Development of cleaning procedures of copper corrosion products by using “green” deep eutectic solvents

Laureando
Shraddha Khaire

Relatore
Dr. Maria Assunta Navarra, Dr. Akiko Tsurumaki

Controrelatore
Prof. Gabriele Favero

ERASMUS MUNDUS MASTER
ARCHMAT

Erasmus
Mundus

SAPIENZA
UNIVERSITÀ DI ROMA

To my parents

Acknowledgement

This thesis is a result of hardship, support, kindness and resilience of a lot of people. People who wish nothing but well for me.

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Abstract

Selection and refinement of a method for copper corrosion removal were undertaken in an environmentally friendly way by using deep eutectic solvents (DES) integrated in a cellulose-based membrane.

DES is a potential "green" solvent based on natural compounds. In this thesis, a DES composed of choline chloride and ascorbic acid in a 2:1 ratio, was prepared and used for copper corrosion cleaning. The DES was diluted with water and the DES to water ratio was optimized in terms of efficiency, time consumption, and selectivity of cleaning.

It was found that DES solutions, having a concentration higher than 70 wt.% were suitable for dissolving copper corrosion products. Meanwhile, they exhibited a supressed dissolution ability of $CaCO_3$ which is a common compound in many of the supporting structures used for copper artefacts.

These solutions were then used for swelling cellulose membranes, and the swelling capacity was monitored for a week. The swollen membrane was put on an electrochemically corroded copper sheet for 24 hours. By removing the membrane, the green malachite layer was successfully removed from the copper sheet while preserving a reddish-brown cuprite layer. This was confirmed by performing X-ray diffraction analysis before and after cleaning the copper sample.

For heritage objects, the defacing copper corrosion products of Cu (II) need to be removed apart from protective layer of cuprite. We concluded that the cellulose membranes containing DES solutions are promising materials for this purpose.

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1. Introduction

General background

The discovery of metal is one of the most important discoveries made by man which allowed us to produce different kinds of materials throughout history and to this day. Not only changing its shape into tools or accessories, but also moulding it into utensils of varying sizes to store and cook as well as use it as a material to showcase art and other technological advancements. The malleability and ductility of metals as well as their strength established them as a vital resource for mankind.

As all things that are created or found on earth inevitably decay and eventually come to an end, metals are no exceptions. Some metals are stable and long-lasting, but they also undergo gradual degradation or corrosion especially in the presence of water, oxygen, acid etc. Most metals corrode, for instance, iron rusts, copper turns green, silver turns black, and lead disintegrates into a white powder. Improper storage of these metals causes their transformation into oxides, sulphides, carbonates or other compounds. The rate of corrosion increases in the presence of chemicals and by the application of electrochemical and mechanical stress.

Copper was the first metal ever discovered on earth. The history of copper dates back to 9000BC. Throughout the chalcolithic period, metalworking means were exponentially developed. The use of copper became frequent and important as it was an alternative to terracotta artefacts, although it did not diminish the importance of terracotta objects. [Hesse, 2007] In archaeological assemblage, many copper objects have been found.

Alike other metals that suffer from corrosion in the presence of oxygen, moisture, and acids, copper also undergoes corrosion and produces greenish-blue residues, which results in deterioration of both metal colour and mechanical strength. Without any specific treatment, the corrosion will spread over the object and invariably destroy it completely. Corrosion is usually characterized by the presence of a bottom layer of cuprite (Cu_2O) and an external layer of Cu (II) salts.

One of the serious issues related to the copper corrosion is the bronze disease, which is a potentially dangerous phenomenon that occurs on the surface of copper or copper alloy. When copper reacts with chlorides, it forms cuprous chloride (CuCl), known as nantokite. This is transforms to a greenish powder of Atacamite ($Cu_2(OH)_3Cl$) and causes progressive and irreversible deterioration of the object.

For the conservation of metal object, we need to find a way of delaying or preventing the inevitable decay and to protect the object from further damage in an adequate way, which must be safe, both for artefacts as well as the person cleaning the object.

Some bio-derived acids, such as citric acids and tartaric acids have been used as cleaning solvents. In addition, chemicals such as benzotriazole (BTA) is known to be an effective corrosion inhibitor. Since BTA is highly toxic, some alternatives such as flavonoid-, terpenoid-, and amino acid-based materials have been proposed. Recently, deep eutectic solvents (DES) have been developed as a solvent for removal of the corrosion products of copper.

In this thesis, DES was used through combining it with a membrane based on carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC). The use of membrane allows us to apply DES on the selected area. The combination of DES and the membrane is supposed to be useful to clean the copper corrosion product from the surface of the object while being non-invasive and environment friendly.

Copper as a metal

Copper in nature is often found as copper ores such as chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) as well as cuprite (Cu_2O). Copper can also be produced from malachite ore via smelting as can be explained by the following equations:

$$Cu_2CO_3(OH)_2 \rightarrow 2CuO + CO_2 + H_2O$$
$$2CuO + C \rightarrow 2Cu + CO_2$$

In the first step, copper compounds are converted by thermal treatment into copper oxide (CuO). Then, at a high-temperature and in the presence of a reducing agent such as carbon, metallic copper is produced by reduction reaction of the copper oxide.

Copper and copper alloys have excellent electrical and thermal conductivities, exhibit good mechanical strength and formability, and have outstanding resistance to corrosion and fatigue. Pure copper has an arrangement of the face centred cubic (fcc) configuration (Figure 1.1). A copper atom locates at each corner as well as in the centre of each face of a cube.

In this structure, the face diagonals are packed closely, and each copper atom is in relation with other 12 copper atoms. [Nielsen, nd.]

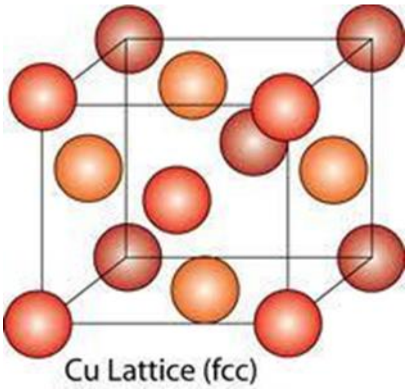


Fig 1.1 3D Electronic structure of copper

Copper alloys

Soon after the discovery of copper, the chalcolithic man realised that the addition of small amounts of other elements makes the resulting product harder, decreases the melting point, and permits the flow of the molten material much easier into moulds. This composite of metals is known as an Alloy.

The formation of copper alloys can be explained in three different ways:

1. Alloying elements substitute for copper atoms in the fcc lattice;
2. Alloying elements are combined with the copper and form localized regions (phases) where the crystal structure differs from the fcc copper crystal;
3. Alloying elements are rejected by the solidifying copper lattice but are trapped within the crystals of the alloy as they freeze and grow.

[Nielsen, nd.]

Phase diagram of alloys generally represents both the change in their crystalline phase and the solid-liquid transition depending on the concentration of alloying elements (x-axis) and temperature (y-axis).

Arsenic was one of the first alloying agents that was added to copper. The phase diagram of copper-arsenic alloy (so called arsenic bronze) is shown in Figure 1.2. The addition of arsenic decreases the melting point of copper from 1084^{o}C to 685^{o}C.

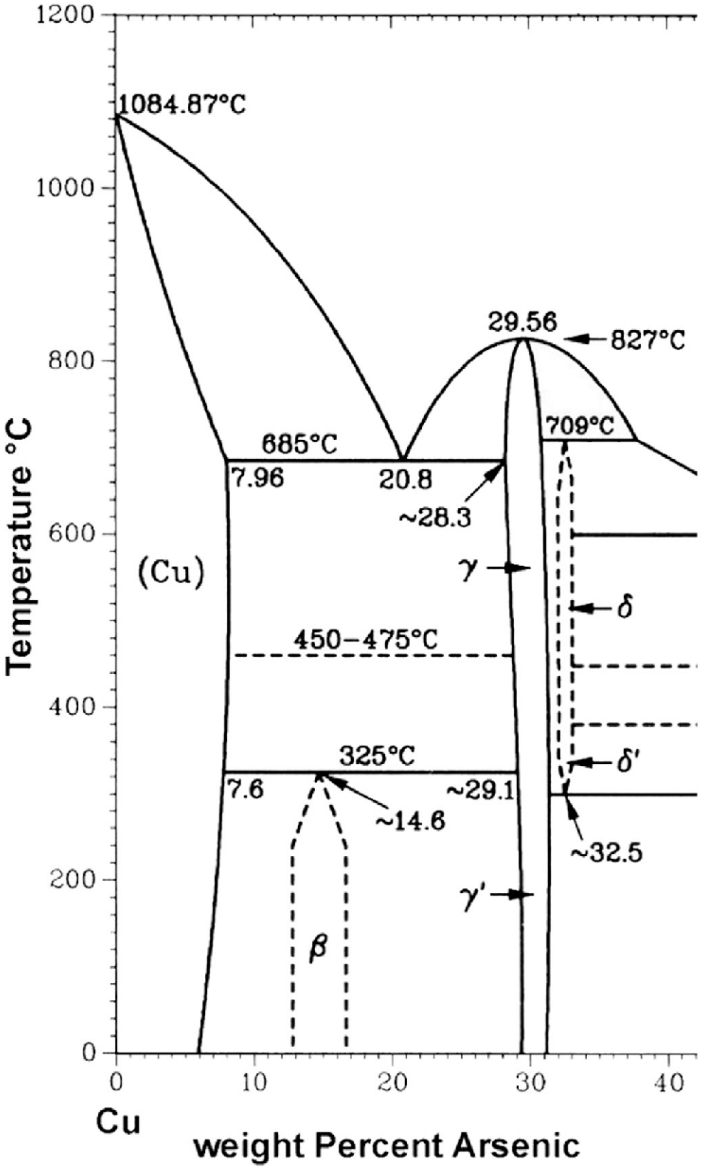


Fig 1.2 Phase diagram of copper-arsenic alloy.

The most common copper alloy is bronze which contains copper and tin and/or arsenic as alloying agents. This discovery gave way to an advanced Bronze Age in history. As shown in Figure 1.3, by increasing the concentration of tin, the melting point of copper decreases. The reduction in the melting point drastically improved the processability of copper. Not only the melting point, but also the colour and mechanical strength vary depending on the tin concentration.

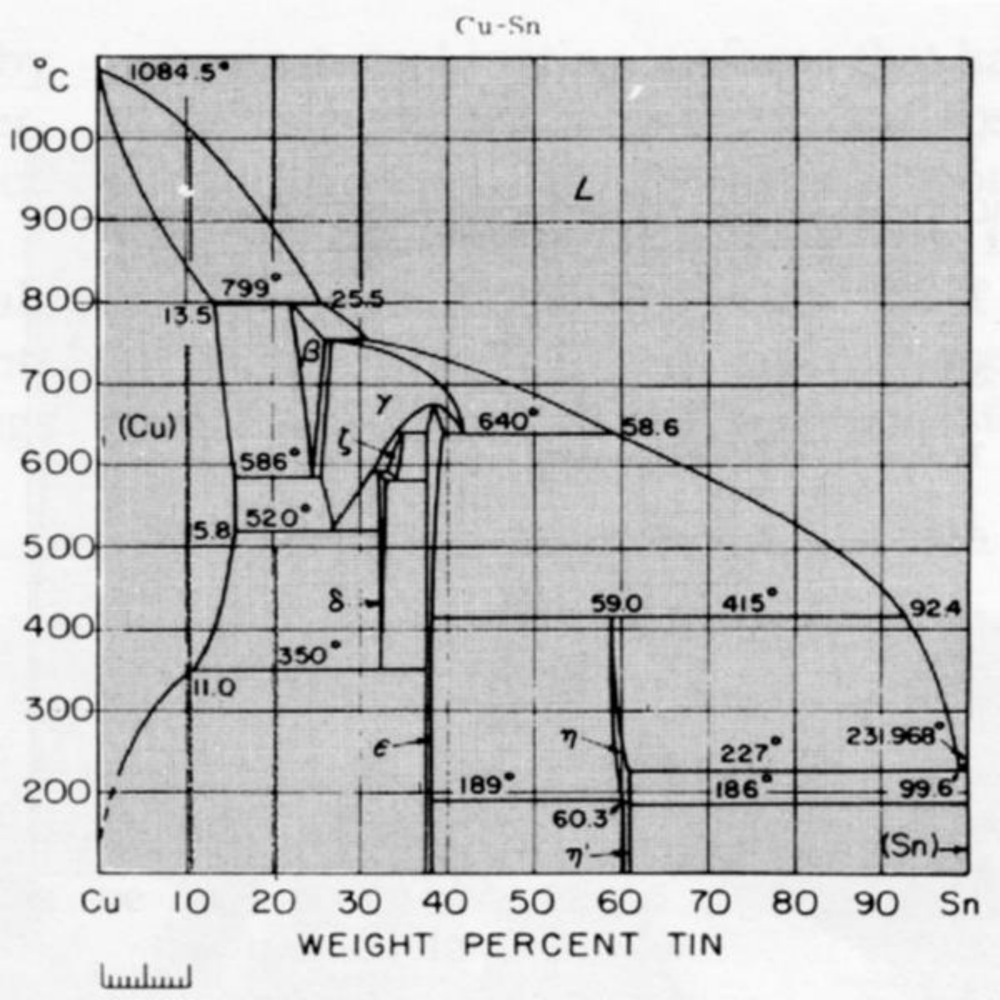


Fig. 1.3 phase diagram of copper-tin alloy system

Through the assessment of the composition and electrochemical properties of natural patinas of outdoor bronze monuments, it was suggested that outdoor bronzes tend to form corrosion layers very quickly as compared to those kept indoors. This patina proves to be relatively protective to the substrate metal. However, because of environmental changes and increasing acidity levels of rain, the patina is unstable. It is often assumed that bronze corrosion in the atmosphere reacts similarly to that of pure copper. However alloying elements induce specific behaviour of bronze which differs from pure copper. The combined action of chemical dissolution and leaching inexorably, leads to an important loss of bronze thickness with time. The patinas which contain copper and tin rich compounds play an important role in the protection of bronze with or without inhibitive treatments. [C. Chiavari, *et al*., 2007]Apart from being protective, it also is aesthetically appealing, especially when it comes to archaeological or historical artefacts. In some cases, like those of coins or embossing, this patination also helps in reading and deciphering the writing on the objects. This is due to the contrast between the shades of patination and the substrate metal.

