The influence of gaseous pollutants in silver artifacts tarnishing.

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Abstract:
The present work aims to study the effect of the common gaseous pollutants on silver artifacts corrosion. The study will be carried out manufactured coupons of silver alloy (91 silver, 9 copper) which have chemical composition similarly to ancient Egyptian silver artifacts. These coupons will be exposed to gaseous pollutants of each individual gas; such as Sulfur dioxide, Nitrogen dioxide, Carbon dioxide, Hydrogen sulfide and Chlorine. The exposure period will be four weeks in a climate chamber with gas concentration 10 PPM. After test Examinations by SEM and PM were used to evaluate the effect of each gas and description the morphology of the corrosion layers. Results revealed that all gases reacted with the surface except carbon dioxide. Formed tarnishing layers varied in coverage and density rate. Corrosion products are analyzed by XRD and results were revealed Ag$_2$S, AgCl, Ag$_2$SO$_4$ and Ag$_2$O as corrosion products.

Key-Words: - Silver, artifacts, atmospheric corrosion, gaseous pollutants.

1 Introduction
Archaeological silver and its alloys have relatively high resistance to corrosion products in the atmospheric environment compared to copper and iron objects. But in the presence of humidity and gaseous pollutants - special Sulphur containing pollutants - Silver is susceptible to tarnish and deterioration occurs. Many corrosion products such as Ag$_2$S, Ag$_2$SO$_4$ and AgCl, have been identified on silver objects either in museum environment (displayed in cabinets and stored in depositories) or extracted from the burial environment. Silver objects corrosion in the atmospheric environmental attributed to the water layers on the surface which provide the reaction of atmospheric gases ionic such as chloride anions, sulphates, carbonates and organics with metallic surface and lead to the metal dissolution [20].

Among the family of ancient metals, the fewest studies on the laboratory and field exposure of the gaseous pollutants were presented to silver. Previous lab exposure tests often focused on silver tarnish due to Sulphur containing pollutants [1-6] these Studies have been agreed in their results which can be summarized in the formation of silver tarnish as black layer consisting of Ag$_2$S as major corrosion product and Ag$_2$SO$_4$ in a negligible quantity. Few lab exposure studies have been presented to impact other gaseous pollutants such as Cl, NO$_2$, and CO$_2$ but results were different and varied. The differences were as follow:

Results of Previous studies indicated that nitrogen dioxide is not considered a corrosion factor of silver because silver does not react with it, but it only acts as an accelerated factor of silver tarnish [7, 8, 9, 10, 11] even though Previous study was found silver nitrate Ag$_2$NO$_3$ as corrosion products in tarnish film of exposed silver to 1.2 ppm NO$_2$ for 40 hours [1]. Also Ag$_2$SO$_4$ as corrosion product was observed on silver coupons in field exposure [12] although the studies indicated that Silver sulfate (Ag$_2$SO$_4$) forms only in artificially high levels of sulfur dioxide [9, 11, 13, 14].

Silver is sensitive to chloride (Cl$^-$) and silver chloride will be formed as a result of the interaction [15, 10, 11, 14, 7, 9, 16]. Also this does not agree with results revealed that silver chloride compound was not identified on surface film of silver coupons after Exposure in an ASTM B117 salt spray chamber [17] and this compatibility with previous studies mentioned that silver does not react directly with chlorine gas and the presence of silver chloride as corrosion product due to burial in a chloride rich environment [18, 19].
Although Ag₂CO₃ is distinguished as corrosion product of silver as result of the interaction with CO₂, and although CO₂ is abundant in the ambient environment of silver artifacts, however - to our knowledge - did not presented lab. Exposure study of CO₂ with silver. Also Ag₂CO₃ has not been detected as corrosion product on the silver artifacts. Ag₂CO₃ was identified one year ago in field-exposure study on the Ag coupons exposed to various outdoor environments and the compound was detected only in one site which distinguished above the temperature inversion layer [20], So Very little is known about the formation mechanism of Ag₂CO₃ Such as it is expected only in strong alkaline solutions [21].

Therefore, in this study, the effects of gases (NO₂, Cl, CO₃) on silver will be presented as a laboratory exposure and compared with previous studies. Also they did not take sufficient laboratory studies although they were common gaseous pollutants in outdoor and indoor atmospheric environment, also hydrogen sulfide and sulfur dioxide were chosen as main gases in silver tarnish and lead to silver sulfide which was often observed as corrosion product of silver.

