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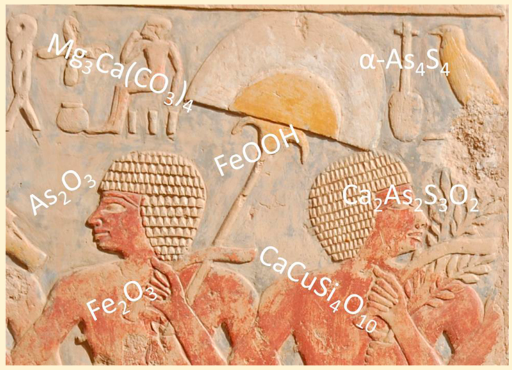
Finding Hidden Chemistry in Ancient Egyptian Artifacts: Pigment Degradation Taught in a Chemical Engineering Course

Javier Giménez*

Department of Chemical Engineering, Universitat Politècnica de Catalunya (UPC), Diagonal 647, 08028 Barcelona, Spain

ABSTRACT: The main objective of this work was to show the application of the study of ancient technology and science on teaching (and learning) chemistry in Chemical Engineering Undergraduate studies. Degradation patterns of pigments used in Ancient Egypt were incorporated in the syllabus of the course entitled "*Technological and Scientific Developments in Antiquity: Egypt and Near East*" (TSDA) (Last year of the Bachelor's Degree in Chemical Engineering at the Universitat Politècnica de Catalunya, UPC). The case studies were discussed following 5 steps which might be a basis for the study of a large number of real cases: (1) Study of the history (Egyptology) related to the case; (2) reading of selected references; (3) description of the degradation pattern; (4) deduction of the chemical mechanism of the degradation; and (5) remediation procedures (if possible). The three degradation patterns observed in pigments used in Ancient Egypt might be used as examples for improving the teaching of chemistry for undergraduate students by applying chemical concepts to real cases in antiquity.



KEYWORDS: *Upper-Division Undergraduate, Interdisciplinary/Multidisciplinary, History/Philosophy, Problem Solving/Decision Making, Applications of Chemistry, Geochemistry*

INTRODUCTION

Learning Chemistry with the Help of Antiquity

In the last year of the Bachelor's Degree in Chemical Engineering at the Universitat Politècnica de Catalunya (UPC-Barcelona Tech), the students have some Optional Courses intended to show applications of chemical and chemical engineering concepts learned during the 4-year Bachelor's Degree. In some of the Optional Courses, an additional objective is to introduce the students to subjects not strictly related to "modern" cases but to humanities, in particular to history. In this sense, the author teaches a course entitled "*Technological and Scientific Developments in Antiquity: Egypt and Near East*" (TSDA), which presents applications of scientific and technological concepts learned during the Bachelor's Degree to some technological and scientific questions related to Ancient Egypt and to other Ancient Mediterranean civilizations, introducing, in parallel, the main characteristics of such civilizations. The teaching/learning of chemistry aided by Egyptology is based on previous research that demonstrated that the interaction between chemistry and art or history had a synergic effect on the learning of chemistry[1−5] and, in particular, when chemistry was taught and learned in combination with the Ancient Egypt.[6−9]

One of the subjects of the TSDA course is the chemistry of the pigments used in Ancient Egypt and the degradation patterns observed in some of the Egyptian paintings. The cases of degraded pigments were carefully chosen considering the experience gained in similar courses taught for the Degree of Industrial Engineering and for the Degree of Chemical Engineering (both at the UPC), especially the course "*Questions of Technology and Civilization in the Ancient Egypt*", taught by the author between 2010 and 2014. The cases accomplished at least two requisites:

(1) The degradation of the color is a real case in Egyptology, and the chemical mechanism of degradation was established. This required a previous compilation of scientific and egyptological papers on the subject and, preferably, the selection of one or two papers that could be read and understood by the students.

(2) The main chemical concepts involved in the degradation process were known by the undergraduate students in Chemical Engineering. In this sense, at the start of the course, the students had already studied different chemistry courses (e.g., Basic Chemistry, Inorganic Chemistry, Organic Chemistry and Analytical Chemistry) and were prepared to apply chemistry to the study of real cases.

