Thermodynamic stability of gilded copper and pigments at high relative humidity and at environmental conditions of Lima, Perú

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Abstract. Cultural heritage materials are affected by diverse environmental agents such as humidity, temperature, and pollution. This work focuses on studying the thermodynamic stability of Peruvian heritage materials such as gilded coppers and pigments within two scenarios: one under ambient conditions and the other under accelerated conditions established by the ASTM D 2247 standard. In both cases, the HSC Chemistry 6 software was implemented. The general results obtained for gilded coppers showed that by varying the relative humidity from 75% and 14 ºC to 80% and 26 ºC, the corrosion products move from CuO to Cu(OH)$_2$. In addition, to Cu$_2$Cl(OH)$_3$ -atacamite- in the presence of chlorin. On the other hand, for hematite (Fe$_3$O$_2$), vermillion (HgS), and Minium (Pb$_3$O$_4$) pigments, we found that at ambient conditions, with NO$_2$ and SO$_2$, they give rise to goethite (FeO(OH)), mercury sulfate (HgSO$_4$) and lead nitrate (Pb(NO$_3$)$_2$), respectively. These changes also modify the natural colour of pigments, where goethite gives rise to a brownish red, mercury sulfate is colorless and lead nitrate is white. This paper is a quick theoretical way to understand how cultural heritage materials can physically degrade. Future experiment trials will contribute to set strategies towards the correct management of these heritage collections.

1. Introduction

Deterioration of materials is often promoted in areas with high humidity, temperature, and pollution. In the case of heritage materials, specifically, there is an interest in understanding the mechanisms of deterioration, so that strategies for its conservation can be designed. Examples of heritage materials in Lima, Peru, are gilded copper which compose pre-Hispanic metalwork and pigments, which compose colonial and republican paintings.

The Inca worldview associates the noblest and abundant metals of the central Andes with the main deities of the Andean pantheon, gold with the sun god and silver with the goddess. From very ancient times, a goldsmith's work was developed based on the work of gold, silver, and copper, linked to a long tradition of gilding and silvering techniques that were used and handled to obtain such appreciated tones [1]. These pieces were part of the clothes and attire that expressed and consolidated the power of important rulers and priests as well as part of the objects that made up the ritual scenario. Evidence of this pattern is found in the elite tombs of Dos Cabezas in the Jequetepeque Valley, La Libertad, Perú,
associated to the Moche culture (100 to 600 AD) [1]. At the time of their excavation, the pieces showed an advanced corrosion process that had caused much of their mineralization and disintegration. Recently, Ingo [2] and colleagues pointed out that the corrosion process formed mainly layered structures containing chlorargyrite (AgCl), cuprite (Cu₂O), nantokite (CuCl), and atacamite [CuCl₂·3Cu(OH)₂] polymorphs. In Peru, also exist an important legacy of pictorial works by artists of the Lima painting from the 18th century, as is the case of Cristóbal Lozano. These paintings are currently exhibited in the “Museo de Arte Religioso de la Basílica Catedral” of Lima, where Petrick & Kuon [3] carried out a study to determine the chemical composition of the red pigments used by the painter. They have identified vermilion (HgS), minium (Pb₃O₄), and hematite (Fe₂O₃) based on the portrait of viceroy Antonio Manso de Velasco, Conde de Superunda. These pigments also degrade during their continuous exposure to environmental conditions, altering their color under the action of temperature, humidity, and pollutants [4-6]. Then, considering that these objects are exhibited in some museums in the city, we decided to perform the present research work, simulating the fluctuating environmental conditions of Lima and their accelerated attack at 100 % of relative humidity (RH).

2. Description of study scenarios and simulation procedure
The objects studied in the case of gilded coppers were selected according to their nature; a sample that simulated a traditional tumbaga sheet [7] and another with evidence of attack by atacamite (Figure 1). This last piece obtained from an exhibition object from Dos Cabezas, Jequetepeque Valley, which corresponds to an embossed and pierced gilt copper sheet. In the case of the red pigments, we selected those identified by Petrick and Kuon [3] in Figure 2: vermilion (HgS), minimum (Pb₃O₄) and hematite (Fe₂O₃).

