

Mini Review

## Corrosion Behavior of Coins in Artificial Sweat Solution: A Review

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Coin materials and time of circulation affect their loss of the original appearance, color, and clear pits of their surfaces. This behavior mainly caused by human sweat that gradually destroys the coins surface. The corrosion behavior of the coins were investigated by many researchers. The wear test might also taking place on the coins before and after immersed in ASS. These coins were investigated in artificial sweat solution (ASS) by chemical and electrochemical techniques. The chemical technique used weight loss (WL) to the minted and sometimes the blanked coins. The electrochemical techniques that used are potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) techniques to test the coins for different periods of time. The ASS analysis were taken periodically by atomic absorption spectroscopy to support the results of the corrosion methods. Also, it help to have a conceptual understanding of the corrosion process during their immersion in the artificial sweat solution. The ions that released from coins in artificial sweat solution were analyzed. The surface morphology was investigated for the coins before and after immersion in ASS by SEM and EDX. Moreover, the corrosion products on their surfaces after immersion in ASS were analyzed by XRD.

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**Keywords:** Coins; Artificial sweat solution; Corrosion behavior; Electrochemical behavior; Weight-loss method

### 1. INTRODUCTION

Coins are made of metal that have standard designs [1]. It is hard to determine the real origin of the earliest coins. The coinage was a Greek phenomenon. The use of coinage was widely spread in Greek

territories [2, 3]. The ancient Pb coin was discovered in 1948 near Parabita (province of Lecce, Italy). It was produced in the 3rd or 4th century BC. The Pb coin was made from two metals (Cu as a rest and plated with Ag). In modern society, Iron was used to recover Cu. Ancient people used simply electrochemical methods to coat coins. Ancient China and Arabic Spain used sulfate solution for coin making. Dissolved metallic Ag in nitric acid to generate Ag containing salt solutions, and then dipped copper blanks into these solutions to make a copper or silver coating [4, 5]. Different types of the hydration process made copper solutions [4].

In Roman times, coating technologies was applied to create Au or Ag layer as thin as possible were developed to save precious metals. The Greeks manufactured Ag plated coins by copying the methods from the Romans. The fragment of a Greek plated coin made by Athens in 404 BC. The silver layer with thickness of approximately 150 μm was placed on the pure copper core. It was believed that a copper blank was first wrapped with a silver foil on both sides then striking force heat were applied to bond and diffuse the bonding. This manufacturing method improved the adherence of the coating layer and copper substrate [6].

During fifth and sixth centuries AD, people in Rome used bronze coins for daily usage. Cu-Sn-Pb alloys were the main elements in these coins. In 1982, Italian Government Mint first produced a large scale of bimetallic coins (500 Lire). The costs of manufacturing the bimetallic coins were higher and the manufacturing steps were more complex. These coins had advantages, for example, ease of distinguishing and good aesthetic features. The coins were produced in two steps: the center was first placed inside the outer ring, and then the two parts were forced together [7].

In Canada, especially in Winnipeg, one of the common minting authorities in the world produces large numbers of “circulation coins”. As shown in Table 1 the several types of coins handled in Canada and its raw materials with chemical compositions [8].

**Table 1.** Chemical composition of “circulation coins” in Canada since 2000 [8]

Type of coins	Elements, wt.%			
	Steel	Cu	Ni	Brass
Five-cent	Rest	3.5	2	-
Twenty-five cent	Rest	3.8	2.2	-
Fifty-cent	Rest	4.75	2.1	-
One dollar	Multi-ply brass-plated steel			

**Table 2.** The several types of coins used in United States [8]

Type of coins	Elements, wt.%			
	Cu (%)	Ni (%)	Zn (%)	Mn (%)
cent	2.5	Rest	-	-

5-cent	Rest	25	-	-
10-cent	Rest	8.33	-	-
Quarter dollar	Rest	8.33	-	-
One dollar	Rest	2	6	3.5

The key processes for manufacturing of coins

Recently, multiply plated steel (MPPS) used as a unique electroplating process which considered one of the cheapest materials with iron. It began to be used in the manufacture of coins and plated with metals that add luster and aesthetics to it, such as brass and nickel. The advantage of this method is to reduce the usage of nickel/copper or bronze than other minting techniques. The MPPS technique is more efficient in saving time during the process [8].

