The Influence of Urban Sprawl on the Corrosion Rate of Buried Archaeological Coins

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ABSTRACT
This article investigates the corrosion of archaeological coins buried in clay and sandy soil saturated with wastewater. Copper-based coins are very sensitive to their buried surroundings. The coins which are the focus of this study were unearthed during an excavation of the Kiman Fares City, in the Fayoum Governorate, by a team from the Faculty of Archeology at the Fayoum University, between 2017 and 2018. They were discovered in a clay-sandy soil, and a visual assessment showed that the coins suffered from voids, visible cracks, fractures, flaking and a complete transformation into corrosion products resulting in the loss of the metallic core. X-ray fluorescence (XRF) analysis detected the presence of elements used to make the coins, such as copper, lead (the major elements of coinage), and iron. Other elements were detected, such as aluminum, silicon, phosphorus, sulphur, manganese, and strontium (minor elements). This is because the coins were discovered in wastewater contaminated soil. Various minerals were identified in the corrosion of the coins by X-ray diffraction (XRD). These minerals were cuprite, atacamite, malachite, and azurite. These are copper-based corrosion compounds. Cuprite for example is copper (I) oxide (Cu_2O), atacamite is copper hydroxychloride ($Cu_2 (OH)_3 Cl$), malachite is copper carbonate ($Cu2CO_3(OH)_2$), and azurite ($Cu_2(CO_3)_2(OH)_2$). In addition, images from a petrography microscope confirmed the presence of quartz and clay minerals. These results revealed that the coins were made of a copper-based alloy. The deterioration of the coins was due to the contamination of the soil where the coins were buried, which contained wastewater, including ions of salt.

INTRODUCTION

Archaeological coins offer a fascinating glimpse into the ancient world and the interaction between different cultures. Although they are the smallest artifacts, they provide a wealth of historical information and valuable insights into the economic, historical, political, cultural dynamics, and dating of a region (Hanegraaf, Larçin, Jonker, Mandley, and Miedema, 2020, 120-140.). The earliest Egyptian coins were created during the Late Dynastic Period, most likely to pay Greek soldiers serving in the Egyptian army around the 3rd century BC (Bolshakov, 1992, 3-9). Over time, the designs on the coins became more intricate, incorporating portraits, historical events, and mythological narratives. Various metals were

used to manufacture the coins according to economic and political circumstances (Flament, 2014, 82) (Salem, Mohamed, Materials, 2019, 247-255). Copper-based alloys were the common metal used to form coins, as well as other tools used in daily activities, such as cutlery (knives, spoons, forks), plates etc. The Ancient Egyptian coins of this study were discovered at Kiman Fares, in the Governorate of Fayoum, by a mission of the Faculty of Archeology, Fayoum University in 2017 and 2018(Fig.1). The coins uncovered date to the Greco-Roman Period. The coins were excavated from clay soil (filled with plant roots and weeds) and flooded with wastewater. The wastewater is rich in organic acids, soluble salts, and carbon dioxide, and there is clear activity from microorganisms. Climate change is already having an impact on heritage. Furthermore, climate change is worsening centuries of damaging human impact (El-Gohary, Moneim, 2021, 90). Corrosion of coins in their buried environment is a natural process that occurs over time due to the physio-chemical reaction with environmental factors. This interaction leads to the formation of corrosion products on the surface and transformation of the metal core into oxides (Wang, Liang, Zhang, Corrosion, 2007, 604-608) (Giovannelli, Natali, Bozzini, 2006, 951-956). Increased reactions produce damage, with the loss of some valuable information (artistic details, historic, scientific, social, etc.). The corrosion layers on Cu-based alloys are generally composed of a thin layer of cuprite (Cu_2O), which growsdirectly in contact with the metal, protecting the metal itself (Barcellos, Di Francia, Sabrina, Gigante, and Ridolfi, 2019). Urban sprawl is the main reason for the accelerated corrosion of the coins. Over time, these coins have been exposed to different environmental conditions from human-made interventions. Most of the coins were subjected to severe corrosion by chemical interactions between metal and the surroundings. In the case of cultural heritage, every object is unique and therefore any loss is irreplaceable. Physicochemical interaction between coins and its environment leads to change in the properties of the coins. Urban sprawl on the ancient cities naturally changes the conditions of the environment, which can lead to the loss of entire cultural landmarks and cities. Ancient cities face challenges related to modern planning and infrastructure development, especially the expansion of urban areas, which results in a rise in the level of ground water and the inability of the soft soil to absorb it. Therefore, surface runoff gathers around the burial artifact (Hagage, Madani, Aboelyamin, Elbeih, 2023, 174). The movement of wastewater saturated with salts and heavy metals causes the morphology of the coins to change. In this study, we analyzed the quantitative chemical composition of the coins, and explored their microstructure, to understand the corrosion by clay and soil contaminated with wastewater and its impact on the preservation of the objects.

Over time, the archaeology of Kiman Fares, like Greco-Roman temples succumbed to the expansion of the modern town. The site has experienced a form of urban sprawl as the modern town has expanded its borders to accommodate a growing population. At the same time sites like Kiman fares, also highlights the enduring challenges of managing urban growth and preserving cultural heritage. Modern urban expansion could also have environmental consequences, such as changes in local ecosystems (Hagage, Madani, Aboelyamin, Elbeih, 2023, 174).

2. Materials and Methods

The coins were investigated to explore the chemical composition, microstructure and corrosion products. As coins are often considered unique and precious objects, analysis involving destructive methods was not permitted. Therefore, non-destructive methods were used such as, X-ray diffraction (XRD), scanning electron microscope (SEM-EDX), X-ray fluorescence (XRF) analysis, and infrared spectroscopy (IR).

Figure 1. (a) Urban sprawl of ancient Kiman Fares city. (b) The general location of the Kiman Fares excavation area in Fayoum. (c) Kiman Fares excavation area in Fayoum and its wild plants.

(After, Manal Mahmoud, 2023)

2.1 Examinations and Analyses techniques of the Coins

The compositional analysis of coins buried in the ground for thousands of years is an important aspect of archeological research in order to ascertain the burial conditions and types of corrosion. The patina layer is the main corrosion product of the coin surface as its composition changes due to the interaction with the environment. The examination of the chemical composition and microstructure of ancient coins is necessary to know the technological background of an ancient population, exploring the evolution of working metals and alloys (Di Turo, Coletti, De Vito, 2020, 104882).

2.1.1 Stereo Microscope (SM)

The structure of corrosion products of coins was investigated using a Leica S9i Stereozoom microscope (50-500x magnification), with visible fluorescent lights, and a digital video camera system. It was used to characterize the features of colored corrosion products and their peculiarities.

