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CONSERVATION METHODS OF IRON ARTIFACTS RECOVERED FROM THE MARINE ENVIRONMENT

Thesis
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By
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ABSTRACT

The survivors of iron artifacts in marine archaeological conditions are rarely in a good state. Long term burial of the artifacts in the marine environment often leads to porous, pits friability, salt encrustation, physical damage and severe corrosion that lead to reduce the lifetime of the metal artifacts. Among the variety of chlorine containing compounds, akaganeite is the only one that was evaluated by XRD in the iron coupons and artifacts. Also, chloride ions were assessed by silver nitrate test and EDS.

The removal of chloride ions is absolutely essential for the conservation of iron artifacts. Desalination treatment is one of the most laborious and time-consuming of conservation treatments. The results by X-ray diffraction, EDS (Energy dispersive spectrometer) and silver nitrate test proved that cast iron artifacts contain chlorides at higher amount than the wrought objects before the treatment. The efficiency of dechlorination treatment methods is often compared by determining the chloride ion removal and the final appearance of the objects by using further methods of investigation and analyses.

We tried in this study to assess desalination treatment methods that can save time and remove a large percentage chloride from the iron artifacts. Many methods of desalination or dechlorination of iron artifacts from the marine environment can be utilized in the conservation laboratories or in marine excavation situ to prevent further damage after being removed from the saline environment. Four methods of dechlorination of underwater iron archaeological objects are used in Demokritos as chemical treatment (NaOH) and/or hydrogen plasma reduction.

Recent successes in hydrogen plasma led us to choose this method for dechlorination. From the literature review of desalination, the chemical solution such as sodium hydroxide is the most effective one in the desalination treatment of iron archaeological objects.

The conclusions of the experimental tests are as follows: The best way for desalination of the marine iron artifacts is by immersing them firstly in 1-2% sodium hydroxide in 13.5-pH combined with plasma reduction. After the application of these methods, it is less probable for the iron artifacts to be re-corroded.

The formation of a stable passivating layer on iron surface artifacts after using 1-2% NaOH combined with plasma reduction was accomplished. At 80 to 300°C, the plasma does not chemically affect the surface or the metallurgical properties. Most of the chloride ions were released during the early stage of desalination.

The objective of the dechlorination is to find out if one of these methods is convenient for the conservator to stabilize the metal artifacts from the marine environment. From our work, we can say that modern technological methods, such as plasma reduction, was used to support the conventional methods of conserving archaeological objects as mechanical and chemical treatment. The percentage of removed chlorides increased with time; and temperature of the plasma. The same dependence on time and on temperature was observed for the desalination with sodium hydroxide.

The few coupons, as well as the two iron artifacts were completely free from chlorides, while the major quantity of chlorides was removed from the others iron objects.

ABBREVIATIONS USED IN THE TEXT

SCUBA	*Self-Contained Underwater Breathing Apparatus*
SDDE	*Surface Demand Diving System*
SONAR	*Sound Navigation Ranging*
GPS	*Global Positioning System*
RH	*Relative Humidity*
SRB	*Sulfate Reducing Bacteria*
MPY	*Mils per year penetration*
DPN	*Diamond pyramid Number*
RP	*Polarization resistance measurements*
MIC	*Microbiologically influenced corrosion*
AAS	*Atomic absorption spectroscopy*
ppm	*part per million*
SEM	*Scanning Electron Microscopy*
EDS	*Energy Dispersive Spectrometer*
SEM	*Scanning Electron Microscope*
XRD	*X-ray Powder Diffraction*
XRF	*X-ray Fluorescence*
CT	*Computerized tomography*
FTIR	*Fourier Transform Infrared Spectroscopy*
DPN	*Diamond Pyramid Number*
HV	*Vicker hardness test*
DI	*De-ionized water*
EN	*Ethylenediamine*
GD	*Glow Discharge*
CP	*Cathodic protection*

VCI	*Vapor phase corrosion inhibitor*
AMP	*Amino-Methyl-1-Propanol solution*
DPL	*Dense corrosion product layer*
DI	*Deionized water*

KEYWORDS

IRON; UNDERWATER; ARCHAEOLOGY; CORROSION; CHLORIDE; CONSERVATION; RESTORATION; DESALINATION; DECHLORINATION; REDUCTION; PROTECTION; PASSIVATION; CORROSION INHIBITORS; EXAMINATION; ANALYSIS; SEM-EDS; XRD.

LIST OF PAPERS

Paper 1

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Paper 2

S. Ahmed Saleh, E. Filippaki, Y. Bassiakos, G. Batis, B. Argyropoulos, 2009. **The hydrogen plasma treatment of corroded iron artifacts from a waterlogged environment,** 12th international symposium on boat and ship archaeology.

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Paper 4

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CHAPTER 1

INTRODUCTION

Conservation in an archaeological context means the investigation, stabilization, and in some cases, reconstruction of the entire spectrum of archaeological materials (Pollar et al., 2007). The protection and management of underwater cultural heritage include the collaboration in the investigation, excavation, documentation, conservation, study and presentation of such heritage (UNESCO 2001). Hamilton (1996) said that shipwrecks are a special kind of archaeological site which has been compared to time capsules. Underwater cultural heritage is a significant aspect of history (Hamilton 1996).

The excavation can be considered as the first stage of any project, and it generates many archaeological artifacts that require much consideration for the dechlorination (the main problem of marine finds) and the preservation treatments. Most of the objects, which survived in immersed seawater for long-term, will be partly or heavily mineralized.

1.1 Introduction

The dechlorination treatment by using sodium hydroxide and/or hydrogen plasma reduction was accomplished in Demokritos, the Plasma Physics Lab of NCSR in Athens. Immersion the iron artifacts in sodium hydroxide is the most widely-used desalination method. From its beginnings, one of the main aims of our work was the desalination by using low temperature plasma. After that the committee changed this plan to be more important. The combination between hydrogen plasma with sodium hydroxide was added.

This thesis deals with the desalination treatment of

- The iron coupons that were cut from a flat into cubic form. The iron coupons were cleaned firstly by a dilute nitric acid. After that they were aged by different methods. They were allowed to dry, weighed before staring the accelerated aging. The coupons state differs from the objects in corrosion compounds, chloride level and the presence of marine compounds.

- Collection of marine cast iron objects retrieved from the wreck, south west from the island of Kea in the Aegean Sea, which sank in 1868. That meaning, the cannonball artifacts were totally immersed in the saltwater for 140 years. *In 2006* the collection of objects was brought up, which were transferred to the Industrial Museum of Syros. Finally, they were delivered to the Metals Conservation Laboratory of the Department of Conservation of Antiquities and Works of art, at TEI of Athens.

- Modern iron artifacts from Paros Island were excavated by “Aegean institute”. That meaning, the wrought artifacts were totally immersed in the saltwater for 150-200 years. The focus of these experiments was to treat 32 marine iron artifacts that have different shapes, different sizes and different rate of corrosion and chloride level. Most of the objects have good state and about four objects are completely corroded.

The removals of the chlorides that are associated with the oxide layer covering the artifacts depend on two factors:

The first factor that depends on the state of the artifact (good state or completely corroded- flat or with surface’s decoration). Most of the marine archaeological objects have a thick exterior layer from the seabed sediments and iron oxides. The kind of iron objects (wrought and cast iron).

The second factor depends on the type and condition of the treatment method. This factor controls final result, because of mechanical, chemical and plasma reduction treatments are probably irreversible if they are used without studying the state of the objects.

1.2 Theoretical background

Corrosion is defined as a gradual wearing or alteration in a chemical or electrochemical oxidizing process. Because the process of corrosion returns metal to its original condition, we must consider the action of degeneration, in its true or primary form (Schweitzer 1997). Iron corrosion is one of the most complicated and costly problems facing the metal artifacts (Riba 1995). Chloride is the biggest problem that we have after excavation. Seawater is an aggressive environment that worsens metal objects conditions within long term. Chlorides in general make many forms of corrosion such as pitting corrosion, so the extraction of chlorides immediately after excavation is considered the most important stage.

Marine iron artifacts recovered from the seawater are usually covered with a protective crust (concretion) that should be preserved until their transfer to the conservation laboratories. The treatment should be immediately by a simple immersion of the encrusted artifact in distilled or fresh water (Hamilton 2000, Rodgers 2004, Degrigny and Spiteri 2004). If the cast or wrought iron object is left to dry out without immersion in distilled water, the crust becomes very hard to be removed.

Weizhen and Chunchun (2005) said the principal aim of any treatment of archaeological iron of marine origin is to eliminate chloride from the corrosion products. If this is done successfully, the development of the corrosion process due to chloride ceases and the rate of corrosion is reduced to a more manageable level, where conventional methods to counter corrosion can operate efficiently (Weizhen and Chunchun 2005).

Many desalination methods are mostly employed in the conservation of marine iron artifacts. These methods are base on the use of conventional methods such as mechanical and chemical cleaning by sodium hydroxide and/or the use of modern techniques like hydrogen plasma.

Dechlorination of the iron artifacts is considered to be one of the most difficult steps of conservation of the iron artifacts. It requires experience, effort and participation of other specialists in the diagnosis and analysis, or when using different technologies such as conventional and modern method or during the use of a hybrid method. The conventional techniques are used in conservation laboratories such as chemical cleaning by using sodium hydroxide that is a common base and mechanical cleaning.

Before, during or after the desalination, the object requires mechanical treatment to remove the adherent corrosion and marine compounds. Mechanical treatment is used to support the desalination methods. Mechanical treatment is important, effective and safe.

There is great importance for the chemical desalination of the iron archaeological objects. The cost of the chemical treatment is very low and most of these solutions in low concentration do not attack the metal or the decoration, but concentrated acids and hydroxides solutions can cause painful burns and serious damage to skin of the object's surface.

The chemical solution is mostly changed every two weeks, unaltered solution is not efficient for removal chlorides, and the immersion treatment is stopped when the chloride ion concentration in the solution (chemical treatment) is low at the range of 0.1% wt. Re-corrosion in storage solution is very rare during the treatment by sodium hydroxide.

Graaf et al., 1995 said that compared with conventional techniques such as sanding there is a huge time advantage. Also finer surface details can be preserved. The second problem, to stop post-corrosion of the artifact, is strongly related to chlorine contamination on the artifact, which catalysis the corrosion process (Graaf et al., 1995).

Hydrogen plasma reduction has been used for dechlorination of metal objects for the past 40 years. Clearly, increasing the use of plasma reduction in the treatment of archaeological materials, nowadays because the good results which achieved. The metal objects are reduced in the Pyrex tube of plasma machine at different temperatures till the chlorides are removed or decreased. The temperature range of 80 –300°C was selected, and based on the phase diagram of iron and the previous work.

Patscheider and Veprek (1986) studied the effect of temperature between 250°C and 350°C and resulted that no significant effect of the temperature on the rate of the reduction could be observed. Therefore all the treatments reported below were carried out at 300°C-400°C for 100 hours (Patscheider and Veprek 1986). This method is very expensive; consequently it has not spread up till now.

In glow discharge plasma, the electrons have sufficient energy to enable them to break the hydrogen molecules in subjects at low temperature and pressure. Plasma reduction treatment results in a considerable decrease the chloride ion concentration of the objects by chemical hydrogen effect. This technique could be considered as a good practice for cleaning of encrustation, desalination and passivation of the objects surface. Hydrogen glow discharge plasma technique has been employed as a cleaning and desalination method for iron artifacts.

However, objects that are completely oxidized must be treated carefully, because treatment may result to be more fragile especially by using high temperature plasma or by using sodium hydroxide after dehydration. Results indicated that iron chloride was present in all of iron objects before the desalination in high level. Sodium hydroxide or/and plasma reduction efficiently to decrease the chloride level and improves their color and shape by formation of magnetite.

Watkinson and Al-Zahrani (2008) resulted that aerated treatment environments extract less chloride than de-aerated systems and have erratic treatment efficiencies, whereas de-oxygenated wash environments aid the removal of chloride from archaeological iron. The best chloride extraction efficiencies are obtained when the wash solution is both alkaline and de-aerated. Average extraction efficiencies for de-oxygenated NaOH solution were similar, irrespective of whether air was excluded by the oxygen scavenger Na_2SO_3 or by nitrogen gas. Consequently the use of nitrogen gas is preferred, as it does not introduce SO_3 and SO_4 ions into the object (Watkinson and Al-Zahrani 2008).

Selwyn and Argyropoulos (2005) used a combination of desalination treatment methods that were based on the immersion of iron in a 2% w/v aqueous solution of sodium hydroxide (NaOH) at room temperature followed by immersion in a 5% v/v 1,2-diaminoethane (ethylenediamine, EN) solution heated to 50ºC. It was developed to preserve the shape of the object and to promote long-term stability by removing soluble salts (Selwyn and Argyropoulos 2005).

Selwyn showed (2004) that non-archaeological iron was possible to reduce newly formed iron corrosion products (e.g. iron (III) oxyhydroxides) to magnetite or $Fe(OH)_2$, it has been noted, however, that archaeological iron artifacts change color from rust red to black during reduction (Selwyn 2004). Davies and others (1954) studied the effect of hydrogen treatment without plasma on the oxidation of iron at 175 to 350ºC. Magnetite was formed below the ferric oxide and has spread out laterally.

Veprek and others (1988) used glow discharge with explosive gases, such as hydrogen and methane. He resulted from experiments that there is no significant removal of NaCl by the plasma treatment in the oxide environment. However, the plasma treatment facilitates a significantly higher degree of chloride removal by subsequent washing in pure water (Veprik et al., 1988). Havlíčková et al., (2008) said that low-temperature chemically active plasma based on electronegative gases is often used in modern technologies (Havlíčková et al., 2008).

