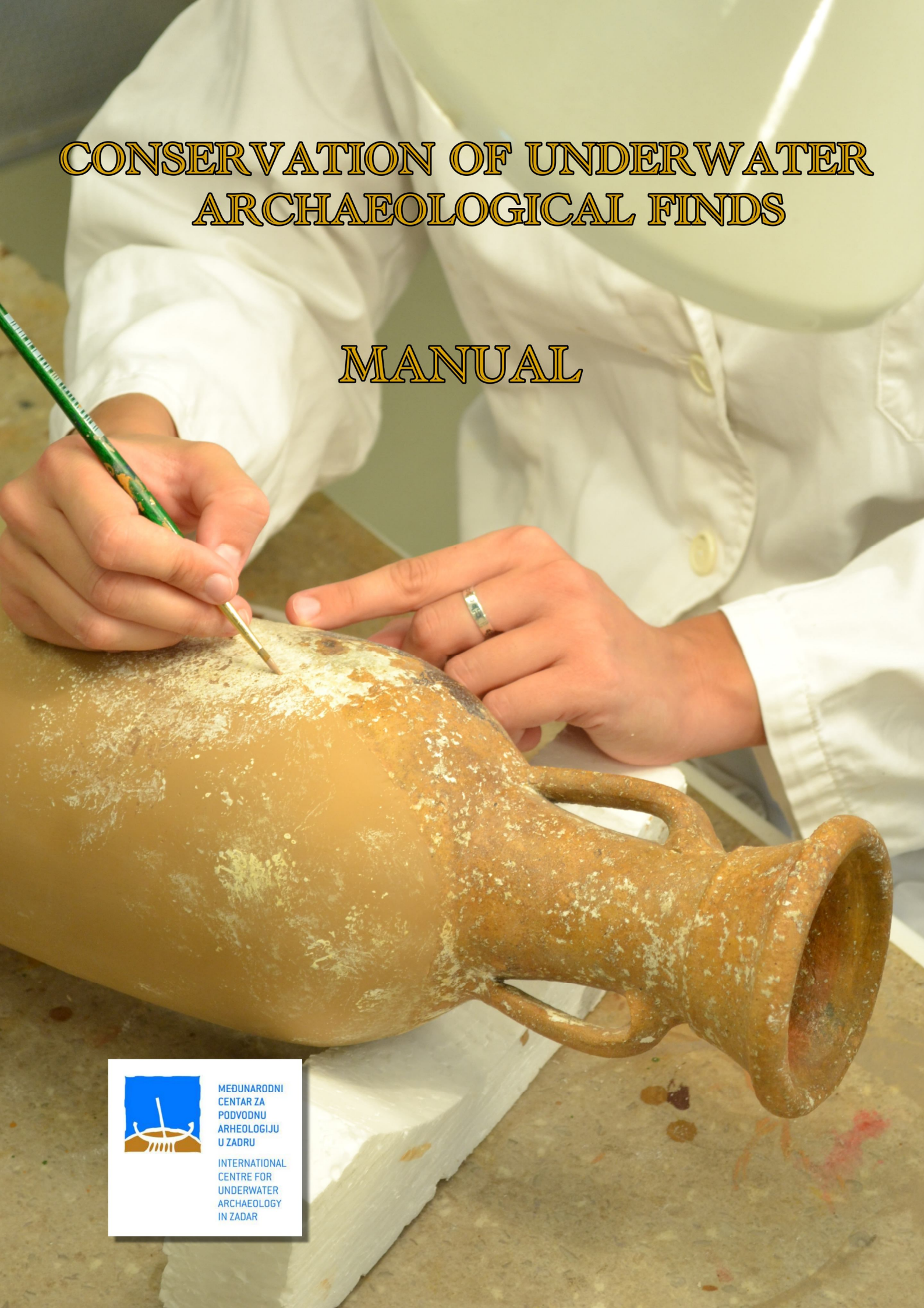
CONSERVATION OF UNDERWATER ARCHAEOLOGICAL FINDS

MANUAL



MEĐUNARODNI CENTAR ZA PODVODNU ARHEOLOGIJU U ZADRU

INTERNATIONAL CENTRE FOR UNDERWATER ARCHAEOLOGY IN ZADAR

International Centre for Underwater Archaeology in Zadar

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CONSERVATION OF UNDERWATER ARCHAEOLOGICAL FINDS MANUAL

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

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CONTENTS

I. Underwater Cultural Heritage and the UNESCO Convention 7
Bekić Luka

II. Guidelines, Ethics and the Methodology of Conservation-Restoration Work 13
Mustaček Mladen

III. Causes of the decay of Archaeological Material 16
Mustaček Mladen

IV. Ceramic, Stone and Glass Archaeological Material 24
Ćurković Martina

V. The Conservation and Restoration of Archaeological Metal Finds 43
Jozić Antonija

VI. Organic Material 55
Jelić Anita

VII. The Handling, Packing, Transport and Storage of Underwater Archaeological Finds 67
Perin Tanja

VIII. *In situ* Protection of Underwater Cultural Heritage 77
Pešić Mladen

LITERATURE 87

INTERNET SOURCES 94

I. Underwater Cultural Heritage and the UNESCO Convention

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Introduction

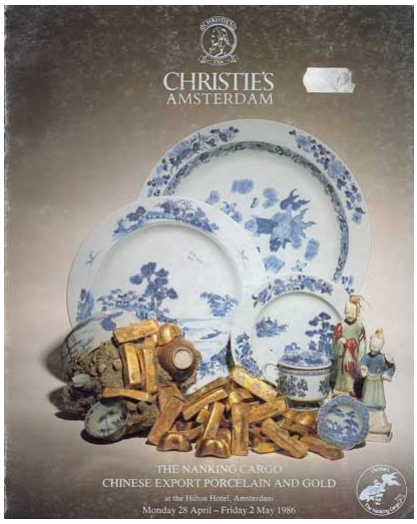
Sunken ships, settlements and various other hidden and valuable finds in the depths of the sea have always stirred the interest of people and their desire to reach them.

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.

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 overcome. 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 submarine finds, whereby the sunken formations have lost their characteristic attributes and disappeared - a fact that has evoked concern.

1. Tek Sing large plate offered for sale (Photo: www.antiquesndynasties.com)

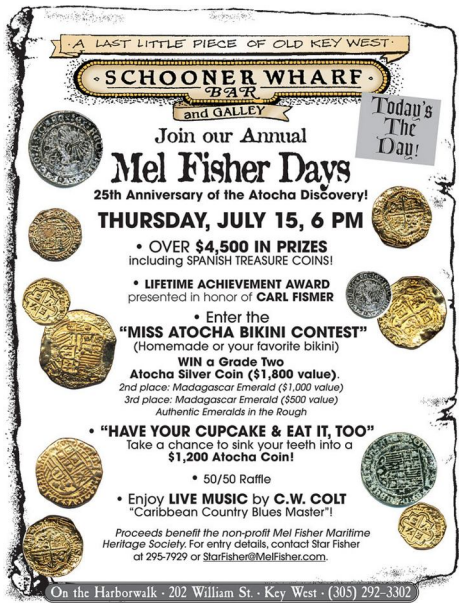
Particularly detrimental were the many activities in which sunken objects were collected solely for their commercial value - a concept that gave no consideration whatsoever to the essence of the find site and its future. There are many examples of various unscrupulous enterprises (treasure hunters) that, 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.



2. Geldermalsen auction catalogue
(Photo: Christies Amsterdam)

As a result, the period following World War II was noteworthy in that consideration was given for the first time of 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.



3. The treasure of the wreck of the Nuestra Señora de Atocha at Mel Fisher Days (Photo: www.schoonerwharf.com)

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 to underwater cultural heritage. These research endeavors, 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.

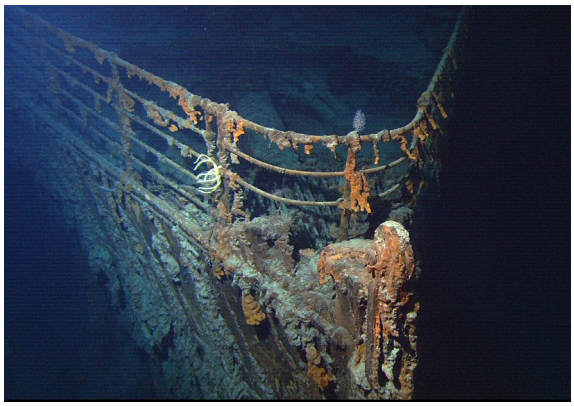
The past few decades have seen numerous initiatives at the national level, and a great many laws and regulations have been adopted governing the methods whereby underwater heritage is protected. These rules were, however, diverse, and, as a result, cooperation at the international level was launched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

Following various initiatives the adoption of the 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.

4. Uluburun wreck - recovering ingots 1, 2
(Photo: www.archaeologyhouston.wordpress.com)

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.

5. Uluburun wreck - reconstruction at Bodrum (Photo: en.wikipedia.org)



6. The bow of the Titanic (Photo: wavesnewsletter.com)

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.

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.

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.

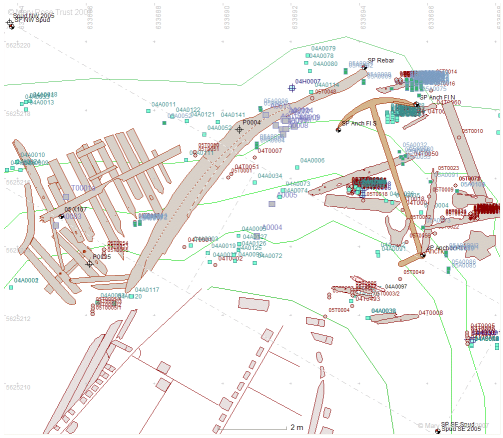
When adopting these principles the Convention also encourages ratifying countries to provide explicit protection to the cultural heritage of inland waters such as rivers and lakes. This paves the way for the participation of landlocked countries in the overall goal of protecting underwater heritage.

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.

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.



7. Mary Rose 2005 Excavation Site Recorder Map (Photo: www.3hconsulting.com)

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.

8. Mary Rose Stem Raise (Photo: ww.3hconsulting.com)

9. Mary Rose Painting (Photo: www.3hconsulting.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 program 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 programs for small finds and features during research, transport and the long-term storage of finds.

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 organization and coordination of these bodies and similar tasks is carried out by UNESCO, the Director - General and the Convention Secretariat based in Paris.

10. 2011 Session of the UNESCO 2001 Convention State Parties in Paris (Photo: L. Bekić)

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 specialized 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 Brodrum in Turkey, the museum housing the once sunken warship Mary Rose in Great Britain and many more.