2.1.2 Scanning Electron Microscopy Equipped with Energy-Dispersive X-Ray (SEM-EDX)

Scanning electron microscopy equipped with energy-dispersive X-ray microanalysis (SEM-EDX) was used to identify the type of alloy. A Quanta FEG microscope was used for this investigation and elemental analysis of the deterioration phenomena. SEM and EDS results of the samples were attained by using a JSM-6380 LA instrument, equipped with a Link EDX operating up to 30 kV.

2.1.3 Polarizing Microscope

The concretions on the coins were investigated using a Leica DM500 polarizing microscope to identify soil sediments that overlap with corrosion products. Separated samples were mounted on glass slides for the investigation. These samples were then polished with silicon carbide emery paper to form thin sections with a flat surface.

2.1.4 Portable X-Ray Fluorescence (XRF)

Spectro X-store was utilized with a 30 keV electron beam. Elemental composition was measured at thicknesses of a few microns to explore atoms with atomic numbers greater than 6, a Si (Li) detector with tiny Be windows was used.

2.1.5 X-Ray Diffraction (XRD)

The chemical microstructure of the corrosion was identified using an X-ray diffractometer, model Philips PW1840 and a CuK radiation source. The crystalline phase was characterized using the database PDF2, tube anode: Cu, start angle (º2 θ): 4.025 and end angle (º2 θ): 59.975.

2.1.6 IR Measurement

IR was used to investigate the intermolecular interaction, molecular geometry, and chemical vibrational bonds of the corrosion, using a Bruker VERTEX 80 combined Platinum Diamond ATR with a diamond disc as an internal reflector and a resolution of 4 cm^{-1} and a refractive index of 2.

3. Results and Discussion

The corrosion studies were conducted on the coins after they had been cleaned, conserved, and repaired. To properly understand the corrosion system, one must consider the coin, the soil, and the transition between the two. This is critical for understanding corrosion processes in different conditions and how they affect the identification and preservation of copper alloy coins.

3.1 Photographic Documentation

Photography is essential documentation, which helps in preserving information about the condition of the coins after excavation from the anthropogenic environment, as shown in Figure 2.
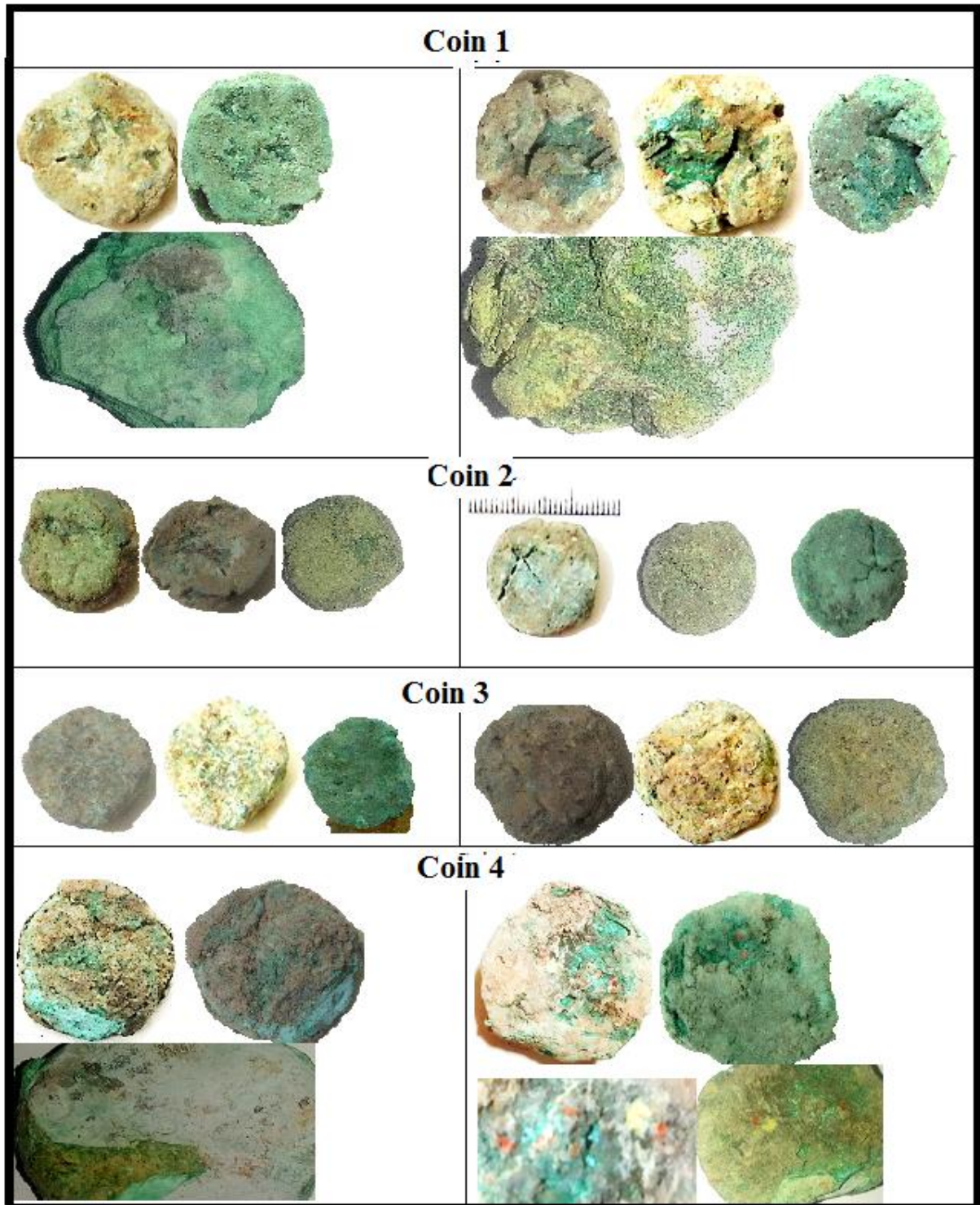
Figure 2. The condition of archaeological coins, coin (1) transformation into corrosion products, coin (2) change in its morphological shape, coin (3) spread of cracks and gaps in it, coin (4) mixing of soil particles with secondary corrosion products.

The distribution of green patina layers, crevices, and pitting of the corrosion was documented. The engineering of the coins were documented to know their original dimension and form (Table 1). Encasing the original form of the coins was a crystallization of

salts and the formation of a thick layer of soil sediments caused by physical-chemical soil characteristic saturated with sewage water.

The dimensions and weight of the coins were altered by the corrosion process in their buried environment. The coins did not have iron and magnetite on the surface, and therefore, they did not connect with a magnet.

Table 1. Weight, diameter and thickness of the heavily corroded coins.