2. Experimental procedures:


Silver coupons should be similar for archaeological silver of ancient Egypt civilization, different concentrations were found in Ancient Egyptian Silver, elemental analysis of a number of Egyptian silver artefacts was showed that 10 objects concentration between 83 to 90%, and 19 objects of silver ratio ranged from 90 to 95% [22, 23]. Also analysis of Babylonian coins from silver copper alloy were about 87–90% purity [21]. So that a composition of coupons was Ag 89.4% and Cu 10.5%. This concentration was not artificial available and was manufactured by alloying a mixture of silver (pieces from the pure silver) with pure copper pieces. The coupons were made by direct addition of silver and copper in a crucible [24]. fig. 1. The dimensions were (3 cm × 5 cm × 0.08 cm) Fig. 2. XRF analysis used to determine the Composition as in fig. 3.

Thin thickness of coupons about 8 m will be suitable and similar to silver artifacts thickness, because most the silver artefacts were manufactured to thin sheets whether by cold-working or casting in moulds such as thin sheets for royal garments, hollow statues, jewellery items, funeral items, Household items of everyday life such as, spoons, jugs, cups, vessels, pots, covered wooden object, bowls and Other usages, so that Successive processes of hammering and ductility with the annealing on alloy rod to obtain thin thickness about .8 m. five new coupons were used For each gas test, a hole was drilled in each sample for suspension in the chamber middle [21].

2.2. Design and Preparation of climate chamber test.

Climate chamber was designed according to ASTM [45]. It is made of 1000 cm diameter Perspex cylinder. The humidity was controlled gradually by the cup of saturated salt solution inside the chamber, the approximately 85%RH was obtained by a saturated solution of potassium chloride [46] and the chamber was only opened to remove coupons. Heating of the air inside the chamber is done by a cartridge heater, the air inside the chamber is continuously mixed by a fan, which was suspended from the ceiling of the chamber, the temperature and relative humidity inside the chamber are continuously measured by dataloger device [47, 48].

A few studies were presented on the silver deterioration tests inside climate chamber, these studies used two types of the deterioration factors: high relative humidity [9, 44] and gaseous pollutants in presence relative humidity [25, 44, 1]. Most studies of silver deterioration were used corrosive solutions as deterioration factors, such as BaS 5 g/l solution for 24 Hours [18] and Na₂S were used as the tarnishing solution [9, 50]. Acetic acid solutions were used as simulation of emissions vapors in wooden cabinets and CuCl₂ 50 g/l for 20 min, and NaCl [50] were used of AgCl silver patina [18].

2.3. The test gases.

The gases for the test were as follows: Sulfur dioxide SO₂, Nitrogen dioxide NO₂, Carbon dioxide CO₂, Chlorine gas Cl and Hydrogen Sulphide H₂S. Those types were the most influence in deterioration of silver artefacts.

2.4. Test procedures.

Each five coupons were exposed to humidified air containing concentration 10 ppm of one gas only. The values of other factors were chosen after surveying 29 previous studies which considered lab exposure of ancient metals family (copper, bronze, silver, steel and lead) as shown in table 1. Their most experiments were performed at room temperature (22 - 25 C), and relative humidity between 80 - 90. There are the other two factors such as:
The gases concentration and the exposure period which were varied from study to another. So accelerated conditions parameters were as shown in table 2.

Cylinders 99.9 % concentration were used to obtain of CO$_2$, SO$_2$ and NO$_2$ gases, The gas flowed from cylinder into the exposure chamber after the calculation of flow and time of the required concentration. H$_2$S and Cl$^-$ were prepared in lab, H$_2$S prepared by the reaction of hydrochloric acid diluted with ferrous sulfide (equation 1) [51] and Cl$^-$ prepared by the interaction of concentrated Cl$^-$ with manganese dioxide (equation 2) [52]. According to the law of Avogadro and Lussac can be calculated Volume which the required concentration of H$_2$S and Cl$^-$ inside the chamber is occupied. Where Molecular weight (one mole) of any gas under standard conditions is occupied 22400 ml (the molar volume, equation 3) [53].

*And by the calculated of molecular weight to H$_2$S equation (4) which occupied 22400 ml can be calculated volume of the required concentration of H$_2$S equation (5).*

$$
\text{FeS} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2\text{S} \quad (1)
$$

$$
4 \text{HCl} + \text{MnO}_2 \rightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \quad (2)
$$

1 mole of a gas at STP = 22.4 liters of a gas \quad (3)