In US, especially in 1793, the first circulation coins were produced. Table 2 presented the several types of coin denominations used. Cu is the base element almost in all types of coins [9]. Copper classified by Environmental Protection Agency (EPA) that decreases viable bacteria so, copper- based surfaces is a commonly used in human products [10].

Manipulation of coins offer a range of advantages, namely (1) increased revenue, (2) significant cost savings, and (3) increased wear-resistance. There are six steps to produce the coin denominations. The first step, the blanking, coins are punched from coiled strips of metal on a blanking press. Annealing is the second step. This step is very important to soften the surface of blanks operated in a special furnace and cleaned using a chemical solution in rotating barrels. After that, the coins were washed, cleaned and dried. The third step is upsetting as called Rimming. The blanks are performed with an edge-rolling operating on the upsetting (Rimming) machine. This machine can roll the edges for the same thickness on coins. The edge is hardened during the upsetting process. It can prevent the soft metal from squirting at the interface between the collar and die during stamping. Finally, striking blanks or is called the coin process which are stamped (minted) with the designed patterns. Most presses can strike more than coin at one time, while others simultaneously strike two coins. After the manufacturing process was completed, the quality control phase inspected the coins using a magnifying glass to check whether they had any defects. Finally, the coins are counted and dropped into a secure container by an automatic counting system.

The chemical compositions of coins, their size, as well as, the thickness of corrosion-resistant coating materials were described. Technical specifications of blanked coins (25P Egyptian coin and 50P Egyptian coin) as illustrated by the importer (British Mint Authority) were given in Table 3. The 25P Egyptian coins coated by 100%Ni with thickness 7.5 μm while the 50P Egyptian coins coated with about 70%Cu and 30%Zn with 25 μm thickness of coating. The steel chemical composition is 0.08%C, 0.15%Mn, 0.03%P, 0.02%Cr, 99.4%Fe and 0.32 others impurities [11].

**Table 3.** Dimensional specification of 25P and 50P blanked Egyptian coins [11]

Blanked coins	Diameter-Cut (mm)	Diameter-Rimmed (mm)	Edge thickness-Rim(mm)	Diameter-Plated (mm)	Weight (g)
50P	$22.74 \pm 0.05$	$22.54 \pm 0.03$	$2.21 \pm 0.10$	$22.6 \pm 0.05$	$6.5 \pm 0.2$
25P	$20.67 \pm 0.05$	$20.47 \pm 0.03$	$1.87 \pm 0.10$	$20.66 \pm 0.05$	$4.5 \pm 0.17$

## 2. EFFECT OF ARTIFICIAL SWEAT SOLUTION ON METALS

Coins lose original appearance and color after circulated for a certain period. During circulation, coins contact with the human skin, the remaining sweat becomes the main reason to vanish the color. The dissolution of coins' material may cause potential allergies [12-18]. Many researchers evaluated the corrosion of metal alloys when they come into direct contact with human body. This problem is linked to the impact of metals due to the absorption of sweat when touching of metal/alloys such as coins, jewels, earrings and piercing [12, 19, 20, 21]. Upon contact of coins with the ASS, the coins can be distorted. On the other hand, upon long-term immersion in ASS increased. A toxic effect started to appear which is due to the ions-release of metal due to dermal-hypersensitivity to typical nickel alloys or nickel [12, 22-27].

As previously mentioned, ASS varied according to different research groups, and this might involve varying compositions, concentrations, and pH levels [22, 28, 29]. The most elements affecting the corrosion behavior on metallic surfaces are urea and NaCl. The chemical composition of Urea is  $\text{CH}_4\text{N}_2\text{O}$ , urea slightly increased "corrosion-potential" ( $E_{\text{corr}}$ ) and significantly decreased "corrosion-current density" ( $i_{\text{corr}}$ ) [50]. NaCl is the most effective compound in the corrosion process. Whereas  $\text{Cl}^-$  ions are active-cathodic ions which can form corrosion products on the surface of metal or alloy like  $\text{NiCl}_2$  [30].