Coin	Weight/gm	Diameter/cm	Thicknesses/cm
1	6.10	2.13	0.57
2	7.41	1.92	0.61
3	5.83	2.05	0.65
4	10.21	2.36	0.63

3.2 Examination by USB Microscope

Bulk samples from the coins were investigated by USB microscope. Greenish patinas were chiefly extant on the surface. Soil deposits as quartz and clay minerals were also detected on the surface. Cuprite, which is usually a liver-red color in mineral form under macroscopic conditions, is expected to appear scarlet-red under the microscope, as shown in Figure 3 (Scott, 1992)
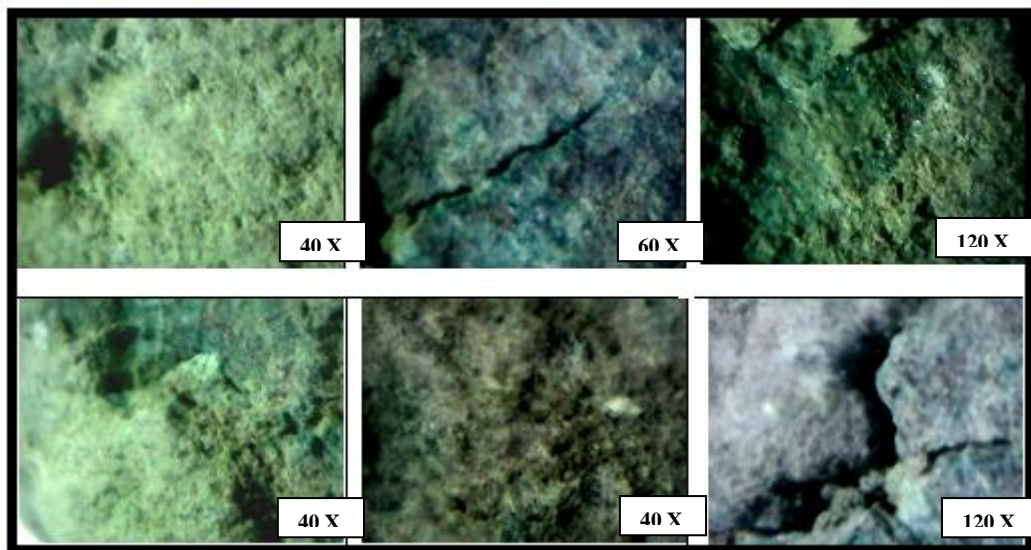

Figure 3. USB microscope images for the coin surface shows pitting and cracking.

3.3 Examination by Stereo Microscope

Visual observations of observe and reverse face of the excavated archaeological coins were shown in figure 4. Visual observation shows that the samples are completely corroded and there are no details of the original surface of the coins as a result of the effect of the sewage water. Also, the presence of the coins in a clay soil saturated with sewage water increased the corrosion process and led to the presence of various corrosion products of different colors. They went through as a result of interaction with external corrosion factors in addition to internal factors. Coin 1 is covered with a heterogeneous thick crust of different colors and corrosion products coexisted with soil particles. Coin 2 is covered mainly with a dark green, compact patina, as a uniform corrosion crust. The observe face and the reverse face of coins 3

suffer from the presence of cracks, and complete transformation into corrosion products resulted from the degradation occurred during long-term underground stay. However, the reverse face of the coin No. 3 suffers from cracks, small voids, and the complete transformation into corrosion products. The observe and reverse face of Coin No. 4 suffer from cracks, calcifications, soil deposits and complete transformation into corrosion products.
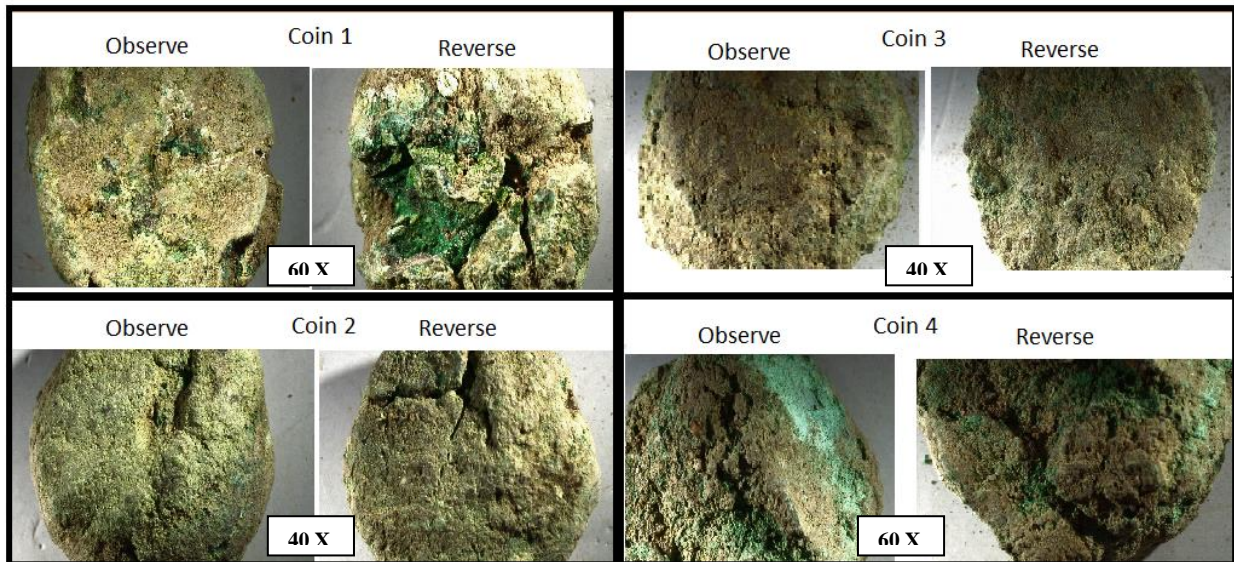
Figure 4. Optical images of the coins excavated from Kiman Fares.

