

Development of Hydrogels for the Conservation of Copper

Laureando
Bianca Werneck

Relatore
Dr. Maria Assunta Navarra, Dr. Akiko Tsurumaki



To my Family, on heaven and Earth.

Acknowledgement

This thesis is the result of many minds put together, through readings, teachings and talks, I learned more than I could have imagined from my supervisors, and with real results from our collective research, it can be said that this was a definite win.

I would like to personally cite these names that have been a positive influence not only on my academic journey but also personally, being them Dr. Maria Assunta Navarra, who has agreed to take me into her laboratory believing in my proposal for work; a special thank you to Dr. Akiko Tsurumaki, who I had the honor to become friends with and with whom I learned so much, having the patience and incredible knowledge to guide me through each and every step of this journey, another acknowledgment to Dr. Lucia Mazzapioda, who was always happy to help me with the experiments; I am also leaving here a recognition to Dr. Maria Isabel Spitz, who suggested me to work on this theme and Dr. Maria Margaret Lopes, who was my undergrad supervisor and the reason I got into this master; This work would not have been possible without these women.

I cannot let aside that my master was made possible because of the Erasmus Mundus Joint master's degrees Program, in which the Archaeological Material Science Master is inserted in, it has been a great experience to get to know incredible laboratories around Europe and such renowned universities and professors, because of all the training that I've received I know feel prepared for continuing on my academic journey.

Lastly, but not least, I would like to publicly thank my family, who have supported me all the way from Brazil, embracing me even from a far when things got hard, believing in my dreams and making everything possible to make them come true, you are the reason I got this far. I would also like to thank my extended family, my friends, who never left my side and stood by checking in and making themselves present even with the distance, I can only be grateful for having such amazing people in my life.

Abstract

In archaeological sites, there are many metals found in different conditions and different levels of damage. The metal artifacts are generally covered by oxide-based corrosion layers. Copper-based artifacts, including bronze products, can be found in a major part of cultural heritage sites, being extremely important to be conserved, as well as in need of careful cleaning procedures and effective means of oxidation protection.

Accordingly, the aim of this work is to develop new chemical methods for the corrosion removal by using a green and environmentally friendly gel that enables both area and material selective cleaning, depending on the additives. Hydrogels are known to be very promising materials for corrosion removal, as they enable cleaning of the parts that are not easily reached or that cannot sustain liquids and can also keep cleaning solvents in the desired area and depth, *i.e.*, high area selectivity. In addition, hydrogels are affordable, friendly and safe for the environment and for the conservators.

The development of the hydrogels has been carried out in the following steps: 1) analysis of the copper surface in terms of hydrophilicity by means of contact angle measurement; 2) selection of the suitable polymer structure that has high wettability and compatibility with copper, such as poly(vinyl alcohol) (PVA) and sodium carboxymethyl cellulose (CMC), and preparation of their aqueous gel having a polymer concentration of 15% (w/w); 3) formation of hydrogel containing 7wt% citric acid as cleaning agent on electrochemically corroded copper surfaces. The cleaning efficiency and mechanism were evaluated using X-ray Diffraction (XRD) analysis and Infrared Spectroscopy (IR).

Throughout these analyses, the desired gel formulation was obtained, which was then tested using chemically corroded coins to confirm the applicability of the gel for the cleaning of different objects.

Sumário

Introduction	1
1.1 General Background	1
1.2 Properties of Copper and its Patina	4
1.3 Copper Preservation	9
1.4 Hydrogels	16
2. Materials and Method	19
2.1 Materials	19
2.2 Preparation of hydrogel	20
2.3 Electrochemical corrosion of copper sheet	20
2.4 Contact Angle Measurement	21
2.5 Characterization methods	25
3. Results and Discussion	26
3.1 Contact Angle Measurement of Pristine Copper	26
3.2 Preparation of Polymer Solutions	28
3.3 Effect of Additives in Hydrogel	31
3.4 Effect of Additive Concentration on the Film	34
3.5 IR Analysis of Hydrogel	35
3.6 XRD Evaluation of Corroded Copper Sheets and Bronze Coins	37
3.7 Cleaning of Copper Corrosion using Hydrogel	38
3.8 Effect of Additive Concentration on Corrosion Cleaning	41
3.9 IR analysis of PVA film Before and After Corrosion Removal	42
3.10 Comparison of Cleaning Efficiency between In-situ and Ex-situ Hydrogel	43
3.11 Application of Hydrogel on Coins	45
4. Conclusion	47
Bibliography	51

Introduction

1.1 General Background

As the world advances, so does technology and the cultural manifestations, that means that our way of producing and understanding some material objects also changes, and there is a development in new ways of analyzing and preserving them.

One of the most significant fields now for archaeological research related to the material itself is archaeometry, where there is a joint of chemical methods and techniques and archaeological questions that can only be answered by combining several fields of expertise.

Archaeometry for the care and research of cultural heritage is a work directly associated with conservation, by using several methods and investigations in order to achieve the best possible results and preserve the object for future generations.

Archaeometric analysis is made by first understanding the object in its significance and historical impact, and then producing the means for a more assertive chemical material analysis in order to prove those thoughts or help on a current investigation.

When analyzing the human production chronology and the development of technology, some materials are very interesting to analyze for they provide a very specific type of production that can only be achieved by some ulterior knowledge, which means that those people (concerning the area that the object was made in) had a great advance and specialization in that type of material.

That specialization may suggest that there was a large amount of the raw material available in that region and, therefore, the people began to form artifacts with it, or it may suggest commercial trading and a higher significance for that material in that society.

The discovery of metal bending could be described as the biggest indication of the development to a modern era, where the objects now have a higher durability and more shaping possibilities, with the implementation of a very demanding and specialized production line, starting the formation of new social relations and economic systems based on the availability of the metal and the level of work done on it (the harder it is to make a type of object using that metal, the rarest it is and, therefore, the more value it has, socially speaking).

Archaeological metal findings are very common for their good durability and are more modern, unlike other types of artifacts made many years before, they have spent less time under hard circumstances (archaeological sites) so they present less degradation, also because of the metal itself, which has a hard surface. They are easily found in the most upper

stratigraphic layers on sites, and since its beginning of manufacturing (metallurgy), have been undertaking advancements and have become a dominant part of human society until these days.

Even though some types of archaeological materials have a high durability and chemical stability, they are in a constant corrosive environment, be it on land or underwater, the chemical reactions with its surroundings are persistently happening, aggravated by no form of protection from unusual climatic events.

Every type of material has a proper temperature and humidity to be stable, they will suffer from natural degradation because of contact with the atmosphere, but it can be retarded by proper care. Considering this, all objects found in archaeological sites are indeed in the said corrosive environments, for their degradation is being attenuated by other external factors, human or nature provoked.

The rate of corrosion depends directly on the artifact composition, and so, their reaction with the surrounding environment where it is deposited.

Based on these factors, even if an object is found in a good conservational state¹ by naked eye analysis, they are definitely fragile, and the removal from the site into a proper environment for their cleaning and storage is very complicated and demands a high level of knowledge on the specificities of that artifact itself and of materials that can be used to clean it.

For some years now, the conservation procedures used on the objects are being reconsidered for their strong chemicals or usage of mechanical strength that could, on a long-term basis cause harm and improve the natural degradation of the object, and because of that, they need constant intervention (even a basic cleaning with brushes is an intervention), which causes some mechanical stress on the object and may generate late chemical reactions.

It may also be bad for the professionals who are in constant contact with these chemicals, causing harm to their health, because of the inhaled gases and the physical contact that may occur; another point to be considered is the environmental protection, for chemical residue disposal is complicated and can cause a lot of prejudice to the nature.

For that and other reasons, the cultural heritage care field has been thinking and developing new ideas of conservation products that are less abrasive, cause less residues and are easy and cheap to produce, for we cannot forget that there is an industry behind every experiment and technology, and even eco-friendly solutions are sometimes left behind for their production costs.

¹ Conservational state is a standard used in heritage sciences to nominate the physical characteristics of a given object; they can be categorized into one of these two states: bad or good. Considering archaeological objects, they will never be excellent, and the "good" designation indicates no considerable losses in the overall structure.

Considering these aspects of innovative conservation methods that are also eco-friendly, this project was conceived, hoping to develop new solutions for the conservation of archaeological materials, specifying the content here on copper, since copper and its alloys are frequently found in archaeological sites, which compose the world's cultural heritage. In this work, these new methods are being expressed through the usage of hydrogels for the cleaning, which implies the removal of corrosion products on its surface. These corrosion products in their formation and composition will be discussed over the next chapters.

Copper composes most archaeological artifacts because it was the first metal to be worked on², and for its great availability in almost every land on the world, even with the discovery of the new metals and alloys, copper was still being used, even if in smaller proportions, to compose the object alongside with these other metallic compounds, in order to lower production costs or to improve malleability.

Copper was and continues to be highly used because of its many characteristics that allows it to be used in several types of materials, these characteristics are mainly: it's high melting point, being useful for materials that need to undertake heat, it is malleable, durable and ductile, which is a good aspect of metallurgical activities, it is hard to corrode, especially because of cuprite, acting as a protective layer, it produces many alloys, such as tin and bronze, along with many other characteristics (Roesky; Möckel, 1996).

These characteristics, especially the high malleability, not only present in copper itself but also on its alloys, were the turning point from making tools and ornaments from stones to metals, because they were easy to shape (by using metallurgical processes) and didn't break as easily. This aspect is described in history by turning from the Stone Age to the Bronze Age.

In fact, this change in making artifacts from bones and rocks to now metals are such a drastic change in history that it can be described as the beginning of "Men Age", where now technology is being developed as so is the economic and social relations.

Considering the importance that these artifacts hold, briefly discussed here, it is essential that they are conserved and treated in the least harmful way possible, so that they can be preserved for the future and continue to provide crucial information about the development of humankind, thus, the usage of polymer-based hydrogels is proposed.

The hydrogels will be explained and distinguished by penetration power, considering that not all times the entire patina needs to be removed, there is the possibility to use a gel with a more surface activeness in order to take out only the selected product, also keeping in mind not to affect the surrounding areas that do not need to undertake this treatment;

² Some studies suggest that gold was being used before copper, but because of its softness and rarity it was not as widely used as copper.

taking this into account, all of the gels here presented have a high area selectivity.

In the case of metallic objects, it is not possible to take samples to do an individual analysis and tests, as it is with paintings, for example (unless there is a detached part), so all the testing in the applicable materials to be used on them should be done at a sampling material that simulates the same conditions as the real one, by using electrochemical corrosion (induced corrosion made on laboratory).

On that note, the use of hydrogels was thought to clean them without leaving chemical traces, and so avoiding possible chemical reactions on the metal, and without penetrating in the material, prolonging its life by resulting in minimal intervention³.

The importance of this project may be determined by the perception that these gels are still a study basis on many different materials; it is somehow a new field for chemistry applied to conservation and it may have a great impact in the copper preservation, as well as other metals to be studied in the future, preventing mechanical scratching and possible human caused damages.

1.2 Properties of Copper and its Patina

Metals are naturally occurring elements that can be found in minerals in different places according to the necessary conditions for their formation (some need extreme heat, some need pressure, and so on). For instance, Copper (Cu) is found in ores in compound compositions, such as chalcocite (Cu_2S) and cuprite (Cu_2O) and can be separated into pure Cu by metallurgical processes such as smelting.

Most of the extraction processes in the past happened in open pits, which are the ores closer to the surface, since to achieve the more internal ones it is needed special equipment that can penetrate the layers, which are available nowadays.

Depending on the region and metallurgical technological expertise of the people, the copper separation processes are different, but they all evolve heat to enhance segregation of compounds. This data on extraction procedures is also an important archaeological evidence of metals usage and civilization knowledge.

³ Intervention standards are used in heritage science in order to analyse the degree of chemical and physical stress that the object is receiving. Minimal intervention is the desired method for it is a surface cleaning with no restoration and using materials that will not be attached or that can be removed if necessary.

All metals⁴ and its alloys are bound to suffer from oxidation reactions by simple exposure to the atmosphere. Historical artifacts of copper suffer from these oxidations, and this is the reason for the corrosion effect, which generates some complex compounds originating from the base metal.

Corrosion means that part of the outer layer of a metal starts to change into complex compounds from the primary element, so their physical structure will suffer from alterations as it decomposes.

Each metal will have different corrosion products and rate of degradation, in fact, even in objects with the same base composition, the thickness and chemical content of the compounds present in the corrosive layers will be a direct response on the exposure time and environmental factors, so they are a result of different extrinsic and intrinsic aspects.

Be it on land or underwater, all objects will try to achieve a chemical stability with their surrounding environment, which in the case of metals, will lead to its oxidation in an attempt to match the surrounding compounds. This characteristic actually slows down the natural degradation that will occur, so they happen at a slower rate, but the object is still fragile.

When the environment has a lot of fluctuation of relative humidity and temperature, that process is accelerated, since the material cannot reach a proper stability, while in a steadier climate, the reaction discussed above occurs. For that reason, it is important to understand the burial place's surroundings.

The corrosion will also be carried out at a higher rate when in direct contact with other elements or acids for a long time, this characteristic can be seen by analysis of tensile strength and length, where both decreases, compared to the original value of a new object with the same composition, after it has been in a corrosive environment for more than 100 years, which is the case for archaeological materials.

Although the alloys do not develop the exact same corrosive products as the pure metal, in the case of bronze (copper alloy) it is investigated that its corrosion compounds are mainly copper based, therefore, by studying the products in copper they can be related in their base composition to the ones on its alloys.

These compounds are formed in the surface of the material, because they are a result of the direct reaction of the external medium with the outermost part that is in touch with it, where the internal layers will only suffer from this decomposition in case there is an extended contact, and the primary products develop to more complex corrosive compounds.