## 3. CHARACTERIZATION OF THE CORRODED COINS

### 3.1. Surface morphology

The optical microscopy is used to investigate the surfaces of coins after immersion in ASS to determine the types of corrosion in formed on surfaces of alloys. Coins were imaged before and after their immersion in ASS [31-33]. The SEM was connected to EDX to analyze the elements on the surface. The protective oxides layer removes from the alloy surface which allows to start of pitting corrosion. That results of the coating failure which is improved by increasing the stability of these protective oxides layers [34].

### 3.2. Phase Identification

The sample corrosion products are formed after immersion of samples in ASS. The phases identification were analyzed by X-ray diffraction analysis.

### 3.3 Wear test

The corrosive wear test is important for coins and engineering applications [35]. ASTM G99-04 was used as the guideline for the wear test [36]. The test machine caused the disk specimen to rotate about the disk center, and therefore left a circular sliding path (wear track) on the disk surface. The revolution speed (number of revolution per minute, rpm) was adjusted according to the pre-set linear sliding speed and the diameter of the wear track [37]. The test was carried out at a normal load of 7 N at a 100 mm/s sliding speed. The total sliding distance was set to 100 m. The frictional force was measured by a load cell, from which the coefficient of friction (COF) was calculated by dividing the friction force by the normal load. The volume ( $\Delta V$ ) of coating removal during the test as shown in Eq. 7 and the specific wear rate ( $W$ ) was determined using Eq. 8 below [11]:

$$\Delta V (mm^3) = \frac{\text{Mass loss (g)}}{\text{Density } \left(\frac{g}{cm^3}\right)} \times 1000 \quad (7)$$

$$W (mm^3/N.m) = \frac{\Delta V}{SL} \quad (8)$$

Where S is the sliding distance (in meter) and L is the normal load applied (in Newton).

## 4. PREVIOUS WORK ON COINS

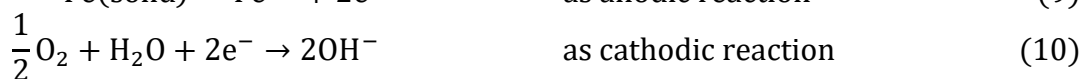
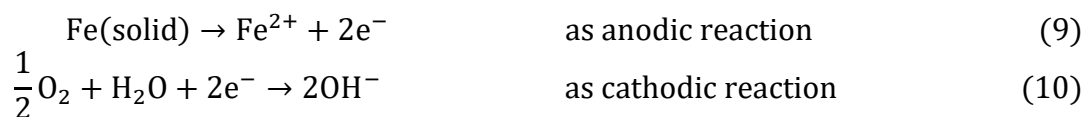
History of coins goes back to more than two thousand years old. The circulation of currency included coins and banknotes, which worldwide have substantially increased during the past few years. Many countries are tending to switch, low value banknotes by coins [38]. There are two sides to compare between them, (a) the manufacturing cost of coins is more expensive compared to banknote manufacturing cost; (b) the circulation life of banknotes are 2-3 years compared to coins which have a circulation life of more than 30 years depend on coins quality [39]. The banknotes come out of the service, they are excluded totally. On the contrary, coins can be recycled again and reused as raw material when they come out of the service [38]. When coins come into contact to human skin, the color of coins may disappear gradually and some ions leached out of the surface of these alloys. On the long period of contact, this may result in dermatitis or allergies [12].

Recently, the most alloys used in coins manufacturing are Ni alloys and Cu alloys [40, 41]. Its price is low compared with porous metals and its decorative appearance. One of the most non-precious metals used to manufacturing of coins is Nickel. The resistance of Ni is unequally by any other metal or alloy except precious metals [42]. The researchers found that Ni is the most common metals causing skin contact allergy, affecting about 10–20% of the general population [24, 33-39]. There are more sources of handling of alloys and metal of Ni such as production and processes, transport, and jewelries

[25, 26, 44, 50]. Ni is classified as one of the most hazardous metal that causes skin sensitivity (may cause an allergy to skin) [51, 52]. When Ni ions reached a  $0.5 \mu\text{g}/\text{cm}^2/\text{week}$  after prolonged contact, this is considered as a restricted limit which causes this skin allergy [19, 34, 43, 53].