## 3.4 Scanning Electron Microscope (SEM/EDX)

SEM/EDX was performed on a sample of soil deposits from the surface of the coins, which showed the morphology of the coin surface (Figure 5 (a & b), 6). The SEM images revealed lumps of semi-detached minerals that were identified using XRD and a polarizing microscope.
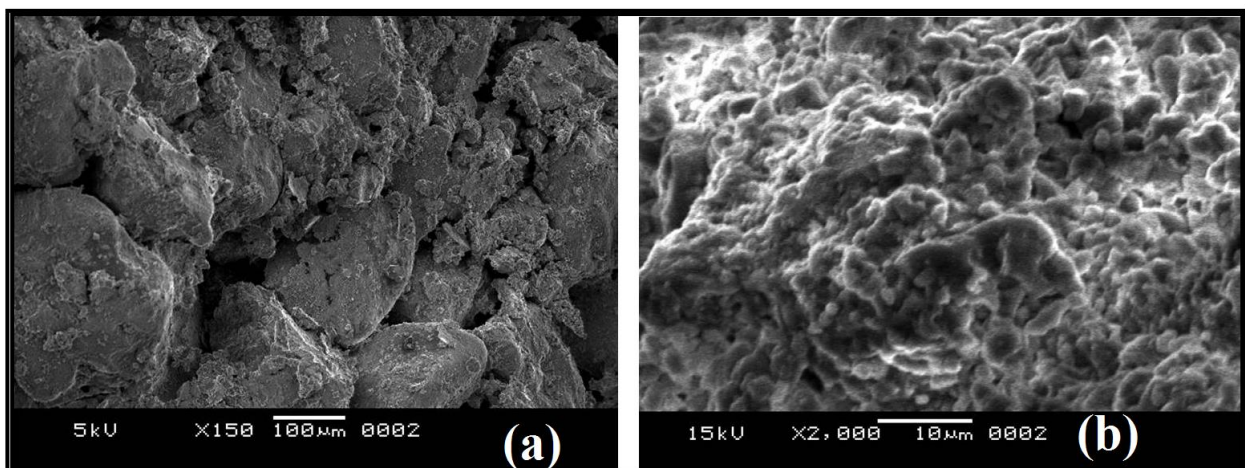
Figure 5. SEM images of the surface morphology, showing their irregular shape and the presence of voids, gaps, and heterogeneous texture components of soil sediments mixed with corrosion products on the coins, (a) low and (b) high magnification.

The morphological changes in the Kiman Fares coins are revealed from the element content of EDX spectrum (Figure 6). As a result, some elements of the coins, type of soil and

wastewater were detected. The presence of peaks were clearly observed, and relate to the elements iron, silicon, aluminum, titanium, sulphur, manganese and oxygen, which are the constituents of some minerals detected in the corrosion.
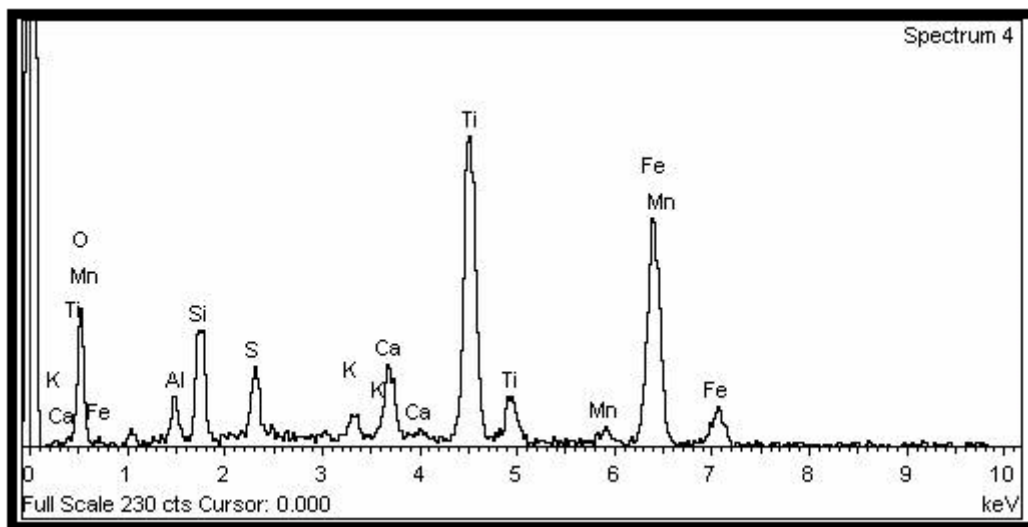
Figure 6. EDX results of the soil encrustations on the coin.

3.5 Polarizing Microscope Measurements

The deposition of soil encrustations adhering to the corrosion on the coins were investigated (Figure 7 (a & b)). This technique presents a qualitative examination for the soil minerals and corrosion grains. The mostly dark areas match with clay minerals like kaolinite. White to yellowish grains corresponds to quartz, feldspar minerals and binder materials like calcite.
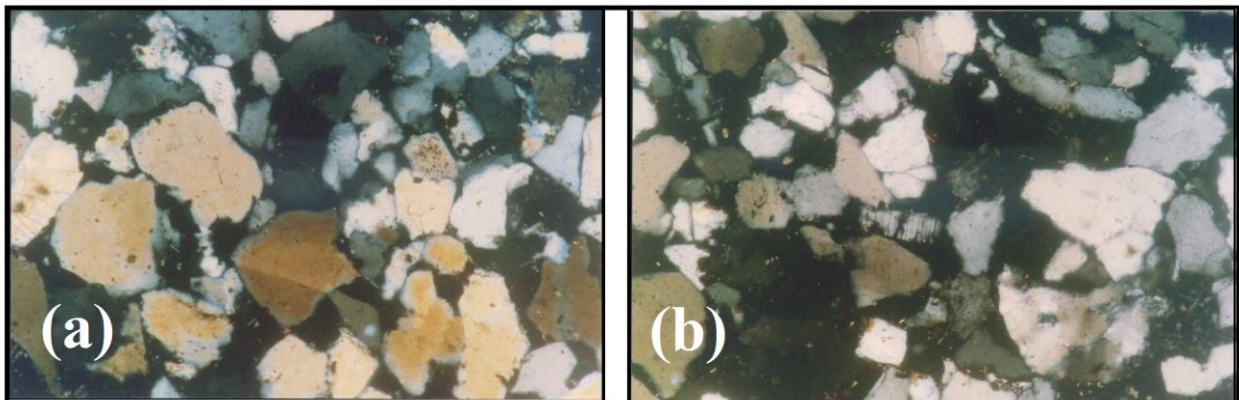
Figure 7. Thin section images of anthropogenic deposits adhered with corrosion products.

3.2 X-Ray Fluorescence Analysis (XRF)

XRF is an excellent non-invasive method for examining the surface layers of metallic materials, such as coins (Torrisi, Caridi, Borrielli, Giuffrida, Torrisi, Mondio, Mezzasalma, Serafino, Caltabiano, Castrizio, 2010, 165, 626-636.) (Caridi, Torrisi, Borrielli, Mondio, 2010, 165, 668-680) (Aiello, Buccolieri, Buccolieri, Castellano, Di Giulio, Leo, Lorusso, Nassisi, Nassisi, Torrisi, 2007, 966-974, SPIE). Figure 8, shows a typical XRF spectrum of the buried environment, with characteristic peaks of aluminum (Al), copper (Cu), silicon (Si),

phosphorus (P), lead (Pb), and iron (Fe). The weight percentage was determined for buried environment ranges of 93.9%, 1.020%, 1.152%, 1.23%, 1.121% and 1.197%, respectively, as shown in Table 2. Some other elements were identified, but their weight percentages were nearly equal or below 0.1%. These elements were, sulphur, titanium, vanadium, manganese, scandium, and strontium.

Table 2. Weight percentage of the elements detected in the soil encrustations.