The objects are placed in a vacuum drying system to remove excess water, a process which took four days. Dry nitrogen is then admitted to the vacuum chamber and the artifact will transfer to a nitrogen dry box. The concretion was removed and samples of concretion, residual metal and corrosion product were drilled out and ground to powder (North 1982).

Nowadays, plasma can be used in the desalination treatment to remove chlorides and corroded surface from inorganic archaeological materials like ceramics, glass and organic archaeological material.

1.3 Aims of the research

This research aims to compare between the methods of dechlorination of iron objects removed from marine environment that is effective to decrease the level of chlorides. Aims of this research are to solve the major problems of dechlorination that face the conservator. It presents a review of the history of developing dechlorinaion methods and techniques. Any method for restoring chlorine-infested iron objects should therefore aim at the decomposition of chloride compounds like akaganeite. The research is concerned with the iron objects from marine excavation, because it is one of the most important objects in this excavation and to compare and describe the rate of corrosion products and chlorides of the iron artifacts in different seawater environments. Also, the purpose of this practical is to understand the effect of the treatment methods. Chloride ions and akaganeite are evaluated by using different methods as silver nitrate, SEM, XRF, and XRD.

CHAPTER 2

ORES AND PROPERTIES OF IRON AND METALWORKING TECHNOLOGY METHODS

Here, we shall deal with the ores and properties of iron and metalwork techniques involve the use of various techniques. The history of ferrous metallurgy began far back in prehistory, most likely with the use of iron from meteors. The smelting of iron began in the 12th century B.C. in India, Anatolia, or the Caucasus. Iron use, in smelting and forging for tools, appeared in Sub-Saharan Africa by 1200 B.C. The use of cast iron was known in the 1st millennium B.C. Moore Said that Although iron is one of the most common elements in the earth's crust (34.6% by mass, 5% by volume) it is not found there in its elemental form. In fact the first source of iron was meteorites, a fact that led to its description as the metal of heaven (Moore 2002).

As Ottaway and Wager (2000) explained the role of the metal and metalworking that played in ancient societies and to integrate “analytical data with theoretical, contextual and ethno-archaeological studies” (Ottaway and Wager 2000). In 1934, Read pointed out that the two words (melting and smelting) may serve as an example of looseness of the language. Their meaning is definite and distinct. Melting is a physical change. A solid is converted to a liquid by heating. Smelting is a chemical change. A mineral is converted into another by heating. Because the final result in both cases is usually a liquid metal or an alloy, and heat is used in both cases, a quite unnecessary confusion of operation that is basically different has arisen (Read 1934). Iron (Fe) is a metallic element and constitutes about 5% of the earth’s crust. The reds, oranges and yellows seen in some soils and on rocks are probably iron oxides. The inner core of the earth is believed to be a solid iron-nickel alloy (http://www.mii.org/Minerals/photoiron.html).

2.1The three sources of iron (The iron ores)

Iron differs completely from other metals used in antiquity. The ores are widespread and abundant, but smelting requires much higher temperatures than other metals. Most smelted iron is inferior to bronze. Steel is an alloy of iron and carbon (Wilson 2006). There are *fifteen iron oxides*, oxide hydroxides and hydroxides known to date. The various Fe oxides differ mainly in the arrangement of the Fe $(O,OH)_6$ octahedral (Cornell 2000). The earliest iron used by man was generally *meteoritic* in origin, as shown by the presence of nickel in most prehistoric objects, as well as in those from the early and middle Bronze Ages. Note that another name for a metallic meteorite is siderite, although this term is also used for an iron carbonate ore. In prehistoric times, meteorites were worked in the same way stone in order to obtain tools (Durand-Charre 2004). Iron ores are found everywhere-a fact often invoked to substantiate claims for this or that region to priority of discovery (Richardson 1934).

2.1.1 The native iron

Native iron comes from two sources, from outer space in the form of metallic meteorites[1], or terrestrial iron in basaltic rock. As a source of metal the letter may be dismissed very briefly (Tylecote 1962). The native terrestrial iron is rare. It is found in igneous rocks, especially basalts (Greenland), also in carboneous sediments (Missouri) and mixed limonite and organic matter in petrified wood (Palache et al., 1944). Generally in the form of small grains or nodules, it often contains considerable quantities of nickel, up to 70%. It is rarer than meteoritic iron, but has also been found in ancient precious objects (Durand-Charre 2004). Meteoric iron contains 5-26% nickel and this allows it to be distinguished from smelted iron. The first piece of non-nickel iron comes from the great pyramid at Giza and is dated ca. 2900 BC (Moore 2002. Knox (1987) categorizes these as siderites, pall sites and mesosiderites. Only siderite is completely composed of iron, the other two contain about 50% iron. There are no clear examples of meteorite use in the old world. Tylecote noted that the structure of meteoritic iron is surprisingly resistant to heat (Henderson 2000).

2.1.2 Iron ores

Iron oxides are common compounds which are widespread in nature. Initially, formation of Fe (III) oxides predominantly involves aerobic weathering of magmatic rocks (mainly on the earth's surface) in both terrestrial and marine environments, redistribution processes between the various global compartments may follow. Iron ore formation and iron oxide precipitation in biota are important examples of redistribution (Cornell 2003). Silica (SiO_2) is almost always present in iron ore (http://www.scrapmetalnow.com/traceelements/te.pdf). The principle ores of iron are Hematite, (70% iron) and Magnetite, (72 % iron). Taconite is a low-grade iron ore, containing up to 30% Magnetite and Hematite (http://www.scribd.com/doc/17346454/IRON-ORE).

2.1.2.1 Hematite

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[1] Meteorites are large meteors that have survived the intense heat of Earth's atmospheric friction and have reached the earth's surface and they are pieces of asteroids, the Moon, Mars or perhaps even comets (Ashley et al., 2009).

Hematite is an oxide of iron having the composition Fe_2O_3. Pure hematite, also called “red ore” (in fact, the name hematite comes from the word “hemo” meaning blood), contains 70% of Fe. But generally it contains various other constituents namely SiO_2, Al_2O_3, P, S, TiO_2, Zn, Cu, As, Sn, Cr and Ni. In nature, its structure is varied starting from compact specula and columnar to foliated (micaceous hematite). When mixed with clay or sand, it is called argillaceous hematite or clay iron stone. The coarse-grained variety with brilliant metallurgical luster is known as “specular iron ore” Hematite is the most widely distributed and mined iron ore. The red hematite often colours soils of tropical and subtropical regions. The ratio of goethite to hematite varies greatly with local conditions and is, therefore, an environment alindicator (Schwertmann and Cornell 2000).

		
Photo (2-1) Hematite	*Botryoidal hematite*	*Photo (2-2) Magnetite*

After: http://www.scribd.com/doc/17346454/IRON-ORE

2.1.2.2 Magnetite Fe_3O_4

Magnetite, a natural magnet, is considered a mixed - valence compound as one third of magnetite’s iron atoms are in the ferric state while two thirds are in the ferrous state ($Fe^{II}\,Fe^{III}{}_2O_4 = Fe_3O_4$). Magnetite is one of the most abundant and wide spread oxide minerals. It is commonly found as minor in igneous rocks; as a magmatic segregation deposit and pyroxene (Berry and Mason 1959).

2.1.2.3 Limonite

Limonite is the greatest part of common yellow-brown ferric oxides. Residual limonite cappings are also found over rock containing ferrous-iron minerals where rock decay has progressed for a long time (Berry and Mason 1959).

Limonite is any impure hydrated iron oxide. Limonite does not have one specific shape. It is usually a pseudomorph of another mineral, such as pyrite. Most of the time Limonite is formed from a mineral containing iron which decomposes and is turned into Limonite. Limonite is mostly clay but also has phosphates and silica also. Most Limonite has a brownish red color (like rust) and leaves a varying streak because each piece of Limonite could be made up of a different amount of phosphates or silica. Limonite has been mistaken for Geothite but can be separated by the exact color and the fact that Limonite has no crystal structure (Guy and Teeter 2009).

2.1.2.4 Goethite

Goethite usually results from weathering of iron minerals, siderite, pyrite, magnetite, or glauconite under oxidizing conditions at ordinary temperatures. It is due also to direct precipitation from marine or meteoric water in bogs or lagoons. Goethite is the main constituent of limonite, which is found as gossans or weathered capping on veins or replacement deposits rich –bearing sulphides. Goethite is often found as crystals, or botryoidal or stalactite, in near-surface features and pockets in many kinds of rocks (Berry and Mason 1959). Goethite minerals are mostly formed in the sedimentary cycle, in the first place by weathering of iron containing oxides, sulfides, carbonates, silicates, or by chemical or organic precipitation from an iron containing solution. A few cases are known where goethite is formed from a hypogenic solution (Govaert 1976).

	
Photo (2-3) Limonite	Photo (2-4) Geothite

After: http://www.scribd.com/doc/17346454/IRON-ORE

2.2 The properties of iron

Artifacts made of iron can usually be distinguished by their dark brown to black colour, hardness, and weight (Rodgers 20004), so the study of the properties is so important in the conservation treatment methods. The proper conservation of any materials requires an understanding of the physical and chemical nature of that material.

- ***physical properties***

Metals are generally hard, malleable, and ductile, possess luster, and are good conductors of heat and electricity. The physical properties of metals are affected partly by the size and shape of grains (Metals are made of crystals known as grains). Apart from the shape of the grains, the physical properties of metals also are affected by the material comprising them. Different phases have different physical properties, and each will lend some of these characteristics to the resultant metal., thus the presence of the brittle compound phase will make the overall metal to some degree brittle. Which phases are present in all alloys will depend on the concentration of alloying elements, the temperatures to which these have been subjected, and the rate at which they have been cooled down. If the metal has been cooled very rapidly, excessive amount of this brittle compound form, but to some extent it can be dispersed by gentle reheating. (Cronyn 1990). Metals scratch easily and it is no longer considered a precious metal. Further evidence for the celestial source of this iron is in the chemical analysis of artifacts. The high nickel content of these artifacts is typical of meteorites, and the nickel content would also account for the lack of oxidation (rusting) (http://www.tf.unikiel.de/matwis/amat/def_en/articles/steel_greece_rome/). Iron is a bright silver-coloured metal with a high melting point. Adding a small amount of carbon to iron makes steel, a harder but more brittle material (Museums galleries Scotland 2009). The melting of iron is in excess of 1500˚C and therefore, in contrast to the case of non-ferrous metal and alloys, artifacts could not be cast from the molten metals in antiquity (Tite 1972 and Hummel 2004). Iron is perhaps the metal most highly susceptible to corrosion (Guldbeck and Macleish 1990) that depends on the type of the metal.

- ***Mechanical properties***

The mechanical properties of given steel are strongly influenced by the microstructure of the steel, and this chapter reviews the common steel microstructures and how they are achieved by the heat treatment of the steel. The mechanical properties of metals are often characterized by listing values of their yield strength, tensile strength, and percent elongation (Verhoeven 2007). Pure iron is soft, but the wrought iron could be hardened by heating in glowing charcoal at temperature above 900˚C represented a major advance in the production of artifacts (Tite 1972). Bloomery iron is a poor substitute for bronze. Its tensile strength is about 40,000 psi. The strength of pure copper is 32,000 psi. Hammering brings the strength of iron to almost 100,000 psi. Iron could be cast only after adding as much as 4% carbon to the bloom, which in turn caused the cast metal to be extremely brittle. One theory suggests that iron's popularity is due to the fact that properly carburized (the addition of carbon), it produces an alloy with desirable cutting and durability properties. This alloy is steel (Herz and Garrison 1998).

- ***Thermal properties***

Thermal conductivity is the ability of a material to transmit heat energy. Different materials can be rated in terms of thermal conductivity.

Good thermal conductor	**Good thermal conductor**
Silver 100	Brass 28
Copper 93	Iron 9

Table (2-1) Relative thermal conductivity (silver taken as standard of 100). After Goffer1980

When the structure of iron was being discovered in the late 19th century, the magnetic transition in iron that occurs at 770°C (1420°F) caused scientists to theorize a structure of iron they called beta iron, which was later shown not to exist. It is helpful to represent the aforementione dide as geometrically on a diagram where temperature is plotted on a vertical scale and identifies the changes that occur at significant temperatures as shown in figure 2-1 (Verhoeven 2007).

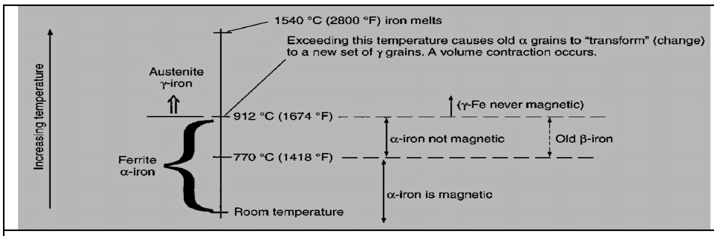
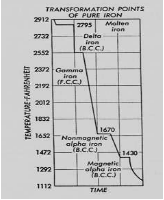


Fig. (2-1) Changes occurring in iron with increasing temperature After: Verhoeven 2007



Cooling curve of pure iron

The C% in structural steels that are subject to cold weather conditions is kept as low as possible to avoid embrittlement problems. A fascinating question is whether or not the steel plate used in the Titanic may have become embrittled at the -2 °C (29 °F) temperature of the saltwater when it struck the iceberg and sank.