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

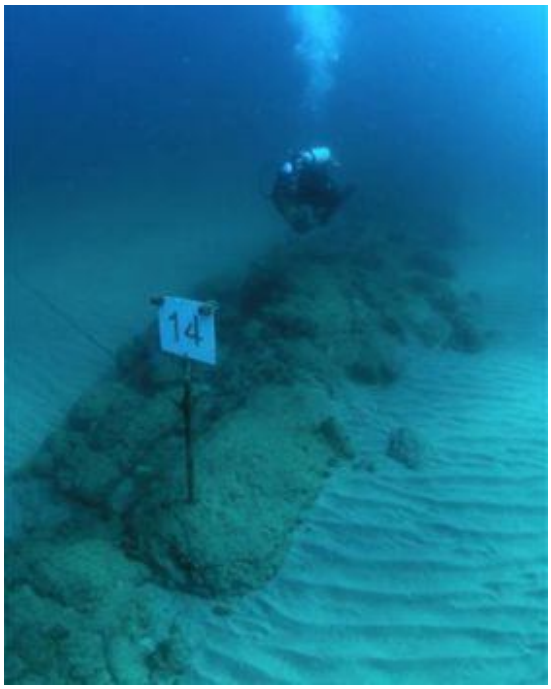
Improvements in diving techniques and equipment has seen a growth in the number of tourist divers who make organized visits to underwater archaeological sites.

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 several shipwrecks, the wreck of the Yongala in Australia and the wreck of the Baron Gautsch in Croatia.

Organized 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.



12. Caesarea location 14 (Photo: www.caesarea-diving.com)

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 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 specializing in the protection of objects collected in wet environments and in developing various procedures and technologies to protect them.

The Underwater Archaeological Finds Restoration and Conservation Department in Zadar, Croatia was founded in 2007. It pools a diverse team of experienced conservators-restorers and chemists who have specialized 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 civilization. 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' Organizations (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, scientific, 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 stabilizing 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 the 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 programmers, 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 programs 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 behavior 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 practiced 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 significant, 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 work 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 provide 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).

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 endeavor 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, archaeological material is exposed over time to the effects of weathering, 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 made of wood, textile, paper and other materials. The living species that inhabit these materials range from microscopic bacterial cells to plants and animals (TIANO 2010, 1). Irrespective of the medium in which they are found, whether on land or the seabed, archaeological material may be preserved in certain conditions. Iron, for example, may be preserved in an absence of water and the presence of phosphate, and wood in the absence of oxygen and the presence of copper salts (CRONYN 1990, 14).

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 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

Fouling

Archaeological material found underwater is exposed to fouling organisms before it is covered by sediment. Fouling organisms are animals and plants that are a component part of the biomass in seas, rivers and lakes.

Fouling may be divided into two groups of organisms:

- Macro fouling, which includes fauna (molluscs and the like) and flora (green algae, brown algae and the like).

- Micro fouling, which includes bacteria and diatoms.

The appearance of a given fouling organism 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. The end of the life cycle of fouling organisms is followed by the accumulation of their remains and the emergence of limestone and other sedimentary rock that form organogenic sediment on materials (ŠESTANOVIĆ 1997, 115). By surrounding the material these deposits may preserve the object from further deterioration by the protection offered by the sedimentary layer from the direct influence of other causes of deterioration from the microclimatic environment.

1. Object covered by organogenic sediment (Photo: R. Mosković, HRZ archives)

Deposition

Once on the bottom of the sea, river or lake, archaeological material is exposed to the inevitable process of sediment deposition. Until their eventual discovery, which may come centuries later, sediments are gradually deposited on the archaeological material. The speed of the sedimentation varies significantly in individual environments and ranges from 1mm to several centimeters 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 material.

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

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 evaporates 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.

Humidity

In its natural state water is found as a gas, liquid and as a solid aggregate. Water in the gaseous state, i.e. water vapour in the air is referred to as humidity.

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 a significant influence on most materials. The influence of humidity and temperature may lead to changes in size and shape, to chemical reactions and biodegradation. Extreme relative humidity levels may have different effects on the state of an object, especially those made of organic materials.

The optimum RH value in which organic materials would suffer the least damage and slowest aging is from 45 to 65%, at a temperature value of from 12 to 18°C. An elevated air humidity level above 65 to 70% favours the development of microorganisms that destroy organic material. It is important to know that many materials stabilize under certain climatic conditions in spite of the fact that these conditions are sometimes extreme (Recollections 1998, 21).

Problems arise when there are changes to the microclimate or when objects are transferred from one microclimatic environment to another. Changes in relative humidity and temperature, especially abrupt changes, are potentially more detrimental to materials than constant extreme conditions.

Water

The physical and chemical effects of water on objects of archaeological heritage are often detrimental. 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 objects of archaeological heritage may be significantly damaged by the activity of other components besides pure water, such as salts, dissolved gases, organic substances and undissolved particles. The abrasive action of sand carried by strong currents can also cause major damage to objects under the surface of the sea. Porous artefacts that contain water in their cavities can be seriously damaged by freezing as a result of the greater volume of ice as compared to water. 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 environment shrinking or swelling may cause damage.

Heat

Heat is a form of energy that is transferred from one body to another and is a part of the internal energy of a body that passes from a body of higher temperature to a body of lower temperature. When the temperatures reach equilibrium, heat is equal to zero. Heat is transferred by conductivity, convection and radiation. *Temperature* is the value in which the heat of a body is expressed. In the case of heat the constant tendency to establish equilibrium in nature relates to an equalisation of temperature, and there is a constant exchange of heat from places of higher temperature to places of lower temperature. On objects of archaeological heritage changes in temperature can cause the expansion and contraction of material, which may lead to temporary or permanent deformation, and finally to fracture. The action of heat causes water to evaporate from materials, and organic materials, for example, become hard, stiff and finally brittle. Heat also quickens and accelerates most chemical processes in materials, and quickens and facilitates the development of micro- and macroorganisms.

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 380 to 780 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 780 nm to 1 mm. This thermal radiation from the sun makes life on earth possible. UV radiation (100 to 380 nm) is vital because of its biological effect, but also particularly detrimental in the UVC range (ozone hole). The detrimental effects of light on organic materials can be very significant. They can cause the partial or complete bleaching of materials and their deterioration. In the present day the damage from light is far more frequent and severe as a result of the growing frequency of ozone holes in the Earth's atmosphere, as a result of which there is more intense penetration of rays of shorter wavelengths than was possible prior to this phenomenon. 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.

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, especially in areas with developed industry. Gases such as sulphur and nitric oxides,

carbon monoxide and dioxide, chlorine, hydrogen peroxide, hydrogen sulphide 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 color. Atmospheric contaminants may, in greater or lesser measure, cause detrimental changes on objects of archaeological heritage. Objects made of organic materials—paper and archival materials above all—are particularly sensitive to these kinds of contamination.

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.

Oxygen

As an elementary substance oxygen is one of the chief components of air, accounting for 21 percent. It is necessary to the sustainment and development of almost all living organisms—it participates in diverse biochemical processes, being most important for oxidation, in the process of which energy is released. Elementary oxygen is produced in nature in plant cells during the process of photosynthesis. Plants use solar energy and chlorophyll to create oxygen from inorganic materials. In the soil strata in which objects are buried oxygen is found for the most part in cavities (pores) in gaseous form.

The quantity of oxygen depends on the porosity of the soil, which determines the soil's capacity to contain gases (air) and water in its pores. In general, the size of the pores in the soil is proportional to the size of the soil particles. The greater, then, the particles of soil, the greater the size of the pores found in that soil. The pores of clay will, for example, be very small. 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. Chemical bonds with oxygen are referred to as oxides, and the chemical reaction of bonding with oxygen, oxidation. Oxygen is a component of many chemical reactions. The presence or absence of oxygen is the chief controlling factor in the activity of organisms and has an indirect role in the deterioration of materials.

Salts

Salts are ionic bonds created by a reaction between an acid and a base. When dissolved, salts split into individual ions, calcium (Ca^{2+}), bicarbonate (HCO_3-), sodium (Na^+) and chloride (Cl^-). The ions that create salts enter soil as a result of the process of rock erosion. This produces Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, HCO_3^- and silicates. HCO_3^- is also present as a product of the decomposition of carbon dioxide from the atmosphere and the breakdown of organic materials. This breakdown creates organic acids that form addition salts (CRONYN 1990, 22). Large quantities of Na^+ and Cl^- can be created from seawater or salt saturated aerosol (windborne seawater). Unlike soil and internal waters, most seawater contains soluble salts. The chief ions present in seawater are Na^+ and Cl^-, and the level of SO_4^{2-} is also high. 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 more soluble at low pH levels, while silicates are more soluble at higher pH levels. Soluble salts crystallize as a result of the evaporation of water leading to an increase in volume. If this occurs in porous material, the pressure may lead to the cracking of the material and of structures. Soluble salts may also accumulate 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 soluble salts causes changes in the color of materials. They also act as an electrolyte, conducting electrical energy and thereby facilitating the electrochemical corrosion of metals, which causes the deterioration of metals.

The biological causes of damage

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 frequently 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 physical 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 deposits 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 materials may also provide a habitat for some organisms.

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 one of the criteria for the classification of multicellular species is the composition of the pigment in plastids. The color of algae varies from red to dark purple, which is the result of a mixture of various pigments found in cytoplasm. The names of individual divisions and classes of algae are derived from their color. 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). Algae can influence the deterioration of archaeological material by causing both 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 supporting 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.

3. The algae covered barrel of a bronze cannon (Photo: HRZ archives)

Bacteria

Bacteria are single-celled organisms, and 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 unfavorable 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. The effects of bacteria on archaeological material, especially those of organic origin, 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 colored blemishes, since many of them create particles of pigment, incrustations and black sediment. Bacteria secrete enzymes that decompose organic substrates and that are, like fungi, entirely aerobic. There is a strain of bacteria that, unlike other organisms, do not require oxygen for respiration and are anaerobic. 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 can be determined by the odour of rotten eggs (hydrogen sulphide) and the blackening of deposits caused by the

4. Black sediment created by the decay and decomposition of iron (Photo: HRZ archives)

formation of metal sulphides (CRONYN 1990, 17).

Moulds

Moulds are multicellular organisms of plant origin at a higher level of development than bacteria. The body of moulds—mycelium—is composed of thin filaments called hyphae. Moulds may be brilliantly colored, 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 very quickly. In favourable conditions new organisms may develop from spores within 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 or high temperatures 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, parchment, 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 colonize 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 for the growth of fungi:

- Physical conditions (temperature, moisture, light)
- Chemical conditions (the presence of oxygen, the pH value of the substrate)
- Biological conditions (the type of material affects the development of some 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 nor 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).

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 color 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. They grow everywhere—from deserts, the moderate belt, to northern areas—and can also be found at high altitudes. 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 mechanically and chemically.