Due to the more variable composition of bronze, the cleaning of bronze is complicated, not universal, and not easy to be analysed. However, because of the high concentration of copper in bronze, the cleaning method used to clean copper is considered to be effective also in cleaning bronze.

Copper in antiquity in the world

As mentioned in a former section, copper has been used for a variety of purposes including decoration, warfare and coinage since 9000 BC. Nuggets of the native form of copper were found in Cyprus and Northern Iran. These nuggets were hammered into ornaments and or primitive tools like knives or axes, etc. Smelting of copper was developed around 3000 BC where in the copper ore was reduced to a metal under high temperature in the presence of a reducing agent. Not long after bronze was firstly discovered, around 4650 BC it was used worldwide until when iron metallurgy was developed in around 1000 BC.

The ancient Indians, Romans, Greeks, and Egyptians used copper not only for the traditional metal uses but also for treatment of diseases and good hygiene. British naval ships had hulls which were encased in copper to protect from biofouling. [Beldjoudi, *et al.*, 2001]

History of copper in India

The first evidence of metal in the Indian subcontinent comes from Mehrgargh in Baluchistan, where a small copper bead was dated to about 6000BC; it is however thought to have been native copper, not the smelted metal extracted from the ore. [Satpathy, nd.]

Using the chronology defined by Shaffer (1992), Kenoyer, *et al.*, mentions that the early chalcolithic age in the Indus Valley Civilization began as early as 5000BC and it matured around 2600 BC which lead the Bronze age.

Metal objects, including those made from copper and bronze, that have characteristics of the Indus Valley tradition, come from the urban sites of Mohenjo-Daro, Harappa and Lothal. They date to the Mature Harappan Phase between 2600 BC and 1900 BC.

The Harappans are said to have sourced their copper ore from the Aravalli hills, Baluchistan or beyond. They soon realised that the addition of tin to copper gives a better and much sturdier metal which they could use for making more durable objects. This new metal thus formed was bronze.

In Harappa, many objects made from bronze like spearheads, blades, figurines, pots and pans, and mirrors, have been found. Highly polished bronze mirrors are still made to this date in the southern Indian state of Kerala in the same way as it was made in Harappa. The Harappan copper smiths are well known for making the 'true saw' and the figurine of a 'dancing girl' from bronze. The figurines were cast using the lost wax technique.The later phase of Harappan culture was marked by the copper hoard which produced a large amount of copper artefacts throughout central and northern India.

During the classical times, the copper and bronze smiths created the most exquisite pieces of art using the metal. One of the most interesting examples is the large bronze statue of the Buddha made around 500 CE in Sultanganj, Bihar.

The word used for metal was Ayas which in particular meant copper or bronze. Later on, as time passed and more metals were discovered and used, copper got a new identity and was called Tamra or the 'Red Metal'.

Since then the metal copper has been used in many religious, administrative and creative books and other works like the Arthashastra, Khadgalaksanam, Rasendramangalam, etc.

Numesmatic data shows that the first uninscribed cast copper coins were minted in the Indian subcontinent as early as 7th Century BC in the Gandhara region as well as Kosambi region. Then inscribed cast copper coins and die struck copper coins from the Maurya period around 4th century BC were found. [Kenoyer, *et al.*, 1999]

Copper in the Ancient times was also used for medicinal purposes. Eating or drinking from copper vessels have been believed and proved to be useful in boosting immunity.

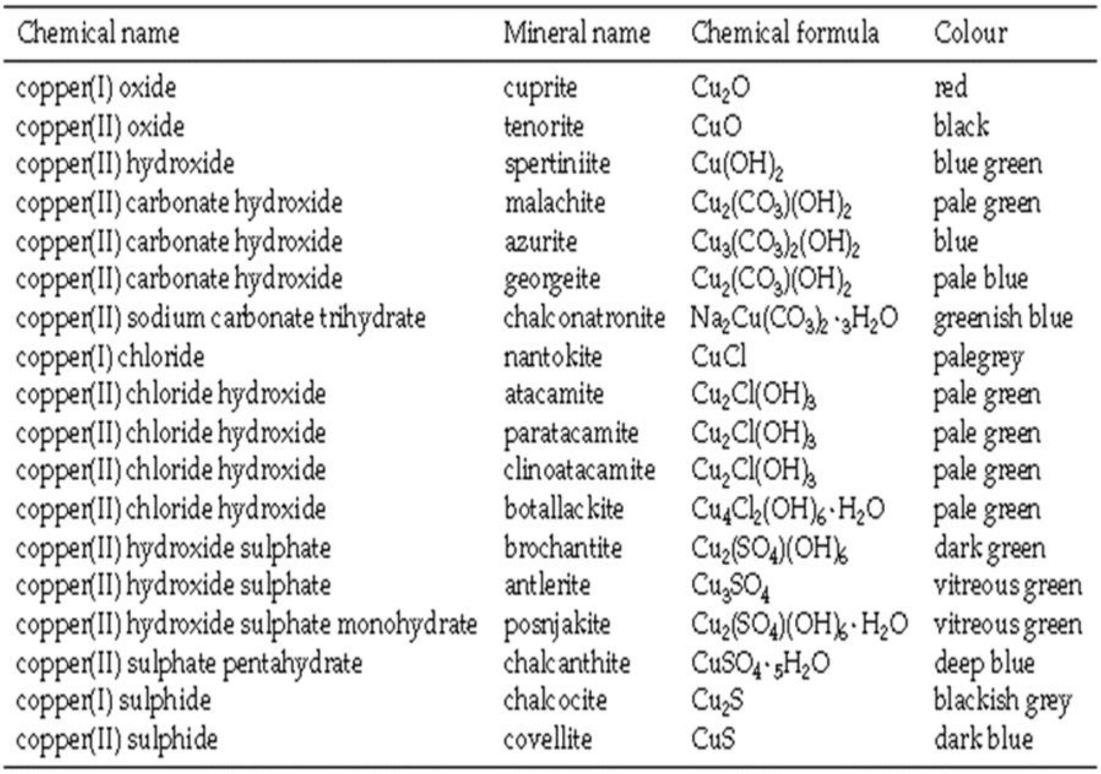
Copper corrosion

Metals vary enormously in their tendency to corrode. All metals tarnish or form an oxide layer when they are exposed to the atmosphere. Most metals develop a darkened surface which, as with stainless steel, may make it difficult to see the underlying base metal colour. The thickness and chemical content of the corroded layer vary as a function of exposure time, atmospheric conditions, and base alloy elements.

In the case of copper, it is quite resistant to the effects from the environment and also from many chemicals, but it is known to be susceptible to acidic media especially when it is exposed for a long time. The tarnish film that is formed over copper is mostly copper oxide which creates a dark base colour.

Table 1.1 summarizes possible products formed as a result of copper corrosion on the surface of the metal. The surface of copper objects can become green in colour, and this is indicative of a patina layer formed by malachite. Sometimes the green patina can be good for the object as it provides aesthetics as well as protection from the harmful effects of the environment. Indeed, malachite green is used as a cationic dye which is readily soluble in water and is used wildly not only in art but also in biotechnology. [Das, *et al.*, 2010]

Table 1.1 Copper Corrosion Products (Selwyn, 2004).



Chemical name	Mineral name	Chemical formula	Colour
copper(I) oxide	cuprite	Cu_2O	red
copper(II) oxide	tenorite	CuO	black
copper(II) hydroxide	spertiniite	$Cu(OH)_2$	blue green
copper(II) carbonate hydroxide	malachite	$Cu_2(CO_3)(OH)_2$	pale green
copper(II) carbonate hydroxide	azurite	$Cu_3(CO_3)_2(OH)_2$	blue
copper(II) carbonate hydroxide	georgeite	$Cu_2(CO_3)(OH)_2$	pale blue
copper(II) sodium carbonate trihydrate	chalconatronite	$Na_2Cu(CO_3)_2 \cdot {}_3H_2O$	greenish blue
copper(I) chloride	nantokite	$CuCl$	palegrey
copper(II) chloride hydroxide	atacamite	$Cu_2Cl(OH)_3$	pale green
copper(II) chloride hydroxide	paratacamite	$Cu_2Cl(OH)_3$	pale green
copper(II) chloride hydroxide	clinoatacamite	$Cu_2Cl(OH)_3$	pale green
copper(II) chloride hydroxide	botallackite	$Cu_4Cl_2(OH)_6 \cdot H_2O$	pale green
copper(II) hydroxide sulphate	brochantite	$Cu_2(SO_4)(OH)_6$	dark green
copper(II) hydroxide sulphate	antlerite	Cu_3SO_4	vitreous green
copper(II) hydroxide sulphate monohydrate	posnjakite	$Cu_2(SO_4)(OH)_6 \cdot H_2O$	vitreous green
copper(II) sulphate pentahydrate	chalcanthite	$CuSO_4 \cdot {}_5H_2O$	deep blue
copper(I) sulphide	chalcocite	Cu_2S	blackish grey
copper(II) sulphide	covellite	CuS	dark blue

The following is the equation that occurs when copper corrodes:

$$2CuCl + H_2O \rightleftarrows Cu_2O + 2HCl$$

$$2HCl + 2Cu \rightleftarrows 2CuCl + H_2$$

Even when there is a standard ambient atmosphere, a thin layer of oxide is formed over the surface of the object. It can be dark, red or turning bluish green in colour (see Table 1.1). The presence of mild hygroscopic salts can accelerate this process.

Copper alloys are generally more stable than pure copper, which resist many saline solutions, alkaline solutions, and organic chemicals. The chemical component of the corrosion of copper alloy is very similar to that of pure copper-based materials. Their tarnishing occurs very slowly in non-aggressive environment (low level of oxidizing acids, oxidizing heavy metal salts, sulphur, and ammonia). On the other hand, the copper alloys are susceptible to corrosion by ammonia, acids, strong alkalis, chlorides, and sulphide gases. In these corrosive media, it first turns dark brown or black and finally becomes green in colour.

After 20 years of exposure to corrosive environment, the tensile strength of copper decreases by less than 5% and the change in length is 10% compared to the original value. The fatigue limit changes depending on the purity of crystallization and is possibly reduced by one-third or more when the crystallize is coarse and not refined. This information is especially important for dealing heritage objects which are usually more than 100 years old. [Knotkova, *et al.*, 2007]

In the case of bronze, the presence of zinc and tin make the bronze sturdier. The inclusion of lead also increases the resistance of the bronze towards corrosion. However, bronze object can suffer from bronze disease, which is a progressive corrosion that seriously affects archaeological copper alloys. It is characterized by the eruption of a light green powder in spots over the surface. Objects displaying bronze disease should be stored isolated to keep the corrosion products away from other artefacts as they are 'cancerous', *i.e.* their growth resembles that of malignant tumours, and quickly spread to other copper-based objects around. [Parisi, *et al*, 2017]

Apart from just chemical exposure, corrosion can also be caused by prolonged physical stress. This phenomenon is known as 'Stress corrosion cracking' or 'Season cracking'. [Das, *et al.*, 2010]

Copper storage

With the technological and scientific progresses that we have achieved in today's world, we can clean and conserve copper and other metals after they are corroded. But as always, as explained by Desiderius Erasmus, "prevention is better than cure", we have to take care of metal objects from the beginning and to store them adequately. Through the conservation treatments, we can increase the life span of these objects and prevent them from corroding for a long time. The use of harmful chemicals for cleaning should be avoided both for the objects and conservators unless absolutely necessary.

According to Canadian Conservation Institute Notes 9/2 – Storage of Metals, it is best to store small copper artifacts in clear plastic boxes padded with acid free unbuffered paper, or in boxes made from acid free or neutral board. Larger artifacts can be wrapped in acid free unbuffered paper, stored in carved Ethafoam supports, or placed on foam shelf liners.