Pure iron melts at an extremely high temperature, 1540°C (2800 °F), and at such temperatures, carbon readily dissolves into the molten iron, generating a liquid solution. When the liquid solution solidifies, it generates a solid solution, in which the carbon (C) atoms are dissolved into the solid iron. The individual carbon atoms lie in the holes between the iron atoms of the crystalline grains of austenite (high temperatures) or ferrite (low temperatures) (Verhoeven 2007).

Heating conditions tended to harden (carburize) the iron, and that further hardening was possible by a water quench. But the subsequent refining and toughening by reheating was be- yond the early Greek iron-workers, as they lacked the proper facilities to determine, or temperature control (Richardson 1934). The elements like phosphorus, sulfur, manganese, chromium, nickel and so on, influence in various ways the physical properties of the material (Turgoose 1993).

- ***Chemical property***

Chemical property of metal is its reaction with water and the other mediums which results in corrosion. The surface is initially protected with a thin transparent layer of iron oxides, but iron and its alloys are the metals that are most vulnerable to damage by corrosion (Museums galleries Scotland 2009). Iron is a chemical element and is rusted easily (Herz and Garrison 1998).

Iron and steel are also magnetic and will carry and electric current. Unlike more noble metals iron readily corrodes, with the corrosion products moving outward into the environment to precipitate on encountering a more basic pH. The precipitated iron corrosion product (mostly FeO(OH), orange rust) cements all nearby debris to the artifact. In aerated moist soil this concretion becomes a brown amorphous mass complete with attached sand and gravel. This concretion may have little resemblance to the artifact hidden inside (Rodgers 2004).

Effect of elements present in iron and its alloy

- **Carbon**

The carbon concentration of the artifact should, in principle, provide the basis for distinguish between wrought iron, cast iron and steel. The carbon combines chemically with some of the iron to form cementite (i.e iron carbide- Fe_3C) and the resulting microstructure consists initially of a mixture of ferrite and pearlite grains, the latter being eutectic mixture of cementite laminate in a ferrite matrix. With increasing concentrations of carbon (i.e. greater than 0.85 percent), the microstructure converts to a pearlite and cementite mixture (Tite 1972). Cast iron contains more than 2% carbon, doesn't resist tension or shocks well (Stambolov 1985).

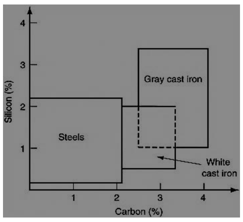


Fig. (2-2) Carbon and silicon % for cast irons, with comparison to steels (most steels have relatively low Si % - cast steels have higher Si %). Ductile iron is formed by special melting and pouring treatment of gray cast iron, and malleable iron is formed by heat treatment of white cast iron.

- **Silicon (0.1-0.2%)**

Silicon is one of the common deoxidizers used during the process of manufacture. It also may be present in varying quantities up to 1% in the finished steel and has a beneficial effect on certain properties such as tensile strength. It is also used in special steels in the rage of 1.5% to 2.5% silicon to improve the harden ability (Paxton and Vierling Steel, 1885). Silicon in amounts up to 2.5% -weight promotes the deposition of graphite, depresses the formation of cementite and imparts to iron hardness and elasticity (Stambolov 1985). The major effect of silicon is to promote the formation of gray iron. Gray cast iron is less brittle and easier to corrode than white iron (http://www.scrapmetalnow.com/traceelements/te.pdf).

- **Manganese (>0.5-1%)**

Next in importance to carbon is manganese. It is normally present in all steels, and functions both as a deoxidizer and also to impart strength and responsiveness to heat treatment. Manganese is usually present in quantities from 1/2% to 2%, but certain special steels are made in the range of 10% to 15% (Paxton andVierling Steel 1885). It raises the yield point, and increases the depth of hardening and tendency to distort or crack upon quench-hardening. Manganese promotes the formation of cementite, obstructs the deposition of graphite and therefore renders the iron only mechanically strong but not elastic (Stambolov 1985).

- **Phosphorus (<0.1)**

The phosphorous concentrations (e.g. 0.4 percent) tend to harden the iron directly while, at the same time, making hardening by means of carburization more difficult (Tite 1972). In addition to increasing yield strength and reducing ductility at low temperatures, phosphorus is believed to increase resistance to atmospheric corrosion (Paxton and Vierling Steel 1885).

- **Sulphur**

It is an important element in steel. The amount generally used for this purpose ranges from 0.06 to 0.30%. Sulphur is detrimental to the hot forming properties (Paxton andVierling Steel 1885).

- **Nickel**

Nickel gives a great weight, and is ductile, but when it amounts to more than one-tenth, it is less ductile. At the same time, it does not rust so easily as iron (Scoffern 1857). In addition, the concentration of nickel can be used to identify those rare artifacts fashioned from meteoric iron since this iron normally contains more than 5 percent of nickel, in contrast to the concentrations of less than 0.1 percent associated with the majority of iron smelted from ores (Tite 1972). Nickel (especially above 36 weight-%) gives iron a low coefficient of expansion (Stambolov 1985).

- **Chromium**

Iron containing 4 weights-% of 15 weight-% chromium it becomes stainless. In addition, iron alloyed with either 0.15-0.3% copper or o.15-0.3% cobalt resists atmospheric corrosion (Stambolov 1985).

2.3 The kinds of iron

Iron has a natural affinity to unite with other elements and so can take on many forms. Ferrous artifacts may have been manufactured from steel, wrought iron, or cast iron. These three types of iron reflect in descending order the carbon content, or in ascending order, the refinement of the metal.

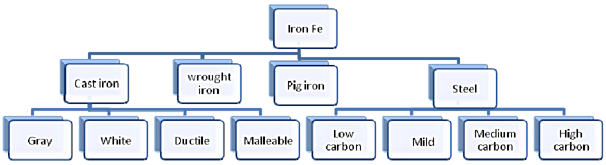


Fig. (2-3) the kinds of iron

2.3.1 Steel: is an alloy of iron and carbon with up to 1.5% C (Tylecote and Black 1980), or steels are over 95% Fe, so a good starting point for understanding steel is to study the nature of solid iron (Verhoeven2007), and is alloyed with other metals to produce a wide variety of alloys which have properties far Ib lkn advance of other metals used in antiquity. However, the antiquities of steel can only be brought about under carefully controlled conditions of temperature and chemical environment (Wilson 2006). The numerous structural transformations that can occur in steels during solidification and cooling complicate the identification and interpretation of the final microstructures obtained. Most ferrite stainless steels have a structure consisting entirely of ferrite at all temperatures. However, the category also includes alloys in which small amounts of high temperature austenite can be removed by annealing below about 800˚C. Ferrite is promoted by high chromium content and low concentrations of austenite stabilizing elements, such as nickel and manganese (Durand-Charre 2004).

Steel could be produced in small amounts for edged weapons early in the history of iron working, and after the mid18th century as crucible steel (in which, measured amounts of carbon were worked into wrought iron). Unlike iron, steel springs back when bent and is lighter and stronger than iron. But steel was not mass-produced before Englishman Henry Bessemer patented his steel making process in 1856. In this process molten iron from a blast furnace is poured into a helmeted bucket mechanism called a converter. Carbon and manganese were added to the iron in the converter and air pumped through it to burn off impurities.

These alloy steels have unique properties and are used for different purposes. In general steel corrodes in large flakes that exfoliate from the surface of the artifact. Archaeological steel includes springs, armor, swords, and the edges of utilitarian tools such as axes (Rodgers 2004).

Steels that are 100% austenite must have temperature-composition coordinates within the upper central dark area of Fig. 2.4. Steels that are ferrite must have temperature-composition 99.98% or purer with respect to carbon. Notice, however, that austenite may dissolve much more carbon than ferrite. At the eutectoid temperature, austenite dissolves 0.77% C, which is roughly 38 times more carbon than ferrite will hold at this temperature. Austenite holds more carbon than ferrite, because the holes between iron atoms are larger in the fcc structure than the bcc structure (Verhoeven 2007).

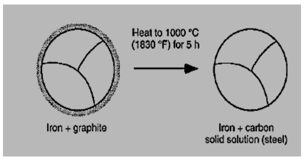


Fig. (2-4) converting a rod of iron containing only three grains to steel by dissolving carbon in it (After: Verhoeven 2007)

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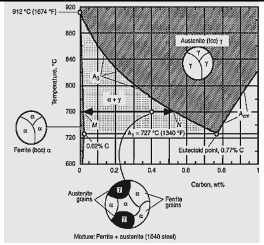
<td>
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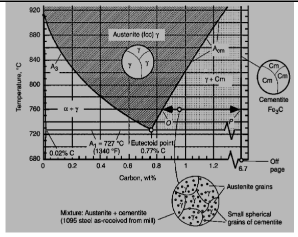
<td>
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<tr>
<td>*Fig. (2-5) Portion of iron-carbon phase diagram for Hypoeutectoid steel alloys (C less than 0.77%) After: Verhoeven 2007*</td>
<td>*Fig. (2-6) Extension of the iron-carbon phase diagram to hypereutectoid steel alloys C% greater than 0.77)*</td>
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The iron-carbon phase diagram extended to higher-carbon compositions where cementite becomes important is shown in fiure (2-6). As before, the region on the temperature-composition map corresponding to austenite is shown as the central dark region. Because cementite exists at only one composition, it is shown on the phase diagram as a vertical line located at its composition, 6.7% C. We can notice that the composition axis at the bottom of the diagram has a break in it just beyond 1.2%, and the value of 6.7% is located next to the break. If the break were not inserted, the 6.7% composition would appear roughly one foot to the right. To envision the true diagram,

imagine extending the right portion approximately one foot, which expands the shaded two-phase region labeled γ + cm into a much larger area. The line on the diagram labeled Acm defines the solubility limit for carbon in austenite. Notice that at 820°C (1508 °F), this line gives a point at1 wt% C, which is the maximum amount of carbon that can be dissolved in austenite at 820°C (Verhoeven 2007).

The steel produced by carburization possesses an additional important property in that it can be hardened still further by heating to a temperature above 750˚C in a reducing atmosphere and then quenching rapidly. This process eliminates the pearlitic structure and in its place a new phase, martenensite, which is a supersaturated solution of carbon in iron and has a needle-like structure, is formed. The quenched steel, although very hard, is reduced, with some loss of hardness, by reheating to a lower temperature. This process referred to as tempering, converts the martensite into a new phase, sorbite, which is a fine dispersion of cementite in ferrite (Tite 1972). Steel is the best alloy of iron, but even to this day, steel cannot be economically made directly from the iron ore.

- ***Plain Carbon Steels***

When a small amount of carbon is added to iron, the properties which give steel its great value begin to appear. As the amount of carbon increases up to .80 or .90%, the metal becomes harder, possesses greater tensile strength, and, what is most important, becomes increasingly responsive to heat treatment with corresponding development of very high strength and hardness (Paxton and Vierling Steel 1885). Plain carbon steels are steels in which the alloying elements do not play a significant role in determining the properties of the metal. The two systems used are both based on carbon content. The phase diagram of the iron/carbon alloy indicates that at 0.8% carbon a eutectoid composition exists, and a pearlitic structure forms upon slow cooling. With carbon content is less than 0.8%, steels are sometimes termed "hypo-eutectoid", and with carbon content greater than 0.8%, we have "hypereutectoid" steels. Unfortunately the classification based on eutectoid structure is coarse and little used for practical purposes. Instead, low, medium and high carbon steel is the preferred groupings used.

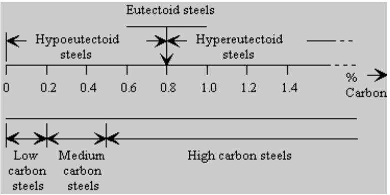


Fig. (2-7) Carbon steel classification

After: Ginzel 1995

With over 2% carbon in an iron-carbon alloy is called grey cast iron. This is no longer considered steel and decarburization must be used to reduce carbon content to below 2% in order that the alloy again will be considered steel (Ginzel 1995). A carbon content of 0.2-0.3% gives steeled iron a strength equal to that of unworked bronze, raised to 1.2%, steeled iron has a tensile strength of 140,000 psi. If the blacksmith then cold-hammers the steeled iron, a tensile strength of up to 245,000 psi can be obtained more than double that of cold-worked bronze. In the bloomery furnace, the fuel and ore charge pass down the stack, where at 800°C, CO reduces the Fe_3O_4 to FeO flakes (Herz and Garrison 1998).

2.3.2 Wrought iron

It is a very variable product. Up to 1500 A.D., it was made exclusively by the direct process of reduction of iron ore to iron at a temperature of around 1200°C. As this temperature is below the melting temperature of pure iron, it meant that the iron was never in the liquid phase, but reduced directly from ore to metal in the solid phase. Since various zones of this reduced metal would be at different temperatures, and surrounded by variable atmospheres, they would absorb or lose carbon at different rates, and in different quantities. Also, since this process didn't occur in the liquid phase, there was little possibility of evening up the composition throughout the metal. This led to great heterogeneity in the resulting material. Therefore, although wrought iron is regarded as more or less pure iron, it is very heterogeneous with high and low carbon regions, but in the main average carbon content is less than 0.1% (very low carbon concentration) (Tylecote and Black 1980).

Wrought iron has a very low carbon concentration and is easily hot rolled into rod, beam, and plate sections. The microstructure of wrought iron is easily recognized, consisting primarily of ductile α-iron (ferrite) matrix with slag inclusions, mostly FeO and SiO_2. The slag is elongated during hot rolling, allowing the flow direction to be identified easily. Although the shape of the slag reveals that wrought iron was severely deformed, the grains are not similarly elongated (Elban et al., 1998).