Table 1 summarizes the input data implemented in the HSC Chemistry 6 software [8] for the two studied scenarios: Lima environmental conditions [9,10] and accelerated conditions described by the ASTM D 2247 standard [11]. As a result, the thermodynamic equilibrium was obtained for the Lima environmental conditions -fluctuating variables- and the phase stability diagrams for the accelerated conditions -fixed variables.
Regarding the found limitations, it is important to highlight that information regarding the concentration of contaminants indoors in the city of Lima, Perú, is scarce and it cannot be assumed as the real conditions where heritage objects are exhibited or stored. Besides, an estimation of a 1000:1 molar ratio to correlate the thermodynamic equilibrium between the environment and the substrate, respectively [12,13]. Furthermore, the obtained results are limited to the interfacial region between the environment and the sample, deeper zones within the substrates respond to different equilibrium conditions.

### Table 1. Simulation conditions implemented in the software HSC Chemistry 6.

|                | Composition (%wt) | Accelerated conditions<sup>c</sup> | Environmental conditions<sup>d</sup> |
|----------------|-------------------|-------------------------------------|--------------------------------------|
|                |                   |                                     | High humidity (RH (%mol)) | Low humidity (RH (%mol)) |
|                |                   | Air saturated with water vapor at 38 ºC (%mol): | Air at 26 ºC and 80%RH | Air at 14 ºC and 75%RH |
| Gilded Coppers | 87 Cu, 10 Au, 3 Ag | 68.9 N<sub>2</sub>, 21.0 O<sub>2</sub> | 73.2 N<sub>2</sub>, 74.7 N<sub>2</sub> | 71.0 O<sub>2</sub>, 1.2 H<sub>2</sub>O |
| Tumbaga<sup>a</sup> | 75.1 Cu, 3.5 Au, 0.9 Ag | 7.0 H<sub>2</sub>O, 3.0 CO<sub>2</sub> | 3.9 · 10<sup>-4</sup> SO<sub>2</sub>, 3.9 · 10<sup>-4</sup> NO<sub>2</sub> | 4.3 · 10<sup>-4</sup> SO<sub>2</sub>, 4.3 · 10<sup>-4</sup> NO<sub>2</sub> |
| Dos Cabezas<sup>b</sup> | 100 HgS, 100 PbO<sub>2</sub>, 100 Fe<sub>2</sub>O<sub>3</sub> | 1.2 H<sub>2</sub>O | 3.9 · 10<sup>-4</sup> NO<sub>2</sub> | 3.9 · 10<sup>-4</sup> NO<sub>2</sub> |

<sup>a</sup> Taken from Lechtman, et al. [7].
<sup>b</sup> Obtained by SEM-EDS analysis.
<sup>c</sup> Taken from the psychrometric chart at ASTM D 2247 conditions [11].
<sup>d</sup> Taken from the psychrometric chart and from references [9], [10].

### 3. Results and discussion

#### 3.1. Gilded objects

The thermodynamic equilibrium results obtained at the environmental conditions showed similar tendencies for tumbaga and Dos Cabezas (DC) gilded sheets (Figure 3 and Figure 4). The behavior obtained for both pieces allows us to deduce that for low humidity values and temperatures above 18 ºC more stable compounds are produced (CuO).

![Figure 3. Stability phase diagram for the gilded coppers at 38 ºC in air saturated with water vapors. The green point indicates our study conditions.](image-url)
Figure 4(a) shows the thermodynamic equilibrium for the high tumbaga piece and Figure 4(b) shows this same tumbaga piece at low humidity. Figure 4(c) shows the piece at Dos Cabezas and Figure 4(d) shows the low humidity within the ambient conditions of Lima, Perú. Each chemical agent has the color corresponding to the actual compound.