$$
2X1+32 = 34g = 22400 \text{ ml} \quad (4)
$$

$$
\text{ppm} \left(19 \text{ mg/m}^3\right) = X \text{ ml} \quad (5)
$$

Gas syringe was used to get the required volume and injected it into inside chamber fig (4), the fan was used for mixing gases and its distribution inside the chamber.
Table 1. Summarizes lap exposure conditions to gaseous pollutants with ancient metals in the previous studies.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Gas</th>
<th>time</th>
<th>Concentration</th>
<th>C</th>
<th>RH</th>
<th>Coupons</th>
</tr>
</thead>
<tbody>
<tr>
<td>[25]</td>
<td>(OCS), H₂S, (SO₂)</td>
<td>5 week</td>
<td>2.5 – 0.26 ppm</td>
<td>22</td>
<td>50</td>
<td>Silver</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.66 - 3.64 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[26]</td>
<td>SO₂, NO₂</td>
<td>30 hours</td>
<td>10–22 ppm, 1.8 ppm</td>
<td>25°C</td>
<td>80–90%</td>
<td>Tin</td>
</tr>
<tr>
<td>[27]</td>
<td>H₂S</td>
<td>22-77 days</td>
<td>50ppb, 2ppm</td>
<td>10,</td>
<td>30, 80, 40 %</td>
<td>Copper</td>
</tr>
<tr>
<td>[28]</td>
<td>(SO₂+NO₂)</td>
<td></td>
<td>75 ppb SO₂ + 120 ppb NO₂</td>
<td></td>
<td></td>
<td>Copper</td>
</tr>
<tr>
<td>[29]</td>
<td>Acetic and formic acid</td>
<td>One, two</td>
<td>formic acid 160 ppb, acetic</td>
<td>22°C</td>
<td>95%</td>
<td>lead</td>
</tr>
<tr>
<td></td>
<td>acid vapors</td>
<td>and four</td>
<td>acid, 170 ppb, CO₂ 350 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>weeks.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[30]</td>
<td>H₂S, NO₂, Cl₂</td>
<td>4, 10 days</td>
<td>10, 200, 10 ppb</td>
<td>30°C</td>
<td>70%</td>
<td>Copper</td>
</tr>
<tr>
<td>[31]</td>
<td>Mixture of NO₂, SO₂, O₃</td>
<td></td>
<td>200 ppb SO₂, 200 ppb O₃, NO₂ ppb</td>
<td>25°C</td>
<td>80%</td>
<td>Copper</td>
</tr>
<tr>
<td>[32]</td>
<td>Vapor HNO₃</td>
<td>7 days</td>
<td>325 μg/ m³</td>
<td>25°C</td>
<td>65%</td>
<td>Copper</td>
</tr>
<tr>
<td>[33]</td>
<td>Mixture of SO₂, H₂S</td>
<td></td>
<td>SO₂ 75 ppb, H₂S 50 ppb</td>
<td>25°C</td>
<td>75%</td>
<td>Copper</td>
</tr>
<tr>
<td>[34]</td>
<td>Mixture of SO₂, NO₂</td>
<td>10, 30, 60</td>
<td>SO₂ 75 ppb, NO₂ 120 ppb</td>
<td>25°C</td>
<td>75%</td>
<td>Copper</td>
</tr>
<tr>
<td></td>
<td>hour</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[35]</td>
<td>Formaldehyde, Acetic and</td>
<td>135 days</td>
<td>0.04, 0.4, 4, ppmv</td>
<td>25°C</td>
<td>54.75%</td>
<td>Copper, lead</td>
</tr>
<tr>
<td></td>
<td>formic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[36]</td>
<td>formic and acetic acid</td>
<td>21 days.</td>
<td>(10, 50, 100, 200 and 300 ppm)</td>
<td>30°C</td>
<td>100%</td>
<td>Copper</td>
</tr>
<tr>
<td>[37]</td>
<td>HNO₃</td>
<td>2 weeks</td>
<td>(126 ppb)</td>
<td>25</td>
<td>65%</td>
<td>copper, zinc and steel</td>
</tr>
<tr>
<td>[38]</td>
<td>NO₂, NO₂+ SO₂</td>
<td>2 weeks</td>
<td>(800 μg/m³), (800 μg/m³ +800 μg/m-²)</td>
<td>30°C</td>
<td>90%</td>
<td>Zinc</td>
</tr>
<tr>
<td>[39]</td>
<td>SO₂</td>
<td>- 4 week</td>
<td>(10 ppm)</td>
<td>25</td>
<td>90%</td>
<td>copper</td>
</tr>
<tr>
<td>[40]</td>
<td>SO₂+O₃</td>
<td>- 4 week</td>
<td>(476 ppb + 500 ppb)</td>
<td>30</td>
<td>70%</td>
<td>Copper</td>
</tr>
<tr>
<td>[41]</td>
<td>NO₂+ SO₂</td>
<td>- 4 week</td>
<td>(200 + 3000 ppb)</td>
<td>25</td>
<td>90%</td>
<td>Steel</td>
</tr>
<tr>
<td>[42]</td>
<td>H₂S</td>
<td>- 4 week</td>
<td>(50-200 ppb)</td>
<td>25</td>
<td>80%</td>
<td>Copper</td>
</tr>
</tbody>
</table>
Table 2. Conditions and procedures of the test.