Some products are formed closer to the copper surface, such as cuprite (Cu_2O), while others are formed closer to the atmosphere, such as malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$), this means that they are formed on top of the cuprite layer, because of reactions from this layer with

⁴ except for the noble metals, such as gold (Au).

altered conditions, in theory, if the object only develops a cuprite layer the corrosion will not increase if in a controlled adequate ambient. The reaction is as follows:



It can be seen from this formula that it is basically impossible to control or avoid the appearance of cuprite on copper, since it is caused by contact with atmospheric oxygen, unless some type of coating is applied, but on normal conditions this layer will develop by simple contact with the atmosphere.

By continuous exposure to a corrosive environment, the following reaction happens on the cuprite, forming the green patina on copper, the sulphates:



As it is known, archaeological objects are not always found in their final deposition place, they can be moved by humans or natural events, and their reactions, resulting in the different products, serve as an indication of the largest time they have passed in a specific place, for example, malachite is usually assigned to soil reactions, while atacamite is associated to water and humid environments, brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) is due to atmospheric pollution (usually sulfur dioxide), and even though they may be found in other places not entirely related to the appearing of the patina, these products are an indication that they were deposited in places with these specific conditions for a large amount of time.

Not only the location makes a difference in the reaction that leads to the occurrence of certain products, but also, as explained previously, the conditions into which the objects are subjected, where an outdoor environment, be it coastal, industrial or rural locations, cause an immediate appearance of them, because of the constant environmental variation; and in another way, in a ventilated shed, only coastal zones will provoke the appearance of corrosion, because of humidity, while the other ones don't have such humid environments, and so the object is better preserved.

These corrosive products that appear in metals are also described as patina. Patinas can be made of two or more corrosion products, depending on the surrounding environment and on the metal's properties and location. The name patina infers that there is a color variation at a surface, in the case of copper, it is used to indicate more than one corrosion product in the same material, if it is only cuprite, it is just described by the name of the product; so, if a copper surface is green it is said to present a patina.

This concept can be more easily described by examination of the different formations, considering, as an example, a copper left in a sheltered condition but in an industrial

environment may develop a cuprite layer or a patina, composed of two corrosions or all four.

Because of all possible environmental and physical variations that result in the production and appearance of different patina, these compounds are divided into general groups for correlation, such as oxides, chlorides and sulfates (salts).

At a first approach and a very general one, these products can be differentiated by naked eye by color, where usually the salts present a greenish or bluish aspect, whereas the oxides present a reddish aspect. By knowing some of them, when looking at a sample it is possible to identify which product it is and the area that it is formed on, but color observation is an aspect that depends on the observer's perception as well as the general conditions at the observation time, therefore, naked eye analysis should not be considered a scientific mean or a proper investigation parameter, thus, it is always recommended to do some analysis by XRD in order to see the compounds composition.

Although all patina products are damaging for the object, for they result of oxidation reactions, there are some studies on cuprite (Cu_2O) that describe the oxide as a natural protective layer preventing further and more dangerous corrosion products when at a stable state, with that in mind, some researchers recommend that the removal of patina is made targeting the salts but preserving the cuprite.

Usually, cuprite is restrained to the surface, so it doesn't really cause physical damage other than higher sensitivity for breakage when in an active state, but the overall structure of the object is not affected.

In light of this aspect, it could be, then, expected that archaeological copper materials are protected from further corrosion products once they develop this cuprite layer overtime, nevertheless, it is necessary to consider that they are in constant environmental change, as these artifacts are not at a stable temperature and humidity ambient, they suffer from acidic alterations and soil interactions with other compounds that cause the appearing of the other patina products.

Considering copper and its alloys, an unnecessary intervention or the lack of ideal environment to safeguard or clean these materials may cause a non-stop chemical reaction, known as "bronze disease", which is triggered by the appearance of nantokite (CuCl) and resulting in a corrosion product called atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), a copper oxychloride that is formed by the oxidation of other products present in the patina; because of this characteristic it is also described as a secondary copper mineral.

When the object presents atacamite in the patina it means that the "bronze disease" has taken place, and so, it must be taken out in order to preserve it, unlike the other patina products, nantokite is highly destructive, and although the damage caused by it is irreversible (since it deteriorates the physical structure), its removal will stop further deterioration. More

generally known products such as cuprite and malachite can be in a stable state, so they don't harm the physical structure of the object, but atacamite is always active.

This product is so dangerous that, if there is one object containing it in a collection, it is important to separate it from the others, for atacamite forms as a powder at the surface of the metal that can easily spread over to its surroundings, allocating itself in the close by metal and cause damage to them; another form that this product may appear is in the form of a film on the surface of the object.

Because the patina is composed of different products, it is important to take into consideration their unique morphology and composition in order to decide on the best treatments for their removal, not prejudicing the surrounding areas and certainly not increasing the problem.

It is also crucial to decide, preceding the conservation actions, the patina layers that will be removed, if the intention is to preserve the cuprite, then the solution applied in the corrosion needs to be of surface removal, if all the layers are to be removed, a solution that penetrates deeper is in need.

The differences in the corrosion measures are related to a straight or rough corroded surface, these are caused by generalized or located corrosion spots; a general corrosion will present an even surface, where the entire patina is the same color and, visually, there are no roughness differences in its parts, whereas a located corrosion will consist of specific spots where the patina will concentrate and then, create, visually, a rough surface with many color differences in between the parts that compose the object.

It is important to clear out that even though these patina seem like they are external to the object, like a coating, they are actually part of it, the outermost part of the copper will react resulting in the formation of cuprite, consuming this part in the formation of this corrosion, the malachite will consume part of the cuprite and so on; this is the reason why it said that cuprite may serve as a protective layer.

Concerning the study of copper reactions according to surrounding environment, it is noticeable that it is a very stable element that doesn't easily decompose, so considering in archaeological terms, the artifacts made from copper bases are generally well preserved, in comparison to other metals from the same time in the same conditions, such as iron (Fe); In order to have an actual decomposition of the material, it is needed a long time exposure to an acidic surrounding, which in sites, that condition can be found in outdoors environments where there is constant changes in the acidity of the rain and an unstable interaction with different soil products, or a high humidity, which provokes the reaction of cuprite with the environment, initiating the appearance of the patina.

Because of all of the variants that can cause corrosion on copper, and the necessity

of a more centered study, this work will focus on the electrochemical⁵ corrosion type rather than ambient-caused because it is a work in development, and it would be risky to test it while it is not definitive at an actual artifact, therefore, all of the tests were made in samples produced in the laboratory following the guidelines of electrochemistry for patina formation, taking into consideration the products usually found in archaeological materials in order to have a reproducibility of them by chemical means, nevertheless, this study can be applied to materials with the same products that were reproduced in the laboratory.

1.3 Copper Preservation

The preservation of artifacts is a subject that is being constantly discussed since the beginning of archaeology as a study field; defining the concern for the object's history and all the extrinsic and intrinsic information that can be drawn from them.

It cannot be put aside that, besides this research factor, there is also the gratification, or jouissance that objects with such representativity can bring. Past civilizations and the progression of humanity have always fascinated us, the understanding of our development in thinking, in social organizations, in manufacturing, and many other aspects that give us a sense of humanity.

The desire for collecting objects can be seen since the development of mankind into a more settled life, for when nomads they couldn't possess many items for it would be hard to carry, but when settling on a land, it is possible to acquire more objects, and now not only for survival purposes, but for delight and religious practices.

When considering the real desire for appreciation of a collection, composed of items that are not necessarily useful in means of survival, for a somewhat beginning of museums is the creation of the "curiosity cabinets", a term that specifies a big movement in Europe, around the XVI and XVII centuries, where the people who went overseas to explore the other lands, be it by foot or ships, would bring back any material they considered peculiar or rare, and those pieces were exposed in these "galleries".

In those times the objects were exposed simply to admire, no actual research or

⁵ Electrochemical corrosion is all corrosion that depends on an electrolytic medium to start the reaction, also called Wet corrosion. This type can be found in underwater copper or samples made in laboratories by means of a solution, while dry corrosion is caused by direct contact of the metal with a reagent, such as gases.

historicity was made on them, other than putting a tag with the information of the place it was found. Since those times, there has been a development in the thinking of material culture and what they symbolize, where nowadays there is the notion that they represent society in their most diverse aspects and can result in the understanding of mankind and its development, which allows us to understand better our cultural differences, where we came from, how the social developments were made, and so on.

From these small private galleries where possessing rare artifacts from around the world was seen as a very noble activity; the bigger the collection, the higher in social status, for in order to acquire these items, it took a lot of monetary power, there is the development of the thinking that this heritage does not and cannot belong to a person, with regard of being a world cultural heritage, and so, there is the buildout of open public galleries, that lead to museums.

Considering those aspects, it is important that the objects are well preserved and kept for the future, and for that, many fields had to unite in order to develop the best strategies for their conservation, and nowadays there is a big connection with the area of chemistry, in order to understand the composition of that object and finding the best methods for its preservation.

To understand better this general aspect that evolves guaranteeing the security and durability of a material for the future, some terms will be here specified for they are the guidelines for all the activities that should be done on any artifact.

Starting with the term that englobes all these tasks, that is preservation. Preservation is a term that exemplifies mainly 2 different activities that can be made with an object in order to help maintain it stable and in an ideal environment (in order to prevent degradation). These 2 activities are conservation and restoration.

Conservation is separated into two forms, the first one is called Preventive Conservation, and it is determined as all activities that are not directly made in the object that help maintain its current conservational state (ex: adequate storage, humidity and temperature); in order to proceed with this action, it is necessary to have a basic knowledge in the material composition of the object, to define how those compounds are better preserved (that is defined by their chemically stable environment).

The second conservation activity is called Curative Conservation or Remedial Conservation (ICOM-CC), and it is explained as all measures that are a direct intervention on the object but don't alter it chemically, aiming to turn the object back at it was in its original state, for example: cleaning, and, to be more specific, in the case of this project, the removal of the corrosive layer in copper, which causes a direct intervention on the surface composition, aesthetically and chemically, also the application of the protective layer to

prevent further damage, although it is a preventive action it fits in this conservative aspect because there is direct contact with the object.

Again, it is vital to understand not only the composition but how they behave and the reactions that may occur, therefore, a general knowledge in chemistry is required.

Restoration is specified as all measures that are a direct intervention on the object and cause physical alterations to it, this is done after the curative conservation if the previous is not enough to retrieve the primary form of the object, revealing its surface and attributes; for example, the reattachment of fallen parts or the reconstruction of new parts to help on its structure, making an effort to resemble the object to its first form.

Although restoration procedures make significant changes in the objects in its attempt to restore it back to its original state, they cannot be a copy, that means that every restoration work should only aim that the physical structure is secured and that the information, the reading of the object, can be done, but without imitating its characteristics; the restored parts must be evident without harming the general structure.

In this work, only conservation activities will be carried out, considering that none of the artefacts treated here are in need of restoration procedures; even more, restoration should only be done by professional restorers that are specialized in that particular material.

It is important to stress out that, considering archaeological materials, be it on land or underwater, it is necessary to have a vast knowledge not only on the material composition itself but also on the surrounding environment, in the case of land objects, to understand the soil deposit in its compounds, the climate and pH of rain (if rainy area), as well as many other aspects.

According to Nord et al. (2002), the deterioration of metal artifacts that are on the soil has gotten worse over the last 100 years, in some cases, artifacts that were recovered from the sites in the early 1900 were in a better conservational state than the ones found now, and this has to do with the acidification of the soil from all types of pollutants that are constantly being deposited by industries; for this, it is important to understand the external factors that determine the degradation of the object, in this case, not only the soil itself but the human behavior that is causing the environmental changes.

The degradation processes that may occur are stimulated also by its own structure, how it was produced, its usage and many other human-related factors that can result in one part of the object being more fragile or have a different composition than the rest; that is why the chemical and historical analysis of it is so important.

Because of this factor of increased acidification, the authors also discuss that an artifact buried 300 years ago has basically the same deterioration as the ones buried 3000 years ago, showing how the pollution and chemical disposal is changing the soil composition

and how this directly affects the objects and nature around us.

It should also be considered that the objects should be kept in a good form for future analysis, and so all interventions should be done with extra care in order to not lose any information or cause deterioration on the material.

All of these aspects are elucidated in the intervention guidelines by UNESCO of minimum intervention, where all of the materials and methods used should be reversible, if necessary, therefore, nothing that alters the object.

Archaeological objects hold a lot of information about the social structure of past societies and product availability, which are the main guidelines into understanding human and nature development, considering that the natural environments were also altered by constant human intervention.

Because of this direct relation with social activities, metal findings are very important for archaeologists, for their throughout analysis may indicate several important evolutionary factors, such as: knowledge of metalworking (analyzed by the level of specialization needed for the working of that metal, by manufacturing practice), provenance, mobility and trading (by analysis of availability of the metal in the site and close by places), social hierarchy (by analyzing the metal composition in its economic value and metalworking, correlated to the place found and other artifacts on the site), cultural practices (by analyzing the usage of that object, if it is for cooking, for armory, for religious purposes, ornamentation, ...), and many others.

When considering metals, copper is indeed one of the vastest utilized in production throughout history, with many alloys and mixed into different types of mineral components because of its physical properties that allow a good shaping and durability.

One of the most common archaeological finds of copper-based materials nowadays are coins, and much as the other objects, they hold very important information, especially on commercial trading and economical activities, therefore, it is a society that is living in a piece of land with some sort of ruler that implicates on this type of lifestyle; the analysis of coins usually even indicates the ruler and the year, which is very helpful in all sorts of investigations.

Copper and Iron objects are more recent, for they result in the discovery of new types of mineral ores that contained those elements, so, in order to extract it from the mineral it is necessary to have a firing process with some specificities, while gold happens naturally, and so it was the first metal to be used in the making of objects.

Metals have different properties and, therefore, different corrosion potentials, it is important that they are separated in their storage place, in order to prevent galvanic corrosion from occurring.