Cu alloys, especially brass, possess strong wear resistance and processing properties, hence it has a wide range of applications, such as in daily hardware, manufacturing of outdoor/indoor machines. Brass usually has a gold-like appearance; however, different colors are often required in many application fields [54-58]. Copper can rapidly kill many bacterial species. Solid copper kills bacteria by contact. This means that bacteria on copper suffer from immediate membrane damage and DNA degradation [59]. High temperature, copper content in the alloys and relative humidity all help increase the efficiency of bacteria killing.

In 1976, Burton et al [60] were interested to know the most effective element in ASS that causes metal corrosion. Iron hydroxide  $\text{Fe}(\text{OH})_2$  appeared in Eqs. 9 and 10 and NaCl does not appear in two reactions. Sodium chloride is an important role in transferring the electrons and also ensures other elements in sweat (organic acids) and participate in breaking the normal oxide film. The low pH of sweat helps in increasing the corrosion process and confirmed their results. The passivity was more in the acidic sweat compared to alkaline sweat [60-62].



Burton et al [60] emphasized the effect of temperature, chloride concentration, person's quality of sweat and the time of the day of the sweat on the corrosion of metal.

In 1987, Randin [22] studied the Ni 200 while it is immersed in ASS as assigned by ISO 3160/2 and sea water NaCl 20 g/L,  $\text{NH}_4\text{Cl}$  17.5 g/L, urea 5 g/L, acetic acid 2.5 g/L, pyruvic acid 2.5 g/L, butyric acid 5g/L, and lactic acid 15g/L. The pH was adjusted to 4.7 with adding drops of NaOH. Table 6 shows the composition of Ni 200. Randin compared these results of Ni 200 with stainless steels at the same experimental conditions [22].

**Table 6.** Chemical composition of Ni 200 [22]

Sample	Element weight (Wt.%)						
	Ni	C	Mn	Fe	S	Si	Cu
Ni 200	Rest	0.06	0.25	0.15	0.005	0.05	0.05

The corrosion potential of Ni 200 was found to be more active in ASS and seawater compared to Ni/Ni<sup>2+</sup> couple (-0.23 VHE). Table 7 showed the value of corrosion potentials in aerated and deaerated solution.

**Table 7.**  $E_{\text{corr}}$  of Ni 200 results [22]

Saturated solution	ASS	seawater
N <sub>2</sub>	- 0.16±0.01	- 0.17±0.02
O <sub>2</sub>	+0.06±0.02	+0.09±0.02

Randin [22] explained that the influenced the reaction of Ni<sup>2+</sup> release where the Ni<sup>2+</sup> increased upon Cl<sup>-</sup> increase which in turn increasing the value of the current density. Consequently, this resulted in shifting the corrosion potential of Ni 200 to active region. The concentration of Ni<sup>2+</sup> in ASS is 10 times higher than the value in seawater solution. Randin recommended not using alloy Ni 200 in applications that has direct contact with human. The investigation of Randin did not include in the test periods and did not specify the release elements rates in solutions. Moreover, Randin did not study the surface changes on the surface of the alloy immersed in the electrolytic solution.

In 1998, Flint [22] was interested in classified the metals according to allergenic metals to four categories. Flint collected data from pervious researches either reaction in ASS or allergenic ions (for the interest to know about these categories [24]. Copper and nickel ions react with ASS and can allergy on human. Zn metal reacts with ASS but not form allergy on human. Flint ensure that the effect of allergenic metal ions on contact person depends on their concentration [24]. Flint [24] used the patch test to test the extent to which the spores are affected by human sweat, which is a well-adhered sample (alloy/metal) to the skin for two days. The patch test helped to reduce oxygen access to this area, thus the interaction is concentrated in this area, and soon the result appears. Flint [24] explained the behavior of the alloys in the sweat can be completely different on the behavior of the components of the alloy itself. Therefore it is necessary to study the effect of the alloys. Specifically those containing elements cause sensitivity of skin to calculate rate of release of the elements. Flint indicated that the concentration of the allergy of metal is not the effective factor to cause an allergy risk. The interaction of metal ions and its development with human skin is the most dangerous in relation to the unit area of the skin. Flint recommended studying the effect of metals on a long enough time to know the reaction from the reaction. Therefore, factors such as time, contact area, and sample shape are very influential and decisive in distinguishing between metals or alloys that cause allergies or others.