Degradation of the Colors of the Ancient Egyptian Paintings

Most pigments used by the Ancient Egyptians were obtained from minerals relatively ubiquitous in the Egyptian landscape; the colors obtained are usually called "earth colors" and are generally characterized by a high stability against weathering and, consequently, the color remains unaltered for centuries or millennia.[10] The procurement of a pigment for the blue color was much more difficult. Ancient Egyptians did not have a mineral with adequate properties for use as a pigment. Because

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J. Chem. Educ. XXXX, XXX, XXX−XXX

of the lack of an appropriate blue mineral, ancient Egyptians synthesized a pigment which is considered the earliest artificial pigment: Egyptian Blue. The chemical synthesis of this pigment was studied in detail[11] and the blue color is due to the presence of crystals of the mineral cuprorivaite ($CaCuSi_4O_{10}$). This mineral had the desired color and was stable under the weather conditions of the Egyptians monuments. A similar chemical synthesis allowed the Egyptians to synthesize a green pigment which is a green frit composed of crystals of wollastonite ($CaSiO_3$) immersed in a Cu-containing amorphous phase.[12]

Although ancient Egyptians mostly used minerals that were stable in various weather conditions, degradation patterns were detected in the paintings of the walls of tombs and temples, and in the paintings of some objects such as papyri. For the TSDA course, the chemical nature of the degradation process was carefully considered so that the students were able to understand the processes with their chemical knowledge at the end of the Bachelor's Degree. The degradation processes are described in this work and correspond to the subsequent color changes detected in ancient Egyptian objects:

1. Whitening of black hieroglyphs in a papyrus on the Warsaw Museum in Poland.
2. Loss of red in some papyri at the British Museum in London.
3. The so-called "copper chloride cancer" in Egyptian Blue in different sites in Egypt.

The Development of the Subjects in the Classroom

During the course, each case of degradation is first presented to the students describing the observations made in different archeological artifacts. In parallel, the historical or mythological/religious background of each object is taught and discussed. Because it was considered desirable that the students had a previous knowledge on the actual process of degradation that was occurring in the objects, one or two scientific articles are previously given to the students. After the empirical description, the chemical aspects of each degradation pattern are taught (with the participation of the students, who had already read the articles), distinguishing between the concepts already learned during the Bachelor's Degree and the new concepts learned from the real case. Therefore, the steps followed during the lessons are mainly based on explanations related to

1. Egyptological and historical data of the place or object where degradation was observed
2. Degradation patterns detected from a "macroscopic" point of view in the place or object and in similar places or objects
3. Description and discussion of chemistry of degradation
4. Likely remediation procedures

Questionnaires were prepared[9] and given to the students about the adequacy of the case study to the egyptological concepts learned during the course, the adequacy to the chemical concepts learned during the Bachelor's Degree, and the usefulness of the case for learning chemistry and Egyptology together. Students provide a rating of 1 to 4 (1 completely disagree, 2 disagree, 3 agree, 4 absolutely agree) to the following questions:

1. I understood the egyptological part of the problem with the papyrus (importance of the colors used, context of the papyrus, provenance...)
2. My chemical knowledge was sufficient to understand the chemical processes involved in the degradation process as well as in the restoration process
3. I have learned/reviewed chemical concepts
4. I have improved my egyptological knowledge

Previous questionnaires on the "*Questions of Technology and Civilization in the Ancient Egypt*" course showed that in general students believe that the study of the Egyptian cases was of interest and allowed the learning and application of chemical concepts. However, the students also judged that in some cases the chemical concepts behind the case studies were too difficult for their acquired knowledge during the Bachelor's Degree.[9]

THE DEGRADATION OF THE BLACK HIEROGLYPHS IN A WARSAW NATIONAL MUSEUM PAPYRUS

The Degradation Pattern

The first case deals with the Papyrus Bakai in the Warsaw National Museum (Poland). Because the usefulness of this degradation pattern on the learning of chemistry (in particular, redox reactions) was already published elsewhere in relation to another course,[9] only a summary is presented here.