These very specific storage materials have been prescribed to store copper by the Canadian Conservation Institute because many natural and synthetic products can emit gases and cause metal to corrode. Hence it is very important to use certificated materials and appropriate ventilation to minimize the build-up of these corrosive gases.

Relative humidity (RH) is of utmost important factor for dealing metal objects as most metals corrode easily in humid or moist environments. The RH in most cases must be kept as low as possible. When it comes to mixed collections including copper objects, it is preferred to keep the RH value between 35% and 55% according to the paper mentioned above.

For museums in humid areas, dehumidifiers should be installed to maintain the average humidity. Apart from this, careful handling of metal objects will also be needed to ensure their protection from physical damage as well as chemical damage (corrosion).

In addition, the life span of copper-based materials can be extended by removing the corrosion products properly. Cuprite is considered as a layer that needs to be preserved and also protects the surface of the copper from further degradations. It generally is reddish orange in colour. [Parisi, *et al.*, 2017]

Apart from this, if corrosion is noticed in any one of the objects stored together, the corroded object must be separated immediately from the group as corrosion (especially in bronze objects) can spread rapidly as discussed above.

Precautions taken while conserving copper

There are a few things that must be taken into account while cleaning copper. While using any method of cleaning, the degree of cleaning must be controlled precisely. One of the well-known issues for cleaning copper is that the removal of the reddish-brown cuprite layer from the surface as this layer works as a protective layer and prevents from further damages.

The malachite and azurite composed of Cu (II), hydroxides, and carbonates must be removed. The preservation of a thin layer of malachite on the surface of the copper object can be preferred as it looks aesthetically pleasing. The level of cleaning, *i.e.* the layer required to be removed, is different depending on the demands of the client, which must be considered and controlled while cleaning and conserving copper.

The cleaning of copper must be followed by conserving it as this will prevent the object from getting damaged again in the future and will also aid in arresting the spread of corrosion which might occur in the case of bronze disease.

Traditional cleaning of copper corrosion

Cleaning of copper has been done traditionally both via chemical and physical ways. For the thick corrosion, physical cleaning is generally done prior to chemical cleaning. This has been done by using a hard and stiff nylon brush or even a nylon bristled toothbrush. As expected, physical cleaning induces some damages because it gives mechanical stress to the object. The cleaning using chemicals is more adequate for precious objects.

Traditional cleaning of copper in India is done using bio-derived citric acids such as those from lemon or tamarind. The reaction between citric acid and malachite can be expressed as follows:

$$2C_6H_8O_7 \rightleftarrows 2[C_6H_6O_7]^{2-} + 4H^+$$

$$Cu(OH)_2 \cdot CuCO_3 + 4H^+ \rightleftarrows 2Cu^{2+} + CO_2 + 3H_2O$$

Other acids used for copper cleaning, such as lactic acid and tartaric acid, follow the same reactions for dissolving the corrosion.

Papita Das *et al.*, reported various factors affecting malachite cleaning by tamarind fruit in her paper on ‘Assessment on the Removal of Malachite Green using Tamarind Fruit Shell as Bio absorbent’.

Tamarindus indica is a common tree that grows in India and such tropical countries. The tamarind fruit shell is the outer shell of the tamarind pulp. It is known that the tamarind fruit shell is composed of carbohydrates with nitrogen, calcium, phosphorous, and iron components. In addition, it contains a certain amount of tartaric acid and hydroxy citric acid. In their experiment, tamarind shells were cleaned, dried, and then sieved to get uniform size particles. By adding refined particles to malachite solutions, the sorption capacity of tamarind shells was evaluated. The best result was obtained when the pH value of the solution was around 5. After adding of adsorbent, the solution pH increased confirming that the ion - exchange occurred, *i.e.* free acids were consumed as shown in the aforementioned equations. Through this research, traditional cleaning method using tamarind shell has been scientifically and experimentally confirmed to be effective, and it was concluded that tamarind fruit shell is one of the low costs and affordable cleaning agent for copper corrosion.

Chemical cleaning of copper corrosion

Apart from the traditionally used and bio-derived cleaning agents as mentioned above, some chemicals are also known to be useful for corrosion cleaning. In the chemical cleaning method, the agents are added as a chelate, which forms complex with copper ions.

Sodium tripolyphosphate (STPP) is able to dissolve malachite and cuprite to a small extend and is used to clean copper. Ethylenediaminetetraacetic acid (EDTA) solution is used to remove the green patination. When the cleaning ability of STPP and EDTA (sodium salts) is compared, STPP is less effective but less harmful to dissolve malachite and cuprite. Benzotriazole (BTA) solution is applied post cleaning to protect the object from further corrosion. Although this chemical works well, it is highly toxic to the environment. A method using more green products should be proposed, and recently some alternatives such as flavonoid-, terpenoid-, and amino acid-based materials have been demonstrated to be effective for copper cleaning.

Deep eutectic solvents

Deep eutectic solvents (DES) were developed by Andrew Abbot and his co-workers when they were looking to create a potentially “green” solvent. They are known to have large asymmetric ions that have low lattice energy and therefore have a low melting point. They are usually formed by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond doner (Figure 1.4). [Smith, *et al.*, 2014]

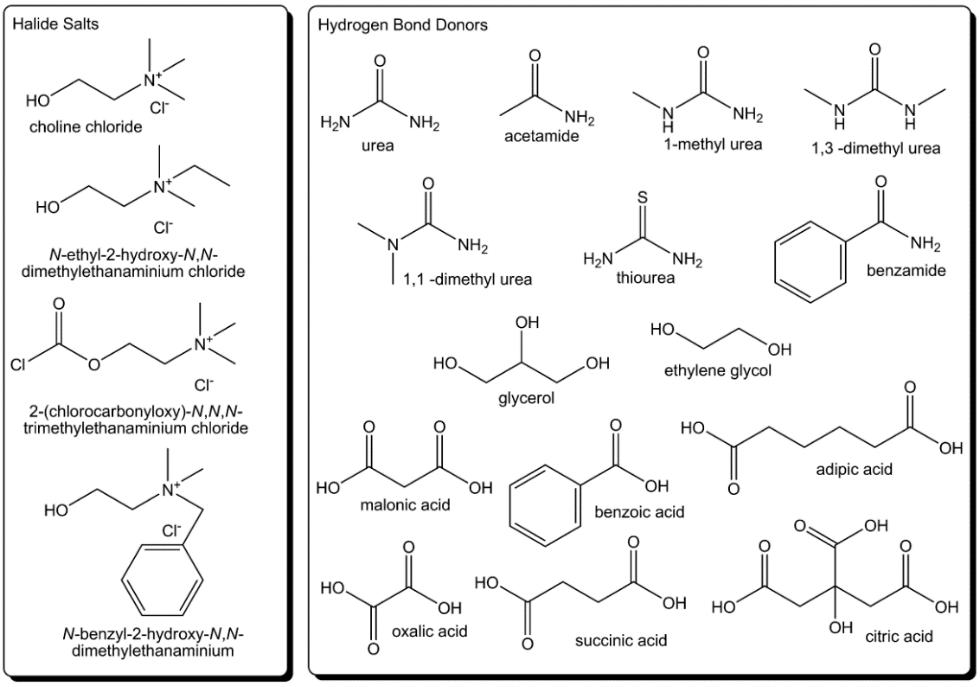


Fig. 1.4 Structures of some halide salts and hydrogen bond donors used in the formation of DES. [Smith, et al., 2014]

In this thesis, we study DES as a cleaning agent for copper. The DES that we used is a mixture of choline chloride (ChCl) and ascorbic acid (AA) in 2:1 ratio. The DES to water ratio to get optimal cleaning effects was optimized.

With respect to the DES formed by ChCl and urea, it is reported that the nanostructure of DES is retained even at a remarkably high level of water (ca. 42

wt% H_2O). The DES-DES interactions, such as the Ch–urea, Ch-Cl, Ch– Ch, urea–Cl, urea–urea, and Cl–Cl, are weakened by the addition of water; however, they are retained until 42wt% of water. Above this concentration (e.g. 51wt%), the segregation of DES becomes unfavourable, and the DES structure is disrupted. In this case, the DES–water mixture is best described as an aqueous solution of DES components. Accordingly, 42wt% of H_2O is the upper limit of water concentration in order to keep the interaction between the components of DES, and the concentration of water should be at or below this water content.

Hydrogel membrane

Hydrogels are soft and wet materials containing a large amount of water in their three-dimensional network structure. Sodium carboxymethyl cellulose (CMC), which is a cellulose derivative with a large number of carboxymethyl groups on the cellulose backbone, is one of the matrices to form the hydrogel.

Because of its non-toxicity, water solubility, low cost, and environment friendliness, CMC has been widely used as a natural ingredient for hydrogels and has been developed for various applications including tissue engineering, drug delivery, wound dressing, plant breeding, and also in heritage conservation. [Zheng, *et al.*, 2015]

The aim of the use of hydrogel in this study is to apply DES on the limited area of copper surfaces by absorbing it in the hydrogel. This also will help the DES to stay on the desired area that needs to be cleaned.

In this thesis, hydrogel based on CMC and hydroxyethyl cellulose (HEC) was prepared. Citric acid was added to to form crosslinking among CMC and HEC (Figure 1.5). The acidic hydrogen in the citric acid is removed, and a covalent bond is formed between the anhydride citric acid and CMC.

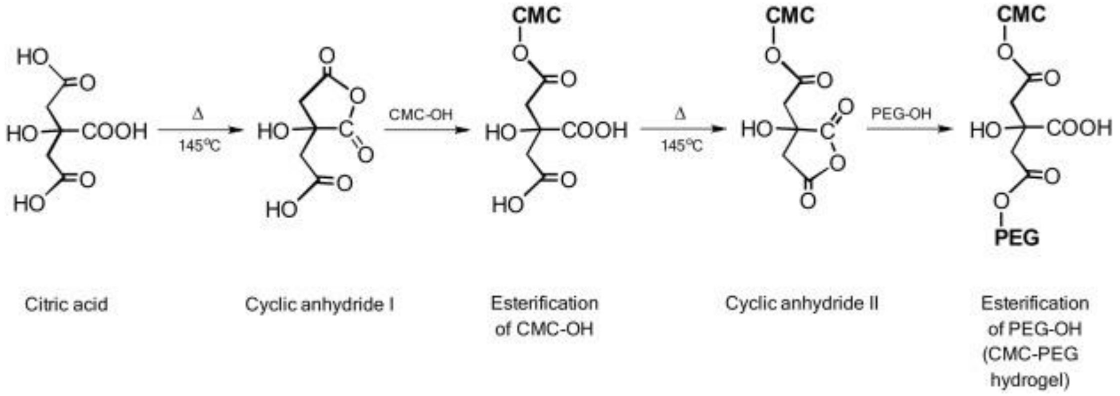


Fig. 1.5 An example of the crosslinking formation between CMC and citric acid. [International Journal of Biological Macromolecules 118, 2018]

We optimised the method of making the CMC membrane containing DES. Specifically, the swelling capacity of the membrane in DES solution was assessed, and the time required to reach the maximum swelling ratio was determined. The swollen membrane was then applied to corroded copper surface, and the time taken for achieving the most effective cleaning was evaluated.

2. Materials and Methods

Preparation of DES solutions

The chemical structure of DES is shown in Figure 2.1 which was prepared by mixing 3.04 g of choline chloride (ChCl) with 1.92 g of ascorbic acid (AA) to reach a ChCl: AA= 2:1 mol/mol ratio. This mixture was then heated at 80° C in a glass container for 30 mins to liquify.

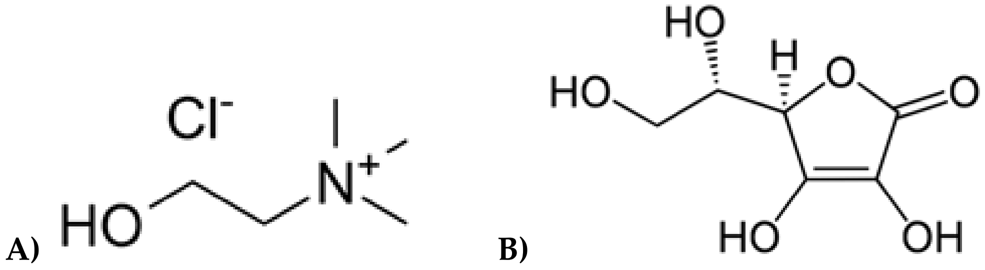


Fig. 2.1 Chemical structures for choline chloride (A) and ascorbic acid (B).

As listed in Table 2.1, the DES solutions were made to achieve the concentration of 10, 30, 50, 70, 80, 90 wt.% of DES in distilled water. Due to the large amount of water, DES10, DES30, and DES50 are considered to be the aqueous solution dissolving ChCl and AA, and the interactions between ChCl and AA are broken. In contrast to this, in DES70, DES80, and DES90, the interactions between ChCl and AA are expected to be preserved as reported in the literature [Hammond Oliver S., *et al.*, 2017]. Therefore, these three high concentration solutions can be considered as the aqueous solution of the DES.

