The conservation of Titanic artefacts
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Introduction
The whole story began in 1985. In September, big headlines in world newspapers declared "The Titanic has been found". Since the catastrophe of 1912, the wreck had never been located. The depth of the ocean and the conflicting testimonies concerning the circumstances of the loss, had prevented its position from being established with any certainty. The perseverance of a French-American scientific team, with the most up-to-date equipment, eventually led to the discovery of the ship on 1 September 1985, thus uncovering one of the great mysteries of the deep.

Numerous drawings and a thousand or so photographs, produced over two expeditions in 1985 and 1986, were to show the reality of the wreck of the Titanic to the entire world: two enormous metallic mountains emerging from the silt, several hundred metres apart. One corresponded to the bow, and the other to the stern of the ship which, during its fall, had broken in two. Despite the years, the structures remained recognizable, but what amazed the first explorers was the multitude of apparently well-preserved objects of all kinds which were strewn around the wreckage. In a landscape of twisted sheet-metal, an intact porcelain plate, a bronze decoration, or a leather suitcase would suddenly appear - amazing objects which, at first sight, created a surrealistic sensation.

Whatever the quality, photographs could not express the emotional effect of these remains. A modest or precious object that has survived such a catastrophe stimulates the imagination more than a simple print. Now, these objects were within arm's reach, but still inaccessible.

In order to bring this terrifying event to the public, a new expedition was planned in 1987. French technology combined with American money were to see these precious remains raised from the Atlantic. The IFREMER, a French organisation specialising in the scientific study of great depths, agreed to undertake the recovery of the objects. The Nautil, a titanium bathyscaphe equipped with articulated arms, carried out the work: delicately gathering often very fragile artefacts and placing them in cages which conveyed them to the surface. The operation was a brilliant success. But, the rescue had to continue, elsewhere and in other ways.

On exposure to air, the degradation and decomposition of the artefacts was inevitable. Removing them from the dark, freezing ocean would disturb the equilibrium which, until now, had ensured their survival. A new equilibrium would have to be established, this time in air, and the objects treated according to their material composition. It was necessary to preserve the material from which the objects were made, otherwise this unexpected collection was at risk of falling apart and turning to powder.

Figure 1. A fork from the Titanic before conservation treatment.

Figure 2. Fork after dechlorination treatment and protective coating.

Electricité de France had the technical facilities for treating these objects. Indeed, since 1983, several procedures had been developed in its research laboratories to guarantee the preservation of underwater archaeological objects. These procedures, based on the use of electricity and electrochemical techniques, had been proven and had gained the confidence of the archaeological teams. In the Spring of 1987, as a result of this reputation, the EDF was approached by the organisers of the new expedition, the society Taurus International, to undertake the conservation. The challenge was exciting but the risks tremendous. The technical interest for the researchers was evident: it was up to them to assess the new problems, to develop new conservation treatments, and to increase the understanding of corrosion phenomenon at great depth. All this, therefore, constituted an extremely interesting scientific project.

In September 1987, the artefacts from the Titanic arrived in the laboratory of the Direction des Etudes et Recherches d'Electricité de France. Immersed in tanks of fresh water and firmly packed with foam, they had travelled by boat in a well-secured sealed container. All the objects were taken out of the container, then from their boxes, recorded and labelled. They were then stored in an orderly fashion according to their material type, and kept under strict security while awaiting conservation treatment. Ceramics and glass were stored in tap water. The progressive desalination of these materials was monitored by regular measurement of the storage water and its chloride content. The metallic objects were also stored in tap water, only a few iron objects, like the safe box, were conserved in a basic inhibiting solution (5% potassium hydroxide). We began the conservation treatments in order of priority, or as soon as the least sign of corrosion was observed.
The burial conditions
It was known that, when the surfaces of objects were not subjected to differential pressure, the physical deterioration due to pressure, would only be slight. This was certainly the case for most of the artefacts from the Titanic. Two particular consequences of the force of the pressure were found: the bottle corks were systematically pushed into the bottles, and the hollow handles of the cutlery were flattened (Figs. 1 and 2). On the other hand, the chemical alterations were very significant. Initial observations in the laboratory confirmed this.

Sea water constitutes a formidable and complex environment (Legal, 1988). It contains salts in solution (chlorides, sulphates, ...), gases and multiple organic substances. As soon as an object is immersed, physical, chemical, electrochemical and biochemical processes of degradation begin rapidly: hydrolytic reactions accompany the action of salts and micro-organisms. These processes combine, but their aggressiveness varies according to the depth and the conditions of immersion. At a depth of 4000 metres, in total darkness, with a low temperature, and reduced oxygen level, the chemical processes are noticeably slower. But, the conditions for chemical alteration of materials still exist at this depth. Deterioration of objects continues, certainly at a rate slowed by the darkness and low temperatures, but the processes of degradation are active and vary according to the materials.

Conservation treatment
Three problems must be overcome if the conservation of objects in their new environment is to be carried out well. It is necessary to eliminate or neutralize the factors causing degradation of the material constituents of the object, to prevent alterations due to the change of environment, and then to consolidate the fragile material in order to preserve its integrity. Different treatments are carried out according to material properties: stabilisation of metals, desalination of porous materials, consolidation of organic materials, drying, and surface protection.