Element	Burial environment Wt.%	Element	Burial environment Wt.%
Al	93.9%	Mn	0.0258
P	1.23%	Ti	0.0488
Fe	1.197%	V	0.0694
Si	1.152%	Sr	0.0022
Pb	1.121%	S	0.1502
Cu	1.020%	Sc	0.0401

Figure 8, shows a typical XRF spectrum on a specific region of coin 1 and listed in Table 3, where characteristic peaks of copper, lead, iron, silicon, and aluminum were detected. The weight percentage ranges of 29.89, 43.2, 93.57, 15.1, and 4.53 %, respectively. These elements are present because coins react with soil components and wastewater, which contains heavy metals and other elements.

Table 3 Weight percentage of the elements detected in the coins.

Element	Average of weight Percentage %			
	Coin 1	Coin 2	Coin 3	Coin 4
Cu	29.89	37	55.42	53.6
Pb	43.29	23.5	4.64	3,27
Fe	3.57	16	4.11	4,2
Si	15.1	19	28.8	25,57
Al	4.53	5.5	4,47	5.46
O	2.32	6	1.54	0.74
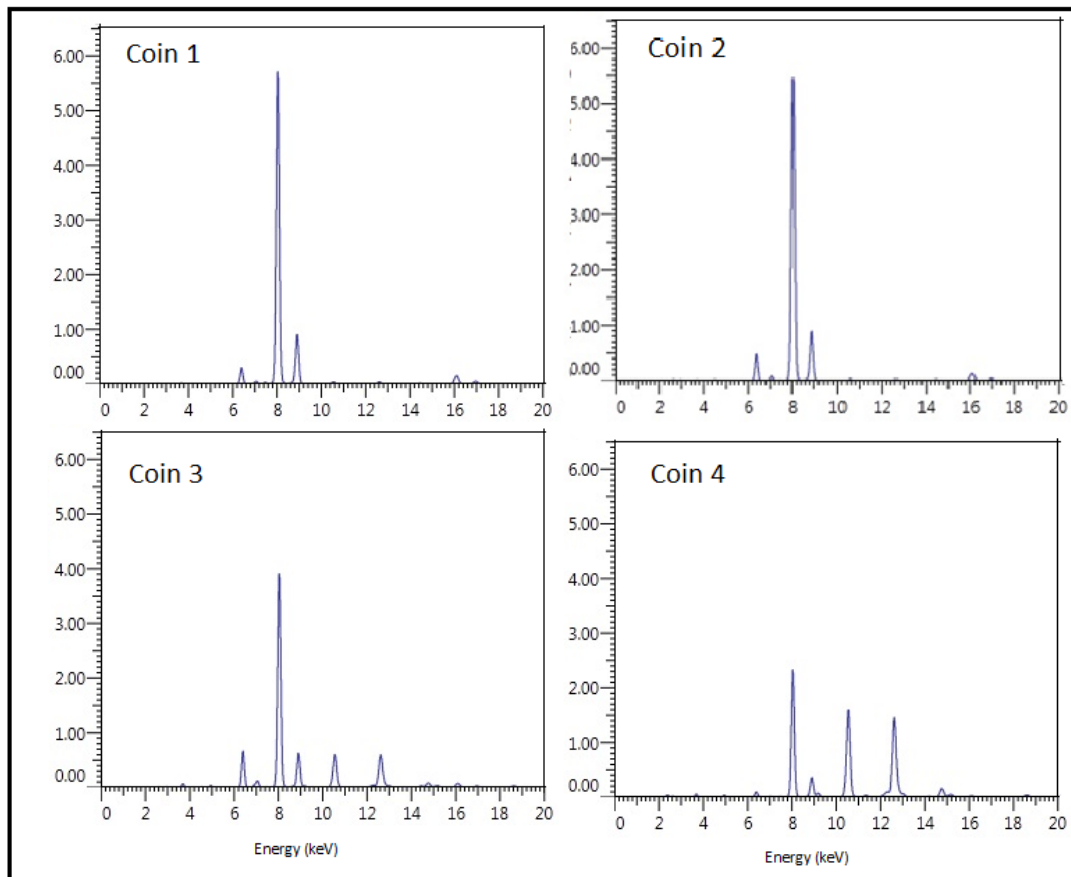
Figure 8. A typical XRF spectrum of the tested coins 1, 2, 3 and 4.

The XRF results of coin 2 (obverse and reverse faces) is listed in Table 2, which shows characteristic peaks of copper, silicon, iron, lead, and aluminum. The alloy Cu-Pb is the main structure of the coin. Tin was replaced by lead in the studied coins A small amount of tin was used where rigidity was required during the casting process, and where a sharp impression was needed (Boev, 2021, 275-279). The weight percentage of copper, silicon, iron, lead, and aluminum were 37%, 23.5%, 16%, 19%, and 5.5%, respectively. In the analysis of historic metal artifacts, the presence of copper, iron, and lead with a high weight percentage is expected, but the presence of aluminum and silicon is the result of soil and wastewater, which had reacted with the coin. There were some other elements identified, but their weight percentages are nearly equal or below 1.5%, like phosphorous, titanium, vanadium, scandium, manganese, strontium. These elements were detected as a result of the coin's contact with soil and wastewater.

Lead has the effect of making copper alloys easier to process, which improves alloy fluidity in the melt. At the same time, a high lead percentage creates a weak point between the grains.

A XRF spectrum on a specific region of the coin 3 (obverse and reverse face), was recorded revealing characteristic peaks of copper, silicon, iron, lead, and aluminum (Figure 8). The weight percentage ranges of the aforementioned elements was 55.42%, 4.64%, 4.11, and 28.8% respectively. The presence of copper, iron, and lead in ancient coins with a high weight percentage is expected, but the presence of aluminum and silicon is due to the soil and wastewater, which had reacted with the coin. Some other elements were identified, but their weight percentages were nearly equal or below 1.5%. These elements were phosphorous,

titanium, vanadium, scandium, manganese, strontium, tin, zinc, and antimony. The presence of these elements is due to the contact the coins had with soil contaminated with wastewater.

The XRF spectrum on a specific region of coin 4 (obverse and reverse face), showed characteristic peaks of copper, silicon, iron, lead, and aluminum (Figure 8). The weight percentage of these elements was 53.6%, 3.27%, 4.2% and 25.57% respectively. Again, the presence of copper and lead with a high weight is expected, but the presence of iron with a high percentage is the effect caused by the burial conditions. In addition, the detection of aluminum and silicon is because of the soil and wastewater, which reacted with the coin. Some other elements were identified, but their weight percentages were nearly equal or below 1.5%. These elements were phosphorous, titanium, vanadium, scandium, manganese, strontium, tin, zinc, and antimony. These elements are present because of the coin's reaction with the soilwastewater. Non-metals, such as silicone (Si), were present, which may be due to sand contamination in the soil.

