

International Centre for Underwater Archaeology in Zadar

# CONSERVATION OF UNDERWATER ARCHAEOLOGICAL FINDS

## MANUAL

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International Centre for Underwater Archaeology in Zadar

CONSERVATION OF UNDERWATER  
ARCHAEOLOGICAL FINDS

**MANUAL**

II. edition

Zadar, 2014.

# CONSERVATION OF UNDERWATER ARCHAEOLOGICAL FINDS

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This Manual is intended for use at Advanced Course on the Restoration and Conservation of Underwater Archaeological Finds

II. edition, Zadar, 2014.

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# I. Underwater Cultural Heritage and the UNESCO Convention

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## INTRODUCTION

Sunken ships, settlements and various other hidden and valuable finds in the depths of the sea have always stirred the interest of people and their desire to reach them. The motivations to access these sunken traces of human presence have been diverse. On the one hand there is the ever-present factor of human curiosity, desire for knowledge and an understanding of events around us and over time and, on the other, a desire to gain wealth, including valuable and rare material property.

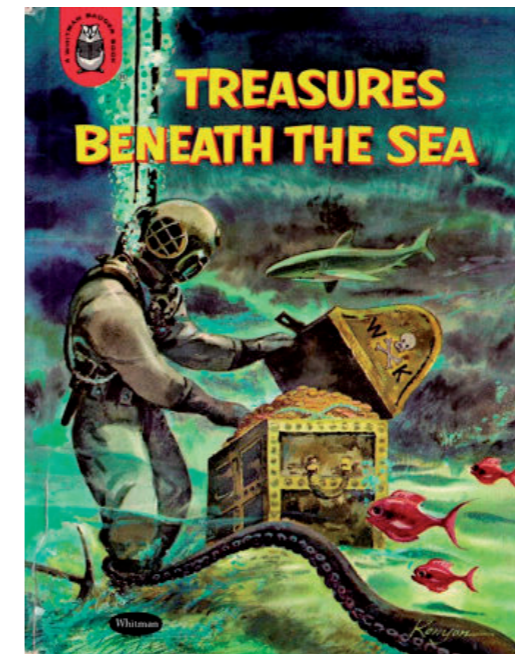


Figure 1. Typical representation of a myth of underwater treasures (www.etsy.com)

The traces of human activity that have disappeared under the waves were once sundered from our onshore existence by the significant obstacle of underwater depth. With time and human progress this obstacle has largely been overco-

me. Sunken human formations (features) became increasingly accessible. And so people, irrespective of the desires that motivated them, found it easier to access the environment of these sunken formations and act upon them. A great deal of this human activity has led to the excavation, relocation, damaging and removal of many underwater finds, whereby the sunken formations have lost their characteristic attributes and disappeared - a fact that has evoked concern.

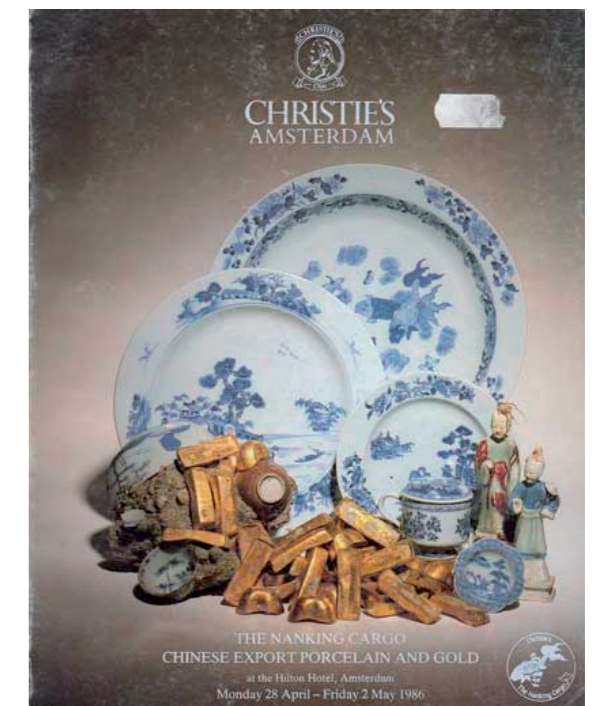


Figure 2. Geldermalsen shipwreck auction catalogue (www.china.org.cn)

Particularly detrimental were the many activities in which sunken objects were collected solely for their commercial value - a concept that gave no consideration whatsoever to the essence of the find site and its future. There are many examples of various unscrupulous enterprises (treasure hunters) that, under sundry arrangements, extracted (salvaged) numerous valuable finds, in the process destroying all the traces and data that might have been collected.

The wreck of the Tek Sing was looted in the South China Sea - over 300 thousand pieces of valuable Chinese porcelain were salvaged in 1999 and later sold at auction. A British operator salvaged over 126 gold bars and 160 thousand porcelain items from the wreck of the Dutch vessel *Geldermalsen* near Nanjing, later sold at auction. Certainly the richest shipwreck is the Spanish galleon *Nuestra Señora de Atocha* found off the Florida coast and ransacked by a private company in a most destructive fashion to extract its cargo of gold and other objects, subsequently sold through various channels. The list of looted shipwrecks is a long one and still growing.

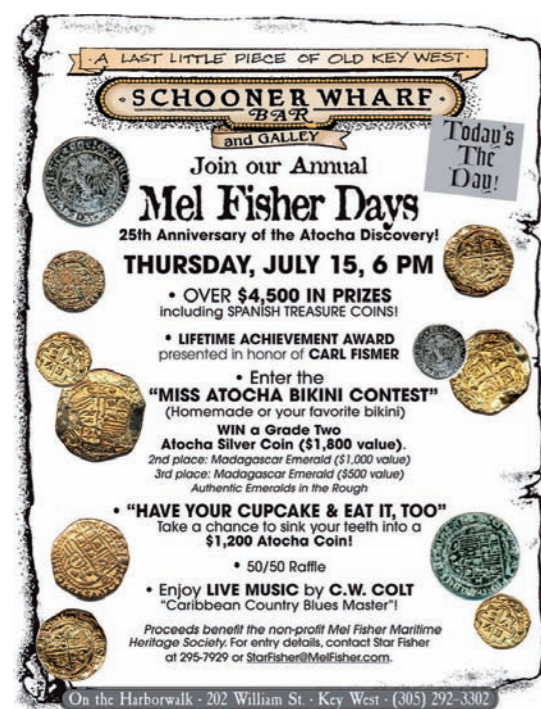


Figure 3. The treasure of the wreck of the *Nuestra Señora de Atocha* at Mel Fisher Days ([www.schoonerwharf.com](http://www.schoonerwharf.com))

As a result, the period following World War II was noteworthy insofar as consideration was given for the first time to the need to afford more care to the methods of accessing individual underwater finds, with the aim of properly protecting and researching underwater human heritage and preserving as much of the remains as possible for posterity. As a counter to the looting undertaken by various private enterprises the past half-century has seen a broadening of the

scientific approach to the research of underwater heritage, which encourages a responsible attitude towards underwater cultural heritage. These research endeavours, crowned by comprehensive publication of the results of research and the exhibition of finds to the wider public have raised the level of awareness of the real value of this heritage.

Estimates put the number of sunken vessels in the world's seas at over three million. A great number of once populated settlements are also now underwater, as are many other diverse and not easily discernable traces of habitation and activity. That truly valuable cultural heritage is to be found underwater is more than evident.

The past few decades have seen numerous initiatives at the national level, and a great many laws and regulations have been adopted governing the methods whereby underwater heritage is protected. These rules were, however, diverse, and, as a result, cooperation at the international level was launched with the aim of harmonising and broadening the efforts targeted to protection to as many countries as possible. Following various initiatives the adoption of the



Figure 4. Uluburun wreck - recovering ingots 1, 2 ([archaeologyhouston.wordpress.com](http://archaeologyhouston.wordpress.com))



Figure 5. Uluburun wreck, reconstruction at Bodrum Museum ([en.wikipedia.org](http://en.wikipedia.org))

1996 ICOMOS Charter on the Protection and Management of the Underwater Cultural Heritage came as a major step forward. It was on the basis of this charter that the UNESCO Convention on the Protection of the Underwater Cultural Heritage was finally adopted in 2001. This was followed by its ratification in some forty countries, making this to date the most important international achievement in the legal protection of underwater heritage. This convention defines underwater heritage as all traces of human activity that possess a cultural, historic or archaeological significance and that were sunk at least 100 years ago. This has set the legal grounds for the preservation of this heritage at the global level.

## THE CONVENTION

The 2001 UNESCO Convention on the Protection of the Underwater Cultural Heritage aims to see states afford better protection to their underwater heritage. The cornerstones of the Convention set out the basic principles for the protection of cultural heritage, foresee a detailed system of cooperation among countries and establish generally accepted rules for the treatment and research of underwater cultural heritage.

## THE PRINCIPLES

The first principle is the obligation to protect cultural heritage for the benefit of humanity. Accordingly, states parties to the Convention (signatories) should protect underwater heritage. Each state implements this protection in accordance with its capabilities, and if it is not able to undertake research of an archaeological site, it is enough that it provides appropriate protection of the site. The Convention encourages scientific research of sites and public access.

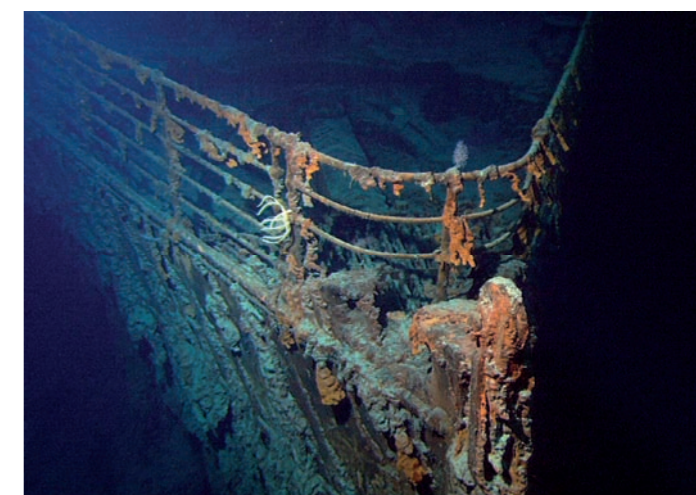


Figure 6. The bow of the Titanic shipwreck ([wavesnewsletter.com](http://wavesnewsletter.com))

## PRESERVATION

The Convention considers the preservation of underwater cultural heritage at its original location, on the seabed, the first option, having precedence over all others. Objects may be collected if this serves to rescue them from unavoidable destruction as a result of, for example, construction work, or if collection constitutes a significant contribution to the protection and research of underwater cultural heritage.

## NO COMMERCIAL EXPLOITATION

The Convention establishes that there may be no commercial exploitation of underwater heritage for the purpose of trade. Finds may also not be dispersed in a fashion that would prevent their subsequent location. These provisions are

in line with the moral principles applicable to cultural heritage on land and do not prevent archaeological research or tourist visits to archaeological sites.

**TRAINING AND INFORMATION EXCHANGE**

States parties to the Convention should promote the exchange of information and the transfer of technology with the aim of improving the protection and research of underwater heritage. It also encourages the provision of training in underwater archaeology and international cooperation in the research, protection and management of underwater cultural property. It in particular emphasises the need to raise public awareness of the need to preserve underwater heritage.

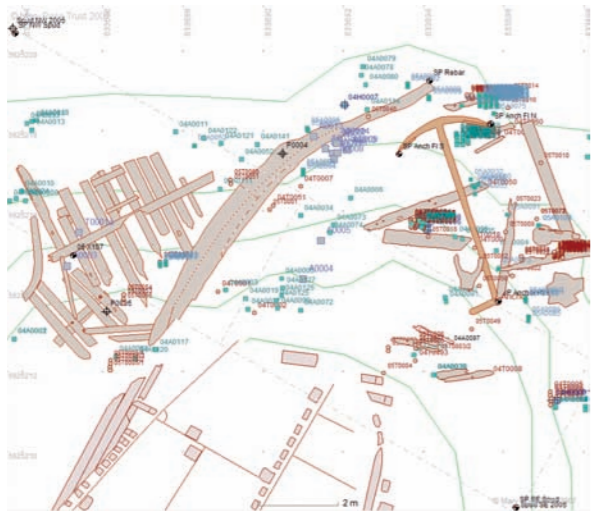


Figure 7. Mary Rose 2005 excavation site recorder map (www.3hconsulting.com)



Figure 8. The stem of the Mary Rose is raised (www.3hconsulting.com)

**OTHER KEY PROVISIONS**

The Convention does not determine the ownership of individual finds and sites, nor does it touch upon issues of state sovereignty and declares that it shall not contradict other international law, including UNCLOS, the United Nations Convention on the Law of the Sea. Any state may sign this convention, independent of whether it is a party to any other convention.

When adopting these principles the Convention also encourages ratifying countries to provide explicit protection to the cultural heritage of inland waters such as rivers and lakes. This paves the way for the participation of landlocked countries in the overall goal of protecting underwater heritage.

States parties are also to notify other countries in the event of the discovery of a shipwreck in the area of their exclusive economic zone or in international waters, with the aim of establishing a coordinating country that will take measures to protect the site.

States parties shall train or develop their own competent bodies that will see to establishing and maintaining a list of underwater cultural heritage. These bodies will also secure the protection, conservation, presentation and management of underwater heritage and nurture study and education in this field.



Figure 9. Mary Rose painting (www.3hconsulting.com)



Figure 10. Mrs Irina Bokova addressing the 2011 Session of the UNESCO 2001 Convention State Parties in Paris (Photo: L. Bekić)

**THE ANNEX**

The adoption of the Convention was followed by the adoption of the Annex to the Convention, which stipulates in greater detail the practical aspects of the protection of underwater heritage. The Annex to the Convention sets out the rules that pertain to various activities directed at underwater cultural heritage. These are generally accepted practical rules that are to be observed during excavation, such as the methodology applied. It also establishes guidelines for how research projects and future preservation should be conceived. The Annex also cites the qualifications researchers should possess to undertake activities related to the preservation and management of underwater cultural heritage. The rules contained in the Annex are one of the more important achievements of the Convention and it is felt that every professional working in the field of underwater archaeology should strictly abide by them.



Figure 11. Vasa Museum Interior (traveling-kids.blogspot.com)

The Annex makes several references to the conservation and restoration of finds. Rule 10, for example, which determines project design, also stipulates the obligation to draft a conservation programme for artefacts and the site in cooperation with the competent authorities. In the chapter dedicated to funding and project duration, in rules 17, 19, 20 and 21, there is specific mention of the need to draft a contingency plan for funding and time required for conservation even in the event of the termination of the project or an interruption of expected funding. Of particular importance is chapter VIII of the Annex, rules 24 and 25, which detail conservation programmes for small finds and features during research, transport and the long - term storage of finds.



Figure 12. Vasa Museum Exterior (it.wikipedia.org)

**IMPLEMENTING THE CONVENTION**

The supreme body of the Convention is the Meeting of States Parties, convened at least once every two years. Expert and advisory support to member states is provided by the Scientific and Technical Advisory Body (STAB), which pools some ten top experts in the field of underwater archaeology. Ad hoc States Parties Working Groups may also be established to discuss, among a limited number of participants, issues and to prepare working materials for Meetings of States Parties. The organisation and coordination of these bodies and similar tasks is carried out by UNESCO, the Director-General and the Convention Secretariat based in Paris.

## CONCLUSION

From the beginnings of underwater research to the present day there has always been great public interest for underwater cultural heritage. In the past souvenirs were collected from shipwrecks, there were exciting articles in the press, and many television and feature length films have been made on expeditions seeking new underwater discoveries.

The number of specialised museums that exhibit restored and conserved underwater finds and even small vessels extracted from the seabed has now grown. Noteworthy are Sweden's *Vasa* Museum, visited every year by three quarters of a million people, the museum at Bodrum in Turkey, the museum housing the once sunken warship *Mary Rose* in Great Britain and many more. Improvements in diving techniques and equipment has seen a growth in the number of tourist divers who make organised visits to underwater archaeological sites.

Underwater archaeological parks have been established where sunken architectural remains can be viewed, such as the Roman period port of Caesarea in Israel and the National Marine Protection Area in the Bay of Pozzuoli in Italy. Much more numerous, however, are the frequently visited locations of shipwrecks such as the Florida Keys Marine Sanctuary with sev-

eral shipwrecks, the wreck of the *Yongala* in Australia and the wreck of the *Baron Gautsch* in Croatia. Organised visits to underwater sites are in line with the guidelines of the Convention, which give preference to the in situ protection of underwater heritage, and it is to be expected that there will be a growing number of underwater sites rendered accessible to visits by divers.

It should, therefore, be in everyone's interest to protect underwater cultural heritage with the aim of preserving it for future generations, and to develop the economic and tourism potential that may emerge from its proper care.

This legal framework, which protects underwater heritage, must be adhered to at the national level, which, besides the adoption of the appropriate laws and regulations, implies practical work targeted to protection. Above all this pertains to people involved in the protection and research of this heritage at the actual sites, most of who are underwater archaeologists. Other people not active in the systems of protection also come into contact with these locations. These are, above all, divers - professionals involved in training and guiding recreational divers. National bodies, such as the maritime police, the port authorities, coast guard and others who, as a result of their competences, may play a key role in the protection of archaeological sites, also need to be included in the system of on - site protection.

Another key aspect - one that is, unfortunately, often overseen - is the protection of objects extracted from the water for the purpose of research. Early efforts to collect and research sunken objects did not give much heed to the conservation and restoration of the objects extracted from the water. Consequently they were damaged or often entirely destroyed as a result of an abrupt change to the environment in which they were situated. This has seen countless very valuable finds collected in the



Figure 13. Baron Gautsch wreck (Drawing: D. Frka; www.rovinj-online.net)

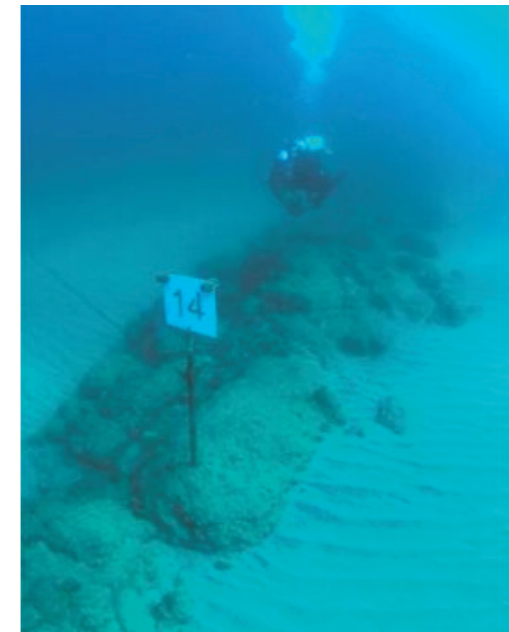


Figure 14. Caesarea location 14 (www.caesarea-diving.com)

past century irretrievably lost, despite being kept in various collections and museum depots.

In recent decades some restorers and conservators of archaeological finds have taken an interest in specialising in the protection of objects collected in wet environments and in developing various procedures and technologies to protect them.



Figure 15. Caesarea visitor's map (www.caesarea-diving.com)

The Underwater Archaeological Finds Restoration and Conservation Department in Zadar, Croatia was founded in 2007. It is now a part of International Centre for Underwater Archaeology in Zadar, a UNESCO category II centre. Conservation workshop pools a diverse team of experienced conservators - restorers and chemists who have specialised in treating underwater finds. This handbook is their work and in it, in a concise fashion, they have endeavoured to outline to those interested the methods whereby various types of objects are protected. This work is largely based on their wealth of practical experience, and on a synthesis of numerous expert papers on the subject from around the world.

## II. Guidelines, Ethics and the Methodology of Conservation - Restoration Work

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### INTRODUCTION

The protection of artistic heritage is as old as the history of our civilisation. It is a complex process that involves human activity and the will to preserve artistic heritage from destruction or loss. The preservation of objects of archaeological heritage is the chief goal of conservation and restoration work. Conservation and restoration is a lengthy process that often requires significant financial resources. It consists of a series of procedures, methods and interventions that prevent the further deterioration of objects, and restores their physical integrity and visual identity. Without the implementation of conservation and restoration interventions most artefacts would decay, and the historic and artistic data would be forever lost.

In their work every conservator - restorer should adhere to the Professional Guidelines & Code of Ethics. The Code of Ethics establishes the terms of reference and the definition of the conservator - restorer's profession as confirmed and broadened at the general assembly of the *European Confederation of Conservator - Restorers Organisations* (ECCO) held in Brussels in 1993. The second version of the Professional Guidelines was adopted at the Brussels general assembly on 1 March 2002, while the second version of the Code of Ethics was adopted at the general assembly held in Brussels on 7 March 2003.

### PROFESSIONAL GUIDELINES

The objects, buildings and environments to which society attributes particular aesthetic, artistic, documentary, environmental, historic, sci-

entific, social, or spiritual value are commonly designated "cultural heritage" and constitute a material and cultural patrimony to be passed on to coming generations.

By definition the conservator - restorer is a professional who has the training, knowledge, skills, experience and understanding to act with the aim of preserving cultural heritage for the future. The fundamental role of the conservator-restorer is the preservation of cultural heritage for the benefit of present and future generations. The conservator - restorer carries out diagnostic examination, conservation - restoration treatment of cultural property and the documentation of all interventions. Diagnostic examination consists of the research of relevant existing information; the identification and determination of the composition and the condition of cultural heritage; the identification of the nature and extent of alterations and an evaluation of the causes of deterioration. Conservation consists mainly of direct action carried out on cultural heritage with the aim of stabilising its condition and retarding further deterioration, while restoration consists of direct action carried out on damaged or deteriorated cultural heritage with the aim of facilitating its perception, appreciation and understanding, while respecting as far as possible its aesthetic, historic and physical properties. Documentation consists of an accurate pictorial and written record of all procedures carried out and the resulting insight. Recommendations regarding storage, maintenance, display or access to cultural heritage should be specified in this documentation.

Furthermore, it is within the conservator - restorer's competence to: develop programmes, projects and surveys in the field of conservation - restoration; provide advice and technical assistance for the preservation of cultural heritage; prepare technical reports on cultural heritage; conduct research; develop educational program-

mes and teach; disseminate information gained from examination, treatment or research; promote a deeper understanding of the field of conservation - restoration. As the primary aim of conservation-restoration is the preservation of cultural heritage, it is distinct from art and crafts. The conservator - restorer is distinguished from other professionals by her/his specific education in conservation - restoration.

### THE CODE OF ETHICS

Every conservator - restorer should adhere to the principles, obligations and rules of behaviour embodied in the code of ethics in the practice of their profession. As the profession of conservator - restorer constitutes an activity of public interest, it must be practised in observance of all pertinent national and European laws and agreements. The conservator - restorer works directly on cultural heritage and is personally responsible to the owner, to the heritage and to society. Failure to observe the principles, obligations and prohibitions of the Code constitutes unprofessional practice and will bring the profession into disrepute. In their work conservator - restorers contribute to a better understanding of cultural property, mindful of its aesthetic, historic and spiritual significance and its physical integrity. By his or her knowledge of the material aspects of objects possessing historic and artistic significance, the conservator - restorer prevents their deterioration and increases the capacity of comprehension by emphasizing the difference between what is original and what has been replaced. In their work conservator - restorers must adhere to the highest standards of the profession regardless of the market value of the cultural heritage. All aspects of preventive conservation should be taken into account before carrying out interventions directly to cultural heritage so that the conservator - restorer may limit the treatment to only that which is necessary. The materials used by the conservator - restorer should be compatible with the materials of the cultural heritage and as completely reversible as possible. Every conservation - restoration treatment of cultural heritage should be documented, and the report should include

written and pictorial records of all conservation - restoration interventions and diagnostic examination with the names of all those who have carried out the work. The conservator - restorer must strive to enrich her/his knowledge and skills and cooperate and exchange information with other professionals with the constant aim of improving the quality of her/his professional work.

### THE METHODOLOGY OF CONSERVATION AND RESTORATION WORK

When initiating conservation - restoration work we must first undertake the careful examination of the object in question and its context. The object must be carefully studied in order to produce as appropriate as possible a determination of what to do and how it should be done. In order to gain the most proper and confident knowledge of the archaeological object under study a conservator - restorer may, during the examination, undertake scientific analysis and special surveys. The study of the archaeological object should yield insight into the kind of materials and techniques used and the intentions inherent in the object's manufacture. Alterations that an object has been subjected to over time should also be ascertained. Respectful of the integral object and of its history and context, the conservator - restorer shall critically assess which alterations act as disfiguring factors, which should - with the aim of facilitating the perception, appreciation and comprehension of the cultural heritage - be removed, and which changes are an alteration of the original material that it would be a mistake to eliminate (VOKIĆ 2007, 261).

The real or potential value of cultural property may be destroyed by conservation - restoration interventions. In order to avoid this the value of cultural property must be assessed and recognized. In order to define a proposal of actions and the order in which they are to be conducted, the conservator - restorer must establish the following: the nature of the original material and

the production technique applied; what changes to the material and which additions to the material have occurred as a consequence of the passage of time; which changes are a disfiguring factor and which are acceptable; what are the reasons for undertaking the intervention on the object; what is the entirety of the object and its context; what was the history of the object, what were the intentions of its author and what value is inherent to the object (VOKIĆ 2007, 262).

The determination of the method in which conservation - restoration work is to be conducted is followed by the selection of materials and procedures to be applied. Materials and procedures are determined for each phase of conservation - restoration work. The following principles are to be respected in the selection of materials and procedures: the principle of minimal necessary intervention; the principle of visual and structural compatibility of the materials and procedures applied with the original materials and original techniques of manufacture; the principle of the reversibility of the materials and procedures applied; the principle of the distinctness of the intervention and the principle of sustainability (VOKIĆ 2007, 263). The professional guidelines divide the concept of preservation into the terms preventive conservation and remedial conservation (PEDIŠIĆ 2005, 12). The preventive conservation of an object of cultural heritage consists of indirect actions, while remedial conservation consists of direct action on the cultural property. Restoration involves direct action on cultural property that is deteriorating or has been damaged, with the aim of facilitating the understanding of the cultural property. To reduce direct intervention on cultural property to the smallest possible measure the conservator - restorer must take into consideration all preventive conservation options when determining restoration procedures.

Written records and photographic documentation based on a defined system must be kept during conservation - restoration work. This system is known as conservation - restoration documentation; it is an integral part of the cultural heritage and must be accessible. Conservation - restoration documentation has as its goal: to provi-

de for and secure a methodological approach to conservation - restoration work; to establish the intention and value contained in the cultural heritage; to determine the material to be preserved and changes that have occurred (VOKIĆ 2007, 258). Conservation - restoration documentation should include: inventory data that establishes the heritage in question, research documentation, work proposal drafts, the documentation of conservation - restoration work, instructions for the method of preservation and maintenance and photographic records of the appearance and condition in all phases prior to and after the intervention (VOKIĆ 2007, 259).

## 5. CONCLUSION

The responsibility and the gradations of the work of a conservator - restorer are established by the Code of Ethics. Given that conservator - restorers work with historic originals, which possess artistic, religious, scientific, cultural, social and economic value, the conservator - restorer has particular responsibility for the preservation of their physical integrity. The professional guidelines establish the fundamental role of the conservator - restorer as being the preservation of cultural heritage for the benefit of present and future generations, and to contribute to a better understanding of its aesthetic and historic attributes (PEDIŠIĆ 2005, 12). According to the code of ethics the work of the conservator - restorer encompasses the technical examination, preservation and conservation - restoration of works of art. When undertaking restoration procedures the conservator - restorer should also endeavour to apply those products, materials and procedures that will not have a negative effect on the work of art. Restoration documentation must contain all relevant data related to the procedures conducted on the cultural property. This restoration documentation becomes a part of the work of art, also as determined by the professional guidelines (PEDIŠIĆ 2005, 13).

## III. Causes of the Decay of Archaeological Material

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### INTRODUCTION

Like other materials in the natural environment, underwater archaeological material is exposed over time to the effects of its environment and is, as such, subject to change. There are numerous and diverse physico - chemical reactions that are referred to as natural aging. The dynamics of these reactions affects the quality and durability of a material. The process of deterioration is a natural one and its speed varies for each material (MUŠNJAK 2008, 132). The nature of the substance from which the archaeological material is made and the microclimatic environment in which it is situated affects the deterioration of the archaeological material. Some types of macro and microorganisms find a suitable habitat for their development on objects of archaeological heritage. The living species that inhabit these materials range from microscopic bacterial cells to plants and animals (TIANO 2010, 1).

In long term exposure to a given set of conditions a material will tend to achieve a state of equilibrium with the environment in which it is deposited. And while it may be slow, the deterioration of archaeological material is inevitable. The extraction of archaeological material from a marine environment leads to a change in the primary microclimatic environment, and upsets the state of balance established between the material and its environment. Atmospheric effects begin to act upon the material that encourage and accelerate numerous decomposition processes. The timely conduct of appropriate conservation procedures is, therefore, necessary with the objective of stabilising the artefact, retarding the further deterioration of the material, and of ensuring its safekeeping until conservation procedures can be undertaken.

The environmental factors that can affect both the deterioration and the preservation of an artefact are: physico - chemical, biological and mechanical.

### PHYSICO - CHEMICAL CAUSES OF DAMAGE

#### WATER

Water is a complex medium consisting of pure water, mineral salts, dissolved gases and micro and macroorganisms (MEMET, 2007, 153). Water is known as the universal catalyst as it activates other causative agents of deterioration, facilitates and accelerates most chemical reactions and allows organisms to develop. Submerged artefacts may be damaged by the activity of other components besides pure water, such as salts, dissolved gases, organic substances and undissolved particles.

The physico - chemical action of water on underwater artefacts causes various types of damage. Water causes ceramic, stone and glass objects to become saturated with the salts present, which leads to the weakening of the material's structure, delamination and the damaging of the surface of the material. The effect of water on objects made of metal encourages the development of a very intensive process of corrosion that destroys the metal structure of the object and irreparably damages it. Artefacts made of wood and other organic materials are most sensitive to the action of water. Besides the fact that water is the chief agent of biodegradation, it also penetrates the organic structure of the object causing the weakening of the organic structure of the object. Many organic materials contain water in the structure of their fibres and cells that is balanced with the surrounding atmosphere.

When they are exposed to a drier or wetter envi-

ronment they are deformed (shrink or swell), whereby the original form of the object is lost.

## SALTS

Salts are ionic bonds created by a reaction between an acid and a base. When dissolved, salts split into individual ions, calcium ( $\text{Ca}^{2+}$ ), bicarbonate ( $\text{HCO}_3^-$ ), sodium ( $\text{Na}^+$ ) and chloride ( $\text{Cl}^-$ ). Unlike soil and internal waters, most seawater contains soluble salts. The chief ions present in seawater are  $\text{Na}^+$  and  $\text{Cl}^-$ , and the level of  $\text{SO}_4^{2-}$  is also high.

Cations (g/L)	Anions (g/L)
$\text{Na}^+$ 11.04	$\text{Cl}^-$ 19.88
$\text{Mg}^{2+}$ 1.30	$\text{SO}_4^{2-}$ 2.74
$\text{Ca}^{2+}$ 0.42	$\text{HCO}_3^-$ 0.18
$\text{K}^+$ 0.39	$\text{Br}^-$ 0.07
$\text{Sr}^+$ 0.008	$\text{F}^-$ 0.015

Table 1. The concentration of the most prevalent ions in seawater

Salinity, i.e. the total mass of dissolved salt, is not the same in all marine environments and differs based on geographic area. The average salinity of global seas is 35‰, while the salinity of the Adriatic Sea is 38‰. All salts are soluble to a certain degree, but the solubility of some is negligibly small, and we refer to these salts as insoluble. Salts of relatively high solubility are: nitrates, chlorides, sulphates, bicarbonates and acetates, while those of low solubility are silicates, oxides, sulphides, phosphates and carbonates. Other factors, such as pH value, also affect solubility. Carbonates, oxides and sulphites are

Origin	Salinity (‰)
Rivers (mean world value)	0.1
Baltic Sea	<17
Black Sea	18–22
Atlantic and Pacific Oceans	32–35
Mediterranean Sea	39–47
Adriatic Sea	38
Red Sea	43–45
Dead Sea	276

Table 2. Salinity in various marine environments

more soluble at low pH levels, while silicates are more soluble at higher pH levels. Salts dissolved in seawater contribute to the formation of a corrosive environment as they act as electrolytes that accelerate the electrochemical corrosion of metals, leading to their decomposition (MEMET, 2007, 152).

Soluble salts on porous archaeological material such as ceramics and stone may cause significant damage, especially upon being brought up to the surface. Artefacts extracted from the sea must be kept submerged in water until the desalination process; otherwise the evaporation of water could lead to the crystallisation of soluble salts, increasing their volume and the fracturing of the structure of the material.

Upon extraction to the surface underwater artefacts are exposed to atmospheric influences that also contain soluble salts. Large quantities of  $\text{Na}^+$  and  $\text{Cl}^-$  can be created from seawater or salt saturated aerosol (windborne seawater). Particular attention should be given to this fact if the underwater artefact is exposed in an open area that is not protected from atmospheric influences. Salt in the air in combination with humidity and other compounds and particles in the air create electrolytes on metals that facilitate electrochemical corrosion and the deterioration of metals (SCOTT, EGGERT, 2009, 109). Soluble salts in the atmosphere are most often deposited on the surface of materials. Surface damage caused by deposits is most frequent in ceramics and stone, but other porous materials are also subject to damage caused by soluble salts (CRONYN 1990, 23). Like soluble salts, insoluble salts may form deposits on any artefact. The exposure of material to the effects of insoluble salts usually causes surface damage and changes in the colour of materials.

## OXYGEN

The presence or absence of oxygen is the chief controlling factor in the activity of organisms that cause the decomposition and deterioration of archaeological material. Oxygen is a component of many chemical reactions that directly or indirectly lead to the damaging of material. A

greater concentration of oxygen in the sea induces an increase in the corrosive potential of metal objects such as copper and iron, and materials at greater depths are often better preserved because of the lower quantity of oxygen present (MEMET, 2007, 155). Chemical bonds with oxygen are referred to as oxides, and the chemical reaction of bonding with oxygen, oxidation.

As an elementary substance oxygen is one of the chief components of air, accounting for 21 percent. It is necessary to the sustenance and development of almost all living organisms - it participates in diverse biochemical processes. The solubility of oxygen in water, i.e. the ability of water to bond oxygen, depends on the temperature. The lower the temperature of water, the more oxygen it can bind, and conversely, the higher the temperature of water, the lower its capacity to bind oxygen. The level of oxygen in water varies significantly but is greater in shallower surface strata and at depths where photosynthesising plants release oxygen or where oxygen-rich water is carried by sea currents.

## HUMIDITY AND TEMPERATURE

Absolute humidity is the quantity of water vapour in the air. The quantity of water vapour in the air depends on the temperature. Warmer air can contain more water vapour than cooler air (MUŠNJAK 2008, 133). A drop in temperature under the dew point leads to condensation in which water vapour changes from a gaseous aggregate state to a liquid. The concept of relative humidity refers to the ratio of absolute humidity in the air at a given temperature and the quantity of water vapour needed to achieve the dew point at the same temperature. Humidity and temperature have an impact on underwater artefacts from the moment they are taken from the sea and are exposed to atmospheric influences. The effect of humidity and temperature on underwater artefacts varies and depends on the type of material and the conservation condition of the object. The impact of extremes in relative humidity or elevated temperature on objects of wood or other organic materials may lead to temporary or permanent deformation of the ma-

terial. These conditions also facilitate various chemical reactions and are favourable to the development of microorganisms that lead to decomposition and the deterioration of the organic structure of materials (UNGER, SCHNIEWIND, UNGER, 2001, 23).

On metal objects a high percentage of relative humidity activates corrosion processes, especially on objects that have not undergone conservation treatment, and to a lesser extent on objects that have undergone conservation treatment. The detrimental impact of humidity on ceramic, stone and glass artefacts is most evident on artefacts that are dried and stored following extraction from the sea without having undergone the desalination procedure. An elevated percentage of relative humidity causes the dissolution and migration of soluble salts in the structure of materials. With a reduction of relative humidity, the salt re-crystallises, which causes it to expand in volume and fracture the structure of materials.