The stabilisation of metal objects
When the objects are exposed to air, corrosion continues as the equilibrium achieved in their former environment is disturbed. This reaction happens as the result of the interaction of the unstable salts in the presence of humidity and oxygen. The stabilisation treatment aims to stop the corrosion processes. Two methods can be considered: either the removal of salts containing aggressive ions, or the isolation of the latter from the air and humidity by the creation of physical or chemical barriers. For certain metal alloys well known in underwater archaeology, such as the copper and iron alloys, or even lead, various procedures have been developed. On the other hand, the stabilisation of modern metals like aluminium and nickel is still the object of research.

Chemical methods are the most commonly used for the desalination of copper alloys. They consist of
Figure 6. Electrolytic brush being used to clean synthetic ivory.

Figure 7. Detail of the iron oxide mark.

Figure 8. Ivory mirror after treatment.

Figure 9. Silver handle before treatment. The concretions may be seen in black.

Figure 10. Silver handle after electrolytic cleaning.

Figure 11. Bronze sculpture during an electrolytic dechlorination.

Immersing the object in suitable products to extract the chlorides (distilled water, sodium sesquicarbonate). The main inconvenience of these methods is their duration, which can take several months. Thus, we have turned toward more rapid electrochemical methods. Most of the objects from the Titanic have been dechlorinated by electrolysis. The principal advantages of this method are a saving in time, and the absence of alteration in the objects and their corrosion products. This procedure, whose different experimental parameters have been the object of specific research, consists of connecting the metal object as a cathode in an electrolytic circuit. A current is then applied, sufficient to extract the chlorides without obtaining a liberation of hydrogen. The dissolved chlorides shift towards the anode throughout the solution.

Equally susceptible to the presence of chlorides, iron needs to be desalinated in the same manner. The methods used in the laboratory are chemical, (such as baths of alkaline sodium sulphite) (Schweitzer and Rinuy, 1982) or electrolytic.

The desalination of porous materials

Porous materials that behave like ceramics, glass or organic materials arrive impregnated with salt-laden water. Moreover, they often present with concretions composed of salts or metallic oxides (sulphides and oxides of iron being the most common) but also carbonates originating from marine organisms.

To ensure the conservation of these materials, it is
advisable to carry out a desalination treatment, that is to say, the extraction of harmful salts. Desalination is generally accomplished by rinsing in distilled water. The salts dissolve only up to a certain point. Electrochemical methods can also be used with good results: electrophoresis is the most suitable. This consists of placing the object in an electric field under the effect of which the salts dissociated into ions are able to shift to the poles of opposite sign to their own.

Organic materials
The collection of organic materials is without doubt the most complex group of artefacts, due to the fact that the objects are often found to be made up of composite materials: leather - fabric - cardboard - wood - metal - hair, and so on.

The objects reached us in various states of conservation. As long as they remain immersed, the degradation that the organic materials are exposed to modifies their form very little. Their structures are weakened, but as long as the water acts as a substitute for the dissolved constituents, they appear in good condition. Handling them proves to be the most difficult.

If, on the other hand, their form is changed, the appearance of these objects is found to be modified. The metallic oxides and sulphides cause a general darkening, especially noticeable on clear materials like papers. Cleaning is therefore one of the most important steps of the treatment. This process must clear the object of its salts while taking into account the chemical sensitivity and the resistance of the constituent materials.

In a number of cases, electrophoresis has been used for cleaning. The conditions of application are quite flexible and very often it is less aggressive than chemical cleaning.

This method has been used successfully for the treatment of paper bank notes, leather, and wooden objects. It must be understood that the intrinsic strength of the object in the electric field must be taken into consideration, and the duration of the treatment and the electric field be adapted to the mechanical resistance of the object being treated.

In every instance, we have worked with a neutral electrolyte (KNO₃ at 0.25% in deionised water), a weak electric field (of 2 to 10 Volts), and clean electrodes (titanium-ruthenium).

The extraction of salts is generally followed by a measurement of the ions in solution. We have noticed that the hygroscopic ions are extracted first, while the metallic salts are not extracted until later.

In the majority of cases, this cleaning has proved sufficient to restore the legibility of the object (especially the bank notes) (Figs 3, 4 and 5). In certain instances, it has been followed by a chemical bath designed to whiten the paper (hypochlorites) or to remove persistent rust stains. Indeed, all these treatments have been achieved by deacidification in a way that will ensure the best conservation of the material.

It should be emphasised that cleaning by electrophoresis is not applicable to all papers. Paper money takes it particularly well because it is chemically very stable and mechanically very solid. It was noted that, when a test was made on a fragment of newspaper, the fibres separated in the electric field.

Cleaning of iron oxide stains
Iron oxide stains on certain ceramics and synthetic ivories have been removed with the help of an electrolytic brush (Figs 6, 7 and 8). The brush acts as a kind of electrolytic cell placed directly on the stain. The object is immersed in an electrolyte (KOH 3%). In addition, a drop of electrolyte can be deposited on the surface of the object if it can not be immersed. The cathode is made of steel wool and the anode of Nickel wire.

Conclusion
This venture was an exceptional opportunity for the Groupe Valestra team, enabling them to fully appreciate the possibilities of electrochemical techniques, to test the efficiency, but also to define the limitations.

Two years of laboratory work have yielded valuable observations, information and technical discoveries, but not without occasional emotion in the face of these fragile remains which appear in a new light.

This wealth of artefacts represents the unique experience of a team who wish now to make it known and share it.

Acknowledgements
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References