Wrought iron is the most refined version of iron, processed from high quality pig iron. This iron is purified and poured over melted sand in order to produce bloomery iron or blooms, as the ingots are called. The silicate slag (sand) introduced into the wrought iron allows this material to be worked and formed into tools and fasteners in a forge. Wrought iron is highly malleable and does not shatter. It is nearly pure with less than .2% carbon content and contains silicate slag in the form of stringy intrusions that run with the grain of the worked metal. Wrought iron is normally brown or dark brown in color. Archaeological wrought iron will have a grainy wood-like appearance as it corrodes along the silicate slag intrusions. Wrought iron will be formed into any worked utilitarian objects that will see hard use, such as fasteners, nails, and anchors (Rodgers 2004).

2.3.3 Pig iron

Pig iron has a carbon content of 3% to 6%, is hard, very brittle and is not useful for tools. Pig iron is an unlikely, though not unheard of find on an archaeological site. It was sometimes transported in ships for refinement and also used as ballast, most often in warships. Pig iron is generally black in color with a rough surface. All iron can be polished to silvery base metal but it rarely if ever appears this way in an artifact (Rodgers 2004).

Pig iron cannot be readily welded. Ability of a metal basis strongly keep condition can be indirectly determined by micro hardness. Concentration chromium from 2.14% up to 5.3% promotes growth of a share ledeburite. Since the contents chromium 2.14% are a marked change of morphology of structure ledeburite (Matveeva and Shapovalova 2006).

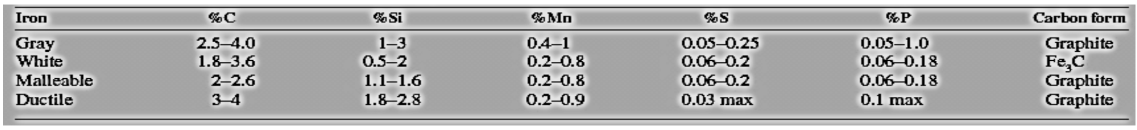
That means cast iron is a refined version of pig iron (Rodgers 2004). Pig iron which has been produced, through reduction from its ores in a furnace, (technical term that means to gain electrons)contains considerable amounts of carbon, silicon, phosphorus, sulfur, manganese and a few other elements. Pig iron in this state isn't useful. Pig iron is therefore remelted with a flux and in this state it is suitable for iron castings (Stambolov 1985).

2.3.4 Cast iron

Cast iron is produced by remelting pig iron in a cupola (a small type of blast furnace) (Jackson and Morton 1984), and cast iron is a refined version of pig iron. It contains a high carbon content of 2% to 6% and remains unworkable and brittle. Yet it can be cast into useful objects such as skillets, pots, piping, stoves, ranges, cannon, machine parts, and cannon balls. Cast iron is very hard but remains brittle due to its micro-crystalline structure. It was not unheard of for cannon shot to shatter on impact with ships or fortifications and certainly most plumbers still realize today that the easiest way to remove cast iron piping is to shatter it with a hammer. Cast iron, like pig iron, is normally black in color and can have a rough or smooth texture depending on them old in which it was formed (Rodgers 2004). Cast iron was the metal of choice throughout the second half of the 19th century. Cast iron is one of the oldest ferrous metals used in construction and outdoor ornament. It is primarily composed of iron (Fe), carbon (C) and silicon (Si), but may also contain traces of sulphur (S), manganese (Mn) and phosphorus (P). It has a relatively high carbon content of 2% to 5%. It is hard, brittle, and nonmalleable (i.e. it cannot be bent, stretched or hammered into shape) and more fusible than steel (Bell and Rand 2006). Cast iron is a complex alloy containing mainly a total of up to 10% carbon as well as varying amount of other elements (Kenawy 2001).

Tylecote and Black confirmed that cast iron is an iron with more than 2.0% C, which usually exit in two forms: white cast iron which contains the phases cementite and pearlite, and grey cast iron which contains ferrite, pearlite and graphite. The usual range of carbon content ranges from 3 to 4%. White cast iron is more common in the early artifacts, but large slow-cooled objects (Tylecote and Black 1980), and the carbon content is combined chemically as carbide of iron. White cast iron has superior tensile strength and malleability. It is also known as 'malleable' or 'spheroidal graphite' iron (Kent et al., 1913).

Cast irons are also alloys of iron and carbon but they contain more carbon than do steels (usually between 2% and 4%) and they contain silicon (typically 1 to 3%). Grey cast iron gets its name from the dull-grey, grainy appearance of a fractured edge caused by the graphite. The presence of these different phases can complicate the corrosion properties of cast irons (Selwyn et al., 1993). The most common traditional form is grey cast iron. Common or cast iron is easily cast, but it cannot be forged or worked mechanically either hot or cold (www.metrum.org/money/contents.htm). Cast iron is well known to endure much better than wrought iron. Silicon also reduced shrinkage and the formation of blowholes, lowering the number of bad castings. As the silicon content of the cast iron increases, the chill depth decreases.



Iron	%C	%Si	%Mn	%S	%P	Carbon form
Gray	2.5–4.0	1–3	0.4–1	0.05–0.25	0.05–1.0	Graphite
White	1.8–3.6	0.5–2	0.2–0.8	0.06–0.2	0.06–0.18	Fe_3C
Malleable	2–2.6	1.1–1.6	0.2–0.8	0.06–0.2	0.06–0.18	Graphite
Ductile	3–4	1.8–2.8	0.2–0.9	0.03 max	0.1 max	Graphite

Table (2-2) The four main cast iron types

Many of the findings from shipwrecks, such as cannonballs, anchors, bolts and iron supports in the main masts were from cast iron (Weizhen et al., 2004)

Though pig, cast, and wrought iron plus steel are primarily made of the element iron, they have widely varying traits and were used for many different purposes throughout history (Rodgers 2004).

2.4 Metalworking technology methods

Metallurgical industries processed ores to recover the useful metals. They used tall furnaces that were often provided with chimneys. Smelters were excavated as pits in the ground. Smelting required large amounts of fuel to reach the desired high temperatures. Technology advanced enough in Roman times to permit reworking of slag from earlier operations (Hughes and Stoll 2005).

In historical times, the mine owners very often held high economic and social positions, manifested in the so-called mine proprietors estates. Their independence and involvement in state politics are well known. Their mining tools, such as for example the mining wedges and hammers, were used as symbols of power in many areas of Sweden. The power structure at this time in Sweden was still based on local and regional authorities, the aristocracy, and the church. Any royal supremacy over larger areas was still at the beginning. The level of production which could be reached by using a bloomery process was not sufficient when the demand for higher output came about. The production of iron was no longer of local or regional interest only (Hjärthner-Holdar and Risberg 2010).

2.4.1 Smelting

The Iron Age dates to approximately 1000 B.C., when our ancestors first learned to reduce the plentiful iron oxide ores found on earth into elemental iron. The iron was made in furnaces that were heated by charcoal fires that were not able to get hot enough to melt the iron (Verhoeven 2007), and in 2002, Moore said that the first record of a smelting process was found on the wall of an Egyptian tomb dated ca. 1500 BC. The Iron Age opened with the production of bloom which through heating and hammering was made into wrought-iron (Moore 2002). But, Herz and Garrison said that the first smelting of iron may have taken place as early as 5000 BC in

Mesopotamia. Throughout the Bronze Age, iron was produced sporadically as iron droplets, a by-product of copper smelting, formed in lumps on top of the slag from the smelting process. This was due to the increased efficiency in copper smelting by the use of fluxes that contained iron oxides mixed in with the copper ores, particularly carbonate ores (Herz and Garrison 1998).

The problem was that the temperature could not be raised enough to melt the iron and the conversion of the ores took place chemically. From the tenth century onwards the smelting process developed steadily; hand operated bellows were replaced with waterwheel driven ones so allowing more air at a higher pressure. Heat recovery started with an increase in the stack and the materials being fed down through the gas stream. By the 15th Century the first blast furnaces appeared and pig iron production became possible. The Stuckofen in Germany was the first furnace that resembled modern blast furnaces in its shape and the use of tuyeres. Production rates were a little different to today; the Stuckofen, a great technical leap forward, produced 100 to 150 tpa. With the blast furnace and pig iron came cast iron and a new route to wrought iron called fining. The development of the puddling furnace in 1784 enabled malleable or wrought iron production to keep up until the development of the hot-blast stove in 1828. The higher temperatures meant that carbon levels in the iron could be raised with the result that the melting temperature fell so opening the way to liquid pig iron and casting. Fascinating is that at this time the pig iron was considered a problem as it was too brittle to be worked with a hammer. It was often recharged or thrown away. The first blast furnace in North America was at Falling Creek in Virginia in 1622 (Moore 2002).

Our ancestors produced an iron called bloomery iron, which is similar to modern wrought iron. Even though charcoal was used in these furnaces, very little carbon became dissolved in the iron. So, to make steel, carbon had to be added to the bloomery iron (Verhoeven 2007). In the bloomery process, which was used in the West until the late Mediaeval period, the smelting produces a spongy mass of metallic iron mixed with slag and charcoal (i.e. the bloom) (Tite 1972). Our ancestors did not know the nature of the element carbon until approximately 1780 to 1790 A.D., and steel and cast iron played a key role in its discovery. Until shortly before that time, the production of steel was primarily the result of blacksmiths heating bloomery iron in charcoal fires. This process is tricky because a charcoal fire can just as easily remove carbon as add it (Verhoeven 2007).

To reduce iron in large amounts required a CO/CO_2 ratio of 3:1, whereas only 1:5,000 CO/CO_2 was required for the reduction of CuO. Forging these lumps of early iron was difficult because the iron contained copper and sulfur. By 1200 BC, the smiths had begun to roast Fe_3O_4 in smelting furnaces. In the process, at 1200°C, the iron did not melt as copper did, but only became pasty. Iron requires 1540°C to melt. The production of iron is not a melting operation, but a reducing operation. The object is to reduce Fe_3O_4 to metallic FeO. In the early days the smiths roasted the iron ore in a forge called a pit forge or later a bloomery forge. To achieve the required temperature, a device was needed to create a draft. The first smiths utilized tuyeres (blow objects). The result of this crude smelting was a pasty mass of iron, slag, and charcoal called a bloom. With further heating and hammering at 1250°C, the bloom could be consolidated into a wrought iron implement. When hammered, the fluid slag and oxides squirted out and the iron particles welded together. This silicate slag gangue was composed largely of fayalite, the iron-rich olivine. With rising temperature, the metal agglomerates and forms wustite FeO, some of which reacts with SiO_2 to form an iron sulfate-fayalite-slag. With high-grade ores, SiO_2 must be added to form the slag. Below the tuyeres, the furnace atmosphere is reducing. Silicate-rich slag flows to the bottom of the furnace, and the bloom forms a layer above the bowl. The bloom is extracted and is ready for the forge, where it can be steeled by the introduction of carbon (Herz and Garrison 1998).

The ancient smiths developed a method to harden the steeled iron even further. This method was quenching or rapid cooling in air or water. Rapid cooling less than 1 second produces the microstructure called martensite hard but brittle. Slower cooling, up to 3 seconds produced fine pearlite, or more than 10 seconds produced coarse pearlite. A third technique for manipulating the end result of forging steeled iron was tempering. After the ancient smiths realized that quenching made hard but brittle steel, they discovered the process of tempering, whereby the steel is heated to the temperature of transformation, 727°C. The temperature attained and the time held at that temperature determines the amount of iron carbide formed and thus the final hardness and ductility of the metal.

The earliest mines worldwide were simple shallow open pits to recover ores found at the surface. With the advance in ingenuity and technology, early miners used picks of durable antler horns and mauls of dijabase to ease the extraction of ores. With tools, miners could advance beyond the surface exposures to follow ore-bearing veins. The melting point of pure iron is 1540°C. Landels points that even by Roman times, European furnaces did not produce heat over 1100°C. Smelting iron, unlike smelting the lower melting point metals, copper, zinc and tin, did not involve turning iron to the liquid state. Instead, it was a solid state conversion requiring chemical reduction of the ore. Ore was placed in a pit and mixed in a hot charcoal fire. Air was forced into the dome covered structure via bellows through a fireproof clay nozzle called a tuyere. After a sustained temperature of 1100°-1200°C, slag (oxidized non-metallics) fell to the bottom leaving the spongy mass containing the iron. Holes forming the sponge texture were a result of the removal of the non-metallics when the slag melted out. The spongy mass is called a bloom by some. This spongy mass was then pounded, usually while still hot, and more slag dropped out as the metal was concentrated into a denser mass. The pounded metal was called wrought iron. Iron is found as pyrite (FeS) and as oxides including hematite which was worked for iron tool manufacture (Herz and Garrison 1998). The bloom was the first forged, by repeatedly reheating and hammering on an anvil while still hot, in order to consolidate the metal and expel some of slag. The resulting iron, which is referred to as wrought iron, had low carbon content (less than 0.5 percent) and could be further forged into the shape required for the artifact (Tite 1972). Descriptions and illustrations in hieroglyphs and on antique Greek painted vases can help to give us insight into the development of metallurgy in the follow figures (2-8, 9, 10). Some Egyptian texts, the Bible, and the Shu King (in which copper is mentioned for the first time) give some insight into the matter as it existed until about 1000BC. The more numerous Greek texts from around the fifth to third centuries BC, together with the remnants of Greek and Roman mines, give a much better idea of developments in those times (Heide 1989).