## LIGHT

There are natural and artificial sources of light. The sun is the most important natural source of light. By sunlight we mean the form of energy we refer to as electromagnetic radiation. This radiation varies in wavelength. Of the total flow of energy radiated from a source of light, the electromagnetic radiation from a wavelength of 780 to 380 nm is referred to as the visible part of the spectrum. Above and below this part of the spectrum are the infrared (IR) and ultraviolet (UV) ranges. The IR range covers the wavelengths from 1 µm to 780 nm. This thermal radiation from the sun makes life on earth possible. UV radiation from 380 to 100 nm is vital because of its biological effect, but also particularly detrimental in the UV-C range (ozone hole).

Photochemical changes to materials are caused by the quantity of light energy that the material is able to absorb. The absorption of light on a material does not always have to lead to chemical changes (SCHAEFFER, 2001, 6). Sunlight has an indirect effect on the deterioration of artefacts in an underwater environment, as it is essential

15-3 µm	3-1 µm	1 µm-750 nm	780-380 nm	380 - 280 nm	280-100 nm	100-10 nm	10 nm-100 pm	100-1 pm
Far IR	MidIR	Near IR	Visible Light	UV A/B	UV-C	Extreme/vacuum UV	Soft X-Rays	Hard X-Rays

Table 3. The electromagnetic spectrum

to the survival of fouling organisms, which have a much more detrimental effect on materials. The effects of light on underwater artefacts are more significant in a dry environment where direct exposure to UV radiation can cause detrimental changes to materials. Artificial sources of light - common light bulbs, halogen wolfram bulbs and fluorescent bulbs - also emit UV and heat radiation. To reduce their detrimental effects they must be covered with special protective films with UV filters (SCHAEFFER, 2001, 26). Damage from direct exposure to UV radiation depends on the sensitivity of individual types of material. UV radiation can cause the bleaching of the surface of an object, the weakening and fracturing of the structure and cause it to fall apart. The inorganic materials ceramic, stone, glass and metal have a low level of sensitivity to UV radiation, while pigments and organic materials such as wood, textile and leather are much more sensitive to UV radiation, and paper is very sensitive. UV radiation can also damage protective coatings such as resins and lacquers on already conserved and restored artefacts, which may activate deterioration process in the material. IR radiation on archaeological material causes it to heat up.

All sources of light cause a certain amount of heating. An increase in temperature impacts the relative humidity in the air and the percentage of humidity of the artefact. Heating caused by artificial sources of light cause drying and an elevation of temperature that accelerates the process of the decomposition of material. The recommended maximum value of light exposure for highly sensitive material such as textile, leather and paper is 50 lux. Materials with moderate sensitivity such as wood, bone, and materials with a protective coating such as resin and lacquers have a maximum recommended exposure value of 150 lux, while artefacts of me-

tal, ceramic, stone and glass, in spite of their low sensitivity to light have a maximum recommended exposure value of 300 lux.

### POLLUTED AIR

By its composition air is a mixture of gases. Its composition changes depending on geographic position and in its natural state it contains a certain percentage of water vapour. Along with the normal gases, air may also contain some other gaseous and solid matter we refer to as atmospheric contaminants. Gases such as sulphur and nitric oxides, carbon monoxide and dioxide, chlorine, hydrogen peroxide, hydrogen sulphide and others cause air pollution. Polluted air may also contain large quantities of water vapour, smoke and dust. Smoke in the air may originate from the incomplete burning of wood, natural gas and petroleum derivatives or coal. Smoke contains tar substances that can accumulate on the surfaces of objects over time, creating a sticky mass of brown or black colour, thus impairing the aesthetic aspect of the object.

There are three chief sources of contaminated air that can have a detrimental effect on archaeological objects:

- The external environment, which produces dust and atmospheric contaminants;
- The environment in a museum or depot which may be exposed to dust or contaminants created by restoration work in workshops;
- Materials used for storage or the exhibition of objects that may contain harmful chemicals.

Elements of atmospheric pollution can cause detrimental chemical reactions on almost all types of material (VAN GRIEKEN, DELALIEUX,

GYSELS, 1998, 2327). On organic material atmospheric pollution can lead to elevated acidity and the weakening of the structure of materials. On metal objects atmospheric pollution can induce detrimental corrosion processes, while on ceramic and stone objects it can lead to the staining and bleaching of surface areas and changes in the colour of the object.

## THE BIOLOGICAL CAUSES OF DAMAGE

### FOULING ORGANISMS

The biological causal agents of the decay of underwater artefacts are fouling organisms, which we can divide into micro fouling organisms and macro fouling organisms. Fouling organisms are animals and plants that are a component part of marine, river and lake biomasses. Micro fouling organisms such as bacteria and algae have a detrimental impact on materials in an underwater environment, while in dry environments, besides bacteria, moulds, fungi and lichens. Numbered among the macro fouling organisms in underwater environments are: corals (*Anthozoa*); molluscs (*Mollusca*); polychaeta (*Polychaeta*); crustaceans (*Crustacea*); echinoderms (*Echinodermata*) and fish (*Pisces*), while in dry environments they include insects and rodents. Fouling organisms inhabit almost all types of archaeological materials, with the exception, for example, of objects made of copper and bronze on which, because of their biolo-



Figure 1. Object covered by organogenic sediment (Photo: M. Mustaček)

gical toxicity, the phenomenon is less prevalent (MEMET, 2007, 164).

The appearance of a given fouling organism on archaeological artefacts depends on various factors, such as temperature and salinity values, the concentration and saturation of oxygen and the type and amount of time the material has been submerged. Fouling organisms on archaeological material causes various kinds of damage. Macroorganisms, such as molluscs, usually cause physical damage to archaeological material, in particular wood and other organic materials, while microorganisms encourage corrosion processes on metal and are the chief causal agent of the effect of biological decomposition that causes surface damage and the weakening of the structure of materials. When the life cycle of fouling organisms on colonised artefacts ends, their remains are deposited and limestone and other sedimentary rock form organogenic sediments on materials (ŠESTANOVIĆ 1997, 115). The formation of sediments on artefacts leads to the creation of a local microenvironment that protects the material from direct exposure to the environment and further accelerated decay. In these isolated environments the process of decomposition is retarded. Sedimentation is the only natural process that provides for the partial preservation of iron finds, which, if directly exposed to the activity of the sea, would completely erode and decay (SCOTT, EGGERT, 2009, 123).

### MICROORGANISMS

Microorganisms are primitive organisms very sensitive to the environment. They are also not resistant to high levels of salts and the toxic products of copper corrosion and certain organic chemicals. Some kinds of microorganisms have adapted and are resistant to extreme pH levels, desiccation and oxygen deficiency. The metabolism of microorganisms is not particularly effective and, instead of carbon dioxide, they secrete organic acids. Individual microorganisms are not visible to the naked eye, but their colonies are (CRONYN 1990, 15). The effects of these organisms on materials, known as biodegradation, are most evident in organic materials and are

part of the natural cycle of decay. The effects of the waste by-products of the metabolic processes of microorganisms such as organic acids on archaeological material may cause chemical weakening and accelerate its decay. The appearance of an artefact may also be visually deteriorated by pigment particles created by mycelium, bacteria or black sulphide created by the activity of anaerobic sulphate reducing bacteria, while the surface of an object covered in microorganisms may be unrecognisable.

## ALGAE

Algae are a broad group of simple, mostly water inhabiting, photosynthesizing organisms (ranging from unicellular to multicellular) similar to plants. Algae are able to live in neutral to weakly alkaline environments, in extremes of temperature and salinity, and in environments ranging from total darkness to sufficient light. Algae are divided into seven classes, and colour of algae varies from red to dark purple, which is the result of a mixture of various pigments. The names of individual divisions and classes of algae are derived from their colour. A common trait of all algae is photosynthesis, which produces oxygen as a by-product and supplies it to aqueous environments. In relation to the substrate they inhabit we can divide algae into two groups: epilithic algae, which grow on the surface of the substrate; and endolithic algae, which penetrate and colonise the interior of the substrate (KUMAR, KUMAR 1999, 18).



Figure 2. The algae covered barrel of a bronze cannon (Photo: M. Mustaček)

Algae can influence the deterioration of archaeological material by causing physical and chemical damage. The effect of algae on archaeological objects is usually the loss of aesthetic value. And while the direct damage to material caused by algae is not always significant, they indirectly influence the deterioration of materials by sup-

porting the growth of biological causes of corrosion such as moulds and lichens (KUMAR, KUMAR 1999, 19). Algae may also cause biodegradation. They produce various metabolites, for the most part organic acids, which have an active effect on materials causing their decay and permanent damage.

## BACTERIA

Bacteria are single-celled microorganisms, and the single largest group of life forms. They are invisible to the naked eye, propagate quickly and can form colonies of several million units in the space of a few hours. Their size ranges from one to several microns. In unfavourable conditions bacteria create special, very resistant cells - spores, which they can also use to multiply. Spores are very robust: they can endure long drought, various chemicals and both high and low temperatures (MUŠNJAK 2008, 138). Bacteria use enzymes to break down organic substances they use as food.



Figure 3. Black sediment created by the decay and decomposition of iron (Photo: M. Mustaček)

The effects of bacteria on archaeological material may lead to permanent damage caused by the degradation and decomposition of materials. When present on an artefact in greater numbers bacteria appear in the form of coloured blemishes, since many of them create particles of pigment, incrustations and black sediment. Bacteria secrete enzymes that decompose organic substrates and, like fungi, are aerobic. There is a strain of bacteria that are anaerobic and that,

unlike other organisms, do not require oxygen for respiration. They secure nourishment by the reduction of inorganic chemicals such as nitrates, carbon dioxide, manganese (IV) and iron (III). This method of respiration is inefficient and ineffective and as a result bacteria secrete organic acids instead of carbon dioxide, which means that they are able to colonise anoxic deposits. A number of these bacteria cause the destruction of organic artefacts, while some have an indirect effect on organic and inorganic materials. Noteworthy among these are anaerobic sulphate reducing bacteria (SRB) such as *Desulphovibrio*, which reduces sulphate to sulphide. The presence and activity of these bacteria indicate the danger of salt efflorescences and acid attack of the object after its drying. It can be determined by the odour of rotten eggs (hydrogen sulphide) and the blackening of deposits caused by the formation of metal sulphides (CRONYN 1990, 17).

## MOULDS

Moulds are multicellular organisms of plant origin at a higher level of development than bacteria. Moulds may be brilliantly coloured, black or white - depending on the species. They are recognisable as white, green, red or black blemishes of circular form, and from the odour of mould. Active mould appears dirty or slimy. Dormant mould is dry, like talc. Moulds are unable to assimilate carbon from the air and live as parasites on other organisms. Moulds reproduce through spores or by the fragmentation of mycelium. Mould spores are created in favourable conditions in four to seven days. Mould spores are light and, like bacteria, they can remain airborne over great distances. In very unfavourable conditions moulds may lay dormant for years, and are very quickly activated in favourable conditions. Mould mycelium die off quickly in unfavourable conditions, while their spores survive. Special disinfection compounds are required to destroy them (MUŠNJAK 2008, 139). Moulds are able to colonise various types of material and may cause damage not only to wooden surfaces, but also to paper, glue, leather, textile and other materials, especially in the presence of relatively high levels of moisture

and heat, while some species may also have a detrimental effect on health (UNGER, SCHNIEWIND, UNGER 2001, 108).

## FUNGI

Fungi are numbered among the most detrimental of organisms responsible for the biodegradation of organic and inorganic materials. The metabolic diversity of this group of microorganisms increases their ability to colonise various types of substrate (wood, glass, stone). Fungi are formed of a vegetative filamentous body of mycelium, composed of series of identical cells called hyphae, and a reproductive system called the fruiting body. Spores develop in the fruiting body that, in ideal conditions for growth, create new hyphae cells. There are certain physical, chemical and biological conditions necessary for the growth of fungi such as temperature, moisture, light, the presence of oxygen, the pH value of the substrate, and the type of material, which have different effects on the development of certain types of fungi.

The fungi that cause the decay of organic material can be divided into two groups: fungi that cause staining (stain fungi) and fungi that cause decomposition/rotting (rot fungi). Staining fungi do not directly degrade cell walls and do not cause a significant reduction in their sturdiness, while rot-causing fungi attack the primary components of the material's cell wall, causing changes in chemical, mechanical and physical traits (LIPANOVIĆ 2009, 2). A high percentage of humidity and an environment saturated with water are the optimal conditions for the appearance of soft rot fungi, which attack the secondary components of cell walls and completely destroy them (ARROYO, 2009, 42).

## LICHENS

Lichens are multicellular composite organisms that are formed by the symbiotic association of two plant organisms - fungi and algae. This symbiotic relationship allows them to survive in extremely dry and wet environments. They differ greatly in colour and shape, and their appearance depends for the most part on the structure of

the fungi. Lichens are the best known of the epiphyte plants. As individual organisms they are aerobic and secrete a significant quantity of organic acids (CRONYN 1990, 16). Their stratified structure guarantees lichens a long life span even after years of drought. A small number of lichens live in waters and seas. Lichens are highly sensitive to air contaminants, especially to industrial pollution high in carbon dioxide. Lichens reproduce by producing spores. They are released into the air to find the right algae in order to establish a new symbiosis.

Lichens can affect archaeological heritage objects both physically and chemically. Physical damage occurs by the penetration of hyphae into pores and the expansion and contraction of the thallus resulting from changes in moisture, in the process of which there is damage to the surface of the object causing the formation of pits and holes (KUMAR, KUMAR 1999, 22). Lichens cause chemical damage to archaeological material by secreting organic acids. They have a corrosive effect on the substrate created by the release of metabolite acids. Metabolite acids cause chemical damage to the material by breaking down and disintegrating the substrate.

### MACROORGANISMS

Macroorganisms such as animals and plants require oxygen for respiration and as such cannot function in an environment lacking oxygen. In order to survive all organisms require water in some degree. Organisms are not resistant to desiccation, extreme cold or heat. Noteworthy among the living communities in the seas are corals (*Anthozoa*); molluscs (*Mollusca*); bristle worms (*Polychaeta*); crustaceans (*Crustacea*); echinoderms (*Echinodermata*) and fish (*Pisces*). These macroorganisms most often cause physical damage to archaeological material. Some molluscs, for example, can bore canals into wood and stone, causing stains, fading and the porosity of the material. Major damage to wooden objects in the sea is caused by the shipworm (*Teredo navalis*). It belongs to a group of molluscs whose development depends on the salinity and temperature of the water, such that a warm climate favours their development, while

cooler temperatures slow their activity. As they use wood as a source of food, they bore canals into it, in which calcareous deposit subsequently form (UNGER, SCHNIEWIND, UNGER 2001, 134). The actual boring of canals into wood weakens its structure, leading to the cracking and fracturing of wooden structures. Besides as a source of food organic and other archaeological materials may also provide a habitat for some organisms.

### MECHANICAL CAUSES OF DAMAGE

Mechanical damage to underwater archaeological heritage is caused by human and natural factors. The leading human factors affecting the degradation of sites are: the non-professional extraction and handling of objects, the looting of archaeological sites, find disturbance by divers, fishing activity (mussels, fishing nets), the anchoring of vessels, underwater construction work, waste dumping at sites and other factors. Numerous natural factors also cause damage to underwater artefacts, such as sea currents, which, for example, carry sand and cause its abrasive action against archaeological material leading to extensive damage to the surface of the artefact, waves, various natural catastrophes and the accumulation of sediment.

Archaeological material, once deposited on the seafloor, riverbed of the bottom of a lake, is exposed to the inevitable accumulation of sediment. Sediments that form over time subject artefacts to significant pressure, which causes the cracking and fracturing of the archaeological material. The action of a strong sea current shifts larger and heavier element of archaeological material and sediment, laying them on more fragile objects, which also leads to their cracking and fracturing. The speed of the sedimentation varies significantly in individual environments and ranges from 1mm to several centimetres per year. Sediments are very diverse and the vast majority of seabed, riverbeds and lakebeds are covered in them. The bottom contains the remains of land erosion, mussels, the organic remains of organisms and salts that have precipitated from seawater. The sedimentary cycle includes

the erosion of rock, the transfer of substances and the deposition of particles. Most of the material that is deposited in the sea comes by way of rivers. These are either particles or dissolved.

There are three basic types of sediment in the sea:

- Lithogenous – particles that are transported to the sea by river, wind and ice and are created by the weathering of all types of rock on land.
- Hydrogenous – are created by precipitation directly from a solution. Marine evaporites are created by deposition for the most part in semi-closed basins such as coastal lagoons. Halite accounts for the majority of precipitated material.
- Biogenous – organisms create organogens. Biogenous sediments consist of the skeletal remains of organisms and of organic substances. The majority of the calcium carbonate that is deposited in the sea is of biogenous origin.

applied to the study of the mechanisms of deterioration on various cultural heritage objects. Physico - chemical and biological factors such as humidity, heat, light, bacteria, organisms and algae are causes of deterioration that have a direct or indirect effect on materials, leading to detrimental changes. The speed at which a material achieves a state of equilibrium with its environment is determined by the characteristics of the microclimatic environment. Climate is for the most part determined by temperature and the relative humidity (RH) of air. Materials gradually change under the influence of environmental factors such as oxygen level, moisture and light. Organic materials such as bone, paper, textile and wood are subject, for example, to the splitting or the polymerisation of molecules and oxidation. These chemical processes are accelerated by elevated temperatures - the higher the temperature, the quicker the aging process. A high percentage of humidity accompanied by elevated temperature favours the development and growth of most biological destructive factors. With an understanding of the mechanisms of deterioration and timely action taken to retard and prevent the further development of detrimental processes on objects of archaeological heritage, we are making great strides with regard to safeguarding their physical integrity and long - term preservation.



Figure 4. A site covered by sediments (Photo: HRZ archives)

### CONCLUSION

An understanding of the mechanisms of the deterioration of materials, combined with an understanding of the factors that cause detrimental changes, is of exceptional importance. A growing number of analytical techniques have become available in recent decades that can be

## IV. The Conservation and Restoration of Ceramics and Pottery

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### INTRODUCTION

Ceramic finds are the most frequent at underwater archaeological sites. The discovery of ceramics profoundly changed the way people lived. Its permeability and durability provided for the preservation, storage and transport of goods, and changed human nutritional habits. The principles of ceramic manufacture have remained largely the same over time. It is based on the modelling of earth, i.e. clay, followed by its firing at high temperature until a firm mass is achieved. Manufacturing techniques have been perfected over time. It all started with the simple manual shaping of a piece of clay, quickly followed by the invention of the manual potter's wheel, the fast potter's wheel, modelling by impressing the clay or pouring liquid clay into moulds, the use of presses and so forth.

Unfired objects can be coated with white liquid clay and then engraved and/or decorated with various engobes or mineral pigments and then fired. The glazes were applied and then fired for the second time, which made the objects impermeable to water.

Clays are formed by the alteration of feldspathic rocks under the influence of atmospheric agents: rain, rivers, winds and the release of gases from the Earth's crust. Chemical reactions turn feldspathic rock into kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). If this process occurs within the rock itself, it is then possible to extract pure kaolinite from the rock. Crushing this into a fine white powder produces kaolin that, with quartz and calcite, is a basic component of porcelain. If this process occurs on the surface of rocks, however, kaolinite is mixed with organic materials, creating what are known as white clays. The drainage of these materials and their accumulation at other sites create common clays, containing many impurities.

After firing most take on a reddish colour as a result of the presence of a large quantity of iron oxides. The chief characteristic of kaolin and clay is its plasticity or ability to retain deformation in spite of the absence of the force that caused it.

Different substances are added to the clay primarily to give the paste greater resistance, to support temperature changes during firing, to accelerate drying, to decrease the retraction that occurs during drying, to reduce the plasticity of the paste and to lower the required firing temperature. These substances include sand, quartz, plagioclase, potassium feldspar, rock fragments, powdered fragments of ceramics (grog), straw, feathers, shale, granulate slags or crushed shells (LOPEZ - ARCE 2013, 2031-2042). It is these particles that are visible in the structure – unique to every piece of pottery – and the type of clay used that are one of the means of differentiating ceramics. The porosity of ceramics depends on the extent to which the minerals have been fused, the size of the particles of the cited tempers, and the quantity of organic materials that will burn away at high temperatures leaving cavities in their place. At lower firing temperatures (800°C) the individual mineral temper grains are easily distinguishable from the clay matrix; at higher firing temperatures (1000-1050°C) the sintering process produces an increase in the interconnection among these grains and the matrix causing the porosity to decrease (LOPEZ - ARCE 2013, 2031-2042).

We can divide pottery into two major groups based on the firing temperature:

- Ceramics fired at lower temperatures (fine and coarse unglazed pottery, glazed pottery, engobed pottery, majolica and other pottery fired at up to 1000 – 1200°C)
- Ceramics fired at higher temperatures (ceramics fired at above 1000 – 1400°C, fire clay; soft - paste, bone china, hard -

paste porcelain, stoneware)

In the first group we can include unglazed pottery dating from prehistory onwards, fired on open bonfires or in primitive kilns that achieved temperatures ranging from 500 to a maximum of 700°C, Roman period, medieval and all other glazed and unglazed ceramics fired in closed kilns that achieved the appropriate temperature for firing ceramics of about 800 to 950°C (e.g. terra sigillata at 900 - 950°C in an oxidation ambient to achieve the bright red colour of the slip), and post medieval and other ceramics fired at high temperatures that do not exceed 1000 - 1200°C. These may be objects with various applied coatings or without, produced from common red or white clay or some other common clay.

We find examples of the second group in hard porcelain already in use during the early medieval period (China, Korea, Japan), the soft-paste and bone china in use since the 18<sup>th</sup> century (Europe), and the stoneware and fire clay that are fired at very high temperatures ranging from 1000 - 1400°C.

### CERAMIC DETERIORATION

Degradation and alteration are natural phenomena in the lifetime of every material. It begins while the material is still in its original form, and continues in the forms humans have shaped it into. The process is constant and unstoppable, and restorers can undertake a series of operations on the object only in an attempt to slow the process. Alteration refers to the aging of objects accompanied by change that does not have a direct effect on the preservation of an object and that does not impair its readability. This category of change includes alterations of colour, the formation of a superficial patina on objects and so forth. Degradation occurs as the advanced process of aging accompanied by a loss of the object's readability.

The degradation of materials occurs as a result of internal and external factors. The internal factors are the characteristics of the material, of

which the greatest roles are played by porosity and capillarity. The external factors of degradation may be divided into two major groups: natural and human. Marine environments are characterised by physical (abrasion, transport, deposition), chemical (dissolution - precipitation, oxidation - reduction) and biological (bacterial or benthic organism growth) processes (LOPEZ - ARCE 2013, 2031-2042).

The degradation of materials is usually accelerated or activated when we remove the object from the environment in which it was deposited and in which it had achieved a state of equilibrium, even if imperfect, and we place it in another environment. The most evident example of this is the extraction of a find from an underwater environment in which it was conserved and quite stable for thousands of years, causing it to dry out in the air, leading to cracking and fracturing. We need to help these objects gradually adapt to the new conditions. The same happens with objects deposited underground. Upon their extraction from the site the objects are exposed to new conditions such light, changes in temperature, changes in the level of humidity and contact with living organisms.

The chief natural factor leading to degradation is water, which acts both as a physical and a chemical factor, and is also a requisite for the presence of biological factors. The physically destructive activity of water in the event of the freezing of water in the pores of material is significant. The ice crystals formed have a volume much greater than that of water, which causes stress within the pore and leads to the cracking of the walls of the pore. The phenomenon of repeated freeze - thaw cycles lead to a loss in the readability of the surface and finally to the complete destruction of an object. Water is also a medium for soluble salts - the most frequent cause for the degradation of porous materials extracted from the sea or environments close to the sea. Seawater contains different types of salts, most prominently sodium, magnesium, calcium, potassium and strontium cations and chloride, sulphate, bromide and bicarbonate anions (LOPEZ - ARCE 2013, 2031-2042).

Over time objects submerged in seawater achieve equilibrium with the surrounding level of pressure, in the process of which air is released from pores and is replaced by salt water. At the moment of the object's extraction from the sea and of the subsequent evaporation of water, the solution in the object becomes concentrated. After a time, when the solution becomes saturated, the process of salt crystallisation begins. The formation of salt crystals has the same effect as the process of forming ice crystals when water freezes. Their growth during formation causes stress within the structure of the object and the breaking of bonds within the material itself. Slower evaporation of moisture from materials causes salt crystals to break out to the surface - this is referred to as efflorescence. This phenomenon is best observed when we remove a non-desalinated object from a moist environment and allow it to dry slowly in a cold place. We can observe the formation of small white crystals on the surface similar to fine hairs. This form of salt crystallisation causes crumbling and sloughing from the object's surface. The speedier evaporation of moisture causes crystals to form inside the object - this is referred to as subflorescence. The result is the cracking and fracturing of the object. The phenomenon of the crystallisation of soluble salts is closely linked with the ambient temperature, which determines the relative humidity and the speed of water evaporation.

The composition and texture achieved with the firing temperature is a key factor in crystallization decay and hence on the durability of these artefacts. Ceramics fired at higher temperature have lower surface area and less connected porosity, which entails a lower absorption of soluble salts. Those fired at lower temperature display lower total porosity but higher surface area rendering them more prone to decay and less durable against weather. These materials usually have more soluble salts and gypsum subflorescence (LOPEZ - ARCE 2013, 2031-2042).

Ceramic archaeological finds from submarine environments are exposed to the accumulation of organic and calcareous deposits (insoluble salts), and the biochemical and physical effects

of living marine organisms. Algae has a biochemical effect as its secretions dissolve the substrate, while marine organisms such as snails, mussels, Cnidaria and polychaetous worms act mechanically upon ceramics, boring into them and scraping their surfaces (JAKŠIĆ, BIZJAK 2010, 231-245). During their life cycles Crambe crambe sponges, encrusting sponges and the Cliona sponge erode the surface of objects with a dense network of tiny holes visible after their removal. These surfaces are then fertile ground for colonisation by lithophagous types of mussels such as the date mussel (*Litophaga litophaga*) and Gastrochaena dubia. We also find the calcareous shells of polychaetous worms on the surface of ceramic objects. Bristle worms belong to the genus Polychaeta and form calcareous shells in the form of a tube around their body. They are able to penetrate deep into porous objects using their jaws or chemically with abrasion (JAKŠIĆ, BIZJAK 2010, 231-245). Accumulations are also created by various types of *Cnidaria* (the best known of which are various corals) and by green, brown and red algae.

We should also note the abrasive effect of the sea, which moves particles from the sea bottom (sand, pebbles) and in this fashion "sandblasts" and wears an object. Objects on the surface of the seabed are more exposed to abrasive action than those found under the surface. This abrasion leads to the rounding of the seams along which fragmentation has occurred and the rounding of edges, and finally to the complete loss of the object.

Objects buried underground are exposed to the circulation of waterborne minerals, causing the accumulation of deposits on objects, most often calcareous, and possibly containing an admixture of sand and soil. Siliceous deposits may form, while the iron and manganese present in soil move to the surface and into porosities of the object, where they form brown blemishes (CAVARI 2007, 66).

The human effects on ceramics and stone objects are also not negligible. These objects are worn while in use, but are particularly subject to the consequences of indirect and unintentional

human influences. Human development is accompanied by an increase in environmental pollution, which results in the formation of acid rains, the accumulation of soot and other impurities on cultural property, the pollution of seas by waste waters and other effects. Another frequent source of problems are the unprofessional and obsolete previous attempts at restoration, which have not only failed to slow the process of deterioration, but have in fact often accelerated it.

## THE CONSERVATION AND RESTORATION OF CERAMICS

Conservation - restoration work on ceramic objects can be divided into phases:

1. Initial documentation, preliminary analysis
2. Cleaning the object
3. Desalination
4. Consolidation
5. Bonding fragments
6. Integration
7. Nuancing/retouching
8. Drafting documentation after conducting restoration work

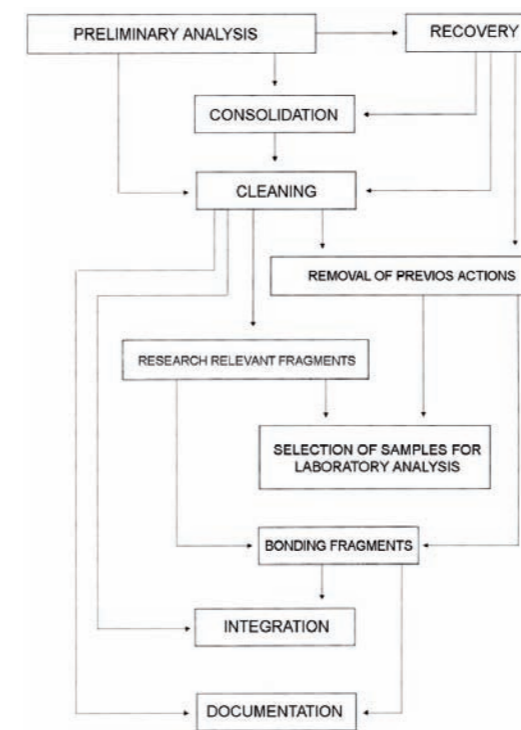


Figure 1. The phases of conservation - restoration work (RAVANELLI, GUIDOTTI 2004, 139)

In Figure 1. we can see that the sequence of conservation - restoration work does not always have to be the same. This depends on the state of the object's preservation, the environment it originates from and the type and quantity of depositions. The order of conservation - restoration interventions may be changed and individual steps may be skipped. In the case, for example, of a well - preserved vessel of firm structure, but in a fragmented state, we can immediately undertake the gluing of fragments without the prior consolidation of the material. In some other cases we will proceed in the opposite fashion, and will undertake all necessary measures to preserve and strengthen the structure of the object while any one of the following procedures may not be required.

Conservation - restoration work also depends on the final location and conditions in which the object is to be stored (we cannot proceed from the same starting point if the object is to be kept in the open, such as at archaeological parks, or in a closed and controlled environment).

Any intervention will leave its trace and cause stress to the object. It is, therefore, important to note that all interventions on the object must be minimal to ensure that our actions do not cause even greater damage to the object and to preserve the historic value of the object (the presence, for example, of marine organism accumulations on the object bear witness to the site at which the object was found, while organic and other remains tell of the object's use).

### 1. INITIAL DOCUMENTATION, PRELIMINARY ANALYSIS

Documentation is the beginning and end of restoration work. The state of the object as it was found *in situ* or upon arrival at the laboratory must be documented, as must all of the phases of restoration work and the final appearance post - restoration. We document every phenomenon visible on the object, fractures, salt efflorescence, deformations, alterations to colour, loss of surface material, deposits accumulated on the surface and all other forms of degradation and alteration, and observations concerning

the object regarding decorations, reliefs and the like. As a preliminary phase documentation has an investigative role, and helps us discover the problems related to the conservation of the object and to find solutions. It may be photographic, written and drawn. Laboratory analysis and radiographic imaging of the object is also undertaken for documentation purposes and to reveal problem areas. As an example we can cite the successful discovery of iron reinforcements within ceramic sculptures using radiographic imaging.

## 2. CLEANING

Cleaning is one of the most delicate phases in conservation - restoration work, followed by consolidation, because both are for the most part irreversible, and as such require a good knowledge and differentiation of foreign materials, i.e. accumulations and stains, from what are integral parts of the object that require preservation, such as patina, irregularities in manufacture and traces of use which should be left untouched on the object.

Cleaning is done mechanically, mechano-chemically, and chemically. We choose the means based on the type of deposit accumulation, the state of conservation and the material of which the object is made. In objects extracted from the sea we differentiate the calcareous and siliceous deposits of marine organisms, the deposits and infiltration of iron and copper oxides and organic deposits (algae, sponges, bacteria).

It is recommended that any cleaning should be-



Figure 2. Ceramic jug fouled by algae and the encrustations of marine organisms (Photo: M. Ćurković)

gin with most delicate techniques, such as brush dusting, cleaning with pads soaked in the mildest solutions such as distilled water or a mixture of distilled water and alcohol and/or acetone. If these techniques do not help in removing deposits and if the conservation status of a find allows it, we can apply slightly more aggressive cleaning techniques – applying them in a controlled manner and localised on the surface of the deposit. We must bear in mind that chemical cleaning, although very effective and faster than mechanic cleaning, has some very significant drawbacks – the process is not always easy to control; the transport of dirty particles in pores is possible and it can leave soluble salts in the interior of ceramics.

### Removing calcareous and siliceous deposits

Calcareous deposits are manifested in the form of the shells of mussels, the skeletal remains of corals, and as white spongy clusters that may contain admixtures of sand and soil materials in their structure. They are often closely merged to the surface and are very hard. They can occur underground by the deposition of calcium carbonate transported by water or in an underwater environment as the result of the life cycle of marine organisms inhabiting the walls of objects. We observe siliceous deposits as low, smooth whitish - transparent accumulations. They are very difficult to remove as they are practically fused with the surface of the object. They are removed mechanically as siliceous bonds are very resistant to chemicals and do not react to mild acids and bases.

As the first choice, the mechanical removal of deposits is always suggested, whenever possible, from objects extracted from the sea while they are still wet and while the deposits have not become entirely petrified in contact with the air. Following minimal intervention we always start with the most delicate techniques, soft brushes, going gradually if necessary and possibly with more aggressive techniques such as surgical scalpels, ultrasonic chisels and pins, pneumatic chisels, laser, microdrills, micro sandblasting, pressurizer water jets and by other means.



Figure 3. A ceramic figurine covered by calcareous deposits and deposits of marine organisms (Photo: M. Ćurković)

When calcareous deposits cannot be removed by mechanical means we are compelled to use chemical means. Cleaning with the use of chemical compounds must be strictly controlled, and mild substances must be used that cannot damage the physical and chemical structure of the object.

Encrustations of calcium carbonate or calcium sulphate on ceramic material may be treated with EDTA disodium (acid) or tetrasodium (basic) salt. A solution of EDTA in deionised or distilled water is a sequestering or chelating agent: complexes are formed with some metallic ions ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Cu}^{++}$  and  $\text{Fe}^{++}$ ) making the

encrustations soluble. The sequestering agent is used to remove insoluble salt deposits, concretions and metal stains by converting the metal into a soluble form that can be rinsed away (PRUNAS, 2012). A solution of tetrasodium EDTA salt (pH 11.5) works best for removing calcareous encrustations, which are more soluble in a basic environment (HAMILTON, 1999). It can be applied by pads soaked in a 10 to 15% solution of tetrasodium EDTA salt in distilled water, and then mechanically removed. After the chemical cleaning procedure the object must be thoroughly rinsed in distilled water to achieve a neutral pH level. For the same objective we can also use ionic (cationic/anionic) exchange resins (AMBERLITE IR 120 H, AMBERLITE 4400 OH). We use them by mixing the resin in the form of powder with demineralized/distilled water and then applying it using a wooden or plastic stick (it must not be of metal) on a layer of Japanese paper, which protects the ceramic from direct contact with chemical compounds. Their advantage is that they do not penetrate into the material's porosity and so do not affect the artefact. This property is at the same time a disadvantage when we need to remove gypsum or other salts from a material's deep porosity. They



Figure 4. A ceramic amphora on which we see the traces of an iron object that had rested against it in the form of iron oxides (Photo: M. Ćurković)

do not have an effect on thick encrustations since they react only with the surface of the encrustation (PRUNAS, 2012).

### Removing iron and copper oxides

Iron and copper oxide stains occur when an oxidised metal object is located near or in contact with a ceramic or stone object and metal oxide particles pass to the structure of the stone or ceramic. Iron and copper oxides are formed by the degradation of metals caused by the combined action of water and air, sometimes aided by atmospheric pollution. Oxides penetrate deep into the pores of ceramic materials and create reddish - brown to black stains in the case of iron oxide, and blue - green stains in the case of copper oxides. We often find iron and copper oxide stains on objects extracted from the sea. They can be cleaned with cotton pads, paper pulp pads or absorbent clays (Sepiolite) soaked with distilled water. A solution of disodium EDTA salt in distilled water is more effective, being the most efficient in removing iron and copper oxide stains, as they are more soluble in an acid environment. We use a 15 to 20% solution in distilled water on ceramics to remove stains, applied in the form of soaked cotton, paper pulp pads or absorbent clays (Sepiolite). When applying soaked paper pulp or absorbent clays it is recommended that a layer of Japanese paper be applied to the object followed by the pulp/clay to prevent the penetration of the material into



Figure 5. A ceramic jug with orange stains caused by the infiltration of iron oxides (Photo: M. Ćurković)

porosities. After the use of disodium EDTA salt we need to liberally rinse the object in distilled water to achieve a neutral pH level (pH 7).