According to the XRF analysis, it was found that some chemical elements were detected in the corrosion products of the Kiman Fares coins, and most of these elements were heavy metals. The elements present at less than 1 wt%, such as magnesium, zinc, silicon, sulphur, and calcium, are most likely pollution from the sand that filled the tomb, along with the other burial goods. In reality, heavy metal contamination of wastewater is expected. This may be because wastewater contains heavy metals, when combined with industrial wastewater (Picciotto, Torrisi, Margarone, Bellutti, 2010,165, 706-712.) (Abdel-Shafy, and El-Khateeb, 2019, 62, 2303-2312), Also, some of the heavy metals, such as Al, Mn, Zn, and Pd have been detected in the Nile River (Abdel-Shafy, 2015, 1-12). This may explain the high weight percentage of some of these metals in the Kiman Fares coins, which have been buried for more than two thousand years (Goher, Ali, and El-Sayed, 2019, 301-312) (Rashed, Toufeek, Eltaher, and Elbadry, 2018,143-159).

Copper alloys dissolve under acidic conditions. In a soil where oxygen is present, copper can corrode. If soil pH not too acidic (usually > 6), basic copper carbonate compounds such as malachite and azurite usually form. These have a characteristic green or green–blue color (Abdel-Satar, Ali, and Goher, 2017, 21-29).

We find that some elements such as chlorine did not appear in the analysis with the EDEX unit, while they appeared in the analysis with X-ray diffraction. This is due to the nature and type of samples that were analyzed in both cases. The samples included layers of rust as well as components of soil adhering to the surface of the coins. Also, covering the samples in the analysis with the EDEX unit was done using carbon, so it did not appear in the analysis results.

3.3 X-Ray Diffraction (XRD) Measurements

The corrosion on the coins represents the conditions of the environment surrounding the coins. According to XRF analysis results, a number of essential elements were detected in the corrosion of the coins. XRD results revealed various minerals in the corrosion of the coins (Figure 9(a & b)). These minerals were cuprite (Cu_2O), atacamite ($Cu_2(OH)_3Cl$), malachite ($Cu_2CO_3(OH)_2$), azurite (CuO), and nantokite (CuCl). Cuprite was the highest component of obverse and reverse face of the coins.

This confirms that the coins were made of copper alloy. Cuprite can be found in a variety of geological environments, such as weathering in copper-rich soils. Weathering of the earth's surface promotes the release of copper ions, which react with oxygen to form cuprite (Caridi,

Torrisi, Borrielli, Mondio, 2010, 668-680). The environment of the Fayoum has experienced this weathering phenomena due to its climate (Huisman, Ackermann, Claes, Eijck, de Groot, Joosten, Kemmers, Kerkhoven, de Kort, and Russo, 2023, 103799) (Huebner, 2020, 486-518). This weathering and release of copper ions leads to corrosion of materials, especially buried archaeological artifacts. The second highest percentage mineral in the corrosion was atacamite, which is a green, bright copper hydroxyl chloride ($Cu_2(OH)_3Cl$) halide mineral (Cameron, Leybourne, and Palacios, 2007, 205-218) (Molahid, Kusin, Syed Hasan, 2023, 1-22). It is a secondary mineral generated by the oxidation of other copper minerals, especially in dry environments. Its hardness is 3 to 3.5 on The Moh's scale, and specific gravity is 3.8. The hardness of atacamite increases the solidity of corrosion, as in the case of cuprite. The green color was covered completely in Figure 1. The formation of atacamite is expected when coins are buried underground, and possibily have contact with wastewater. The area of Kiman Faris, where the coins were found is near the wastewater. The third mineral in the corrosion was malachite. This mineral is a copper carbonate, and its chemical formula is $Cu_2CO_3(OH)_2$. The fourth mineral was azurite, and is also a copper carbonate mineral, but its chemical formula has more atoms than malachite, $Cu_3(CO_3)_2(OH)_2$ (Huisman, Ackermann, Claes, Eijck, de Groot, Joosten, Kemmers, Kerkhoven, de Kort, and Russo, 2023, 103799) (ameron, Leybourne, and Palacios, 2007, 205-218). Its color is deep blue to violet-blue. It was used in the production of blue glaze in ancient Egypt (Huisman, Ackermann, Claes, Eijck, de Groot, Joosten, Kemmers, Kerkhoven, de Kort, and Russo, 2023, 103799) (Molahid, Kusin, Syed Hasan, 2023, 1-22). The fifth mineral was tenorite, which is copper (II) oxide (CuO). It has a gray-to-black metallic color and has monoclinic-prismatic crystals. Ultimately, the minerals detected in the XRD pattern confirm that the composition of the coins was dominated by copper.
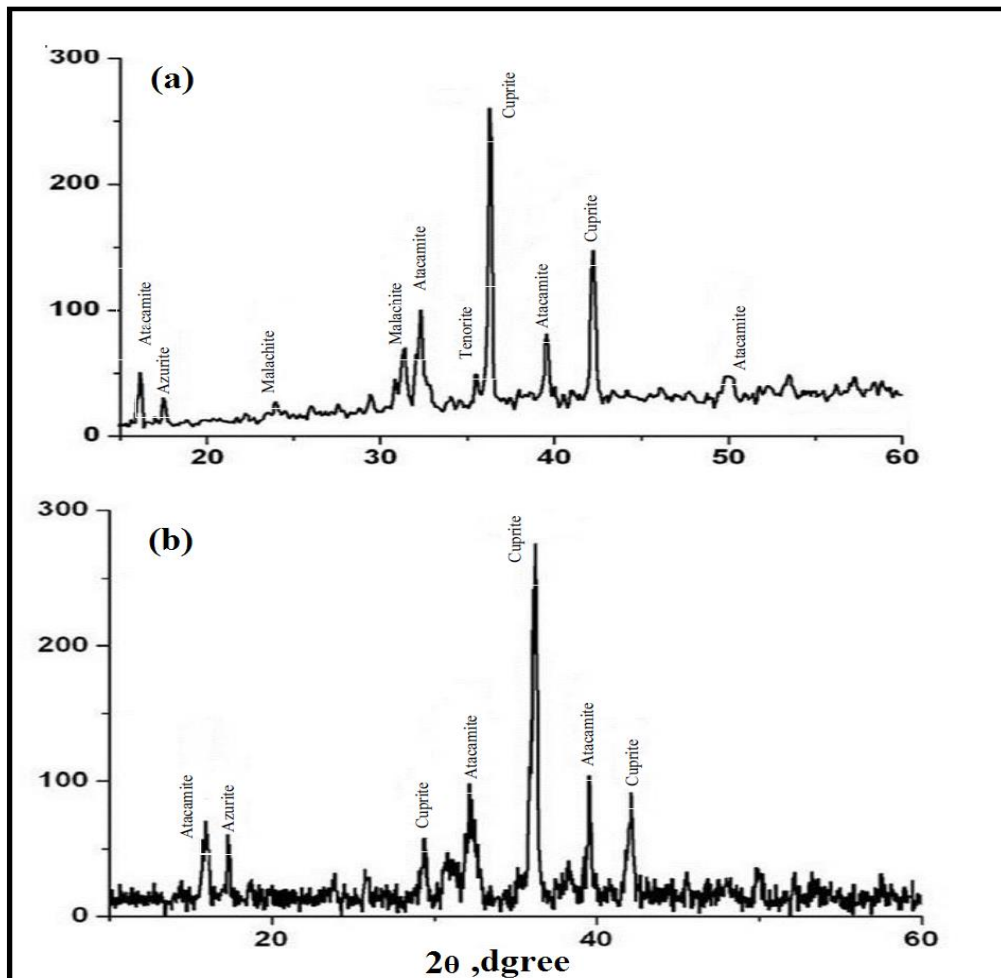
Figure 9. XRD pattern of the coin No. 1, a) observe face, and b) reverse face.