Mechanical 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 physical 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.

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 archaeological objects, such as: sea currents, waves, various natural catastrophes and the effects of plant and animal organisms. Sand from the seafloor borne on a strong sea current, for example, has an abrasive effect on objects, causing extensive surface damage.

Likewise, sediments that accumulate on objects over time subject it to significant pressure, which causes the cracking and fracturing of the object. 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.

Conclusion

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

IV. Ceramic, Stone and Glass Archaeological Material

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Introduction

This chapter shall describe the causes of degradation and the methods of conservation and restoration of ceramic, stone and glass archaeological objects extracted from marine and land sites. We shall cover these materials together because they share some common characteristics—the method of their manufacture and their mineral composition. These are inorganic compounds that contain a large percentage of silicates, which account for 28% of the Earth's crust. They are created by the manipulation of sand, feldspar, clay, talc and silicates into other forms under high temperature, produced by both humans and nature. As such we can group them into the same category of "siliceous and related materials" (Cronyn, 1990: 102-159). The materials of this category are of crystalline or glassy structure and are brittle. These materials vary from very high to low levels of porosity, and range from very soft to very hard. By their composition we can divide them into materials of siliceous and calcareous base. Based on their characteristics we shall see how various materials degrade, above all in terms of their porosity, and the problem of soluble salts and their migration through the pores of the material.

We find an abundance of ceramic and stone and somewhat less glass material under water and on land. This is indicative of the very early use of ceramics and stone as materials for the manufacture of commonplace objects, beginning with tools, small artistic objects and utensils, vessels for the storage of food and water, other ware, and other objects of various functions. Glass appears somewhat later and in smaller quantity. Noteworthy as the most frequent underwater finds are the ceramic amphorae we find as scattered cargo or as part of a shipwreck. Large and small fragments of stone sculptures and utensils are frequently found at submarine sites, while glass objects are found in smaller numbers and for the most part in a fragmented state.

Ceramics

Ceramic finds are the most frequent at underwater archaeological sites. The discovery of ceramics profoundly changed the way people lived. Its impermeability 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, the technique of pouring clay into a mould, the use of presses and so forth. Engraved and drawn decorations were added to the basic form. The objects were coated with glaze and other protective coatings to ensure impermeability.

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 ($Al_2Si_2O_5(OH)_4$). 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 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 color 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.

Substances that reduce plasticity and/or lower the required firing temperature are added with the purpose of improving the attributes of clay: sand, calcite, feldspar, chamotte, silica, organic particles and so forth. It is these particles that are visible in the structure, unique to every piece of pottery, and the type of clay used is one of the means of differentiating ceramics. The fusing of minerals occurs in the structure of a clay object during firing at high temperatures. 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.

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

1. Ceramics fired at low temperatures (fine and coarse unglazed pottery, glazed pottery, engobed pottery, maiolica and other pottery fired at up to 1000 - 1200°C)

2. Ceramics fired at high temperatures (ceramics fired at above 1000 - 1400°C, fire clay; soft-paste, bone china, hard-paste porcelain, stoneware)

The first group includes prehistoric and all other unglazed pottery 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 (terra sigillata at 900-950°C in an oxidation ambient to achieve the bright red color 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.

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

The degradation of ceramics is closely bound with the composition of the clay, and especially with the temperature at which the ceramics are fired. Ceramic fired at high temperature is more compact and of firmer structure than that fired at lower temperatures because of the better fusing of minerals. The result is better preservation over time, while ceramic fired at lower temperatures is, precisely as a result of its greater porosity, subject to degradation, and we often find it in a worse state of conservation. As an example we can cite the difference between porcelain and the maiolica that is aesthetically very similar to it. Porcelain is fired at very high temperature at which all the minerals are successfully fused into a single compact and impermeable mass. At these high temperatures the surface coating (glaze) is also completely bonded to the substrate to form an integral body. The formation of calcareous, organic and other accumulations may occur when these objects are submerged in seawater, but these do not present a problem, as they are unable to penetrate into the structure of the object, and do not affect the degradation of the object. In the case of maiolica fired at lower temperatures we have a ceramic body consisting of a substrate of terracotta to which a layer of glaze is adhered. With use cracks may appear on the glaze layer, which become a medium for the infiltration of water, salts and impurities, which then cause the layer of glaze to separate from the substrate layer. This porous surface is then a perfect target for marine organisms that can penetrate and destroy the already damaged surface.

Stone

Rock can be divided into three categories indicative of physical characteristics arising from formative processes.

They are divided into:

1. Igneous or volcanic rock (basalt, granite, pumice, obsidian)
2. Sedimentary or deposited rock (limestone, tufa, arenite, sandstone, breccia)
3. Metamorphic or transformed rock (gneiss, dolomite, marble, slate, gypsum)

Igneous rock forms by the cooling and/or solidification of magma and the formation of a dense network of crystals—below the Earth's surface as intrusive rock or on the surface as effusive rock. The formation of subterranean igneous rock occurs under high pressure and temperature. Rocks formed by these processes are very compact and of low porosity. The rapid cooling of molten material often forms obsidian and pumice.

Sedimentary rock is created by the deposition of the remains of other rock caused by the action of atmospheric influences, the deposition of marine and other organisms, and the deposition of dissolved limestone. We find calcium carbonate or limestone as the chief constructive element of these rocks, or in the role of cement binding rock particles of various granulation of igneous, sedimentary or metamorphic nature. They are divided into clastic, biochemical or chemical by the processes that create them.

Metamorphic rock is created by the transformation of existing rock through the action of temperature and pressure, which cause profound physical and/or chemical changes. Metamorphic rock may be sedimentary or igneous by its composition. In most cases igneous rock is the least porous and thereby the least subject to degradation over time. More porous rock is sensitive to changes in climatic conditions—changes in temperature and relative humidity, and is thus more readily degraded. The workability of the surface is linked to its porosity. Unlike porous sedimentary rock, easily worked because of its characteristic softness and porosity, impermeable igneous rock is very hard and difficult to work. Stone is polished after being worked to reduce surface porosity. This procedure is easier to perform on impermeable igneous rock, while the highly porous surface of sedimentary rock is almost impossible to polish. Marble has the characteristic of moderate hardness and low porosity, and is as such easy to work and polish. This is why it has become a favoured stone among sculptors.

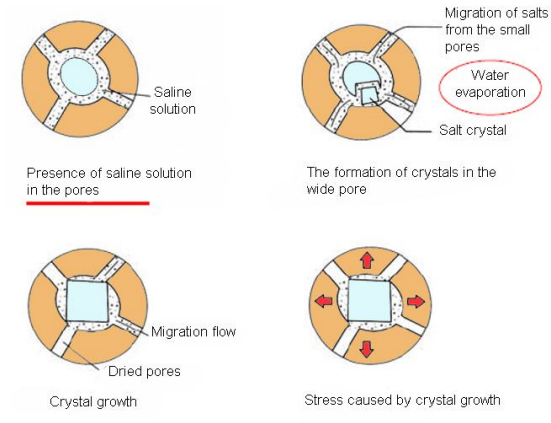
Other materials, such as metal parts, the pigments with which sculptures and walls are often painted and waxes used to coat marble statues, are often added to stone objects. Each of these materials has its characteristic behaviour over time. The speed at which individual materials degrade can affect the stone object, accelerating its degradation. This is when particular attention should be given to the conservation of these materials or their removal if they compromise the stability or aesthetic appearance of the object itself (the removal of oxidized iron spikes and couplings and their replacement with new stable materials).

Ceramic and stone 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 people 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.

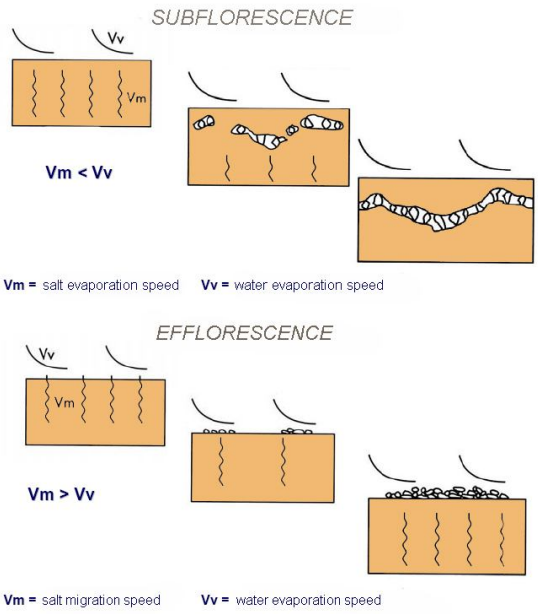
Alteration refers to the aging of objects accompanied by change that does not have a direct effect on the preservation of an object and that does not impair its readability. This category of change includes alterations of color, the formation of a superficial patina on objects and so forth. Degradation occurs as the advanced process of aging accompanied by a loss of the objects readability. The degradation of materials usually happens 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 phenomenon is the extraction of a find from a submarine environment in which it was successfully conserved 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 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. The natural factors are further subdivided into three categories: physical, chemical and biological. 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 well known. The ice crystals formed have a volume much greater than that of water, which causes stress



1. The formation of salt crystals in the pores of porous materials (Sketch from the lecture by prof. arch. Paolo Pieri Nerli, Palazzo Spinelli, Florence)

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. Salts appear in the form of chlorides, sulphates and nitrates; we find chlorides in objects deposited near or submerged in seawater, while sulphates and nitrates are most often formed in the presence of organic substances (CAVARI 2007, 66).



2. and 3. Efflorescence and subflorescence (Sketch from the lecture by prof. arch. Paolo Pieri Nerli, Palazzo Spinelli, Florence)

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 crystallization 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 an object from a moist environment and allow it to dry in a cold place. We can observe small white crystals on the surface similar to fine hairs. This form of salt crystallization 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 crystallization of soluble salts is closely linked with the ambient temperature, which determines the quantity of moisture in the objects and the speed at which water evaporates.

A frequent phenomenon in ceramics fired at lower temperatures is the absorption of large quantities of water and the reversion of the fired material into clay, as a result of which the objects become frangible and subject to deformation.

The presence of slightly acidic water can significantly weaken the structure of carbonate stone. An acidic environment accelerates the dissolution of calcium carbonate, which is then leached from the object by water, weakening its structure. A similar process takes place in stone kept in the open where it is subject to leaching and acid rain (an indirect human factor). Calcium carbonate is transformed into calcium sulphate and gypsum. The surface becomes powdery and granular and also becomes an ideal substrate for the deposition of salts, soot, bitumen and other impurities, which will later develop into the very problematic and well-known black stain.