Iron oxides can be removed from objects by submerging them in a 10 to 25% solution of hydrogen peroxide. The amount of time required to remove a stain varies from a few seconds to several hours. Rinsing is not required after the use of hydrogen peroxide. We must be aware that bubbles produced by the reaction of hydrogen peroxide with the stains can detach



Figure 6. Large Iznik plate covered with iron oxides before and after conservation - restoration treatment (Photo: M. Ćurković)

the glaze or damage the surface of the ceramic if it is not really well preserved and sound.

### Removing organic deposits

Organic deposits are created during the decomposition of living organisms or by the sedimentation of organic substances. Larger deposits are removed mechanically, while infiltrated deposits can be removed by submerging the object in a 10 to 25% solution of hydrogen peroxide. Smaller deposits can be removed by applying a pad soaked in a 10 to 25% solution of hydrogen peroxide over affected areas. Washing the object in a 5% solution of tensioactive hygienic compound (C 2000) in distilled water with brushing is recommended for the removal of carbonaceous, fat and oily substances and proteic materials. The object can be cleaned with a tensioactive concentrated preservative (New Des) based on quaternary ammonium salts, which has an effect on microorganisms and biological patina. It is used as a solution of 5% preservative in distilled water. It does not need rinsing in tap water after the treatment.

Enzymes (amylase, lipase or a mix of enzymes) may be used on fats, carbohydrates and proteins to enable them to be washed away.

### 3. DESALINIZATION

We have already touched upon the problem of soluble salts and moisture in porous materials in previous chapters, in this case affecting ceramics and stone. Soluble salts are most often present in objects extracted from the sea, but we also find them in objects that were found in the open or underground in seaboard areas. They are removed by the desalination process. Desalination is defined as the maximum possible reduction of the salt content of a material effected through its extraction. Extraction is undertaken to achieve three principal objectives: minimise the deterioration of the material caused by the process of crystallisation/dissolution of soluble salts, prevent future deterioration and avoid the alteration of subsequent restoration procedures such as consolidation or integration (ZORNOZA - INDART, 2009, 2031-2042).



Figure 7. The fracturing of ceramic caused by the presence of soluble salts (Photo: M. Ćurković)

The desalination of an artefact from a marine environment is most efficiently carried out by submerging the object in a bath of clean water that is periodically changed. Tap water is used in the initial phases of desalination, followed by distilled water in subsequent baths. It is important to proceed gradually in order to avoid the overly rapid release of salts, which could cause additional damage to the object. The conductivity of the water is measured before and after every change of water with a conductivity meter and/or potentiometric titration as an indicator of the quantity of salts that have been secreted. When the quantity of salts (conductivity) has been reduced to a minimum constant value the process of desalination can be completed, i.e. the object can be taken out of the bath and allowed to dry in a shaded location. Care should be taken that the object is not exposed to significant oscillations in temperature during drying.

There are a number of methods of desalination by soaking:

- Desalination in closed baths with frequent changes of water and measurements.
- Desalination in baths with pumps that improve water circulation. This prevents the

occurrence of salty pockets in hard to reach places under and inside the object and thereby facilitates and accelerates the process of salt secretion. Water conductivity measuring is carried out at every change of water.

- Desalination in flowing water baths. This is the most effective, but also the most expensive procedure. The large quantities of tap and distilled water used presents a problem. Conductivity measurements are made during the entire process.

In the case of low - fired or extremely large objects it may be preferable to undertake desalination using packs. Packs of paper pulp, Sepilote or Laponite RD soaked with distilled water are used to extract soluble salt from pores. Their effect is much slower than the soaking methods as less water is employed.



Figure 8. Seeking the appropriate fragments (Photo: M. Ćurković)

#### 4. CONSOLIDATION

The consolidation of materials is carried out only if necessary, i.e. when the surface and structure of an object are damaged, powdery and frangible or in the case of glaze falling off a ceramic object. Consolidation consists of the impregnation of material that has lost its structural soundness using liquid solutions that, once they have penetrated into the structure of the object, solidify, thereby strengthening the walls of the pores. The optimum protective agent should retard or stop the absorption of water into the material without creating a barrier that would prevent the exchange of gases between the in-

terior and the outer surface of the material. The choice of consolidant is based on its penetration characteristics, permeability to water vapour, the final appearance it imparts and the heightened mechanical durability it imparts to the material after treatment (BORGIOLO 2002, 8).

The consolidant should always penetrate as deep as possible into the pores of the material in order to avoid creating a belt of discontinuity between treated and untreated sections. The existence of a discontinuity belt causes stress between the two sections, and leads to structural damage. A very diluted solution with small molecules (ethyl silicate is noteworthy in this respect) is used with the aim of deeper penetration. Objects with greater porosity can be impregnated with more viscous solutions in very low concentrations.

The optimum consolidation agent should be reversible in solvents enabling easy repeated interventions on the object if they become necessary in the future. Solutions and emulsions of organic and inorganic compounds are used for the consolidation of materials: acrylic resins and micro emulsions, polyvinyl acetates, ethyl silicate and others. They are applied in various percentages by immersion, spraying, coating and under a vacuum.

Acrylic resins – Paraloid B72 is a 100% acrylic resin based on ethyl methacrylate with excellent properties in terms of hardness, brightness and adhesion to a substrate. Paraloid B72 is soluble in ketones, esters, aromatic and chlorinated hydrocarbons, and can be applied in various percentages by immersion, spraying, coating and under a vacuum.

Acrylic emulsions – Acril 33 (ex Primal) is a 100% pure acrylic resin in aqueous dispersion characterized by excellent resistance to atmospheric agents and chemical stability. ACRIL ME is a micro acrylic emulsion characterized by the reduced size of its particles (around 50 microns). This causes a low viscosity and a greater capacity of penetration into porous substrata than normal acrylic emulsions. Both can be ap-

plied on wet artefacts, as they are aqueous dispersions. They can be applied in various percentages by immersion, spraying, coating and under a vacuum.

Polyvinyl acetates – are swollen by water, becoming opaque white but reverting to a clear film on drying. Of all the polymers available for conservators, PVAC has been shown to be one of the most stable to light ageing (HORIE, 1987). Mowilith 50 can be used both as a consolidant and as glue if prepared in different percentages. Mowilith 50 is readily soluble in many solvents such as acetone, esters, ketones, aromatic hydrocarbons and the lower alcohols (the latter require the addition of a low level of water as a co-solvent). After application it may slightly darken the original colour of the ceramic. It can be applied in various percentages by immersion, spraying, coating and under a vacuum.

ESTEL 1000 is a ready - to - use consolidant based on ethyl silicate and polysiloxane oligomers in white spirit D40 solution. It can be applied by immersion, brushing or spraying until saturation is achieved. The curing of the consolidant is completed after about four weeks at an ambient temperature of 20°C and a relative humidity of 40-50%.



Figure 9. The process of bonding fragments (M. Ćurković)

#### 5. BONDING

Objects are often found in a fragmented state. Fragments are bonded to achieve the stability and integrity of the object, which will allow a normal observer or scientist to read and understand

the object as a single logical entity.

The phase of preliminary bonding in which we attempt to locate the exact position of every fragment involves joining the fragments with paper adhesive tape prior to final gluing. Sensitive surfaces, such as glazing and painted decorations should be specially protected to avoid breaking off and "tearing" the surface with paper adhesive tape. Permanent bonding is performed after all fragments have been precisely located.

Reversible adhesives that solidify by the evaporation of the solvents in which they are dissolved and that can be dissolved again are used for bonding. Stronger glues with greater adhesive strength should be used when gluing fragments of large ceramic objects. In these cases we are compelled to use non-reversible two-component epoxies of exceptional firmness and great adhesive strength. Epoxies can be used in the restoration of porcelain for gluing and as filling material for integrations.

Mecosan L-TR is a solvent based artificial resin adhesive. Adherences carried out with Mecosan L-TR are resistant to water, oils, grease, gasoline and alcohol. After drying it shows a translucent adhesive film.

Archaeocoll is a special adhesive for archaeological ceramics and other porous materials. It consists of pure cellulose nitrate. Its speciality is the total absence of any softening agents, so a maximum of aging stability is obtained. The volatile solvents (ethyl acetate and acetone) are non - toxic. Objects to be joined must be dry and dust free. The adhesive can be removed any time by solvents such as acetone, ethyl acetate or propylene glycolmethylester.

Mowital B 60 HH is a vinyl butyral polymer chiefly used in archaeological restoration for bonding and consolidating ceramics. Mowital B 60HH answers very well to the following properties: reversibility, resistance to ageing, transparency, setting rapidity and minimum shrinkage. It is diluted in alcohol with percentages varying according to use and is reversible in alcohol and acetone.



Figure 10. Gluing ceramics (Photo: M. Ćurković)

Polyvinyl acetate – PVA – K 40 and K60 is a thermoplastic resin based on polyvinyl acetate homopolymers soluble in alcohols, esters, ketones, toluene and chlorinated hydrocarbons, and is particularly suitable for heat - sizing/gluing of archaeological finds and ceramics.

Paraloid B 72 and Mowilith can also be used as glue when dissolved with acetone in a higher percentage.

Cyanoacrylate glues (Supper Attack, Super Bond and others) are used for immediate and only temporary bonding because they are brittle and do not have a long lifetime.

Epoxy resins (Araldite 2020, HXTAL NYL-1, EPO 121 and others) have the quality of great adhesion and strength but are difficult to reverse, which makes them a second choice in conservation. We often use them for gluing porcelain and glass objects because of the similar physical characteristics they obtain after the curing process and refinishing (hard and shiny surface). Bonding porcelain objects is done in the same manner as described for glass (pages 43-44).

## 6. INTEGRATION

After the gluing procedure fragmented objects often lack material/fragments lost while deposi-

ted at the site (underwater or underground) or as a result of unskilful handling and extraction from the site. Intervention on an object is required when the stability and readability, i.e. its physical and aesthetic integrity, have been compromised. Objects are reconstructed only when all of the elements required for reconstruction are available. Integrations can be made directly on the object or indirectly, fitting the integrated part in the original after it's refinished. The direct method is more invasive than the indirect method as there is a greater possibility of damaging the object during the process of integration. In the indirect method a cast is made in order to replace the missing section. After the integrated part has been treated it is inserted into the original part. This method is less invasive to the original object but it takes more time and several attempts are required to effect the successful insertion of the integrated part into the original one. Integrations are made from materials that should, by their physical characteristics and appearance, be as similar as possible to the original and be chemically stable. When integrating ceramics we can use different materials: different type of plasters (dental, alabaster), cellulose strengthened binders (polyfilla), wax mixtures such as integrant I 76, synthetic clays (Glinamol, Das) or others.

Dental plaster is a natural plaster with all-purpose possibilities in modelling techniques,



Figure 11. Fabricating an integration on a potter's wheel (Photo: M. Mustaček)

excellent hardness and fidelity of detail reproductions. It has a low expansion ratio when hardening (0.05%). Alabaster plaster is a natural plaster with excellent features, used to make moulds and, generally for artistic work (expansion: 0.15%). They are both good integrants in restoration because of the minimal expansion ratio and physical appearance and characteristics similar to ceramic. Ceramic fragments can be protected from eventual salt release from the plaster by coating/sealing the joints with a consolidant applied by brush. The external walls of the ceramic can be protected by liquid latex, which can be peeled away after integration is finished. Moulds of clay, plasticine, wax leaves, adhesive tape, silicon rubber putties and pastes, and various other materials are made as a support to integration. Silicone moulds are used to make casts for more elaborate decorations. When a large part of a (ceramic) vessel is missing, integrations may be made of plaster on a potter's wheel, modelled with the aid of the internal and external casts of the object. Plasters can be pigmented by adding natural pigments to plaster before mixing it with water. Several samples of pigmented plaster must be made before deciding on the right mixture because the real colour of the pigmented plaster can only be seen after it cures and dries. We can mix the plaster with a 5% water based consolidant (for example Acril 33) to improve its hardness and inertness.

Integrations are worked with files, scrapers and other hand tools while still wet, and are polished

with sandpaper of various granulations or a microdrill after drying. Plaster is easily reversible as it softens with the addition of water, and is then easily removed mechanically.

Polyfilla is an inert cellulose based filler. It is usually used for filling smaller gaps because of its lack of firmness. In some restoration laboratories we find the use of wax mixtures for modelling integrations. Integrant I 76 is a mixture of virgin beeswax, colophony, paraffin wax, dental plaster and zinc oxide. Each of the mentioned waxes must be melted at the required temperature and then mixed together. The remaining ingredients are then added to the liquid mixture as powders. It is applied to the object while warm, and can be refinished and remodelled with a heated instrument. This type of integrant endures the higher temperatures that often occur in showcases, and can be detached from the ceramic body.

## 7. NUANCING / RETOUCHING

Retouching has a predominantly aesthetic role it does not prevent or retard the object's deterioration, but rather restores its aesthetic integrity and its aesthetic value. The goal of retouching is to nuance integrated parts of fragmented objects and to assimilate them, in a greater or lesser extent, with the surrounding material. Retouching should be limited to the integrated part, avoiding the overpassing of colour along the edges of the original material. There are several approaches to how restored objects should be retouched.

Archaeological objects should be retouched in a



Figure 12. The process of filling joints (Photo: M. Ćurković)

way that keeps the integration visually distinguishable from the original part. This is achieved by colouring the integrated surface in a colour that is two or three shades lighter, but very similar to the tone of the original. In some cases the patterns and nuances present on the object can be reproduced on the integrated surfaces, but always in a lighter tone. The application of "invisible" retouching is frequent when dealing with antiquary objects, where every shape of decoration, relief and any visual effect of the original parts of the object are faithfully reproduced. This kind of retouching is not recommended as it can easily become false. All materials used in retouching must be reversible. The most frequently used are water - based acrylic colours easily soluble in acetone, water - soluble tempera and powdered pigments mixed with acrylic emulsions. They are applied with a brush, sponge, brush-spattered, airbrush and other methods. After drying, the coloured areas can be protected with a matte protective coating (acrylic emulsion, matte sprays) or a glossy coating in the case of glazed ceramic vessels (glossy lacquer, glossy sprays). These may be applied by brush or spraying.

## 8. DRAFTING POST - RESTORATION DOCUMENTATION

Comprehensive written and pictorial (sketch and photo) documentation should be drafted as the final step in conservation - restoration work. This documentation must contain all data gathered prior to, during and after restoration work. The initial situation of the object as found is documented, with photographic and written records of its state of conservation, the presence or perhaps absence/lack of decoration, the presence of deposits and infiltrations, traces of previous restoration attempts, the object's dimensions and number of fragments, the origin and period of its creation and all other observations related to the object. Materials and procedures used on the object during restoration work are recorded, as are the results of their application. When conservation - restoration work is completed the

object is photographed from all angles, and a written description of its final state is drafted. Sketched documentation and recommendations for the preservation of the object in future storage and depositing are appended. Also appended to this documentation are the eventual results of laboratory analysis related to the object.



Figure 14. A pot after conservation - restoration treatment (Photo: M. Ćurković)

## V. The Conservation and Restoration of Glass

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### INTRODUCTION

Glass is an amorphous substance that is created by the cooling and solidification of the melt without crystallisation. We differentiate natural glass (volcanic) from artificial glass (technical). Natural glass is created in volcanic eruptions (obsidian) or when lightning strikes sand (fulgurite) in cases where the melted stone/sand cools quickly enough that there is no crystallisation. Humans first manufactured artificial glass about 3000 BC as a glaze to coat vessels and brick. The manufacture of independent glass objects began around 1500 BC (RODGERS 2004, 145-146). Glass is also present in the form of opaque enamel on metal surfaces, and as Egyptian faience. Glass is artificially coloured by the addition of metal oxides of manganese, cobalt, chrome, copper, iron and others in the blend prior to melting. Decolourisers were also used, usually Mn which produces a complementary colour to neutralize the blue/green tone produced by Fe, with the result of a virtually colourless glass.

Glass made only of silicate crystals ( $\text{SiO}_4$ ) is the most solid and resistant to acids and bases. Because of its very high melting point (about 1710), glass had to be made with a lower melting point, as it was technically very difficult to produce glass from pure silicate. Thus to silicate ( $\text{SiO}_4$ ), as the chief ingredient, network modifiers ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ) have been added to break the bridges between the network formers (Si) and oxygen, thereby lowering the melting point of the glass. This breakdown of the network at several points weakens it and affects the properties of the glass. Network stabilizers ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) are added to give strength to the glass structure. They also break the bridges between network formers ( $\text{SiO}_4$ ) and oxygen but link at the strongest bonds because of their ionic potential and their smaller dimensions. These basic materials

for the manufacture of glass vary and can be exchanged for other ingredients. By its composition we divide glass into these groups: soda-lime glass, crystal glass (lead), borosilicate glass, aluminosilicate glass and silicate glass (quartz) (LEMAJIČ 2001, 2). The quantity of these added ingredients will determine the character and quality of the glass. In general, glass durability decreases for increasing amounts of network modifiers.

Glass is processed at high temperatures. A solid block of glass is placed in a furnace where it is melted and then placed on the tip of a pipe. Blowing through the pipe creates a bubble that is then, in further processing, shaped into a bottle or vase, and then removed from the pipe. Throughout the entire process of manufacturing, glass objects need to be heated, i.e. the glass mass must be melted by periodically returning it to the furnace. There is also a method of shaping glass with the aid of moulds where a heated glass mass on a pipe is introduced to a wooden mould, and thereby modelled by being blown into various shapes.



Figure 1. Matted glass beads, beads with surface iridescence (Photo: M. Ćurković)

### DEGRADATION OF GLASS

Glass is a material that was created from a crystalline form using high temperatures (energy), and has the characteristic of becoming

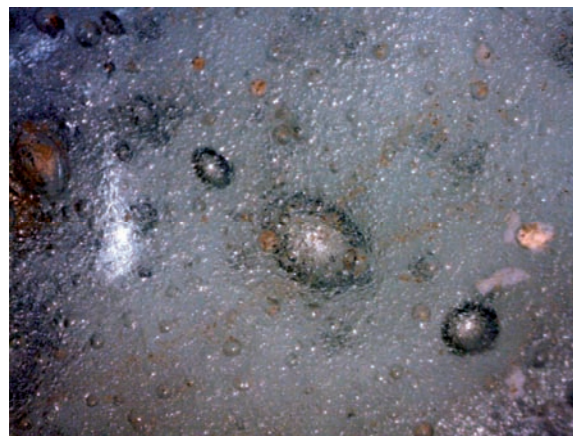


Figure 2. An eroded glass surface, magnification 50 x (Photo: M. Ćurković)

crystalline again, to return to the state of lower energy. This process is a very slow but can be stimulated by various factors. The degradation of glass is caused by three factors: as a result of physical damage, changes to the surface (deposits) and chemical damage. Because of its brittle nature glass is subject to damage caused by mechanical activity. We find the causes of physical damage in production defects, impact or falls, thermal shock, abrasion or previous attempts at restoration (DAVIDSON 1989, 169-170).

Foreign substances may also accumulate on the surface of the object or inside glass vessels. Deposits are created by the use of the object, the deposition of material when buried or deposited in a marine environment, the deposition of the products of metal corrosion, atmospheric pollution or from an excess of material used in a previous restoration procedure. In the case of deposits created by the use of the object these are the remains of cremation, food, drink, medications, paints and the like. Soil, calcareous, siliceous and black sulphide stains on the object may occur during interment. If a glass object is located near a metal object there may be a deposition of iron oxides. On glass objects submerged in a marine environment we find calcareous and siliceous deposits composed of the skeletal remains of marine organisms, deposits of algae and of other living marine organisms, and the already mentioned iron oxides. Previously restored objects may have the residue of adhesives, adhesive tape and fillers on them, which we

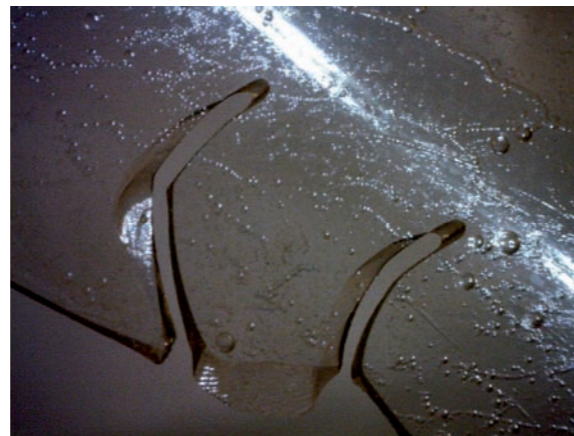


Figure 3. Micro fractures, magnification 50 x (Photo: M. Ćurković)

today also consider depositions that should be removed (DAVIDSON 1989, 171-172).

The greatest chemical damage to glass is caused by water and water solutions (sea). In contact with water chemical changes are initiated on the surface of glass, a process that then continues within the structure of the glass material (CRONYN 1990, 131). Chemical degradation occurs as a result of weak chemical bonds within the structure of glass between the base of silica and added substances, i.e. the modifiers and stabilisers.

Contact with water leads to the leaching of positive  $K^+$  and  $Na^+$  ions, followed by  $Ca^+$  and  $Mg^+$  ions. They react with water to form hydroxides. Positive hydrogen ions replace the positive ions of the modifiers that have leached out, which hydrates the glass. After drying they react with

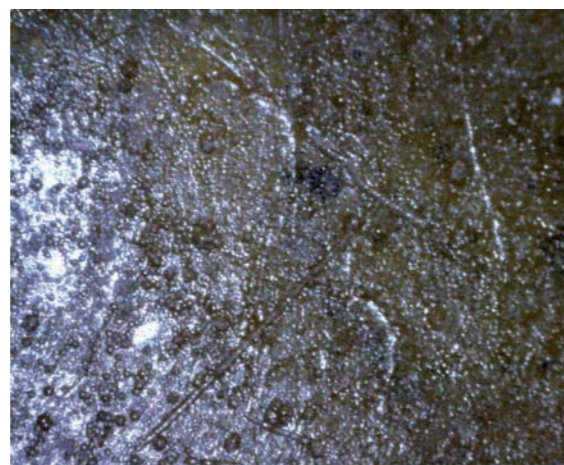


Figure 4. A scratched and eroded surface, magnification 50 x (Photo: M. Ćurković)

carbon dioxide and form sodium and potassium carbonates. The carbonates thus formed continue to absorb water from the environment, perpetuating the reaction and the deterioration of the glass. As a result we have a weakened structure consisting only of silica ( $SiO_4$ ). The following step in the degradation of glass is the dissolution and decomposition of this weakened structure.

Dramatic physical damage can occur to objects extracted from the sea during the drying process as a result of the activity of soluble salts. In the process of evaporation soluble salts in the structure or on the surface will crystallise and cause the object to fracture.



Figure 5. The flaking of a glass surface (Photo: M. Ćurković)

The visible symptoms of glass degradation are: rainbow lustre (iridescence), a matte surface with the formation of flakes, the loss of the glass nature of the object, discoloration, incrustation and deposits and spontaneous fracturing.

The presence of rainbow colours on the surface (iridescence) occurs as a result of a delaminated glass surface caused by its chemical degradation. Because of the uneven and delaminated surface, light is reflected at different angles, causing it to shine in the colours of the rainbow. This lustre can only be observed when the object is completely dry, i.e. when the water between layers is dried out. Thin layers of degraded glass flake off upon drying, damaging the surface up to the level of complete decay. The damaged surface is uneven, matte and given to sloughing and flaking. A similar matte surface



Figure 6. Glass iridescence (Photo: A. Jelčić)

effect is achieved by physical means, by the abrasive action of sand and other substances in the underwater environment. Poorly preserved glass may survive in the form of a chalky silica gel, having lost the characteristics of glass – clarity and transparency, and is as such very difficult to identify as glass. Discolouration occurs when metal oxides are leached from glass, when metal oxides in the glass are oxidised, or by the absorption of metal oxides from the environment. Spontaneous cracking is frequent in the presence of a damaged hydrated glass surface. Cracking occurs when a hydrated surface is reduced in volume as a result of drying. Fractures can occur on the surface of the glass, but may also affect deeper layers. These surfaces are even more sensitive to external factors, i.e. humidity, and as such subject to further degradation.

## THE CONSERVATION AND RESTORATION OF GLASS

Conservation - restoration work on glass objects can be divided into phases:

1. Initial documentation, preliminary analysis
2. Cleaning the object
3. Desalination
4. Consolidation
5. Bonding fragments
6. Integration
7. Drafting documentation after conducting restoration work

As in the case of the restoration of ceramics and stone, the sequence of restoration procedures may vary depending on the level of an object's preservation and the conditions in which it was deposited.

### 1. INITIAL DOCUMENTATION, PRELIMINARY ANALYSIS

Photographic and written documentation of the state of an object as found must be made before the start of restoration work. The remains of colour, gilding, engraving or a painted surface often adhere to the layer of deposits. If a decoration is not identified there is a significant possibility that the cleaning process will unintentionally remove it together with the accumulated deposits or damage it. We can use radiography or filming under UV light to reveal decorations on the surface.

### 2. CLEANING

When cleaning glass it is important to know that cleaning implies the removal of soil and deposits accumulated on the surface, but not the removal of the products of glass degradation. Doing so would be considered the destruction of a part of the original object, because the removal of these damaged surface areas may significantly and detrimentally affect the original dimensions of the object. The selection of material that shall be used in cleaning depends on the level of preservation of the glass, decorations present on the surface and on the types of deposits we intend to remove. It is always better to not undertake



Figure 7. A test cleaning of calcite deposits (Photo: M. Ćurković)

cleaning, and leave the deposits on the object, than to go ahead with removal that could damage a degraded surface or the object as a whole. In the case of highly damaged glass the priority is to consolidate the material, and then to undertake mechanical cleaning. Deposits can be removed with a soft brush, scalpel and cotton swabs soaked in solvents while the object is still wet. Painted decorations, colours and gilding on glass surfaces should be protected with a coating of consolidant - they must not by any means be cleaned using water.



Figure 8. Glass neck covered with marine organism deposits (Photo: M. Ćurković)

Preserved archaeological glass may be treated with mild chemical cleaning. Objects extracted from muddy sites may be cleaned with tap water, distilled water or other solvents before the object dries and is consolidated. The best choice would be a mixture of solvents with different evaporation points, such as a mix of acetone, alcohol and water (1:1:1). An oily film on the surface of the object can be cleaned with a 25% solution of hydrogen peroxide in water.

Deposits of metal oxides can be removed mechanically or by the controlled use of chemicals in the same manner as in the case of ceramics (page 32). Metal oxides are often firmly bonded with the damaged glass surface, and as such it is sometimes better not to remove them.

Calcareous and marine organism deposits can be mechanically removed with a scalpel while the object is wet. Chemical cleaning is done as

described in the case of ceramics with EDTA salts and ionic exchange resins.

### 3. DESALINATION

Glass objects extracted from a marine environment must pass through the process of desalination to remove soluble salts. Desalination is conducted in the same fashion as with ceramics, by submerging the object in a tap water bath, later in distilled water, with regular changing of the water. The desalination process is completed when measurement of the water's conductivity establishes a minimum constant quantity of salts (i.e. the lack thereof). The object is then ready for air-drying and/or to undergo consolidation only in special cases when this is indispensable.

### 4. CONSOLIDATION

Consolidation is conducted only when indispensable, in the event of the sloughing, flaking and crumbling of the surface. It should always be kept in mind that consolidation is an only partly reversible procedure and that it is better to avoid it if there is not an unequivocal need to undertake it. Removing consolidants is only partly possible because there is a decline in reversibility, and because of the damage that may be caused by the use of solvents that would engender the repeated wetting and drying of the object. Consolidation is carried out to preserve and improve the sturdiness of the object and to restore the transparency a glass object has lost by the degradation of its surface. A consolidant penetrates into the structure of the object and fills minute cracks, smoothing out unevenness and imparting transparency. It should be noted that it is not enough to consolidate only the damaged surface of the glass object, but rather that the consolidant must penetrate deep into the structure and bond with the preserved glass core. An object that appears dry may contain water molecules within its structure. Drying this kind of object, or a wet object, by heating or under a vacuum, leads to the dehydration of the hydrated surface, shrinkage and the loss of the material.

A degraded wet glass object can be consolida-

ted by exchanging the water (also referred to as dehydration) by submerging the object in another solvent (acetone, alcohol) following by immersion in a consolidant soluble in the same solvent or with a water-based consolidant. Silicone oil is a consolidant applied to objects dehydrated in acetone. It is applied under pressure to improve the penetration of the consolidant and to facilitate the evaporation of acetone. The same method can be used to consolidate with solutions of acrylic and polyvinyl resins. Dry objects can be consolidated with the same substances by coating, spraying, immersion or under pressure. The most frequently used consolidant for glass is still acrylic resin Paraloid B72.

### 5. BONDING

Bonding fragments secures the object's stability and aesthetic integrity. Materials used for gluing must possess the characteristics of transparency, good adhesion, and reversibility and must not be damaging to the object. Paraloid B72 acrylic resin has been used for this purpose but does not have a long lifetime and lacks satisfactory adhesive strength. Epoxide resins such as Araldite 2020 and HXTAL NYL-1 have successfully replaced it. They are very transparent and have physical characteristic similar to glass.

Prior to gluing, the object must be cleaned of dust to ensure the better adhesion of the glue. Fragments may initially be joined with very small strips of adhesive tape. If the surface of the glass has been well preserved, the strips are replaced by metal clips that are applied to the outer wall as bridges linking two fragments, and are affixed with little drops of cyanoacrylate glue (Super Attack) only to the places where clips touch the surface of glass.

These small bridges enable the application of liquid glue along the whole length of the joint. Liquid glue enters the joints by capillary action. Therefore it is important that the fragments have been joined as well as possible and that there are no pores between them, so that the glue can be absorbed into the joints by capillary action. For this purpose the most frequently used



Figure 9. Joining fragments with adhesive tape (Photo: M. Ćurković)

epoxide glues are Araldit 2020 and HXTAL NYL 1. Araldit 2020 is more economical in terms of cost and dries quicker than HXTAL glue (HXTAL has a very long setting time – an entire week is required for complete curing) but tends to yellow more readily than HXTAL. Any excess glue can be removed using cotton swabs soaked in acetone and well drained in order to prevent any excess acetone from affecting the speed of resin solidification. After the glue has completely dried, the metal clips can be removed mechanically or by softening their bonds with the aid of cotton swabs soaked in acetone.

## 6. INTEGRATION / GAP FILLING

Integrating a glued glass object restores its stability and aesthetic value. Integration is possible only when there is sufficient data on the object and its original appearance. Complete and partial reconstruction is possible. Complete reconstruction is done with objects when most of the original parts are present and some gaps need to be filled, or when only a small part of the



Figure 10. Joining fragments with metal clips, detail (Photo from Museum of Ancient Glass in Zadar)

fragments are present but there is a model of the original appearance. Partial reconstruction is carried out on objects where there is insufficient information about the original appearance. Reconstruction then has the role of linking fragments and ensuring stability.

In both cases to fabricate integrations we use the same epoxy resins as are used for bonding (Araldite 2020, HXTAL) because of the excellent characteristics they demonstrate after drying. These are fluid resins that are easily toned and upon drying becoming transparent masses very similar to glass. The negative side of these epoxy resins are their long hardening times, which results in the resin flowing from the place it was intended to dry in and a reduced possibility of manoeuvring the resin when fabricating an integration.

Integration can be done directly, by filling the gaps directly on the object, or indirectly when the missing part is fabricated separately and then joined to the artefact. Pigment is added to one component of a quantity of two - component glue that will be, once mixed, sufficient for all required integrations.

Powdered pigments are used as colorants, first dissolved in a small quantity of solvent (Microlith pigments for glass) or as already prepared glass paint (Vitrail by Lefranc & Bourgeois, Pebeo or others).

In the direct method, a cast is made directly on the object into which liquid resin has been poured. For the successful fabrication of an integration, we need a solid preparatory phase involving the fabrication of appropriate moulds. Casts may be done using wax leaves or dental silicone.

For the wax leaf method, the leaves have been cut with a scalpel in the shape that will cover the cavity – one from the inside, the other from the outside.

The leaves can be modelled and curved using a hot air blower. First we place the leaf on the inner side, creating a good seal by pressing the

warm putty onto the object. We can put some two - component vinyl polysiloxane impression material around the leaf to seal the borders. We then apply the outer leaf, affixing it in the same manner. We then cut out two holes – one through which the resin is poured, the other enabling bubbles of air to escape from the cast (in order to not be captured in the resin). At these holes we install two wax cylinders, affixing them with melted wax. When the cast is completely sealed and its functionality has been checked (simply by blowing through the cylinder) we can start pouring the resin into it. Once the resin has fully hardened, the cast may be removed, and we can undertake the finishing of the integration. The integration must be finished using abrasive paper or a microdrill, exercising caution in order to avoid damaging the surface of glass.

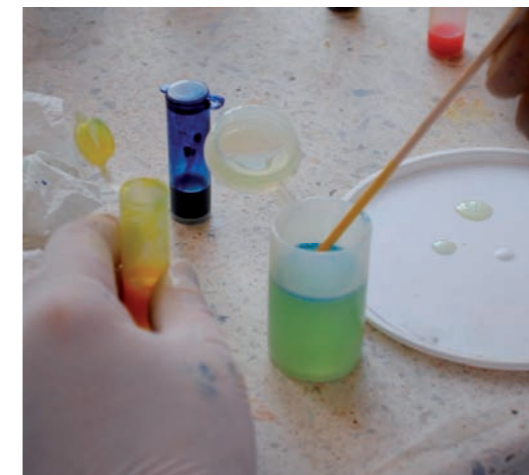


Figure 11. Toning epoxy resin (Photo: M. Ćurković)

Integrations done using silicone casts are more precise, and there is no need for finishing. The drawback of dental silicone is its high price in comparison with wax leaves. We make the silicon cast by putting two separate layers of silicone on the inner and outer surfaces of the glass over an area the same size and shape of the missing part (we immediately produce the two walls of the mould – inner and outer). The first layer is a two - component vinyl polysiloxane impression material, which is laid out thinly, so that it authentically reproduces even the tiniest details of the surface. While it is not completely dried out, we apply the other layer of compatible silicone putty onto it, which serves to give hardness to the cast. After drying, the silicone wall is set apart from the glass and cut by scissors



Figure 12. Integration using epoxy resin with the aid of a silicone mould (Photo: M. Ćurković)

into a shape that effectively covers the gap (in the shape of the gap, but a little wider to extend over the edges). The cast is attached to the inner side of the object using a compatible glue for silicon casts, while the edges of the cast are well sealed using impression material in order to prevent the loss of resin through holes. Two holes are made in the front cast using a needle, one for pouring in the resin, the other for the outflow of excess resin. The holes have to be placed in specific positions in order to allow the resin to enter the mould at a lower point and exit at a higher point in order to evacuate all the air inside and avoid the creation of bubbles (FERUCCI, 2012). The front section is glued to the object as described for the inner part; then drinking straws are applied at the holes to serve for pouring in and out. The straws are glued using cyanoacrylate glue and then permanently affixed using the same impression material. The validity of the cast can be tested by blowing through the straws (air must be heard coming out on the other side). Epoxy resin is poured into the lower straw until resin begins to pour out through the upper straw.

These methods (silicone and wax) can be combined when, for example, the missing portion, or a decorated surface, does not permit to use the silicone. It is possible then to make the walls with wax and seal them with silicone and add the straws.



Figure 13. Integrating small imperfections using the indirect method (Photo: M. Ćurković)

In the case of ovoid closed forms (balsamarium, bottles, vessels) for the inner mould we can use a balloon inflated from the inside of the object.

In the indirect method a sheet of epoxy resin is cast that is of the same thickness as the glass wall at the missing section. A form identical to the gap/missing section is then cut out and affixed to the original with adhesive tape. Epoxy resin is poured in at the joint of the original glass and fabricated epoxy resin plate to glue in the integration. This method is very effective with thin-walled glass artefacts, as the thinly poured



Figure 14. A partially reconstructed artefact (Photo: M. Ćurković)

epoxy resin sheets can then be easily adapted to the form of the artefact.

The other indirect method is done by reproducing and modelling the missing part in plaster to achieve the desired shape. It is then removed from the artefact and a silicone cast made from it. Epoxy resin is then poured into the silicone cast and, once hardened, removed from the cast and then integrated and glued into place. This method presents the danger of damaging the artefact during the modelling of the plaster.

### 7. DRAFTING POST-RESTORATION DOCUMENTATION

As is described in the previous chapter on the restoration and conservation of ceramic and stone material, comprehensive written and pictorial (sketch and photo) documentation should be drafted as the final step in conservation - restoration work. Restored glass objects should be stored in constant conditions, away from direct sources of heat.