3.4 Chemical Reactions between Metal and Surroundings

Chemical reactions to form the aforementioned minerals are expected because of the presence of the required conditions, such metal cations (M^+, and M^{2+}), oxide ion (O^{2-}), sodium chloride (NaCl), and water (H_2O) (Huisman, Ackermann, Claes, Eijck, de Groot, Joosten, Kemmers, Kerkhoven, de Kort, and Russo, 2023, 103799) (Cameron, Leybourne, and Palacios, 2007, 205-218).

Formation of cuprite or copper (I) oxide as a result of oxidation was the first copper corrosion product to form on the surface of the coins, prior to their burial (equation 1). Alternatively, oxygen in the soil would soon form the oxide layer. The red, cuprous oxide layer, which adhered to the metal core, usually covered the other Cu(II) salts as shown in equation 2.

Cuprite (Cu_2O) is formed when copper

$$2Cu^+ + O^{2-} \rightarrow Cu_2O \qquad\qquad \text{equation (1)}$$

Cuprite is the primary patina of the coins - the first layer formed on the surface.

Simple equation to form tenorite mineral is as follows:

$$Cu^{2+} + O^{2-} \rightarrow CuO \qquad\qquad \text{equation (2)}$$

The presence of water, carbon dioxide and chloride ions in the environment help in the formation of atacamite (copper (II) hydroxy chloride) as shown in equation 3.

$$2Cu^{2+} + 3OH^- + Cl^- \rightarrow Cu_2Cl(OH)_3 \qquad \text{equation (3)}$$
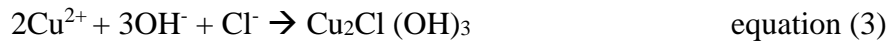
Malachite mineral is formed as shown in equation 4.

$$2Cu^{2+} + CO_3^{2-} + 2OH^- \rightarrow Cu_2CO_3(OH)_2 \qquad \text{equation (4)}$$

The chemical reaction of azurite formation is as follows:

$$Cu^{2+} + 2CO_3^{2-} + H_2O \rightarrow Cu(CO_3)_2(OH)_2 + H^+ \qquad \text{equation (5)}$$
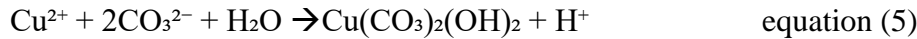
Analysis of the diffraction patterns suggests that the main phases are Cu-alloys, namely CuPb. Additionally, high amounts, of cuprite 12 % (wt) and of nantokite 6% (wt), confirm the high degree of corrosion of the coins. Secondly, traceable phases of pyromorphite, chalcopyrite, and Fe oxides, suggest extensive environmental interaction with either phosphorous enriched, or anaerobic and humus soil (Debernardi, Corsi, Borghi, Cossio, Gambino, Ghignone, Scherillo, Re, Giudice, 2022, 133). Electrochemical processes further contributed to the degradation of Cu-Pb coins, and groundwater saturated with salts, Figure 10, shows the main reason of the degradation of the coins.

Figure 10. The field conditions of the excavated coins.
(After, Manal Mahmoud, 2023).

3.5 Analysis of Wastewater from Kiman Fares

A sample of wastewater was taken from the excavation site at Kiman Fares and analyzed to determine its salt components and pH. The results of the chemical analysis of the wastewater sample are presented in Table 4.

**Table 4.** The results of the chemical analysis of the wastewater sample from Kiman Fares.

Chemical Composition	(ppm)
Total dissolved salts	7989
Sodium bicarbonate NaHCO$_3$	1378
Sodium chloride NaCl	3827
Sulfur trioxide SO$_3$	1274
pH	8.9

Dissolved salts were the main components of the wastewater in the excavated area. The impact of the movement of wastewater on the surface of the coin has implications for the alteration of surface morphology, for weight loss, and for the transformation of the metal completely into corrosion. The pH value of the wastewater is alkaline which relies on the equilibria of carbonic acid and the concentration of carbon dioxide, bicarbonate and carbonate (Luklema,1969, 913-930), as shown in Table 3. Sodium chloride (NaCl) solution is a type of electrochemical reaction which increased the corrosion rate of the coins. These salts showed the presence of cuprous chloride, CuCl, as a corrosion product adjacent to the metallic surface of the coins, creating long-term problems for the stability of the object (Scott, 2002).

3.6 Analysis by IR Spectroscopy

The IR spectrum showed evidence of various corrosion products on the coins, as shown in figure 7. As discussed earlier, XRD data confirmed the presence of copper-based minerals, cuprite, atacamite, malachite, and azurite. The absorption peak at 472 cm^{-1} is a significant peak for the metal–oxygen (Cu–O) (Bouachma, Ayouz-Chebout, Kechouane, Manseri, Yaddadene, Menari, and Gabouze, 2022, 1-13.). The spectrum showed this peak at about 472 cm^{-1}. The peaks at 427 cm^{-1} and 503 cm^{-1} · are the adsorption peaks for CuO (Ethiraj, and Kang, 2012, 1-5). The peak at 678 cm^{-1} may represent Cu-O-Cu because as mentioned, there is a significant peak in the 605-660 cm^{-1}, which relates to Cu-O-Cu (Voinea, Vladuta, Bogatu, Duta, 2008, 76-80) (Kim, Woo, Hung, Lebbai, 2006, 320-328). The strong absorption peak at 1008 cm^{-1}, and the absorption peak at 3330 cm^{-1} corresponds to malachite (Schuiskii, and Zorina, 2013, 576-580). Also, the strong absorption peak at 1008 cm^{-1} can be considered for Si-O. The spectrum showed the broad band near 3442 cm^{-1}, which corresponds to the O-H stretching vibration of incomplete silanol group (Si-OH) condensation, as well as remaining absorbed water (Buti, Rosi, Brunetti, Miliani, 2013, 2699-2711). The bands around 3332 and 3440 cm^{-1} are assumed to originate from stretching vibrations of hydroxyl groups of paratacamite. A strong band around 1105 cm^{-1} is allocated for brochantite, as well as those at 608, 878 and 980 cm^{-1} (Mendoza, Corvo, Gómez, and Gómez, 2004, 1189-1200).