Galvanic corrosion is the reaction that occurs when two metals with different

properties are in contact, directly or through a medium, where one of them has a higher corrosion resistance, the noble metals, so the one with less resistance, less noble, will suffer more attacks and will decay faster, which creates sort of a protection to the other metal, since the later will not be targeted by the corrosion products.

“For metals, washing an object free of salts is a significant step towards stabilization, however, most metals also require a corrosion inhibitor and coating systems to further promote stability. The corrosion inhibitor locks up metal ions that could react with the environment to form stable corrosion products. The coating system impedes the access of oxygen and water to the metal surface, which limits the rate at which corrosion can occur. Depending on the material and its condition, other steps may be needed before an artefact is exhibited, stored or studied.”

(Viduka, 2012; pg. 11).

For the development of these protective measurements, it is important to analyze at first the state of corrosion; they are separated into stable or active. The first one indicates the patina that has found chemical stability, and, therefore, is not acting as a corrosive medium for the metal anymore, meaning that the corrosion seen will not increase (considering it is in an ideal storage place), whilst the second one indicates a patina that is still corroding the metal, and so, increasing; those can be differentiated by observing the physical damage, with possible detachments of parts, and the presence of powders on the surface (indicators of active corrosion).

Visually this differentiation can be made by analyzing the surface of the object, where at an active corrosion the object will present roughness, with non-even spaces, and a stable corrosion object will present a more flat or smooth surface; at a microscopic observation both of them will indicate some roughness, but at naked eye analysis only the active will be visible (see Figure 1.1).

In the case of copper and its alloys, another indication that the corrosion is active, besides the powdery aspect, is the color of the corrosion, while a stable corrosion is colored in dark green, brown, or red, the active ones present a light green color, almost white.



Figure 1.1 Examples of stable (top) and active (bottom) corrosion on copper nails.
Government of Canada, Canadian Conservation Institute.

Taking into account the aspects described above, conservators are in constant debate on whether it is important to remove a stable corrosion or not, in any case, for active corrosion it is always recommended to remove it before causing any more harm.

A common point is that intervention is needed when the reading of the object is compromised; the reading of an object is a museological term to describe the visual characteristics of an artifact that result in the understanding of its cultural representation, which is the main point of preserving cultural heritage, to be conscious of the significance of that piece in its human and environmental indications, for example, on a coin the reading is related to the numismatic, the drawings and engravings in it, that indicate a time period and region in which that coin would circulate, besides trading and element availability.

Considering this importance of preservation, as discussed previously, it is crucial to think about not only cleaning processes but also on the preventive conservation, that, in the case of collecting institutions, is the space that is predetermined to hold the collection, the technical reserves.

The technical reserves work better if the collections are separated by composition, so, for example, paintings stay separated from metals; when designing these ambient, for the majority of materials, metals included, the most important areas to be controlled in the selected environment are temperature and humidity, for more specific measures, after understanding how the corrosion of copper happens, it is also essential to use air filtration systems to avoid pollutants and avoid direct contact with hands because of grease. For metals the desired numbers for controlled relative humidity between 30% and 45% and a temperature in between 20 and 30.

Corrosion inhibitors are being more and more used in institutions in order to prevent constant cleaning and with this coating, even in variations of temperature and humidity there

is not much need to worry, since the coating will not allow the reaction of the copper and its alloys with the external factors, although this is in fact a good method, many inhibitors may increase the dirt or react when at a given Ambiental factor, so it is important to remember that they are not a completely effective method, it is always best to prevent the degradation by external factors than apply something on the object.

The agents of deterioration may not only be from the atmosphere itself, but natural causes, like flooding, firings or earthquakes, or human causes such as physical contact, poor management and incorrect interventions; therefore, it is important to think about measures for all of these aspects, taking into consideration what the institution has available for the care of the collection. In the case of institutions that don't have professionals specialized in metals it is recommended to get in touch with other institutions such as universities in order to have proper care, in case that is not possible, it is important to follow the guidelines dictated by UNESCO and ICOM in the best possible way.

With the aim of the project being the removal of corrosion products, also known as patina, from archaeological copper materials with new hydrogels, the testing for the best combination for this cleaning was made not on original archaeological objects but in recreations of these products by electrochemical means, as described in the chapter above.

These artificial patinas are very close in composition and structure from the patinas found in archaeological materials, so they work well for testing and prevent the real object from getting damaged.

In order to achieve the similarity of patina from an archaeological copper material, the XRD of a reference spectrum of an archaeological coin was analyzed in order to understand the compounds present and, with that, attempt to recreate them electrochemically.

Depending on the corrosive environment, different types of patinas will appear on the copper surface, and they can be separated into two main groups that we will refer to as simple and complex compounds.

Simple compounds are the products that are easily formed, the oxidation takes place by atmospheric contact, and they form a flatter, even, surface, found in most copper materials, even more recent ones, being them: cuprite (Cu_2O) and malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), and in less cases, atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$).

Complex compounds are the products that are only formed by a significant exchange with a corrosive environment, so with a long exposure, they form more uneven surfaces, with different layers, mostly found on archaeological materials; they comprise the three compounds described above plus many others, such as: azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) and posnjakite ($\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot (\text{H}_2\text{O})$).

It is important to point out that one object may contain one or many corrosion

products, as said, it depends on the exchange and reactions with the surrounding environment. It may be possible to find an object that has only Cuprite, while others have four types of products in the patina and so on.

In this work, artificial corrosion, containing the patinas found in archaeological artefacts, was formed by electrochemical polarization. By using the standards for patina formation given by Beldjoudi *et al.* (2001), the copper sheet was immersed in the ASTM D1384 solution as a corrosive medium, which contains 0.01M Na₂SO₄, 2.8*10⁻²M NaCl, and 16.1*10⁻²M NaHCO₃, and an anodic potential of 0.15V (vs Ag/AgCl) for 2h was applied, followed by 96h at 0.38V (vs Ag/AgCl).

By using this procedure, it is possible to test the hydrogels safely without any harm to the actual object until the final gel formulation is ready.

It is important to point out that this standard was made by using the results of European archaeological copper, from bronze age to roman times, so, if similar research is being made in America it is necessary to have a standardization of the corrosion products that are developed there, better yet, from country to country, since soil and climatic conditions, as well as production means vary a lot.

1.4 Hydrogels

The wrong usage of cleaning materials or strong solvents may increase the degradation of the object, especially considering archaeological materials that are already very delicate and fragile.

Because of that, the object's characterization, on their chemical composition and conservation state are very important in order not only to do a proper cleaning but also to establish an adequate conservation plan for them, which should include all of the preservation measures.

The cleaning of land archaeological artifacts usually starts with a mechanical process, using brushes and spatulas in order to remove dust/soil crusts and dried corrosion products. After this first approach, the chemical cleaning procedures take place in order to remove all of the products and maybe detain some degradation processes.

Chemical cleaning procedures may consist of the use of strong solvents that, on a long-term basis, will need to be removed or will slowly enhance the natural degradation, not

visible in daily monitoring.

On that note, it is thought of the importance to use solvents that are more natural and not very abrasive and that won't leave any residues, preventing the occurrence of continuous reactions on the object; this thinking works accordingly to the UNESCO guidelines of minimum intervention for cultural heritage, with the priority being the conservation of the stable areas and trying to keep the intervention on the parts in need, where the object requires stabilization of its physical structure or chemical cleaning to be well preserved and be able to provide the historical information it contains.

Another aspect to consider is the environmental pollution caused by the disposal of chemical residues that cause a lot of harm to the environment itself and to the atmosphere, by increasing the toxicity levels into which we are daily exposed to.

Considering these aspects, this work proposes the use of hydrogels as an alternative for usual chemical solvents, by using only natural solvents and chemicals that are eco-friendly.

Hydrogels basically consist of water, polymers and selected additives for cleaning, so they are easy to make and don't require much time, the only thing to consider is the solubility and properties of the selected polymers and the composition of the material that is need of the cleaning, in order not to cause any wrong reactions.

Polymers are used in these gels because of their many mechanical and chemical characteristics, such as elasticity and stability. It is important to do research and test the correct polymer formulations, for their differences in crystallinity, molecular weight and thermal transition affects the properties of the polymer matrix⁶. (Kasalkova et al, 2015).

The benefits of developing this hydrogels are many, such as that they are environmental friendly and non-flammable, economical (basically everything that is needed for their formulation is already available at chemistry and conservation laboratories, and if not they are easily reached), the preparation is fast and minimum, it is good for the conservators health (they retain gases that may be toxic, also they don't require strong acidic solvents), they emit less pollutants and generate less residues, they allow a more controlled and selective cleaning for they diminish the penetration power of the solvents and increase the retention time, and also allows the cleaning of materials that can't undertake mechanical cleaning (such as scratching) or traditional strong solvents.

Selectiveness is one of the most seeked advantages of these gels, especially when dealing with metals patina, since there is a need of a selective removal of corrosion products, after analysis of which layers should be removed or left; that is a common case on copper

⁶ A polymer matrix is a polymer-composed medium that presents a cross-linked solid structure that holds the agents in their place.

for cuprite, for example, that sometimes is left on the object to prevent further corrosion.

This aspect is important specially when considering archaeological objects that, usually, don't present an uniform corrosion, because of the variations of the environment they are left in, so the corrosion is normally located in a specific part of the object, and so, it is necessary to act only in the part in need.

Some institutions even require that other products besides cuprite are left in the artifact for historical purposes, for they believe that these oxidation products are now a part of the object history and compass its esthetic. This is a debatable point, but if the removal of the most dangerous compounds such as Atacamite is done, it is possible to leave the other products if it is determined that the corrosion is stable and there is a constant observation of the degradation state.

Accordingly, it is understandable that this selectiveness for a very controlled cleaning is important, and the amount of patina to be removed really depends on the researcher or requesting institution.

In order to form a hydrogel, the components of the solution need to be carefully designated so that they will properly interact with each other forming a polymer matrix and functioning according to the object's demands.

With that in mind, before selecting the agents for the gel, the polymer and additives, it is important to understand the composition of the recipient's areas that require the application of this gel medium, be it for cleaning or preservation, so that the gel has the expected reaction.

A base hydrogel is composed of water and a thickening polymer, in order to increase the viscosity of the solution and actively become a gel. Water is the main element in this formulation, for it will complete the hydrolysis and so provide the dissolution of that polymer in the medium, enhancing its basic properties.

The combination of these two form a base gel. After this step, other organic substances may be incorporated, called additives, such as plasticizers and acids, so it is very important that all the chosen elements have an affinity between them and are water soluble.

The gel can be applied directly on the object with basic instruments like a pipet, or even a swab in the case of art works such as paintings, differently from membranes, the drying of these types of hydrogels, and so, formation of a film, is done directly on the object, instead of outside.

In the case of metals, the main degradation they encounter is corrosion, and given the complexity of these patina structures, the gel here is expected to act as an adhesive medium, so the products are transferred from the patina to the gel via chemical reaction, since the goal is to avoid physical removal.

The film formation happens when there is a loss of volatile compounds on the gel by evaporation, and so, the gel dries and a thin elastic film is formed and when peeled off, the corrosion layers are removed with it by chemical transfer.

It is recommended that the hydrogels are made on the same day of application, or at maximum at 24 hours prior to application, in order to avoid atmospheric contamination and excessive loss of volatile compounds within the matrix.

The removal of the film is done by peeling, and in order for that process to be effective and non-damaging for the object, the peeling needs to be gentle, for that, the film cannot be too rigid, so the elasticity needs to be high, in order to not remove some patina physically instead of chemically, through the medium.

Another interesting point on the drying of these gels is that, because they are directly applied they are not homogenous in the surface of the object, and so, their drying occurs firstly by the conners, where there is less amount of gel, and then to the middle, which can cause a problem on the removal; in order to overcome this aspect, it is recommended that some paper is put, cut on the shape of the area to be cleaned, and with this, the drying is equal and the removal is easier, since it is not even needed tweezers.

2. Materials and Method

2.1 Materials

Polymers, such as carboxymethyl cellulose sodium salt Mw: 90,000 (CMC), polyvinyl alcohol Mw: 130,000 99% hydrolyzed (PVA), and polyethylene oxide Mw: 100,000 (PEO), were purchased from Sigma-Aldrich and used as received. The structure is shown in Figure 2.1.

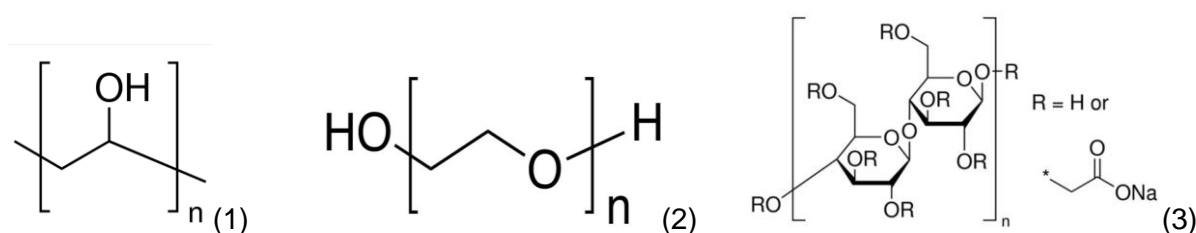


Figure 2.1. Chemical structures of PVA (1), PEO (2) and CMC (3).

Polyethylene glycol (PEG), boric Acid (BA), glycerol (GLY), and citric acid were purchased from Sigma-Aldrich and used as additives for hydrogels. The structure is shown in Figure 2.2.