With underwater archaeological finds in the presence of soluble salts there is also the problem of the accumulation of organic and calcareous deposits, and the biochemical and physical effects of living marine organisms on the object. Algae has a biochemical effect as its secretions dissolve the stone substrate, while marine organisms such as snails, mussels, Cnidaria and polychaetous worms act mechanically upon stone and ceramics, boring into them and scraping their surfaces (JAKŠIĆ, BIZJAK 2010, 231-245).

During their life cycles Crambe sponges, encrusting sponges and the Cliona sponge erode the surface of objects with a dense network of tiny holes visible after they are removed. These surfaces are then fertile ground for colonization by lithophagous types of mussels such as the date mussel (Litophaga litophaga) and Gastrochaena dubia, which bore deep into stone destroying its internal structure.

4 and 5. Various kinds of sponge on ceramics (Photo: A. Jelić, R. Mosković)

Larvae grow into a mussel in the already present holes, and proceeds to dissolve stone from acid gland secretions, penetrating deeper by a circular motion. We also often find the calcareous shells of polychaetous worms.

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 stone and ceramic 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.

6. Canals formed by polychaetous worms (Photo: A. Jelić)

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 (such as ceramic and glass pebbles on a beach).

7. The eroded surface of a stone ball (Photo: M. Ćurković)

8. Mussels on the surface of a ceramic plate (Photo: T. Perin)

9. The remains of algae, encrusting sponges and the shells of polychaetous worms (Photo: M. Ćurković)

10. Objects fouled by algae and the encrustations of marine organisms (Photo: R. Mosković)

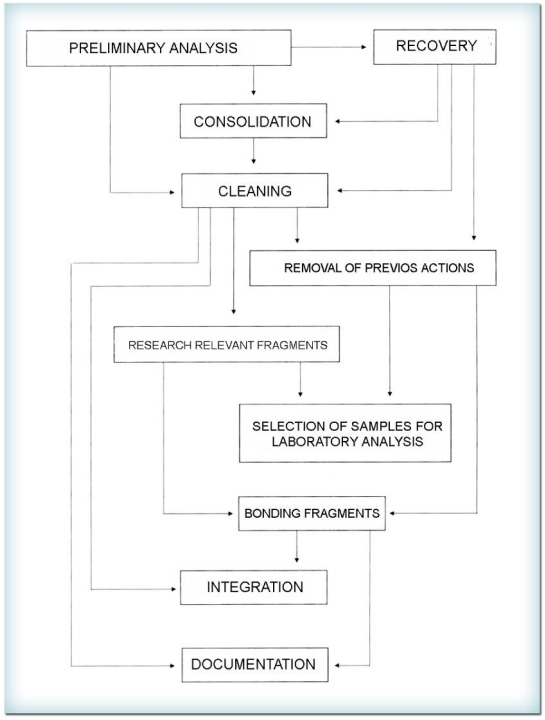
Dissolved minerals circulate underground, causing the accumulation of deposits on objects, most often calcareous, and possibly contain an admixture of sand and soil. Siliceous deposits may form, while the iron and manganese present in soil move to the surface of the object, where they form brown blemishes (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 and stone

Conservation-restoration work on ceramic and stone 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.



11.The phases of conservation-restoration work (Sketch from: Ravanelli, Guidotti 2004, p. 139)

In Figure 11 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 stone fragments in 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).

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 color, 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 sketched. 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 stone sculptures using radiographic imaging.

Cleaning

Cleaning is the most delicate phase in conservation-restoration work because it is irreversible, and as such requires a good knowledge of 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.

Cleaning is done mechanically, mechanico-chemically, and chemically. We chose 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).

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 a submarine environment as the result of the life cycle of marine organisms inhabiting the walls of objects.

12. The mechanical removal of deposits (Photo: M. Ćurković)

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.

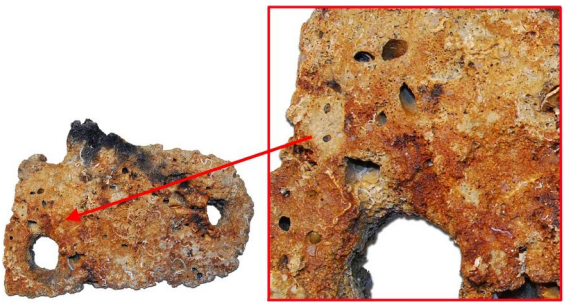
13. A stone ball covered by calcareous deposits (Photo: R. Mosković)

As the first choice, the mechanical removal of the 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.

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

The deposits are removed using surgical scalpels, ultrasonic chisels and pins, pneumatic chisels, pressurized water jets and by other means.

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. Calcareous deposits on ceramic material are softened with pads soaked in a 10 to 15% solution of EDTA salt in water, and then mechanically removed.



15. A stone anchor with marine organism deposits, an eroded surface and mussels present in cavities

Great care is required when working with stone with a high ratio of calcium carbonate content and we should avoid the chemical removal of calcareous deposits as the compound, once it has dissolved the calcareous deposit, can easily penetrate the object and damage the original surface and structure of the stone. A localized application of pads of controlled duration on prominent deposits is permitted. EDTA salt is used in an AB 57 solution to remove black stains on stone. After the chemical cleaning procedure the object must be thoroughly rinsed in distilled fresh water to achieve a neutral pH level.

Removing iron and copper oxides

Iron and copper oxide stains occur when an oxidized 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 and stone 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.

16. Fragments of a ceramic jug covered in iron oxides (Photo: A. Jelić)

17. A porcelain lid covered in iron oxides (Photo: M. Pešić)

We use EDTA salt solution in water to remove these metal salts. EDTA salts bond predominantly with iron and copper, but are also significantly active on calcium. Particular caution should, therefore, be exercised in removing stains from calcareous type stone. If this is the case we use a mild solution of 3 to 5% EDTA salt in a water solution, and a 15 to 20% solution in water on ceramics, to remove stains, applied in the form of soaked cotton or paper pulp pads. After the use of EDTA salt, which is naturally alkaline, we need to liberally rinse the object in distilled fresh 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.

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

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 are 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 in water with brushing is recommended for disinfection.

Desalination

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 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:

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.

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 interior 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 (BORGIOLI 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, polyvinyl acetates, silicone resins, ethyl silicate, barium hydroxide, microcrystalline waxes and others. They are applied in various percentages by immersion, spraying, coating and under a vacuum.

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 common 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.

19. Assembling a ceramic vessel using adhesive tape (Photo: M. Ćurković)

Sensitive surfaces such as glazing and painted decorations on stone and ceramics 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 in the same solvent are used for bonding (Mecosan, PVA glues, Paraloid B72). Stronger glues with greater adhesive strength should be used when gluing fragments of large ceramics and almost all stone objects. In these cases we are compelled to use non-reversible two-component epoxies of exceptional firmness and great adhesive strength.

Integration

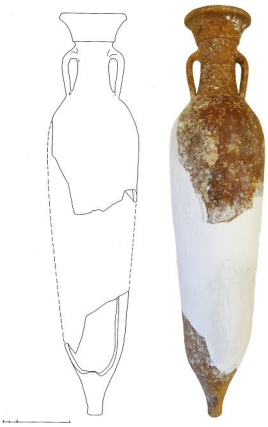
After the gluing procedure fragmented objects often lack material/fragments lost while deposited at the site (underwater or underground) or as a result of unskilful handling and extraction from the site. Intervention on an object is required when the stability and readability, i.e. its physical and aesthetic integrity, have been compromised. Objects are reconstructed only when all of the elements required for reconstruction are available. Integrations are made from materials that should, by their physical

characteristics and appearance, be as similar as possible to the original. When integrating ceramics we most often use dental plaster.

20. Fabricating an integration on a potter's wheel (Photo: M. Ćurković)

Dental plaster is an ideal integrant for ceramics because it is not hydroscopic, and as an inert material does not attract or release water/soluble salts into the ceramic material. Alabaster plaster, wax mixtures and various blends of plaster with admixtures (crushed brick, sand) are also used for integration. Stone objects are integrated with polyester putty/mortars for stone integration (artificial stone) and using natural mortars strengthened by the addition of consolidants.

Moulds of clay, plasticine, wax leaves, adhesive tape and other materials are made as a support to integration. Silicone and clay moulds are used to make casts of complicated 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.



21. Reconstruction based on a sketch (Sketch & photo by: M. Čurković)

Integrations are worked with files, scrapers and other hand tools while still wet, and are polished with sandpaper of various granulations after drying.

22. Reconstruction of an amphora (Photo: M. Ćurković)

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, without the application of color along the edges of the original material for better assimilation.

There are several approaches to how restored objects should be retouched. Archaeological objects are for the most part retouched in a way that keeps the integration visually separate from the surrounding material. This is achieved by coloring the integrated surface in a tone somewhat lighter, but very similar to the color of the original material's substrate. In some cases the patterns and nuances present on the object are indicated on the integrated surfaces, but always in a lighter tone. The differences in nuance between the original and integrated surfaces do not

necessarily have to be very evident—it suffices that the difference between the two is discernable upon closer inspection. The application of "invisible" retouching is frequent when dealing with antiques, where every shape of decoration, relief and any visual effect of the original parts of the object are faithfully reproduced.

23. Objects after restoration (Photo: M. Ćurković)

All materials used in retouching must be reversible. The most frequently used are water -based acrylic colors 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 colored 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.

Drafting post-restoration documentation

A 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.

The following conditions are recommended for the maintenance and storage of ceramic and stone objects after conservation-restoration procedures (*Atto di indirizzo sui criteri tecnico-scientifici e sugli standard di funzionamento e sviluppo dei musei*, VOKIĆ 2007):

Material	*Tempera-ture (°C)*	*Humidity (RH%)*	*Lighting (lux)*
Ceramics	-	45—65	>200
Low-fired ceramics	-	<45	>200
Stone	-	45—65	>200

Glass

Glass is an amorphous substance that is created by the cooling and solidification of the melt without crystallization. We differ natural glass (volcanic) from artificial glass (technical). Natural glass is created in volcanic eruptions (obsidian) or when lighting strikes sand (fulgurite) in cases where the melted stone/sand cools quickly enough that there is no crystallization. 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. Early glass was most often of a blue color as a result

of the frequent presence of copper oxides in the glass blend. Glass is artificially colored by the addition of metal oxides of manganese, cobalt, chrome, copper, iron and others in the blend prior to melting.

The chief ingredient of glass is silica (SiO_2) to which flux—soda (Na_2 O) and potash (K_2 O)—is added as a modifier to lower the melting point (from 1700°C to under 1000°C), and stabilizers—magnesium and calcium from limestone—to improve its durability (CRONYN 1990, 128). 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.

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 modeled into various shapes.