Table 2.1. DES solutions made of varying concentrations

Sample name	Concentration (wt.%)	
	DES	Water
Water	0	100
DES10	10	90
DES30	30	70
DES50	50	50
DES70	70	30
DES80	80	20
DES90	90	10

Preparation of CMC/HEC membrane

The membranes were prepared by using cellulose derivatives such as sodium carboxymethyl cellulose (CMC) and hydroxy ethyl cellulose (HEC). The structures of the starting materials are shown in Figure 2.2.

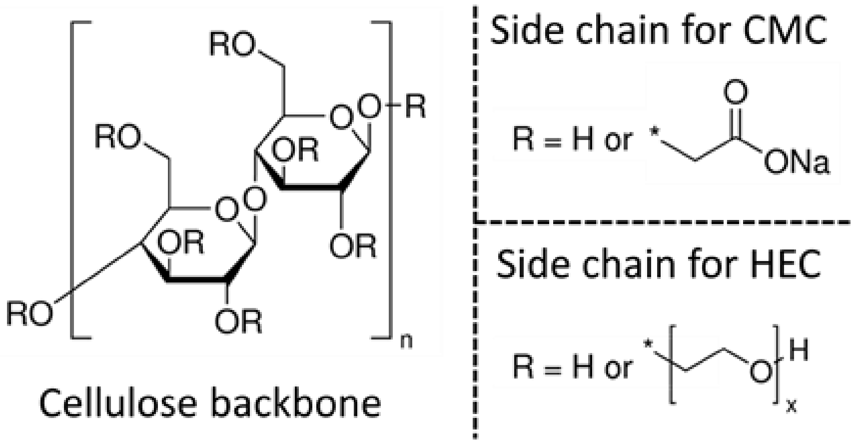


Fig. 2.2 Chemical structures of carboxymethyl cellulose (CMC) and hydroxy ethyl cellulose (HEC).

The membrane was made using the following methodology: To 98ml of distilled water, 115mg of citric acid was added in a weighing bottle with 8cm diameter. This mixture was kept for magnetic stirring. Once the citric acid was completely dissolved, 1.5 mg of sodium CMC and 0.5 mg of HEC were slowly added to the mixture. The mixture was then stirred eight hours or overnight without heating. The stirring magnet was then removed and the weighing bottle with sample was covered with aluminium foil and kept in the oven at 40° C for drying water. It took around five days for the membrane to dry. Then, crosslinking formation was carried out at 80° C for 24h.

Dissolution test of copper corrosion products

For the sake of simplicity of the experiment, a dissolution test of copper corrosion powder was performed prior to the cleaning of copper corrosion using CMC/HEC membrane. 3 mg of copper corrosion powder was added to 300 mg of the DES solutions and mixed manually. The solubility was checked immediately after addition of the powder and after three days without any stirring. The changes in colour of the solutions, release of gas, presence of insoluble powders, and formation of precipitate after dissolving were evaluated. This experiment would tell us which DES concentration would give us optimal results in terms of cleaning copper corrosion.

Dissolution test of calcium carbonate

As calcium carbonate ($CaCO_3$) is the main component in lime stone, which is sometimes used as a base for copper artefacts like statues, plaques etc., dissolution tests were also performed with respect to $CaCO_3$ in order to understand how the application of DES solution causes the damages of lime stone. Hence the solubility of $CaCO_3$ was checked in the solutions with varying DES weight percentages.

We added 3 mg of $CaCO_3$ powder to 300 mg of the DES solutions. They were stirred manually, and their solubility was observed soon after dissolution as well as after three days without any stirring.

The objective of this experiment is to identify which of the DES concentration would effectively clean copper corrosion product but also cause little to no damage to a limestone base that the copper artefact may be attached to.

Swelling test of the membrane

Once the membrane was completely dry, it was then cut into 1cm diameter circles. These disks (having the weight between 10.1 – 13.1 g) were then immersed in 500 mg solutions having 70, 80, and 90 wt.% of DES. These specific concentrations were selected because they are proved to be the effective concentration in the copper corrosion product dissolution tests. The time taken for the membranes to swell and the amount of solution absorbed by the membrane were evaluated. The swelling ratio was calculated according to the following equation:

$$\text{Swelling ratio (\%)} = \frac{w_s - w_d}{w_d} * 100$$

In which, w_s and w_d are the weight of swollen and dried membrane, respectively. The membrane was also immersed in water as a control.

Swab cleaning test

This test was performed in order to assess the effectiveness of the DES solutions as a cleaning solvent by using them with a standard swab stick. The results were also compared with the results obtained with a usa of the DES integrated within a CMC/HEC membrane.

A cotton ball (diameter ~5 mm and weight ~15 mg) was taken using tweezers. Each cotton ball had the capacity of absorbing around 60 mg of the solution, which changed depending on the viscosity of the DES solution. This cleaning was repeated four times for each copper sample, using a different cotton ball every time. Other cotton balls were also used to wipe out the copper surface with ethanol and distilled water after each cleaning. This step is necessary to avoid build-up of the cleaning product and also to see appropriate results after each cleaning steps that exclude an over lapping effect of all four rounds of cleaning. The cleaning with ethanol is also necessary to remove the excess product and excess solvent after the cleaning is completed. When this step is not done, there is a possibility that the remanent product staying on the copper surface for a long time starts affecting the copper adversely. To avoid this, after wiping the copper surface with DES, the surface must also be wiped with plain distilled water and ethanol for assuring that that there is no residue left.

Copper cleaning test using DES with membrane

The synthesized CMC/HEC membrane was cut into 1 cm diameter circles. They were placed into 500 mg of DES70, DES80, and DES90 for swelling. After the membranes were swollen sufficiently (24 hrs for both DES70 and DES80 and 1 week for DES90), they were then placed on the surface of a copper sheet which were electro chemically corroded as mentioned above.

The degree of cleaning was visually evaluated every day. The membranes were removed after 24 hrs in the case of those swollen in DES70 and DES80, while the membrane swollen in DES90 was removed after 4 days. The most time efficient as well as the most capable composites of DES and membrane was determined.

3. Characterization methods

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a quantitative analytical technique that monitors the mass of a sample from 1 mg to several g during an increase in temperature from a room temperature to as high as 1000° C under a stable or changing gas flow. [Saadatkhah, *et al*., 2019]

The logic of this analysis lies in the fact that as the sample decomposes, its mass drops. This occurs because the volatile compounds are formed through the decompositions. The balance in TGA records the weight change of sample as a function of time and temperature.

Since the balance is very sensitive, TGA can be used not only for the evaluation of thermal stability of the sample, at which the volatile compounds are formed, but also can be used to measure the weight of volatile component in the sample.

In this thesis, we have used TGA to determine the water concentration in pristine DES and also to evaluate the thermal stability of an aqueous solution of DES. For the former analysis, isothermal program was used. Several mg of the pure DES sample was put in the Al_2O_3 crucible, which was then placed in a TGA furnace. The sample was heated from room temperature to 110° C at a heating rate of 10° C/min and the isothermal analysis was carried out at 110° C for 60 min. For the latter analysis, thermodynamic analysis was employed. The sample put in the crucible was heated from room temperature to 400° C at a heating rate of 5° C/min.

X-ray diffraction

X-ray diffraction (XRD) is a non-invasive technique for analysing heritage objects which normally and preferably don’t permit large scale sampling. This technique is useful to understand the composition of materials, which can be determined in relation with the crystalline structure of solid materials such as metal, ceramic, and polymer

When the wavelengths of X-ray are similar to the spacing of planes in a crystal lattice in which diffraction occurs. The interaction of the incident rays with the sample produces a diffracted ray, and constructive interference occurs when the conditions given by the Bragg's Law are fulfilled:

$$n\lambda=2d\ \sin\theta$$

in which, n is a constant value known as the order of the diffracted beam, λ is the wavelength of the beam, d denotes the distance between lattice planes, and θ represents the angle of the incident wave.

By performing XRD, it is possible to study different crystalline phases in the same chemical formula. Because of this, XRD is useful technique to detect different crystalline phase in unrefined copper corrosion. In this thesis, we have done XRD analyses of electrochemically corroded copper sheets before and after treatment with the DES. We did this in order to understand the component in the pristine copper corrosion and also the change in the component before and after DES treatment. Through XRD analysis, we have analysed the cleaning capabilities as well as cleaning selectivity of DES solutions with different concentrations.

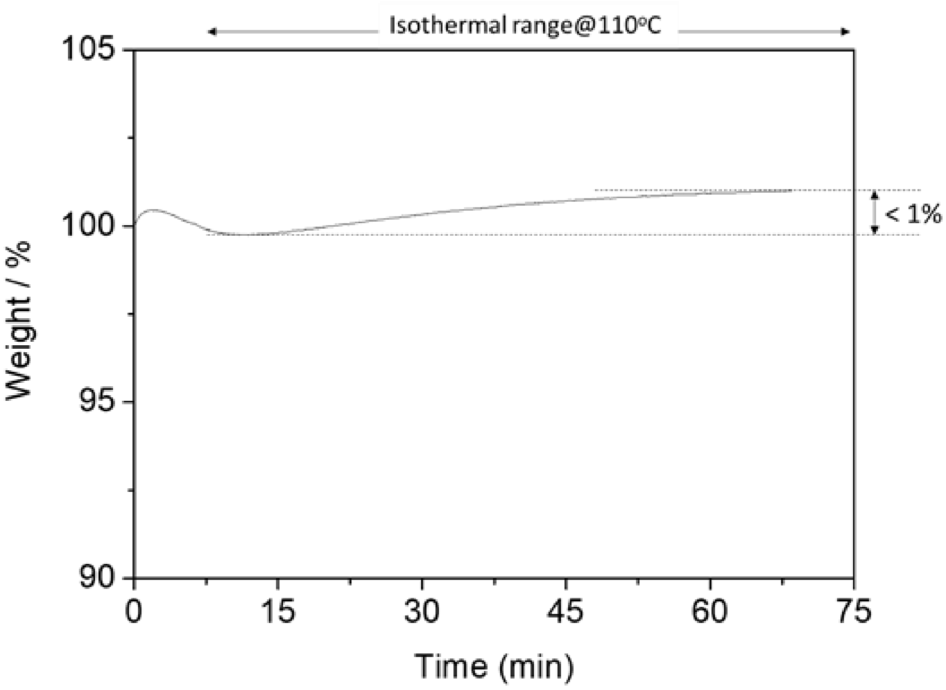
4. Results and discussion

TGA analysis of DES

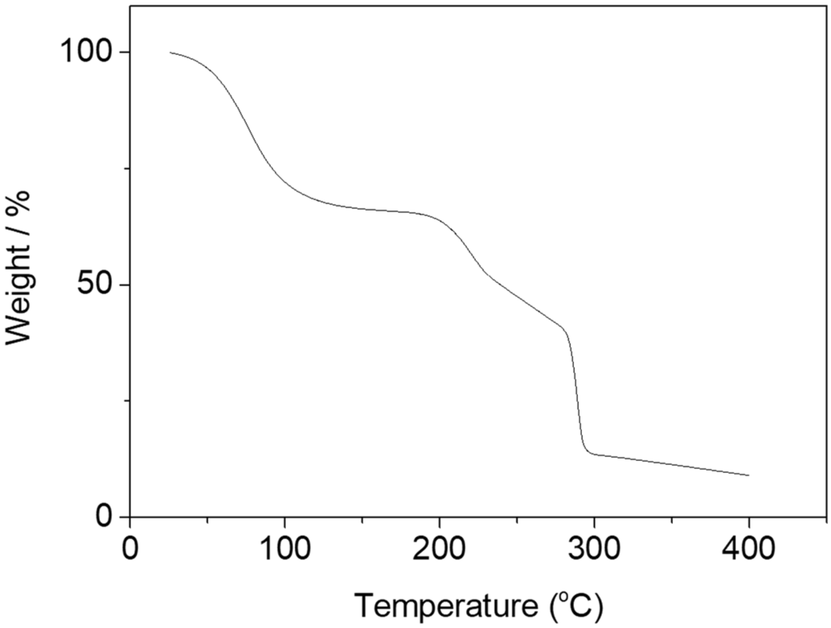
Latent absorbed water in DES is unavoidable because its components are generally hygroscopic. The presence of water has a great impact upon the physicochemical properties of DESs, such as the melting point and viscosity [Delgado- Mellado Noemi, *et al.*, 2018]. Accordingly, it is important to evaluate the water content in DES in order to obtain the results with high reproducibility.

Figure 4.1 (a) shows the isothermal TGA analysis at 110^{o} C of pure DES, which was done to evaluate its water concentration. Through this analysis it was found that the weight changes through the course of isothermal treatment of the DES was less than 1wt%. This confirms that the water contamination in our DES is very limited.

Thermodynamic TGA was also done with respect to DES70 (Figure 4.1 (b)). The weight loss around 100 ^{o} C is related to the evaporation of water, while the weight losses around 200^{o} C and 300 ^{o}C are related to the decomposition of AA and ChCl, respectively.