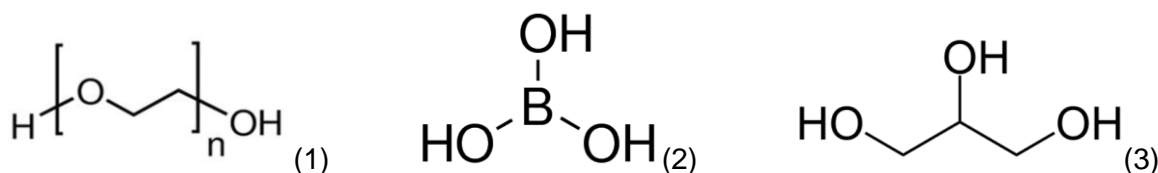


Figure 2.2. Chemical structures of PEG (1), Boric Acid (2) and Glycerol (3).

2.2 Preparation of hydrogel

The 5, 10, 15, 20 and 30 wt.% polymers were added to 5mg distilled water. The solutions from 5 to 15 wt.% polymer were mixed using a magnetic stirrer and those with the higher concentration, 20 and 30 wt.% were mixed by hand. The hydrogels with PVA were heated up to 80C° for 15 minutes while being stirred by the magnetic stirrer for complete dissolution.

After polymer dissolution and cooling, the plasticizers and cleaning agent (citric acid) are added to the gel and mixed by hand. The plasticizers were added in different concentrations, varying from 1 to 30 wt.%, while the cleaning agent was always maintained at its 7 wt.%.

2.3 Electrochemical corrosion of copper sheet

Prior to electrochemical treatments, copper sheets (0.127cmm thickness, 3 cm width x 6 cm length) were rinsed with 0.01 M H₂SO₄. Then, they were immersed in the ASTM

D1384 solution as a corrosive solvent which contains 0.01 M Na₂SO₄, 2.8 × 10⁻² M NaCl, and 16.1 × 10⁻² M NaHCO₃. An anodic potential of 0.150V (vs Ag/AgCl) for 2 h, followed by a potential of 0.380V (vs Ag/AgCl) for 96 h, was applied to the copper sheet using platina as a counter electrode.

For the coins, the chemical corrosion was made by using 0,5mol of HCl (Hydrogen Chlorite) directly applied on the coins in a glass container and leaving them exposed to the atmosphere for one month, in the same container. This caused the corrosion that can be seen in the XRD spectra of figure 3.6.

2.4 Contact Angle Measurement

When first analyzing a material for coating, gels, or adhesives application, it is important to have a general notion on how the medium interacts with the surface, which can be characterized by the surface free energy when in contact with the applied medium.

This surface energy is defined in its reaction to a water medium; thus, it is categorized into hydrophilic (water affine) or hydrophobic (water repellent). This characteristic happens because of attraction and repulsion forces from the material itself and from the liquid medium, and they can be enhanced by distinct treatment methods, such as the Wenzel type, which states that surface roughness enhances its chemistry.

If the surface energy on the material is high, it is expected that it will “pull” the liquid, because the liquid will be attracted to the surface, and so, the applied medium will spread over it, but if the liquid is more attracted to itself than to the surface, it is said to be a low surface energy material, and with that, the liquid tends to remain in a round shape that can easily be separated from the material.

As the Wenzel type suggests, the roughness and oxidation layers enhance the normal hydrophilic properties that a copper sheet presents at constant temperature and humidity, the value for a clean copper is the highest because the sample doesn't have any type of alterations on its surface.

These properties are seen by contact angle (C.A θ_{eq}). Contact angle enlightens the relation between the surface energy (solid) and the liquid by placing a droplet of the medium into the surface of the material and calculating the angle between the droplet outline and the

solid surface exactly at the point where the intersection occurs.

The angle is where the dome touches the sample, where hydrophilic is $C.A < 45^\circ$ and hydrophobic is $C.A > 90^\circ$. Visually, in hydrophilicity there is a spreading of the liquid, and in hydrophobicity there is no spreading, but instead, formation of a high liquid dome on top of the material; that spreading property is called wettability, where a liquid that spreads well is so said to have a good wettability.

The morphology of the surface defines the scope of the coating's wettability property; morphology here is defined as any alterations from the main crystalline structure of a clean material in comparison with the ones from the same composition that have suffered some type of damage, be it physical or chemical.

In order to have a good relative measurement, it is important that all of the samples and droplets are at a stable constant temperature, for the heating or cooling of the liquid and sample surface may cause alterations in the droplet dome measurement. Another important point is to make sure that all the droplets being applied are the same size, for different dimensions may also cause alteration in the numbers.

“Contact angle refers to a method of calculating surface free energy by evaluating the interface of a liquid and a solid surface. A contact angle (also referred to as a wetting angle) is formed when a drop of liquid is placed on a material surface and the drop forms a dome shape on the surface. The angle formed by the connection point at the edge of the dome the water makes on the surface is called the contact angle.”

(BTG Labs, <https://www.btglabs.com/what-is-contact-angle>)

It is also needed to clear out that atmosphere interferes with the angle, the contamination of the solid or the liquid medium may result in different numbers, therefore, it is recommended that the analysis is done in a clean sample, or when is the case of a corroded sample, to be sure that the liquid medium applied is not contaminated.

It is important to evaluate not only the direct contamination itself, but the exposure to variants humidity and temperature for some amount of time, which may also generate differences for metal objects, for there is a reaction in their surface caused by the water interaction; in the case of copper, this interaction results in the formation of a cuprite layer. (Yekta-fard; Ponter, 1985).

Copper oxides have different wetting properties, although they all present a hydrophilic behavior, because of the differences in the morphology and compounds.

In this work, some polymeric matrixes were analyzed in their contact angle in order to understand their wetting properties, on the recognition that the chemical composition, structure, and morphology of the polymer within the matrix directly affects the wetting property; This effect is caused by their different influences on the surface free energy. (Kasalkova et al, 2015).

Besides this wetting analysis, the measurement of the polymeric matrix contact angle may also be used to determine the surface stabilization of the material.

Because the main concern of this work is to determine wettability properties, static contact angle was used as a measure, static C.A means that the calculation was done by a stable and still liquid on the solid surface, opposite to dynamic C.A, where the analysis is done overtime with the spreading of the liquid, and roughness C.A, meaning the effect of the surface morphology on the final angle value. (Biolin Scientific, Contact Angle Measurement).

When it is not possible to make all the droplets the exact same size, as it is by using specially designed equipment, an average number can be achieved by measuring 3 drops on the same sample, considering that the variation is less than 5°. After taking pictures of the domes formed on the surface it is possible to calculate the angles by using a simple computer program.

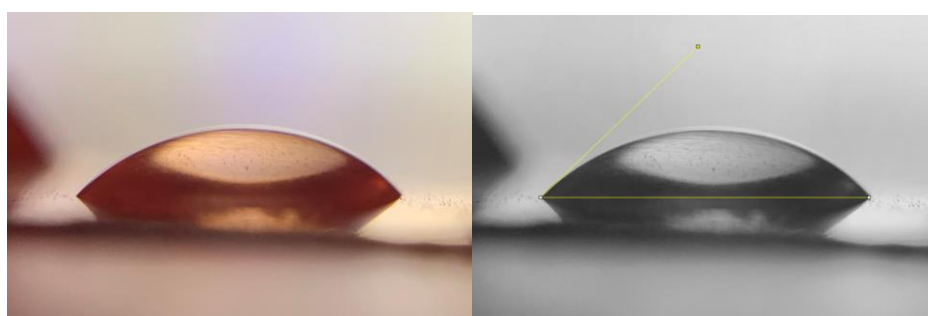


Figure 2.3. Distilled water droplet on a damaged copper sheet.
From left to right: picture with magnifying lens; treated image for
calculation of contact angle ($\theta = 46.708$).

As shown in the image above (figure 2.3), the treatment for the calculation of the angle starts by changing the color of the picture into a black and white font in order for the program to be able to recognize better the edges of the droplet dome and so, to form the angle for the mathematical calculation. The magnifying lenses are important so that the image doesn't lose the resolution, which is very important because the analysis is made on

a small spot, so it needs to be clear.

Overall, this is a very simple procedure to be done, the basic instrumentation for the determination of the C.A, be it on an already assembled equipment by a scientific material company or built in the laboratory, are a camera with microscopic lenses, a lighted background for sample visualization and a pipet for droplet application.

The experiment was done by using an empty box with a semi-transparent background with a light directly applied on the back, where the sample, a copper sheet, was placed horizontally and a droplet of pure water was applied on its surface.

Because the equipment was made by hand, the numbers presented here are an average calculation based on the measurements of 3 droplets on the same sample, where the variation was less than 3° on angle.

In the case of this experiment, the equipment was built in the laboratory taking into consideration what was needed in order to have a good picture; with very simple materials that were easily accessed, such as:

- Tea box, small.
- Magnifying lenses for the cellphone.
- Thin transparent parchment paper.
- Flash light.
- Glass pipette.

First, the box was cut on the shape of a dome and the parchment paper was placed on the back, after that, the flashlight was put and adjusted for the best focus and vision of the sample; the solutions were placed on the copper samples by using a thin glass pipette and the pictures were taken with the magnifying lenses.

The box used in this experiment has a pattern inside, but this does not alter the desired results, for the picture will focus on the cut transparent background with the light source, therefore, any box can be used, but dark colors are preferred in order not to have much refraction of light inside and the shape of the dome of the droplet can be easily distinguished.

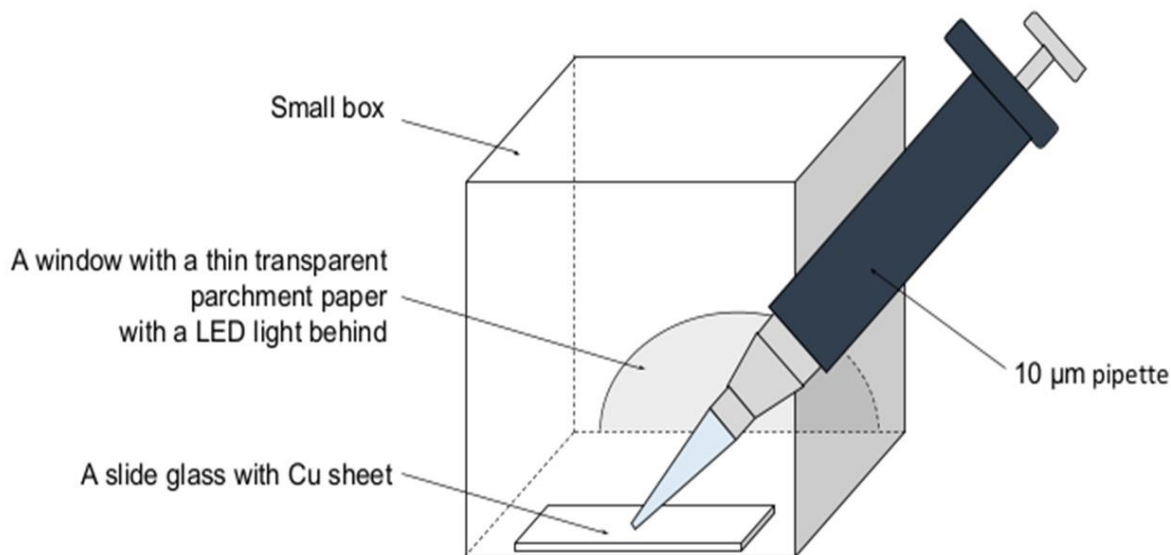


Figure 2.4. Assembly of contact angle equipment.

As can be seen in the picture above (Figure 2.4), it was a simple and non-demanding process that can be used for the optimization of gels and adhesives, it is seen how the equipment looks like after everything is put together, the flashlight had intensity control, and after some attempts, it was seen that a lower light gives better results in the quality of the image; The pictures were taken before any treatment in the computer, by the use of the lenses it is possible to have good results in the quality and overall structure of the sample even when approximated in the computer program afterwards.

By consideration of the results of these experiments, not only in actual results for the research but also by the durability of it, it is recommended for laboratories and conservation / restoration facilities to do this experiment as well before applying the solutions in the metals and other materials that the conservators are not entirely sure which additives works best with them.

2.5 Characterization methods

In order to better understand the copper in its patina, defining the products present in

there, X-Ray Diffraction (XRD) technique was used; and for the bonding between the polymer and the additives, understanding their behavior in different concentrations and linkage with water, the Attenuated Total Reflectance Fourier transform infrared (ATR- FTIR) spectroscopy technique was used.

XRD is a widely used technique in the field of materials science and archaeometry, and it works by irradiating the sample with X-rays and measuring the scattered angles, while the FTIR measures the infrared region of the spectrum.

To better explain, in this thesis, XRD was done on electrochemically corroded copper and clean copper for comparison of products, it was also done on the coins that were used for the hydrogel test. FTIR was done on the gels to understand the bonding and have a determination of concentrations in their formulation.

These techniques were chosen for their potential to bring out the desired information in a non-invasive manner, non-destructive even, although the FTIR does require a small proportion of the sample for analysis, while in the XRD the sample was placed in its entirety.

Both techniques are widely used in the field of archaeometry for they help determine and understand better the material that is being worked on, avoiding damages caused by mixtures that could react in a bad way with some of the elements present in the sample; for this reason it was vital to determine what kind of products were present in the electrochemically corroded copper and have a correlation of the achieved products in the laboratory with the ones of actual archaeological objects, since the goal of this thesis is to determine hydrogels that can be used in these objects in a safe way.

3. Results and Discussion

3.1 Contact Angle Measurement of Pristine Copper

The experiments started with the evaluation of four clean copper samples with different properties on surface, where the first one had a pristine smooth surface, the second one was treated with 0.5 M H₂SO₄ soln. to produce fresh copper surface, the third one was polished with a 240 grind sandpaper sheet, and the fourth one was polished with a 800 grind sandpaper sheet in order to evaluate the alterations in the wettability angle depending on the level of damage that the sample presents. Accuracy of the measurement was confirmed by

repeating the experiment three times for each sample.

Below (Figure 3.1), the results of these first measurements can be seen, and with them it was proven that the contact angle of water on the copper, stored in an environment with no significant ambient variations (constant humidity, temperature, and composition of air) was 75.2° . According to the literature (W.A. Zisman, 1964), highly hydrophobic materials, such as fluorinated polymers, show a contact angle with water higher than 120° . Compared to this, pristine copper presents hydrophilic properties.