Figure 15. An artefact after conservation - restoration work (Photo: M. Ćurković)

## VI. The Conservation and Restoration of Metal Finds

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### INTRODUCTION

Throughout history what are now metal archaeological finds have been manufactured for the most part from iron, copper, silver, gold, lead and tin. These metals, with the exception of gold, rarely occur in nature as elements, and are found for the most part in the form of ores that are their stable state. As a result, from the moment of their production, the cited metals and their alloys tend to return to their initial state, reacting with the environment and initiating the process of corrosion, converting them into stable compounds.

The corrosion of metal is a spontaneous process of unintentional destruction caused by physical, chemical and biological agents. It can be classified on the basis of the environment in which it occurs, based on the appearance of the corrosive attack and based on the mechanism of its action. When conserving and restoring metal objects we must, therefore, bear in mind that metal corrosion is a spontaneous mineralisation and that the process is almost impossible to stop entirely, but that, with proper protection, we

can slow it as much as possible (KLARIĆ 1998, 53).

The proper choice of materials, tools and methods with which to treat metal objects depends greatly - besides on the analysis of damage and the state of the object - on a knowledge of the nature of the products of the corrosion of a given metal, and thereby of the characteristics of the metal from which the object is made.

### THE CHARACTERISTICS AND MECHANISMS OF THE CORROSION OF BASIC METALS IN ARCHAEOLOGY

The metals can be graded in reactivity from highly corrodible (base) to unreactive (noble).

**IRON > TIN > LEAD > COPPER > SILVER > GOLD**  
 Most base Most noble

The corrosion of metal products in an underwater environment (seas, lakes, rivers, swamps and the like) occurs in an electrolyte and is as such, by the mechanism of its action, electrochemical, which means that there is

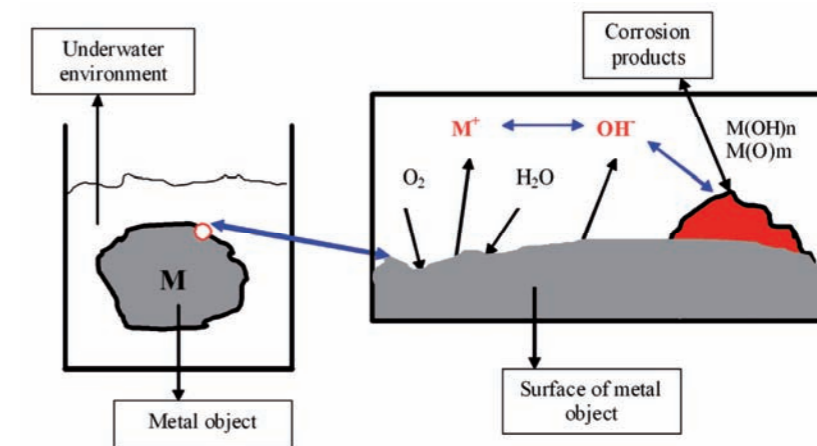


Figure 1. A schematic depiction of the electrochemical mechanisms of corrosion in an underwater environment (Drawing: A. Jozić)

initially an oxidation of an atom of metal into a free cation, which only by secondary processes produces a molecule compound that is a corrosion product (HAMILTON 1999, File 9). The chemical composition of corrosion products will depend on the reactants present in the environment. The products may be laid down as amorphous powders but it is more common for crystals to be formed.

Depending on the solubility of the corrosion formed, products can be developed in two situations:

- Active corrosion - the metal forms soluble products that move away from the metal into the surrounding environment. This usually occurs in very acid or extremely alkaline environments when all trace of the metal is lost.
- Passivation - the metal forms solid corrosion products that adhere to its surface and prevent or restrict further attack. Metals sometimes corrode in environments where it would be supposed that passive films would develop to prevent attack.

This may be due to the presence of certain aggressive ions, chlorides being a prime example. Unlike other ions, chloride ions migrate through protective films and cause the metal beneath to corrode (CRONYN 1990, 168-171).

The process of corrosion in an underwater environment may be manifested as:

- Uniform corrosion - corrosion resulting from an electrochemical reaction that occurs on the entire metal surface at almost the same rate.
- Galvanic corrosion - occurs when two different metals or alloys are in electrical contact through the action of an electrolyte (corrosive substance). The less noble metal in this pair corrodes significantly faster than it would if it alone were present in the same electrolyte.
- Fouling corrosion - corrosion caused by marine organisms, occurs when marine organisms, such as limpets and molluscs, grasp on to a metal surface, develop, and then separate small pieces of metal from the surface. This process causes pits to form on the metal under the marine orga-

nism, which is the first phase of autocatalytic pitting corrosion.

## IRON AND ITS ALLOYS

Iron is the most important technical metal. In its pure form it is a white, brilliant and relatively soft metal. In nature it is very widespread (about 5% of the Earth's crust), and occurs for the most part as oxide (magnetite  $\text{Fe}_3\text{O}_4$ , haematite  $\text{Fe}_2\text{O}_3$ , limonite  $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), carbonate (siderite  $\text{FeCO}_3$ ), siliceous and sulphide ores. It is rarely used as a pure metal, and it is most often alloyed with other elements (FILIPOVIĆ; LIPANOVIĆ 1995, 1024-1036). Archaeological iron is in most cases wrought iron (up to 0.35% carbon), and iron archaeological finds at underwater sites are most frequently anchors, cannons, cannon balls, nails, razors, knives and various other tools.

Of all the metals in extensive use, iron is the most susceptible to corrosive processes. The corrosion of iron is caused by oxygen and moisture. Initially, three oxides occur successively in iron in contact with air and oxygen:  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . With the introduction of moisture  $\text{Fe}_2\text{O}_3$  converts to  $\text{FeO}(\text{OH})$ , which is, unlike the first three, amorphous in structure and no longer protects the metal from further corrosion. The chlorine and sulphur dioxide compounds present further intensify this process, and various aerobic and anaerobic bacteria certainly play a role (KLARIĆ 1998, 69-70).

The activity of moisture also leads to the separation of metallic salts, which act as an electrolyte, and an electrolytic reaction is created with anodic and cathodic areas.

Iron oxidises at the anode creating ferrous chloride, while hydrogen is reduced at the cathode. Hydrogen, which is weakly conductive, gathers at the cathode and prevents further corrosion. In the presence of oxygen, however, hydrogen combines with oxygen as water or hydrogen peroxide eliminating the protective layer and the electrolytic reaction continues until the entire surface is covered in the products of corrosion, which then allows for the unimpeded activity of



Figure 2a. Iron legionary spear, Lenovac site, prior to intervention (Photo: A. Jozić)



Figure 2b. Iron legionary spear, Lenovac site, post-intervention (Photo: A. Jozić)

chloride, which completely destroys the metal core. It should be noted that a strong corrosive layer occurs on objects with inserts and applications of metal that are nobler than iron. A whole range of corrosion processes occur during corrosion in a fluid medium, i.e. sea or fresh water - the presence of carbonic acids creates carbonates of iron, while contact with sand and phosphates has a stabilising effect, and the compounds created are relatively non-aggressive towards the metal itself. Water rich in magnesium and calcium acts to strengthen the corrosion layer, while a relatively high chloride content in seawater causes a strong corrosive attack which is only increased when the object is extracted. The characteristics of an advanced stage of corrosion are a blistered surface, cracked crust and a bulging accumulation of products on the surface of the object (BUDIJA 2002, 83-84; HAMILTON 1999, File 9).

The common products of corrosion on archaeological objects made of iron alloys:

IRON(II) HYDROXIDE -  $\text{Fe}(\text{OH})_2$   
 LIMONITE - IRON OXIDE-HYDROXIDE -  $\text{FeO}(\text{OH})$   
 IRON(II) CHLORIDE -  $\text{FeCl}_2$   
 HYDRATED IRON(II) CHLORIDE -  $\text{FeCl}_2 \cdot \text{H}_2\text{O}$   
 IRON(III) CHLORIDE -  $\text{FeCl}_3$   
 HYDRATED IRON(III) CHLORIDE -  $\text{FeCl}_3 \cdot \text{H}_2\text{O}$   
 FERROUS SULPHIDE -  $\text{FeS}$   
 MAGNETITE -  $\text{Fe}_3\text{O}_4$   
 HYDRATED MAGNETITE -  $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$   
 HAEMATITE - IRON(III) OXIDE -  $\text{Fe}_2\text{O}_3$   
 HYDRATED HAEMATITE -  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

It should be noted that iron chlorides are always a component part of the corrosive products of iron and that metal objects from underwater en-

vironments, besides having accumulations of corrosion products, are almost always also covered in incrustations characteristic of the environment from which they were extracted (rock, sand, molluscs, skeletal remains of dead marine organisms and the like) (HAMILTON 1999, File 9).

## COPPER AND ITS ALLOYS

Copper is a metal of characteristic light reddish colour. It is relatively soft, very malleable and an excellent conductor of heat and electricity. It occurs naturally as an ore, most frequently a sulphide ore (chalcopyrite, covellite, chalcocite, bornite...), oxide ore (cuprite, tenorite...) and carbonate ore (malachite, azurite...). Because of its very high tendency to corrode and difficult casting it is most often alloyed, above all with tin and zinc.

- An alloy of copper and zinc is known as brass. If the amount of zinc does not exceed 20% the brass is yellow in colour, while further increasing the proportion of zinc renders the brass whiter.
- An alloy of copper and tin is known as bronze and is of reddish-brown colour. Bronzes with over 20% tin are white in colour, and were used in the Roman period for the manufacture of mirrors. Bronze with about 30% tin is known as speculum metal, which is very hard, fragile and brittle (BUDIJA 2001, 137).

The most frequent bronze finds at underwater sites are cannons, nails, weapons, various parts of ship's equipment and - depending on the sunken ship's cargo - wether bells, vessels, small boxes, medallions, coins, needles, fibulae, various tools and jewellery.

When bronze corrodes there is an initial layer of red copper(I) oxide (cuprous oxide) that forms on its surface mixed with tin oxide. Cuprous oxide then hardens in the form of the mineral cuprite, which is reddish - brown in colour. This layer is porous and the action of CO<sub>2</sub> bonds an external layer of basic carbonates to it. The layer of copper carbonate is green - blue in colour, and its bases are the minerals green malachite and blue azurite. These minerals create a noble patina, uniformly distributed, showing all the detail and protecting bronze from further corrosion. Changes occur in the presence of chlorine which converts basic carbonate (malachite) into nantokite. It acts upon metal making its surface powdery and mottled green. Nantokite is hydrolysed to create hydrochloric acid, which further reacts with the uncorroded copper. A further reaction in the presence of moisture and oxygen creates a pale green powdery patina of basic cuprous chloride (paratacamite). This kind of corrosion is often referred to as bronze disease, bronze cancer, bronze plague and malignant patina. Malignant patina is recognisable by the bumpy protrusions it creates by the blistering of the patina under the influence of chlorine. The process usually affects smaller or larger areas of the object, and the focal area of the process is raised in relief and similar in appearance to layered scabs. With time the affected area spreads through the depth and breadth of the object. For the most part metal objects extracted from the sea have active chlorides present and thereby bronze disease, which may result in pitting corrosion and the complete decomposition

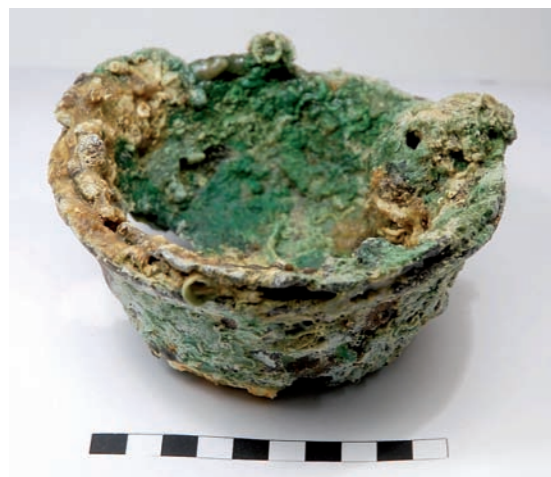


Figure 3. A bronze bowl, Veruda site (Photo: A. Jozić)

of the object (BUDIJA 2001, 138-139; KLARIĆ 1998,63-64; MAZZEO 2005, 29-43).

The basic patinas present on archaeological objects made of copper alloys are:

COPPER(I) OXIDE, Cu<sub>2</sub>O, CUPRITE – a reddish-brown compound; it always lies directly on the metal.

COPPER(II) OXIDE, CuO, TENORITE – a black copper oxide; a transitional form to more stable forms of patina.

MALACHITE, Cu<sub>2</sub>(OH)CO<sub>2</sub> – one of the green basic copper carbonates.

AZURITE, Cu<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> – a blue copper carbonate; appears together with malachite.

CHALCONATRONITE, Na<sub>2</sub>Cu(CO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O – a blue-green sodium copper carbonate.

ATACAMITE and PARATACAMITE, Cu<sub>2</sub>(OH)<sub>3</sub>Cl – of the same composition, but of different crystal structure; a basic copper chloride of light green colour; soft, often powdery structure; occurs on objects from soils rich in salts and on objects extracted from marine environments.

BOTALLACKITE, Cu(OH)<sub>3</sub>Cl·H<sub>2</sub>O – of blue-green colour; related to paratacamite.

NANTOKITE, CuCl – forms a whitish waxy layer on bronze. We find it only accompanied by paratacamite. One of the causative agents of cyclic corrosion, known as bronze plague (BUDIJA 2001, 139-141).

### SILVER AND ITS ALLOYS

As an elementary substance silver is a lustrous white noble metal, unusually malleable and ductile. It has lower electric resistance and greater heat conductivity than any other metal. There are relatively small amounts of silver in nature. It is found for the most part accompanying lead and copper ores or as argentite Ag<sub>2</sub>S. Because of its softness it is rarely used in its pure state for the manufacture of works of art, and it is normally alloyed, most often with copper, tin or gold (FILIPOVIĆ, LIPANOVIĆ 1995, 1079-1085). The most frequent archaeological underwater finds made of silver are coins and various kinds of jewellery.

Sulphur compounds are the leading cause of silver corrosion. Of the sulphur compounds the

most significant to silver corrosion are hydrogen sulphide and sulphur dioxide. In aerobic conditions the oxidation of silver always involves oxygen, but is assisted by hydrogen sulphide, which bonds the created Ag<sup>+</sup> ion to highly insoluble silver sulphide.



In the process the contact of silver with oxygen also creates a layer of the also black silver oxide parallel to the layer of silver sulphide. In seawater a layer of silver bromide is also frequent. The cited sulphide and oxide compounds provide silver with a degree of protection from further corrosion, and provide an aesthetically pleasing patina the preservation of which is always desirable. Changes occur in the presence of chlorine. Silver objects suffer most from reactions with the chlorine contained in the ground and in seawater. This creates silver chloride or "horn silver" that, unlike sulphides and oxides, does not have the characteristic of protecting the metal, and the process of corrosion lasts until all the silver is converted to a chloride making this corrosion destructive. When silver alloyed with copper (or some other metal) is corroded, the entire process is more complex as the appropriate copper compounds are formed parallel to the silver compounds. In these cases the less noble metal is always decomposed first and these objects have a patina that is more characteristic of copper than of silver (BUDIJA 2001, 5; HAMILTON 1999, File 13).



Figure 4. Silver coins, Sveti Pavao site near Mljet (Photo: M. Pešić)

The visual characteristics of the corrosion of silver objects:

BLACK LUSTROUS PATINA – this patina occurs on objects of pure silver that have been exposed to extended atmospheric action in a dry and saltless environment.

PALE GREY PATINA – characteristic of a thin layer of silver chloride on the object.

BLACK-GREY or BROWN SCALES – the ad-

vanced stage of corrosion typified by hard scales and a disfigured, fissured surface. These scales are the result of the chloride and bromide frequent in salty environments. Chlorides react with the silver creating a layer of "horn silver," while brown scales form in the presence of excess bromide.

COPPER CORROSION SURFACE – copper corrosion may completely cover the surface of a silver-copper alloy, giving it the appearance of corroded copper. In the less advanced phase points of copper corrosion can be seen on the surface of the object (KLARIĆ 1998, 107).

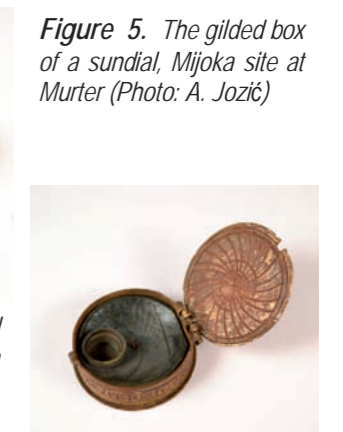
### GOLD AND ITS ALLOYS

Gold is a soft and ductile metal of lustrous yellow colour. It is a very rare element. In nature we find it almost exclusively in its metal form, while a small quantity of gold is found accompanying copper and silver ores. Gold is the most noble of metals and is as such exceptionally resistant to corrosion. It is overly soft in its pure state and is most often alloyed with silver, copper, or some other metal (FILIPOVIĆ, LIPANOVIĆ 1995, 1085-1089). The archaeological finds made of gold most frequently found at underwater sites are various kinds of jewellery.

The noble nature of pure gold lies in its prevention of natural corrosion - it is absolutely stable in air and does not bond with oxygen at any temperature. Pure gold does not corrode. Gold alloys that contain over 20% of other, as a rule less noble metals, are subject to corrosion - particularly sensitive to corrosion are gilded objects where only a very thin surface layer is gol-



Figure 5. The gilded box of a sundial, Mijoka site at Murter (Photo: A. Jozić)



den. Gold, as the most noble metal, is always cathodic in relation to other metals in a corrosive medium - they dissolve and the corroding alloy becomes increasingly porous and brittle, and thereby increasingly subject to corrosive processes. Objects made of these kinds of alloys acquire the patina of the metal that has been added to gold (KLARIĆ 1998, 115; BUDIJA 2003, 78-82).

The visual characteristics of archaeological gold: UNCORRODED – pure gold is relatively easy to visually identify.

COPPER CORROSION – visible on the surface of objects made of an alloy of gold and copper.

SILVER CORROSION – visible on the surface of objects made of an alloy of gold and silver.

SCRATCHED SURFACE – gold is an extremely soft metal and small scratches are easily visible on archaeological object



Figure 7. Lead anchor stock, Čiovo site (Photo: A. Jozić)

## LEAD AND ITS ALLOYS

Pure lead is a heavy, silver-blue, lustrous metal. It is very soft, very dense and has a low melting point. In relation to other metals it is a relatively poor conductor of electricity and heat. Lead and its compounds are very toxic. It occurs most frequently as a sulphide, PbS, the mineral galena. Frequent lead finds at underwater sites and shipwrecks are weights, cannon balls, various ship's repair patches, cartridges for weapons and anchor stocks.

Lead is a quite stable metal that turns grey in contact with air relatively quickly by the formation of an oxide - carbonate layer that protects the lead from further reaction with the environment. In natural waters, in which oxygen is present, lead undergoes corrosive dissolution as the result of electrochemical processes. But, because of the common occurrence of hydrogen carbonate and sulphate in natural waters, a highly insoluble layer of basic lead carbonate and sul-

phate forms on the surface of the lead protecting it from further corrosion. Mechanical damage of this layer can lead to a stronger corrosive attack and the conversion of the object to basic lead carbonate.

The most frequent corrosion products on archaeological objects made of lead are various oxides (PbO, PbO<sub>2</sub>), basic carbonates (2PbCO<sub>3</sub> x Pb(OH)<sub>2</sub>), chlorides (PbCl<sub>2</sub>), sulphides (PbS) and sulphates (PbSO<sub>4</sub>). Corrosion products on lead objects extracted from marine environments are stable. They may visually disfigure the object, but they do not participate in chemical reactions leading to the further corrosion of lead. These objects require cleaning exclusively for aesthetic reasons and to reveal surface detail (FILIPOVIĆ, LIPANOVIĆ 1995, 849-855; HAMILTON 1999, File 14).

## TIN AND ITS ALLOYS

As an elementary substance tin is a silver - white metal, not overly hard and very malleable. At normal temperatures it undergoes practically no change either in air or water. One of the key uses of tin is to create alloys, bronze above all. Objects of pure tin are very rare finds at underwater archaeological sites. While it is relatively resistant to corrosion, it is sensitive to changes in temperature that cause changes in the structure of the metal.

Initially this is visible as a loss of surface lustre and later as the formation of expanding grey-



Figure 8. A tin box, Mijoka site at Murter (Photo: A. Jozić)

black stains. At these areas the metal is converted to a powdery grey dust, the object is rendered frangible and breaks easily - this process lasts until the object is entirely decomposed. In seawater it has been demonstrated that the presence of sodium chloride promotes and accelerates the corrosion of tin (HAMILTON 1999, File 14).

## CONSERVATION - RESTORATION INTERVENTION ON UNDERWATER METAL ARCHAEOLOGICAL FINDS

Conservation - restoration work on underwater archaeological metal finds can be divided into phases:

1. Photographic documentation and a detailed description of the initial condition
2. Desalination of the object
3. Preliminary investigation
4. Cleaning the object
5. Active stabilisation
6. Gluing broken objects and possible reconstruction
7. Applying protective coatings
8. Drafting technical documentation on interventions conducted

The cited phases of conservation - restoration intervention can be applied with equal effectiveness on archaeological metal objects found in underwater environments and at those found in other environments, the only difference being that the lack of marine incrustations and the lower chloride content significantly reduces the time required to process and stabilise these objects.

### 1. PHOTOGRAPHIC DOCUMENTATION AND A DETAILED DESCRIPTION OF THE INITIAL CONDITION

Metal objects, like all artefacts must be recorded before they receive any treatment. The ethics of conservation - restoration intervention dictates the documenting of the relationships between the original state of the object and all changes that are the consequence of conservation - res-

toration procedures, in order to avoid unknowns in some future procedure, i.e. so that the level of interventions conducted, the dimensions and scope, can be precisely determined. The preliminary phase, consequently, involves taking measurements of the object, photographing it, makes sketches and documenting the state in which it was found.

### 2. DESALINATION OF THE OBJECT

After initial documentation the objects are isolated in polypropylene nets and placed in desalination baths. Desalination involves submerging the objects in vats filled with tap water with the addition of the appropriate inhibitor, and regular renewal with fresh solution. The addition of the inhibitor is an appropriate cautionary measure to prevent the continuation of corrosion processes, or their acceleration, which, as a rule, is the case when metal objects are extracted from a marine environment. The most frequently used are alkaline inhibitors such as sodium carbonate, sodium sesquicarbonate and sodium hydroxide. The amount of inhibitor added must be such that it maintains the pH of the solution above 8 (HAMILTON 1999, File 9). The water in the baths is changed, as a rule, every four weeks, i.e. when the concentration of secreted salts reaches a constant maximum. The concentration of salt is monitored via electrical conductivity, which grows proportionally with the increasing quantity of salt in the solution. The water is changed successively, with the maximum concentration dropping with every new change. It is important to proceed gradually to avoid the overly speedy release of salts, which could cause further damage to the object. In the last few changes tap water is replaced with distilled water, which accelerates the desalination effect. When desalination is completed objects are taken out of the water and left to air dry, taking care to avoid significant oscillations in air temperature during the drying procedure.

### 3. PRELIMINARY INVESTIGATION

The selection of materials, tools and the methods of treating an object should, along with an understanding of the characteristics of the metal

of which an object is made, be preceded by an analysis of the damage and the state of an object. The examination of excavated material is fundamental to archaeological conservation. The conservator looks at any remaining original material together with its deterioration products and any adhering associated material. In order to understand what s/he is looking at, a conservator must have a good knowledge not only of materials and how they decay, but also of historical technologies. Objects should be examined to establish the number of layers, chemical composition, state of the surface, the possible presence of decorations, inserts of other metals, the remains of gilding, silver plating and other parameters. This information is then used not only to determine the mode of treatment for the artefact but also to reveal how it was originally made, what it was used for, and even the significance of the context in which it was found (CRONYN 1990, 58).

Preliminary examination includes a visual inspection of the object and an inspection under magnification (5X, 10X, 20X, 40X). Based on the acquired information we can decide on possible laboratory or chemical analysis of the metal archaeological object and radiographic filming.

To establish the state of the interior of a metal object it is best to make use of x-rays. X-rays pass through metal oxides more readily than through the metal itself, and an x-ray gives a much better picture of the extent of oxidation than any other method. On an x-ray we can observe the thickness of the layer of corrosion, the presence of other metals and materials and opt for the most appropriate conservation method. X-rays provide us with a two-dimensional image of the object. A step beyond imaging archaeological objects using x-rays is the use of CT. This is a modern method that produces a three-dimensional image providing us with insight deep into the object. We can calculate the thickness of the metal core, the oxide crust or of a non-metal lying on the original object. These kinds of images tell us much more about an object hidden under calcareous, oxide and corrosive accumulations (DONELLI, MIHANOVIĆ 1997/1998, 459-477).

#### 4. CLEANING METAL OBJECTS

The cleaning of metallic archaeological finds is a non-reversible stage in the conservation and restoration process. What is removed cannot be recovered. In the entire process this is the most sensitive phase, as the thickness of calcareous, oxide and corrosive accumulation above the surface that is to be removed has to be well judged. Various corrosion products form over the centuries on archaeological metal objects and their surface is, as a rule, preserved in a mineralised form. This is referred to as the original surface. The original surface is one of the corrosion layers that delineate the original shape of the object and may be only a few millimetres thick, but is of exceptional importance to the restorer and archaeologist as it contains information about the object from the time when it was in use. This layer must, therefore, be preserved and only the corrosion products and accumulations above it are to be cleaned (DORAČIĆ 2000, 133).

##### Mechanical cleaning

The mechanical method is recommended and used to remove corrosion products and to clean an archaeological metal object to its original surface. Wherever possible, the cleaning of metallic archaeological objects is carried out mechanically as these methods are the most controllable when done by skilled hands.

Mechanical cleaning is the basic form of work on metal archaeological objects and is done using a wide range of small hand-held tools and tools powered by electricity, compressed air, or ultrasonics.



Figure 9. A micro sandblasting device and chamber (Photo: A. Jozić)

Small hand-held tools include: various chisels, pins, scalpels and brushes. To avoid marking the artefact, the tool should be softer than the material being cleaned but care should be taken to avoid using tools that, when abraded, could adhere to the material. Ultrasonic vibrations can be used either transmitted from small mobile heads as in dental descaling units or in tanks into which objects are immersed in a liquid. A dental micromotor is the most commonly used power tool; it can be fitted with a variety of grinding wheels and burs of various shapes and sizes. The use of micro sandblasting devices is widespread and it is the most useful tool powered by compressed air. The actual micro sandblasting procedure is very simple. The object is held by hand in the micro sandblasting chamber. The other hand is used to control the nozzle from which sand is ejected under pressure. The air and sand pressure is set using a regulator and should be reduced when approaching the original surface. When applying micro sandblasting one should bear in mind the proper choice and granulation of the abrasive substance. The selection of the appropriate type (corundum, glass beads, walnut shells...) and size (50-110 µm) of abrasive depends on the kind of metal and the level of corrosion on the object. During sandblasting the abrasive strikes the surface of the object, entering the smallest pores and slowly removing the accumulated cor-



Figure 10. Mechanical cleaning an iron object under a microscope (Photo: M. Mustaček)

rosion. These provide high cleaning power but minimal stress and vibration to the object. Mechanical cleaning should be done carefully, with full concentration and great caution and always using a magnifying glass or microscope. Carelessness can very easily destroy details and cause the object to lose its authenticity.

##### Chemical cleaning

The chemical cleaning of archaeological metal objects is nowadays for the most part avoided. It is used sometimes to clean objects made of lead, silver or gold that are, as a result of their softness, easily damaged by mechanical cleaning. The most frequent chemical cleaning agents are mildly acidic or alkaline and neutral water-based solutions, while other solvents are rarely used. The most important attribute of these agents is that they eliminate corrosion accumulations but do not erode the metal we are cleaning. Their key drawback is that they, as a rule, also remove the original layer of patina and that objects thus treated lose their original brilliance. In general, however, chemical cleaning is difficult to control, as the agents often penetrate micro-cracks to reach the weakened artefact. It is vital that objects are thoroughly rinsed with water after chemical cleaning to eliminate any soluble product and any remains of the chemicals used so that they do not contribute to further corrosion.

##### Cleaning by electrolytic reduction

Electrolytic cleaning involves a current flow that is almost the reverse of what occurs during electrochemical corrosion. Electrolytic reduction is a method involving the flow of electric energy between two metals submerged in and electrolyte developing hydrogen, which then acts as a reductive substance. In electrolytic reduction electricity is introduced from an external source such as a battery or transformer rectifier.

Corroded metal objects serve as the cathode (negative electrode) while the anode (positive electrode) is made of stainless steel. The most frequently used electrolyte is a water solution of sodium hydroxide. The intensity of the reduction is proportional to the strength of the electricity.

When the current is turned on, the inert metal becomes the anode whilst that to be cleaned is the cathode being fed with electrons. The main reduction reaction at the cathode is the formation of hydrogen gas which – forming as bubbles on the metal surface below the corrosion crust – tends to force this layer off into the bath, thereby "mechanically" cleaning the metal.

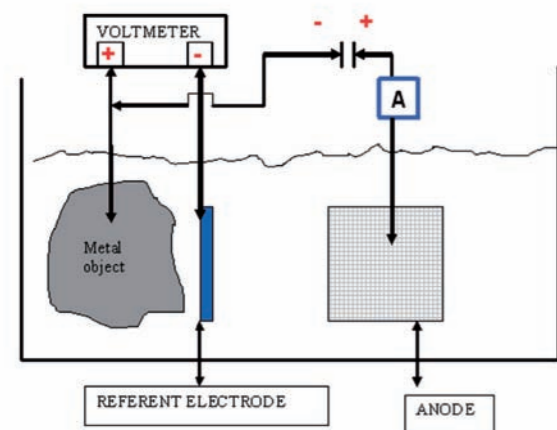


Figure 11. Schematic depiction of the electric circuit of electrolytic cleaning (Drawing: A. Jozic)

Secondary reduction reactions of the corrosion crust form either more easily removed corrosion products or powdery metal, which is then brushed off. Hydrogen forms on the cathode, which reduces and decomposes the corrosion layers of salt while the chlorides from the cathode migrate to the steel anode. The strength of the electricity and the duration of this procedure must be controlled by monitoring the corrosion potential (voltmeter, referent electrode), as it would otherwise completely remove all corrosion layers from the metal object exposing the stripped metal core, which is not our goal.

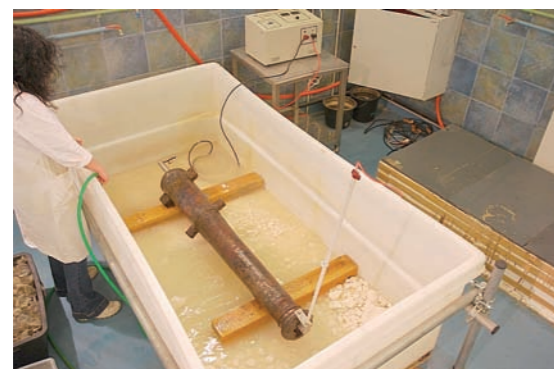


Figure 12. Setting of a bronze cannon for electrolytic reduction process (Photo: A. Jelic)

Archaeological metal objects usually lack a metal core and are preserved for the most part in a mineralised form and where electrolytic reduction is used in preference to mechanical methods because it is "cheaper," being less labour intensive, the cost to the artefact itself must be taken into account (CRONYN 1990, 174).

### 5. ACTIVE STABILISATION

After the removal of a metal object from an environment in which the metal and the corrosion products have been in equilibrium for centuries, attempts must be made to stabilise it. The active stabilisation of archaeological objects implies procedures that involve direct intervention on the object to stop decomposition processes. This includes, for example, eliminating chloride ions, using corrosion inhibitors, synthetic impregnation materials and the like. In contrast to active stabilisation, passive stabilisation does not intervene directly on the metal object, but in the environment around it (microclimate control, use of dehumidifiers etc.).

The role of chlorides is significant in the corrosion of metal objects and we can say that the problem of their removal is one of the key problems in the conservation of metal archaeological objects. The most successful method of eliminating chloride ions from iron objects is the standard procedure in a solution of sodium sulphite. The procedure itself involves isolating the objects in polypropylene nets and placing them in a sulphite procedure vat. The vat is then filled with a solution of sodium sulphite (6.3%) and sodium hydroxide (2%) in distilled water. The conditions of the procedure are anaerobic (the vessel is hermetically sealed) to prevent the oxidation of sulphite into sulphate, which would destroy the material. The cited solution circulates in the vat at a temperature of 50°C and extracts the chloride ions responsible for deterioration from the object. A high pH level and elevated temperature encourage the speedy and effective migration of chloride ions from the object in the solution (HAMILTON 1999, File 10B).

The concentration of chloride is determined by potentiometric titration. The solution in the bath



Figure 13. An iron object isolated in a polypropylene net after the sulphite procedure (Photo: A. Jozic)

is changed once a month for as long as chloride presence can be demonstrated. Once the desalination is completed the treated objects are rinsed in copious quantities of distilled water.

The active stabilisation of bronze objects is usually achieved by submerging them in a 3% alcohol solution of benzotriazole. When bubbles stop evolving, after about 24 - 48 hours, the objects are extracted from the solution and allowed to dry. Upon drying the excess benzotriazole is removed with a pad soaked in acetone. Benzotriazole is a vapour phase corrosion inhibitor that effectively inhibits the anodic reaction of copper dissolution in an acid medium, and stabilises an oxide film in an alkaline medium and thereby increases its corrosion protection. By bonding to

the cation  $Cu^+$ , benzotriazole blocks the formation of nantokite, a basic copper chloride, and thereby the further cyclical corrosion reaction (HAMILTON 1999, File 12; BUDIJA 2001, 147). Benzotriazole has been demonstrated as a very effective copper and copper alloy corrosion inhibitor. Research has, however, shown the compound to be toxic - new effective, but ecologically acceptable corrosion inhibitors should be found.

### 6. GLUING BROKEN OBJECTS AND POSSIBLE RECONSTRUCTION

Damaged metal objects, meaning above all broken and cracked objects received in two or more fragments, are simply glued together. The recommended method is to first undertake a preliminary bonding of the fragments with reversible cyanoacrylate glue, and then to strengthen the binding with two - component, also reversible, glue, in the process of which we may also apply reinforcement in the form of glass fibres. The damaged surface of metal objects may, if required with the aim of achieving structural stability, be filled with the same two - component glue with the addition of the appropriate pigment. Missing pieces are most readily fabricated from a plastic mass. The most frequently used are two - component epoxy resins to which the



Figure 14a.



Figure 14b.

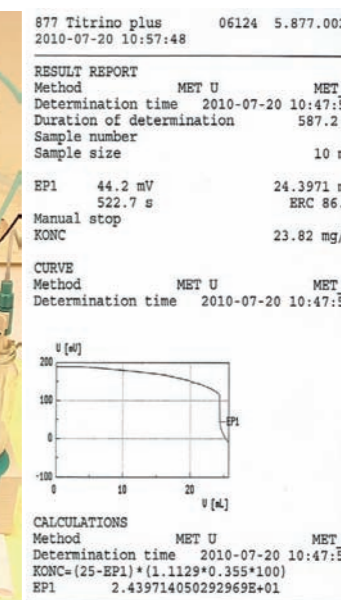


Figure 14c.

Figure 14a, 14b and 14c are showing the device that determines the concentration of chloride and a schematic depiction of the results (Photo: A. Jelic)

appropriate pigment is added and a possible admixture of the appropriate powdered metal. This is a relatively easy procedure and, what is most important; these kinds of supplements are completely reversible. We should only undertake the reconstruction of metal objects if we have a very good grasp of the processing of this material and if the original appearance of the object is evident from the fragments, and we should keep in mind that our actions must not alter the authenticity and condition of the object.

## 7. APPLYING PROTECTIVE COATINGS

Protective coatings on metal objects may be applied by coating, spraying and immersion. Applying a coating with a brush is an acceptable method if the object in question has a smooth surface. Otherwise working with a brush does not allow us to cover and fill small pores and there is a great likelihood that air could be trapped in them, and with it the potential danger of the blistering of the coating and the development of corrosion foci. When applying the coating by brush the layer of coating must be as uniform and thin as possible, as this allows us to apply several layers and achieve a durable multi-layered coating. By spraying a protective coating on the surface of a metal we achieve a uniform thickness and a relatively good filling of pores, but insufficiently good if working with a very porous or rough metal surface. The best results are achieved by applying the protective coating by immersion. Besides the fact that the coating fills every pore, this method also has the effect of reinforcing the object, especially an object of porous structure.