(a)



(b)

Fig. 4.1 (a)Isothermal TGA of the pure DES and (b) thermodynamic TGA of DES70

Dissolution test for copper corrosion products

Before utilizing DES solutions as a cleaning agent for copper corrosion, we have screened the concentration of DES in water to optimize it. For this purpose, dissolution test of copper corrosion powders in DES solution has been carried out. Figure 4.2 shows the photos of dissolution test that were taken immediately after adding 1 wt% copper corrosion power to the mixtures. As can be seen in the reference photo, copper corrosion powders merely dissolved in water. Similarly, DES10 did not dissolve the copper powders and the powders remained at the bottom of the vial. Immediately after adding the copper powders, there was white and green coloured precipitate left at the bottom. However, after several days, blue crystalline substance was seen as shown in Figure 4.3. This is considered to be due to the formation of Cu (II) complex including Ch cations and Cl anions, e.g. $Cu(Ch)Cl_3$, as reported in the literature [Kataev Evgeny, *et al.*, 2012].

DES30, DES50 and DES70 worked well for dissolving the copper corrosion products. In fact, they dissolved the copper corrosion products quickly and completely. While dissolving, it was also noticed that bubbles were formed in all three concentration solutions. The bubbles lasted for a shorter time in the DES30 and DES50. This may be because they are more fluid than DES70. This designate that these DES solutions are acidic (will be discussed in a following section), and following reaction is expected to occur for dissolving corrosion products, e.g. malachite:

$$Cu_2(OH)_2CO_3 + 2C_6H_8O_6 \rightarrow 2CuC_6H_6O_6 + CO_2 + 3H_2O$$

As shown in Figure 4.3, in the case of DES30 and DES50, the formation of blue crystalline was observed similar to as in the case of DES10. Only DES70 did not form the blue crystalline (the photo was not taken) among these solutions.

DES80 and 90 took a longer time to dissolve the copper corrosion as they are very viscous. Immediately after adding the corrosion power, white and green precipitations were observed (Figure 4.2). However, after several days, the corrosion was completely dissolved, and the formation of blue crystalline, which was observed for DES10, 30, and 50, was not observed in the case of DES80 and DES90.

It can be concluded through this experiment that DES70, DES80 and DES90 gave the better results in terms of supressed formation of blue crystalline products after the dissolution. They dissolved the corrosion slowly but completely. These three concentrations of DES can be used as a cleaning solvent of copper corrosion for varying purposes depending on the demand of the client and or object.

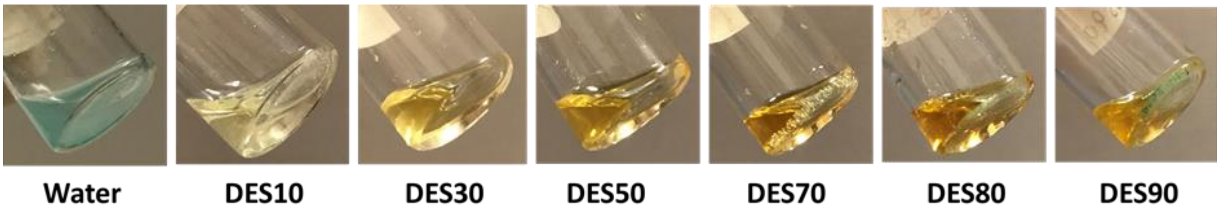


Fig. 4.2 Photos of the dissolution test taken immediately after adding copper corrosion power to the mixtures. The result of water is also shown as a reference.

Fig. 4.3 Photos of the dissolution test taken after several days after adding copper corrosion powder to the mixture.

Dissolution test for calcium carbonate

From the dissolution test of the copper corrosion products, it was suggested that the DES solutions possess acidic natures. The acidic solution is known to corrode calcium carbonate, which is the main component of limestones. For example, when citric acid (as a cleaning agent) comes in contact with calcium carbonate and copper corrosion, it dissolves both of them and releases carbon dioxide. [Shabani, *et al.*, 2012]

These can be expressed by the following equations:

$$3CaCO_3 + 2C_6H_8O_7 \rightarrow Ca_3(C_6H_5O_7)_2 + 3CO_2 + 3H_2O$$

$$Cu(OH)_2{\cdot}CuCO_3 + 2C_6H_8O_7 \rightarrow 2Cu_2 + 2C_6H_6O_7 + CO_2 + 3H_2O$$

For instance, for the copper corrosion removal from marble statues, the selective dissolution of the corrosion from the stone surface becomes important. Therefore, we have also carried out the dissolution test of calcium carbonate in the DES solutions (Figure 4.4).

It should be noted that the weights of $CaCO_3$ added to the solutions were not constant because $CaCO_3$ immediately formed CO_2 gas. The amount of added $CaCO_3$ might include some errors. During the dissolution test, it was noticed that DES10 formed gas immediately but there was some precipitation visible and the dissolution was not complete. This is considered to be because there was low concentration of DES and hence the DES was too diluted to dissolve $CaCO_3$.

DES30 and DES50 dissolved $CaCO_3$ quickly and completely through the formation of a lot of gas. The gas was ejected easily from the solution and was not visible in the photo. There was no precipitation left.

DES70 dissolved $CaCO_3$ slowly but completely. Bubbles were produced and they remained in the solution even after dissolution. This is due to the slightly high viscosity of this solution. There was no precipitation left after dissolution.

DES80 and DES90 dissolved $CaCO_3$ very slowly but it was not successful in dissolving the powder completely. Some precipitation was still found in DES80 after two days of leaving the mixture in ambient condition. In the case of DES90, major part of $CaCO_3$ as a precipitation remaining after two days of leaving the mixture untouched.

It was realised that DES30, DES50 and DES70 dissolved calcium carbonate quickly. DES80 dissolved calcium carbonate very slowly whereas the dissolutions in DES10 and DES90 were not complete. The reason why DES90 did not dissolve the calcium carbonate even though it had a higher concentration for DES might be because it has high viscosity or low water content to dissociate acid.

Keeping these results in mind, it was found that DES80 and DES90 are a good concentration for cleaning copper from objects that are attached to a limestone base as they can remove copper corrosion from the copper object and are not harmful for calcium carbonate surface. This gives us selectivity while cleaning copper.

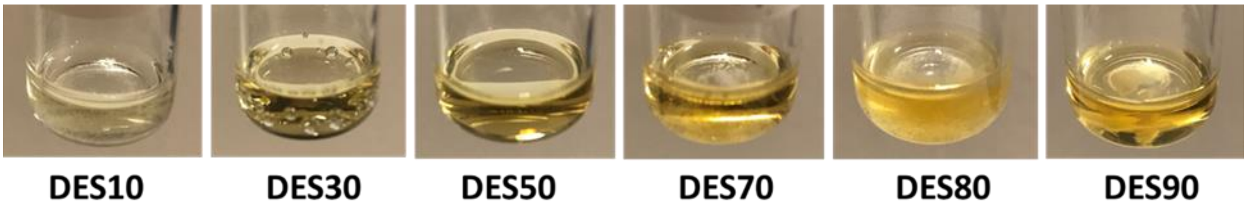


Fig. 4.4 Immediately after adding $CaCO_3$ powder to the solutions.

Acidity of DES solutions

Through the dissolution test of copper corrosion products, an experiment was performed to measure the acidity levels of the different DES weight percentages. For any cleaning agent, moderate acidity is preferred as high acidity levels tend to work well but they can damage the object and also are harmful for conservators, while low acidity levels sometimes not enough for copper cleaning.

As shown in Figure 4.5 and Table 4.1., the lower water content in the mixture resulted in the higher acidity.

It was noticed that when the concentration of DES is low, such as DES10 and DES50, the solution is more acidic after dissolving the copper corrosion powders. In the case of DES 70, DES 80, and DES90, they were less acidic after the dissolution test. This can be interpreted as the consumption of acidic component and the formation of water during the dissolution:

$$Cu_2(OH)_2CO_3 + 2C_6H_8O_6 \rightarrow 2CuC_6H_6O_6 + CO_2 + 3H_2O$$

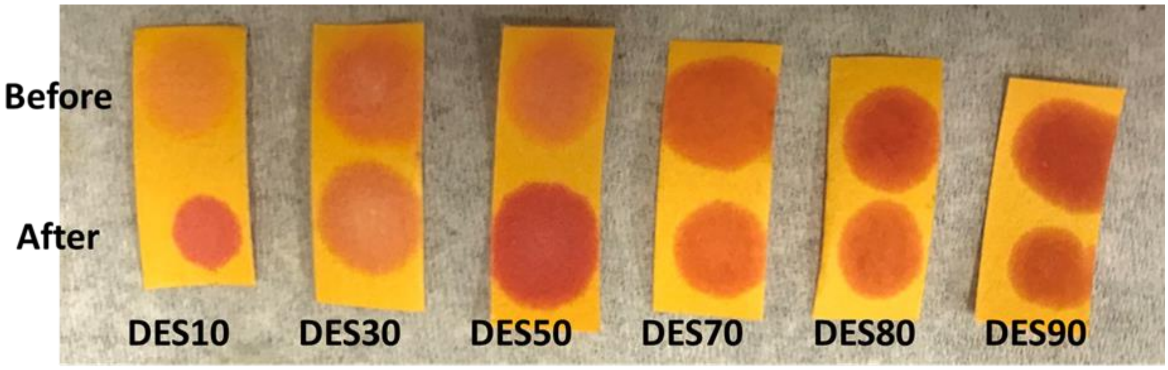


Fig. 4.5 Litmus paper test done on the DES before and after dissolution of copper corrosion powder.

Table 4.1 pH values of DES solution

pH values of DES solution						
	DES10	DES30	DES50	DES70	DES80	DES90
Before	3	2	2	1	1	1
After	1	2	1	2	2	1

Swelling test

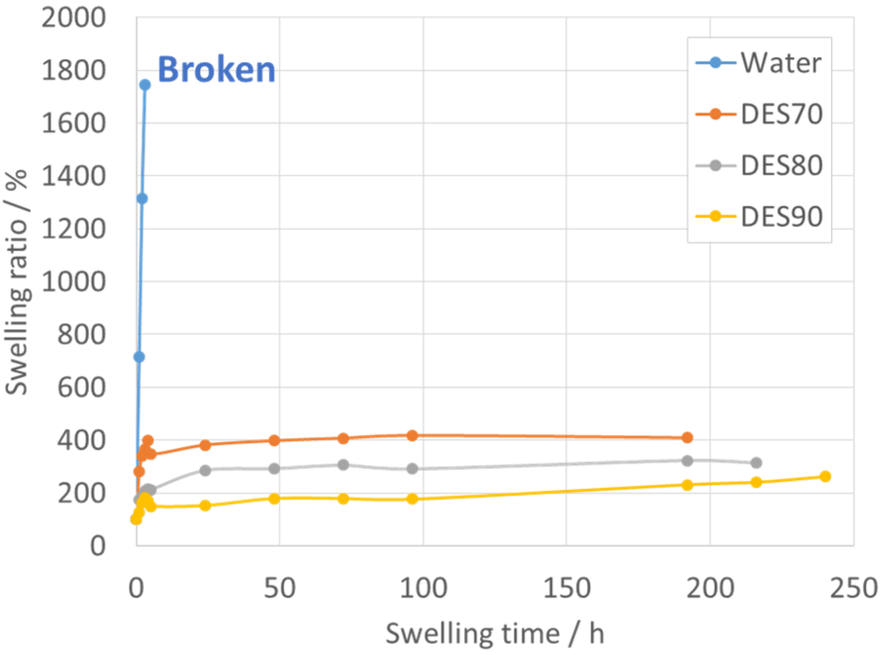
The original CMC/HEC membranes are rigid and self-standing, which turn to a gel form by immersing them in the cleaning solvent. The time required for gelation was different depending on the concentration of DES in the cleaning solvent. When the swelling test was performed on the membrane, it was noticed that the membrane is not stable in water. As shown in Figure 4.6, after 4 hours of soaking, the membrane absorbed 18 times of water compared to its original mass, became a fragile gel, and did not retain its original shape. The quick disintegration suggests the crosslinking density of the membrane is not sufficiently high.

When the membrane is soaked in the series of DES solutions, the disintegration was supressed. In the case of DES70, the membrane rapidly absorbed the solution in the first four hours and swelling degree reached 400 %. After five hours of immersion, the swelling degree of membrane once decreased to 350 %. We suppose this is due to the temperature change during the experiment or partial dissolution of membrane. The swelling ratio of membrane reverted to 400% after 24 hours, and became plateaus after 48 hours. In this range, there is a slight gain in weight of just 1mg during the 8 days of experiment.