To understand how the wetting properties are altered depending on the conditions that present on the surface, another test was made using the copper plate with different roughness conditions.

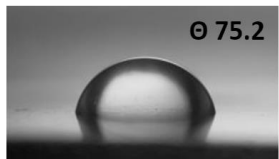
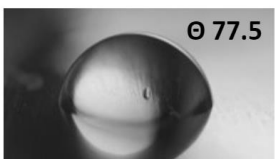
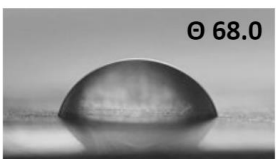
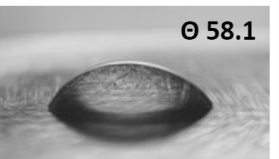
Pristine Cu	Cleaned Cu	Sandpaper 800	Sandpaper 240
			

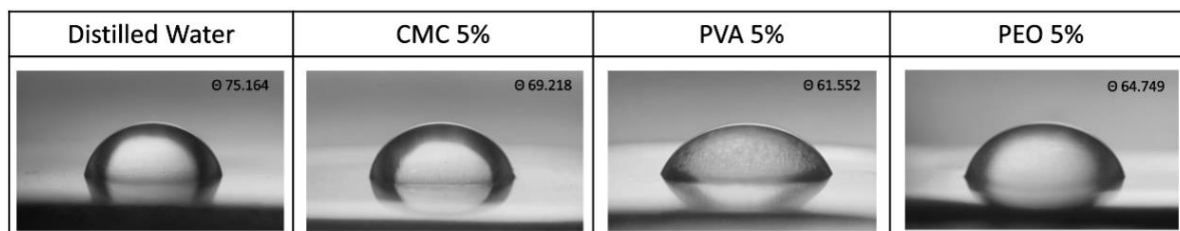
Figure 3.1. Contact angle of distilled water droplet on different copper sheet samples. From left to right: Normal Cu; Cleaned Cu; Cu Scratched with Sandpaper 240; Cu Scratched with Sandpaper 800.

A copper sheet left at room temperature, without any modifications (pristine Cu), exhibited a water contact angle of 75.2° , which is slightly smaller than that of the copper sheet cleaned with H_2SO_4 . It is known that copper in ambient starts to develop some patina, specially Cu_2O (cuprite), and this circumstance is seen by the measurement of their contact angles. Considering this patina formation, it is expected that the hydrophilicity will increase, because hydrophilic copper is formed.

Because not only the conditions of copper but also the solution applied on the top of the sample affects the contact angle, the other test was made by using the aqueous solutions containing polymers selected for the preparation of the hydrogels. This analysis is important also for the selection of a suitable polymer structure that has good compatibility with copper, as it is expected that the gel with a high wettability shows a good penetration ability in the porous corrosion products, resulting in the removal of inner corrosion.

The solutions containing 5% (w/w) polymer were prepared for his analysis. This low concentration value was decided in order to keep a low viscosity of the liquid solution to make

the measurement, since the solution with a higher polymer concentration is more viscous and harder to form a droplet with a precise volume.



***Figure 3.2. Different solution droplets on normal copper sheets.
From left to right: distilled water; CMC 5% solution; PVA 5% solution; PEO 5% solution.***

As can be seen above (Figure 3.2), the presence of polymers in the applied medium made a difference in the angle compared to the distilled water. The contact angle decreased in the following order: water > CMC 5% solution > PEO 5% solution > PVA 5% solution, meaning the solution has a greater wettability when polymers are evolved. This is a good result considering that the addition of polymer contributes to the higher wettability, and the gel is expected to be able to penetrate in porous corrosion layers.

3.2 Preparation of Polymer Solutions

For the selection of suitable polymers for the preparation of hydrogels, the chemical structure was taken into consideration from the point of view of the solubility in water, the interactions with hydrophilic copper surface, also the stability in the presence of acid, because citric acid is used as the cleaning agent. Based on this definition, three candidates of polymers: PVA, CMC and PEO were selected. These polymers are also known to be not harmful for the environment and the copper.

In the first phase of the testing, quick screening of these polymers was done in terms of the viscosity of the hydrogel to keep the gel in the applied area and the property of a film which was obtained by casting and drying the gel on a clean copper sheet. For this analysis,

the solutions containing 10% (w/w) polymers are prepared, and citric acid was added in a concentration of 7% (w/w); these concentrations were defined according to literature, in order to have a primary understanding of the physical properties of the polymers in the state of gel (wet) and film (dry).

Table 3.1. Property of the gel and the film obtained by drying the gel coated on the clean copper.

Polymer	Gel (Wet State)	Film (Dried State)
PVA	Highly viscous and area selective	Flexible and adhesive on copper
PEO	Fluid and spread on the copper sheet (not area selective)	Very fragile solid layer
CMC	Highly viscous and area selective	Fragile film

As summarized in Table 3.1, PVA and CMC formed highly viscous gels which can remain in the applied area, *i.e.*, area selective, while the gel of PEO was fluid because PEO was not solubilized completely. After applying and drying the gel on the copper, films were obtained but none of them were particularly good in terms of adhesiveness and elasticity. The film of PEO was especially fragile and could not be pulled off. Therefore, PEO was excluded from further evaluation.

Then, a new experiment was made at an attempt to define the best concentration of polymer for this gel formation in a way to enhance the properties, since it was noticed from the previous experiment that the thickness of the polymer film was too thin and not good for a corrosion removal. For this optimization test, the polymers were individually added to pure water in a proportion of 5%, 10%, 15% and 20% (w/w), and mixed with magnetic stirring until gel formation, where PVA was heated up to 80°C for about 15 minutes in order to diminish its dissolution time and have a homogeneous mixture.

As it can be seen in Table 3.2, there was a lot of difference in the properties of the gels depending on the amount of the polymer, where 5% (w/w) polymer was not enough to change the solution from liquid to gel form, whereas the gels with 10 and 15% (w/w) polymer presented a good viscous property and allowed a good area selectivity, but the 15% gels can be obtained by hand mixing rather than magnetic stirring, differently from the 10% (w/w) gel,

that presents a less viscous aspect. This difference can be more easily understood visually by the images of the physical appearance of the gels in their different concentrations (Figure 3.3). The 10% gel was slightly fluid and expected to be area-selective only when it is applied on the horizontal area, while the 15% gel was enough viscous to remain in the area which is not horizontal.

Table 3.2. Effect of the polymer concentration on the possibility of magnet stirring of polymer solution (top) and thickness of the film (bottom).

	Concentration of polymer / wt. %			
	5	10	15	20
PVA	Easy	Easy	Possible	Hard
	Too thin	Thin	Thick	Not uniform thickness
CMC	Easy	Easy	Possible	Hard
	Too thin	Thin	Thick	Not uniform thickness

The gel with 20% polymer was also very viscous but it did not become homogeneous even after a hand mixing. The transparency of the gels is a good indication of complete dissolution of the polymer. The 20% gels were slightly turbid, suggesting that this concentration is too high to dissolve the polymers completely.



Figure 3.3. Pictures of the gel based on CMC with different concentrations.

During the drying experiment, where the gels were put on a copper sheet and dried to obtain a film, it was noted that thicker and mechanically stronger films were obtained by increasing the polymer concentration from 5% to 15%. The films obtained from the 20% gels were not uniform due to the presence of the insolubilized polymers. It should be noted here that some of the polymer films became too adhesive upon drying, and in order to try to fix this issue the use of plasticizers is discussed in the next section.

To summarize, PVA, CMC and PEO were selected as candidates to form the hydrogels because of their hydrophilic structure, chemical stability, and environment-friendliness. However, viscous gel was not obtained with PEO, and this was excluded from further assessments. By increasing the concentration of PVA and CMC, the gel became more viscous, which is favorable for the area selectivity, and the films became thicker. However, 20% was too high in order to obtain a homogeneous gel. As a result, from this experimental part, there is the defined concentration of polymers in a solution, and that is a 15% (w/w).

3.3 Effect of Additives in Hydrogel

In the previous experiment, the film was successfully formed from the hydrogels. However, the obtained film was rigid and not flexible. Baglioni *et al.* reported that the use of plasticizers makes the final films flexible, elastic, and less rigid. Also, adhesiveness of the film is improved with respect to neat PVA films, and the films are thus more suitable for peeling off from a delicate surface. In addition, by using the additives with hygroscopic properties, the time required for water evaporation increases and the gel can react with the patina for a longer time, which is expected to be advantageous for the corrosion cleaning. For the plasticizer's experiments, again some literature review was made in order, trying to compare the most used plasticizers with the polymers previously chosen; after this, analysis on their chemical structure, water solubility and interaction with the polymers and the citric acid was also investigated.

Also, by considering the easy access and environmental factors, the testing on the plasticizers to be used in the gel formulations with CMC and PVA were BA, GLY, PEG, and their mixtures.

Table 3.3. Effect of the plasticizers added to the 15% (w/w) PVA gel on the viscosity of the gel and the elasticity of the film obtained by drying the gel coated on the clean copper.

Additive	Concentration (wt%)	Consistency of Solution	Film Formed on clean Cu
-	-	Viscous gel	Non-extendable
B.A	0,5	Non-fluid gel	Non-extendable
GLY/B.A	4,5/0,5	Non-fluid gel	Extendable
GLY	5	Viscous gel	Extendable
PEG	5	Viscous gel*	Non-extendable
PEG/GLY	2,5/2,5	Viscous gel*	Extendable

* the gel was turbid.

As described in Table 3.3, when considering PVA based gels, their viscosity increased by the addition of BA because of the crosslink formation between PVA and BA. The other additives did not alter the viscosity of the gel. When PEG was added, the gel was slightly turbid, suggesting that PEG was insoluble in the gel (Gadhav et al, 2020).

When the focus is placed on the film, the ones containing GLY have shown to be more extendable than the ones with only BA and PEG. The gels containing BA usually presented this non-extendable characteristic, but the gel where BA was put together with GLY was removable from the copper, this is because of the GLY properties. The PEG basically presented the same characteristics as BA, although the film made by the addition of PEG was not as brittle as the one with BA, it was still hard upon removal. Therefore, BA was discarded as a possible additive for PVA.

As for the CMC based hydrogels (see Table 3.4), it was noted that the gel containing BA almost completely dried, leaving a very rigid and adhesive film on the copper, presenting the same characteristic seen before in the PVA based hydrogels, and so it was again discarded as a possible additive for CMC. The gel formulations containing PEG were the most easily peelable, in fact, it even looked like they were already kind of detached from the copper plate. This is not a good property for corrosion removal, because corrosion cleaning takes place at the adhered interface. Also, there is a fear of contamination of copper surface with the remaining PEG. In order to solve this problem, an analogous of PEG with lower molecular weight and terminal methyl groups, namely PEG DE, is used. Employing PEG DE, the bleed out of the additive was successfully controlled, and the film including PEG DE was

found to be elastic. The gel formulation with no additive and the one with only GLY showed similar properties in terms of a good viscosity and elasticity of the capabilities of the peeled film; Based on these observations, for the following tests, it was decided to use these two formulations: CMC without additive and CMC with PEG DE.

Table 3.4. Effect of the plasticizers added to the 15% (w/w) CMC gel on the viscosity of the gel and the elasticity of the film obtained by drying the gel coated on the clean copper.

Additive	Concentration (wt%)	Viscosity of the gel	Elasticity of the film
-	-	Viscous gel	Extendable
BA	0,5	Viscous gel	Rigid
GLY/BA	4,5/0,5	Viscous gel	Rigid
GLY	5	Viscous gel	Extendable
PEG	5	Viscous gel	Extendable*
PEG/GLY	2,5/2,5	Viscous gell	Extendable*
PEG DE	5	Viscous gell	Extendable

* PEG remained on the copper surface

In conclusion to this experiment, and as a guideline to the following tests that will be made using the final formulation that were outlined here as the best ones, in what concerns the PVA based hydrogels, the addition of the GLY helps in the enhancement of the elasticity of polymer, and this will be used together with PVA in all the following formulations. For CMC, in the following experiment, CMC with no additives will be taken into consideration in addition to the CMC with PEG DE as an additive.

3.4 Effect of Additive Concentration on the Film

The next step after defining the type of additives was to define the best concentration of them on the hydrogel, by considering an ability to form a peelable film on clean copper after drying and the elasticity of the peeled films (Table 3.5); The evaluations were made using only the one additive for each polymer that worked better in the previous results, specifically PVA with glycerol and CMC with PEG DE. Considering that citric acid is used as a cleaning agent for copper corrosion in the following sections, the evaluation has been done with respect to the hydrogel including 7% (w/w) citric acid.

Table 3.5. Film formation ability (top) and elasticity (bottom) of hydrogels.

<i>Polymer</i>	<i>Additive</i>	<i>Concentration of additive / wt%</i>			
		<i>0 – 1 - 3</i>	<i>5 - 7</i>	<i>10 - 20</i>	<i>30</i>
<i>PVA</i>	<i>GLY</i>	<i>Adhesive</i>	<i>Peelable</i>	<i>Peelable</i>	<i>Peelable*</i>
		<i>-</i>	<i>Rigid</i>	<i>Elastic</i>	<i>Elastic</i>
<i>CMC</i>	<i>PEG-DE</i>	<i>Adhesive</i>	<i>Peelable</i>	<i>Peelable</i>	<i>Peelable</i>
		<i>-</i>	<i>Rigid</i>	<i>Elastic</i>	<i>Elastic</i>

In the evaluations with both PVA and CMC, it can be noted that the concentrations of 10 and 20 had the best results, giving a formation of a peelable elastic film. By decreasing the concentration of additives, the peeled film became rigid with 5 or 7% (w/w) additive concentration, and the film was adhesive and not peelable when the concentration of additive was less than 3% (w/w). For the PVA + GLY formulation, the addition of 30% (w/w) resulted in a n elastic film but the gel was too fluid to keep the gel in the selected area. When considering CMC, the results for the 30% (w/w) were different, where it basically presented the same characteristics as the gel with 10 to 20% additives.