Glass deterioration

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 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

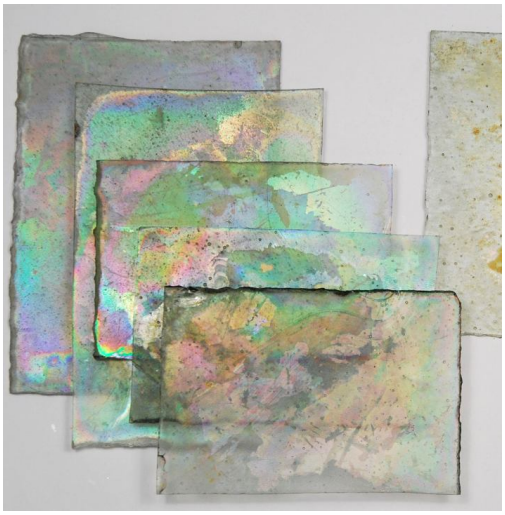
24. Beads joined by calcareous and other depositions in a conglomerate (Photo: M. Ćurković)

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 stabilizers.

Contact with water leads to the leaching of positive K^+ and Na^+ ions, followed by Ca^{2+} and Mg^{2+} ions. They react with water to form hydroxides. Positive hydrogen ions replace the positive ions of the modifiers have leached out, which hydrates the glass. After drying they react with 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_2). 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 crystallize and cause the object to fracture.

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.



25. Glass iridescence (Photo: A. Jelić)

The presence of rainbow colors 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 colors 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 after 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 effect is achieved by physical means, by the abrasive action of sand and other substances in the submarine 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.

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

Discoloration occurs when metal oxides are leached from glass, when metal oxides in the glass are oxidized, or by the absorption of metal oxides from the environment.

27. A glass lid with iron oxide deposits (Photo: M. Pešić)

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.

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

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.

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 color, 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.

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, and also 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 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, colors and gilding on glass surfaces should be protected with a coating of consolidant - they must not by any means be cleaned using water.

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. 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. Metal oxides are often firmly bonded with the damaged glass surface, and as such it is sometimes better not to remove them.

Removing calcareous deposits from glass objects is a significant problem. The mechanical removal of these deposits using a scalpel while the object is still wet is recommended. There have been attempts to remove calcareous deposits using chemicals (hydrochloric acid, EDTA, acetic acid) but these methods have always turned out detrimental to the glass object.

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 way as with ceramics and stone, by submerging the object in a tap water bath, later in distilled water, and to exchange the water regularly. 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.

Consolidation

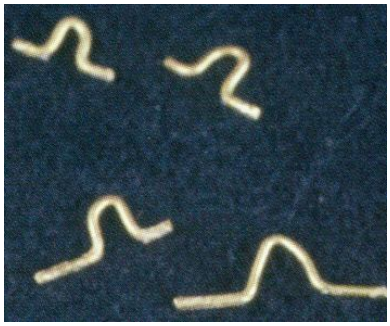
Consolidation is conducted only when indispensible, in the event of the sloughing, flaking and crumbling of the surface. It should always been kept in mind that consolidation is an only partly reversible procedure and that it is better to avoid it if there is not an unequivocal need to undertake it. 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 consolidated 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.

Bonding

Bonding fragments secures the object's stability and aesthetic integrity. Materials used for gluing must posses the characteristics of transparency, good adhesion, reversibility and must not be damaging to the object. The Paraloid B72 acrylic resin, or more frequently the Araldite 2020 epoxy resin, preferred for its greater duration, is used for this purpose.

Prior to gluing, the object must be cleaned of dust to ensure the better adhesion of the glue. Fragments may initially be joined with adhesive tape or metal omega clips. The metal clips are applied to the outer wall as bridges linking two fragments, and are affixed with drops of cyanoacrylate glue (Super Attack).



29. Metal clips (Photo: Koob, 2006, p. 60)

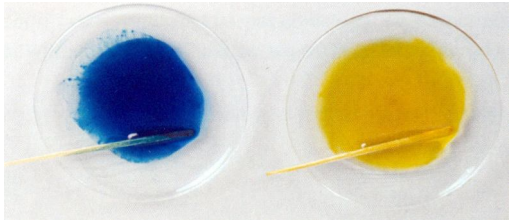
A prepared epoxy resin (Araldite 2020) or diluted acrylic resin (Paraloid) in acetone is poured into the joints, penetrating the fractures by capillary action, and allowed to dry. After the glue has hardened the clips can be removed using a scalpel or a pad soaked in acetone.

30. *Gluing a glass vessel with the aid of metal clips (Photo from Museum of Ancient Glass)*

Integration

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 fragments are present but there is a model of the original appearance. Reconstruction can then be undertaken with the aid of a cast mould. 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 an integration we use epoxy resin (Araldite 2020) because of the excellent characteristics it demonstrates after drying. Araldite 2020 is a fluid resin that is easily toned by adding powdered pigment or acrylic color during preparation—upon drying it becomes a transparent and brittle mass similar to glass. The negative side of this epoxy resin is its long hardening time, 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.



31. Toning epoxy resin with pigments (Photo: Koob, 2006, p. 87)

As a result, for the successful fabrication of an integration, we need a solid preparatory phase involving the fabrication of appropriate moulds. With larger integrations silicone casts of the inside and outside of the object are taken into which a fluid resin is then poured. Larger integrations can be done in several phases, integrating a part each time, and continuing with the work only when the previous section has dried well. Balloons inflated from the inside of the object are used with ovoid closed objects (balsamarium, bottles, vessels) as a support for the integration. After the resin is applied and has dried, the balloon is simply deflated and withdrawn from the object.

32. Reconstruction with the aid of an inflatable balloon (Photo: Koob, 2006, p. 85)

Wax leaves, adhesive tape, plasticine, clay and the like can also be used as support for the integration. If necessary, the epoxy resin may be treated mechanically after drying with sandpaper or a scalpel. Care should be taken in the process that pressure applied or the use of a tool does not damage the glass object. An integration can be coated with acrylic resin (Paraloid B72) diluted in acetone to improve transparency and protection.

33. The partial reconstruction of an object (Photo: M. Čurković)

34. The complete reconstruction of an object (Photo: Koob, 2006, p. 103)

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.

The following conditions are recommended for the maintenance and storage of glass objects after conservation-restoration procedures (*Atto di indirizzo sui criteri tecnico- scientifici e sugli standard di funzionamento e sviluppo dei musei*, VOKIĆ 2007)

Material	***Tempera-ture (°C)***	***Humidity (RH%)***	***Lighting (lux)***
Well pre-served glass	-	45—65	>200
Unstable glass	-	15—40	>200

V. The Conservation and Restoration of Archaeological 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 mineralization 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.

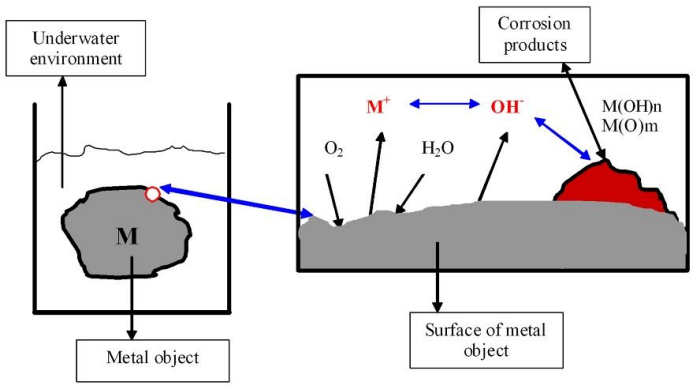
The characteristics and mechanisms of the corrosion of basic metals in archaeology

The 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 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 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



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

corrodes significantly faster than it would if it alone where 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 organism, 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 Fe_3O_4, haematite Fe_2O_3, limonite $2Fe_2O_3 \times H_2O$), carbonate (siderite $FeCO_3$), 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: FeO, Fe_3O_4 and Fe_2O_3. With the introduction of moisture Fe_2O_3 converts to FeO(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 oxidizes 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 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 stabilizing 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

2.a. Iron axe—prior to intervention; Kupa River site (Photo: M. Pešić)

2.b. Iron axe—post-intervention; Kupa River site (Photo: M. Pešić)

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 - $Fe(OH)_2$

LIMONITE – IRON OXIDE-HYDROXIDE - $FeO(OH)$

IRON(II) CHLORIDE - $FeCl_2$

HYDRATED IRON(II) CHLORIDE - $FeCl_2 \times H_2O$

IRON(III) CHLORIDE – $FeCl_3$

HYDRATED IRON(III) CHLORIDE – $FeCl_3 \times H_2O$

FERROUS SULPHIDE - FeS

MAGNETITE – Fe_3O_4

HYDRATED MAGNETITE – $Fe_3O_4 \times H_2O$

HAEMATITE – IRON(III) OXIDE – Fe_2O_3

HYDRATED HAEMATITE – $Fe_2O_3 \times H_2O$

It should be noted that iron chlorides are always a component part of the corrosive products of iron and that metal objects from underwater environments, 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 color. 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, chalcozine, 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 color, 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 color. Bronzes with over 20% tin are white in color, 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.

3. A bronze cauldron - Saint Paul site near Mljet (Photo: A. Jozić)

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 color. This layer is porous and the action of CO_2 bonds an external layer of basic carbonates to it. The layer of copper carbonate is green-blue in color, and its base is the mineral 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 hydrolyzed 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 recognizable 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 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_2O, 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, $Cu_2(OH)CO_2$ - one of the green basic copper carbonates.

AZURITE, $Cu_3(OH)_2(CO_3)_2$ - a blue copper carbonate; appears together with malachite.

CHALCONATRONITE, $Na_2Cu(CO_3)_2$ x $x3H_2O$ - a blue-green sodium copper carbonate.

ATACAMITE and PARATACAMITE, $Cu_2(OH)_3Cl$ - of the same composition, but of different crystal structure; a basic copper chloride of light green color; soft, often powdery structure; occurs on objects from soils rich in salts and on objects extracted from marine environments.

BOTALLACKITE, $Cu(OH)_3Cl$ x H_2O - of blue-green color; 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_2S. 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^+ ion to highly insoluble silver sulphide.

$2Ag + H_2S + 1/2O_2 \rightarrow Ag_2S + H_2O$

4. Silver coins - Saint Paul site near Mljet (Photo: M. Pešić)

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).

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 advanced 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 color. 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 is 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 golden.

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).

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

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 objects.

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.

6. Lead anchor stock – Čiovo site (Photo: A. Jozić)

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 sulphate 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_2), basic carbonates ($2PbCO_3$ x $Pb(OH)_2$), chlorides ($PbCl_2$), sulphides (PbS) and sulphates ($PbSO_4$). 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.

7. A tin box – Mijoka site at Murter (Photo: A. Jozić)

Initially this is visible as a loss of surface lustre and later as the formation of expanding grey - 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 stabilization
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 stabilize these objects.

Photographic documentation and a detailed description of the initial condition

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-restoration 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.