Paraloid B72 and Cosmoloid H80 are the most frequently used protective coatings for archaeological metal objects. Paraloid B72 lacquer is a long-lasting thermoplastic, acrylic resin that does not yellow and is resistant to alkalis, acids and mineral oils. It is prepared as a solution (2 or more percent) in the appropriate organic solvent (acetone, xylene, toluene). Cosmoloid H80 is a microcrystalline wax prepared as a solution with a percentage of toluene. Bronze, silver and possibly gold objects are protected with Paraloid, while a mixture of Paraloid and Cosmoloid is used as a protective coating for iron and lead objects.

It should be noted that a protective layer on archaeological objects does not guarantee permanent protection and that they need to be periodically renewed. Conserved and restored metal archaeological objects need to be handled with care and their state monitored, and a professional should be promptly notified of any changes. It is particularly important to avoid greater oscillations of temperature and relative humidity and to continually monitor the microclimatic conditions in the space in which the objects are kept.

## 8. DRAFTING TECHNICAL DOCUMENTATION

The original condition of the object and all changes that are the result of conservation-restoration interventions should always be documented, and drafting technical documentation should always follow the completion of conservation - restoration work on metal archaeological finds.



Figure 15. Documenting the gradual removal of corrosion and calcareous accumulations from the head of the ancient Apoxyomenos statue – a valuable underwater bronze find (HRZ photo archives)

Technical documentation must, above all, include photographs of the object prior to, during and after interventions undertaken, sketches of the object, reports on laboratory analysis that may have been conducted and radiographic images of the object. To reduce unknown variables in any future procedure, i.e. to precisely determine the level of interventions undertaken, proper documentation should describe all interventions undertaken on the object and all materials used. The importance of properly drafted technical documentation is unquestionable, and a step further should be to organise the documentation in well-designed and broadly accessible databases. This would allow easy access to a great quantity of valuable data and thereby to a better assessment of individual methods of protection.

## CONCLUSION

Conservation - restoration intervention on archaeological metal objects is a very sensitive and demanding operation and should not be undertaken without an understanding of treatment ethics. The success of the intervention depends on a commitment to recognise the original surface under corrosion accumulations, to ensure that the vital interventions undertaken are reversible and that they do not, in the final tally, alter the character of the object. Technological and scientific progress brings with it new development in all fields of activity, including in the fields of conservation and restoration. Every restorer should, therefore, keep abreast of current developments, accept new methods, new experiences, perfect their craft, exchange information and do everything they can to provide the best possible research of objects from archaeological sites and their high quality and professional conservation and restoration.

## VII. Organic Material

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### INTRODUCTION

Organic material is a category of materials that include all artefacts made of plant fibres, animal tissues or bones. The most frequent underwater archaeological material of organic origin found in rivers, lakes, the sea or wetlands are wood, bone, ivory, leather, textile and cord. The level of preservation of archaeological objects of organic materials that have been underwater or in wet soil for years differs, and depends on the type of material, the conditions of the environment in which they were found, and above all of their biodegradation by various microorganisms. The conservation of artefacts of organic materials, from their extraction from water or wet soil to storage and display, is a long process that demands competence, patience, commitment and dedication to the undertaking. The organic materials found are most often from a shipwreck and we find small ship's gear, ship parts and partial or entire sections of a ship's structure.

In this chapter organic material has been divided into wood, as a category unto itself, and other

organic materials, which encompasses all other artefacts made of plant fibres, animal tissues or bone.

### WOOD

Archaeological wood refers to all finds of wooden artefacts and other old wooden manufactured goods that reveal information about people and culture. Because of its mechanical properties, workability and relatively easy accessibility, wood has from time immemorial been used in the most diverse applications characteristic of the period from which they originate. But while it has been very extensively used, its susceptibility of decomposition under the influence of atmospheric conditions, microorganisms and other destructive factors has seen only a small percentage of wood preserved (MALINAR 2007, 85).

Wood, as a substance produced by plants, is chemically composed of: carbohydrates (cellulose, hemicellulose), lignin (phenolic substances) and other components (aliphatic acids, alcohols, proteins and inorganic substances) in a significantly smaller amount. Cellulose is the most important of these molecules and accounts for the majority of the cell, about 40 to 50% of

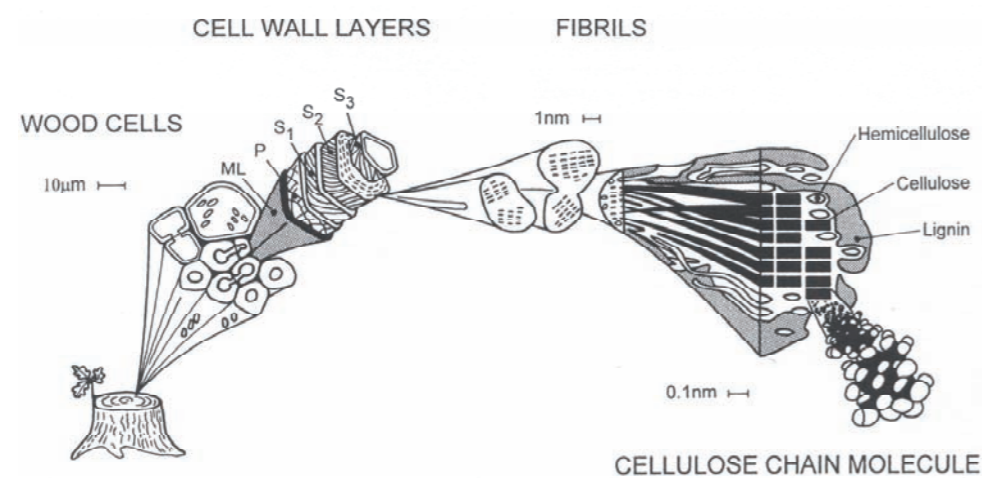


Figure 1. The structure of wood (JONES 2003, 54)

the total mass of wood. Cellulose molecules join to form microfibrils, and they in turn form fibres that give a wood cell its strength and durability. Within the structure of wood, cellulose is surrounded by hemicellulose and lignin. Hemicellulose is the second most important carbohydrate present and accounts for 20 to 30% of wood's cell mass. The function of hemicellulose is not yet fully understood, but it is presumed that it serves as a binding structure between cellulose and lignin. Lignin, which accounts for 20 to 30% of wood's cell mass, serves as the "glue" that holds the microfibrils together, and gives wood its strength. It is also the most stable chemical compound in the structure of wood (Figure 1) (JONES 2003, 53, 54; FORS 2008 13, 14).

The basic element in the structure of wood is the cell that, in its living state, consists of a membrane and protoplasm. When cells die, the protoplasm gradually disappears. What remains is only the membrane - i.e. the walls, which have thickened and lignified - and the lumen (the cell cavity) filled with air or water, depending on the level of moisture in the wood. The cell walls, which are hygroscopic, absorb or transpire moisture, depending on the ambient humidity. This is the process of water absorption and desorption, which results in changes to the dimensions and volume of wood. The moisture level of raw

wood, depending on the ambient humidity, can range from 25 to 65%, where about a third is made up of hygroscopic or bound moisture (MALINAR 2007, 86).

### ARCHEOLOGICAL WATERLOGGED WOOD

Wood extracted from water (rivers, lakes or seas) and wood extracted from wetland is referred to as archaeological waterlogged wood. It can be defined as wood that does not contain or contains little air within its cells, capillaries and micro capillaries. Its structure is also weakened by biological decomposition (RODGERS 2004, 39).

Archaeological waterlogged wood often looks well preserved; an appearance contributed to by inorganic, cold and dark underwater conditions that slow biological decomposition. Waterlogged wood is, however, very weak and deteriorated because water soluble substances such as starch and sugar, mineral salts, pigments and tannins are the first to be dissolved in underwater conditions. Cellulose passes through the process of hydrolysis and attacks by anaerobic bacteria that decompose it leaving only the lignin network. Over an extended period of time the lignin will also decompose. The result of cellulose and lignin decomposition is an increase in the space between cells and the molecules within cells, rendering the wood more porous and more permeable to water. All of the cavities are filled with water, and it is this absorbed water and the remnants of the lignin that maintain the original form of the wood. This, seemingly well preserved wood is soft and spongy to the touch and will only retain its original form while it is wet. Abruptly exposing wet wood to air will cause excess water to evaporate, in the process of which the force of water surface tension causes already weakened cell walls to rupture. Significant changes in dimensions take place, i.e. the contraction, delamination and deformation of the wood. The changes in dimension depend on the level of decomposition and the amount of water present. As the wood dries the changes in dimension are greatest in the direction of the wood's annual growth rings (tangential shrinkage), somewhat less in the direction of the

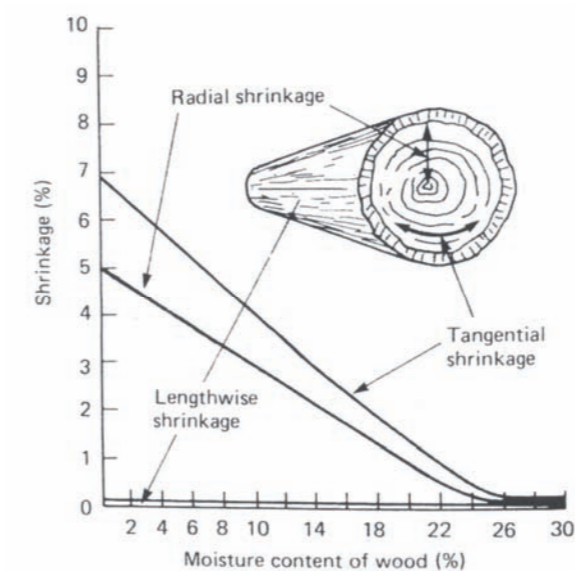


Figure 2. Graphic illustration of raw wood shrinkage (JONES 2003, 64)

medullary rays (radial shrinkage), and in insignificant amounts parallel to the grain of the wood (longitudinal shrinkage) (Figure 2). Dimensional changes which are due to moisture loss or dehydration are present even at freshly cut wood but in smaller percentage, for instance freshly cut oak can shrink 4% radially and 8% tangentially when air dried, while waterlogged oak can shrink over three times more. It is valid in general that dimensional changes depend on the degree of degradation and amount of water present, in fact more water present means less cellulose and lignin and that is also the normal result of the biological and chemical decomposition of the wood. Changes in the wood resulting from dehydration are permanent because subsequent hydration of the wood will not return the cell to its original state. Leaving the wood at the find site is, therefore, recommended until the required conditions for its conservation have been secured, with the necessary protection of the site from possible devastation. If the wood has already been extracted from the water it should be submerged in a pool or some other water-filled vessel to prevent the process of dehydration until the conditions required for its conservation have been secured (CRONYN 1990, 248-254; SMITH 2003, 22, 23).

## THE CONSERVATION OF WATERLOGGED WOOD

The conservation of archaeological wood allows for its further study and exhibition. An important aspect of the conservation of artefacts of waterlogged wood is their stabilisation, i.e. strengthening their structure and maintaining their appearance and original dimensions. It is a complex process that includes replacing water with an impregnating substance that will strengthen the structure of the wood and to undertake the removal of the water in a fashion that will not cause the wood to shrink or come apart. There are a number of methods of conservation known to us that differ one from the other by the impregnation substance used and the process whereby it is applied, and each of these methods should conform with the basic principles of conservation such as the reversibility of the process, a minimum level of

intervention and that it does not alter the character of the object (FORS 2008, 6, 7).

The basic conditions that must be secured for the process of conserving waterlogged wood are the area in which the process is to be conducted and the financial means for both the process of conservation itself and for the fabrication of a pool and the procurement of the impregnation substance. It is also important that space be provided for the exhibition of the object after the conservation process has been completed - a requisite disregarded in most cases. Given that the process of waterlogged wood conservation demands a significant amount of time, we recommend initiating the process only after the necessary conditions have been provided for (MALINAR 2007, 93).

Conservation - restoration work on archaeological waterlogged wood can be divided into the following phases:

1. Photographic documentation and a detailed description of the initial condition
2. Cleaning the object
3. Preliminary investigation
4. Desalination
5. Impregnation
6. Drying
7. Drafting technical documentation



Figure 3. An example of taking measurements and producing a drawing (Photo by: A. Jelić)

### 1. Photographic documentation and a detailed description of the initial condition

The conservation process begins with the initial

documentation of the state of the object as it was found. This phase involves photographic documentation prior to the start of conservation-restoration interventions, a scale drawing is made or at least a sketch with indications of the basic dimensions (Figure 3). Written documentation is also drafted with a detailed description of the object's appearance.

### 2. Cleaning the object

Wooden artefacts extracted from wet soil, muddy riverbeds or the seafloor may be covered by accumulations of impurities and sediments. These accumulations are removed slowly under a slow stream of water (Figure 4). Use soft brushes and increase the temperature of the water to 30°C to remove tougher incrustations. The calcareous shells of marine organisms are a frequent component of accumulations on the surface of wooden objects extracted from a marine environment - they are removed mechanically using scalpels of various profiles and sizes. Traces of iron elements may also be present on wooden objects - visible as rusty orange to reddish-brown accumulations on their surface. These kinds of accumulations are removed by treating the object with a 5% solution of disodium salt of ethylenediaminetetraacetic acid (EDTA:  $C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O$ ) in water. Cleaning is often carried out in parallel to desalination - which also has the effect of accelerating the latter process (JONES 2003, 35, 36).

### 3. Preliminary investigation

Preliminary investigation always includes a visual examination and in some cases taking samples, determining the moisture content, the type and age of wood and x - ray imaging. Besides describing the appearance and shape of the wood, a visual examination also describes its texture, durability and hardness.

Sampling precedes every analysis, and the size and method of sampling depends on the analysis. For most analyses sampling needs to be undertaken while the wood is in water, after cleaning, prior to or during desalination, but certainly prior to the process of impregnation.

The quantity of moisture, i.e. the relation



Figure 4. Cleaning under a slow stream of water with brushes (Photo: M. Mustaček)

between solids and water contained in the wood is an important piece of information in the conservation of archaeological waterlogged wood because, besides being an indicator of the level of the wood's degradation, it also determines the quantity of impregnation substance required in some conservation methods. Wood with higher moisture content, i.e. fewer solids, will, for example, require a greater quantity of impregnation substance than wood that contains less moisture. The moisture content of wood is determined by the thermogravimetric procedure. A wood sample of several grams is first weighed in its waterlogged state and is then dried in a dry kiln up to a constant mass. After weighing the dried sample the percentage of moisture contained in the wet sample is calculated with the following equation (MALINAR 2007, 93):

$$\Psi = [(A - B) / A] \times 100 (\%)$$

Where: A = the mass of the wet sample

B = the mass of the dry sample

The greater the percentage of moisture in the sample of waterlogged wood, the smaller the quantity of solids, i.e. cellulose, in the structure of the wood, and a greater quantity of impregna-

tion substance required.

The moisture content of wood can also be determined as the ratio of water to dry sample, where the formula is:

$$U_{max} = [(A - B) / B] \times 100 (\%)$$

The results are frequently over 100% but it is not uncommon to find wood that contains more than 500% or even 1000% of water. Wood containing more than 200% of water is considered to be degraded. According to the amount of water present waterlogged wood is often classed as:

- Class I: Wood containing over 400% of water. This material is very soft and almost no hard core is present.
- Class II: Wood containing 185 - 400% of water. A hard core is present, but relatively small.
- Class III: Wood containing less than 185% of water. A hard, little deteriorated core is present below a thin decayed surface layer. This class of wood is the most difficult to conserve (JONES 2003, 57; DE JONG et al 1979, 23).

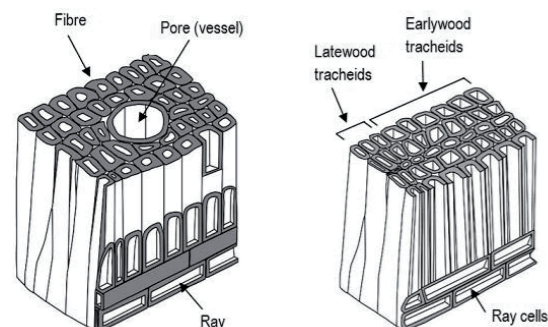


Figure 5. Graphic illustration of hardwood and softwood, magnified 250 times (Image from <http://toolboxes.flexiblelearning.net.au>)

The species of a wood artefact is determined by ascertaining its macroscopic and microscopic characteristics. There are two broad categories of wood, hardwoods and softwoods (Figure 5). Hardwoods are more dense and classified as angiosperms, which refers to broadleaf trees or deciduous trees. They are considered "porous" because they have vessel pores. Typical examples of hardwoods are oak and birch. Softwoods are less dense and classified as gymnosperms and they are needle-bearing trees or evergreen trees. They are considered

"non-porous" because they lack vessel pores. Typical examples of softwood are pine and spruce. This classification is not really related to the hardness of the wood because some softwoods are harder than hardwoods, it is actually based on plant reproduction (JONES 2003, 51).

The age of wood is not essential data to the conservation process. The age of a wooden artefact may be approximately determined from sources such as the dating of the site or shipwreck. More precise data on the time the wooden artefact was created is acquired using technical methods such as the radiocarbon dating method, i.e. dating by way of the radioactive isotope of carbon,  $^{14}\text{C}$ . This method can determine the age of other organic substances such as the age of textile or bone. The age of wooden objects can also be determined by the dendrochronological method, which establishes age by measuring the growth rings of wood and their pattern.

X-ray imaging is used to establish the presence of metal within wooden artefacts, or on their surface if we speculate that metal may be present under calcareous deposit layers. X-rays penetrate wood with more intensity than metal and these images provide us with precise data on the presence of metal. Determining the age of wooden artefacts, the species of wood and x-ray imaging are analyses done in specialised laboratories.

Markers for measuring changes in dimension (radial and tangential shrinkage) can be placed at characteristic points on the wood in this phase of the conservation procedure. The data from measurements before and after impregnation will establish the percentage of the wood's shrinkage (MALINAR 2007, 93).

#### 4. Desalination

Besides water, wood extracted from the sea contains salts, and desalination is essential. Salt is hygroscopic and would absorb water from the air after the conservation process if not eliminated. That would wet the impregnation substance and dissolve it at elevated relative humidity levels. Also it may adversely affect other materi-

als, mostly metals, in the same room or environment in which the treated wood is stored. Desalination is carried out by submerging the wood in a pool of clean tap water to which a disinfectant has been added to prevent the development of harmful microorganisms. The disinfectant may be a fungicide, algicide, orthophenyl phenol, but the most commonly used is a mixture of boric acid and borax because of its lesser toxicity. A 2% solution of a mixture of boric acid and borax in a ratio of 7:3 is added to the desalination water. The water in the desalination pool is changed, as a rule, every four weeks, until the concentration of excreted salts reaches its constant maximum. With successive changes of the water, i.e. with every new change of water, the concentration maximum drops. This process is monitored by determining the quantity of excreted salts, i.e. chloride, in a sample of the water used for desalination. The electrical conductivity of the water sample is measured with a conductivity meter - it grows proportionally with the increase of salts in the solution. More precise values are arrived at by measuring the concentration of chloride in the sample by potentiometric titration (Figure 14; page 57). When the measured value falls to the value for clean tap water, the desalination process is deemed completed. If possible, continuing desalination in distilled water is recommended to reduce the quantity of chloride in the wood to a minimum (BORRELLI 1999, 3; MALINAR 2007, 93).

#### 5. Impregnation

The conservation of waterlogged wood is a complex process that involves impregnating wood, i.e. replacing water with a material that will strengthen the structure of the wood and to undertake the removal of the water in a fashion that will not cause the wood to contract or come apart. There are a number of methods of conservation known to us that differ one from the other by the impregnation substance used and the process whereby it is applied. The most common techniques for treating waterlogged wood are discussed below.

##### Polyethylene glycol (PEG) method

Polyethylene glycol (PEG) is a synthetic polymer constructed of the monomers ethylene oxide

and water with the general formula  $\text{HO}-(\text{CH}_2\text{OCH}_2)_n-\text{H}$ , where "n" is the number of monomers in the PEG molecule - PEG 200, for example, has four monomers in its chain, and  $n=4$ , while PEG 4000 has ninety monomers and  $n=90$ . It is used in the conservation of waterlogged wood as a replacement for water in the structure of wood because it forms hydrogen bonds and provides mechanical support of deteriorated wood. There are several kinds of polyethylene glycol that differ one from the other by molecular mass. Polyethylene glycols of lower molecular mass, such as PEG 200 to PEG 600, are liquid at room temperature, and penetrate the structure of wood deeper, while polyethylene glycols of greater molecular mass, such as PEG 1500 through to PEG 4000, are in a solid state, and while they penetrate less they are superior in terms of stabilizing the structure of wood. They are soluble in water, alcohol, benzene and other organic solvents and, because of their low toxicity, are numbered among substances that do not present a health risk (HAMILTON 1999, File 6; JURIĆ 1995, 79; <http://www.maryrose.org/>)

Conservation of waterlogged wood with polyethylene glycol simultaneously eliminates water and impregnates wood. Wood, if necessary previously isolated in a polypropylene net, is placed in a vat containing a PEG solution.

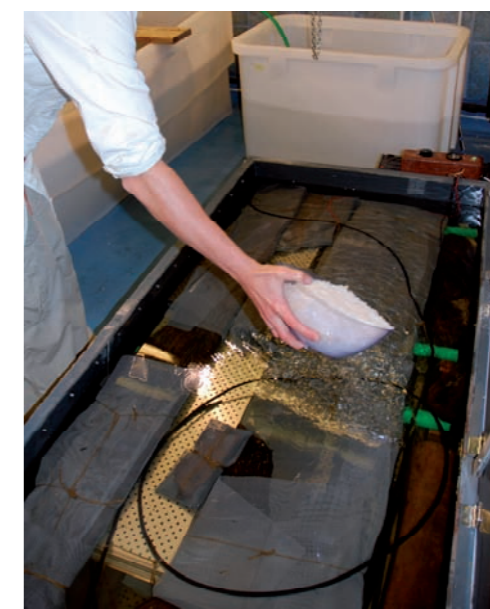


Figure 6. Adding PEG in vat containing waterlogged wood (Photo: A. Jelić)

Disinfectant is used if water is used as the solvent - for example a 2% solution of a mixture of boric acid and borax in a 7:3 ratio. If alcohol is used as the solvent disinfectant is not required. The temperature of the solution in the vat, thermally isolated and covered, is gradually increased until, after a few days or weeks, it reaches a temperature of 60°C. During that time the percentage of PEG is increased as new and previously calculated quantities of PEG are added to the solution on a daily basis (Figure 6). The size of the PEG increments is dependent upon the condition, size and species of the wood being treated (HAMILTON 1999, File 6; MALINAR 2007, 94-105).

Two techniques of adding PEG are used, and we differentiate between the two - phase and parallel methods. In the two - phase method PEG of a lower molecular mass is first added to the solution, followed by PEG of greater molecular mass. The parallel method involves simultaneously adding PEG of smaller and greater molecular mass as a mixture. What is common to these methods is that the PEG slowly penetrates into the wood and replaces water in its structure. By measuring the concentration of PEG in the solution we can determine the quantity of absorbed PEG at any given time (Figure 7). When the concentration of PEG reaches a level of 70 to 90% no new PEG is added, and the wood is left in the solution for a time. Usually, if a minimum concentration of 70% PEG is achieved, the wood will remain stable. In some cases, if the percentage of PEG in the solution is more than 70%, water may be drawn out of well-preserved wood without being replaced by PEG, which will cause the wood to collapse. After the wood is saturated with the impregnation substance it is taken out of the vat and gradually dried (FORS 2008, 7, 8; MALINAR 2007, 105).

For smaller objects alcohol can be used in the

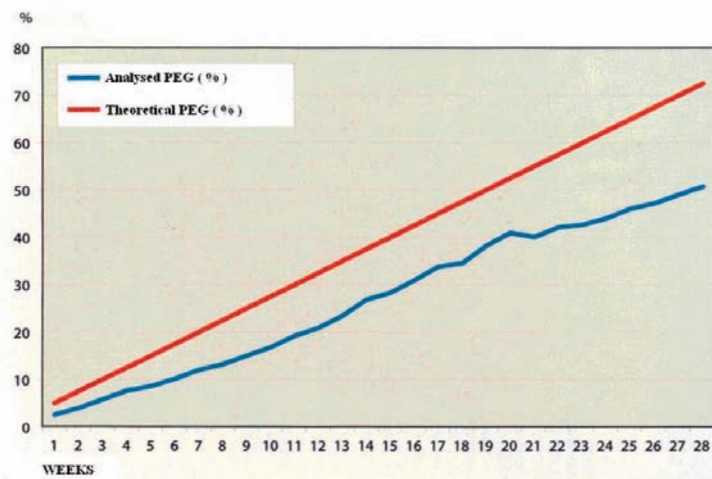


Figure 7. An example of the graphic depiction of the relation between theoretical PEG concentrations in a solution through a 28-week period and those established by analysis (MALINAR 2007, 106)

PEG solution instead of water. It is recommended that the wood be dehydrated before being placed in the PEG/alcohol solution. Dehydration is done by placing the wood in at least three baths of ethanol. However, it is not critical that all the water must be removed from the wood before the treatment because PEG is soluble in both water and alcohol. The use of alcohol instead of water considerably reduces treatment time and the finished product is lighter in both weight and colour. However, the treatment process is more expensive and there is always the risk related with heating the alcohol because of its

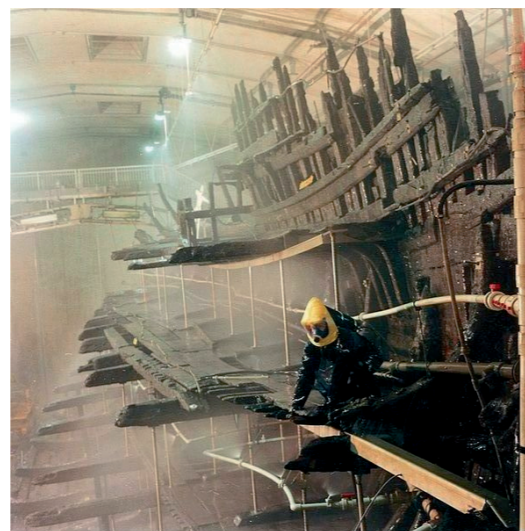


Figure 8. Conservation of the remains of the wooden structure of the Mary Rose using PEG solution spraying ([http://en.wikipedia.org/wiki/Mary\\_Rose](http://en.wikipedia.org/wiki/Mary_Rose))

flammability (HAMILTON 1999, File 6).

The method of conservation with polyethylene glycol is one of the first and the most frequent methods used. However, laboratories that intend to conserve large artefacts of waterlogged wood must be prepared to make major investments in both equipment and chemicals. A substantial vat must be constructed with the capability to heat and circulate the solution and there is also a considerable amount of PEG required, while conserving small artefacts is a simpler process. Small vats are needed that can be placed in a thermostatically controlled oven and only a small amount of PEG is required (HAMILTON 1999, File 6). Regardless of investment it is still the most suitable method for the conservation of large artefacts of waterlogged wood. The well-known 17<sup>th</sup> century warship *Vasa* (Figure 11; page 11) and the 16<sup>th</sup> century warship *Mary Rose* where conserved using this method. Wooden ship's structures are conserved first by spraying with water to effect the essential process of desalination, and then with a PEG solution in the impregnation procedure (Figure 8). The conservation of finds of this size usually requires the construction of special hangars in which the process of conservation is to be carried out, as is the cases of the two examples cited.

The drawback of the method is the length of the process. It is lengthy and the heating involved consumes a great deal of energy and material. As an impregnation substance PEG is good at stabilizing wood, but it does render it darker in tone, heavier and gives it the appearance of having been coated with wax. PEG also causes metals such as iron, lead, copper, bronze and aluminium to corrode. It must, therefore, not be used as an impregnation substance for wood in combination with any of the cited metals (UNGER et al 2001, 420-422).

Also, after conservation and with the passage of time, the elementary sulphur that is a constituent element in the structure of wood oxidises. Sulphur oxidation synthesises sulphuric acid and its salts, which increases the acidity of wood and causes its degradation. The synthesis of sulphuric acid and its salts is visible as a light yellow

powder on the surface of the treated wood (Figure 9). Preventing this synthesis and eliminating synthesised sulphuric acid and its salts is a major problem affecting wooden finds conserved using the PEG method.

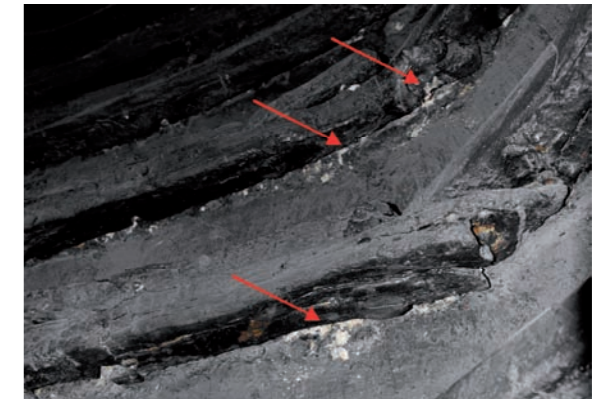


Figure 9. An example of the synthesis of sulphuric acid and its salts on the surface of wood conserved using the PEG method (Photo: A. Jelić)

#### Sucrose method

The method of conserving waterlogged wood with sucrose (sugar) was developed as an alternative to more expensive methods. The sucrose, i.e. sugar used is white refined sugar because it is less hygroscopic than brown or unrefined sugar and will, therefore, attract less airborne moisture.

Wood is submerged in a bath of prepared 1 to 5% solution of sucrose in water to which an antimicrobial substance and insecticide has been added. The concentration is increased by the regular addition of set quantities of sucrose to the solution. The addition of modest percentages (1 to 5%) is recommended until its concentration reaches 50%. After that the sucrose doses are increased to 10% until a 70% concentration is achieved. When the wood achieves equilibrium with the achieved concentration of sucrose in the solution, it is taken out of the solution and slowly dried (HAMILTON 1999, File 6).

This conservation process is similar to the PEG method. The apparatus required is similar with the difference that metal vats can be used since sucrose does not cause metal corrosion. The wood is stable after conversion and it largely retains its natural appearance. This is one of the

cheapest methods of wood conservation, as it does not entail heating the solution given that sugar is dissolved at room temperature. The shortcomings of the method are the length of the process, as with the PEG method; the danger of a possible attack on the treated wood by insects and other pests; and a lack of data on the success of the method over a longer span of time (UNGER et al 2001, 426-428).

#### Acetone - rosin method

The method is based on replacing the water in wood with a natural resin, in this case, pine rosin also called colophony as the impregnation substance. Mostly it is used to conserve well-preserved hardwoods. The rosin is insoluble in water, and is dissolved in organic solvents, the most frequently used being acetone or alcohol. For the method to be successful it is important to use only lump, technical - grade rosin and pure acetone or alcohol.

Since rosin does not mix with water it is important to remove the water from the structure of the wood. The dehydration of waterlogged wood is achieved by submerging the wood in three successive acetone baths. The process of dehydration in each of the baths lasts from two to four days until all of the water is replaced by acetone. For objects of 5 to 10 cm thickness the dehydration process last four days, while for objects thinner than 5 cm the process lasts for two days in each of the acetone baths. The dehydrated wood is then placed in closed containers with a saturated solution or rosin in acetone. The solution contains 67% rosin, with a 52° C process temperature. The process of impregnation lasts from two to four weeks, depending on the thickness of the object, upon which the wood is taken out of the solution and the excess rosin removed with rags moistened with acetone.

In some cases, usually when conserving very well preserved hardwood, the

artefact can be pre-treated with 10% hydrochloric acid (HCl) after washing but before dehydration. Artefacts with a thickness of 5 - 10 cm should be submerged in the solution for about four days, and artefacts thinner than 5 cm for about two days. After this pre - treatment the treated artefacts need to be neutralised by rinsing them under running water for about 3-5 days. In treating the wood with hydrochloric acid, the organic acids – which are one of the structural components of wood – break down, which can improve the penetration of rosin into the wood. However, hydrochloric acid can cause damage to an artefact by cracking its surface after conservation so the pre - treatment is often eliminated.

The acetone - rosin method can be carried out in ethanol instead of acetone, especially if treatment is carried out in PVC vessels. Also it can be carried out at room temperature but for a longer period to ensure the complete saturation of artefacts with the colophony solution.

The advantages of the method are the stability of the treated wood and wood that is dry, strong and low in weight that can be easily glued and repaired (Figure 10). Since rosin does not react with metals this method can be used for conservation when wood is present in combination with metal. The drawbacks are the flammability of acetone and the high cost of the process. This method is recommended for the conservation of smaller waterlogged wood artefacts of considerable significance (HAMILTON 1999, File 6; UNGER et al 2001, 399).



Figure 10. Wooden pulley before and after conservation with acetone - rosin method (Photo: A. Jelić; Drawing: O. G. Eibar)

#### Lyophilisation (freeze - drying) of waterlogged wood

Lyophilisation, or drying by sublimation, is a process of dehydrating substances by freezing whereby the water present within the substance passes into the solid state, and then reducing the surrounding pressure and increasing the temperature to create conditions that allow the water to sublime directly from the solid to the gaseous state (Figure 11).

This method of dehydration is used in the conservation of waterlogged wood. The process is modelled to account for the fact that freezing water creates crystals of ice that have a greater volume than water in the liquid state, which causes the degradation of the cell walls within the structure of wood. To prevent this degradation the waterlogged wood is treated with a low percentage PEG solution prior to the lyophilisation process. The PEG absorbed from the solution works within the structure of the wood as an inhibitor to the growth the ice crystals during the freezing process, and as a protection against possible changes in dimension. A 10% PEG solution will prevent the growth of ice crystals, while for the conservation of waterlogged wood a PEG solution of at least 40% of is needed before the dehydration process. The dehydration process is carried out in a lyophilisation chamber (Figure 12) with pressure and temperature regulation until all the water is eliminated or until a constant mass is achieved in the wood being



Figure 12. A freeze drier ([http://www.kambic.com/produkti\\_liofilizatorji.php](http://www.kambic.com/produkti_liofilizatorji.php))

treated (JONES 2003, 62; HAMILTON 1999, File 6).

This conservation method is applicable on smaller waterlogged wood artefacts since the process is limited by the size of the lyophilisation chamber. The method can also be applied on larger artefacts when they are disassembled or cut because they cannot be extracted from the find site in their integral state as was the case with the Bronze Age ship found in the port city of Dover in England, or with the remains of the ancient Greek ship *Kyrenia*. In this case it is possible to dry smaller sections, if sufficiently small, in a lyophilisation chamber after which they are reassembled (BRUNNING et al 2010, 30; KATZEV 2005, 73, 74).

This conservation is the shortest, but also the most expensive because of the high cost of the device indispensable to the process. Conservation using this method can only be undertaken in restoration workshops that possess this device.

#### Silicone oil treatment

The use of silicone oil for the stabilisation and conservation of organic materials has been conducted and tested for over 20 years. This

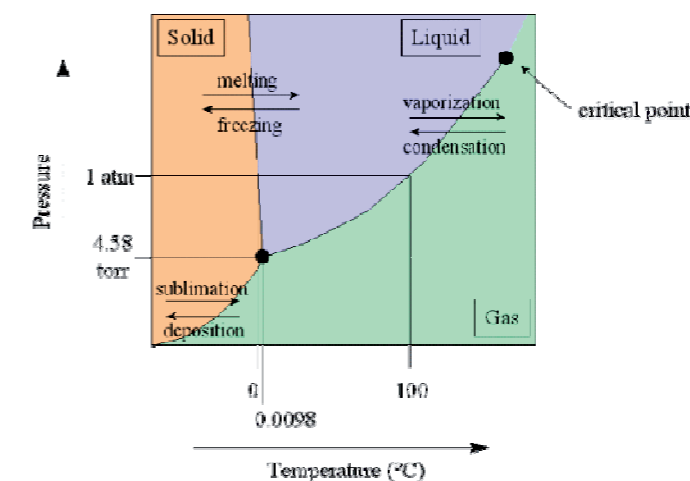


Figure 11. Water phase diagram (<http://eskola.hfd.hr/clanci/pahuljice/faznidijagram.htm>)

is a new preservation technology and it should be considered when choosing an appropriate conservation method.