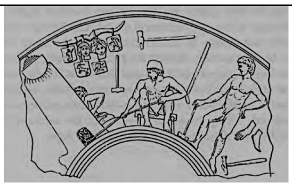
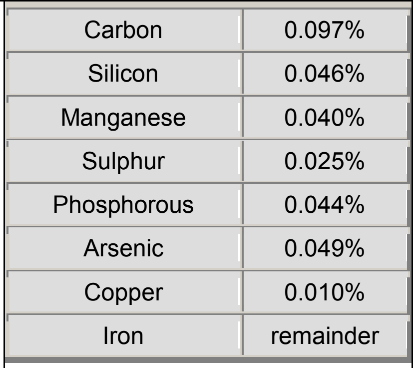


Fig. (2-8) Picture of a Greek smith on an Attic amphora from about 550 BC. One of the oldest and most informative Greek pictures of a smith's workshop. The master smith holds the work piece with a pair of tongs as his apprentice strikes it with a large hammer. Two important visitors look at the work of the smith	*Fig. (2-9) Decoration on a Trojan bowl. In a smelting workshop two enormous figures arise. They are being shaped with various tools, such as a forging hammer and a shaving and burnishing tool.*

After: Heide 1989

Fig. (2-10) A shaft furnace from Greece (6th century BC) depicted on a vase showing a smith forging a bloom in front with the bellows behind
Aftre: Tylecote 1992



Carbon	0.097%
Silicon	0.046%
Manganese	0.040%
Sulphur	0.025%
Phosphorous	0.044%
Arsenic	0.049%
Copper	0.010%
Iron	remainder

Table (2-3) Mean composition of a typical bloom

Aitchison gives a mean composition of a typical bloom but this could vary widely, depending especially on the origin of the ore (table 2-3). Steel industry existed in ancient Greece and Rome (up to about 500AD). Contrary to some, there was in fact a developing steel industry in the ancient Mediterranean world. We can define irons and steels by the carbon content method (Ginzel 1995), but Reynolds and Weidmann found something over 4 wt% carbon, about 1wt% each of manganese, silicon and smaller amounts of highly undesirable sulphur and phosphorus (Reynolds and Weidmann 1990).

Cast iron can be produced by the easiest possible method of obtaining iron from the ore that of placing alternate layers of broken ore and burning charcoal. This method has the advantage of extreme simplicity, since iron flows to the bottom in a molten state, but it presents the disadvantage that, while flowing through the fuel, the iron absorbs carbon and thereby becomes cast iron. All this proves that the method of producing cast iron was known during the Greek Dark Ages, but was forgotten in historical ages. Cast iron is not fit for the manufacture of objects which have to withstand repeated shocks or need a sharp edge (www.metrum.org/money/contents.htm).

2.4.2 The forging methods of metals

2.4.2.1 Technique of casting[2]

The production of shaped articles by pouring molten metal into moulds

The first known leaden casting, a little Egyptian figure from about 3800 BC, was made earlier than the first known silver object from the same country-a necklace from about 2400 BC. After smelting, casting the metal is the next step. This technique had become very important by the Bronze Age, and smiths were able to make the desired alloy very accurately, having developed the skills needed to control the percentage of tin necessary to make the bronze suitable for special purposes (Heide 1989). At the outset the sand caster made his sand molds, then smelted virgin ore in a wide variety of homemade smelters or blast furnaces and did his casting. As the demand for castings grew the foundry man had to devote more and more time and energy to the actual production of sand castings, thus he had less time to devote to the collection of ore and the smelting end of the work. The metal smelter, who devoted his time and skills to the efficient production of pig iron ingots which he sold the ever increasing number of sand foundries. At this point the foundery man became a metal re-melter and caster as it is today. There has been much development in sand casting methods, but the basic system is the same today as it was at the outset. A sand mold is made into which the liquid metal is cast and when the metal has solidified, the mold is broken up (shake out) and you have the casting (Ammen 1979).

Traditionally, clay or plaster has been popular, as was gutta-percha until the arrival of synthetic materials in the mid-twentieth century (Craddock 2009).

- ***Sand casting*** is the most widely used process for both ferrous and non-ferrous metals. Depending on the moulding method, it may be classified as green sand, dry sand or shell mould process. A typical green sand foundry involves three groups of activities. Pre-casting includes sand preparation, core making, moulding and mould assembly. The casting stage involves furnace charging, melting, holding, melt treatment (such as inoculation) and pouring into moulds, which are then left to cool. Post-casting involves shakeout, cleaning, fettling, shot-blasting and inspection. Further operations may include heat treatment and machining (Ravi 2004).

2- Casting is a 6000-year young process.

Complex objects were often cast in molds made of two, three, or even four pieces, and it is quite clear from the chemical composition of some of the weapons and ornaments that the smiths had been experimenting quite extensively with various alloys to such lengths that they had hit upon the idea of joining one piece of metal to another with an alloy of different composition and had thus in effect begun to experiment with solders. But excellent though their technique of casting was, much of the work was still accomplished by laborious hammering and chasing, while the size of castings they were able to make was still severely restricted and seems to have been limited by the quantity of metal that they could melt at any one time (Hodges 1992).The fuel was usually charcoal (Richardson 1934).

- ***Hollow castings*** will have been poured around clay cores. The mineralogy of the clays and fillers can be traced to specific regions. Core material of statuette has come from Rome indeed contained clays that were likely to be from the Tiber.
- **Plaster casts**

Traditionally, plaster of Paris has been the main material for making both the moulds and the casts. Dry plaster was carefully mixed to a creamy consistency and applied to the surface to be moulded. To protect the surface of the original a releasing agent of grease or of oil had to be applied (Craddock 2009).

2.4.2.2 The hammering method (Mechanical working)

These metalworking techniques seem to be the first and perhaps the most important techniques, because they could be applied to all metals. Any metal which can be found in its native state could have been flattened between two stones, in a manner resembling the effect of a hammer and anvil. By this means the metal becomes thinner, changes shape, and hardens at the same time. When annealed in fire, it becomes malleable again, and can be further hammered and flattened. Objects have been found which were made in about the eighth century BC, using these methods. Metal smiths were thus able to make sheet 0.2 mm thin. The only method for making a seamless tube at that time was with the technique of raising, a brief description of which appears below. At that time steel was unknown, but iron was mentioned for the first time by Hamurabi in his law book (ca. 1750 BC). Iron daggers dating as early as the fourth century BC have been found in Egypt. The slightly conical shape of the tube lends plausibility to the idea that this piece might have been made by raising.

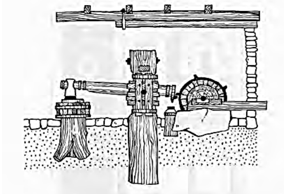


Fig. (2-11) The oldest type of water driven tail-hammer
After: Heide 1989

Fig. (2-12) Brass and copper hammer workshop with annealing furnace, tail-hammers, and (flying-) shear. With a stretch hammer, the sheet is struck. With a doming hammer it is driven into the shape of a vessel

In about 1500 the first rolling-machines-used for rolling the leading for glass windows came into use (Fig. 2-11). By 1700 lead plates were being made in a rolling mill (Fig. 2-12). However, the making of sheet metal continued to be done with hammer-mills until about 1800. Not until 1816 in Germany was the first cold rolling machine put into use. The making of seamless tubing was developed in 1820 by T. Burr, but the process was used only for lead tubes. In 1880 it finally became possible to make seamless tubes of a metal harder than lead by crossing the rolling wheels (Heide 1989)

The shaping of metals in the solid state by plastic deformation above or below the crystallization temperature by hot or cold working. The stresses that build up within the metal that cause the cracking can be relieved by heating the metal in a fire at high temperature at which the metal begins to glow red. On cooling, the metal can then be hammered again to shape it until it begins to harden, when it must be heated once again to relieve the stresses that have built up (Ginzel 1995).

Finishing the Surface

All of the above-mentioned techniques and procedures were used for the primary purpose of shaping the object. An important secondary goal, almost from the beginning, was to make the piece as beautiful as possible. In order to do so, metalworkers developed many other techniques. An object could be made smooth and shiny by means of rubbing with very fine sand. There are many minerals which display very different grinding and sanding qualities. Pumice, for example, is a soft volcanic rock which leaves small scratches on the metal, after which finer polishing can be done with rouge, a ferric oxide made in different grades of fineness. All this sanding and polishing was done by rubbing, sometimes with the aid of rotating on a lathe. *Agate and hematite* are very suitable minerals for this purpose when polished to a smooth, flawless surface. The combination of shaving or scraping and burnishing gives the old instruments their typical appearance: shiny, but with longitudinal small facets.

Embossing, striking or stamping designs into walls of an article in such a way that motifs in relief result is called "embossing." An object made of thin sheet metal is filled with a mixture of pitch and sand, or sand and bitumen. It is also possible to push the object into or onto a mixture of pitch which has been softened by heating. This work can also be done on a flat surface of lead (Heide 1989).

- ***Etching***

Some acids will affect metals in such a way that the metal dissolves and disappears. This is how the characteristic rough and pitted surface is formed. The surface of an article can be covered with a protective coating, called a "resist," and after this has dried the design is scratched through it to expose the metal underneath, which will be affected by the acid or mordant. The depth of the lines depends on the length of time the object is immersed in the acid. By removing more of the resist again after a period of etching, the process can be repeated, and new parts of metal will dissolve. In this way it is possible to make a kind of relief in the metal surface. Sometimes this technique was used in signing instruments and in preparation for the niello or emaille technique. Etching was also an important process in printing (Heide 1989).

CHAPTER 3

CORROSION OF THE MARINE IRON ARTIFACTS IN THE SEAWATER

This chapter offers a clear view of how the changes in marine environment affect the state of iron objects. Plenderleith and Werner said that the condition of an antiquity depends on two main factors; the materials of which it is composed, which vary enormously, and the conditions to which it has been subjected in the course of its life history (Plenderleith and Werner 1979).

Iron artifacts will, of course, also deteriorate and behave in widely variable manners and must be conserved accordingly. Underwater, the concretion process is more complex but will result in the complete concealment of the iron object within a calcium carbonate shell (Rodgers 2004).

Perkins explained that corrosion is a natural process which can attack any metal or alloy under the right conditions. Corrosion eats away iron and its alloys, causing unattractive appearance and eventual (Perkins 1996). Corrosion is the deterioration of a material by its reaction with the surroundings. It adversely affects those properties that are to be preserved (Sidhu et al., 2005). Watkinson (1983) confirmed that chlorides are drawn into the object to take part in the corrosion cycle and remain there until corrosion is complete (Watkinson 1983).

Iron rusts can be classified into harmful and harmless, according to the effects on the corrosion of iron. Harmless rusts usually do not develop on the iron matrix in the normal environment and do not need to be removed from the iron antiquities. Harmful rusts are able to accelerate the further corrosion of the metal core in the normal environment (Zise et al., 2007).

Corrosion has classified in many different ways. One method divides it into high temperature and low temperature corrosion. Another classifies it into wet and dry corrosion. Corrosion has been defined as a chemical or electrochemical reaction between a metal or alloy and its environment (Bayliss and Deacon 2002).

3.1 Electrochemical corrosion of iron artifacts in the seawater

The essential features of such a cell are two electrodes, an anode and a cathode, joined to an external conductor (Bayliss and Deacon 2002). In order for corrosion to occur must be there a complete circuit between anode and cathode. The current flows in two phases: in the solid phase electrons flow from the iron anode to the magnetite cathode, and in the liquid phase the current is carried by iron (II) and hydrogen ions moving outwards from the anode, and by hydroxide and other anions moving inward. The hydrogen ions are formed by partial hydrolysis of iron (II) ions, which occurs readily even at low pH (knight 1997). In high purity water, where no other electrolyte is present to any significant extent, it is the solubilisation action of water on a metal surface like iron, which is the first step in the corrosion process. The polarisability of the water molecules on contact with the iron surface leads to the weakening of the O-H bond and gives rise to reactions below, which show the combined effect of solubilisation and hydrolysis (Kenkateswariu 1996).

During burial, chloride is attracted to anodes as a counter ion to balance charge from Fe^2. In damp burial conditions it exists as a Fe^{2+} /Chloride ion^- solution at the metal surface. Chloride content may be typically 0.1-1.5wt % of object, but can be significantly greater for marine metals 7.10–12 wt %. Soluble chloride acts as an electrolyte making the iron inherently unstable. Overlying the corroding metal core is a dense corrosion product layer (DPL) identified as comprising a goethite (α- FeOOH) or sometimes a siderite ($FeCO_3$) matrix in which are embedded magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) strips. This is effectively the marker layer for the surface of the object and is also present in totally mineralized objects, which present no ongoing corrosion problem, but remain a conservation problem due to their fragility and the need to reveal their original shape (Watkinson 2010).

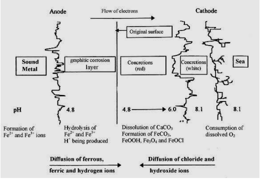
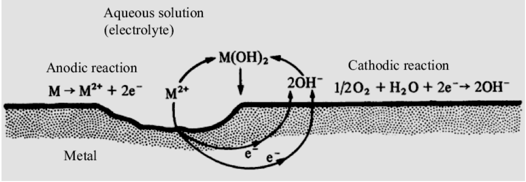
	

Fig.(3-1) The mechanism of corrosion in sea water *After: Degrigny and Spiteri 2004*	*Fig. (3-2) Wet corrosion of a divalent metal M in an electrolyte containing oxygen.* *After: Bardal 2004*

The current in the solution is carried by migration of anions, e.g. chloride or sulphate in natural environments and hydroxide from the cathodic reaction, towards the anodic sites and of cations towards the cathodic sites. If the anodes and cathodes are spatially separated, then this results in a build up of anions at the anodic regions. Since any portion of the solution must be electrically neutral, the charge on the anions must be balanced by the presence of cations, and these are the ferrous ions produced by the corrosion process. The extent to which an individual ion carries the ionic current, and thus becomes concentrated at the anodic regions, depends on its concentration and its mobility. Since the mobility of chloride is much higher than that of ions such as sulphate it is the chloride that predominately carries the ionic current except in environments where the sulphate to chloride concentration ratio is high (Turgose 1993).