<table>
<thead>
<tr>
<th>Period</th>
<th>T</th>
<th>RH</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 weeks</td>
<td>25</td>
<td>85%</td>
<td>10 ppm</td>
</tr>
</tbody>
</table>

3. Results and discussion.

3.1. Examination of the samples after the test.

The Coupons were examined after each test by Visual examination, Polarizing Microscope and Scanning Electron Microscope to identify the morphology and composition of the formed layer and evaluate the interaction between the coupons surface and the test gases. The investigation revealed that all the coupons surfaces interacted with the gases from the first week except the exposed coupons to carbon dioxide. The reaction began as a very thin layer on the surface, and the surface appearance turned from light interference tones to a grey and, finally, black film. Also the tarnishing rate was increased with H$_2$S, Cl, decreased with SO$_2$, NO$_2$.

3.2. The analysis of corrosion products by x-ray diffraction.

The coupons were exposed to x-ray diffraction to analyze the formed patina. This was showed many of corrosion products as in Fig. 7. Silver sulfide (Ag$_2$S Acanthite): they were identified as abundant on silver artifacts. The reaction behavior between gas H$_2$S and the silver surface to form these products explains equations (6, 7).

\[
4\text{Ag} + \text{O}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{Ag}_2\text{S} + 2\text{H}_2\text{O} \quad [54, 55] \quad (6)
\]

\[
2\text{Ag} + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + \text{H} \quad [24] \quad (7)
\]

Silver chloride (AgCl Cerargyrite, chlorargyrite): In this case, the dominant theory in the interpretation of formation mechanism of chloroargyrite AgCl is the transformation of Ag$_2$O to AgCl as equation (8) [12, 15].

\[
\text{Ag}_2\text{O} + 2\text{Cl}^- + \text{H}_2\text{O} \rightarrow 2\text{AgCl} + 2\text{OH}^- \quad [12] \quad (8)
\]
Fig. 5. The coupons after the test, (a) the coupons exposed of H$_2$S, (b) the coupons exposed of Cl, (c) the coupons exposed of SO$_2$, (d) the coupons exposed of NO$_2$, (e) the coupons exposed of CO$_2$. 

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Silver sulfite \((\text{Ag}_2\text{SO}_4)\): This product was identified in a previous study as corrosion product of silver 20 and the equations (9-12) were suggested for the mechanism of its formation on silver coupons surface.

\[
\begin{align*}
2\text{Ag} + 2\text{OH} & \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} \quad (9) \\
\text{OH} + \text{SO}_2 & \rightarrow \text{HSO}_3^- \quad (10) \\
\text{Ag}_2\text{O} + \text{HSO}_3^- & \rightarrow \text{Ag}_2\text{SO}_3 + \text{OH}^- \quad (11) \\
\text{Ag}_2\text{SO}_3 & \rightarrow \text{Ag}_2\text{SO}_4 \quad (12)
\end{align*}
\]

Silver oxide \(\text{Ag}_2\text{O}\): Silver artifacts react with oxygen either by the electrochemical reactions in the presence of humidity (equations 13-15) or by chemical reactions in the absence humidity (equation 16). Therefore \(\text{Ag}_2\text{O}\) and \(\text{AgO}\) are formed on silver artifacts surfaces.

\[
\begin{align*}
\text{Ag} & \rightarrow \text{Ag}^+ + e^- \quad (13) \\
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + e^- & \rightarrow 2\text{OH}^- \quad (14) \\
2 \text{Ag}^+ + 2\text{OH} & \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} \quad (15) \\
\text{Ag} + \frac{1}{2} \text{O}_2 & \rightarrow \text{AgO} \quad (16)
\end{align*}
\]

Silver ammine nitrate \((\text{Ag(NO}_3)_2(\text{NO})_3)\): previous studies of filed and lab. exposure were identified only one product \((\text{AgNO}_3)\) from nitrates anions as corrosion products on silver surface. Therefore this compound was expected of \(\text{NO}_2\) gas, but analysis showed Silver ammine nitrate \((\text{Ag(NO}_3)_2(\text{NO})_3)\).

Copper Nitrate Hydroxide (Rouaite, \(\text{Cu}_2(\text{NO}_3)(\text{OH})_3\)): Silver and copper are the coupons alloy elements, the formation of Rouaite corrosion product is contributed to selective corrosion of copper by the interaction of cu (as the main alloying element) with \(\text{NO}_2\) gas.
4 Conclusion
Silver in atmospheric environmental and presence humidity are susceptible to formation of surface tarnishing layer. The tarnishing is formed not only in the presence of Sulphur containing pollutants but also in presence other gaseous such as Cl and NO₂. Except the coupons of CO₂, all the test coupons were exposed to tarnishing layer which was formed on the surface as a blackish thin film caused by the interaction of the metal surface with test pollutants. But highest layer in density and tarnishing was to H₂S gas.

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