3.5 IR Analysis of Hydrogel

The hydrogels based on PVA and GLY, as well as ones based on CMC and PEG DE were analyzed by means of IR spectroscopy. The samples are composed of water-based solutions, and so in the spectra of PVA - based hydrogels, the water peaks can be seen at 1700 and 3400 cm^{-1} and they overlap the peaks of OH bond in PVA and GLY. The intensity of these peaks decreased by increasing the concentration of GLY.

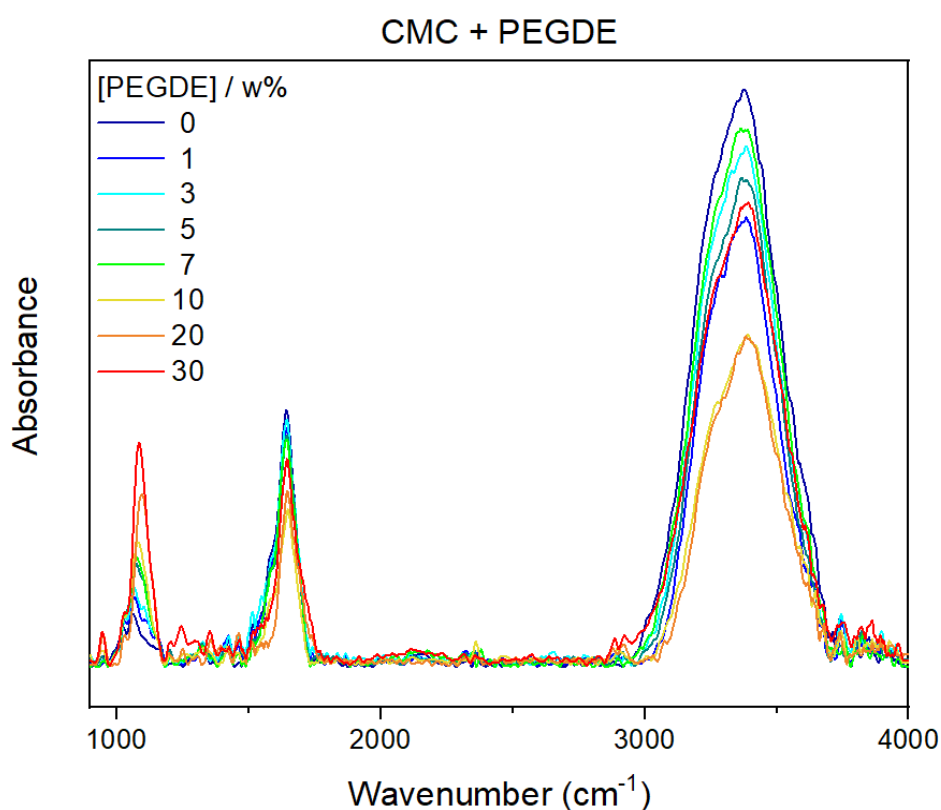


Figure 3.4. FTIR spectrum of PVA based solutions with different concentrations of GLY

Given that there was no shift in these peaks, a proof of a formation of interactions is not easily detected (Figure 3.4). Around 1100 cm^{-1} , a peak of C-O stretching in PVA is observed when the additive is absent. The increase in the additive concentration can be seen by the appearance of two new peaks at 1050 and 1150 cm^{-1} and by the increasing of their peak intensities.

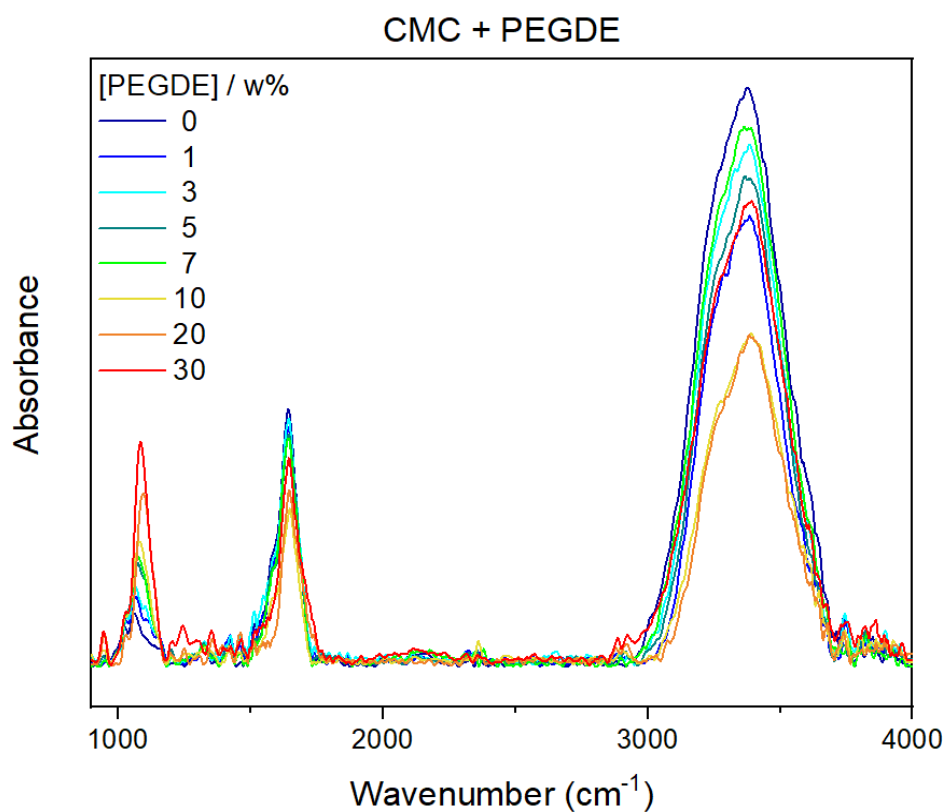


Figure 3.5. FTIR spectrum of CMC based solutions with different concentrations of PEG DE

Similar to the IR spectra of the PVA gels, in Figure 3.5 the peaks around 1700 and 3400 cm^{-1} are because of the presence of water, as well as the OH groups in CMC. Around 1700 cm^{-1} , there is also a peak related to the C=O bonds in CMC. The most important peak to be analyzed is around 1100 cm^{-1} , arising from the C-O bonds in both CMC and PEG DE. There is a peak shift to a higher frequency by increasing the concentration of PEG DE from 1% to 20% suggesting the formation of the interactions between CMC and PEG DE such as ion-dipole interaction. Further addition of PEG DE up to 30% caused a peak shift to a lower frequency. This suggests that the presence of 30% additive is excessive to enhance the interactions in the gel.

3.6 XRD Evaluation of Corroded Copper Sheets and Bronze Coins

The analysis of an electrochemically corroded copper sample and chemically corroded coin was done by using XRD technique. The XRD spectra serve as indicators of corrosion products present in the sample.

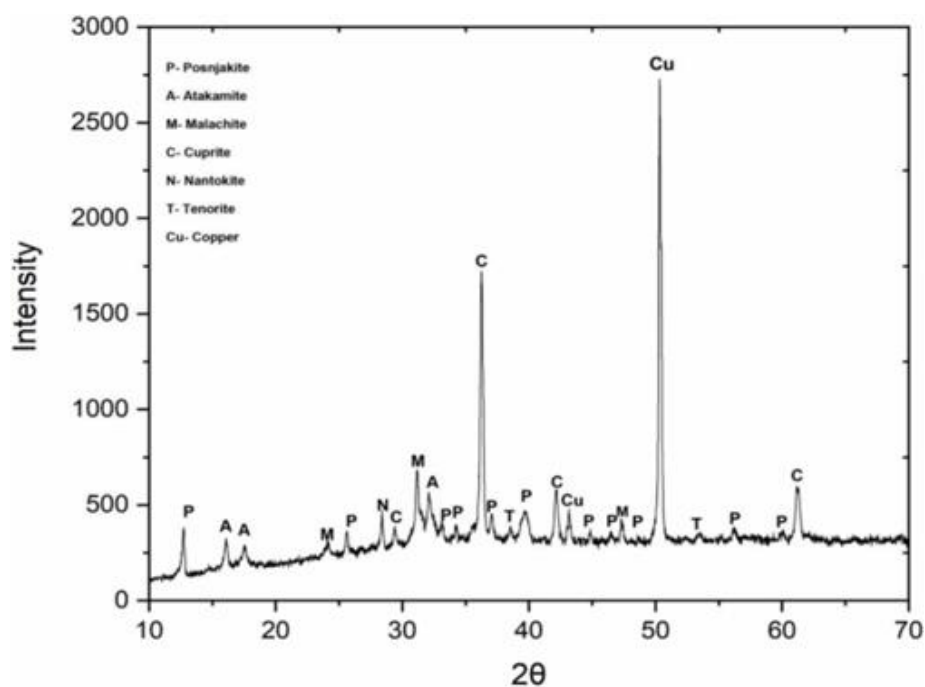


Figure 3.6. XRD pattern of electrochemically corroded copper.

In the electrochemically corroded sample, peaks related to cuprite (C: Cu_2O), malachite (M: $\text{Cu}_2\text{CO}_3(\text{OH})_2$), atacamite (A: $\text{Cu}_2\text{Cl}(\text{OH})_3$), posnjakite (P: $\text{Cu}_4\text{SO}_4(\text{OH})_6(\text{H}_2\text{O})$), tenorite (T: CuO), and nantokite (N: CuCl) were observed (Figure 3.6). By analysis of the patina present on the corroded copper, it was confirmed that patina present in archaeological copper objects, such as malachite and cuprite, was possible to be reproduced by the electrochemical corrosion, and it was confirmed that the electrochemically corroded copper is a good standard material for corrosion removal.

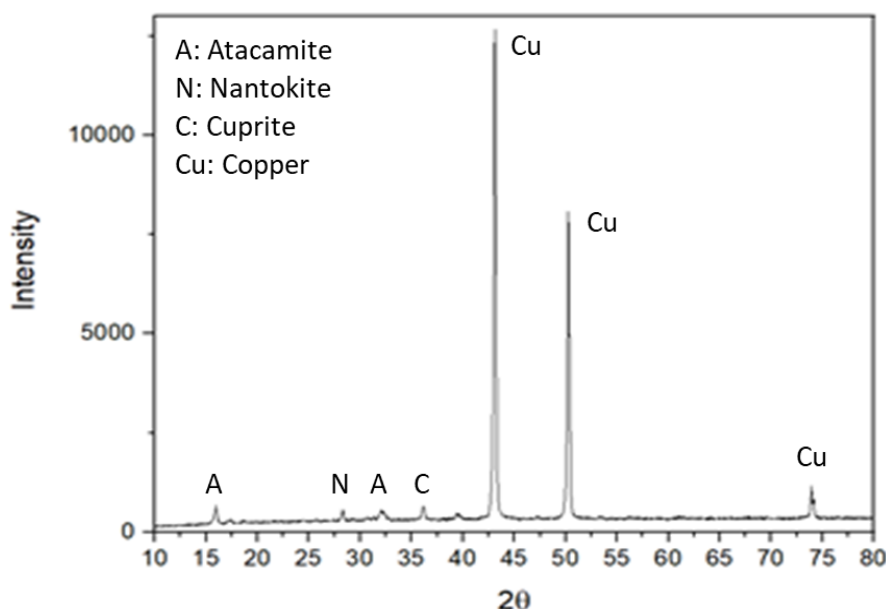


Figure 3.7. XRD of chemically corroded copper-covered steel coin.

In the XRD patterns of chemically corroded coins (Figure 3.7), two strong signals of copper are observed at 43.3° , 50.4° , and 74.4° (2θ) corresponding to (111), (200), and (220) planes. In this case, the patina containing Cl such as atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$) and nantokite (CuCl) was present in addition to cuprite. This is because the coin was exposed to the atmosphere containing HCl.

3.7 Cleaning of Copper Corrosion using Hydrogel

After the definition of the additives to the polymer gels, new tests were made using them directly in the electrochemically corroded copper sheets, in order to evaluate their ability of patina removal in relation to the time taken for the formation of film on the copper and the types of removed corrosion (only surface corrosions or also internal corrosions). The assessment was made by applying 0.04 g gel with 5wt% additive and 7 wt.% citric acid on a circle area with 1cm diameter on electrochemically corroded copper (Table 3.6).

It should be noted here that it is important to consider that the environmental factors directly affect the time for removal, where an increase in temperature will diminish the time for the film formation, for it will promote a faster evaporation of the volatile compounds on the

gel. The experiments depicted here were made at room temperature of about 17° Celsius and the humidity was considerably high. Accordingly, the evaporation of water is expected to be slow.

The gel containing only CMC was applied first, where it was noted that the best time for its removal is between 4 and 5 hours after application and the gel presented a film with complete removal of malachite and cuprite with no residues left. The gel with PEG DE presented more adhesive film on copper which removed mainly the surface malachite layer and a part of the bottom cuprite layer. The gel containing CMC and GLY was not a good mixture for this type of application, given that, in between 1 and 3 hours the gel was still soft and did not form a film, at 4 hours a thin film was formed but not homogeneous, some parts were still soft, but at 5 hours it formed a film which is very adhesive on the copper. The film retained a desirable property, specifically peelable and elastic, only in a very small window of time. After 5 hours of drying, the removal of the film required physical stress. For the CMC gels there was a good result for no additives, but it completely removed all of the corrosion products, which may be a problem if the conservator's intention is only partial removal of the patina. In this case, the addition of PEG DE is expected to be useful for the removal of selected corrosion products.