The hieroglyphs of the papyrus were originally written in black but today there remains a mixture of black and white hieroglyphs (see Figure 1). Wagner et al.[13] studied the papyrus

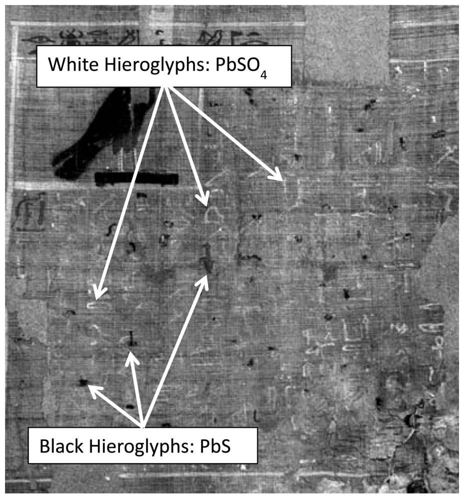

Figure 1. Black hieroglyphs and white hieroglyphs in the Bakai papyrus. Image adapted from ref 13 and republished with kind permission from Springer Science and Business Media.

in order to determine the processes behind the color change in order to propose a methodology to restore the original color of the hieroglyphs.

The Degradation Mechanism

After the study of the composition of the black and white hieroglyphs, Wagner et al.[13] determined that galena (PbS) was used to paint the black hieroglyphs. The electrochemical reaction explaining the whitening of the hieroglyphs was a redox reaction where sulfide (from galena) was the reducing reagent and oxygen from the atmosphere was the oxidizing species, because it is assumed that during the storage the papyrus was in contact with air and with a certain degree of humidity:

$$PbS(s) + 2O_2(g) \leftrightarrows PbSO_4(s) \quad (1)$$

Students have to explain the process by using a Pourbaix diagram of the Pb−S system. In previous courses of the Bachelor's Degree (in particular during the first semester of the first course and during the first semester of the second course), students learn to construct Pourbaix diagrams "by hand" and they deduce the mathematical expressions that are behind every line of a Pourbaix diagram. After this learning, they apply codes such as the Medusa code that allow building Pourbaix diagrams. As it can be seen in the Pourbaix diagram of Figure 2, oxygen oxidizes lead sulfide to lead sulfate.

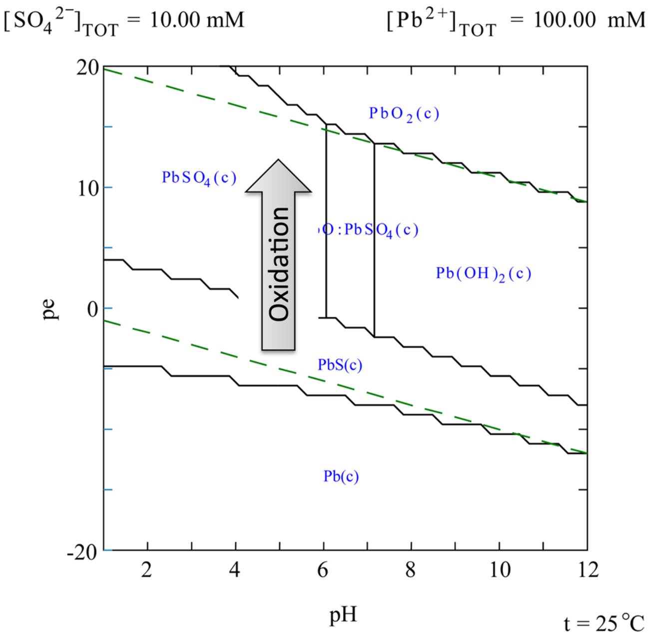

Figure 2. Pourbaix diagram[14] of the Pb−S system. The arrow shows the PbS oxidation by oxygen. pe = E(V)/0.059. The diagram was made considering a high total lead concentration in solution in order to represent only solid phases.

The (Pretended) Restoration of the Papyrus

After the exploring of the electrochemical mechanism of color alteration, Wagner et al.[13] proposed a treatment to restore the original aspect of the papyrus. They proposed as a reagent sodium borohydride ($NaBH_4$) which has two main advantages, its theoretical hydrogen content is relatively high and the reaction products are not aggressive with the archeological artifact.

Although the results of the treatment were positive from a "macroscopic" point of view (hieroglyphs changed their color from white to black), the reducing species used in the restoration of the papyrus, $NaBH_4$, could reduce Pb^{2+} to Pb(s) instead of reducing SO_4^{2-} to S^{2-}, and Pb(s) would be responsible for the black color of the hieroglyphs:

$$4PbSO_4(s) + BH_4^- + 2H_2O \leftrightarrows 4Pb(s) + 4SO_4^{2-} + BO_2^- + 8H^+ \quad (2)$$

The Students

Before explanations of the degradation pattern and the importance and mythological sense of the papyri introduced in the tombs of the Ancient Egyptians, the article given to the students is from Wagner et al.[13] and the students applied their knowledge on:

- Stoichiometry of redox reactions and how to balance chemical redox reactions.
- Oxidation, reduction, oxidizing species and reducing species. In particular, the oxidizing nature of the atmosphere due to the presence of oxygen.
- Constructing and interpreting Pourbaix diagrams. Students made the diagrams from the values of the equilibrium constants included in the Hydra database,[18] which defined the chemical system. Once the system was defined, students created the Pourbaix diagram by using the MEDUSA code, both programs, developed at the Royal Institute for Technology (KTH) in Stockholm, are freely downloadable.[14]

THE DEGRADATION OF THE RED COLOR IN BRITISH MUSEUM PAPYRI

The Degradation Pattern

Research at the British Museum (London, U.K.) showed a degradation pattern on the As-containing pigments used by the ancient Egyptians.[15] Arsenic sulfides were used as pigments because of the vivid color of the minerals, especially realgar (α-As_4S_4) and orpiment (As_2S_3). In ancient Egypt, realgar was used from the New Kingdom (from ca. 1500 BC) as a pigment in the walls of the tombs and on other artifacts, especially on papyri, where realgar was detected by using different analytical chemistry techniques, especially Raman spectroscopy.[16]

Daniels and Leach[15] found that in some papyri, the original red color obtained by using realgar had changed to orange, yellow or white. Figure 3 shows a fragment of the Ani papyrus,

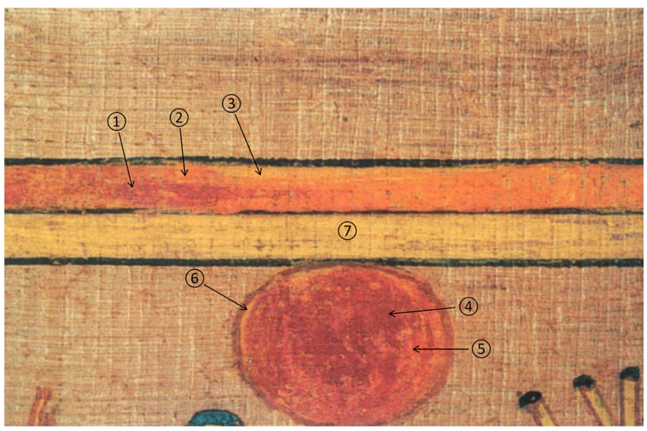

Figure 3. Papyrus Ani at the British Museum showing different zones of color (see text for more details). Numbers 1 and 4, red realgar; numbers 2, 3, 5, and 6, degraded realgar (formation of pararealgar); number 7, orpiment. Image adapted from ref 15 and republished with permission of Maney Publishing. http://www.maneyonline.com/sic (accessed Jan 2015).

where different zones of color might be observed. Numbers 1 and 4 indicate zones with the original red pigment; numbers 2 and 5 show zones with orange pigment; and 3, 6, and 7 show yellow zones. The yellow color indicated by number 7 is different from 3 and 6 because it was originally yellow, obtained by using orpiment (As_2S_3).

The Chemical Process of Realgar Degradation

To explain the degradation of the color, the existence of stable arsenic sulfides different from realgar should be considered.[17] Red realgar (monoclinic) is transformed to its yellow

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J. Chem. Educ. XXXX, XXX, XXX−XXX

polymorph pararealgar (monoclinic prismatic) through an intermediate phase (called χ-phase) when it is exposed to visible light.[18] The alteration from realgar to pararealgar depends on the wavelength of the incident light, the shorter the wavelength the higher the proportion of pararealgar formed. Under unfiltered sunlight, all the realgar alters to pararealgar. In the presence of oxygen, the transformation of realgar to pararealgar occurs via the reaction:[19]

$$5As_4S_{4(\mathrm{realgar})} + 3O_2(g) \leftrightarrows 4As_4S_5 + 2As_2O_3 \quad (3)$$

followed by the loss of one atom of S:[19,20]

$$As_4S_5 \leftrightarrows As_4S_{4(\mathrm{pararealgar})} + S \quad (4)$$

The sulfur atom released reacts with another molecule of realgar to produce another molecule of the As_4S_5 phase:[21]

$$As_4S_{4(\mathrm{realgar})}S \leftrightarrows As_4S_5 \quad (5)$$

which produces one molecule of pararealgar through reaction 4 and one atom of sulfur which reinitiates the mechanism.