In 1999, Colin et al [63] were interested in the chemical composition of corrosion products formed on the surface of B48A, nickel silver, and Monel alloys. The chemical composition of alloys showed in Table 8. Colin investigated the surface morphology of these alloys after six weeks of immersion in synthetic sweat with pH 6.5 by XPS and AES. The chemical composition of solution used was (NaCl 0.5%, 0.1% lactic acid, 0.1% urea) [63].

**Table 8.** Chemical composition of samples [63]

Sample	Elements, wt %				
	Ni	Cu	Zn	Tn	Fe
B48 (A)	2	83	10	5	-
Nickel Silver (B)	23	62.5	12	2.5	-
Monel Metal (c)	66	32	-	-	2



The Colin et al results, showed that the percentage of oxidation of Cu-Ni alloys decreased by increasing Ni content, and there was no zinc in the analyzed oxidation layer. The corrosion products of these alloys contained copper (I) chloride (especially when the alloy has a high content of copper). For Ni-based alloys, Ni hydroxide and Ni oxide present on the surface as corrosion product. The results of Colin et al showed that the layer of film formed on the alloys B48 and Nickel Silver contain a small percentage of  $\text{Cu}^{2+}$ , but the percentage of zinc oxide is the most. This mean that a dezincification process was occurred. With the analysis of corrosion film declared that formation of Ni- ( $\text{Ni}(\text{OH})_2$ ;  $\text{NiO}$ ) especially in Ni-rich alloys. Colin et al ensured that with increase of concentration of Cu metal in alloys increase the thickness of the corrosion film. The research of Colin et al [63] focused only on the analysis of the surface of the surface of these alloys and did not confirm with other analytical.

In 2003, Fournier et al [64] were interested in the studying of metallic impurities (Ni, Zn, and Cu) on human hands resulted from handling of Francs and Euro coins. Their appearance and composition appear in Table 9. Leaching and manipulations are two different techniques were used to investigate these impurities.

**Table 9.** Composition of Francs and Euro coins [64]

Denomination	Appearance	Composition (wt.%)
Francs' coins		
Francs	Yellow outer ring and white in center	Ring: Al-Bronze Cu 92%, Al 6%, Ni 2% Centre: Pure Ni
10 F	White	Pure Ni
0.50 F; 1 F; 2 F; 5 F	Yellow	Al-Bronze Cu 92%, Al 6%, Ni 2%
Euro coins		
One	Yellow outer ring and white in center	Ring: Ni-brass Cu 75%, Zn 20%, Ni 5% Centre: Cu 75%, Ni 25%
Two	white outer ring and yellow in center	Ring: Cu 75%, Ni 25% Centre: Cu 75%, Zn 20%, Ni 5%
10 ct; 20 ct; 50 ct	Yellow	Nordic-gold Cu 89%, Al 5%, Zn 5%, Sn 1%
1 ct; 2 ct; 5 ct	Red	Cu- plated steel

Leaching method used a solution of HCl or NaOH. Fournier et al [64] immersed Coins in that solution for a specific period. Fournier et al [64] analyzed the ions, which released in the solution. Manipulation method presented a simulation of real situation of the coins as a sum of volunteers handled the coins. The time of handling from 2 to 3 s before handled to each volunteer. Fournier et al [64] results shows that Cu released was faster than that of Ni and Zn while the last two ions were released in equal amounts.

Fournier et al [64] collected three groups of 2 Franc coins for several years and another set of 2 Euro coins manipulated for 2-5 months. The first and second groups consisted of 58 coins each. They



were immersed in 5 to 6 flasks filled with 100 mL of demineralized water, then they placed in ultrasonic bath for 10 min. Samples left in air to dry then they washed. The third group consisted of 58 coins prepared to have a final shiny polish. Volunteers manipulated of coins. The fingers of every volunteer were rubbed well with fiber wipe. Fournier immersed the wipe in 100 mL of HCl solution at room temperature for 24 hr, after that they measure the concentration of ions in solution. The result of their tests summarized in Table 10.