Table 3.6. Time for the formation of film on corroded Cu (top) and species of removed corrosion (M: malachite and C: cuprite) after peeling the film (bottom). All solutions contain 7w% of citric acid as a cleaning agent.

	Additive	1h-3h	4h	5h	>12h
PVA	GLY 5%	gel	Peelable film	-	Adhesive film
			M		M and C
CMC	-	gel	Adhesive film	-	-
			M and C		
	GLY 5%	gel	Too soft film	Adhesive film	-
			M and C		
	PEG DE 5%	gel	Adhesive film	-	-
			<u>M and C (minor)</u>		

It can also be seen that in this test, there was a good result for the PVA with GLY as an additive. In 4h the film was formed, but the film was semi-wet and there was only malachite removal, whereas in 12h after application the film was completely dried and it was able to remove cuprite, which is in the bottom of the malachite layer. However, the removal of cuprite was physical and not chemical. Therefore, depending on the fragility of the artifact, if this type of removal can be done or not, the drying time of the gel needs to be controlled.

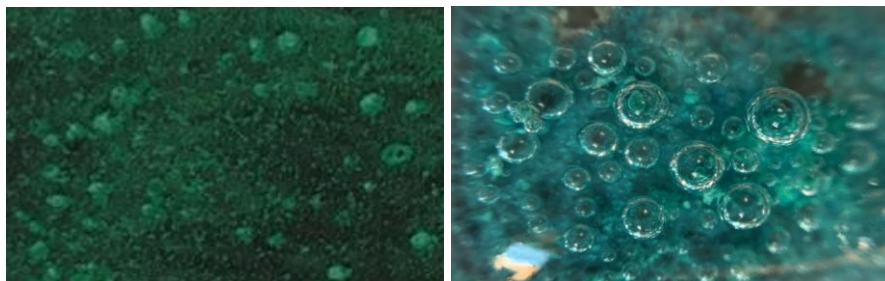
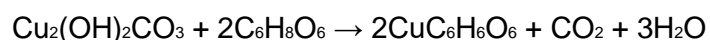


Figure 3.8. Electrochemically corroded Cu before (left) and after (right) application of hydrogel containing citric acid.

It is also important to point out that in all films the malachite layer was removed via chemical reaction with citric acid, as can be seen above (Figure 3.8). This removal is expressed on the formula below:



The formation of CO_2 can be confirmed by the formation of bubbles on the copper patina once the gel is put on top (see Figure 3.8). Also, in Figure 3.8. on the right, there is a noticeable extraction of the malachite layer from the copper to the gel. When the film is peeled, the malachite is within its matrix, which proves that there was a dissolution of malachite at the interface of Cu and the gel medium. In this reaction the polymer does not take part in it, but it is used as a matrix in order to retain citric acid on top of the layer for a time long enough to provoke a successful reaction and have an easy removal by peeling. The use of polymer contributes to the removal of cuprite. In the case of cuprite, the removal was done by physical means, and was achieved only when the film dried and became enough adhesive on the copper.

3.8 Effect of Additive Concentration on Corrosion Cleaning

In both tests in the former section, the gels had the addition of citric acid in the fixed concentration of 7% (w/w) and the polymers also had a fixed concentration of 15% (w/w) as defined in the section 3.2. Here, an effect of the different concentration on the cleaning efficiency was assessed. As for the cleaned copper sample (section 3.4), it was seen that the similar concentrations did not show a big change in the gel properties, only the concentrations of 1, 5, 10, 20 and 30 % (w/w) were tested (Table 3.7).

Table 3.7. Effect of concentration of additives on species of removed corrosion (M: malachite and C: cuprite). All gels contain 7 wt.% citric acid.

Component	Concentration of additive / wt%			
	1	5	10	20 – 30
PVA + GLY	M and C(minor)	M and C (minor)	Mainly M	Only M
CMC + PEG DE	M and C	M and C(minor)	M and C (minor)	Only M

Although the elasticity of the film is improved by increasing the amount of the additives, there was not much difference in the concentration range above 10%. For PVA, cuprite was removed from the corroded copper as a minor species regardless of the additive concentration, and the removal was effective especially for malachite. Because the smaller concentration should be considered in order to avoid the high usage of chemicals, we concluded that 10% is adequate for the improvement of flexibility of the film and for the selective removal of corrosion in the case of PVA-based hydrogel.

For CMC, no additives, or the smallest addition of them can remove cuprite, whereas the higher concentration of plasticizer results in a partial removal of cuprite. If the goal is to not remove the cuprite layer, CMC should not be considered, because it promotes the removal of cuprite. When this is the problem, the conservator needs to consider increasing the PEG DE concentration on CMC. However, after peeling the film, we found that copper is slightly wet, probably because of the bleed out of PEG DE. Because the addition of PEG DE on the CMC gel didn't cause much difference in the film formation or in the drying time, the following experiments to define the final gels were made with no additives for CMC.

3.9 IR analysis of PVA film Before and After Corrosion Removal

Another analysis using IR spectroscopy was made on the membranes that were formed by the gels on clean and corroded copper (Figure 3.9). The effect of water on the spectra is less compared to the results shown in section 3.5 since the film is dried at room temperature overnight.

As shown in the red curve, the peaks for O-H groups in PVA and GLY can be seen in between 3000 and 4000 cm^{-1} . In addition, the peak of C-H stretching vibration is visible around 2900 cm^{-1} . Below 1500 cm^{-1} , vibrations such as C-O stretching are visible. By the addition of citric acid (yellow curve), it can be noted that a stretching vibration of the C=O in citric acid appeared around 1700 cm^{-1} , which is shifted to a smaller wavenumber (around 1550 cm^{-1}) after the used of the film for the corrosion removal (blue curve). The presence of malachite in the post-cleaning film can be confirmed by the increase in the peak intensity around 1400 cm^{-1} related to the carbonate groups in malachite.

The shift of C=O peak of citric acid can be understood by the analysis of the structure of citric acid. Pedroni *et al.* (2013) reported that when the H^+ of citric acid is replaced with Na^+ , its peak shifts towards a lower frequency. In the present case, since citric acid reacts with malachite, the H^+ is considered to be replaced by Cu^+ . Although the species of cations are different, the replacement of H^+ with metal cations is considered to cause a similar peak shift. Indeed, in the FTIR spectra of copper citrate reported by Zhang *et al.*, a strong peak is confirmed around 1558 cm^{-1} , which corresponds to the FTIR spectra made from the post-cleaning membranes.

This result shows us that the gel successfully extracted the malachite layer from the copper via a chemical reaction, which was our primary intention, since a physical removal is not a good treatment for patinas from fragile artifacts.

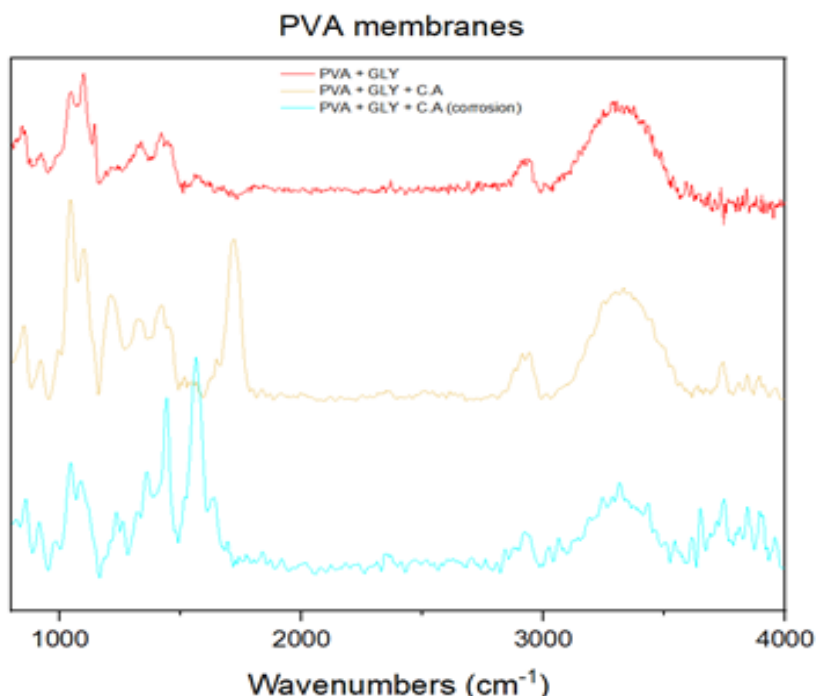


Figure 3.9. IR spectra of PVA membranes: the one with addition of GLY (red), the second and third one with the addition of GLY and citric acid (CA) before (yellow) and after (blue) the removal of corroded copper.

3.10 Comparison of Cleaning Efficiency between In-situ and Ex-situ Hydrogel

In order to understand the best way to approach the corrosion removal is really the by film formation upon drying directly applied to the corrosion, comparisons were made between a film that is formed on the sample (*in-situ*), meaning that it is applied still in a gel state and dried within the patina, and a film formed outside (*ex-situ*), meaning that a dry film is initially prepared from the gel put in a solution containing citric acid, and then placed on the patina.

It is important to point out that for this experiment the room temperature was higher than the previous experiments and the drying was faster. In the previous experiments with a temperature of 17° Celsius, the drying time was 4 hours, now with a 23° Celsius, the drying time lowered to 40 minutes to 1 hour; more specifically, for CMC the removal was done in the 40 minutes and for PVA, because of the addition of glycerol, that maintains water for a longer time, the removal time was in the 1 hour.

For this experiment, another modification in the removal was made. The analysis of the previous removal, which was made by tweezers to peel off the film, could cause some damage to the object in case we are dealing with a sensitive piece. This is because the edges of the film are thinner and dried faster, and in turn it is necessary to force a little on the edge for the peeling. This problem was solved by using glassine-paper cut in the shape of the desired application area. By applying the hydrogel over the glassine paper with a cut, when removing the paper, the gel comes out with it. In this way, it is not necessary to touch or force the object at all. Figure 3.10 compares results of cleaning of electrochemically corroded copper by *ex-situ* and *in-situ* films. In the same figure, the shape of glassine paper can be better understood.

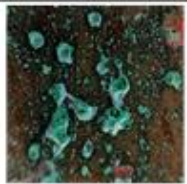
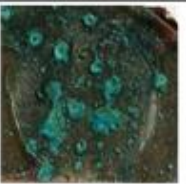
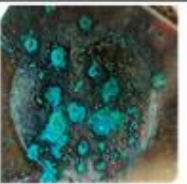
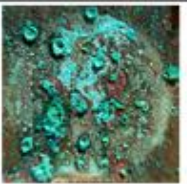

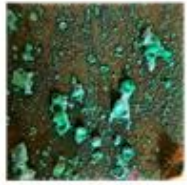
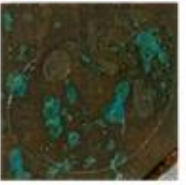
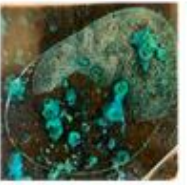
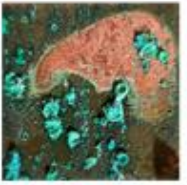

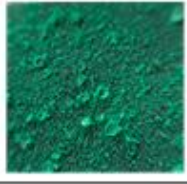

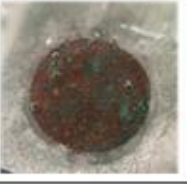
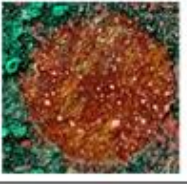

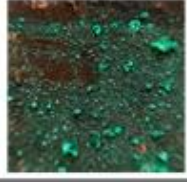
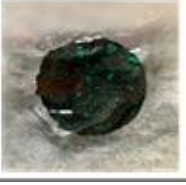
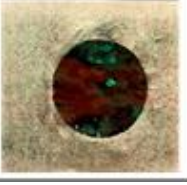
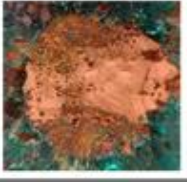
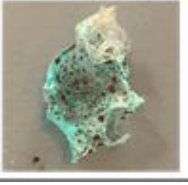
	Corroded Cu	During cleaning		After cleaning	
		After 0 min	After 10 min	Cu	Film
<i>Ex-situ</i> PVA+GLY					
<i>Ex-situ</i> CMC					
<i>In-situ</i> PVA+GLY					
<i>In-situ</i> CMC					

Figure 3.10. Efficiency of corrosion removal from electrochemically corroded copper using *in-situ* and *ex-situ* films.

When *ex-situ* CMC film is applied on the corroded copper, only the upper half of the film was in contact with the copper because the *ex-situ* CMC film was not flexible enough for adhering to the copper. The film was possible to remove cuprite, but only in the areas where there was contact between the film and copper, causing a non-uniform cleaning. In the case of *ex-situ* PVA, the whole film was in contact with the copper. However, cleaning efficiency was not high; only a small amount of malachite and atacamite were removed but leaving the cuprite layer. This is because the *ex-situ* films cannot penetrate the porous corrosion. Therefore, the depth of cleaning was not sufficient when *ex-situ* films were used.

As shown in the 3rd and 4th lines of Figure 3.10, the *in-situ* films can remove deeper patina layers, while the *ex-situ* can only remove the more external ones. For *in-situ* CMC, the gel was dried fast and a little brittle on removal, as can be seen in the picture in Figure 3.10 by the fact that the shape of the membrane is not consistent to the shape of the hole formed on the glassine paper. The cuprite removal was not complete as can be seen in the cleaned copper and in the membrane with the red tiny spots. In the case of *in-situ* PVA, the film was easily peeled off from the corroded copper. In this case, cuprite removal was minor, confirming the presence of GLY, which improved the softness of the film and controlled the adhesiveness of the film on the copper. In order to leave the cuprite layer and remove only malachite, the PVA+GLY gel is the better one.