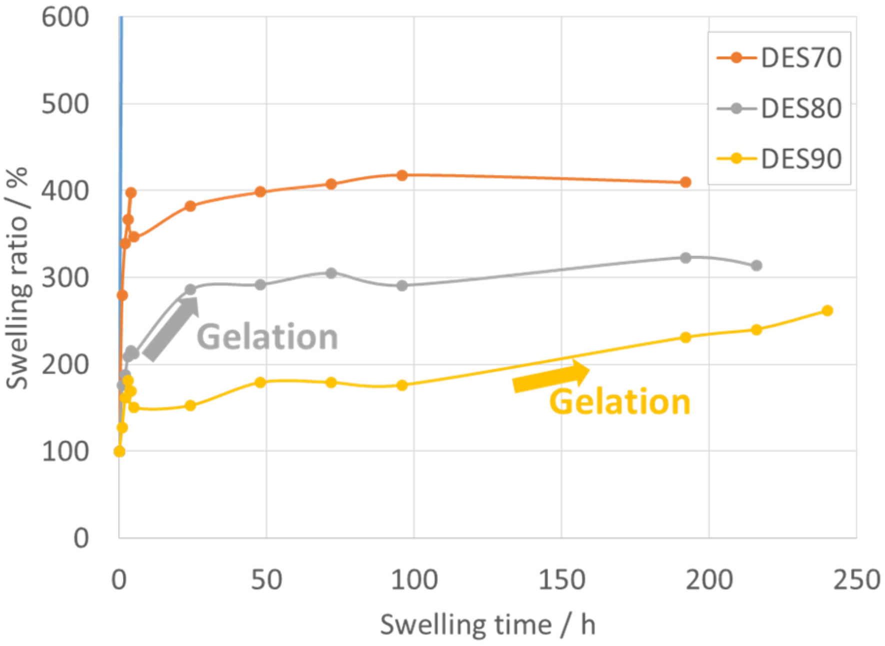
On the other hand, the membranes in DES80 and DES90 became gels after 24 hours and 192 hours, respectively (see Figure 4.6 (b)). The membrane in DES90 took longer time to become a gel than DES70 and DES80. The gel after 8days weighed 30.3 mg, being equivalent to the swelling ratio of 250%. Moreover, the weight did not stabilize even after 10 days of the membrane swelling. This may be because of the high viscosity of DES90. In addition, taking the hydrophilic property of the cellulose membranes into account, the low water content in the mixture is expected to cause the low swelling degree.

The membrane in DES90 remained very rigid for the first few days, which is not favourable for the cleaning of copper surface because a rigid membrane will not attach to the copper surface properly. On the other hand, the membrane become gels within 1 day in the case of DES70 and DES80. These swollen membranes are expected to be suitable for copper cleaning.

From the swelling test, it can be concluded that DES70 and DES80 are the best option when it comes to swelling of the CMC/HEC membrane because the membrane can soak a higher amount of the DES in a shorter period of time.



(a)



(b)

Fig. 4.6 (a) Swelling ratio of the CMC/HEC membrane during the swelling procedure in various DES solutions and in water and (b) an enlarged figure including the results of only DES solutions

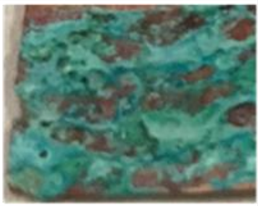
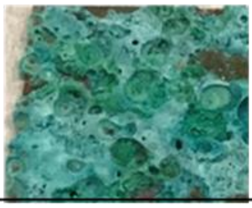
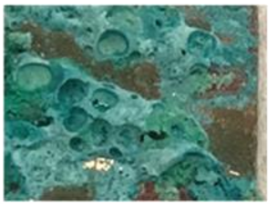
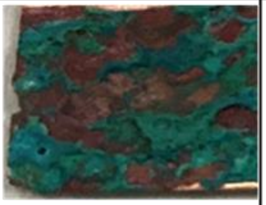
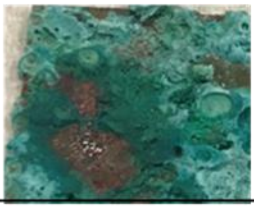
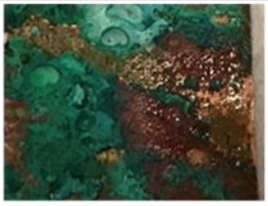
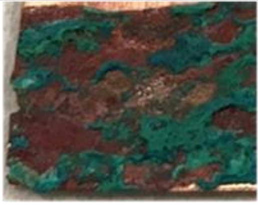
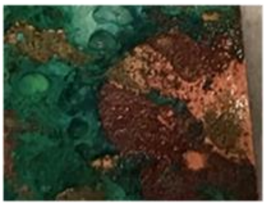
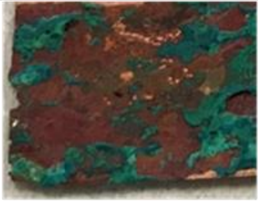
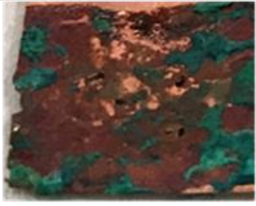
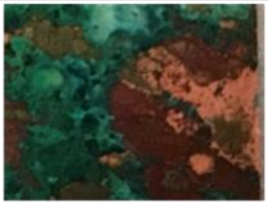
Swab cleaning test

The DES solutions were assessed in terms of the ability to remove copper corrosion from copper metals. First, the cleaning test was carried out simply by absorbing the DES solutions into the swab. For one cleaning, four cotton balls were used with a diameter of around 5mm which contained about 60 mg of the solution. Each time before using the new swab, the corroded copper surface was rinsed with ethanol.

As summarized in Table 4.2 it takes three to four rounds of cleaning to see the metallic copper surface underneath the corrosion layers. All solutions are effective for removing the corrosion and no significant difference was observed among the three different concentrations. When DES70 was used, the green malachite layer was successfully removed but the red cuprite layer was preserved. This result can be beneficial for the selective cleaning of malachite from copper because as it is mentioned earlier, a thin cuprite layer formed over copper prevents the copper metal from further corrosion or degradation.

DES90 also worked well and the cleaning was quicker than DES70 as well as DES80. It pulverized the copper corrosion easily. This is considered to be due to the high concentration of DES in the solution. The original copper metal was seen after the first round of swab cleaning. However, it was also noticed that DES90 was also strong enough to remove some of the reddish-brown cuprite layer along with the green malachite layer.

We can conclude that all the three concentrations of DES work properly as a cleaning solvent. They only were different in terms of proficiency and selectivity of cleaning. This will be beneficial for practical usage for the conservator to achieve the desired level of cleaning depending on the demands of the client or circumstances.

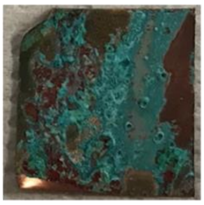
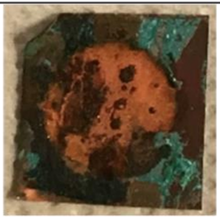
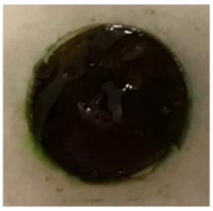
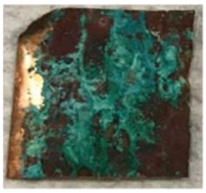
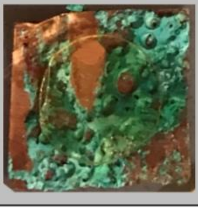
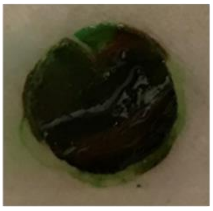
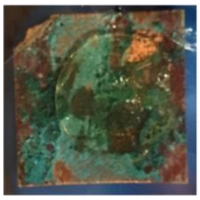
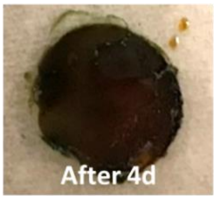
DES70	DES80	DES90
		
		
		
		
		

<u>Table 4.2 Result of cleaning with the swab stick saturated with the DES.</u>

Cleaning test using membrane

The cleaning of copper was then undertaken by using membrane swelled in the DES solutions. The swollen membrane was layered on the corroded copper sheet. It can be noticed that DES70 and DES80 sufficiently removed corrosion after 24 hr of the treatment, and especially DES70 removed most of the green malachite layer of copper corrosion (Table 4.3). In the case of DES70, the formation of bubbles was observed soon after putting the membrane on the corroded copper due to the formation of CO_2. Based on visual observation, the efficiency of cleaning was better for DES70 than DES80, which left most of the dark green corrosion. In both cases, the colour of the membrane turned dark green when they were removed from the copper surface after 24 hours.

On the other hand, a sufficient effect was not obtained after 24hrs. As shown in Table 4.3, DES90 took 4 days to remove the corrosion. In the swab cleaning test, DES90 exhibited a strong cleaning ability and removed also red cuprite corrosions. In contrast to this, in the membrane cleaning test, DES90 showed a weaker cleaning ability compared to DES70 and DES80, and the red cuprite layer was more preserved when the condensed DES solutions were used. This is probably because of the facts that DES90 is more viscous and the weight of DES90 absorbed in the membrane was lower than DES70. Therefore, the amount of DES90 was not enough for enhancing the cleaning ability. Also, during the membrane cleaning, infiltration of DES90 is considered to be insufficient to reach the cuprite layer, which locates below the green malachite layer (see the discussion about corrosion compound in the next section). Accordingly, the DES70 and DES80 give better results compared to DES90 when these solutions were integrated with CMC/HEC membrane.

	Pristine Cu	Soon after putting membrane	After 24h Only Cu	After 24h Only membrane
DES70				
DES80				
DES90				

<u>Table 4.3 Comparison of cleaning ability of DES absorbed in CMC/HEC membranes. The photos in the grey cells were taken using different piece of copper.</u>

X-ray diffraction results

XRD was performed on three samples of copper which were electro chemically corroded. The pristine sample was analysed prior to any cleaning to use as a control. For the preparation of the pristine copper corrosion, electrochemical corrosion technique was used as mentioned in the experimental section. The electrochemical treatments in the ATSM D1384 solvent allow the production of the corrosions including oxide, carbonate, sulphate, and chloride [Beldjoudi T., *et al.*, 2001]. The absence of tenorite (CuO), azurite ($Cu_3(OH)_2(CO_3)$), brochantite ($Cu_4SO_4(OH)_6$), antlerite ($Cu_3SO_4(OH)_4$), melanothallite (Cu_2OCl_2) was confirmed due to the absence of the peaks related to these products, while the peaks related to cuprite (Cu_2O), malachite ($Cu_2(OH)_2CO_3$), atacamite ($Cu_2Cl(OH)_3$), posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$), nantokite (CuCl) were observed during the experiment. Figure 4.7 summarizes the references of the XRD patterns of these components. The Powder Diffraction Files (PDF) were taken from the International Centre for Diffraction Data (ICDD). Only the spectrum of posnjakite was taken from the RRUFF database.

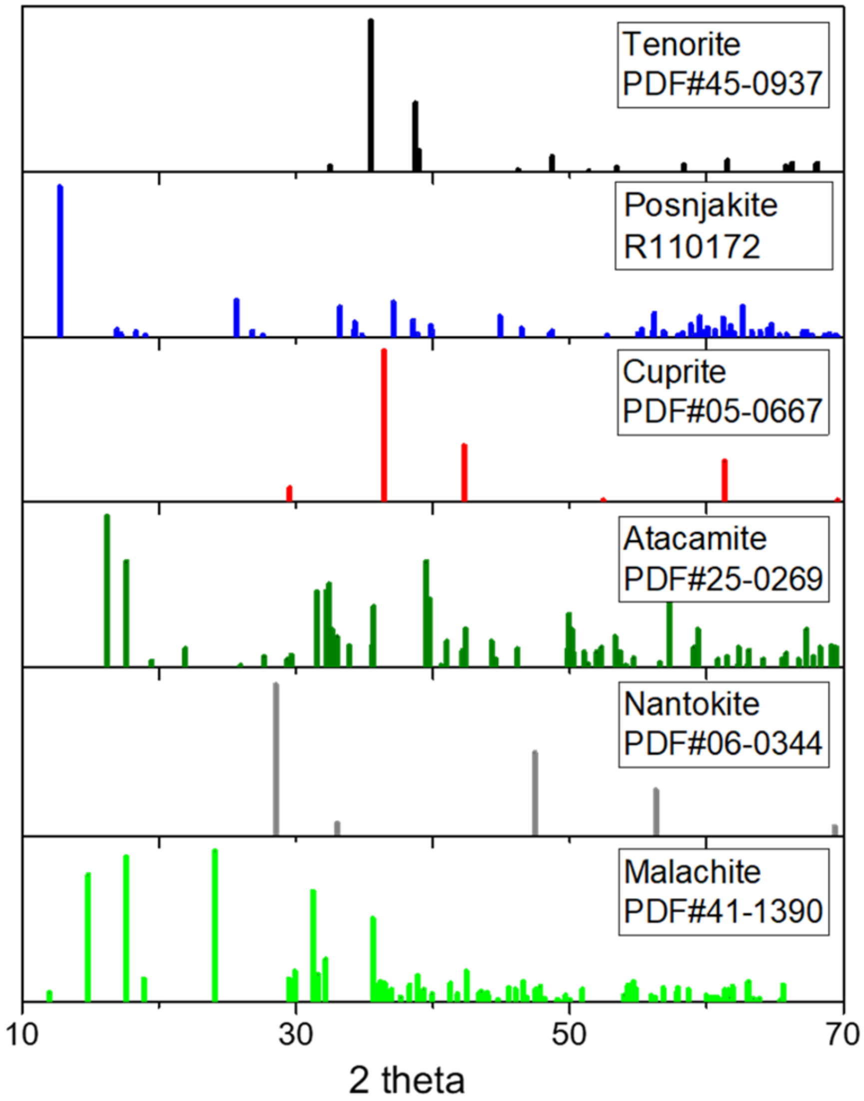


Fig. 4.7 Reference patterns of copper corrosion products.