Possible Misidentification of the Pigments Depending on the Analytical Technique Used

The formation of yellow pararealgar as a degradation product of realgar might confuse the determination of the composition of the pigment if an elementary analytical chemistry technique is used, because orpiment, realgar and pararealgar have the same elementary composition (As and S) and the same formula (As_4S_4) although different molecular structure.[17] The pigment actually used could then be misidentified depending on the analytical technique.[22] For example, Olsson et al.,[23] Abd el Aal et al.,[24] and Nagashima et al.[25] deduced the presence of orpiment on yellow pigments after the determination of arsenic by Particle-induced X-ray Emission (PIXE) while Bonizzoni et al.[26] arrived at the same conclusion from the arsenic detected by XRF in yellow pigment in an Egyptian coffin. In such cases, the original use of realgar and its degradation instead of the use of orpiment should not be discarded, at least from the chemical point of view.

The students have to realize at this point the importance of the type of data given by the different analytical techniques. One of the objectives of the Analytical Chemistry course is related to the ability of the graduates in Chemical Engineering to select the appropriate instrumental analytical technique depending on the sample; this example on the Ancient Egyptian red-yellow pigments helps to differentiate between techniques that allow elemental analysis and species analysis.

The Students

In this case, before the explanations on the degradation pattern, two articles were given to the students:

1. Daniels and Leach.[15] In this paper, the color changes in papyri painted with realgar are described.
2. O'Day.[17] This article describes the chemistry and mineralogy of arsenic, in particular the chemistry of the arsenic sulfides.

From this case, students practice chemical concepts learned in subjects as Inorganic Chemistry and Analytical Chemistry. They learn about mechanisms of reaction, in particular solid-phase chemical reactions (during the Bachelor's Degree the students learned reaction mechanisms mainly in the aqueous phase).

On the other hand, they confront the use of different analytical techniques to determine the composition of different solids. In particular, students should be aware of the information obtained by the techniques for elemental analysis (e.g., XRF, PIXE) and the techniques that allow the elucidation of the solid composition (e.g., XRD, Raman) and their applications in the analysis of solids.

■ THE COPPER CHLORIDE CANCER IN THE "EGYPTIAN BLUE" PIGMENT

The Degradation Pattern

In spite of the stability of the Egyptian Blue pigment against weathering, minerals found mixed with the pigment appeared to be a result of degradation. In particular, basic copper chlorides,[27,28] $Cu_2(OH)_3Cl$, were found in some archeological samples. The formation of these minerals from blue pigments is the so-called "bronze disease" or "copper chloride cancer", which results in a change of color, from blue (pigments) to green (basic copper chlorides).

The formation of basic copper chlorides was detected not only where Egyptian Blue was used but also in artifacts painted with Green Frit and in objects made of faience.[29] In these objects, it seems that the degradation started with the devitrification of the glass phase followed by the decomposition of the residual material to form the basic copper chlorides. The degradation was high in objects from the Egyptian Old Kingdom (ca. 3050–2200 BC), medium to high in objects from the Middle Kingdom (ca. 2050–1650 BC) and low to medium in artifacts from the New Kingdom (ca. 1550–1050 BC).[29] In particular, the degradation of some of the faience tiles found under the king Djoser (first pharaoh of the Third dynasty, ca. 2700 BC) step pyramid in Saqqara was very high, and the tiles believed to be green seemed to actually be blue tiles which were severely degraded. In some cases, the glaze disappeared and the tiles became white due to the color of the core of the faience. The authors affirmed that green faience was never used by the Egyptians; on the contrary, all the green faience in Egyptian objects was the result of the chemical degradation of the copper compounds to basic copper(II) chlorides. A recent work, focused on the degradation patterns of the king Djoser faience tiles, corroborated these findings and, in addition, showed that in some of the blue tiles the glaze was composed of Egyptian Blue.[30] Basic copper chlorides, especially atacamite, were also found on other Egyptian artifacts, and it was even believed that they were pigments used by the ancient Egyptians for the green color.[26,31]

The Chemical Mechanism of Degradation

In copper or bronze artifacts, basic copper chlorides are formed following the subsequent set of reactions:

Step 1. Oxidative dissolution of metallic copper in chloride media:[32,33]

$$2Cu(s) + 4Cl^- + O_2(g) + 4H^+ \leftrightarrows 2CuCl_2(s) + 2H_2O \quad (7)$$

Step 2. Reverse disproportionation reaction of the freshly formed $CuCl_2(s)$ with metallic copper:

$$Cu(s) + CuCl_2(s) \leftrightarrows 2CuCl(s) \quad (8)$$

Step 3. CuCl(s) oxidation by oxygen to produce the basic copper chloride:

$$4CuCl(s) + O_2(g) + 4H_2O \leftrightarrows 2Cu_2(OH)_3Cl(s) + 2H^+ + 2Cl^- \quad (9)$$

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J. Chem. Educ. XXXX, XXX, XXX−XXX

The consequences of this mechanism can be visualized in Figure 4, where the Pourbaix diagram shows the transformation

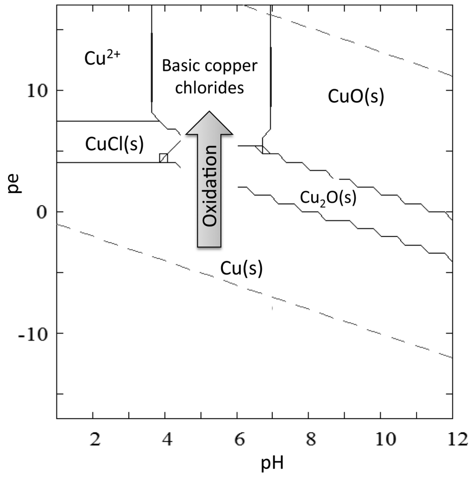

Figure 4. Pourbaix diagram[14] of the Cu−Cl system. The arrow shows the oxidation of metallic copper by oxygen. pe = E(V)/0.059. The diagram was made considering a high total copper concentration in solution in order to represent only solid phases.

of metallic copper to basic copper chlorides due to the oxidation of the metallic copper in the presence of chloride and in acidic medium.

In the case of the Egyptian Blue, the mechanism should be different because copper is already in the +2 oxidation state in the cuprorivaite, although the presence of chloride at acidic pH is necessary considering the global transformation reaction of cuprorivaite to basic copper chlorides (reaction 10):

$$2CaCuSi_4O_{10}(s) + 5H^+ + Cl^- \leftrightharpoons Cu_2(OH)_3Cl(s) + 2Ca^{2+} + 8SiO_2 + H_2O \quad (10)$$

According to Scott,[33] atacamite (orthorhombic) or other polymorphs such as clinoatacamite (monoclinic) would be formed depending on chloride concentration in the solution in contact with the solids, precipitating atacamite when the concentration of the $CuCl^+$ complex was higher than the 20% of the total copper concentration in solution.[34] This is obviously depending on the free chloride concentration in solution needed for the atacamite precipitation. Figure 5 shows two diagrams which represent the relative concentrations of the different copper species present in the solution as a function of chloride concentration. The first one shows the speciation of the copper(II)−chloride complexes in solution and the second one the speciation of copper(II) solid phases. As it can be seen, atacamite is the predominant copper(II) solid phase at free chloride concentrations higher than ∼0.05 mol/L, and at this concentration, $CuCl^+$ accounts for more or less the 20% of the total copper(II) in solution. According to Sharkey and Lewin,[34] at higher chloride concentrations in solution (at which $CuCl_2$(aq), $CuCl_3^-$ or $CuCl_4^{2-}$ predominate), the formation of other polymorphs is favored, without dimorphic inter-conversion.

The Conditions for the Formation of Basic Copper Chlorides in Egyptian Monuments

The presence of solutions with high chloride concentration in contact with the walls of tombs and temples is not unusual in the Egyptian monuments, because of the geological character-