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.

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. 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. 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; MIHANOVIÆ 1997/1998, 459-477).

Cleaning metal objects

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 mineralized 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 micrometers 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. Mechanical cleaning is the basic form of work on metal archaeological objects. It involves the use of various chisels, pins, scalpels, dentistry micromotors, and various rotation and vibration tools. The use

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

of micro sandblasting devices is widespread.

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 ìm) 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 corrosion.

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.

9. Micro sandblasting an iron object under a microscope (Photo: A. Jelić)

Chemical cleaning

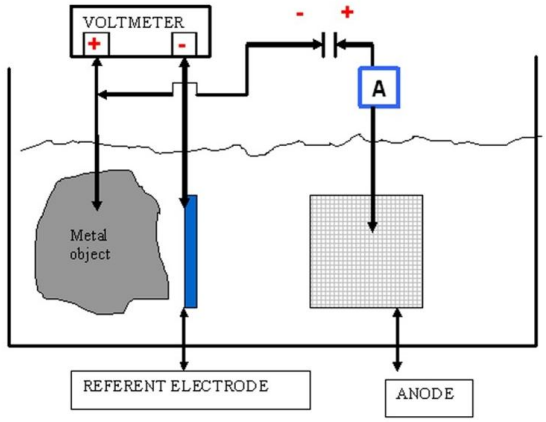
The chemical cleaning of archaeological metal objects is nowadays for the most part avoided. It is used sometimes to clean objects made of lead, silver or gold that are, as a result of their softness, easily damaged by mechanical cleaning. The most frequent chemical cleaning agents are mildly acidic 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. It is vital that objects are thoroughly rinsed with water after chemical cleaning to eliminate any remains of the chemicals used so that they do not contribute to further corrosion.

Cleaning by electrolytic reduction

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. 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.

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.



10. Schematic depiction of the electric circuit of electrolytic cleaning (Sketch: A. Jozić)

Archaeological metal objects usually lack a metal core and are preserved for the most part in a mineralized form and electrolytic reduction, which could cause them to fall apart, is not recommended as a cleaning method (BRADLEY 2004, 89-92; HAMILTON 1999, FILE 10A). This kind of cleaning is, as a rule, used successfully only on newer and better preserved metal objects.

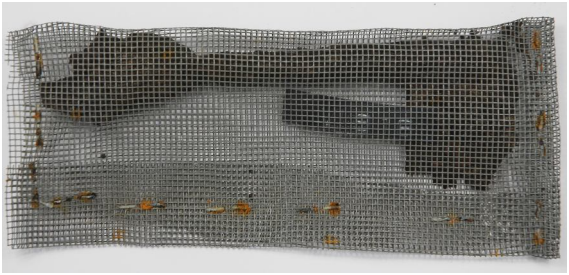
Active stabilization

The active stabilization 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.

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.



11. An iron object isolated in a polypropylene net after the sulphite procedure (Photo: A. Jozić)

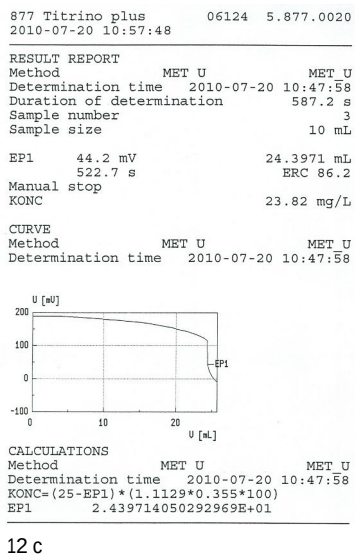
The vat is then filled with a solution of sodium sulphite (6.3%) and sodium hydroxide (2%) in distilled water. The conditions of the procedure are anaerobic (the vessel is hermetically sealed) to prevent the oxidation of sulphite into sulphate, which would destroy the material.

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 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.

12 a

12 b



12 c

12. The device that determines the concentration of chloride and a schematic depiction of the results (Photo: A. Jelić)

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 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.

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.

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.

13. Documenting the gradual removal of corrosion and calcareous accumulations from the head of the ancient Apoxyomenos statue – a valuable underwater bronze find (Photo: 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 organize 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.

VI. Organic material

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Introduction

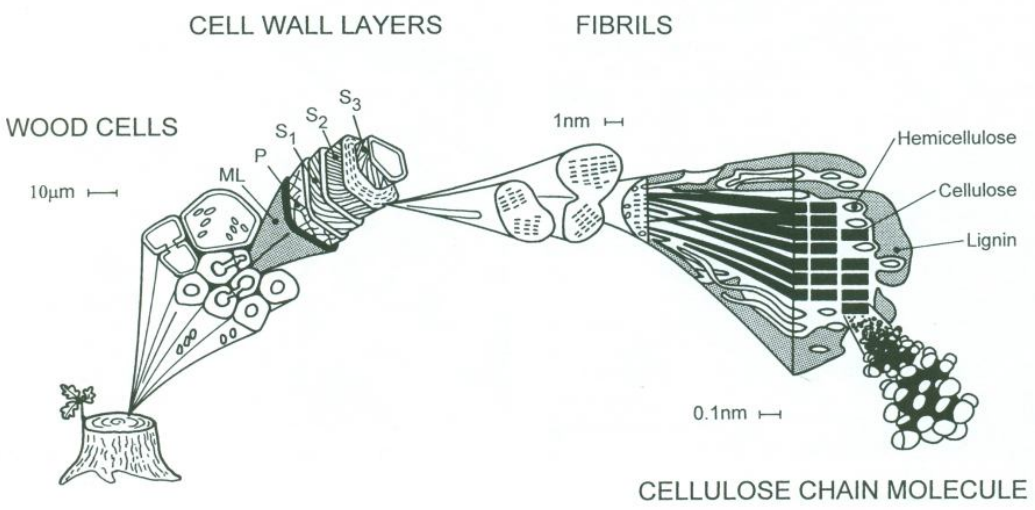
Organic material is a category of materials that include all artefacts made of plant fibers, animal tissues or bones. The most frequent underwater archaeological material of organic origin found in rivers, lakes, the sea or wetlands are wood, leather, bone, textile and rope. The level of preservation 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 fibers, 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 wood preserved (FORS 2008, 4; 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 the total mass of wood. Cellulose molecules join to form microfibers, and they in turn form fibers that



1. The structure of wood (Photo: JONES 2003, p. 54)

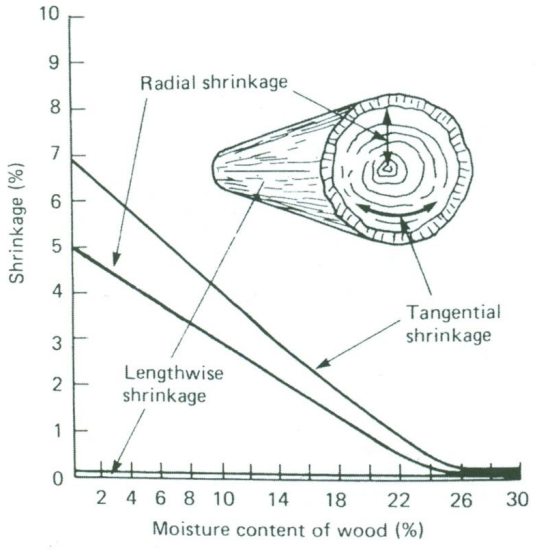
give a wood cell its strength and durability. Within the structure of wood, cellulose is surrounded by hemicellulose and lignin. Hemicellulose is the second most important carbohydrate present and accounts for 20 to 30% of wood's cell mass. The function of hemicellulose is not yet fully understood, but it is presumed that is 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 microfibers 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; FOST 2008 13, 14; MALINAR 2007, 86).

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 (MALINAR 2007, 86). Wood moisture can be expressed as a percentage of water in relation to dry matter, but more frequently as a percentage of water in relation to the wet mass of the wood. As such 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 (HAMILTON 1999, File 6; MALINAR 2007, 86).

Archaeological 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 microcapillaries. Its structure is also weakened by biological decomposition (MALINAR 2007, 85; 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, delaminating and deformation of the wood.



2. Graphic illustration of raw wood shrinkage (Photo: Jones 2003, p.64)

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 medullary rays (radial shrinkage), and in insignificant amounts parallel to the grain of the wood (longitudinal shrinkage).

It is valid in general that the more water there is the less cellulose and lignin, and this is 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; FOST 2008, 4, 5, 17; JONES 2003, 64; JURIĆ 1995, 79; JURIĆ et al 1994, 45; MALINAR 2007, 86, 87, 93; SMITH 2003, 22, 23).

The conservation of archaeological 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 stabilization, 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).

3. An example of taking measurements and producing a drawing; (Photo: Malinar 2007, p. 107)

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:

- Photographic documentation and a detailed description of the initial condition
- Cleaning the object
- Preliminary investigation
- Desalination
- Impregnation
- Drying
- Drafting technical documentation

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 (MALINAR 2007, 92).

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. 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: $C_{10}H_{14}O_8N_2Na_2 \times 2H_20$) 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; SMITH 2003, 23).

Preliminary investigation

Preliminary investigation always includes a visual examination and in some cases taking samples, determining the moisture content, the age and type 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 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 thermo-gravimetric 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:

$$Ø = [(A – B) / A] \times 100 (\%),$$

Where:

A = the mass of the wet sample

B = the mass of the dry sample (MALINAR 2007, p. 93).

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 impregnation substance required.

The age of wood and its species are 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}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. The species of a wood artefact is determined by ascertaining its macroscopic and microscopic characteristics (MALINAR 2007, 87-89).

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 specialized laboratories.

Markers for measuring changes in dimension (radial and tangential shrinkage) are 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).

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. 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, algacide, orthophenyl phenol, but the most commonly used because of its lesser toxicity is a mixture of boric acid and borax. 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 salt in the solution. More precise values are arrived at by measuring the concentration of salt in the sample by potentiometric titration (Figure 12 in the chapter on the Conservation and Restoration of Archaeological Metal Finds). 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; HAMILTON 1999, File 6; MALINAR 2007, 93).

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.

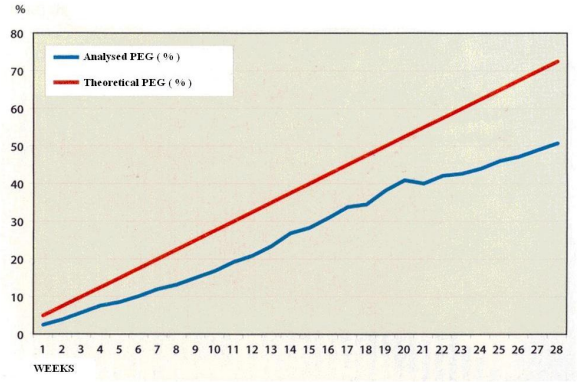
Polyethylene glycol (PEG) method

Polyethylene glycol (PEG) is a synthetic polymer constructed of the monomers ethylene oxide and water with the general formula $HO\text{-}(CH_2OCH_2)_n\text{-}H$, 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 forty-five monomers and n=45. 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; JONES 2003, 64; JURIĆ 1995, 79; MALINAR 2007, 94; *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. 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 (HAMILTON 1999, File 6; MALINAR 2007, 94, 96, 97, 105).