The iron objects had corroded away in the marine environment, the water associated with hydrated Fe^{+2} ions can react (e.g. undergo hydrolysis) and cause local acidification

$$[\text{e.g. } Fe^{+2}(aq) + H_2O \rightarrow Fe(OH)^{+}(aq) + H^{+}(aq)]$$

The corrosion of iron is an electrochemical process. The anodic process, equation (1), the dissolution of iron, need not occur at the same location as the cathodic process, oxygen reduction, equation (2a), or hydrogen evolution, equation (2b).

$Fe = Fe^{2+} + 2e^{-}$ (1)

(Iron metal) (Ions) (Electrons)

$O_2 + 2H_2O + 4e = 4OH$ (2a)

$2H_2O + 2e = H_2 + 2OH$ (2b) (Turgoose 1993)

Chloride anions diffuse to the anodic places for charge balance and are hydrolyzed to an acidic and concentrated ferrous chloride solution. After long burial periods, the main stable corrosion products on iron finds are magnetite Fe3O4 and goethite α-FeO(OH) (Schmutzler and Ebinger-Rist 2008). An archaeological iron object is usually covered by a layered structure of corrosion products. The outer layer is a mixture of iron corrosion products (e.g. iron (III) oxyhydroxides, typically goethite) and extraneous material such as small rocks, sand, clay and soil minerals. Below this is another layer of iron corrosion products in a lower oxidation state, usually magnetite, lying on top of any remaining metal. When iron corrodes in a marine environment, it usually becomes covered with concretions, primarily calcium carbonate CaCO3. The Fe2+ ions tend to react and precipitate in the concretion rather than on the surface of the object. Because of the acidity that develops beneath the concretion of marine iron, there may not be many corrosion products retained on the surface of wrought iron or cast iron. Wrought iron will have its characteristic fibrous structure; while cast iron will usually have its original shape maintained by the remaining porous matrix of soft graphite filled with some iron corrosion products (Selwyn 2004). Absorbed from the marine environment, they destabilize iron and accelerate corrosion. They also crystallize when they dry, and can break an iron object a part from the inside to the outside (http://www.monitorcenter.org/preserving/process/). The chloride ions are trapped in the lattice of β-FeOOH, in microcrack and probably chemisorbed on iron oxide and iron oxyhydroxide surfaces (Scott and Seeley 1987).

When metals with different corrosion potentials are in electrical contact through an electronic conductor while submerged in seawater, the metal having the higher (negative) potential can range from a few millivolts to over 1.5 V. The greatest damage will occur when the area of the less noble (more negative) metal is relatively small as compared to the nobler metal. This relative area effect is usually more important than the magnitude of the initial potential difference (Jenkins 1978).

For iron in steel corroding in water at room temperature, is reaction would be

$Fe \longrightarrow M^{n+} + ne^-$ (Hack 2005). Corrosion cells do not always require two separate electrodes of dissimilar metals, however, the electrodes may be have two different phases within the surface of the same piece of alloy. Provided the two phases have different electrode potentials, and are bridged by an aqueous electrolyte, they can form a microscopic cell on the surface and the anodic phase is attacked (Reid 1990).

Corrosion in an aqueous system occurs due to the interaction between the surfaces of the materials which come into contact with the aqueous environment, many times under conditions of stress. The stress could be chemical in the sense that the aqueous environment may be acidic or alkaline. It might be thermal stress as in a steam generating system (Kenkateswariu 1996). A series of complex reaction follows, in which iron (II) ions are partially hydrolyzed and oxidized to iron (III), leading to the precipitation of an inner layer of magnetite $Fe(II)\ Fe(III)_2\ O_4$ and an outer layer of goethite, α-Fe(III)OOH, mixed with minerals, eg. quartz and clays (Knight 1997). The corrosion of iron artifacts is a complex electrochemical process; localized corrosion is the main corrosion format. Chloride ion is one of the important factors induced to localized corrosion of iron artifacts, due to the deep penetration and electronegativity.

The corrosion of metals submerged in salt water, as is the case with most shipwrecks, is a complex electrochemical process (Bayliss and Deacon 2002) with the anodic and cathodic reactions occurring at spatially separate points (Weizhen 2004). It has often been explained in terms of large galvanic cell which is based on the electromotive series of metals. Stated in general terms, all the metals are compared in all electrochemical cell with a hydrogen electrode, which is given an arbitrary electrode value of 0. Metals that have a potential more negative than hydrogen in a galvanic cell are said to have a negative electrode potential more positive to hydrogen have a positive electrode potential (Hamilton 1976).

The electrochemistry of oxygen -in the form of oxidation of metals- is a main cause of *damage to shipwrecks*. It's only fitting, therefore, that electrochemical reduction should be one of conservator's main tools to reverse that damage (Arnaud 2007). The decrease in corrosion rate with time is a direct result of an oxide scale layer forming on the metal's surface, which then deters further corrosion from occurring (Craig 2006).

When cast iron is attacked by seawater, it undergoes so-called graphic corrosion or graphitization. What happens is that the iron matrix goes into solution leaving a more or less adherent and porous residue, which consists mainly of the graphite in the iron mixed with insoluble iron corrosion products. Cast iron parts that have suffered this type of attack generally retain their original form and appearance even though they may have lost much of their original strength (Calvert and Laque 1975).

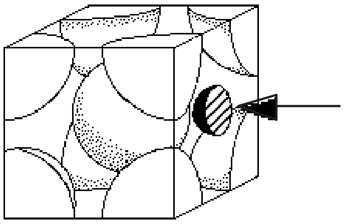
3.2 The factors influence rusting of iron objects

Objects in the marine environment setting are fully exposed to almost all of the factors that cause damage and deterioration. The corrosion of marine iron artifacts is dependent on many different and of ten interrelated factors as follows:

3.2.1 Endogenous factors

Iron objects are usually classified as wrought iron or cast iron.

Cast iron corrodes in layers from the surface inward and may crack and exfoliate. The key to cast iron corrosion is that the metal cools onto a carbon graphite matrix after casting, giving it a crystalline structure as structure in figure (3-3). As their on corrodes and migrates from the matrix the artifact will retain its shape but the outer layer may only be very soft graphite. Conserving the archaeological surface in this case may mean (Rodgers 2004). Cast iron usually corrodes by graphitization which leaves behind a metal core within an outer shell of graphite that contains iron corrosion products. Iron that has reached this level of decay is considered highly unstable and will corrode rapidly at the graphite/metal core boundary once it is exposed to the atmosphere. This rapid corrosion will force the flaking of the outer layers of the iron object. This type of corrosion is considered exothermic, which produces heat that speeds up the rate of decay for an artifact. There are numerous examples of iron objects which once recovered from the sea literally became “too hot to handle”. These exothermic reactions can actually explode the surface layer of an iron object (cannon, cannonball, etc.) before it reaches its conservation receptacle. Sometimes this destructive process may only take a few hours in warm to tropical conditions (Macleod 1989).



Intersitial Carbon in Iron
Since the interstitial sites are so small, the maximum solubility in BCC iron is only one carbon atom for 5000 iron atoms.

Fig. (3-3) BCC iron showing the location of interstitial carbon atoms

- ***Wrought iron*** tends to corrode differently than cast iron. Wrought iron, fabricated in layers subjected to repeated heating and shaping that burns off much of its carbon content, contains only trace amounts of carbon, and therefore does not have a graphitized surface layer like cast iron items. Wrought iron corrodes along the layers formed as it was shaped, known as slag lines, which tend to look like long ropy strands (Yeager 2005).

3.2.1.1 The influence of carbon in iron object

The melting point of iron is depressed by the addition of carbon. With lower carbon content than 4.2 % weigh-the solid solution (austenite) separates from the melt of iron (Stambolov 1985). The presence of carbon increases the hardness and brittleness of the iron alloy. It decreases the melting point from (1530° to 1130°C). The graphite flakes in the cast iron maintain the shape of the artifact, but can also act as a cathodic site, since graphite is an electronic conductor. Thus the iron matrix can corrode away, all the iron surface acting as an anode, with the fact that much of the cast iron is excavated from seawater environments, can lead to extremely high chloride levels in the inner graphitized regions (Turgoose 1993).

A phase diagram is a temperature versus composition map that locates on the map the temperature-composition coordinates where the various phases can exist (Verhoeven 2007)

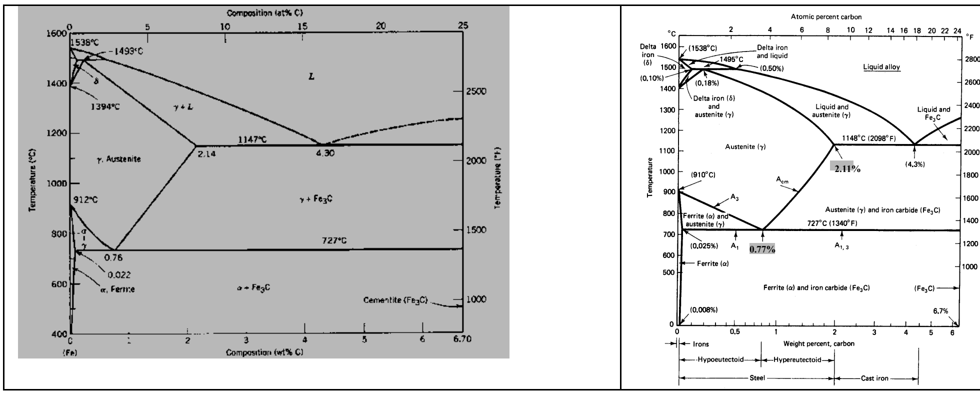


Fig. (3-4) The iron –iron carbide phase diagram
After: Callister 1990.

In iron at room temperature, the cubes have an atom at each of the eight corner sand one atom right in the middle of the cube. Iron with a bcc structure is called ferrite. Another name for ferrite is alpha iron, or α-iron, where α is the Greek symbol for the first letter in the Roman alphabet, "a.". When the ferritic iron is heated to 912°C (1670 °F), the old set of ferrite grains changes (transforms) into a new set of austenite grains. Imagine that the ferrite grain structure is shown in figure (3-4) has just reached the transformation temperature. One would first see the formation of a new set of very small austenite grains forming on the old ferrite grain boundaries, and then the growth of these grains until all the old ferrite grains were gone. Two important effects occur when ferrite changes to austenite:

(1) Just as it takes heat energy to transform ice to water; it takes heat energy to change the ferrite grains into austenite grains. Therefore, on heating, their on temperature will remain close to 912 °C (1670 °F) until all the ferrite grains are transformed.

(2) The ferrite-to-austenite (α-to-γ) transformation is accompanied by a volume change. The density of austenite is 2% higher than ferrite, which means that the volume per atom of iron is less in austenite (Verhoeven 2007).

3.2.2 Exogenous factors (Marine environement)

The stabilization of archaeological iron presents difficult problems, because it is a relatively reactive metal, and in the presence of an electrolyte such as seawater, it mineralizes to a greater or lesser extent. The minerals formed will vary depending on burial conditions. In anaerobic conditions, corrosion may proceed to a much lesser extent. Such objects often appear extremely well preserved and are sometimes assumed to be stable (Keene 1994).

Miller said that seawater contains substantial concentrations of CO_3, SO_4, Mg, and Ca. These doubly charged ions create stronger electrostatic interactions than the singly charged ions found in a simple NaCl solution (Miller 2000). In sea water, the presence of aggressive anions like chloride and seawater is an extremely complex and non-homogeneous medium that contains nearly all of the known elements. In addition, seawater contains large amounts of complex organic substances, both living and nonliving. The chemical factors in the environment, other physical factors must be considered in order to predict and control corrosion of the object. Many chemical constituents of the environment vary considerably with location and depth (Jenkins 1978). Many sea bottoms off Mediterranean coasts are extensively with a thick growth of *posidonia*. The marine plants, of the phanerogam family, have a subterranean stem with a network of roots and a cluster of ribbon-shaped leaves, which may be as much as 80 cm in length. The *posidonia* beds, known as *mattes*, extend from the shore over the sea bottom to a depth of 40 m. They are not everywhere uniformly distributed, and sandy-bottomed hollows, called intermattes, are found whose depth and width may range from 0.5 m to 3 m. These hollows form winding or rectilinear trenches that may extend for several hundred meters (Dumas 1972). At the bottom of the sea, in total darkness, with a low temperature, low salinity (sometimes, the springs can be found) and reduced oxygen level, the chemical processes are noticeably slower.

The corrosion of iron in sea water proceeds in a similar yet greatly accelerated manner because water generally becomes more corrosive as its salt content increases

$$V_{corrosion}(\text{sea})\ \textit{x10 faster}\ \text{than}\ V_{corrosion}\ (\text{air})$$

$$V_{corrosion}\ (\text{sea})\ \textit{x5 faster}\ \text{than}\ V_{corrosion}\ (\text{soil})$$

The corrosion rate of the specimen was calculated using the formula

$$\text{Corrosion Rate (mpy)} = (534 \text{x} W) / D\ A\ T$$

W = Weight loss in mg,
D = Density of the specimen in gm/cc,
A = Area in square mm,
T = Exposure time in hours
mpy = million parts per year (Prasanna 2009).