Silicone oil is a collective term for any polymerised siloxanes with organic side chains. The basic formula is  $[R_2SiO]_n$  with R being an organic side chain such as methyl or ethyl. The silicone oil treatment is comprised of three components; a silicone oil, a cross-linker and a catalyst. When these three components are combined a cross-linking with each other and with the cellular walls of the treated object will occur creating scaffolding for the cell, but leaving the rest of the cell empty of bulking agents. In fact, the cross-linker in this combination links with the carbinols (-COH) in the cell structure, with the silicone oil and with itself, creating a three-dimensional network inside each cell. The catalyst in the combination speeds up this polymerisation that will fix the network in place and provide the strength and support of the cell walls.

The silicone oils are mainly silanol-terminated polydimethylsiloxane polymers, and they are present in different viscosity from very low to very high. Which one to use mostly depends on viscosity. The conservation of organic materials such as wood and bone will require a silicone oil of low viscosity. Mostly it is used as a mixture of two silicone oils with different molecular weight and therefore viscosity. One is a low viscosity polymer and the other is slightly thicker. This way the different needs of the material being conserved can be provided for, for example wood that has a soft exterior zone surrounding a harder and possibly structurally sound core. The lower viscosity polymer will penetrate the tight, solid matrix of the less structurally damaged core wood, while the more viscous polymer will easily penetrate the softer exterior.

Methyltrimethoxysilane and isobutyltrimethoxysilane are considered as good cross-linkers for this polymerisation and they are added in a small percentage to the silicone oil. Dibutyltin-di-acetate is mostly used as a catalyst, and can be applied topically or vaporised in an airtight environment.

As silicone and water do not mix, water must first be eliminated from the waterlogged wood. That can be accomplished using a series of dehydration baths, starting with ethanol and working through to several baths of fresh acetone. To make sure all water is eliminated water is first exchanged with ethanol and then ethanol with acetone. The length of time in each bath is dependent on the material, size and condition of the artefact. Dehydration can also be done under a vacuum to ensure complete dehydration.

Once dehydration is complete, the artefact is transferred to the silicone oil/cross-linker solution while thoroughly soaked with acetone. The solution is mixed by adding 3-4% of cross-linker, by weight, to the silicone oil or to a mixture of two silicone oils with different viscosities. It is often necessary to weigh down an immersed artefact to prevent its flotation. This can be done with a plastic or aluminium mesh with weights. The artefact can be kept in the solution for a long time but usually six weeks is more than enough, while smaller ones require an even shorter treatment time. Sometimes the solution with the artefact can be put in a gradual and slight vacuum to speed up the acetone/silicone oil solution displacement process. A vacuum must be used carefully and only if the artefact is well preserved, otherwise it can cause damage and the collapse of the wood cells. With severely damaged artefacts, it is better to conduct the displacement process at ambient pressure. At ambient pressure, acetone will vaporise more slowly from the cells of the wood, allowing the polymer solution slowly into the cells. After the displacement process the artefact is removed and patted dry with a dry rag to remove excess silicone oil from the surface.

The silicone oil/cross-linker mixture can also be applied topically on the surface of the artefact. The simplest and most gentle way of applying is by rolling a cotton swab dipped in the solution onto the surface, then following with a clean swab to remove the excess. This can be done more than once on a surface for a deeper penetration. To ensure that there is no excess in the material before catalysing, it can be carefully wrapped in absorbent paper towels and left to

rest, until no more oil comes out.

An artefact cleansed of excess silicone oil has to be placed in a closed environment with a small dish containing small volume, approximately 10-15 ml, of catalyst. A resealable plastic bag or a sealable plastic container can be used as the closed environment. The catalyst has to be exchanged every 24 hours as it has a limited working life. Large objects require daily changing for about two weeks; smaller objects need less time. Also, everything can be placed in oven heated to 52°C which will accelerate catalyst vaporisation and thus reactivity with the polymer solution in the artefact. After catalysis, it is recommended that the artefact be placed under a fume hood for one or two days (LUDWICK 2012, 11-16; SMITH 2003, 23-26).

The advantage of silicone oil treatment is in naturally coloured and lightweight wood that is strong enough for handling in any environment. Dimensional changes are small and the conserved wood is stable, making storage climate control unnecessary. Silicone oil can also be used when wood is in combination with metal because it has no negative impact on metals. Silicone oil is recyclable, so the solution can be used again, which reduces the long-term costs. The main drawbacks are that this treatment is not reversible and that the initial costs of materials are considerable (<http://nautarch.tamu.edu/Theses/pdf-files/Cox-MA2008.pdf>).

## 6. Drying

Once the process of impregnating artefacts of waterlogged wood has been completed they can be dried without dimensional changes such as contraction, delamination and deformation. What is important is that the drying process is conducted slowly in controlled conditions. The best results with regard to achieving the least changes in dimensions are achieved at a relative humidity of 50-55%, achieved by gradual reduction from 100% relative humidity, and a temperature of 20°C. If the wood is conserved with the PEG method the objects are sprayed intermittently with a low percentage PEG solution, for example 20% solution of PEG 4000, during the drying process. The excess PEG is removed from the

surface with a jet of hot water or air until the structure of the wood is visible. The drying process conducted at specified controlled conditions can last for months or even years depending on the size of the artefacts (JONES 2003, 71-73; SMITH 2003, 25).

After drying, if necessary, the artefact can be reassembled. If the artefact is large or conserved using the PEG method the parts should be connected with wedges because they can hold two large pieces or two waxy pieces together. The wedges should be made of stainless steel or another strong and noncorrosive material. If the artefact is small or can be glued then the use of cyanoacrylate glue is recommended, although other types of adhesive that adhere well to treated surfaces can also be used. The fragments of the artefact can be connected without gluing or connecting with wedges. This is usually the case with the fragments of a ship. In this case they are properly arranged and placed in a specially designed bracket in the shape of the ship in question.

If cracks have occurred or if an object needs correction the gaps are filled with putty for wood. Araldit SV 427 with Hardener HV 427, a two-component epoxy resin paste for manual application is usually used for filling gaps but other commercial putties can be used as well (Figure 13).



Figure 13. Filling the gaps (Photo: A. Jelić)

### 7. Drafting technical documentation

Technical documentation should be drafted upon the completion of conservation - restoration work on waterlogged wood artefacts. This documentation must, above all, include photographs of the object prior to, during and after interventions undertaken, reports on laboratory analysis that may have been conducted and radiographic images of the object. All interventions undertaken on the artefact must also be described in detail, indicating all materials used. Good documentation provides information on all changes to an artefact that are the result of conservation-restoration work, and reduces the number of unknown factors in any future procedure.

The cited are only some of the known methods of conserving archaeological waterlogged wood most often implemented. The choice of treatment depends on several factors:

- The size of the object (only few laboratories are available to treat large objects or have any kind of freeze - driers, although many laboratories have different types of treatment tanks);
- The degree of degradation (the varying remaining ratios of lignin to cellulose in wood will determine the type of treatment);
- The species of wood (a very porous wood is easier to impregnate than a non - porous one);
- Composite objects (when wood is in combination with metal only particular methods can be used);
- The preservation of surface detail (if there are details on the wood surface one has to consider which method to use) (<http://www.kolo5200.si/conservation>).

The substances used for wood conservation should also satisfy some general requirements such as good penetration into the wood, the strengthening and stabilisation of wood, the long-term dimensional stability of wood, minimal impact on the wooden object and the reversibility of an intervention. However, reversibility as a desirable aspect of the conservation process is actually misrepresented because it is impossible to remove all of the treat-

ment substance from a conserved piece of waterlogged and badly deteriorated wood. Some of the treatment substance will chemically bond with the remaining lignin and cellular structures of the wood or will simply be trapped in cellular voids. Furthermore, the process of removal will cause more damage than benefit to the already weakened structure of the wood. The reversibility of an intervention should refer to the ability to re - treat an artefact that has already been treated, if re - treatment is necessary.

Whatever the method we decide to use, however – after conservation treatment the wood must be kept in controlled microclimatic conditions, which is common to most conservation methods. The most commonly cited values are a temperature of  $18^{\circ}\text{C} \pm 2^{\circ}\text{C}$ , a relative humidity of  $55\% \pm 2\%$  and lighting that does not exceed an intensity of 200 lux (BRUNNING et al 2010, 30; HAMILTON 1999, File 6).

### OTHER ORGANIC MATERIAL

Organic materials are substances that originate from once living organisms, and are constructed of chains of animal protein molecules and of cellulose or other polysaccharides of plant origin. By their chemical composition these substances are organic polymers, the fundamental building block of which is the element carbon. In general organic material is built of large molecules, i.e. complex polymers, formed by the chemical bonding of the same or similar smaller molecules called monomers. The chemical bonding of monomer molecules creates chain molecules, which, bonded to one another, form microfibrils. Microfibrils group to form the fibres that give organic material its sturdiness and durability (CRONYN 1990, 238).

Bone and ivory, and sometimes leather, are the most frequent of the other archaeological materials of organic origin conserved at our workshop.

### BONE AND IVORY

Bone and ivory are sturdy binding tissues, the interior of which is built of collagen fibres, calci-

um and other minerals such as phosphorous, magnesium, sodium and carbonates. Bone is perforated with tiny canals together with a number of larger holes. Ivory does not have a canal system, but rather a layered structure caused by growth rings. It also has a structure of very fine tubules typical of ivory. The organic tissue of both bone and ivory is ossein and it constitutes at least 30% of the total weight of the material. It is often difficult to distinguish between bone and ivory unless the material is examined microscopically. Bone is granular tissue with characteristic pores while ivory is hard and has very dense tissue. Their structure is porous, which makes them sensitive to salts and impurities. This structure also promotes microorganisms that decompose organic substances, i.e. collagen fibres. Also in waterlogged sites, ossein is decomposed by hydrolysis and the inorganic framework is disintegrated by acids, rendering them into a very soft material (CRONYN 1990, 275, 276; HAMILTON 1999, File 3).

### Bone and ivory artefact conservation

The conservation-restoration process consists of the same phases described for the conservation of waterlogged wood. The purpose of the process is to prevent physical damage to bone/ivory artefacts, such as their cracking and splitting which are the consequences of uncontrolled drying. They can only be cleaned, strengthened and stabilised, while the need for an impregnation process depends on the level of decomposition present in an osseous artefact. Most of the time satisfactory restoration is impossible.

### Cleaning and desalination

Bone or ivory artefacts extracted from a marine environment must be desalinated to eliminate soluble marine salts, which are hygroscopic and the crystallisation of which causes physical damage to non - desalinated artefacts.

Desalination is carried out in tap water over an extended period with frequent changes of water. For more important artefacts it is recommended that desalination be carried out gradually in a mixture of seawater and fresh water. The percentage of fresh water is gradually increased to

100% and is then changed as many times as required until the soluble salt level reaches that of fresh water. Finishing desalination with several changes of distilled water is recommended to reduce salt to a minimum value. The level of salts is measured using a conductivity meter, which shows the presence of all soluble salts and is therefore a more reliable indicator of salt presence than an individual test for a specified salt.

The removal of insoluble salts or stains is done prior to or during desalination. It is recommended that they be removed mechanically using picks or other tools instead of by chemical cleaning. If chemical cleaning is necessary then the material must be thoroughly soaked with water before applying any chemical to prevent chemical absorption and to ensure it remains on the surface of the artefact. The chemical cleaning should be localised on the stain and done with a brush or swab in as many steps as are needed to clean the area. Calcium carbonate stains can be removed by using 5-10% hydrochloric or formic acid, iron stains with 5-10% oxalic acid and sulphide stains with 5-10% hydrogen peroxide. When using chemical cleaning the artefact must be rinsed in water to remove all residue of the treatment chemical (HAMILTON 1999, File 3).

### Impregnation and drying

Bone and ivory are materials prone to cracking and splitting during the dehydration process, i.e. drying. If it is established that the osseous structure of the artefact has been weakened and that dehydration could cause the cracking of the osseous structure, the osseous artefact is impregnated prior to drying. The consolidation can be carried out in a 5-10% solution of a suitable synthetic resin such as polyvinyl acetate (PVA) or Paraloid B72 in organic solvent alcohol or acetone or toluene. The consolidant can be applied by brush to the surface several times, each time allowing it to dry, by immersing the artefact, or by immersion under a vacuum for the best results. Before consolidation the water has to be removed from the artefact in a series of alcohol baths. The alcohol content in an alcohol/water bath should be gradually increased until the final bath is of 100% alcohol. After several

baths of 100% alcohol it is recommended that the artefact be immersed in two baths of acetone to ensure that all the water is removed (HAMILTON 1999, File 3).

Bone can also be consolidated by immersion in a 50% solution of polyvinyl acetate (PVA (C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>)<sub>n</sub>) in distilled water for a period of two weeks. In this case total dehydration is unnecessary. This is followed by gradual drying in a closed chamber over a period of one week.

If the osseous artefact is well preserved and its structure not significantly weakened, impregnation prior to gradual drying is not required. For example, the bones and the ivory from the wreck of the *Mary Rose* were only cleaned and desalinated before gradually drying at a temperature of 20°C and a relative humidity of 50%. If an osseous artefact needs to be glued then a concentrated solution of Paraloid B72 or PVA dispersion can be used (JONES 2003, 100; RODGERS 2004, 173). After conservation - restoration treatment, osseous artefacts should be kept at a temperature of 15 to 22°C, a relative humidity of 45 to 65% and lighting of 100 to 200 lux (VOKIĆ 2007, 36, 59, 71).

## LEATHER

Leather artefacts in an aqueous environment deteriorate over time. The water - soluble substances such as tannins, fats and oils, that are a constituent part of leather material, dissolve in an aqueous environment as a result of which collagen fibre is rendered more susceptible to hydrolysis, i.e. decomposition in reaction with water. If waterlogged leather is dried without prior conservation the weakened collagen fibre means that there will be changes in dimension, i.e. the leather will contract. The consequence of this is that the leather becomes very fragile and weak and susceptible to bio-decomposition and the negative effects of environmental factors such as light, air pollution and changes in relative humidity. Besides this, the great quantity of soluble salts that have diffused into the structure of the leather from the sea, besides rendering the leather hygroscopic, may also cause abrasion to the leather (SMITH 2003, 60, 61).

### Leather artefact conservation

The conservation of leather artefacts endeavours to stabilise the structure of leather and retard its further decomposition. The conservation - restoration process consists of the same phases previously cited for the conservation of wooden artefacts, and those already described will not be repeated here.

#### **Cleaning and desalination**

The conservation of leather artefacts begins with the essential process of desalination and cleaning. Only once the soluble salts, sediment and impurities have been eliminated the collagen fibre, which may react with other materials besides water, is stabilised.

Leather artefacts are cleaned mechanically under a soft stream of water - soft brushes and sponges may also be used. In the case of persistent impurities the leather may also be cleaned by chemical means - the use of small quantities of non - ionic detergents (a solution of about 1%) is permissible in these cases. The chemical cleaning of artefacts must be followed by a thorough rinsing under a stream of water. When cleaning one should bear in mind that it is often better to not remove a stable impurity than to damage the leather by the very process of cleaning (JONES 2003, 97; SMITH 2003, 62).

Desalination is done in tap water over an extended period of time with frequent changes of water. Changing the water every week is recommended, as is using distilled water for the last changes of water.

#### **Impregnation and drying**

The conservation of waterlogged artefacts may be undertaken with the aid of a number of different methods. The conservators involved in the conservation of remains from the wreck of the *Mary Rose*, for example, have treated leather using seven different methods. The result of the research has revealed two methods to be superior in the conservation of waterlogged leather artefacts. One of these two is the polyethylene glycol method (JONES 2003, 98, 99).

### **The polyethylene glycol (PEG) method**

Desalinated and cleaned leather artefacts are immersed in a 10% PEG 400 solution in water or alcohol at room temperature. The percentage of PEG is increased every week by 10% until a 30% solution is achieved. After a week of soaking in the 30% solution the artefact is taken out, the excess PEG is removed from the surface using toluene or water and the artefact is gradually dried in a controlled atmosphere, i.e. at a temperature of 20°C and a relative humidity of 55%. Artefacts whose surface remains soft even after impregnation may be subject to further superficial consolidation by coating them with a solution of Paraloid B72 in toluene (JONES 2003, 100).

The conservation of leather artefacts using PEG is considered a satisfactory method even though it has been demonstrated that it is better if the leather is dehydrated in a freeze drier (Figure 12), as was the case in the conservation of leather artefacts from the wreck of the *Mary Rose*. In that case it suffices that the leather artefacts are treated with only a 10% PEG solution over a two - week period prior to their dehydration in a lyophilisation chamber (JONES 2003, 100).

### **The glycerine method**

A frequently used method for the conservation of waterlogged archaeological leather is the glycerine method. Artefacts are immersed in a 10 to 40% solution of glycerine in alcohol or water for a period of two weeks. The artefacts are then dehydrated by immersion in an acetone bath three times for three hours each time. Since glycerine does not mix with acetone it remains in the structure of the leather after the dehydration process (HAMILTON 1999, File 7).

After drying leather artefacts are kept at a temperature of 15 to 22°C, a relative humidity of 45 to 65% and an illumination intensity of 100 to 200 lux (VOKIĆ 2007, 36, 59, 71).

The successful conservation of waterlogged leather artefacts establishes the stability and elasticity of the artefact, restoring their shape and form while not altering the chemical or physical character of the leather.

## CONCLUSION

The treatments discussed in this manual are used to conserve waterlogged material and material from marine sites. Every artefact is different and requires a different method of conservation, which can, to a degree, be modified. With most methods, it is not a question of which treatment is better or preferred. The conservator-restorer has to be familiar with various treatments and be able to decide in which situation particular treatments are the most appropriate. After the careful study of the object it is up to the conservator - restorer to select which of the existing conservation methods to apply. The decision depends on many factors such as: the desired outcome of the conservation process the wood should be light in colour, glueable, flexible or rigid, insensitive to fluctuations of humidity; if the wood is part of a compound wood/metal artefact; the degree of degradation of bone or ivory; the equipment and chemicals available in a workshop; the resources and facilities available to the conservation - restoration workshop. After treatment the organic artefacts should be chemically stable which can be ensured only if the artefacts are stored or displayed under optimum conditions. Otherwise they can become chemically unstable and re - treatment could be required. Organic artefacts should, therefore, be periodically inspected and evaluated during proper storage so that re - treatment is delayed as long as possible or, if necessary, reduced to simple and brief re - treatment.

The conservation method selected should be the least detrimental to the artefact, but also satisfy the basic principles of the conservation process, such as its reversibility in relation with possible re - treatment, minimum intervention, compatibility of used materials and that the process does not alter the character of the object. The right choice of method is the result of a solid understanding of the problematics of conservation and many years of experience in the conservation of archaeological waterlogged wood and other archaeological organic materials.

## VIII. The Conservation and Restoration of Stone Finds

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### THE DETERIORATION OF STONE AND REASONS FOR CLEANING

The most common causal agents for the deterioration of stone are: the human factor, natural catastrophes, climate change, soluble salts entering the pores of stone via moisture and the action of the sea and marine organisms. Stone artefacts in the sea are protected from abrupt changes in temperature or moisture levels, but are, however, exposed to sea currents, corrosion, abrasion and the activity of marine organisms that have a detrimental effect on stone surfaces. Thus we differentiate organisms that act chemically and mechanically, destroying the surface of stone (algae, sponges, bacteria, molluscs etc.). Besides the detrimental effects of marine organisms, we also know of the detrimental effects of soluble salts on stone, especially in situations when a find is taken from the sea to land. The drying of the stone leads to the crystallisation of the detrimental soluble salts we find in seawater – primarily sodium chloride in large quantities, while potassium chloride, magnesium chloride, calcium sulphate and magnesium sulphate are found in small quantities, but may also be detrimental to the "health" of stone.

Besides this "health" - related reason for cleaning stone, the aesthetic reason is equally important. Encrustations of marine organisms cover fine details in the surface, and with the accumulation of thicker encrustations, details are lost from view. Thus at times the natural relationship of indented (shadowed) and protruding (lit) surfaces is altered.

It is very important to note the fundamental difference between impurities and patina. The imprecise use of these terms often leads to misunder-

standings, whether in planning cleaning operations, or in carrying them out.

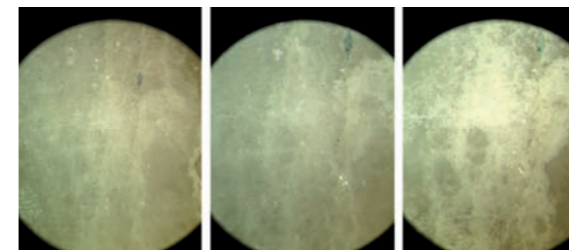
"True" or primary patina is the result of natural and "normal" processes on the surface of stone that occur as the result of slow physical and chemical processes. This produces a thin natural protective layer that, depending on its composition, may be of various colours. The most frequent component of this layer is calcium oxalate, which is less soluble than mineral calcite and, as such, acts as a natural protection from external forces. From the scientific - technical aspect it is, therefore, easy to argue in favour of preserving primary patina when cleaning stone. From the art history position it constitutes the most significant part of the stone artefact – onto which a history has accumulated on the artefact or ancient building in the aesthetically most valuable form. In contrast, impurities are a layer of accumulated calcification, encrustations of marine organisms, various types of discolouration that occur when stone is in contact with other materials (iron, bronze etc.) and compounds that occur as the result of the aggressive action of sulphates, chlorides and nitrates. Before undertaking cleaning the origin and composition of impurities and their possible detrimental effect on stone must be ascertained. A decision then needs to be made on whether to clean the stone of encrustations and, if so, in what manner and to what level. Cleaning is directly associated with the conservation of stone, as the consolidation of a damaged surface sometimes needs to be effected prior to cleaning, while often the true state of an artefact, i.e. the level of damage, can only be determined after cleaning. The choice of cleaning method depends on many factors: the type, quality and condition of the stone, the nature and intensity of impurities, the size and type of stone surface (a straight façade, a simple architectural decoration and a valuable sculpture demand different approaches).

The cleaning of stone is one of the most

complex conservation problems, as it involves numerous factors (type, quality and preservation condition of the stone, the nature and intensity of impurity, the microclimate of an edifice and its individual parts etc.). Around the world it is customary for this work to be undertaken as an interdisciplinary effort, by a team and for comprehensive preparations to be undertaken in advance of cleaning. Each case has to be observed individually as there are no set solutions for individual local situations that may differ significantly.

### DOCUMENTATION AND PRELIMINARY ANALYSIS

Detailed documentation of the condition of stone (visual observation, photographic documentation, the type of stone has to be ascertained – mineralogical - petrographic analysis, an analysis of impurities – chemical, x - ray (x - ray diffraction), microscopic analysis) has to be undertaken prior to cleaning. Samples for mineral - petrographic analysis can be chiselling off, drilled out with a core bit or by the removal of spalled flakes of stone (MALINAR, 1998). This analysis establishes the type of stone of which the artefact is made and its geological age. This can ascertain with a high level of certainty the stone quarry from where the stone originates. Samples for chemical analysis are taken in the same manner as sampling for mineralogical-petrographic analysis. Chemical analysis determines the chief components of the stone. Semi-quantitative x-ray analysis of soluble salts in stone are carried out with the evaporation residue of the aqueous extract of salts from stone using X - ray diffraction. This is an exceptionally useful analysis as it determines the types of salts pre-



*Figure 1. Microscopic image of a sample of Proconnesian marble (Photo: I. Martinović)*

sent in the stone.

In microscopic analysis the procedure begins with the taking of a sample of the marble material that satisfies the conditions for analysis. This is primarily done by mechanical removal with masonry tools or by taking a small piece of the stone that originated from breakage during the discovery of the artefact. The sample for analysis is dipped in epoxy resin, which is then polished to a high shine. Thus prepared, the stone sample is placed under a microscope and photographed. The image is created by radiation which is reflected off the sample and returns to the initial radiation. This analysis is done to obtain a better insight into the structure to facilitate determination of the type of stone. Once the condition has been established, the reasons for cleaning and a precise objective must be established, i.e. the point up to which cleaning will be done.

### DESALINATION

Stone that has lain in wet soil or the sea for an extended period of time was wet with water that contained greater or lesser quantities of soluble salts. Having been brought to the surface, the stone begins to dry. With the escape of moisture through pores in the stone and its evaporation into the atmosphere, soluble salts remain on and under the surface of the stone. As the stone dries out they accumulate here and crystallise. The critical moment occurs when the size of the crystals achieve the size of a pore. New quantities of salt coming from the interior of the stone to the surface increase the size of existing crystals. Crystallisation pressure, which now exceeds the hardness value of the stone, begins to destroy its structure. This is manifested as surface crumbling, sloughing or the delamination of entire crust sections. The salts in stone may be of diverse chemical origin. By type of anion, the most frequent salts are from the sulphate, chloride and nitrate groups. Sulphates may originate from a polluted atmosphere or as windborne aerosol; nitrates may originate from soils; and chlorides most often from the sea, but may also be found in continental areas where

they are contained in the soil.

There are several ways in which salts can successfully be removed from stone material. The most widespread procedure used for small fragments is desalination by submersion. Water in the bath enters the pores of the stone and gradually dissolves soluble salts. The dissolved salt is extracted into the water by diffusion, while clean water continues to penetrate the stone and dissolve salts. This goes on until a balance is achieved between the concentration of salt in the desalination bath and the concentration of salts in the stone. When this balance is achieved



Figure 2. An example of desalination by submersion in a vat (Photo: I. Martinović)

ved the procedure is halted. The salty water is taken out and replaced with new clean water. Monitoring of the procedure is conducted by quantitative chemical analysis, by measuring pH values, and by measuring the electrical conductivity of the aqueous extract. Another procedure involves the coating of the stone with various compresses made of a porous powdery or fibrous material soaked in water. This may be a mash of cellulose fibres or paper, attapulgit, sepiolite, or clay, kaolin, stone dust and the like. Water from the compresses first enters the stone and dissolves salts there. As the compresses dry out the moisture evaporates, drawing salts out to the surface where they remain. When the compress is saturated with salts, it is removed and replaced with a new clean compress. The desalination process is monitored by chemical analysis of the salts both in the saturated compresses and in the stone itself. The third method

of eliminating detrimental soluble salts is by chemical procedures, such as the process of converting harmful calcium sulphate into insoluble barium sulphate. This is the Lewin method of treating stone with a solution of barium hydroxide.

## CLEANING WITH WATER

Cleaning water may be tap water, but distilled or deionised is better (DONELLI, ŠTAMBUK-GILJANOVIĆ, 2004). Large quantities of water are undesirable for a number of reasons (the presence of iron, polychrome, the risk of dirtying, the loss of fragile material, the problem of the migration of salts and the penetration of water, the danger of freezing). Washing with pressurised water is not recommended on sensitive surfaces, especially where architectural plastic, sculpture and the like are present, and where the stone surface has been damaged, where stone is crumbling off and where erosion has occurred. Pressurised steam is sometimes used, especially in the removal of greasy impurities. Care must be exercised in the process, as the steam may rapidly heat up the surface of the



Figure 3. Cleaning with pressurised water (Photo: M. Mustaček)

stone causing damage.

Washing, i.e. moistening, stone with water vapour, known as nebulising, is done with a fine spray of water under high pressure (100 bar) using a system of pipes and sprayers that keep the rock wet over an extended period of time, without excessively wetting it, until such time as the impurity has softened sufficiently to be removed with light brushing.

This is usually achieved by time control of the washing (four seconds of wetting followed by a four minute dry interval). The impurity is progressively softened to the point where it can be removed with a brush.

## CLEANING WITH ABRASIVES

Abrasive cleaning mechanically removes the layer of impurity, but besides removing dirt it also tends to destroy the natural patina of stone that protects its epidermis, which is sometimes damaged and softened. After abrasive cleaning the epidermis is exposed to accelerated damage caused by reactions with detrimental components of the atmosphere. Often sandblasting itself damages this soft epidermal layer. Abrasive cleaning also destroys traces of the dressing of the stone, and rounds edges. In the exceptional cases when abrasive cleaning is approved, it must be performed by a highly specialised person who must have a good knowledge of why cleaning has been undertaken and in what measure it is to be effected. The cleaning of complex architectural decoration and sculpture is done separately, as a restoration operation with somewhat different, i.e. more precise techniques. This refers to micro abrasive blasting. Abrasive procedures can be wet or dry. The level of abrasion, i.e. the possibility of effecting control, depends on several factors: the hardness of the abrasive, the shape and size of the particles, the pressure, i.e. speed at which the particles hit the surface and the width, distance and angle of the stream. The abrasive used can be harder than stone (aluminium oxide – corundum is the hardest at 9 Mohs), and is by composition pure calcium carbonate, shaped into ro-

und particles with coarse surfaces (NIKŠIĆ, 2004). As a result dirty surfaces are cleaned in a much gentler fashion than with "classic" abrasive cleaning in which the abrasive is crushed rock or sand with sharp-edged grains. The dry procedure is now increasingly used as it provides for easier control of work and avoids unnecessarily wetting the stone, but does require special conditions (use of a mask by the operator, the isolation of the work area). Because of the complexity of the operation and its relatively slow pace, this procedure is used primarily for the cleaning of sculptures.

There are several ways in which abrasive cleaning is controlled: by the hardness, shape and fineness of the abrasive grains; air pressure, the blast nozzle aperture diameter; the distance of the nozzle from the surface of the stone; the angle of the stream in relation to the stone surface.

## CLEANING WITH COMPRESSES

Cleaning with compresses is used especially when salts have to be removed from stone, or when the impurities are difficult to dissolve and need to be kept in contact with the solvent for an extended period, and then drawn out. Compresses are made of absorbent materials that are mixed into a paste. The most frequently used are: specialty clays – sepiolite, attapulgit, diatomaceous earth, talc and chalk, non-acidic binder such as scrap cotton or paper pulp and bread (MALINAR, 1998). Because of their three-dimensional (porous) structure these materials are able to absorb water up to 1.5 times their own weight, without changing in volume. The most frequently used medium (binder) in compresses is water, although other solvents are also used. The principle by which they work is that the medium (reagent) softens the unwanted substances on the surface of the stone and draws them into the mass of the compress while the cleaning substance evaporates from the outer surface. The compresses may additionally be covered with plastic film to retain moisture and prolong the cleaning action. Compresses of slaked lime clean the surface of limestone by the

combined action of mild alkalinity and softening by moisture. Mora AB-57 paste is a mild chemical compress, very effective in cleaning limestone and marble. Its ingredient EDTA facilitates the dissolution of calcium salts. The compress contains: ammonium bicarbonate, soda bicarbonate, EDTA (ethylenediaminetetraacetic acid), carboxymethyl cellulose and disinfectant, all dissolved in water. Monumentique is a paste similar to Mora's paste in which the chief ingredient is also EDTA and that is marketed as a finished product under the names Monumentique paste S and Monumentique paste C+ polymer.

## CLEANING WITH CHEMICAL AGENTS

Chemical agents for cleaning stone are usually used when other procedures have failed, especially when impurities have penetrated deep into the pores of stone. This procedure can entirely remove natural patina, but also some soluble components of stone, which weakens its surface structure. Sometimes chemical procedures combine two cleaning agents (acid and base) with the idea that they will neutralise one another. However, a reaction may occur between them creating salts within the pores of stone. The salts crystallise and swell in the process exerting a pressure of about 1,000 atm. In chemical cleaning methods it is impossible to control the depth of the penetration of chemicals into stone, or the reaction of chemicals and stone. In conservation practice the rule is that all materials that are applied to the surface of stone must be inert and reversible.

## CLEANING USING THE CAVITATION METHOD

The cavitation method is borrowed from dentistry and is used to remove thin calcite deposits. The principle upon which it works is that the surface that is to be cleaned is sprayed with a fine stream of water while the tip of a pin or fine spatula vibrates at a very high frequency. This vibration creates a cavitation effect (the sudden evaporation of water in bubbles and the-



Figure 4. Cleaning using the cavitation method (Photo: I. Martinović)

ir condensation creates a cavitation vacuum) on the surface of the stone, which separates a calcite crust from the surface of stone.

The cavitation method allows for very precise work in separating a crust or various discolorations on the surface of stone, causing no damage to the surface of the stone in the process. The drawback of the method is its slowness (only small surfaces can be treated) and, as such, it is not recommended for large objects.

## CLEANING WITH LASER

Laser cleaning is the latest procedure in which laser beams of a given frequency react upon the dark colour of impurities, creating resonance in them and converting them into fine dust that is removed as smoke. Laser is an electromagnetic wave, like all light, but monochromatic (NIKŠIĆ, 2004). Each laser has a characteristic wavelength. A laser used to clean sculptures emits in the range close to infrared radiation,

beyond the visible part of the spectrum, usually at a wavelength of 1,064 nanometres. Lasers used for other applications emit in the ultraviolet range, i.e. in the visible part of the spectrum. There are currently in Europe some ten types that differ in terms of the source of light, wavelength, emitted energy and duration of impulse.

Cleaning lasers consist of three main components: a generator, the cooling system and the laser unit. The beam is transmitted via an articulated arm with mirrors or a fibre optic delivery system. An articulated arm allows for the transmission of high - power beams, while optical fibres allow for a regular beam cross - section, which is important when working with sensitive objects where a low energy density is used. An optical fibre also allows for the transmission of a laser beam over greater distances (tens of metres), which is practical when working on edifices, as there is no need to move the device along scaffolding.

Laser emits an intense, pure form of light in a very short interval. When the pulsing light is directed at a stained surface, the foreign, impure material significantly absorbs the energy, creating a photomechanical effect. When the light impact is very short (in an order of magnitude of several nanoseconds), there is insufficient time for the heat to pass to the substrate. The result is that impurities are freed and ejected from the surface, leaving the substrate untouched. As a result the removal of impurities using laser can be described as self-limiting. This means that the removal of material from a historical substrate is stopped as soon as the impurity has been removed. Even artefacts that have been impacted by advanced deterioration processes, and

are as a result very fragile, can be carefully cleaned with a laser, without prior consolidation.

Laser can be used to remove impurities of the most diverse origin: black encrustations formed by deposition from a polluted atmosphere, biological layers (mosses, lichens, algae), sediments of movable dirt, prior surface treatments, corrosion layers and impregnated stains (graffiti). Experimentation is also being done on the cleaning of polychromes, using different parts of the light spectrum (ultraviolet, visible light) or significantly shorter impulses. The desired cleaning effect is achieved by the targeted choice of wavelength, energy density (fluence) and impulse duration.

The advantages of laser cleaning are that there is no contact, that it allows for direct and precise control, that the procedure is selectivity - self-limiting, ecologically clean and complementary. The chief drawbacks to laser cleaning are: limitations on thick scum, on counter conical relief surfaces, and the cost and lengthy duration of the process in relation to other methods.

Laser cleaning preserves the total layer of several microns that constitutes the patina, and thereby the natural protection of the stone. Unlike in all other cleaning techniques, degraded stone surfaces – at times very unstable – do not require prior consolidation when undertaking laser cleaning, moreover, it would be unfavourable as it would retard the action of the laser. This advantage of the laser is significant, as a consolidant can attach some of the impurity to the stone and thereby render cleaning more difficult. Likewise, if polychrome is present on the stone, prior consolidation could bond part of the pigment to the impurity and thereby prevent discri-

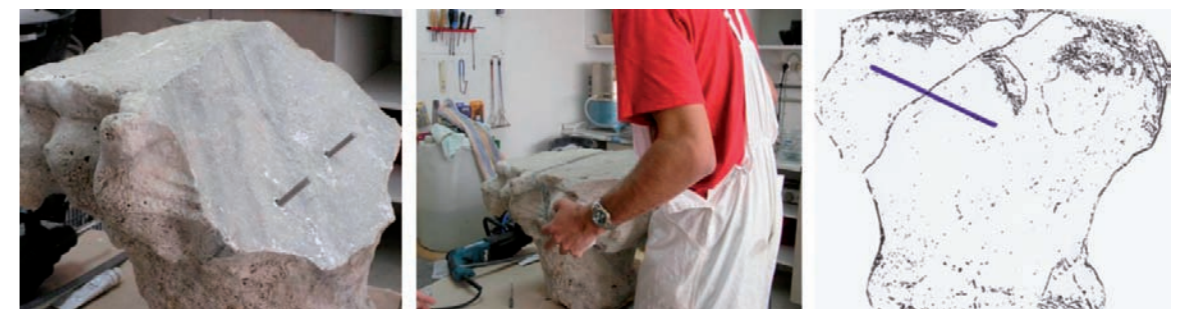


Figure 5. Joining, and the positions of inserted stainless steel rods (Photo: I. Martinović)



Figure 6. Stone wheel before, during and post-treatment (Photo: I. Martinović)

minative cleaning. If a very degraded and unstable stone surface is revealed upon cleaning, its consolidation should immediately be undertaken.