Two techniques of adding PEG are used, and we differentiate between the two-phased 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 4).



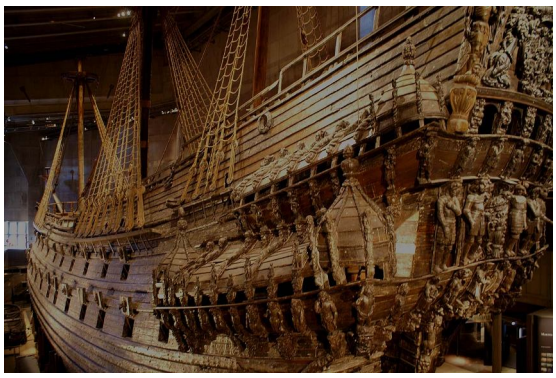
4. An example of the graphic depiction of the relation between theoretical PEG concentrations in a solution through a 28-week period and those established by analysis (Sketch from: Malinar 2007, p. 106)

When the concentration of PEG absorbed reaches a level of 70 to 90% no new PEG is added, and the wood is left in the solution for a time. 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).

5. Conservation of the remains of the wooden structure of the Mary Rose using PEG solution spraying (Photo: http://en.wikipedia.org/wiki/Mary Rose)

The method of conservation with polyethylene glycol is one of the first and the most frequent methods used. It is most suitable for the conservation of large artefacts of waterlogged wood such as the well-known 17th century warship *Vasa* (Figure 6) where the complete wooden ship structure was conserved using this method, or the 16th century warship *Mary Rose*, where the conservation of the remains of the wooden ship's structure using this method is still ongoing. Wooden ship's structures are

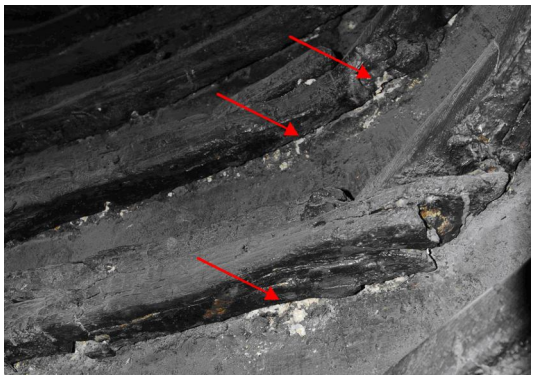
conserved first by spraying with water to effect the essential process of desalination, and then with a PEG solution in the impregnation procedure (Figure 5). The conservation of finds of this size usually requires the construction of special hangars in which the process of conservation is to be carried out, as is the cases of the two examples cited.



6. The ship Wasa after conservation using the PEG method

(Photo: http://www.bloggersbase.com/travel/stockholm-an-overview/)

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 (HAMILTON 1999, File 6; FOST 2008, 29-31; UNGER et al 2001, 420-422).



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

Also, after conservation and with the passage of time, the elementary sulphur that is a constituent element in the structure of wood oxidizes. Sulphur oxidation synthesizes sulphate acid and its salts, which increases the acidity of wood and causes its degradation. The synthesis of sulphate acid and its salts is visible as a light yellow powder on the surface of the treated wood (Figure 7). Preventing this synthesis and eliminating synthesized sulphate acid and its salts is a major problem affecting wooden finds conserved using the PEG method.

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 percentiles (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 conservation and it largely retains it 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

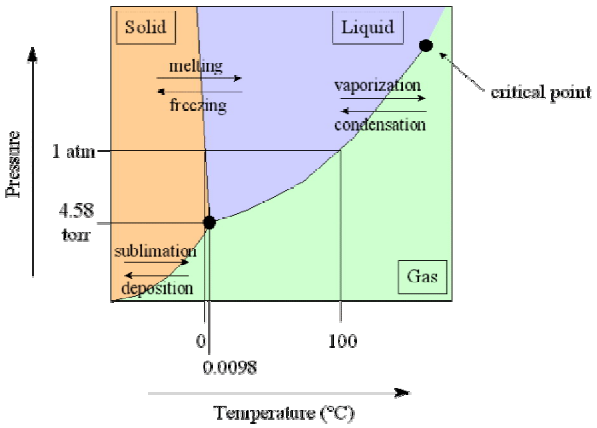
wood by insects and other pests; and a lack of data on the success of the method over a longer span of time (HAMILTON 1999, File 6; UNGER et al 2001, 426-428).

Acetone-rosin method

The method is based on replacing the water in wood with a natural resin known as rosin or colophony as the impregnation substance. The rosin is insoluble in water, and is dissolved in organic solvents, the most frequently being used 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 centimetre 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 of 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 (HAMILTON 1999, File 6). The advantages of the method are the stability and low weight of the treated wood, and the ability to use the method when wood is present in combination with metal, as rosin does not react with metals. 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).

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.



8. Water phase diagram (Photo: http://eskola.hfd.hr/clanci/pahuljice/faznidijagram.htm)

This method of dehydration is used in the conservation of waterlogged wood. The process is modeled 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. The dehydration process is carried out in a lyophilisation chamber (Figure 9) with pressure and temperature regulation until all the water is eliminated, i.e. until a constant mass is achieved in the wood being treated (JONES 2003, 62; HAMILTON 1999, File 6).

9. A freeze drier (Photo: http://www.kambic.com/produkti_liofilizatorji.php)

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.

Drying

Once the process of impregnating artefacts of waterlogged wood has been completed they can be dried without dimensional changes such as contraction, delaminating 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 55% 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, 20% for example, 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 (JONES 2003, 71-73; JURIĆ et al 1994, 48; MALINAR 2007, 105; SMITH 2003, 25).

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. What is common to all methods, however, is that upon conservation wood must be kept in controlled microclimatic conditions - the most commonly cited values are a temperature of 18°C ± 2°C, a relative humidity of 55% ± 2% and lighting that does not exceed an intensity of 200 lux (BRUNNING et al 2010, 30).

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 microfibers. Microfibers group to form the fibres that give organic material its sturdiness and durability (CRONYN 1990, 238).

Leather and bone are the most frequent of the other archaeological materials of organic origin conserved at our workshop.

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 (JONES 2003, 97; SMITH 2003, 60, 61).

Leather artefact conservation

The conservation of leather artefacts endeavours to stabilize the structure of leather and retard its further decomposition. The conservation-restoration process consists of the same phases previously cite 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 is the collagen fibre, which may react with other materials besides water, stabilized.

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 (HAMILTON 1999, File 7; 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 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 (HAMILTON 1999, File 7; JONES 2003, 100; RODGERS 2004, 171).

The conservation of leather artefacts using PEG is considered a satisfactory method even though it has been demonstrated that it is better of the leather is dehydrated in a freeze drier (Figure 9), 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 (HAMILTON 1999, File 7; SMITH 2003, 63).

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 60 to 90% 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 from 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 (JONES 2003, 98).

Bone

Bone is a sturdy binding tissue the interior of which is built of collagen fibres, calcium and other minerals such as phosphorous, magnesium, sodium and carbonates. Bone has a porous structure, which makes it sensitive to salts and impurities. This structure also promotes microorganisms that decompose organic substances, i.e. collagen fibres (JONES 2003, 100; RODGERS 2004, 172; SMITH 2003, 112).

Bone 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 artefacts, such as their cracking and splitting—the consequence of uncontrolled drying. The need for an impregnation process depends on the level of decomposition present in a bone artefact.

Cleaning and desalination

Bone and bony artefacts extracted from a marine environment must be desalinated to eliminate soluble marine salts, which are hygroscopic and the crystallization of which causes physical damage to non-desalinated artefacts (JONES 2003, 100; SMITH 2003, 113). Desalination is carried out in tap water over an extended period with frequent changes of water. Finishing desalination with several changes of distilled water is recommended. The mechanical cleaning of bones and bony artefacts is done prior to or during desalination.

Impregnation and drying

Bone is a material prone to cracking and splitting during the dehydration process, i.e. drying. If it is established that the bone structure of the artefact has been weakened and that dehydration could cause the cracking of the bone structure, the bone artefact is impregnated prior to drying by immersing it in a 50% solution of polyvinyl acetate (PVA $(C_4H_6O_2)_n$) in distilled water for a period of two weeks. This is followed by gradual drying in a closed chamber over a period of one week. If the bone artefact is well preserved and its structure not significantly weakened, impregnation prior to gradual drying is not required. The bones from the wreck of the *Mary Rose*, for example, were cleaned and desalinised, and gradually dried at a temperature of 20ºC and a relative humidity of 50% (JONES 2003, 100; RODGERS 2004, 173).

After drying, bone artefacts are 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).

Conclusion

Every artefact is different and requires a different method of conservation, which can, to a degree, be modified. After the careful study of the object it is up to the conservator-restorer to select which of the existing conservation methods to apply, which depends on the facilities and resources available to the conservation-restoration workshop. The method selected should be the least detrimental to the object, but also satisfy the basic principles of the conservation process, such as its reversibility, minimum intervention and that it does not alter the character of the object. The right choice of method is the result of a solid understanding of the problematic of conservation and many years of experience in the conservation of archaeological waterlogged wood and other archaeological organic materials.

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

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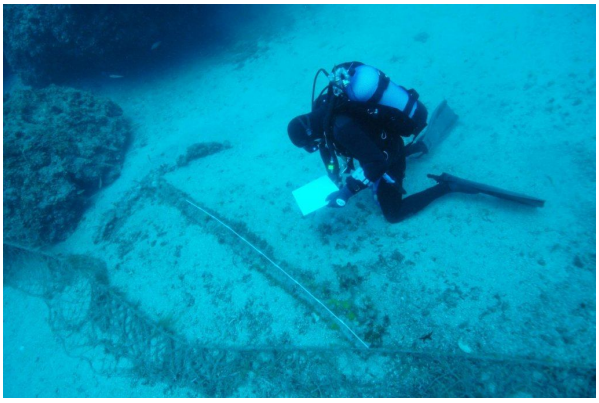
Introduction

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 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.



1. Drafting documentation at the site (Photo: M. Marukić, HRZ archives)

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 organization 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 stabilization 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.