**Table 10.** Released ions from 2 Franc and 2 Euro coins [64]

Released ions (µg/mL)	2F coins state			2 Euro coins state		
	Un washed	washed	Polished	Un washed	Washed	Polished
Ni	0.38 ± 0.1	0.46± 0.16	0.009± 0.004	0.23± 0.06	0.26± 0.07	0.012± 0.006
Cu	0.44± 0.1	0.2± 0.07	0.013± 0.004	1.4± 0.2	1.3± 0.2	0.10± 0.01
Zn	0.14± 0.03	0.12± 0.04	0.012± 0.003	0.26± 0.03	0.28± 0.05	0.02± 0.03

Table 10 shows that the rinsing process of coins before handled coins had significant effect on the results. Fournier et al [64] showed that the friction of coins between hands is the main reason that cause allergy and transfer pre-existing ions that found surface of metal coins.

In 2004, Nucera et al [53] were interested in studying nickel allergy on humans, especially from coins of 1 and 2 Euro; 1,2- and 50-Euro cent; 100 and 500 Italian lire coins. The composition of these coins used is in their work shown in Table 11. Table 12 shows a patch test on 25 patients (8 men and 17 women) with different age range (16-72 old) found that 19 patients had more allergies.

Nucera et al [53] showed that the ASS is much stronger than the water on the surface of the coins. Especially the Ni element, because the percentage of Ni ions released increased significantly. They proved the theory after studying the effect of the sweat solution on two metal coins one and two Euro. The percentage of Ni-released was in ranges between 23.2–65.1 µg/cm<sup>2</sup>/week. The alloy Cu-Ni (75/25) immersed the largest amount. Nucera et al [53] recommended that the only solution to avoid dermatitis resulting from coin handling.

**Table 11.** Composition of coins used in Nucera et al work [53]

Sample	Composition
Euro coins	
1 cent	Cu-plated Fe
2 cent	Cu-plated Fe
50 cent	(Cu 89%, Al 5%, Zn 5%, Sn 1%)

One Euro	Core: Cu 75%, Ni 25%, Ring: Cu 75%, Zn 20%, Ni 5%
Two Euro	Core: Cu 75%, Zn 20%, Ni 5%, Ring: Cu 75%, Ni 25%
Italian lire coins	
100	Fe 81.5%, Cr 18.5%
500	Core: Cu 92%, Al 6%, Ni 2%, Ring: Fe 81.5%, Cr 18.5%

**Table 12.** Classification of allergy sensitivity result according of ICDR<sup>a</sup> [53]

Reaction	Sensitivity degree		
	1	2	3
1 cent	4%	-	-
2 cent	4%	-	-
50 cent	16%	-	-
One Euro	28%	44%	4%
Two Euro	28%	24%	24%
100 Lire	-	-	-
500 Lire	40%	4%	8%

<sup>a</sup> International Contact Dermatitis Research Group

In 2007, Milošev and Kosec [25] were interested in studying Cu-18 Ni-20 Zn alloy which is known commercially copper silver alloy and commonly used as base metal for jewelry. This alloy was studied in ASS for 30 days. The Ni ions released by this group was confirmed by atomic absorption technique. The alloy surface analyzed by XPS techniques. Moreover, electrochemical techniques were used to support the results [25]. From Table 13, notice that the amount of released ions were much higher when this alloy immersed in ASS compared to its immersion in Ringer's solution. It was 14.5 higher for Cu, around 7 time higher for Ni, and around 14.8 higher for Zn.

**Table 13.** The ions released in ASS and Ringer's solution in Milošev's work [25]

Solution	Ions release ( $\mu\text{g}/\text{cm}^2/\text{week}$ )		
	Cu	Ni	Zn
ASS	145	269	133
Ringer solution	10	38	9

Milošev and Kosec [25] monitored the concentration of Ni ions released in solution for 30 days. The Ni ions released was rapid in the first days of immersion then it started to slow down. After the 30 days of immersion in ASS, the surface analyzed by XPS showed that the percentages of C and O ions in corrosion product were higher than the main ions of alloy (Cu, Ni and Zn). The small percent of Cl<sup>-</sup> ion ensure that oxide film formation was from Zn, Ni, and Cu.