As shown in Fig 4.8, the pristine sample had a variety of copper corrosion products. These include cuprite, malachite, atacamite, posnjakite, nantokite and tenorite. The peaks of pure copper were observed at 2θ values of 43.3° and 50.4° corresponding to (111) and (200) planes of Cu.

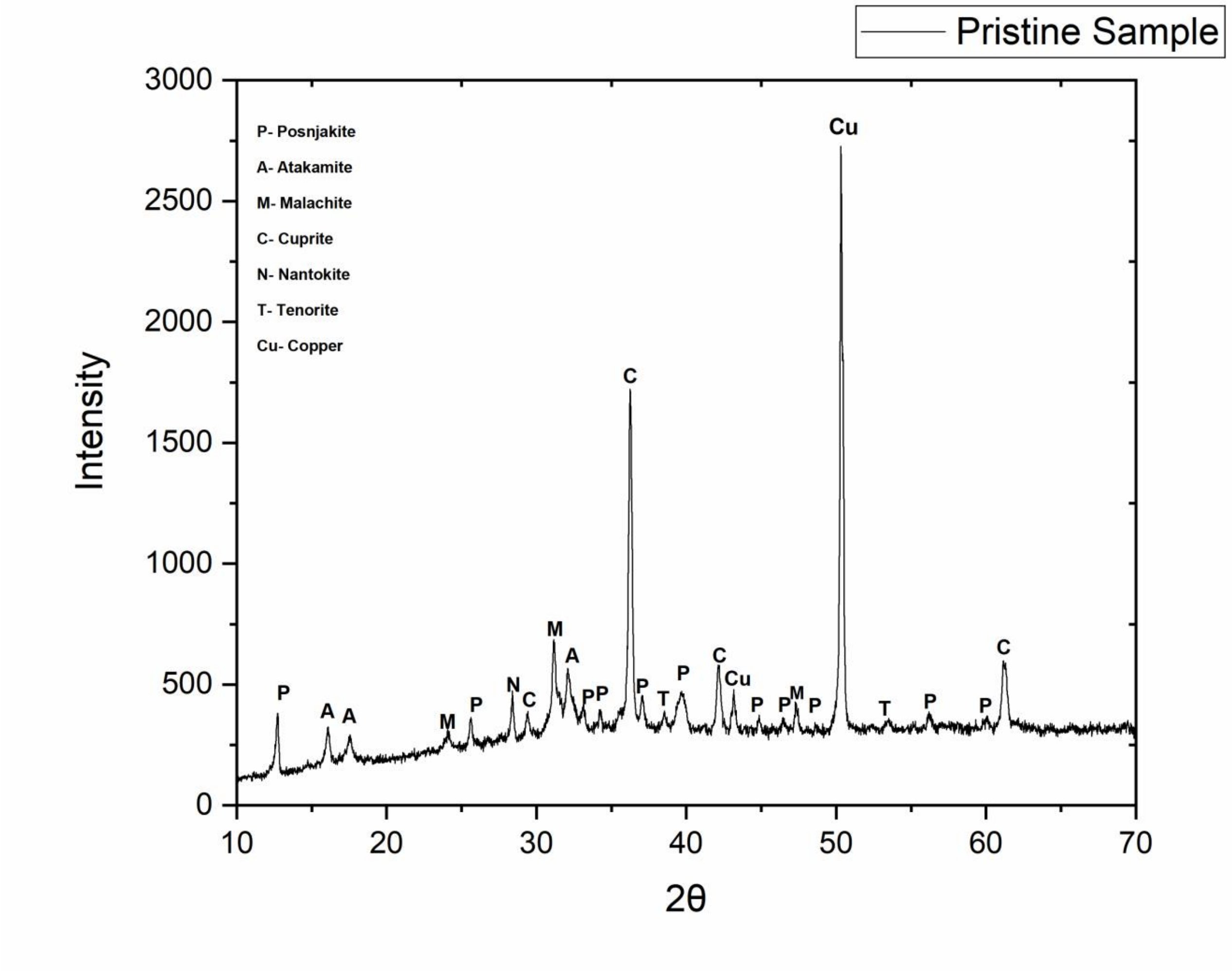


Fig. 4.8 XRD pattern of the pristine corrosion sample before cleaning.

The other two samples were of the corroded copper sheets after treatment with the DES80 and DES90 cleaning membranes. The results of XRD were compared to those of pristine copper corrosion to assess the change during the removal of copper corrosion products.

As shown in both Figure 4.9 and Fig 4.10, DES80 and DES90 removed major part of the copper corrosion. In the case of the sample treated with DES80 membrane, the peaks of copper were predominant, and small peaks related to cuprite were observed. The new small peaks observed around 18° are probably related to the atacamite derivatives such as paratacamite. [Lopesino Patricia, *et al.*, 2018] Not only the membrane removed most of the copper corrosion, but they also preserved the protective cuprite layer. DES90 preserved cuprite better than DES80. However, many small peaks related to the copper patinas were observed, which are due to the weaker cleaning ability of DES90 as discussed above.

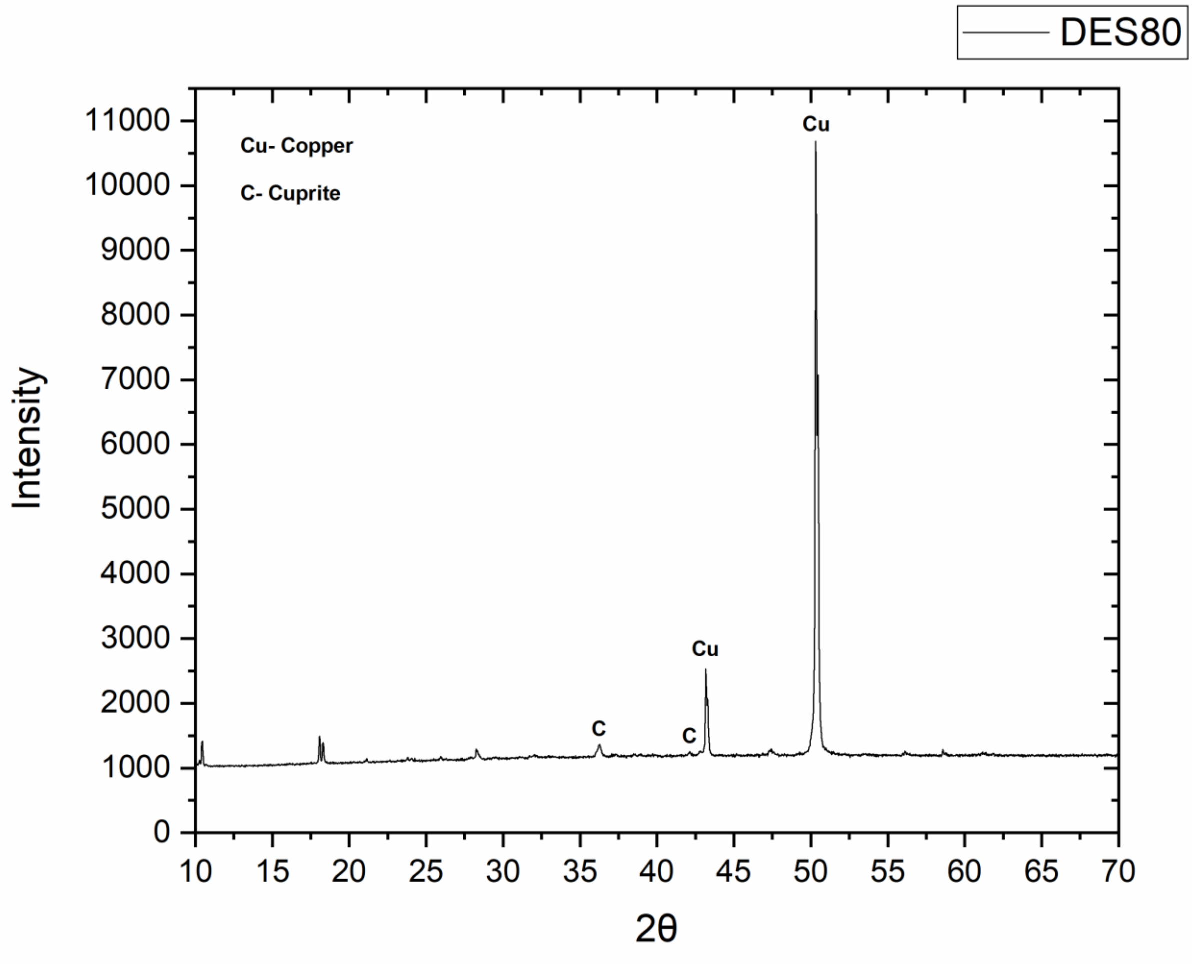
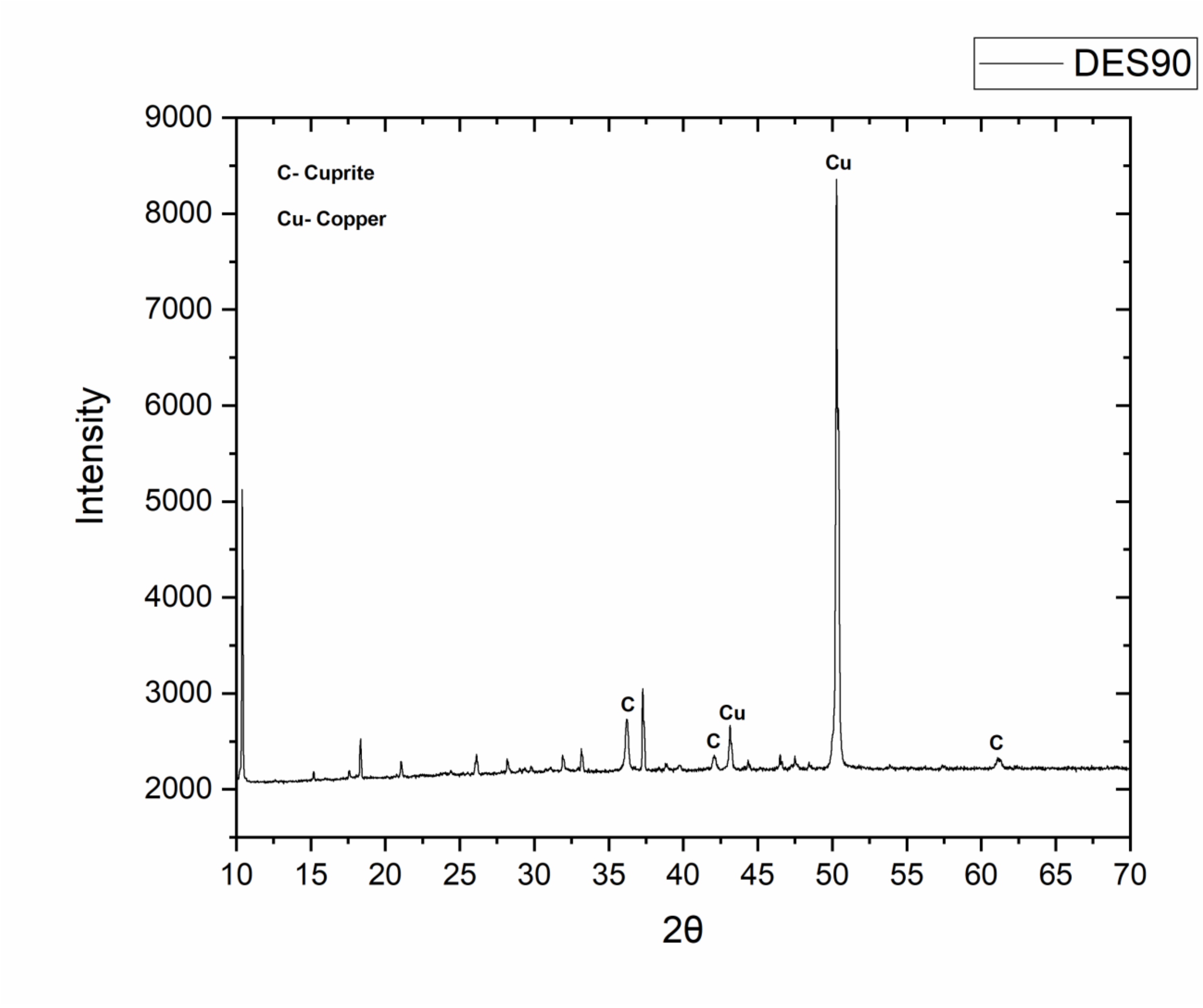


Fig. 4.9 XRD patterns of the copper sample after the cleaning procedure using membrane with DES80.