2. *Drafting documentation at the site (Photo: I. Miholjek, HRZ archives)*

The presence of a specialized 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 outmost 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 extraction 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 consideration 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

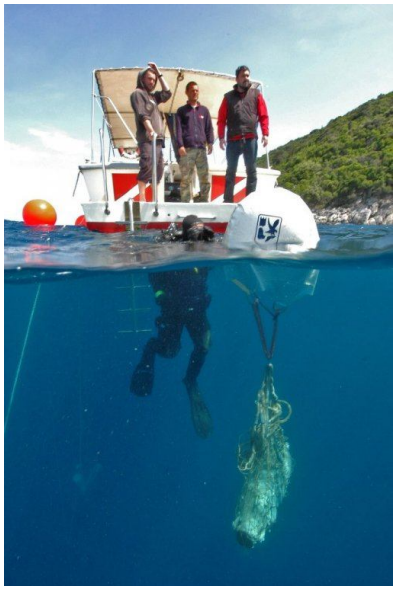
which designations are written with water resistant markers or labels made using a Dymo device. Given the great number of various situations we may encounter during underwater archaeological research, it is difficult to provide a description of procedures for every specific situation or every individual 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 plastic self-adhesive bags or plastic canisters that can be closed shut. If the object is sufficiently sturdy it can simply be wrapped in bubble wrap or in polyethylene film and raised to the surface. In the case of very fragile small finds we need to provide the appropriate support prior to raising, as they could break under their own weight or water pressure. 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.

Heavy and large finds

To be able to visualise this type of find 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 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.



3. Extracting amphorae using air balloons (Photo: R. Mosković, HRZ archives)

Dolia, as a particular type of amphorae, are placed in sturdy nets that are then raised using cranes on a ship's deck. Besides the cited cranes, we can also use air-filled balloons. There are many commercially available air balloons of varying sizes. They can be used to raise cargos 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 filled, therefore, the air in it expands as it rises and the lift increases, which results in an uncontrolled and very rapid ascent. Most balloons have a vent a diver can use to release air to control the speed of the ascent. 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.

4. Extracting a bronze cannon (Photo: R. Mosković, HRZ archives)

Fragile finds

When dealing with an exceptionally fragile find we should bear in mind that any pressure applied to the object could cause it to fall apart. With these finds we need to proceed with the outmost care. Prior to extraction they must be provided with the appropriate support. 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 a 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 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.

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

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.

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

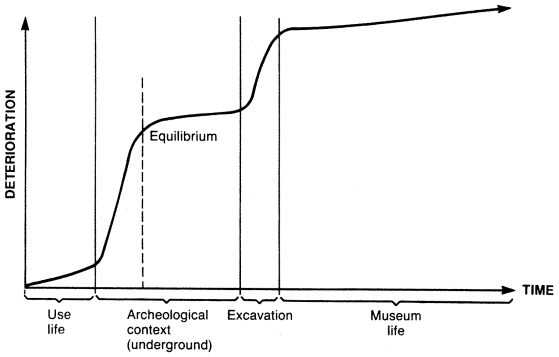
The procedure involved excavating tunnels under the ship's keel through which heavy cables were then drawn and affixed to pontoons placed above both sides of the sunken vessel. Water was then pumped into the pontoons until their decks were level with the surface of the sea. When water was then pumped 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 metres 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 were treated using standard conservation procedures.

Stabilized 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 stabilization of finds to prevent their deterioration. This process must begin immediately after the object has been taken from its natural environment and inclu-

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



7. A graph of the decomposition process over time; (Photo: http://www.nps.gov/museum/publications/MHI/AppendI.pdf)

A key element in this stabilization 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):

- The 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 fresh water in the case of very stable and sturdy objects.

- 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 color 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 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 stabilized 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 adequately tagged. 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. If using solutions that dissolve Dymo labels or plastic markings, we can use non-corrosive metal labels.

- Objects must be sorted by their composition. Sorting finds based on their composition is particularly important when dealing with metals, since storing two different metals together crates a galvanic effect between them leading to corrosion.

- 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. 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 (JONES 2010, 10). To ensure the maximum possible protection during transport we should follow these guidelines when packing (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.

- 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.

- 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.

- 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 methods 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 wooden finds

In ideal conditions the temporary storage of finds ahead of their active conservation should be as brief as possible—this kind of temporary storage, however, very often lasts for years

until funds and conditions are secured for appropriate treatment. The basic conditions for the storage of wooden finds are as follows:

- The wood 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.

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.

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

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.

Passive storage of leather finds

During the passive storage of leather 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 (JONES 2003, 47). Keeping leather finds wrapped in hermetically sealed polyethylene film 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 deionised water (BOWENS 2009, 157-158; JONES 2003, 47).

Passive storage of textile

The temporary storage of textile finds follows the same parameters as those for wood and leather, i.e. finds are packed in polyethylene bags or submerged in containers with fresh water. The water in the containers must be changed on a regular basis and possible microbiological activity controlled (JONES 2003, 47).

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 outmost 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).

Silver, gold, 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 glass, ceramic and stone

Glass, stone and ceramics are stored by submerging them in containers filled with water. After extraction these finds must under no circumstances be immediately submerged in tap or deionised 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 (HAMILTON 1999: File 4, 1-2; JONES 2003, 48-49).

Permanent find storage

Once the process of the active conservation and restoration of a find has been completed it 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 colors. 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. Keeping relative humidity at a level ranging from 40 to at most 70 percent with maximum variations of ±2% is recommended. For organic underwater archaeological finds the recommended relative humidity range is within the narrow boundaries of from 55 to 58 percent, while with metal underwater finds the recommended constant value is about 40% (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. It is recommended that 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.

VIII. *In Situ* Protection of Underwater Cultural Heritage

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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, and a dearth of exhibition space in museums 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 with the aim of the best possible and longest lasting solution for the preservation of our heritage.

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 signifycantly 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, and to various natural factors that constantly (sea currents, tides and waves) 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 submarine 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, 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 (harbour, shipwreck, structures, buildings, artefacts and human remains, objects of prehistoric character, aircrafts and vessels), 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 population 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 museum.

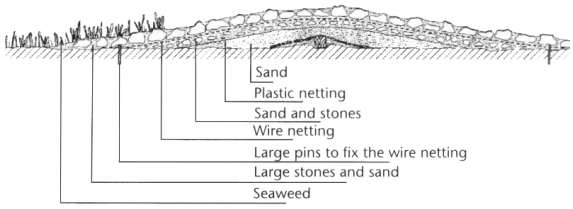
When dealing, for example, with the remains of a wooden ship structure on the seabed one of the methods of burying with sand would be ideal. For a Roman period shipwreck with the remains of a large number of amphorae implementing protection by the use of a cage would be an appropriate solution, while 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 sea grass at a site are being perfected of late with the purpose of exploiting the sediment that moves with water currents. Since natural sea grass 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 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).



1. A complex method for the burial of a site using natural and artificial materials (Photo: Negueruela 2000., p.112)

If there is a need the site may also be covered, besides with sand, 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 sandbags

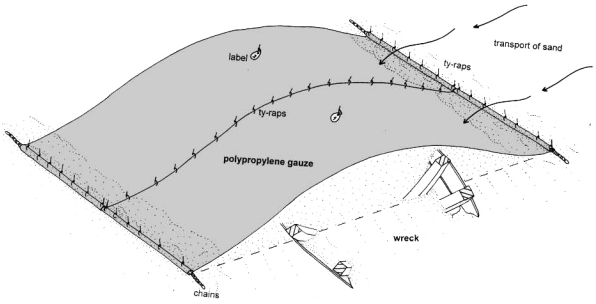
This is a method of protection used at sites where there is strong erosion, mostly as a result of various natural processes, and where the simpler method of depositing a layer of sand would not provide long-term protection. This method of physically protecting a find or site involves the use of polypropylene 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 fashion 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 (DAVIDE 2004: 143).

2. Protecting site Orud with sandbags and geotextile (Photo: R. Mosković / HRZ archives)

Covering the site with canvas 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.

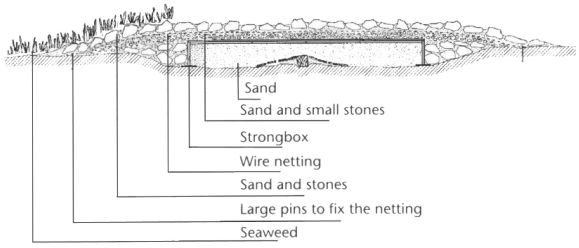


3. Protecting a site using polypropylene netting (Sketch: Manders 2008, p.36)

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 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.



4. A site is protected with a closed box (Sketch: Negueruela 2000., p. 115)

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.

5. The Mijoka Shallows site off Murter protected with metal netting (Photo; I. Miholjek / HRZ archives)

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 of these is the fact that the netting corrodes quite quickly, and requires systematic monitoring and replacement when the necessity arises. Another problem is that, since the netting is usually installed directly above it, 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 in 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 amphorae.

Their significance and level of preservation make them ideal examples for this type of physical protection (ZMAIĆ 2009: 18-19).

6. A protective cage over a Roman period shipwreck at rt Makarac (Photo; I. Miholjek / HRZ archives)

In situ conservation and stabilisation

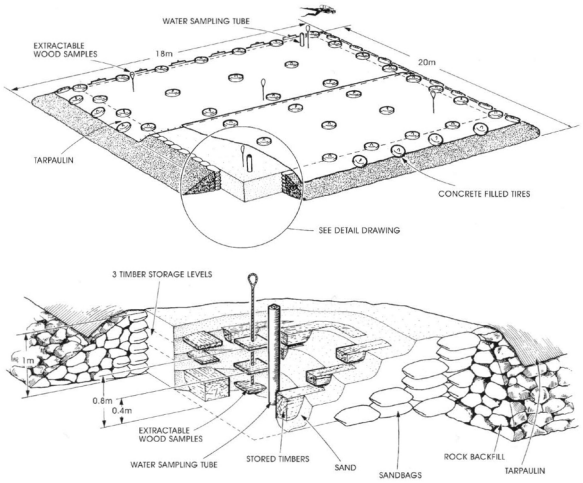
With the development of the conservation-restoration profession and the application of knowledge from other branches of science, some methods that have been applied primarily in other fields have made their way into the practical *in situ* protection of archaeological sites. Their goal is to act directly 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 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, ORTMAN 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 Australia, 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 (BARTULI 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 significance 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 deterio-ration. 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



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

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. These may be independent archaeological sites, several archaeological sites in close proximity that 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 Ancorage and other shipwreck sites within Biscayne National Park in Florida (SKONWRONEK 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: 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, Safeguarding and Visualising North-European 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 material yielded by archaeological research, and upon its extraction from an underwater environment was often not afforded proper care, conservation, storage and preservation. It is, therefore, vital that before undertaking any underwater research we secure the prerequisite conditions to ensure the long-term preservation of underwater cultural heritage 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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