Finally, it should be noted that the laser is a technology that is quickly assuming an ever more important role in conservation - restoration practice. Laser is not a universal cure; it is only one more technique that can be successfully applied in combination with other cleaning and conservation techniques.

The great diversity of methods is accounted for, on the one hand, by the great number of different situations present in practice, and on the other, by the desire to avoid the negative effects each of the cleaning techniques is inevitably accompanied by. For example, all methods that involve the application of large quantities of water are not recommended because of the direct or potential damage they can cause through massive infiltration into the stone substrate, not to mention the impossibility of working in cold weather. The threat of abrasive methods – including micro sandblasting – to the original surface of a stone artefact is well known, and this method is thus used only when all others have been exhausted. Chemical methods in general have two drawbacks: on the one hand the likely infiltration of unnatural substances into the stone mass with varying degrees of harmfulness, and on the other, the necessity of rinsing these components out with large quantities of water.

As a result it is natural that people involved in stone cleaning try to identify the negative consequences of individual methods, and work to find new ways that could, to the greatest

extent possible, eliminate undesirable collateral effects.

### BONDING AND RECONSTRUCTION

As artefacts are for the most part found in a fragmented state, they require gluing and the reconstruction of missing sections in order to restore the artefact, in the greatest measure possible, to its original condition.

Epoxy resin and adhesives based on polyester, to which fillers are added depending on the type of stone (marble dust, talc, finely ground limestone etc.), are primarily used when gluing, i.e. bonding fragments. The speed of adhesion of glues based on polyester can be regulated by the addition of accelerators and catalysers. When joining larger fragments gluing is aided with the use of serrated non - corrosive (stainless steel) pins/rods.

Depending on the type and condition of stone, reconstruction is effected with diverse materials and the use of various tools. Acrylic emulsions are used with additives of stone dust acting as fillers, polyester and epoxy resins (also with the addition of an appropriate filler), various mixes of white cement, stone dust, slaked lime etc. When reconstructing stone finds we can also fabricate a "patch" of true stone when we are able to determine the type of stone with certainty. "Patching" with true stone is done by finely trimming the stone with masonry tools and then gluing it to the original find. It is important to differentiate among traditional masonry tools (martellino/mason's hammer, bushing chisel, tooth chisel etc.), i.e. to recognise the traces

they leave when dressing stone in order to render the reconstructed surface as close as possible to the original artefact.

state and that it preserves the artefact as such from further deterioration.

### CONSERVATION

With regard to impregnation, i.e. the protection of stone from the effects of moisture, the atmosphere and other detrimental substances, there is a broad range of protective materials and application methods. A decision on a type of protective material and the method of its application depends mostly on the type and condition of stone and on the conditions the stone artefact will be kept in following conservation - restoration work (JAKŠIĆ-BIZJAK, 2010). Stone protection substances differ in their chemical composition, newly formed products, effectiveness of protection and durability. It is very important that materials for the protection of stone allow water and vapour to pass, that they create a barrier to external influences, that they are compatible with the petrographic and physico - chemical characteristics of stone and that they have as little as possible impact on the appearance of the treated stone artefact.

### CONCLUSIONS

Cultural monuments, because of their importance to the human community, require particular care and very high financial expense to be preserved for future generations. Many of them have, over the centuries, from their creation to the present, suffered various forms of damage and contamination. Each of the methods cited has advantages and drawbacks. Some allow for the relatively speedy treatment of large stone surfaces, while others are very slow. Some require significant human interaction, some less. When undertaking conservation - restoration work on stone monuments the chief criteria for the choice of method is: that it must not be harmful to stone, i.e. that it must not cause damage to the stone or create secondary products that may cause damage. The purpose of conservation - restoration work is to restore the appearance and condition as close as possible to the initial

## IX. The Handling, Packing, Transport and Storage of Underwater Archaeological Finds

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### INTRODUCTION

The conservation of archaeological underwater finds is not limited only to the process of an object's active stabilisation in specialised laboratories or workshops - conservation and conservators themselves should be involved in all project phases; from preparatory examination and the extraction of the object, right up to and including the final exhibition of the object to the general public. In underwater archaeology conservation is not just a collection of specific procedures and treatments - conservation also provides us with answers to important questions concerning our history. It is the task of every conservator to care for the preservation of an object's integrity as an important piece of historical evidence.

The following section will discuss the proper handling of objects and the need for special techniques and guidelines that reduce the possibility of damaging objects to the lowest possible degree. The proper handling of finds includes the procedures applied at the find site itself, during the extraction of the find, immediately following extraction on the surface and during transport. All of the procedures and guidelines that set out proper handling are a sort



Figure 1. Drafting documentation at the site (Photo: M. Marukić)

of first aid for finds and are very important in ensuring that finds are delivered to specialised institutions in an unaltered state, where the further course of conservation procedures will be determined. Proper storage prior to complete conservation procedures, known as passive storage, is necessary to stabilise the object and maintain it in the same state in which it was delivered from the find site, while proper storage after conservation is necessary to ensure the long term stability of treated objects - the exhibition of conserved objects in inadequate conditions may lead to deterioration and the activation of undesirable processes.

### HANDLING UNDERWATER ARCHAEOLOGICAL FINDS

Major and irreversible damage may be done if objects are handled in an inadequate fashion in the early stages of research, resulting in the loss of significant information, which may affect the further stages of the object's conservation. It is, therefore, important to pay a great deal of attention precisely to proper procedures towards objects at the site, and the further handling of a find after it has been extracted from its natural environment. When discussing the proper handling of objects we need to keep in mind the course of an entire underwater research effort, because the handling of objects will differ in the various phases of a project.

The first phase of research includes all of the preparatory work whereby data is collated pertaining to the site and the objects present. This is a key phase, as it provides a complete picture of the site, which will determine the further course of the research. Preparatory examination is essential, as the information retrieved will determine the significance of the site and of individual finds and a possible decision to extract individual objects. The essential prior preparation of containers for the short - term and long - term storage of extracted finds and the organisation

of a team of appropriate experts will be based on these decisions. In this phase the conservator must secure adequate materials for packing and transport and make preparations for the stabilisation of extracted finds - vital to the phases that follow as it will reduce the detrimental effects of extraction. It would be ideal if an experienced conservator diver were present at the site during the entire underwater research effort to provide advice and determine further steps in our actions, treating the objects and the site as a whole. The presence of a specialised conservation expert during the actual extraction of the object is tremendously important - proper treatment will ensure the long - term stability of the object. Intervention during research depends on whether a decision has been made to leave the objects and the site in situ, or if there are plans to undertake the extraction of finds. Reasons for extracting an object must be defined in advance, before any kind of excavation and the extraction of objects to the surface, and they must weigh considerations of the possible detrimental consequences extraction may cause.

### LEAVING OBJECTS AT THE SITE (*IN SITU*)

Moving objects alters the integrity of the site and it is, therefore, of the utmost importance that detailed documentation be kept so that the historical significance and the integral context is not lost. In many cases the wisest course of action is to leave the site untouched to allow future generations the opportunity to study it. If a decision has been made to leave the objects at the site, thereby preserving its integrity, measures must be taken to prevent its further deterioration and possible looting.

### HANDLING OBJECTS DURING EXCAVATION TO THE SURFACE

Bringing objects up to the surface is a very complex operation that demands detailed planning for the safety of all participants of the research effort. Before making a decision to extract a given object, especially a large one, research must be undertaken that will, in the final tally, answer the question of whether extracting the object is beneficial. This must include considera-



Figure 2. Drafting documentation at the site (Photo: I. Miholjek)

tion of a set of criteria that includes financing, the project's feasibility, whether the object will ever be exhibited, i.e. whether an adequate site for exhibition and storage exists, and what evidence is gained by extraction that could not be procured through in situ observation (CRONYN 1990, 44). The determination of a plan and procedures to be implemented will depend above all on the fragility, significance, location, size and mass of the object, the goals of the project, the available time, the available sources of financing and the possibilities of further conservation (BOWENS 2009, 154).

Every effort must be made during extraction of an underwater archaeological find to ensure that the object is preserved and that it retains its integrity. At all times we should bear in mind the fact that these are exceedingly fragile objects that appear much sturdier than they actually are.

The first step in any underwater archaeological research where a decision has been made to bring finds to the surface is to draft detailed documentation. Photographic documentation of the position of every find must be made, and of their orientation with regard to one another. If possible a video record should also be made, and every find should be numbered. Numbering is important so that the relationship between individual finds and the site can be determined later in the laboratory. For marking purposes the most frequently used are plastic boards or film on which designations are written with water resistant markers or labels made using a Dymo device. Finds should also be sketched at the site

using plastic board and pencil. The sketch should show the positions of finds at the site and state the distance between the finds and control points at the site.

Given the great number of various situations we may encounter during underwater archaeological research, it is difficult to provide a description of procedures for every specific situation or every individual object. What follows, therefore, is an overview of the most frequent situations we encounter when extracting underwater archaeological finds (FELICI 2002, 203-215; BOWENS 2009, 154-156).

### Small objects

Before being raised to the surface, small objects are placed in net receptacles, usually plastic baskets, which can be pulled by rope onto the boat or lifted by a single diver when full enough. If the objects are very small they are placed in self - adhesive bags or plastic canisters that can be closed shut. Fragments of a single artefact are also placed in self - adhesive bags or sealable plastic canisters. This way they are stored apart from other finds. If the object is sufficiently sturdy it can simply be wrapped in bubble wrap or in polyethylene film and raised to the surface.

### Heavy and large finds

Before undertaking any heavy lifting, the vessel and lifting devices should be tested to determine stability for safe operation. Heavy and large finds can be raised in several ways. They can be lifted using a winch or endless chain hoist if the ship or the platform is directly over the site or by a hand - operated trailer that can be installed on board a ship. Financially more acceptable solutions, however, are to use a cord from the deck of the ship or to lift with the aid of air - filled balloons. There are many commercially available air balloons of varying sizes. They can be used to raise cargoes ranging from several hundred kilograms to several tonnes. The basic principle on which these balloons function is to inflate the balloon until full and the maximum lift is achieved. When possible it is better to use several smaller balloons rather than one large one. This is because the air in the balloon expands as it rises. If the balloon is only partially



Figure 3. Extracting amphorae using air balloons (Photo: R. Mosković)

filled, therefore, the air in it expands as it rises and the lift increases, which results in an uncontrolled and very rapid ascent to the surface. The balloon may lose its buoyancy, which results in the fast return of the object to the seabed. By using several smaller balloons, a loss of buoyancy may occur in one balloon while the buoyancy of another will remain the same. Most balloons have a vent control that a diver can use to release air to control the speed of the rise. In this manner a single diver can lift quite large objects (GREEN 2004, 268-274).

To be able to visualise heavy and large finds we can take the example of amphorae, lead or stone anchor stocks and cannons. In the case of amphorae particular care should be given to their contents, and amphorae must under no circumstance be emptied at the site, and should rather be extracted with their entire contents, as it is from them precisely that important information will later be gained. When faced with a site with a large number of amphorae the best method of extraction is to arrange the amphorae in the vertical position in a metal basket sheathed in a material that will prevent the amphorae from hitting into one another or moving during



Figure 4. Extracting a bronze cannon (Photo: R. Mosković)

extraction to the surface. In the case of individual finds, amphorae may be raised using a cord from the deck of a ship - if this is the case great care should be taken to properly attach them to the rope, i.e. it is important that they are raised with the neck facing upwards, avoiding the use of the handles as fixing points.

Dolia, as a particular type of earthenware container, are placed in sturdy nets that are then raised using cranes on a ship's deck.

When raising anchor stocks it is important to bind them well with rope so that they do not break under their own weight while being raised. Noteworthy as particularly difficult are very long and fragile objects, where simply binding them well with rope will not suffice. The appropriate support must be secured prior to their extraction. A wooden receptacle within which the object is fixed is most often used for this purpose.

### Fragile finds

In the case of very fragile finds we need to provide the appropriate support prior to raising as they could break under their own weight or water pressure. With these finds we need to proceed with the outmost care. Prior to extraction they

must be provided with the appropriate support. Various means can be used to provide support, from simple straight wooden or plastic boards to specially constructed supports whose form follows the shape of the object.

When raising very long and fragile, but relatively light objects we use a plastic support onto which the object is transferred and then fixed by binding it with strips of textile. Because of the length of these object using several balloons is recommended to provide balanced lift in as horizontal position as possible.

In the case of fragile ceramic finds, especially if they are fragmented, one of the methods is immobilisation in plaster directly at the site. The find and the surrounding material is sheathed in nylon or aluminium foil, then a layer of cotton wool and finally wrapped in gauze or jute. A bag of plaster is emptied on the wrapped find and the resulting block is simply transferred to a bag or basket and raised to the surface.

Very effective techniques have been developed to raise wooden and metal finds where there is a great danger of their imminent breakup. Depending on the shape and size of the object a sturdy



Figure 5. Extracting Apoxyomenos from the sea in a metal crate (Photo: D. Frka)

base is prepared that is subsequently encased with lead leaf onto which a layer of cotton wool is placed. The object is placed on this layer of cotton wool and itself clad in cotton wool. Everything is additionally fixed into place by encasing them in lead leaf that, because of its pliancy, simply adapts to the shape of the object.

### The remains of ships

The remains of ships and of various other craft should certainly be mentioned as a separate category of underwater archaeological find. These finds are very interesting because ships, when they sink, are a sort of time capsule and together with their entire contents become a witness to their time. It is impossible to give a universal rule when extracting the remains of ships because the procedure will vary from case to case depending on the dimensions, structure, age, location, level of preservation and the possibility for its housing after extraction.

If the wood is in very poor condition any attempt to extract the ship in one piece would result in a complete breakup, and the best solution is to extract individual pieces. In these situations it is of the outmost importance that comprehensive documentation is drafted and that every piece be carefully marked so they may be reassembled as a whole later during treatment.

The extraction of the remains of a ship in a single piece has been undertaken successfully in some cases, the best known such case is that of

the Swedish ship *Vasa*. The principles applied in that case were later successfully used with other similar finds. The procedure involved excavating tunnels under the ship's keel through which heavy cables were then drawn and affixed to pontoons placed above both sides of the sunken vessel. Water was then pumped into the pontoons until their decks were level with the surface of the sea. When water was then pumped out of the pontoons the *Vasa* began to rise from the bottom. The procedure was repeated several times and the *Vasa* was literally pumped out of the water. A floating construction was built around it within which the *Vasa* floated to the museum where further conservation was undertaken and where it was accessible for viewing by visitors. The success of this procedure in the case of the *Vasa* was contingent on the relatively good condition of the wood, a fact related to conditions in northern seas.

When dealing, however, with very fragile wood that could easily break under its own weight the above cited method cannot be implemented. In these cases the weakened structure must be provided with an appropriate support that will adapt to the shape of the ship's structure. This method of extraction was used in Marseilles during the extraction of the remains of Greek ships from the ground. Wooden beams were placed horizontally under the remains of the ships until a platform of sorts was achieved, which was then raised together with the remains. When faced with cases like this of very fragile finds there is another recent technique that was employed to extract the wooden remains of the *Sea of Galilee* boat in Israel. Layers of resin were applied along the entire length of the boat, about 8 m long, until a sturdy casing had been achieved. Canals were also dug under the keel of the vessel, into which resin was also injected until a sturdy support bracing was achieved. The resin dried in the air and the entire block, encasing the wooden remains, simply navigated the lake. After being delivered to the processing site the resin was removed, and the remains of the boat



Figure 6. Raising the *Vasa* to the surface (<http://www.vasamuseet.se/en/The-Ship/Life-on-board/>)

were treated using standard conservation procedures.

### STABILISING EXTRACTED OBJECTS

Extracting an individual object disrupts the natural equilibrium achieved between the object and its environment. At the moment of submersion every object is exposed to the intense influence of the surrounding environment, which includes chemical reactions with water and the soluble salts present, colonisation by fungi and algae, and erosion caused by sand. Extended exposure to these factors leads to the significant degradation of the object. A natural equilibrium is achieved after a time between the object and all of these environmental factors, which results in a relative halt of the decomposition process.

This natural balance is disrupted upon the excavation and movement of the object. Exposing the object to a new set of conditions initiates a chain of physical and chemical reactions that can in the end lead to the complete destruction of finds. The chief causes of accelerated deterioration are visible light, UV radiation, changes in temperature and relative humidity, insects and inadequate transfer, transport and storage (CRONYN 1990, 69-70).

The chief task of the person handling finds, ideally a conservator, upon extraction is the stabilisation of finds to prevent their deterioration. This process must begin immediately after the object has been taken from its natural environ-

ment and includes all of the actions taken by a conservator or other professional staff during temporary storage and transport to a specialised laboratory in which active and permanent conservation of the find will be conducted.

A key element in this stabilisation process is to ensure that every object is maintained in the same or almost identical conditions to those it was extracted from the moment it leaves the water. The following are the chief guidelines to follow at the site when handling freshly extracted underwater finds (BOWENS 2009, 153; KARSTEN 2009, 20-22):

- Objects must be kept submerged or wet the entire time. Drying may have catastrophic consequences for objects as it causes surface cracking, breakage and the growth of moulds, which may lead to the complete destruction of the object and very quickly reduce it to a pile of dust. The objects are best kept in water from the original location, or in a mixture of the original water and freshwater, or in freshwater in the case of very stable and sturdy objects.
- Objects must be stored in suitable inert containers. Polyethylene vessels, boxes and bags are suitable containers for the storage of freshly extracted finds. Within these containers objects can be additionally stabilised and secured using protective layers of foam or sandbags. These containers must be sealed hermetically to prevent the evaporation of the solution in which the objects are placed.
- Objects must be sorted by their composition. Finds are usually stored in plastic bags, plastic nets and plastic boxes with or without covers based on their composition. This is particularly important when dealing with metals, since storing two different metals together creates a galvanic effect between them leading to corrosion. If finds from different period – usually ceramic finds – are found at a site it is re-

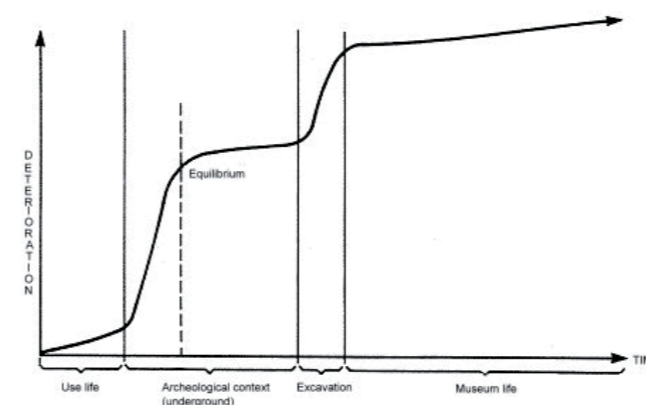


Figure 7. A graph of the decomposition process over time (<http://www.nps.gov/museum/publications/MHI/Appendl.pdf>)

commended that they be stored separately according to their particular periods. It is also recommended that fragments of the same object be stored together but separate from other finds. Organic materials should also be stored separately and by their composition.

- Objects must be adequately tagged. Stored objects must be appropriately tagged and catalogued. To this end we must use a system of tagging that will remain stable in the conditions in which an object is temporarily stored. Two methods of tagging that have proven to be stable in aqueous solutions are plastic ribbons imprinted using a Dymo device and writing on plastic labels or containers using water resistant markers which will not fade away with time. If using solutions that dissolve Dymo labels or plastic markings, we can use non - corrosive metal labels. If a label is tied to an object, i.e. the handle of a pot, an inert twine, like polypropylene, must be used for securing, as cotton twine will rot. Labels tied on wooden samples should be tagged using stainless steel pins because staples or pins made of other metals will corrode. For objects placed inside a plastic bag, plastic net or plastic box, labels should also be put inside the bag, net or box. When using a plastic box it is also recommended that the box also be labelled. Labels should state the name of the archaeological site and date of excavation, and also with other site-relevant information such as quadrant, stratigraphic unit and depth and a description of the object.
- Objects must be kept cold. A rise in temperature increases the speed of decomposition, promotes the growth of fungi and moulds and activates corrosive reactions in metals, which again has as its consequence the visible damaging of the object or a weakening of its structure. Objects must, therefore, be stored in as cool an environment as possible upon extraction, ideally in a refrigerator.

- Objects must be shielded from direct sunlight. Increased exposure to light causes photochemical reactions, changes to colour and the fading of the surface, accelerates the speed of decomposition and promotes the growth of algae. Upon extraction objects should be kept in the dark as much as possible.
- Objects must be secured. Weapons and potentially explosive materials should be handled with care and pursuant to the safety guidelines prescribed in a given country. In Croatia the Weapons Act (Official Gazette 63/07, 146/08) is currently in force.

### PACKING FINDS FOR TRANSPORT

To avoid the possible damaging of finds during transport to a place of temporary storage or to a laboratory where conservation will be undertaken, a great deal of attention must be paid to proper packing. The packing method must protect against shock and vibration, while at the same time the find should be protected against drying. Even slight drying can cause saturated and near-saturated marine salts, including calcium sulphate and calcium carbonate, to deposit within the artefact, leading to surface damage. Several factors need to be taken into consideration when packing, above all the distance a find is to be transported and the place where the find is to be stored. For most artefacts it stands that they should spend at least 24 hours in mixture of 50% original salt water and 50% freshwater before packing for transport. Also the material used for wetting an artefact during transport should be soaked in same mixture. To ensure the maximum possible protection during transport we should follow these guidelines when packing (BALLARD 2008, 78-80; BOWENS 2009, 154-156, JONES 2010, 10):

- All materials and containers used for packing and additional means of immobilising an object must be of chemically inert materials. Polyethylene canisters with lids, various polyethylene wrapping films, self-

adhesive polyethylene bags, special bubble wrap materials and boards of expanded polyethylene foam have been shown most appropriate to this function.

- Objects must at all times be kept wet to prevent them from drying out, especially if transport to a storage facility lasts several days. Objects are wrapped in textile that is thoroughly soaked in water and then additionally wrapped with film to reduce the evaporation of the liquid.
- For a long transport period, i.e. up to two months, objects wrapped in soaked textile should be placed in three layers of polyethylene films, which are checked for leaking, and then well - sealed with package sealing tape. Afterwards, the objects are wrapped in two to four layers of bubble wrap and placed in cardboard cartons.
- If the transport time to the storage site is short, the objects need not be additionally wrapped to prevent evaporation, rather finds are sprayed and covered in layers of polyethylene film to keep them wet.
- For ferrous and cuprous metals it is recommended that they be immersed in a reducing solution, i.e. 5% sodium carbonate or 2% sodium hydroxide, before packing to slow their further corrosion.
- Besides proper packing, organic material should be refrigerated to slow the rate of biodeterioration caused by microorganisms during transport.
- Transporting finds in containers filled with water should be avoided, as objects may be carried by the movement of water in the container, which may lead to damage. If finds are transferred in such containers, they should be so arranged as to prevent any movement and impacts between objects.
- Several objects of the same composition that form an ensemble may be transported

in a single container to preserve the integrity of the site. These objects must be separated from one another, either by individually wrapping them in polyethylene film or by using special plastic partitions and should be additionally immobilised to stop them from hitting one another.

- In the case of exceptionally fragile and sensitive materials it may be necessary to fabricate a made - to - measure support of wood or polyethylene foam to provide them with adequate support and protection.
- The packing must keep the object clearly visible to avoid the need to unpack it during transport.
- Objects must be properly tagged - double tagging is recommended, i.e. one tag in the packing or container and another on the outside.
- At no time should wet archaeological artefacts be allowed to freeze.
- It is important to know that underwater finds, especially in the case of organic materials, dry out quickly and all of the procedures cited above are intended for transport only and should by no means be used for longer storage. Finds should be deposited in the precisely stipulated conditions provided in the following section 5 on passive find storage immediately following transport.

### PASSIVE FIND STORAGE

Passive storage is defined as a method of safe storage of extracted archaeological finds that should prevent the further deterioration of an object until active conservation is undertaken at a specialised laboratory. These storage facilities would ideally be situated close to a find site to allow for immediate storage in optimal conditions immediately following extraction. The following are the minimal conditions these storage met-

hods and facilities must meet (JONES 2003, 35):

- Deterioration should be stopped or reduced to the smallest possible measure during passive storage.
- The storage method applied should in no way affect further conservation procedures.
- Containers used in passive storage must be easy to maintain. Objects must be easily accessible to specialised staff while in passive storage.
- Finds must be accessible to the general public, especially if the finds are of great significance or of high interest.

Temporary or passive storage will differ based on the kind of material a find is composed of.

#### PASSIVE STORAGE OF CERAMIC, GLASS AND STONE

During the passive storage of ceramics, glass and stone it is important to control soluble salts by controlling relative humidity. Relative humidity must be kept high (100%) to prevent crystallisation of salt; otherwise formed crystals can cause physical damage. Finds made of these materials must be stored by submerging them in containers filled with water. After extraction these finds must under no circumstances be immediately submerged in tap or deionized water, but rather in seawater, which is then gradually replaced with tap water over a period of several weeks. This kind of wet storage ensures the stability of the object over an extended period of time - the only thing required is to undertake regular monitoring and changes of the water to prevent the growth of biological organisms. Also, during extended storage of glass the pH of the solution gradually begins to rise which can be harmful to glass. Buffers can be added to keep the pH down, as can bactericides to prevent damage from bacteria (CRONYN 1990, 137; HAMILTON 1999: File 4, 1-2; JONES 2003, 48-49).

#### PASSIVE STORAGE OF METAL FINDS

While they may appear to be very solid and in good condition metal finds, iron especially, are very often highly unstable and it is, therefore, very important that metal finds be stored in stable conditions immediately upon extraction to prevent active corrosion (BOWENS 2009, 157-158; JONES 2003, 48-49).

##### Iron

The extraction of iron finds accelerates the corrosion process because of the change to environmental conditions, above all the available amount of oxygen, percentage of moisture and the presence of chlorides. To control these conditions iron objects must be stored in tap water to which a corrosion inhibitor has been added immediately upon extraction. The most frequently used corrosion inhibitors in this type of passive stabilisation are sodium hydroxide, sodium carbonate and sodium sesquicarbonate. Water solutions to which these substances have been added will prevent iron corrosion as long as the solution's pH value is maintained above 8 and up to 12. For short-term storage, which should not exceed six months, a 5% solution of sodium carbonate (pH 11.5) is used, or a 5% solution of sodium sesquicarbonate (pH 9.7). For long term storage the best results have been achieved with a 1% solution of potassium dichromate in water to which sodium hydroxide is added until a pH value of 9 to 9.5 is achieved. When working with these kinds of solutions the toxicity of chromate presents a major problem and they need to be handled with the utmost caution and only by a professional (HAMILTON 1999: File 9, 10-13; JONES 2003, 48).

##### Copper and its alloys

As with iron the process of corrosion is rapidly accelerated upon extraction because of the disruption of the equilibrium achieved. These objects are, therefore, also passivated by depositing them in a 5% solution of sodium sesquicarbonate or sodium carbonate in water. This kind of storage is recommended for no longer than 6 months prior to desalination and active conservation (HAMILTON 1999: File 12, 2; JONES 2003, 48).

#### Gold, silver, lead, tin and their alloys

Further corrosion of these metals after extraction has not been observed, i.e. exposure to atmospheric conditions does not affect them. As a result these finds do not need to be stored in a water-based solution but may, rather, be dried and stored until their active conservation. If there are significant deposits on an object it is good to keep it in a 5% solution of sodium sesquicarbonate or sodium carbonate in water to prevent the deposits from hardening before they are removed (JONES 2003, 48).

#### PASSIVE STORAGE OF ORGANIC FINDS

In ideal conditions the temporary storage of organic finds should be as brief as possible before their active conservation. However, this kind of temporary storage very often lasts for years until funds and conditions are secured for appropriate treatment, especially for larger wooden finds. The basic conditions for the storage of organic finds are as follows:

- They must be kept in a 100% moisture level the entire time.
- Exposure to light must be kept to a minimum to prevent the development of algae.
- The growth and development of bacteria, fungi and pests must be prevented or reduced to the minimum possible level.

#### Passive storage of wooden finds

Small wooden finds can be stored wrapped in polyethylene bags or film, with the addition of a minimum quantity of water, and the thermal bonding of the ends to prevent the entry of air. The packed object is then placed in a further two polyethylene bags to prevent the loss of water. It has been observed that this method of storing keeps finds from drying out, but does not prevent microbiological activity. The only way to reduce microbiological activity in finds thus stored in polyethylene bags is to treat the wood with biocides and storage in a cold place, ideally a refrigerator at 4°C. In the case of very large wooden finds, such as wooden ships, a major problem during passive storage is preventing them from drying out. Constructing large containers in which these types of finds would be

entirely submerged is economically very unfeasible, and in these cases the only alternative is to use spraying. It has been demonstrated that the best results are achieved when spraying water cooled to a temperature between 2 and 5°C.

Wooden finds may be stored temporarily in containers filled with water. Plastic canisters with lids are used for smaller finds, while specially fabricated polypropylene or polyethylene containers with covers to prevent the penetration of light are used for larger finds (BOWENS 2009, 156-158; JONES 2003, 36-47; BRUNNING 2010, 20; SINGLEY 1981, 8).

In many cases temporary storage becomes long-term, which may lead to the degradation of wood resulting from the postponement of active conservation and stabilisation treatment.



*Figure 8. Improper storage of a wooden find has caused it to dry out and crack accompanied by the growth of mould on the surface (<http://www.english-heritage.org.uk/publications/waterloggedorganicmaterials/waterlogged-organic-materials-guidelines-draft.pdf>)*

#### Passive storage of bone and ivory

Artefacts made from these materials must be stored in freshwater to prevent the crystallisation of salts, which often cause physical damage. They also have to be stored at a low temperature of 2-5°C and the water must be changed on a regular basis with possible control of microbiological activity (JONES 2003, 48).

#### Passive storage of leather finds

During the passive storage of leather the loss of water must be prevented and the conditions must be as similar as possible to those from

which the find was extracted, which means that they must be kept in controlled conditions of temperature, pH, salinity and microbiological activity. Keeping leather finds wrapped in hermetically sealed polyethylene film or in sealed containers is recommended to prevent drying out, and at a temperature of from 2 to 5° C to reduce biological growth. In case of significant biological activity we can use quaternary ammonium salt as a biocide, with copious rinsing of treated finds using deionized water (BOWENS 2009, 157-158; JONES 2003, 47).

## TRANSPORT AFTER CONSERVATION

After conservation finds are usually transported to the owner, museum or some other facility. Before transportation finds should be properly packed and secured. Packaging finds before transport and unpacking after transport should be carried out very carefully. This should be handled calmly, deliberately and systematically.

Finds are packaged separately; they should be wrapped in paper – acid - free paper is recommended – and then be placed in polyethylene bags, bubble wrap, or smaller boxes made of plastic, wood or cardboard depending on the find. Several separately packaged smaller finds are packed together in larger boxes, and then in shipping containers. It is important that the packaging is done systematically, that the packaged material from one site does not interfere with material from another site unless otherwise noted. Systematisation is possible within material from the same site, and then according to their composition.

Every empty space inside packed boxes or containers for transportation must be filled in order to avoid shock and vibration during transportation. Foam materials are used for filling – usually sponges, bubble wrap, foam, paper etc., as this fixes all material in place and prevents slipping during transport that could lead to mechanical damage. "Fragile" or "Handle with Care" labels should be affixed to containers or some other indication that the material must be handled with the utmost care.

Containers that serve for transportation should protect finds against external influences such as temperature, relative humidity and light on route to the destination. The type of container used for transportation is selected based on weather conditions, the length of transport and the means of transport. Usually a wooden containers for longer transport and cardboard boxes for short distances. It is recommended that transport containers not be overly large or heavy while transporting. It is also recommended that these containers have handles for easy handling. In means of transport such as a lorry (truck) it is essential that containers be secured in order to prevent their movement during transport.

In the case of large and clunky finds they are also packaged separately. Finds must be protected from all sides either with bubble wrap, sponge or sponge - like material, and then fixed to the base, in a manner that makes them easy to handle. The shocks that are present during transportation and the vibration of means of transport cannot be completely avoided, but their harmful effects can be reduced and alleviated with proper packaging.

## PERMANENT FIND STORAGE

Once the process of the active conservation and restoration of finds has been completed and once, if necessary, they have been transported, they must be stored in the appropriate conditions, irrespective of whether a decision has been made to store it in a depository or to exhibit it in a museum or similar facility. The object has been stabilised by the conservation process, but we need to bear in mind that only the regulation and constant control of the storage conditions will provide for long-term protection. The microclimatic conditions that require strict control to ensure the long - term stability of materials are temperature, air humidity, illumination and contact with detrimental materials and substances.

## TEMPERATURE

Fluctuations in temperature may lead to the

expansion or contraction of materials, which may cause permanent damage to an object. Elevated temperatures lead to photochemical reactions that may result in the fading of colours. Permanently elevated temperatures in combination with high humidity values promote the development of fungi, bacteria and insects. Keeping the temperature in areas in which objects are stored or exhibited between 18 and 20°C is recommended (JONES 2003, 117-119; VOKIĆ 2007, 14-16).

## RELATIVE HUMIDITY

Inappropriate relative humidity is considered the leading cause of the deterioration of objects. Humidity can be inappropriate in three cases: if it is too high, too low or if there are significant fluctuations in relative humidity.

- If relative humidity is constantly above 70% it will significantly accelerate biological activity, which will result in the appearance of mould and fungi, lead to the corrosion of metals and to dimensional changes on objects, especially those of organic origin.
- Relative humidity constantly below 40% leads to significant structural changes in objects of organic origin.
- Significant and sudden oscillations in relative humidity will cause dimensional oscillations in organic materials.

To ensure the long - term stability of finds relative humidity must be kept within precisely defined boundaries. In general, keeping relative humidity at a level ranging from 40-70% with maximum variations of  $\pm 2\%$  is recommended. The recommended value of relative humidity for ceramic, glass and stone is from 45-65%, except in the case of unstable glass. In that case the relative humidity should be between 15 and 40%. For metal underwater finds relative humidity should be constant, with a value of about 40%, although for iron the recommended value is 15% and 35% for copper and its alloys. The recommended range of relative humidity for

organic underwater archaeological finds is 45-65%, while for wooden finds only the range should be within the narrow boundaries of 55-58% (JONES 2003, 117-119; VOKIĆ 2007, 14-16).

## LIGHT

Objects, especially those of organic origin, are sensitive to exposure to both visible light and to UV radiation, which cause them to undergo various photochemical changes. To prevent the deterioration of finds during exhibition or storage, finds should ideally be stored in darkness, i.e. exhibited in strictly controlled lighting conditions. For ceramic, glass, stone and metal the lighting should be under 300 lux while for organic material lighting should not exceed an intensity of 50 lux. Given that the detrimental effects of light on objects are cumulative, it is recommended that objects be returned to a dark place or that the premises be kept dark when a museum is not open (JONES 2003, 117-119; VOKIĆ 2007, 14-16).

## BIOLOGICAL ACTIVITY

Finds in storage or part of an exhibition in a museum must be constantly monitored for possible insect or rodent attack or the possible growth of fungi, mould and bacteria. Biological activity is controlled by the above-cited microclimatic conditions, which must be kept in precisely defined boundaries (JONES 2003, 117-119).

## CONCLUSION

This section has endeavoured to present the basic guidelines we must adhere to when handling underwater archaeological finds, both at the site and following the extraction of finds. The importance of proper handling during the transport of finds has been emphasised with the aim of ensuring the integrity and stability of extracted objects prior to their active and complete conservation. The last section cites the conditions for the permanent depositing and storage of finds - only proper procedures and storage in appropriate conditions, after a find has been completely conserved, can ensure its long term stability.

Proper management of finds is vital - adequate handling at the site and immediately following extraction serves as a sort of first aid for finds and guarantees that they are delivered in an unaltered state to the institution at which they will be adequately stabilised and protected from the inevitable and rapid onset of further deterioration.

## X. *In situ* Protection of Underwater Cultural Heritage

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with the aim of the best possible and longest lasting solution for the preservation of our heritage.

### INTRODUCTION

*In situ* protection refers to the concept of preserving underwater cultural heritage at its original site, regardless of whether it is on land or underwater. There are many reasons why the *in situ* protection of underwater sites should be given preference as the first option, above any invasive activities directed towards the research of underwater cultural heritage. We can only underline that the process of the conservation and restoration of underwater archaeological finds is a costly and demanding job and that, as a rule, the process is never completed as a result of the tendency of archaeological finds to continue deteriorating. Another reason is a dearth of exhibition space in museums, which is frequently the reason why archaeological finds sit forgotten in depots.