In 2010, Rathish et al [18] were interested to study the corrosion behavior for three different metals. The three metals tested were mild steel, galvanized steel and 316L SS in ASS at according to

ISO 3160-2. Rathish et al [18] used the electrochemical techniques in the studying. Table 14 shows polarization parameters obtained from these three samples. Rathish et al showed that SS 316L is a better to making things which direct contact with skin [18].

**Table 14.** Potentiodynamic polarization results for three ferrous samples [18]

Metal	$-E_{\text{corr}}$ (mV)	$\beta_a$ (mV/dec)	$\beta_c$ (mV/dec)	$J_{\text{corr}}$ (A/cm <sup>2</sup> )
Mild steel	704	89	328	$181 \times 10^{-6}$
Galvanized steel	412	126	128	$877 \times 10^{-9}$
SS 316L	443	665	134	$1224 \times 10^{-8}$

In 2011, Song and Hong [65] were interested in finding a suitable alternative alloys for Cu-Ni (75/25) alloy coin. Alternative alloys suit same operating conditions, mechanical, physical and chemical properties. Song and Hong [65] measured the hardness of four alloys as shown in Table 15. The strength of these alloys showed that the use of Cr element in these alloys resulted in increase in hardness, strength and therefore wear resistance. With respect to the cost of materials, the alloy making with high percentage of Cu and low percentage of Ni is less cost than the alloy Cu-Ni (72/25).

**Table 15.** Hardness of alloys [65]

Alloy's composition (wt. %)	Hardness (Hv)
Cu-Zn-Ni-Fe (65/18.5/15/1.5)	111
Cu-Zn-Ni-Fe-Cr (64.8/18.5/15/1.5 /0.2)	126
Cu-Zn-Ni-Fe (60.5/25.5/12/2)	138
Cu-base Zn-Ni-Fe-Cr (25.5/12/2.0/0.26)	150

Song and Hong showed the price of metals Cu, Ni, Zn in\$/ton which was 8309, 23,405 and 2489 respectively [65]. Song and Hong could calculate the cost of new alloys as appeared in Table 16. The alloy Cu base-Zn-Ni (25.5-12) saving approximate 30% when compared to Cu-Ni (75/25).

**Table 16.** Material cost of alloys per ton [65]

Alloy	Material cost per ton (US \$)
Cu-Ni (75/25)	12,080
Cu base-Zn-Ni (18.5/15)	9372
Cu base-Zn-Ni (25.5-12)	8512

The work of Song and Hong did not include any allergic studies or any information concerning the release of ions in the environment. Their evaluation of new alloy depended only on mechanical, optical properties and economical studying [65].

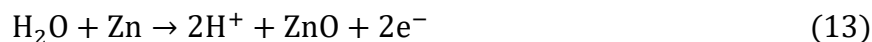
In 2012, Chen et al [40] designed a new copper-based alloy ((wt %) 74.2 Cu, 0.8 Al, 0.5 Ni, 0.3 Me, 0.1 Re, balanced Zn). They compared the alloy with the alloy that used in china for manufacturing coinage materials through corrosion resistance in 3.5% NaCl solution. Chen et al [40] used WL technique, electrochemical tests and (SEM and EDX) to characterize the corrosion products on the surface. The results showed that this new alloy has an average of corrosion rate of 0.01304 mm/y as examined by WL technique. This rate is considered much less than of H7211 alloy (0.04664 mm/y). The result gained from WL technique was confirmed by potentiodynamic polarization technique. The corrosion product formed after 8 days of immersion was O and Cl, their amount were less. Those formed after 30 days of immersion, as anticipated. This may be attributed to the cathodic reaction presented in Eq.11 and the contribution of Cl ions from the NaCl.