3.2.2.1 Description of marine environment

Seawater, the earth's most abundant resource, covers 71% of the earth's surface. This electrolyte approximates a 3.5 wt. % sodium chloride solution, but is much more complex, containing almost all naturally occurring elements. The major chemical constituents of seawater, listed in table (2), are consistent throughout the world. The minor constituents, including dissolved trace elements and gases, can vary substantially. Seawater also contains biological organisms, which often control the rate of the corrosion reactions occurring in metals in the seawater.

Constituent	**Concentration g/kg of seawater**
C^{l-}	19.353
Na^+	10.76
SO_4^{2-}	2.712
Mg^{2+}	1.294
Ca^{2+}	0.413
K^+	0.387
HCO_3^-	0.142
Br^-	0.067
Sr^{2+}	0.008

Table (3-1) Major seawater constituents

(35 parts per thousand (%) salinity)

After: Aylor 1995

Water is presented chemically as H_2O but, there are many salts, solids and gases in the various waters. The pH of water usually falls within a neutral range (pH 4.5-8.5), but some types are acidic, and these can be particularly corrosive to steel. Generally, however, the main factors in determining the type and extent of corrosion are the dissolved solids (which influence the conductivity, hardness and pH of the water), dissolved gases (particularly oxygen and carbon dioxide) and organic matter. The conductivity is important and the presence of salts, such as sodium chloride (NaCl) tends to make seawater more corrosive than fresh water (Bayliss and Deacon 2002). Seawater contains salts in solution (chloride, sulphate), gases and multiple organic substances. As soon as object is immersed, physical, chemical, electrochemical processes of degradation begin rapidly: hydrolytic reactions accompany the action of salts and micro-organism. These processes combine, but their aggressiveness varies according to the depth and the conditions of immersion. Sea and lake water contains carbonates, chlorides, sulphates and other dissolved salts derived from dissolution of rock particles. Because they are fairly well mixed, the salt content of the seas is much the same everywhere (about 3%) (Cater 2002).

The sea is immense, about 1.413×10^{21} Kilograms of a moderately concentrated aqueous electrolyte solution. In this gigantic body of water there are unlimited geographical and local variations in the parameters of the marine environment. At wreck sites, the part of the marine environment, which is most significant in respect to deterioration or change or artifact material is immediately associated with the artifact. This environment is usually a solid/liquid interface. For example artifact/atmosphere-sea spray; artifact/seawater; or artifact/sediment-interstitial water of sediment. Such interface boundaries are sites for a wide variety of chemical, physical and biological reactions (Florian 1987). That means the object in the marine environment has three mediums. Sea water constitutes a formidable and complex environment (Pennec 1989).

3.3 The forms of corrosion

For all the combinations of metals, marine environments, and structural applications, only a few forms of corrosive attack occur. Several corrosion mechanisms may result in the same form of attack in various situations (Jenkins 1978). All corrosion forms take place at the anode, where the metal, MO, loses electron(s) and becomes a positive ion. This oxidation will proceed only if the produced electrons and ions are removed at the cathode. These reactions occur as anode-cathode, reaction pairs, and each is called a "half-cell reaction."(Fodor 1985).

3.3.1 General corrosion (Uniform corrosion)

Uniform corrosion is responsible for the largest amount of corrosion damage. When a metal corrodes at substantially the same rate over its entire exposed surface, uniform corrosion is occurred. As for all natural phenomena, the attack is not strictly uniform. Surface roughening always occurs. The amount and distribution of this roughening vary considerably, and can grade into pitting corrosion.

Weight loss is a valid measurement of uniform corrosion. Typical materials that are subject to uniform corrosion in seawater are carbon steels and most alloy steels (when mill scale has been removed (Jenkins 1978).

3.3.2 Localized corrosion

This term implies that a part of an exposed surface area corrodes in a suitable electrolyte. This form of corrosion is more difficult to control than general corrosion (Perez 2004). Localized corrosion is the main factor of deterioration of the metals archaeological objects.

Localized corrosion can be classified as:

3.3.2.1 The erosion corrosion is the attack of a metal caused by the rapid flow of a fluid past or the impingement of a fluid on the metal surface. Steels and iron alloys are most subject to this form of attack in seawater (Jenkins 1987). The term erosion refers to deterioration due to mechanical forces. When the factors contributing to erosion accelerate the rate of corrosion of a metal, the attack is called erosion corrosion. Erosion corrosion is usually caused by a corrodent, aqueous or gaseous, flowing over the metal surface or impinging on it (Philip and Schweitzer 2004).

3.3.2.2 Stress corrosion cracking results in the failure of a component in a shorter time at a given load or a lower load in a given time when exposed to static stress in a particular environment as compared to failure loads or times. Stress corrosion cracking can occur rapidly and often occurs due to residual fabrication stresses rather than service loading. High strength materials are most susceptible to this form of attack. Failures of structures by stress corrosion cracking can be predicted by fracture mechanics techniques (Jenkins 1978).

3.3.2.3 Pitting corrosion is an extremely localized corrosion mechanism that causes destructive pits (Perez 2004). The major deterioration reactions of archaeological iron are closely associated with chloride ions. Iron and particularly steels undergo pitting corrosion in high chloride environments. Pitting is a form of localized attack where the corrosion rate is substantially greater on some areas of a metal surface than on others. The result of pitting attack can range from broad, shallow cratering to narrow, deep pits resembling drilled holes. The surfaces surrounding the pits can remain virtually unattacked. Weight loss cannot be used to evaluate pitting corrosion. Pit depth and frequency measurements, tensile tests, and visual observations are normally used to evaluate pitting attack. The gradation of uniform corrosion into the broad, shallow cratering form of pitting attack can be subtle. The two forms of attack can be differentiated by use of the pitting factor (P.F.) where

P.F = Depth of Deepest Pit / Average Depth of Attack

When the pitting factor is less than two, uniform corrosion is said to have occurred. When the pitting factor is greater than two, then pitting corrosion is said to have occurred (Jenkins 1978).

3.3.2.4 Crevice corrosion is associated with a stagnant electrolyte such as dirt, corrosion product, sand, etc. It occurs on a metal /alloy surface holes, underneath a gasket, lap joins under bolts and under rivet heads (Perez 2004).

3.3.2.5 Corrosion Fatigue is the dynamic analogy of stress corrosion cracking. In this form of attack, failure occurs at a lower stress level or in a fewer number of cycles when exposed to cyclic loading in an aggressive environment than when exposed to cyclic loading in air (Jenkins 1978).

3.3.2.6 Graphitic corrosion caused by micro-cells, formed by different phases in an alloy, which is also called graphitization or spongiest, is a form of corrosion unique to grey cast iron. The iron is transformed to rust which together with graphite flakes forms a spongy mass. *This type of corrosion is common in grey cast iron in contact with water* (Warnglen 1985).

3.3.2.7 Cavitation corrosion is the result of the impingement and collapse of vacuum bubbles on a metal surface. The bubbles are normally formed in areas of low pressure in a high velocity stream, such as are commonly found downstream of obstructions to the fluid flow. Cavitation corrosion is particularly severe on iron and steels and should be avoided by proper hydraulic design (Jenkins 1978).

3.3.2.8 Fretting corrosion is attack accelerated by relative motion between two surfaces in close contact. The attack may be due to the repeated rupture of inherently protective corrosion product films, or may be due to direct abrasion effects with the corrosion products serving as an abrasive. Fretting corrosion can result in rapid attack and should be avoided by design, such that relative motion between faying surfaces is avoided (Jenkins 1978).

3.3.2.9 Intergranular corrosion is the internal attack of a metal at or adjacent to the grain boundaries. The areas where these grains meet are called grain boundaries. In some metals, the grain boundaries themselves are more active than the bulk material. In other alloys, such as the stainless steels, improper heat treatment (sensitization) can lead to rapid attack of the material adjacent to the grain boundaries. In both cases, the structural integrity of the alloy is essentially destroyed in the affected area with a very small amount of actual material loss. Weight loss cannot be used to evaluate this form of attack (Jenkins 1978).

3.3.2.10 Galvanic corrosion is attack accelerated by electrical coupling of two or more dissimilar metals can occur rapidly and can result in either uniform or localized attack. Not only the composition of the metals involved, but also their relative exposed surface areas, distance apart, geometric distribution, and the resistance of the electrical contact, determine the rate and type of attack that will occur. Galvanic corrosion tendencies in seawater can be predicted. Although nearly any metal can be subject to galvanic corrosion, steels are most prone to this type of attack due to their relatively high activity in seawater (Jenkins 1978).

3.4 The factors which increase the rate of corrosion in the marine environment

The corrosion resistance in natural seawater is rather different and better than that in brackish water with the same total salinity. This forms a very complex medium, in which the influence of each factor, whether chemical (such as composition), physical (such as temperature) or biological, on the corrosion of metals cannot be readily separated, unlike that in salt solutions (Vargel 2004).

3.4.1 Flow effect

Water movement is also a major factor in determining the micro-environment. Flow has a major impact on the acceleration of corrosion damage (Cove 1993). Deeper sea floors, beyond the influence of storm waves, tend to be muddy, with occasional deposits of sand flowing off shore during major storm events. The flows become less common further from the shoreline where quiet-water muds predominate (Carter 2002). Sea and air environments interact in complex ways. Wave action resulting from wind friction is probably the most obvious product of such interaction and is a constant to mariners. The surface of the sea also responds to long-term or distant wind effects by producing sustained waves, termed swells, which may persist in spite of contrary local winds, resulting in waves and swells of different amplitudes from different directions at the same time (Gould 2000).

3.4.2 Biofilm effects on corrosion

McNeil and Little (1999) stated that the role of the microbiological in the biofilms play an important role in determining the corrosion or alteration of such objects, particularly archaeological artifacts. Mineral deposits on the surface of these objects can provide useful insights into the processes of degradation and, in cases of severe degradation, sometimes into the nature of the original objects (McNeil and Little 1999).

Biofilms can stimulate corrosion in two main ways: a) by initiating corrosion through the formation of differential aeration cells and, b) by increasing the rate of the cathodic reaction. Generally, biofilm-metal interactions on a corrosion-resistant alloy can lead to the initiation of localized corrosion that would not occur in the absence of biofilms (Videla 1996). Marine organisms can affect corrosion by creating corrosion indirectly by partially plugging or creating obstructions. Microorganisms represented most importantly by sulfate reducing bacteria are very commonly encountered in seawater (Laque 1975). **As much as 60 percent** of the corrosion of iron in salt water can be attributed to bacterial action (Hamilton 2000).

Corrosion by Sulphate-Reducing Bacteria

When certain bacteria produce substances such as sulfuric acid, ammonia, the resulting corrosion is known as bacterial corrosion (Philip and Schweitzer 2004). Iron sulfides occur as a result of this corrosion, both as an adherent corrosion product, for example, on iron objects, and also in the surrounding environment. From the occurrence of iron sulfides, the presence of sulfate-reducing bacteria may be deduced. The black corrosion products thus formed liberate hydrogen sulfide (H_2S) on acid treatment, which distinguishes them from black iron oxide (magnetite). The corrosion products often are loose and, when dislodged, pits lined with bright metal, which correspond to areas of anodic dissolution, are visible (figure 3-10). With cast iron, graphitization has sometimes been seen, in which the iron becomes dislodged, leaving only the graphite structure and corrosion product (Stott et al., 1988).

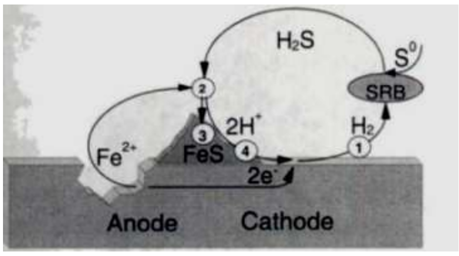


Fig.(3-5) Role of hydrogen-consuming SRB in the anaerobic corrosion of iron and steel. This diagram uses elemental sulfur rather than sulfate as electron acceptor for SRB to demonstrate a possible mechanism for proton recycling after precipitation of hydrogen sulfide with ferrous iron sulfide deposit.

After: Lovely 2000

The mechanism of anaerobic corrosion caused by ***the sulfate-reducing bacteria*** has always been controversial. There are several iron sulfides that are known to be cathodic to iron. The main roles of the bacteria to be:

(1) Generation of sulfides by their growth.

(2) Regeneration of fresh iron sulfide (FeS), enabling it to remain cathodic to iron.

Depolarization of FeS cathode, thus bringing fresh surfaces constantly into contact with steel by their movement (Stott et al., 1988).

$8H_2O \rightarrow 8H^+ + 8OH^-$ Hydrolysis

$4\,Fe \rightarrow 4Fe_2+ + 8e^-$ Anodic reaction

$8H+ + 8e^- \rightarrow 8H_{BIOL}$ Cathodic reaction

$8H_{BIOL} + Na_2SO_4 \rightarrow Na_2S + 4\,H_2O$ Sulphate reduction

$Fe_2{}^+ + Na_2S \rightarrow FeS\downarrow + 2Na^+$ Insoluble products precipitation

$3Fe_2{}^+ + 6OH^- \rightarrow 3Fe(OH)_2\downarrow$

$4Fe + Na_2SO4 + 8H_2O \rightarrow 3FeS + 3Fe(OH)_2 + 2Na(OH)$ Total reaction

(Bartuli et al., 2008).