The rules of *in situ* protection emphasise the importance of, and respect for, the historical context of a cultural object, its scientific significance, the importance of preserving underwater cultural heritage for future generations and preventing the mistakes that have been committed in the past to the detriment of underwater cultural heritage as a result of the improper handling and care for cultural objects. *In situ* protection also stresses that cultural objects, under normal circumstances, have achieved a certain level of stability owing to low rates of deterioration and oxygen levels, and are, as such, in many cases not threatened. If threatened, of course, there is a need to protect these sites, but again in these cases, preference should be given to various non-destructive methods and the methods of *in situ* protection that will be discussed further in the text. Given the truly high level of diversity among the classes and types of underwater sites, each of them requires an individual approach to protection, conservation and presentation

### WHAT AFFECTS THE DEGRADATION AND CHANGES TO *IN SITU* OBJECTS

The formation of individual archaeological sites under water is the result of the sinking of land sites, individual objects or artefacts. Once an individual find or site is placed in this new environment it becomes subject to various physical, chemical, biological and mechanical factors: the infiltration of water (sea) into the object's structure, the effects of oxygen and chemical reactions in water, corrosion, the effects of various marine organisms, algae and bacteria, erosion, the sedimentation of sand, hydrolysis and other factors, depending on the actual surroundings in which the object is found.

After a time, however, there is a relative stabilisation of degradation processes in an aqueous environment, and it can be said that the process of an individual object's deterioration has - owing to the agency of physical, chemical and biological factors - attained a relative stagnation, more precisely - that it is significantly retarded. There are, however, factors that may still effect changes to the stability of a site or artefact that has attained this level of stability. This pertains above all to the destructive activity of people whose work is tied to the sea and the seabed, such as treasure hunting, sports diving, fishing, underwater construction works, dredging (MANDERS 2012, Unit 9.10), and to various natural factors that constantly (sea currents, tides and waves, marine organisms) or intermittently (natural catastrophes) have a negative effect on underwater heritage.

## THE LEGAL PROTECTION OF UNDERWATER CULTURAL HERITAGE

Throughout history most underwater cultural heritage was protected from human activity by the inaccessibility of the underwater environment - sites located at greater depths, as a rule, enjoyed a greater chance of being preserved. The development of professional diving equipment opened access to these locations to the wider public, which increased the danger of their devastation. This development demanded of the professional community that it develop legal measures and regulations that will help preserve underwater cultural heritage. Countries adopted legislation that encompasses the legal protection of underwater cultural heritage with more or less success. A few of the noteworthy acts in effect are the Historic Shipwreck Act in Australia, The Protection of Wrecks Act in Great Britain, Portugal's legislation on marine and underwater archaeological heritage or Croatia's Cultural Property Protection and Preservation Act and its Ordinance on Archaeological Research. The lack of harmony among these laws prompted professionals to draft and adopt a single regulation to treat the protection of underwater cultural heritage. The 1996 ICOMOS Charter for the Protection and Management of the Archaeological Heritage was a key step in formulating an international legal framework. This was followed by a 2001 session of UNESCO when the body adopted its *Convention on the Protection of the Underwater Cultural Heritage* and the Annex to that document. The Convention laid out the fundamental principles for the protection of underwater cultural heritage, provided a framework for cooperation between countries and expounded the rules that relate to activities directed at underwater cultural heritage. The Convention also established some basic principles such as the obligation to preserve underwater cultural heritage, encouraging *in situ* protection as the primary method of preservation, opposing commercial exploitation, and promoting information sharing and professional training with the aim of raising public awareness of cultural heritage preservation. The Annex to the

Convention sets out the rules that pertain to activities directed towards underwater cultural heritage. It includes practical and applied regulations that should be adhered to when undertaking excavations, provides guidelines on how to design research and preservation projects and emphasises the qualifications researchers should have to undertake activities related to the preservation and management of underwater cultural heritage.

Another key factor alongside the legislation provided by individual countries in preserving underwater cultural heritage is the cooperation of competent authorities charged with its care. In Croatia, for example, this pertains to the principal cultural institution - the Ministry of Culture - and to conservation departments, museums and institutes and other competent institutions whose cooperation with the police and port authorities aims to create favourable conditions for the best possible organisation of the protection of underwater cultural heritage. Furthermore, one should not disregard the potential of diving clubs and local populations, whose interest should be that underwater cultural heritage is protected, all with the aim of preserving it for future generations, and for the development of the economic and tourism potential that may arise from the proper care of underwater cultural heritage.

## THE PHYSICAL PROTECTION OF UNDERWATER CULTURAL HERITAGE

Various methods of physical protection safeguard sites from physical damage and to a certain degree may limit the damage caused by natural factors. When selecting a method of protection we must take various parameters into consideration, unique to each site. The first parameter pertains to the general characteristics of the site itself: the type of site (harbours, shipwrecks, structures, buildings, artefacts and human remains, objects of prehistoric character, aircraft), the predominant type of material at the site (wood, ceramics, metal, glass), the depth at which it is situated, the level of threat to the site, its state of preservation, its accessibility to the general po-

pulation and the historical and archaeological value of the site. The second parameter pertains to the conditions affecting the site and influencing its survival or degradation, among which we may number physical, biological and chemical factors. The third parameter pertains to the possibilities for and feasibility of *in situ* protection, and the financial framework on which a final decision concerning the protection of a given site often depends. It is on the basis of the study of these parameters that we can determine the methods and strategies that will be implemented to protect and conserve the site or, perhaps, to present it *in situ* in the form of a museum.

When dealing, for example, with the remains of a wooden ship structure on the seabed one of the methods of burying with sand would be ideal. For a Roman period shipwreck with the remains of a large number of amphorae implementing protection by the use of a cage would be an appropriate solution, while for a large modern sunken vessel legal protection and presentation in the form of an archaeological park would be the suitable method of protection. Further in this section we shall elaborate the most frequent methods of physical protection with examples of sites at which they have been implemented.

### COVERING THE SITE WITH A LAYER OF SAND AND STONE

As a result of the natural processes present on the seabed underwater sites are often covered in sand during their formation, which creates a physical protection barrier above them. Exceptional situations may, however, uncover and expose a site. The phenomena that create a threat to these sites are most often natural changes such as strong waves, currents and natural catastrophes and only sometimes are they related to human activity. The principle of repeated protection is very straightforward - exposed finds are covered in a layer of sand that has the purpose of securing the site from visual and physical contact with external factors. The effectiveness of this method may be limited because of the possibility of a repetition of the process that was the initial cause of the destabilisation of the site. There is also the problem that when

building up fine sediment such as sand, it may happen that it does not manage to stabilise at the site before being carried away by sea currents. Various kinds of barriers may be used with the purpose of improving and increasing the duration of the depositing of marine sediments, thereby expediting the process. These may be low bulwarks set perpendicular to the direction of the movement of underwater currents that serve as barriers along which broken off algae and seaweed is deposited, facilitating the deposition of sediments (STANIFORTH 2006, 53). Methods of implanting artificial seagrass at a site are being perfected of late with the purpose of exploiting the sediment that moves with water currents. Since natural seagrass does not take well to replanting on the sandy bottom once disturbed, artificial grass is used in its place to encourage the deposition of sediment. Certain conditions have to exist at the site for this kind of protection to be effective, notably an optimal depth, a relatively flat bottom and regular and optimal currents. Without a relatively strong sea current there is not enough moving sediment to be deposited, and accumulations form on the artificial grass that prevent its movement and sediment gathering, whereby it loses its purpose. An example of the ineffective use of this method is at the Legare Anchorage shipwreck site in Florida (SKOWRONEK et al. 1987, 316-317), while a positive example is the protection of the wreck of the William Salthouse in Australia (STANIFORTH 2006, 54). There are also examples of when, as a result of the natural conditions and strong sea currents, this kind of protection has not proven effective enough to create a stable environment for the site, and other methods also had to be implemented for effective protection, as was the case at the Hårbøllebro site in Denmark (GREGORY et al. 2008, 17-18).

Another application of the sand burial method is a customary practice in underwater archaeological research. Upon the completion of every archaeological research campaign there is a need to protect excavated areas. Covering already excavated trenches with sand ensures the protection of this part of the site, and also provides us with reference positions for the continuation

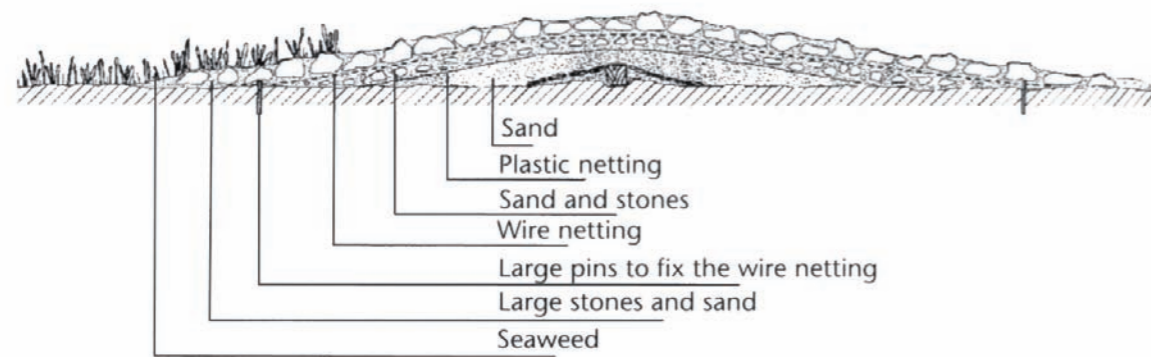


Figure 1. A complex method for the burial of a site using natural and artificial materials (NEGUERUELA 2000, 112)

of research during the next archaeological campaign. Covering parts of a site is often associated with the use of geotextiles; textiles made of polypropylene or polyester fibres. Geotextile needs to be installed at the site prior to burial in sand to isolate the researched area of a site from the deposited sand. This is very important to avoid the contamination of the site by the secondary deposit whereby the geotextile is stabilised above the finds, and to avoid the unwanted disturbance of archaeological strata. This method of temporary protection has been proven inexpensive and beneficial in archaeological practice (DAVIDDE 2004, 142).



Figure 2. Part of a shipwreck near Oruda island, Croatia protected with sandbags (Photo: R. Mosković)

If there is a need, besides with sand, the site may also be covered with a heavier aggregate (gravel, rock), taking care not to damage archaeological finds in the process (BOWENS 2009, 167). There are a number of variations to this method of protection. The most complex method involves burying the site with a layer of sand,

followed by a polypropylene netting, a layer of gravel and sand, metal netting fastened to the bottom with spikes, followed by heavier stones and the camouflaging of the entire area with seagrass (Figure 1) (NEGUERUELA 2000, 112). This creates an artificial hummock, incorporated into the natural surroundings and protected from looting and unwanted visitors.

#### COVERING THE SITE WITH SAND BAGS

This is a method of protection used at sites where there is strong erosion, mostly as a result of various natural processes, and where the simpler method of depositing a layer of sand would not provide long-term protection. This method of physically protecting a find or site involves the use of polypropylene bags filled with sand (bags of organic materials have a shorter life span). The bags are arranged at the site with the aim of entirely covering it up, providing physical protection (Figure 2). The sandbags are able to resist the water current and may mitigate the effects of wave action on the site. They are most effective when installed in greater numbers, densely packed so that their edges overlap. They should be placed on the seabed in as low a profile as possible to allow the water current to flow gently over them, since arranging them in the form of a hillock could have the effect of destroying fringe areas of the site by the action of sea currents (BOWENS 2009, 168). Covering a site in sandbags cannot be considered a lasting solution, since the bags in which the sand is packed will deteriorate over time - sites protected in this fas-

hion should be subject to monitoring and regular supervision. The method of covering a site with sandbags has been implemented successfully at a number of sites such as at the Solway wreck in South Australia (CORONEOS 2006, 55-57), Duart Point in Scotland (MARTIN 1955, 19) and at several sites in Italy (DAVIDDE 2004, 143).

#### COVERING THE SITE WITH CANAVAS OR POLYPROPYLENE NETTING

This method involves installing fine mesh canvas or polypropylene netting over a threatened site with visible surface finds on the seabed so that the netting is not taut, but rather gently moves with maritime currents (Figure 3). Polypropylene netting has been demonstrated as superior in this application because of its greater strength and longevity. To keep it in place this netting needs to be weighed down or affixed to the bottom, usually with sandbags or spikes along the edges. Over a short period of time (one to a few weeks), as a result of the activity of sea currents and waves, fine sand enters the eyes of the netting and accumulates over the site. Over time this creates an artificial embankment over the site.

This buries the site in a layer of sand, protecting it from the actions of waves, sea currents and marine organisms (shipworms, mussels, fish) and human factors. This system shields the site from the view of potential looters and also keeps

the finds in an anaerobic environment, which contributes to stabilising archaeological material. This method, of course, is not appropriate to every site and a set of conditions have to be present to warrant its implementation. This pertains, above all, to the strength of the sea current and the quantity of sediment available. Because the eyes of the netting through which sand is to pass may be blocked by the growth of algae and other marine organisms that tend to colonise the netting, this method is limited in its application to appropriate sites. Nevertheless, regular monitoring of the processes at a given site and timely intervention can address most of the problems that arise during the sedimentation process. This very effective and inexpensive method of protecting sites has been used in places like Sri Lanka on the wreck of the Avondster (MANDERS 2006a, 58-59), in the Netherlands at the Burgzand Noord 10 wreck (MANDERS 2003, 18-20; MANDERS 2006b, 72) and at the site of the Hårbøllebro wreck in Denmark (GREGORY et al. 2008, 19-22).

#### COVERING THE SITE WITH A CLOSED BOX

This is a very interesting protection solution that may also be used during archaeological research, and upon its completion is a basis for long term in situ protection. The system of covering a site with a closed box is an in situ site protection principle that consists of several steps. A permanent metal frame that surrounds the area we

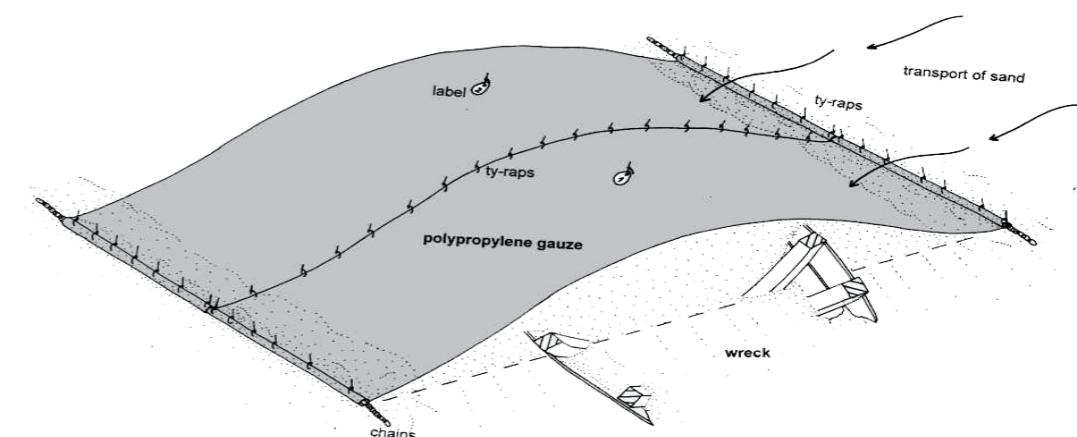


Figure 3. Protecting a site using polypropylene netting (MANDERS 2008: 36)

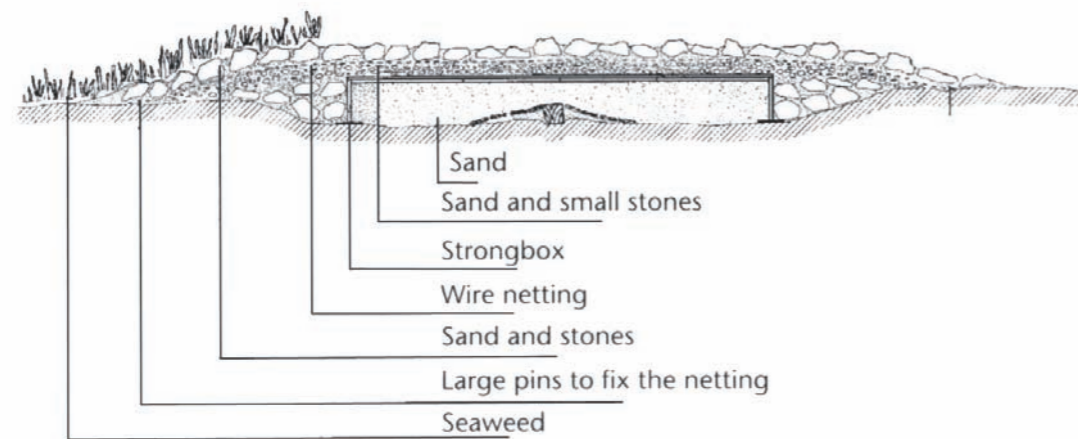


Figure 4. A site that is protected with a closed box (NEGUERUELA 2000, 115)

wish to protect is first installed on the bottom. Metal plates are then affixed to the frame on its vertical and horizontal sides. These plates are moveable, and may be removed during research allowing archaeologists to study the area under them. This structure is useful during research as it also provides a working surface on which hand tools may be placed, divers are able to navigate it safely and it also prevents damage to those parts of the site still covered by other parts of the structure. At the end of research and documentation the space between the finds and the metal structure is filled with sand to stabilise the finds, and the plates are fixed to the metal frame to completely close the site and finds, which are left in situ. The box is then covered in successive layers of sand, protective netting and stones. A grassy covering may also be installed, which protects the site and blends into the site's natural surroundings (Figure 4). Covering a site in this fashion is most effective for shipwreck finds and ship structures that form a smaller, closed context, and that require longer, systematic and precise documentation. The closed box protection system has been successfully implemented on a Phoenician vessel from the 7th century BC in Spain's Mazarron (NEGUERUELA 2000, 112-116).

### PROTECTION USING METAL NETTING

Protective metal nets are usually used as physical protection from an immediate threat to

an archaeological site by impeding undesirable access to archaeological finds. Galvanised iron nets, additionally coated in corrosion inhibitors, are installed over a site to provide protection (Figure 5). The netting has to be affixed to the bottom with spikes, or weighed down with concrete blocks to ensure they remain fixed in the desired place.

Marine organisms will quickly colonise the netting and they will be completely overgrown in a relatively short period of time, creating visual protection of the finds we want to safeguard. And while this kind of in situ protection is inexpensive and ideal for very shallow sites, it should not, because of certain shortcomings, be considered a final solution. The greatest drawback of this method is the fact that the netting corrodes quite quickly, and requires systematic monitoring and replacement when



Figure 5. The Mijoka Shallows site off Murter protected with metal netting, Croatia (Photo: I. Miholjek)

the necessity arises. Another problem is that, since the netting is usually installed directly above the site, potential looters can quite easily cut the protective netting and devastate a site. This method of protection is most effective if combined with some other method such as burial with sand or sandbags. This method of protection is frequently implemented in Italy (DAVIDDE 2002, 83-84; DAVIDDE 2004, 143-144) and in Croatia (JURIŠIĆ 2006, 154-155).

### PROTECTIVE CAGES

This method has as its purpose the physical protection of a site achieved by covering the entire site with protective cages. A cage consists of a sturdy metal structure onto which steel netting of various sizes is affixed and joined. This method of fabrication allows us to create a cage of the desired size, depending on the size of the area we wish to protect. The cage is attached to the seabed and additionally weighed down with concrete blocks to ensure its stability (Figure 6). The top of the cage has locked openings for authorised persons providing them with direct access to finds with the purpose of further documentation or find maintenance. Protective coating is applied to the nets to retard corrosion, as are zinc protectors in the role of sacrificial anodes to provide cathodic protection of the cage (MESIĆ 2008, 96). Their purpose is to corrode before the steel cage, increasing its life span. An info plate is affixed to the cage providing basic data on the site and providing a further aspect of legal protection as it indicates that the site constitutes protected cultural property. The examples of protection cited so far have aimed to conceal sites from the public and thereby protect them from external influence. Protective cages, however, have a different role in that they serve to present the site. A site thus protected offers the broader diving community the possibility of accessing underwater heritage without posing a threat to its safety. There are legal regulations in place to govern protected sites in Croatia. The competent ministry issues a multi-year concession to interested diving clubs who lead groups of tourists to a site. The club in question undertakes the obligation to carry out frequent monitoring of the cage to prevent undesired visitors

and to see to the upkeep of the cage, which is, besides, in the club's best interest. This approach has achieved a level of site self-sustainability, as it provides benefit not only to the responsible diving club but also to the local community. The shortcoming of this method is the limited lifetime of the netting, estimated as some twenty years - continued materials and degradation inhibitor development may extend their useful lifetime (JURIŠIĆ 2006, 155-156). This model of protection has been implemented in the Croatian Adriatic since 1990 - eight sites with the remains of shipwrecks have been protected to date. These are Roman period shipwrecks with a large number of integrally preserved amphore. Their significance and level of preservation make them ideal examples for this type of physical protection (ZMAIĆ 2009, 18-19).



Figure 6. A protective cage over a Roman period shipwreck off the island of Zirje, Croatia (Photo: M. Pešić)

### IN SITU CONSERVATION AND STABILISATION

With the development of the conservation-restoration profession and the application of knowledge from other branches of science, some methods that have been applied primarily in other fields have made their way into the practical in situ protection of archaeological sites. Their goal is to act directly upon the stabilisation and retarding of degradation processes in targeted archaeological objects. One of these is cathodic protection, applied only on metal finds. The principle upon which the method is based is that the object we wish to protect (the cathode) is placed into electrical contact with a sacrificial

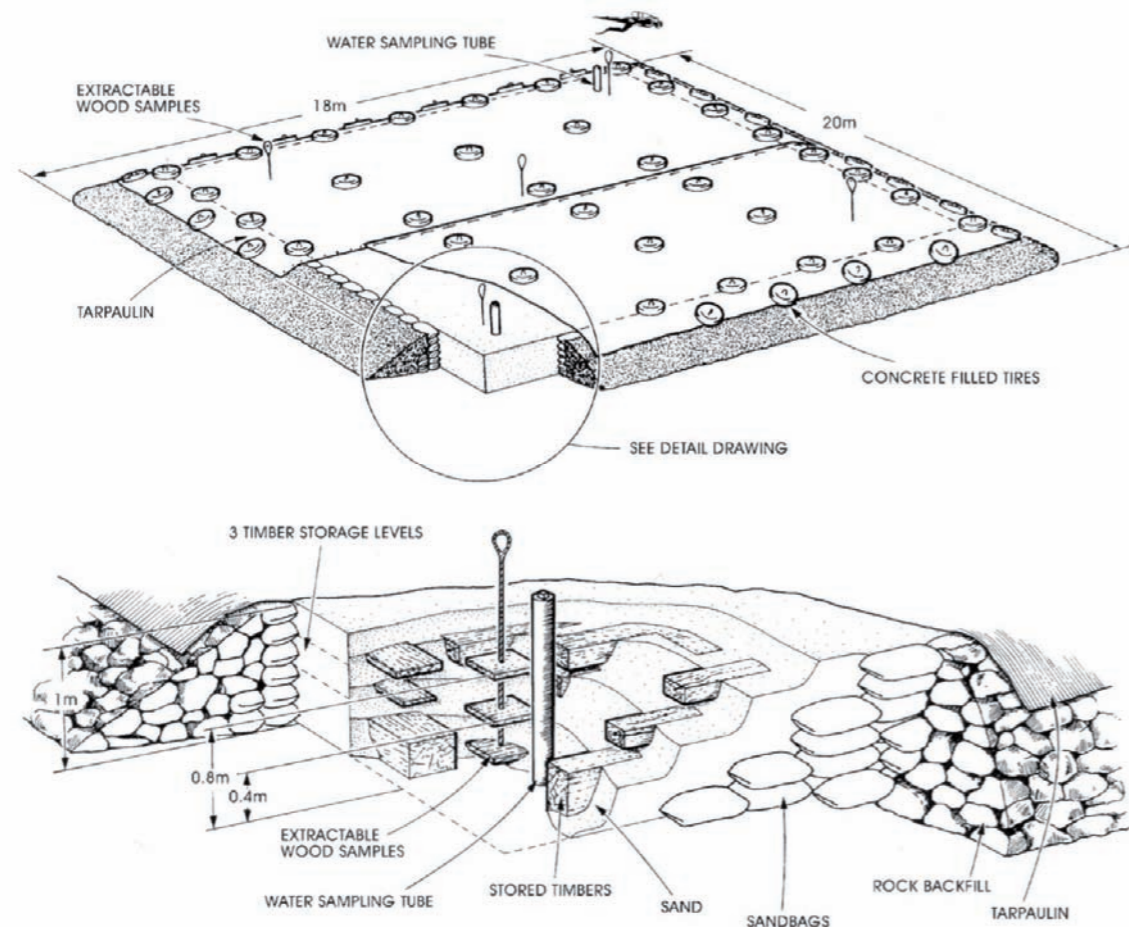


Figure 7. Sketch of a hummock with buried wooden elements from the Red Bay site in Canada (WADDELL 2007, 149)

anode. The sacrificial anode is a metal that corrodes more readily - more precisely has a higher negative potential - usually this is zinc, magnesium or aluminium. The two metals create an electrochemical cell as a result of which the anode corrodes in favour of the protected cathode, whereby the degradation of the metal find we wish to protect is significantly retarded (MacLEOD 1987; ORTMANN 2009, 17). The stabilisation of objects *in situ* also significantly shortens the process of conservation if a need arises to extract the object from the site (MacLEOD 1995, 58-59). The shortcomings of this method are that it is applicable only to metal finds, that the sacrificial anode has a limited lifetime and needs to be regularly monitored and replaced, and that the method is suitable only for smaller objects (cannons, anchors) since human and financial potential may be a limiting factor when dealing with larger objects. This method of protection has been applied for many years in Aus-

tralia, at the Duart Point shipwreck for example (MacLEOD 1995; GREGORY 1999). There is also the recent example from Sicily, where iron cannons have been protected in this fashion at the Cala Spalmatore site with the purpose of presenting the site as an underwater archaeological park (BARTULLI et al., 2008).

#### REBURIAL OF ARCHAEOLOGICAL MATERIAL

While it cannot in essence be considered a method of *in situ* protection since the archaeological finds are researched and their original position altered, this is one of the methods that ensures the stability of underwater archaeological material in its natural environment, and we will treat it in the context of protecting finds under water. A scarcity of financial resources, modest prospects for the restoration and presentation of archaeological material, and the low historical significan-

ce of certain artefacts has made burial in sand one of the frequently applied methods of protecting already researched archaeological material (BERGSTRAND et al. 2005, 9).

The purpose of this method is to store archaeological material in a stable environment to retard physical, biological and chemical deterioration. Once research and documentation has been completed, archaeological materials are arranged in a trench prepared in the seabed and buried in sand - alternatively, a special structure is fabricated for the same purpose (Figure 7). Certain standards must be observed in the process, the most important of which are that the objects must constantly be kept in a wet environment during documentation to prevent their deterioration, that each object must be properly tagged prior to burial to facilitate the work of those who will one day access the material again. The purpose of this procedure is that the reburied material achieves a stable condition providing for many years of storage, until the need arises for its extraction and restoration (DAVIDDE 2004, 139; ORTMANN 2009, 11-13). This method is applied for the most part on wooden ship structures the conservation and restoration of which is a lengthy and demanding undertaking - meaningless without proper presentation. One of the more complex examples of this kind of protection of researched archaeological material, wood in this case, was implemented at the Red Bay site in Canada where over 3,000 pieces of wood were reburied in the seabed (WADDELL 2007, 149-151; ORTMANN 2009, 12-13). Another example of this method of protection is in Marstrand harbour in Sweden where, after several research campaigns, about 85% of various archaeological finds of metal, ceramics, glass, wood and other organic material were reburied. Here protection is carried out in the frame of a 50-year RAAR (Reburial and Analyses of Archaeological Remains) project the aim of which is to collect data on the processes and intensity of deterioration of various kinds of archaeological materials based on the monitoring of a broad range of parameters. This kind of research wishes to comprehend the causative agents of the degradation of archaeological materials for their more effective future protection

and preservation (BERGSTRAND et al. 2005).

#### MUSEUMS AND PARKS *IN SITU*

Once archaeological material is extracted from the water and undergoes conservation-restoration treatment it is exhibited in museums and collections specialised in caring for this kind of material. Of late there is a growing tendency towards presenting underwater cultural heritage *in situ* in the frame of underwater archaeological parks or underwater museums. The presentation of cultural heritage is closely linked to, and an inseparable component of, archaeological finds, and it is important that a person involved in the protection of heritage is knowledgeable in the basics of presentation. Furthermore, because of the constant tendency for archaeological material to continue deteriorating, the conservator-restorer must be familiar with the conditions and methods of preserving objects and to be in a position to act in a timely fashion towards their preservation. We shall look here in brief at a few of the methods of presenting archaeological finds related to underwater archaeological heritage.

Underwater archaeological parks are one of the most popular methods of *in situ* presentation and can be found around the world. Among these we can number all underwater sites or objects that enjoy legal protection and have been developed for visitor access (Figure 8). These may be independent archaeological sites, several archaeological sites in close proximity that

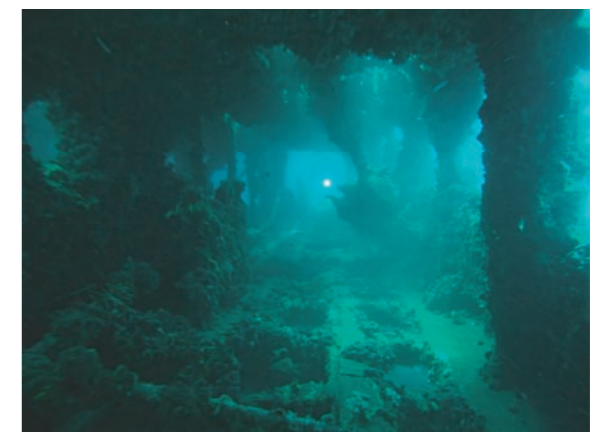


Figure 8. Inside the protected shipwreck Baron Gautsch, Croatia (Photo: N. Starčić)

together form one large underwater park or archaeological sites in the frame of nature parks and reserves. What is common to them is that they have been researched and documented by experts and that visitor access to these sites, with constant supervision, does not constitute a threat of damage or the destruction of the archaeological finds that are a constituent part of an underwater park (DAVIDDE 2002, 84).

Individual cases that may be characterised as underwater parks have already been cited, including sites protected by steel cages in Croatian waters - but we can also number various shipwrecks, harbour complexes or sunken architecture among the archaeological parks. There are a great number of underwater archaeological parks around the world and as examples we can cite the underwater archaeological park off the island of Ustica in Sicily and Baia to the west of Naples in Italy, the Legare Anchorage and other shipwreck sites within Biscayne National Park in Florida (SKOWRONEK et al. 1987), the sunken harbour of Caesarea Maritima in Israel (RABAN 1992). In these parks visitors are guided to small finds and features by signs, and the finds themselves are accompanied by information boards that describe them and provide information concerning their origin and function, and offer visitors other interesting information related to a given site (DAVIDDE 2002, 85).

Underwater museums are structures in which underwater cultural heritage is presented in situ and that are accessible to the broader public and not only to divers. Currently the largest underwater museum in situ is the Baiheliang Museum in China - built on dry land prior to the Three Gorges Dam going operational and now lying underwater at a depth of 43 metres. It features inscriptions up to 1,200 years old recording the movement of the Yangtze River (XIURUN 2011, 2). Another major project is an underwater museum in Alexandria, Egypt that aims to present submerged Egyptian culture, including small finds and features, the remains of the Alexandrian harbour and the famed lighthouse on Pharos (MORCOS 2000, 33, 40-41).

There are also a great number of museums that directly link their content to underwater cultural heritage. Noteworthy are the Mary Rose Museum in Portsmouth, Great Britain with its presentation of a 16th century warship, the Vasa Museum in Sweden's Stockholm or the Bodrum Museum of Underwater Archaeology in Turkey.

## SITE SUPERVISION

The supervision of underwater archaeological sites is a key step towards preserving underwater cultural heritage. As has been emphasised several times, the greatest threats to the preservation of archaeological sites are those coming from human or natural factors. We have already described in some detail the legal and physical protection of sites, and we shall now briefly touch upon the methods of supervising them. There are several methods whereby sites can be monitored and protected. We should above all emphasise the role of experts whose regular observation, inspection and collections of samples from a site will enable them to notice changes on time and properly respond to them. Sometimes the wider population is not aware of the location of underwater archaeological heritage, and these places should, therefore, be properly indicated to reduce the negative effects on heritage. Indicating protected zones, which can be visibly identified with buoys, is the basic method of marking off zones in which activity that could damage cultural property is not permitted. These areas can have info signboards that indicate the reasons for protecting the site and the sanctions foreseen for those who do not abide by the stipulated restrictions. Of course it is the competent legal authorities that play a key role in this system and who need to conduct periodic monitoring of the site. The deployment of sonar buoys is also one of the methods that can be used to monitor the site. Installed at the site they can warn approaching vessels that they are approaching a protected zone and send the competent authorities notifications of unwanted entry to the site. The movement of vessels in protected archaeological zones may also be monitored by satellite, based on which maps of the movements of ships in

protected zones can be drafted, which may later be used as evidence if a site is looted. Monitoring of sites may also be undertaken using various geophysical methods that monitor the appearance and changes to the natural surroundings such as erosion of the seabed, and that may also be beneficial in documenting changes to archaeological finds and sites. It is, of course, impossible to protect and monitor the situation at all underwater archaeological sites, and this kind of monitoring can only be deployed to a limited number of key areas. This is why educating the local community and interested groups is yet another crucial element of the principles of protection and monitoring. Presentations, lectures, publications, courses and workshops are only a few of the aspects of education that can bring underwater heritage closer to the broader public with the aim of raising awareness and care for its protection.

Supervision of the state of underwater archaeological finds in situ is yet another key determinant in which experts from the conservation-restoration profession should take an active role. Monitoring the processes of degradation and decomposition, changes to the surrounding environment and to the natural conditions that influence the state of archaeological finds, and analyses of all influences on them, help us understand and take timely action against the causative agents. Different causative agents affect every kind of archaeological material - metal, ceramics, stone, wood - in varying intensity, and each requires a specific approach to monitoring these parameters. Given that these causative agents are described elsewhere in the text, we will only cite a few of the major projects here that are engaged in studying and monitoring the causes of the deterioration of archaeological material *in situ*.

Besides the already cited and broad - reaching RAAR project that includes particular study of all subgroups of materials most frequently found at archaeological sites, also noteworthy are the MoSS Project (Monitoring of Shipwreck Sites) the aim of which it is to better understand the processes of shipwreck deterioration (PALMA 2005), BACPOLES (Preserving cultural heritage

by preventing bacterial decay of wood in foundation piles and archaeological sites) which is studying the degradation of archaeological wood, and the research conducted on the wreck of the James Matthews (RICHARDS 2001; ORTMANN 2009, 28-32).

## CONCLUSION

Protecting cultural heritage is the primary task of every archaeologist, historian, conservator-restorer and every other person who comes into contact with the historical context of finds and sites and the underlying premise that should guide any research effort and the care of archaeological material. The protection of underwater cultural heritage in situ is one of the chief guidelines set out in the *UNESCO Convention on the Protection of the Underwater Cultural Heritage* and its Annex, and it should, as such, also be the first choice when engaging in research. This section has outlined the various methods of legal and physical protection of underwater sites *in situ*, and the methods of their presentation and supervision. Archaeological research is, however, often undertaken because of a threat to a site, because of its historical significance or simply because of a need to fill in gaps in historical knowledge. The result of these research efforts is material extracted from an aqueous environment, which, at the moment of extraction, is in an exceedingly sensitive state and requires the immediate attention of an expert. In the past it has often been the case that materials yielded by archaeological research, and upon its extraction from an underwater environment, was often not afforded proper care, conservation, storage and presentation. It is, therefore, vital that, before undertaking any underwater research, we secure the prerequisite conditions to ensure the long-term preservation of underwater cultural property in a state as similar as possible to that in which it was found. The in situ method of protection is certain to see further development in the future, as will the methods that both preserve and present underwater cultural heritage in its original form.

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