To conclude these results, the *in-situ* formation of films is better meant to remove the inner products in the porous corrosion. When the additive is absent, the CMC membrane is dried quickly and completely resulting in the physical removal of cuprite in addition to the removal of malachite. By using the additive, the resulting film of PVA and GLY retained a semi-wet state, and the cuprite removal was controlled. Based on our results, depending on the demand of conservators in terms of the corrosion species required to be removed, the hydrogel formulation can be controlled.

3.11 Application of Hydrogel on Coins

Using the optimized gel formulations that were selected, namely, PVA + 10%GLY and CMC, the possibility of applying them to an object was assessed. In order to understand and evaluate the reproducibility of the gel in a little closer to reality, since the aim of this work is that the gels can be applied in archaeological objects, the final gel formulation was tested

on chemically corroded coins to have a test on a real object (Figure 3.11). The other aim of this analysis is also to understand if the gel behaves differently on a copper combined with other metals.









According to the information from the European Central Bank, 1 cent coins are composed of copper-covered stainless. Therefore, the coin is not alloy but its chemical stability can be different from the pure copper we have tested.

Prior to the corrosion removal, XRD was made in one of the coins (see section 3.6), where the peaks observed in the spectra were related to mainly atacamite, malachite and cuprite.

As explained in section 2.3, these coins were made in the laboratory by chemical means, where they were kept in the airtight container with a 0,5 mol solution of HCl and left at room temperature (about 26° Celsius) for one month. The coins were cleaned by using 0.5 M H₂SO₄ solution before the formation of corrosion, and therefore, all patina was produced during the corrosion treatment.

The application of gel was done in the entire object and there was no need to use the paper protection / area selection-because the corrosion was formed uniformly.

Figure 3.11. Chemically corroded 1 cent coins during corrosion removal using the hydrogel.

	Pristine	During cleaning	After cleaning	
		After 10 min	Removal	Coin
PVA +GLY				
CMC				

Similar to the results on the copper sheet, the films maintained the expected aspect, where the PVA + GLY film was easy to peel and very elastic, and the CMC film was a little

more brittle and had breakage, but still came out very easily. The problem with this breakage of the film, especially when dealing with archaeological artifacts, is that it is necessary to keep trying to get the edge of the film on the object, and that can cause harm and scratching, while by removing it starting from the edges of the objects and having a single peeling doesn't cause harm at all. For the coin with a high hardness, the property of both films is acceptable.

When analyzing the cleaning of the coin, both gels provided a complete removal of the green patina, returning the coin to its original color. It is important to point out that the cuprite layer of the coin was thinner compared to that formed on the electrochemically corroded copper. As can be seen on the films being pulled out, no red spots are observed, but the copper was able to return to its original color due to the thinner cuprite layer. Even though the coin has a fine carving design on its surface, the gels were able to remove the patina also from this structure, confirming the advantage of *in-situ* film.

4. Conclusion

The purpose of this thesis was the development of new hydrogels for the cleaning of the copper patina, with a focus on the type of corrosion, respecting the different demands in terms of layers to preserve and remove, and considering the environmental factors as a main guide for the choice of the elements present in the gel.

For this purpose, the tests were divided into two focus areas: corrosion and gel. For the corrosion analysis, XRD experiments were made in order to understand the products present in the patina and contact angle measurements with corroded and non-corroded copper were made in order to understand the hydrophilicity of metal surfaces and interaction with the gels. For the characterization of the gels, different concentrations and additives were assessed.

The contact angle analysis regarding the gel formulations was performed and it was proven that copper has a high surface energy, and that the chosen polymers in the solutions have a good controlled spreadability on it, even considering the roughness and corrosion differences in the surface.

For the gel analysis, as a first step after some of the formulations were done, was to do experiments with FTIR-ATR, in order to understand the interaction of the polymers with the citric acid and with the additives, also, membrane testing were made after removing the films from the corrosion to understand the chemical process of this removal.

For the formulation of the gels itself, in the investigation steps of this work, the first part was to research on polymers on their chemical structure and water solubility, considering also their interaction with the copper; after defining the desired polymers for the conduction of the experiments, more research on possible additives was made by previous studies using hydrogels in archaeological materials, as well as the type of reagent used to provoke the chemical reaction and so, remove the desired patina.

Contact angle measurements were made in order to understand the hydrophilicity of copper and the wettability of the solutions. The contact angle experiment showed the following order: water > CMC 5% solution > PEO 5% solution > PVA 5% solution, meaning the solution has greater wettability when polymers are evolved. This is a good result considering that the addition of polymer contributes to the higher wettability and the gel is expected to be able to penetrate in porous corrosion layers.

The second step for the gel formulation was to test different concentrations of polymers and additives until find the one with best viscosity and selective application; this was made by using copper samples, both clean and corroded, to understand the behavior of the gel in these different situations and if, in fact, it could remove the patina without causing any harm to the copper itself (no reaction with the metal).

After testing in electrochemically corroded copper sheets, the two final gel formulations were also tested in chemically corroded bronze coins in order to analyze the applicability of the gel in real objects and understand its behavior in a copper alloy (bronze is composed of copper and tin, but the main products it develops in its patina come from copper reaction).

Considering the results from all of the testing, with emphasis on the final test on the copper sheets and on the coins, it is possible to say that both of the gels presented here in the experimental part, with PVA and CMC as the polymer matrix (PVA with the addition of glycerol), presented successful results and can be used depending on the desired results, while the PVA gel has a more selective cleaning, usually leaving intact the cuprite layer, the CMC gel has a complete removal of the patina, and so, it is up to the conservator to choose which one suits the project better.

After the testing with the different concentrations and of optimization, the final formulation that works best is on 15% w/w of polymer and 7% w/w of citric acid, with the possible incorporation of 10% w/w of additives depending on the polymer being used, which can be increased into 15% w/w in case the cuprite really needs to be preserved.

As it is shown by the results in this thesis, the CMC gel formulation works better when no additives are present, while the PVA gel worked better when glycerol was put in the formulation as an additive, which prevented the fast drying, allowing a better layer selectivity.

As for area selective, both gels shown to be capable of not spreading to the surrounding areas, especially when using the paper for a better selectiveness, which also assists in the removal, since when using the glassine paper it is not necessary to use tweezers, causing even less harm, since tweezers may scratch the object; with the paper, when pulling it out of the object, the gel comes out with it, for its edges are somewhat glued to the paper.

The gels present the intended characteristics of environmental-friendly and easy to make that were the main point of this project, as well as area selective and even selective removal, in the case of PVA, combining, in this way, all the concepts on patina conservation that are currently being discussed among the professionals of the area.

Bibliography

H.W. Roesky; K.Möckel. **Chemical Curiosities**. 1996, VCH.

M. Yekta-fard; A. B. Ponter. M. (1985) **Surface Treatment and its Influence on Contact Angles of Water Drops Residing on Teflon and Copper**, The Journal of Adhesion, 18:3, 197-205.

Nikola Slepickova Kasalkova; Petr Slepicka; Zdenka Kolska; Vaclav Svorcik. **Wettability and Other Surface Properties of Modified Polymers**. 2015. INTECH Open Science; chapter 12, Wetting and Wettability.

Biolin Scientific. **Contact Angle Measurement**; available at: <https://www.biolinscientific.com/measurements/contact-angle>.

G.m. Ingo; T. de Caro; C. Riccucci; E. Angelini; S. Grassini; S. Balbi; P. Bernardini; D. Salvi; I. Bousselmi; A. Çilingiroglu; M. Gener; V.K. Gouda; O. Al Jarrah; S. Khosroff; Z. Mahdjoubi; Z. Al Saad; W. El-Saddik; P. Vassiliou. **Large scale investigation of chemical composition, structure and corrosion mechanism of bronze archeological artefacts from Mediterranean basin**. Appl. Phys. A 83, 513–520 (2006).

T. Beldjoudi, F. Bardet, N. Lacoudre, S. Andrieu, A. Adriaens, I. Constantinides & P. Brunella (2001) **Surface Modification Processes on European Union Bronze Reference Materials for Analytical Studies of Cultural Artefacts**, Surface Engineering, 17:3, 231-235

Chiara Riedo, Fabrizio Caldera, Tommaso Poli and Oscar Chiantore. **Poly(vinyl alcohol)-borate hydrogels with improved features for the cleaning of cultural heritage surfaces**. Heritage Science, (2015) 3:23.

Teresa Guaragnone, Andrea Casini, David Chelazzi, Rodorico Giorgi. **PVA-based peelable films loaded with tetraethylenepentamine for the removal of corrosion products from bronze**. Applied Materials Today 19 (2020) 100549.

Ravindra V. Gadhave; Vineeth S.K; Pritam V. Dhawale; Pradeep T. Gadekar. **Effect of boric acid on poly vinyl alcohol- tannin blend and its application as water-based wood adhesive**. Designed Monomers and Polymers Volume 23, 2020 - Issue 1.

Rita Reale; Susanne H Plattner; Giuseppe Guida; Maria Pia Sammartino; Giovanni Visco. **Ancient coins: cluster analysis applied to find a correlation between corrosion process and burial soil characteristics**. Chemistry Central Journal 2012, 6(Suppl 2):S9.

Alessandra Giumlia-Mair. **On surface analysis and archaeometallurgy**. Nuclear Instruments and Methods in Physics Research B 239 (2005) 35–43.

I. Constantinides; A. Adriaens; F. Adams. **Surface characterization of artificial corrosion layers on copper alloy reference materials.** Applied Surface Science 189 (2002) 90-101.

Ravindra V. Gadhave; Prakash A. Mahanwar; Pradeep T. Gadekar. **Study of Cross-Linking between Boric Acid and Different Types of Polyvinyl Alcohol Adhesive.** Nuclear Instruments and Methods in Physics Research B 239 (2005) 35–43.

M. Pedroni; F. Piccinelli; T. Passuello; S. Polizzi; J. Ueda; P. Haro-Gonzalez; L. Martinez Maestro; D. Jaque; J. García-Sole; M. Bettinelli; and A. Speghini. **Water (H₂O and D₂O) Dispersible NIR-to-NIR Upconverting Yb³⁺/Tm³⁺ Doped MF₂ (M = Ca, Sr) Colloids: Influence of the Host Crystal.** Crystal Growth & Design; American Chemical Society 2013, 13, 4906–4913.

Arjun Manoj; Rahul Ramachandran; Pradeep L. Menezes. **Influence of Abrasive Load on Wettability and Corrosion Inhibition of a Commercial Superhydrophobic Coating.** Coatings 2020, 10, 887.

Ian Donald MacLeod. **Conservation of Corroded Copper Alloys: A Comparison of New and Traditional Methods for Removing Chloride Ions.** Studies in Conservation, Feb. 1987, Vol. 32, No. 1 (Feb. 1987), pp. 25-40.

Mahmood R.S. Shirazya; Sonia Blais; Luc G. Fréchette. **Mechanism of wettability transition in copper metal foams: From superhydrophilic to hydrophobic.** Applied Surface Science 258 (2012) 6416–6424.

C. Leygraf; T. Chang, G. Herting; I. Odnevall Wallinder. **The origin and evolution of copper patina colour.** Corrosion Science 157 (2019) 337–346.

Antonio R. Mendoza; Francisco Corvo; Ariel Gomez; Jorge Gomez. **Influence of the corrosion products of copper on its atmospheric corrosion kinetics in tropical climate.** Corrosion Science 46 (2004) 1189–1200

Lucilla Pronti; Anna Candida Felici; Marcella Alesiani; Ombretta Tarquini; Maria Paola Bracciale; Maria Laura Santarelli; Giacomo Pardini; Mario Piacentini. **Characterisation of corrosion layers formed under burial environment of copper-based Greek and Roman coins from Pompeii.** Appl. Phys. A (2015) 121:59–68.

N. Souissi; E. Triki. **Early stages of copper corrosion behaviour in a Tunisian soil.** *Materials and Corrosion* 2010, 61, No. 8.

Werner Gerwin; Roland Baumhauer. **Effect of soil parameters on the corrosion of archaeological metal finds.** *Geoderma* 96 2000 63–80.

Emiliano Carretti; Scilla Grassi; Manuela Cossalter; Irene Natali; Gabriella Caminati; Richard G. Weiss; Piero Baglioni; Luigi Dei. **Poly(vinyl alcohol)-Borate Hydro/Cosolvent Gels: Viscoelastic Properties, Solubilizing Power, and Application to Art Conservation.** *American Chemical Society, Langmuir* 2009, 25(15), 8656–8662.

Enas M. Ahmed. **Hydrogel: Preparation, characterization, and applications: A review.** *Journal of Advanced Research* (2015) 6, 105-121.

F. Clarelli; B. de Filippo; R. Natalini. **A mathematical model of copper corrosion.** 2000 *Mathematics Subject Classification: 76V05 (35R35, 65M06).*

Claudia Mazzuca; Leonardo Severini; Fabio Domenici; Yosra Toumia; Francesca Mazzotta; Laura Micheli; Mattia Titubante; Benedetta Di Napoli; Gaio Paradossi; Antonio Palleschi. **Polyvinyl alcohol-based hydrogels as new tunable materials for application in the cultural heritage field.** *Colloids and Surfaces B: Biointerfaces* 188 (2020) 110777.

Erica I. Parisi; Nicole Bonelli; Emiliano Carretti; Rodorico Giorgi; Gabriel M. Ingo; Piero Baglioni. **Film forming PVA-based cleaning systems for the removal of corrosion products from historical bronzes.** *Pure Appl. Chem.* 2017; aop.

Hailong Fan; Jiahui Wang; Qiuya Zhang; Zhaoxia Jin. **Tannic Acid-Based Multifunctional Hydrogels with Facile Adjustable Adhesion and Cohesion Contributed by Polyphenol Supramolecular Chemistry.** *ACS Omega* 2017, 2 6668-6676.

Rita Reale. **Monete Antiche: Studio assistito da metodi chemiometrici e multivariati della corrosione in relazione alle caratteristiche del suolo.** Thesis, 2008. Sapienza Università di Roma.