<u>Fig 4.10 XRD patterns of the copper sample after the cleaning procedure using membrane with DES90.</u>

Comparison of the two cleaning procedures

When the swab test was performed, it was observed that although cleaning of the copper surface with a cotton swab soaked in the DES gives good results, we noticed that it also requires a lot of solution. This is because a cotton ball tends to soak up a lot more of the solution than a membrane. As a laboratory scale, the difference in quantity of DES is small between these techniques, but it would be large when the larger artefacts are the target of treatment. A lot of the soaked solution is also lost when the DES soaked cotton ball touches the surface and especially when a pressure is applied to clean it, which wrings the cotton ball and causes bleed out of the DES solutions. There is a possibility that the use of cotton swab mechanically damages fine structures of copper artefact because the copper patinas need to be wipe out by applying slight force. This needs to be assessed by means of SEM in the future. In contrast, the use of swab stick method is highly useful for quick cleaning. As explained in the experimental section, the preparation of membranes takes time. In addition, since swab cleaning method needs to be carried out by human hands, the level of cleaning can be controlled by conservators. As shown in Table 4.2, when DES90 was used, the metallic copper surface was achieved after 2 rounds of cleaning. For DES70, it needed several times of cleaning, but we have succeeded in the preservation of cuprite layer.

In contrast to these properties of swab cleaning techniques, the use of a membrane ensures that not much of the cleaning solution is wasted. It would also help in precise area selective cleaning as the membrane can be cut in varying shapes and sizes depending on the need of the object. The membrane would also come in handy when the need arises to clean copper corrosion from hard to reach places. This might occur in the case of intricate pieces of art. However, it requires a lot of time for synthesizing the membrane. Accordingly, we can conclude that this technique is more adequate for precious materials.

5. Conclusion

The purpose of this thesis was the optimization of the cleaning method for copper corrosion by using DES and cellulose-based membrane. Ratios of the DES aqueous solutions which are suitable to remove copper corrosion from an archaeological or historical artifact in the most effective way which is not harmful to the object and gives the desired results in a shorter time were identified.

A series of DES solutions of different concentrations ranging between DES10 to DES90 were compared to one another on the basis of results achieved by using various methodologies and experiments.

The dissolution tests were performed in two steps: one to check the dissolution of copper corrosion products and the other to check that of calcium carbonate. Through the copper corrosion dissolution test, it was found that when the concentration of DES was lower than 50 wt.%, the solution dissolved the corrosion powder quickly but formed blue precipitate after a few days suggesting the dissolution state is not stable. DES70 dissolved the copper corrosion powder completely and quickly although it formed a small amounts of CO_2 gas. DES80 and DES90 dissolved the powder slowly but completely and the solubilized copper was stable and there was no precipitation. The dissolution test of calcium carbonate was done as it is a common compound in limestone supporting structures used for copper artefacts. DES30 and DES50 dissolved $CaCO_3$ quickly, designating that they are harmful to be used on limestone. DES70 dissolved $CaCO_3$ slowly but completely, DES80 dissolved it slowly but not completely where as DES90 showed no change in the amount of powder that was added to it. DES90 has the least solubility of $CaCO_3$.

Results of the swelling test of the membrane showed that when immersed in DES70, it took 5 hours for the membrane to reach gelation and took 48 hours to reach constant weight. The membranes in DES80 and DES90 took 24 hours and 192 hours to become a gel, respectively. The membrane in DES90 was rigid in a few days and its weight did not stabilize even after 10 days of immersion. The swelling capacity of the membrane was much higher with DES70 than with DES80 and DES90.

The DES solutions were assessed in terms of their ability in removing copper corrosion from copper metal. In the swab cleaning test, it was found that DES solutions with concentrations of 70, 80 and 90 wt.% were successful in removing copper corrosion. DES90 worked quicker than DES70 and DES80 but unlike the other two concentrations, it also removed the protective cuprite layer along with the malachite layer.

Through the aforementioned experiments, we have confirmed the DES solutions especially containing DES more than 70 wt.% are effective for copper cleaning.

When the swollen membrane was used to clean copper corrosion, it was found that DES70 and DES80 took 24 hours to show results. DES70 gave better results than DES80 whereas DES90 took four days but showed similar results to DES70.

XRD results showed that post cleaning with the membranes, DES90 preserved cuprite better than DES80 but has weaker cleaning ability.

We can successfully conclude that DES concentrations above 70 wt.% are suitable to clean copper corrosion. In addition, from the dissolution test of $CaCO_3$, we can conclude that DES90 can be used for artefacts which are bound or attached to a limestone as it is the safest option among the other potent DES concentrations. In cases where there is no calcium carbonate involved, DES70 as well as DES80 can be used to clean copper corrosion. Cleaning can be done by using both swab stick as well as a cellulose membrane. They also make it permissible to have selectivity in terms of time taken to gain results as well as the degree of cleaning achieved.

6. Future Scope

In this study, I used crosslinked cellulose-based membrane because of its good mechanical stability and chemical stability in water solution. Alternatives to the membranes can be considered in the future. In addition to cellulose derivative, another polysaccharide such as Agar Agar is considered to be useful. Agar Agar as a membrane is suggested because it is also nature derived and eco-friendly affordable polymer. For the specific usage with copper, the compatibility between these polymers and copper should be considered. For example, the contact angle measurements of these components need to be carried out in the future for investigating other promising polymer matrices.

Another idea that should be considered is direct application of membrane solutions with cleaning agent to copper objects before it turns to a gel form, like a mask. The membrane can then be solidified by evaporating the solvent using an oven or even solar heat. Also, modification of polymer back bone structure using DES solution will be advantageous because it reduces the acidity level of the DES and eliminate the need of swelling procedure of membrane in cleaning solution. These techniques will help the solution to stay on the surface of the object longer time and help in removing more stubborn corrosions.

An appropriate and equally eco-friendly method of protecting and conserving the cleaned surface must be devised to complete the procedure. This would ensure that not only is the object cleaned but it will also prevent the object from relapsing into corrosion and will protect it for a longer period of time.

References

1. Andrew C., Etim E.E., *et.al.*, 2017, *Deep Eutectic Solvents: An Overview of its Application as a "Green" Extractant*, Pgs.23-30.
2. Anirudhan T. S. and *et al.*, 2008, *Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell* in The Journal of Chemical Thermodynamics, Vol. 40, Issue 4, Pgs. 702- 709.
3. Hammond Oliver S., *et al.*, 2017, *The Effect of Water upon Deep Eutectic Solvent Nanostructure: An Unusual Transition from Ionic Mixture to Aqueous Solution,* Angewandte Chemie, Vol. 129, Pg. 9914- 9917.
4. Antonijeic M.M. and Petrovic, 2008, *Copper Corrosion Inhibitors in A review* in International Journal of Electrochemical Science 3, Pgs.1-28.
5. Bastidas J.M., Mora N., and *et al.*, 2001, *Characterization copper corrosion products originated in simulated uterine fluids and on packaged intrauterine devices* in Journal of Materials Science: Materials in Medicine 12, Pgs.391-397.
6. Beldjoudi T., Bardet F. and *et al.*, 2001, *Surface Modification Processes on European Union Bronze Reference Materials for Analytical Studies of Cultural Artefacts* in Journal Surface Engineering.
7. Calister William D., 2013, *Materials Science and Engineering: An Introduction*, Wiley Publication.
8. Carlo G. Di, Giulliani and *et al.*, 2017, *Artificial patina formation onto copper-based alloys: Chloride and sulphate induced corrosion processes* in Applied Surface science 421, Pgs.120-127.
9. Chiavari C., Rahmouni, *et al.*, 2007, *Composition and electrochemical properties of natural patinas of outdoor bronze monuments* in Electrochemical Acta 7760-7769.

10. Constantinides I., Adriaens A., Adams F., 2001, *Surface characterization of artificial corrosion layers on copper alloy reference materials* in Applied Surface Science 189, Pgs. 90-101.

11. Das Papita, *et al.*, 2010, *Assessment on the Removal of Malachite Green Using Tamarind Fruit Shell as Biosorbent* in CLEAN- Soil Air Water, Pgs. 437- 445.

12. Delgado- Mellado Noemi, *et al.*, 2018, *Thermal stability of choline chloride deep eutectic solvents by TGA/FTIR-ATR analysis,* Journal of Molecular Liquids, Vol. 260, Pgs. 37- 43.

13. Demitri Christian, Sole Roberta Del and *et al.*, 2007, *Novel Superabsorbent Cellulose-Based Hydrogels Crosslinked with Citric Acid* in Wiley InterScience.

14. Edwards Mark and *et al.*, 1996, *Alkalinity, pH, and copper corrosion by-product release* in Regulatory Girdlock.

15. Gioventu Eleonora, Lorenzi Paola, *et.al.*, 2012, *Bacterial Cleaning Technology or marble surfaces affected by black crust: Comparison with Chemical and Laser Treatment* in 12th International Congress on the Deterioration and Conservation of Stone Columbia University, New York.

16. Kataev Evgeny, et al., 2012, *Fluorescence Detection of Adenosine Triphosphate in an Aqueous Solution Using a Combination of Copper (II) Complexes,* Inorganic Chemistry, Vol. 53, No. 9, Pgs. 4885- 5494

17. Kenoyer Jonathan M. and Meller Heather M.L., 1999, *Metal Technologies of the Indus Valley Tradition in Pakistan and Western India.*

18. Knotkova D. and *et al.*, 2007, *Corrosion and conservation of copper and bronze in* Environmental deterioration of materials, Vol. 21, WIT Press.

19. Liu Xun, Hu Wenyuan and *et al.*, 2015, *Severe corrosion of copper in a Highly alkaline egg white solution due to a biuret corrosion reaction* in Corrosion Science 94, Pg. 270-274.

20. Lopesino Patricia, et al., Corrosion of Copper in Unpolluted Chloride-Rich Atmospheres in Metals, Vol. 8.

21. Macchia A., Sammartino M.P., Tabasso Laurenzi M., 2011, *A new method to remove copper corrosion stains from stone surfaces* in Journal of Archaeological Science 38, Pgs. 1300-1307.

22. Mödlinger, Marianne & Sabatini, Benjamin, 2016. A *Re-evaluation of inverse segregation in prehistoric As-Cu objects* in Journal of Archaeological Science. Vol. 74, Pgs. 62-74.

23. Parisi Erica Isabells, Bonelli Nicole and *et al*., 2017, *Development of an innovative film-forming cleaning system for the removal of corrosion products from copper alloy artifacts* in METALS, ICOM-CC 18th Triennial Conference.

24. Parisi Erica I., Nicile Bonelli, *et al*., 2017, *Film forming PVA-based cleaning systems for the removal of corrosion products from historical bronzes*.

25. Radetzki Marian, 2009, *Seven thousand years in the service of humanity-the history of copper, the red metal* in Resources Policy.

26. Saadatkhan Nooshin, Garcia Adrian Carillo, and *et al*., 2019, *Experimental Methods in chemical engineering: Thermogravimetric analysis-TGA* in The Canadian Journal of Chemical Engineering.

27. SavrikarShriram Sheshgir, Ravishankar Basavaiah, 2011, *Introduction to 'Rasashaastra'-The Iatrochemistry of Ayurveda* in African Journal of Traditional, Complementary and Alternative Medicines.

28. Schock Michel R., 1996, *Alkalinity, pH, and copper corrosion by-product release* in Journal American Water Works Association-Jamer Water Work Assn, Pgs. 88,81-94.

29. Scostt Cindy Lee Scott, 2012, *The use of agar as a solvent gel in objects conservation* in Object Specialty Group Postprints, Volume Nineteen, Pgs. 71-83.

30. Selwyn, L., 2004, *Metals and corrosion: a handbook for the conservation professional,* Ottawa: Ont: Canadian Conservation Institute.

31. Singh Poonam, Magalhaes Solange and *et al*., 2018, *Accepted Manuscript, Cellulose-based edible films for probiotic entrapment* in Food Hydrocolloids.

32. Shabani M.A., M.Irannnajad, and *et al*., 2012, *Investigation on leaching of malachite by citric acid* in International Journal of Minerals, Metallurgy Materials.

33. Smith Emma L. and *et al*., 2014, *Deep Eutectic Solvents (DESs) and their Applications* in Chemical Reviews, Pg. 11060- 11082.

34. Szakalos Peter, Gunnar Hultquist, 2007, *Corrosion of Copper by Water* in Electrochemical and-Solid-State Letters

35. Vrese Peter De, Brooks Neil R. and *et al*., 2012, *Speciation of Copper (II) Complexes in an Ionic Liquid Based on Choline Chloride and in Choline Chloride/Water Mixtures* in Inorganic Chemistry.

36. Watson Keith, *An Introduction to the Metals from the Mary Rose*.

37. Nielsen Willium D, *Metallurgy of Copper- Base Alloys, Copper Development Association Inc*.

38. Zheng Wen Jiang, Gao Jie, and *et al*., 2015, *Facile fabrication of self-healing carboxymethyl cellulose hydrogels* in European Polymer Journal, Vol. 73, Pgs. 514-522.

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