The XRF analysis showed that Si is present in the corrosion of the coins. The presence of Si in the corrosion is due to the coins having been buried in clay and sandy soil. Also, the presence of water is expected as a result of the coins being surrounded by groundwater (Gehan Adel Mahmoud, et al., 2020, 250-262) figure11.
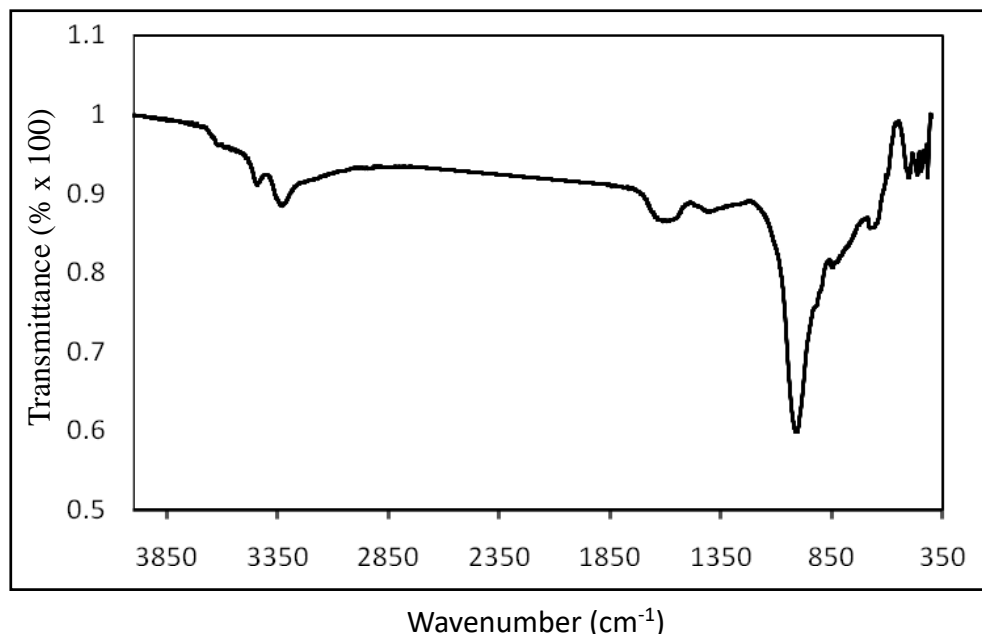
Figure 11. IR spectrum of corrosion products of the coins.

Organic compounds were not detected on the exterior area of the coins. The area from 2800 cm⁻¹ to 3000 cm⁻¹ represents stretching bands of –CH2– groups of the organic compound. (Mendoza, Corvo, Gómez, and Gómez, 2004, 1189-1200)

Conclusion

The urban sprawl of Kiman Fares city along with the physiochemical characteristics of soil saturated with wastewater affected the ancient coins. Layered, pitting and crevices are the main deformations of the studied coins, which was caused by the burial conditions. XRF detected various elements in the corrosion and soil, which comprised mainly copper, silicon, aluminum, lead, and iron. The coins were made of Cu-Pb alloy enriched in Fe, with copper and lead being the primary components of the coins. Investigations showed that the physical and chemical properties like the high density of the remaining core and cracking of the surface were changed with a high percentage of lead. XRF also detected some heavy metals with weight percentages less than 1%, such as titanium, vanadium, manganese, tin, cobalt, and zinc. XRD indicated that the corrosion products were composed of some minerals, including cuprite, atacamite, malachite and azurite. This analysis confirms that the crystallinity of these minerals on the coins, which are copper-based compounds. The petrography microscope indicated the red and greenish color of these minerals, such as cuprite, atacamite, and malachite; deep blue of the azurite mineral, and grey-to-black. The effects of the soil and wastewater on the coins is reflected in the heavy corrosion and complete transformation into copper-based minerals. Stabilizing the coins is a significant concern. However, with proper preventive conservation strategies, effective monitoring, and innovative preservation techniques, these coins will be preserved for the future.

Author Contributions

SMS and GAM collected the coin samples and carried out the investigations by measurements, USB and stereo microscopes and analyses by XRF, XRD and SEM-EDS. AAE and AMA conceived the overall research and carried out IR, fitted spectra, elaborated data, and drafted the manuscript in the light of referenced work. They also delivered some basic information on the investigation techniques.

AMA, RMA, and MMS contributed to the study conception, the design and implementation of the research, the analysis of the results, and the writing and approval of the final manuscript

Declarations
Conflict of interest, the authors declare that they have no conflict of interest

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تأثير التوسع العمراني على معدل صدأ العملات الأثرية المدفونة

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الملخص

يركز هذا البحث على دراسة نواتج التآكل للعملات الأثرية المدفونة تحت الأرض والمتصلة بالطين والتربة الرملية المشبعة بمياه الصرف الصحي. تم الكشف عن عملات أثرية في أعمال التنقيب بمدينة كيمان فارس بمحافظة الفيوم من قبل كلية الآثار بجامعة الفيوم، ٢٠١٧- ٢٠١٨، حيث تم اكتشافها في تربة طينية / رملية. تم قياس وزن وقطر وسمك كل عملة. تُظهر الملاحظات البصرية أن العملات تعاني من فراغات وشقوق مرئية وكسور وتقشر وتحول كامل إلى مركبات تآكل؛ فقدان اللب المعدني. كشف التحليل بتفلور الأشعة السينية (XRF) عن وجود عناصر مستخدمة في صنع العملات الأثرية، مثل النحاس والرصاص (العناصر الرئيسية للعملات) والحديد، كما تم الكشف عن عناصر أخرى، مثل الألومنيوم والسيليكون والفوسفور والكبريت والمنجنيز والسترونشيوم (عناصر ثانوية بسبب وجود العملات في تربة ملوثة بمياه الصرف الصحي، كذلك تم التعرف على معادن مختلفة بواسطة التحليل بطريقة حيود الأشعة السينية (XRD)، هي الكوبريت (Cu2Oوالأتاكاميت ((Cu2 (OH) 3Cl))والملاكيت ((Cu2CO3 (OH) 2))، والأزوريت (Cu2 (CO3) 2 (OH) 2)، بالإضافة إلى ذلك، أكد الفحص بالميكروسكوب المستقطب وجود معادن الكوارتز والمعادن الطينية. كشفت هذه النتائج أن العملات المعدنية مصنوعة من سبيكة أساسها النحاس. يرجع تدهور العملات المعدنية إلى التربة التي اكتشفت فيها في منطقة الحفائر، والتي تحتوي على مياه الصرف الصحي، بما تحتويه من أيونات أملاح.