Then anodic and film formation reactions Eqs. 12 and 13:



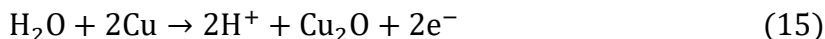
Or



and Cu formed  $\text{Cu}_2\text{O}$  [88] as shown in Eqs 14 and 15:



Or



Then after oxide films of Zn and Cu covered the surface, the Cu(I) chloride appeared on the surface as indicated in reaction Eq. 16:



In 2013, Julander et al [19] were interested in studying the effect of amount of released Ni-ions precipitation onto the skin during circulation of Ni-plated coins. After their immersion for an hour in artificial sweat, they found that the amount of Ni released from Ni-plated coins was  $7.5 \mu\text{g}/\text{cm}^2$ . This mean that Ni-ions released of Ni-plated coins were larger four folds than from Cupro-Ni coins. Julander et al showed that the initial Ni release rates  $>$ Ni released after one week of immersion (10–27 times). They also confirmed that people handled Ni-alloy in a short time were constantly more susceptible to injury. The comparison between Ni-plated coins and cupronickel coins showed that Ni deposition of Ni-plated is the highest level of nickel onto skin. Consequently the risk of allergy, which in turn means that the danger of handling Ni-plated is more increased than handling of cupronickel alloy coins. They also indicated that the study of Ni deposition in ASS for one week is not enough time to compute the circulation risk of items with high Ni content that come into people handled Ni alloys in short time [19].

In 2015, Liang et al [66] were interested in studying the behavior of brass alloy (70% Cu, 30% Zn), which commonly used in coinage manufacturing. In their work, they studied ASS that has four different compositions as provided in Table 17.

**Table 17.** Chemical composition of ASS at pH 6.5 according to Liang et al [66]

Solution No.	Solution composition
1	NaCl 5 g/L, Urea 1 g/L, Lactic acid 1 g/L
2	NaCl 5/L, Lactic acid 1 g/L
3	Urea 1 g/L, Lactic acid 1 g/L
4	NaCl 5 g/L.

Liang et al [66], after samples were immersed for 28 days, interesting phenomenon appeared which the formation of Zn-coated samples resulted from dezincification process. This was accompanied by pitting corrosion, which was attributed to the presence of chloride ions (Cl<sup>-</sup>) that accelerates the anodic reaction. Liang et al [66] expected that lactic acid and NaOH are the main species contributed in corrosion process while urea had little effect. They analyzed the corrosion products on surface, which were Cu (II) chloride hydroxide, Cu (I) oxide and urea with Cu<sup>2+</sup>. Liang et al did not mention their sample geometry details and limited their study for 28 days only.

Elzohry et.al [11] discusses the corrosion behavior of the Egyptian coins alloys in ASS by WL and electrochemical (open circuit and potentiodynamic polarization) techniques up to 7 days. WL of the minted coins after 7 days indicated that the 25P Egyptian coins were rapidly corroded in comparison to 50P Egyptian coins. The atomic absorption spectroscopy after 7 days for minted coins cleared that the released Ni-ions concentration from the minted 25P Egyptian coins exceed the safe limit of Ni release. OCP showed clearly a possibility of the formation of oxide film on the surface of 25P and 50P coins thus 25P coins are more active than 50P coins in ASS. Potentiodynamic polarization indicated that  $I_{corr}$  values increased which was attributed to the specific dissolution of Zn for 50P coins (dezincification). The specific wear rate of the corroded minted coins demonstrated that the 50P Egyptian coins was about 3 times larger than that of 25P Egyptian coins. The surface morphology of these coins after immersion in ASS followed by wear showed that increasing the immersion time, there was a consequent increase in the depth of the scratching of the two types of coins.

#### 4. CONCLUSION

The review focus on the effect of the artificial sweat solution (ASS) on the coin materials and time of circulation. Coins were investigated in artificial sweat solution (ASS) by chemical and electrochemical techniques in different times. The corrosion behavior were investigated by using WL method, polarization test, open circuit, impedance and atomic-absorption spectroscopy which showed the concentration of ions released in the solution. The surface morphology for the coins before and after immersion in ASS were characterized by using OM, SEM/EDX analysis. The results were confirmed by electrolytic solution analysis, which was taken periodically from ASS while the coins were immersed in

the ASS by atomic absorption spectroscopy. The phase identification of the coins after immersed were analysis. The specific wear rate of the coins were also studied.

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