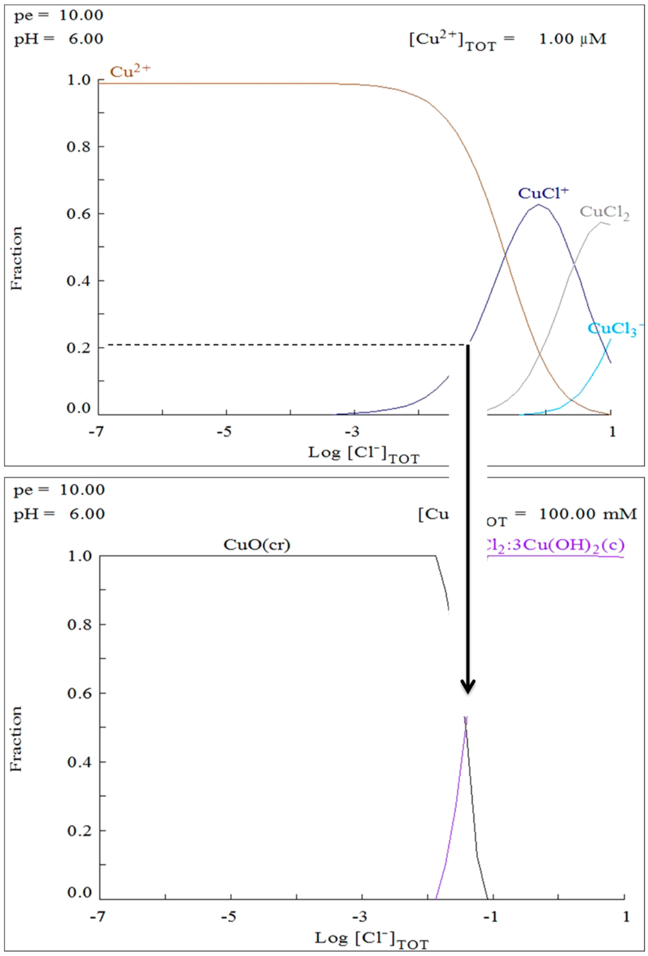

Figure 5. Fraction diagrams[14] of aqueous copper species and solid copper species. The arrow indicates the chloride concentration at which basic copper chlorides are the predominant solid species.

istics of Egypt. For example, the shales and marls in the Valley of the Kings contain a relatively high amount of NaCl (up to 5.1%), which is easily dissolved in water.[35] Actually, 1 cm^3 macro-crystals of halite were found in the Nefertari tomb.[36] In addition, the porosity and permeability of the Egyptian geological formations enhance the migration of water and brines.[37] Water in contact with the walls of the temples or tombs derives from groundwater, flash floods or transpiration and respiration of human beings. Chlorides are the first salts to be dissolved and the existence of a relatively high quantity of solid NaCl in contact with small quantities of water results in high-chloride brines, which would favor the formation of the basic copper chlorides.

The Students

The suggested readings for the students before the start of the teaching of this degradation process are

1. Schiegl et al.[29] This article describes the actual process of degradation in Ancient Egyptian monuments, and the important consequences that the disease can cause. The degradation from a mineralogical point of view is also described.
2. Pollard et al.[27] Describes the mechanism of formation of the basic copper(II) chlorides and the basic properties and chemical behavior of the three main basic copper(II) chlorides.

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J. Chem. Educ. XXXX, XXX, XXX−XXX

Explanations in the classroom are mainly focused on complexation of metals with inorganic ligands, the degree of formation of complexes, and the fraction diagrams, which have to be made by the students using the Hydra database and the MEDUSA code.[14]

The students also learn that the use of analytical techniques that give the elemental composition has a limited applicability, because the determination of the presence of copper and silica might be due not only to the presence of cuprorivaite but also of atacamite. Only techniques such as XRD provide the actual composition of the pigment.

■ CONCLUSIONS

Chemistry and Egyptology are taught together and a symbiotic effect seems to be obtained. The teaching of basic knowledge on both subjects opens a wide range of educational aspects, but feedback with students is critical. It is important to know the opinion of the students, especially about the adequacy of the course and the examples to their knowledge at the end of the Bachelor's Degree.

Case studies involve chemical knowledge related to redox reactions, reaction mechanisms, formation of metal complexes, and Pourbaix diagrams. In addition, the students can see how the different techniques learned in the course of Analytical Chemistry are applied to ancient artifacts.

The examples described in this work contribute to the achievement of the specific competence "Capacity to understand and apply basic knowledge principles of general chemistry, organic and inorganic chemistry and their engineering applications" and to the transversal competence "Efficient oral and written communication. Communicating verbally and writing about learning outcomes, thought-building and decision-making. Taking part in debates about issues related to the own field of specialization" in the Bachelor's Degree and are related to one of the course objectives, the capacity of the students "to identify the materials used in the antiquity in pigments, glass objects and jewels". The students are evaluated during the classes and in different written exams and the results are very positive.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: francisco.javier.gimenez@upc.edu.

Notes

The authors declare no competing financial interest.

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J. Chem. Educ. XXXX, XXX, XXX−XXX