This claim is based on the instability of copper hydroxide (II) since it has the possibility of reacting with CO$_2$ and Cl salts in the environment to give rise to malachite and atacamite [14,15]. This last compound is catalogued as the cause of the accelerated mineralization of gilded pieces. Namely, atacamite generates a type of continuous corrosion that takes advantage of the humidity of the environment to grow while the substrate is consumed [14,15].

On the other hand, under accelerated corrosion conditions, similar results were obtained, except for the formation of silver oxide (IV). However, this result skips the participation of CO$_2$, which alters the equilibrium to generate AgCO$_3$. This phase stability diagram is read considering the following values established from the study conditions: pO$_2 = 2.1 \cdot 10^{-1}$, pH$_2$O = $7.0 \cdot 10^{-2}$, pN$_2 = 6.9 \cdot 10^{-1}$, and pS$_2 = 1 \cdot 10^{-36}$.

3.2. Pigments

The results of thermodynamic equilibrium for pigments led to simpler graphs (Figure 5 and Figure 6). Hematite proved to be a predominant pigment under Lima's environmental conditions. Nevertheless, Figure 5 shows that as humidity increases the presence of goethite increases, changing the original pigment color to a more brownish red.

In the case of vermilion and minimum pigments, we found that their stability depended more on the air pollutants than on the humidity and temperature variables. These compounds gave rise to mercury
(II) sulphate and lead nitrate (II), which are colorless and white, respectively. The equilibrium graphs described for these last compounds were omitted in the study due to their invariability.

\[
\text{Fe}_2\text{O}_3 \text{ Low Humidity} \quad \text{Fe}_2\text{O}_3 \text{ High Humidity} \\
\text{FeO(OH) High Humidity} \quad \text{FeO(OH) Low Humidity}
\]

**Figure 5.** Thermodynamic equilibrium for hematite and goethite when experiencing the fluctuating environmental conditions of Lima, Perú. Each chemical agent has the color corresponding to the actual compound.

**Figure 6.** Stability phase diagram for the studied pigments at 38 °C in air saturated with water vapors. The different points indicate our study conditions.

On the other hand, under accelerated corrosion conditions, the phase stability diagram indicated the same trend for minimum and vermilion while hematite was finally displaced by goethite (Figure 6). Similar results have been published by other authors, pointing out that high percentages of humidity in the environment tend to degrade hematite [6], whiten minimum [5] and destabilize vermilion [4]. Therefore, as a general premise, it was obtained that red pigments require low humidity and the absence of contaminants for their correct conservation.
4. Conclusions
This research work assesses the deterioration of gilded coppers and pigments belonging to the historical heritage of Peru through the simulation of Lima's environmental conditions and air-saturated at 100% of relative humidity. The HCS Chemistry 6 software led us to conclude that when displacing the equilibrium stability from 75% RH and 14°C to 80% RH and 26°C, diverse corrosion products can be favored. Copper compounds shift from Cu(OH)$_2$ to CuO when decreasing humidity and increasing temperatures. Furthermore, pieces with Cl gave place to atacamite [Cu$_2$Cl(OH)$_3$], which cause the well-known bronze disease phenomena. In the case of pigments, hematite -Fe$_2$O$_3$-, vermilion -HgS-, and minimum -Pb$_3$O$_4$- showed new phases when reaching the thermodynamic stability, forming goethite -FeO(OH) -, mercury sulfate (II) -HgSO$_4$-, and lead nitrate (II) -Pb(NO)$_3$-, respectively. Consequently, red pigments changed their hue or intensity as they deteriorate. Meanwhile, vermilion, and minimum pigments proved to be more sensitive to environmental pollutants than to temperature and humidity variables. As a general recommendation, according to the results obtained, we propose to control the presence of pollutants and the use of low humidity in the exhibition or storage environments to contribute to the conservation of these historical pieces. These results highlight the importance of the correct management of Peruvian heritage collections. In future studies, experiments will be carried out to validate the obtained results. Besides, we will consider the effect of other pollutants such as Cl salts on the care of these heritage objects.

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