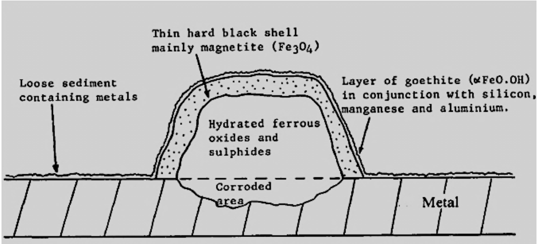


Fig. (3-6) Cross section through an iron object

After: *Ringas and Robinson 1987*

The concentration of organic material in sea water is important in many corrosion processes. The effect of this concentration on the corrosion of metals in surface seawater has not been well studied. There is a greater variation in chemicals and corrosion behavior between surface waters and waters at depth than that between surface waters at various locations. Oxygen content, pH, and organic material concentration and type are the major variables affecting corrosion at depth (Jenkins 1978). Color in natural waters is due mainly to organic matter.

3.4.3 Silica

Silica can also strongly impact the chemistry of iron hydroxides. For example, the presence of silica can affect the crystallinity and size of iron oxide formed strongly impacts the chemistry of iron hydroxides. Silica sorption to iron hydroxides produced a highly negative surface charge, which in turn led to the creation of smaller iron particles from larger particles. Dissolved silica in water might also increase detachment of particles from rust on the surface of a corroding iron object. The presence of dissolved silica in water may have a significant influence on both iron corrosion and iron release to waters. Cast iron contains approximately 2.5% silica by weight, so corroding iron can release silica to the water, which could explain the increase in silica with time. A few different processes may be responsible for silica removal from the water. First, silica could have been incorporated into the scale by simply adsorbing to the iron surface. Secondly, the relationship that appears to exist between the rates of iron release and silica removal implies the formation of an iron–silica solid on the surface of the iron scale. Finally, some other factor in the system with the corroding cast iron could have catalyzed the formation of a crystalline form of silica (Rushing et al., 2003).

3.4.4 Temperature

Temperature has a significant effect on fouling organisms and, on fouling rates. In warm, tropical waters the fouling rates are typically high, whereas they are typically lower in temperate waters. A rapid temperature change on the order of 20 to 401ºC can inhibit or prevent fouling. It is possible that the effect of heating may be significantly greater on deep ocean organisms than on common surface organisms (Jenkins 1978). At a depth of 400 meters, in total darkness, with a low temperature, and reduced oxygen level, the chemical processes are noticeably slower. Deterioration of objects continues, certainly at a rate slowed by the darkness and low temperature, but the processes degradation is active and varies according to the materials (Pennec et al., 1989).

If the oxide film initially is porous, the oxygen is able to pass through and continue to react at the oxide-metal interface. Iron (II) sulfides are known to oxidize and produce acid relatively fast in a humid environment. Thermodynamically, the stepwise oxidation process of iron sulfides may end at hydrated iron (II) sulfates while releasing acid, as for pyrite (Fors and Sandström 2006).

3.4.5 pH

Sea water is a complicated system. However, its pH value is quite consistent with an average value of 8.0 in normal sea water. The pH value could be changed in polluted sea area. The oxidation of elemental sulphur results in the formation of sulphate and hydrogen ions and sulphur oxidation characteristically results in lowering of pH. Within this pH range, it is favorable for propagation of anaerobic bacteria (Wang, et al., 2007). First, consider the exposure of iron to aerated water at room temperature (aerated water will contain dissolved oxygen). In the range of pH 4 to pH 10, the corrosion rate of iron is relatively independent on the pH of the solution. In this pH range, the corrosion rate is governed largely by the rate at which oxygen reacts with absorbed atomic hydrogen, thereby depolarizing the surface and allowing the reduction reaction to continue.

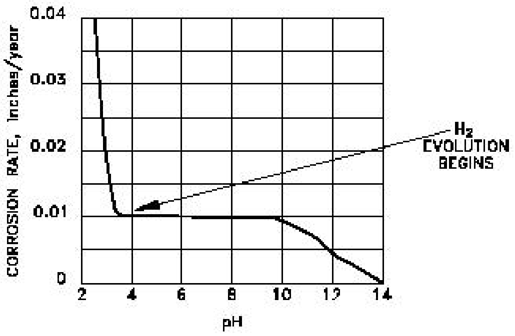
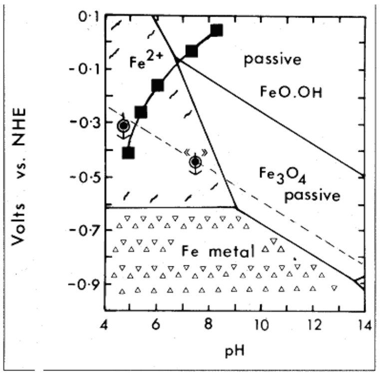


Fig.(3-7) Effect of pH on the corrosion of iron exposed to aerated water at room temperature



Pourbaix diagram for iron in sea water. The ■ data points relate to measurements on a *Rapid* cannon, the ⚓ symbol is for the predisturbance corrosion potential of the *Sirius* anchor and the "⚓" is the $E_{corr.}$ value prior to removing the sacrificial anode after one year of treatment

For pH values below 4.0, ferrous oxide (FeO) is soluble. Thus, the oxide dissolves as it is formed rather than depositing on the metal surface to form a film. In the absence of the protective oxide film, the metal surface is in direct contact with the acid solution, and the corrosion reaction proceeds at a greater rate than it does at higher pH values. For pH values above about pH 10, the corrosion rate is observed to fall as pH is increased. This is believed to be due to an increase in the rate of the reaction of oxygen with $Fe(OH)_2$ (hydrated FeO) in the oxide layer to form the more protective Fe_2O_3 (note that this effect is not observed in deaerated water at high temperatures) (http://www.tpub.com/content/doe/h1015v1/css/h1015v1_117.htm).

3.4.6 Salinity

Salinity is a measure of the degree to which the water in the sea is salty, and is a function of the weight of total solids dissolved in a quantity of sea water (Chester 2003). Salinity can also vary over the year, depending on the season. The aggressiveness of seawater and of marine environments, in general, is due to the abundance of chlorides. It contains about 19 compounds such as potassium chloride, sodium chloride NaCl and magnesium chloride MgCl (Vargel 2004).

3.4.7 Alkalinity of seawater

The pH of seawater usually has an average of 8.0 for all oceans commonly occur in surface water where three is equilibrium between atmosphere and surface water. About 95% of the ionic strength of seawater is due to salts whose ions are neither acid or bases and are not involved in proton exchange and thus do not contribute to the pH of seawater. It is the minor constituents of carbonates, borates, phosphates and silicates which are largely responsible for alkalinity of seawater. Of these the CO_3^{--} carbonate equilibrium system is the most important (Florian 1987).

3.4.8 Dissolved oxygen

Seawater contains 6–8 mg (ppm) dissolved oxygen. The oxygen concentration of seawater varies significantly with the depth of the ocean, but also with the temperature and the biological activity of the medium (Vargel 2004). The amount of oxygen in the atmosphere is far in excess of that in saturated seawater. Hence wherever there is contact between the two, oxygen is bound to diffuse into water till the saturation point is reached. This rate of diffusion is hundred times greater if the sea surface is agitated. Although seawater receives oxygen only at or very near the surface, life exists everywhere (http://www.uae.gov.ae/uaeagricent/Fisheries/ocean_e.stm).

$Fe \rightarrow Fe^{2+} + 2e^-$ Anodic reaction

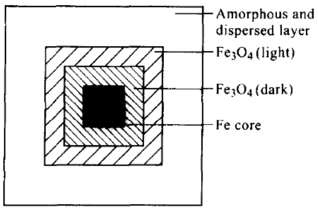
$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$ Cathodic reaction (Bartuli 2008).

Oxygen concentration cells can be created from deposits on a metal's surface or may be due to improper component design, which introduces crevices. Differences in oxygen content due to discrete films or deposits randomly scattered along a metal surface can cause pitting and/or crevice corrosion at these localized sites (Shifler and Aylor 2005).

3.5 Corrosion products of iron (Decay products)

The corrosion products are unsightly, and the swelling and deformation of the objects may be severe. The layer of corrosion products produced from reaction between the object and water, oxygen or biological organisms in the marine environment (Caple 2001). A layer of corrosion products made of iron oxides, oxyhydroxides and/or carbonates (Neff et al., 2004). Variety of corrosion products can be formed depending on the species present in their environment (soil, sea water, atmosphere, etc.) (Peulon et al., 2004). North (1982) discussed the exact nature of marine iron corrosion products. It is necessary to consider at least four distinct stages in the history of marine iron artifacts, due to differences in micro-environments and corrosion products. These stages are (1) initial immersion, (2) concreted with residual metal, (3) concreted with no residual metal, and (4) post-excavation. In stages (2) and (4) characterization of the corrosion products is complicated by their reaction with the atmosphere, thus necessitating the use of specialized sampling and measurement techniques (North 1982).

The outer layer, the thickest one, is very porous and looks like a mosaic of chloride and rust containing globular cemented together by network of silicates and other minerals. At some points this layer is easy to scrape off, and its surface displays crevices and cavities. But there are no gaps or capillaries observed which pierce the rust right to metal. ***The middle layer*** consists of striated, hard dark-brown, hard rusty red and softy yellow streaks which overflow in one another in circular pattern, but appear nevertheless sharply outlined. The streaks are arbitrarily distributed throughout the middle layer, and are again arbitrarily intersected by fine racks. After 1 or 2 days in humid chamber, only the soft and porous yellow streaks are covered with chloride blisters. ***The inner layer*** represents rust embedded in the iron core, rust and iron; being positioned next to each other. In the humid chamber rust blisters spring up at the boundaries between iron and adjacent rust areas as well as from the rust areas themselves (Stambolov 1985). The presence or absence of an oxide on a corroded surface, the color of an oxide, and its location on the metal surface provide clues to the mechanism of attack (Escalante 2005). It is well known that oxides and oxyhydroxides (FeOOH) and amorphous matter are main products of atmospheric rusting, marine corrosion and passivation of iron (Misawa et al., 1974).

	
Fig. (3-8) Colors of iron oxides *After: Schwertmann and Cornell 1991*	*Fig. (3-9) The layers of iron corrosion* *After: Novakaova, et al., 1997*

The nature of the corrosion products on marine iron changes both with time and with changes in the environment. From the chemical viewpoint, the 'lifetime' of marine iron can be considered as four distinct periods, although all four will not necessarily occur with every marine iron artifact (North 1982). Rust is iron oxide. Common salts are listed in table (3-2).

Soluble salts	**Insoluble salts**

Chlorides	carbonates
Nitrates	Sulfides
Sulfate	Phosphates

Table (3-2) Common salts affecting porous materials

from archaeological sites

Buchwald and Clarke (1989) studied the major corrosion products are chloride ion containing akaganiete, and goethite with minor amounts of lepidocrocite and maghemite by metallographic examination (Buchwald and Clarke 1989).

Literature indicates that the most common corrosion products found in the marine environment are:

3.5.1 Magnetite: ($Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$) remains stable in its anaerobic environment, and is therefore somewhat protective of the iron, as long as the external corrosion products and concretions remain intact. Once the outer rust layer is ruptured, the magnetite can oxidize to maghemite, Fe_2O_3 then to the iron oxyhydroxides mentioned above and can be found in the inner layers. According to Knight, the magnetite layer on the metal core is covered by a maghemite layer (γ- Fe_2O_3), which cannot be separated clearly from the goethite layer. The objects original surface lies between the magnetite and maghemite layers. Magnetite can be found in the inner layers near to the metal core (Schmutzler and Ebinger-Rist 2008). High fractions of sulphur have been detected in the magnetite layer, owing to bacterial activity in a low oxygen environment found in the massive ore (Buchwald 2005). *Figure (3-16) shows the idealized magnetite.*

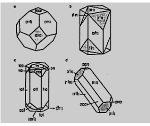


Fig. (3-10) Idealized magnetite (cubo-octahedrons), (b and c variations of pseudo-hexagonal prisms and (d Elongated cubo-octahedron). (After:Lovely 2000)

Stambolov added that magnetite is the protective layer of iron objects, the red-brown layers can be reduced into the black double compound magnetite. A further reduction leads to the black ferrous oxide FeO (Stambolov 1985).

3.5.2 Hematite Fe_2O_3 the color of hematite is brown-red instead. This is ionic compound in which the metals exist as positive ions. The oxidation state of iron in hematite is +3.

3.5.3 Maghemite Fe_2O_3 is a form of hematite with the crystal form of magnetite which causes the magnetic anomalies (Wilsom 2006). Maghemite has a similar crystalline structure to magnetite and the same chemical composition as hematite being a metastable phase between magnetite and hematite. In the crystalline structure of magnetite and maghemite, oxygen ions are cubic close packed with both octahedral and tetrahedral sites occupied by iron, whereas in hematite, oxygen ions are hexagonally close packed, and iron is present only in octahedral sites (Chirita and Grozescu 2009).

3.5.4 Wustite *FeO* is the lowest oxide of iron*, films are significantly enhanced compared to bulk FeO, and that its magnetic properties lead to remarkable (*Couet et al., 2008). Wustite is the most iron-rich oxide, forming adjacent to the metal, whereas hematite is the most oxygen-rich, forming next to the atmosphere (Fell 2004).

3.5.5 Lepidocrocite γ-FeOOH is ferric oxyhydroxide) (Argo 1981). Although a common terrestrial iron corrosion product, is rarely found on corroded marine iron. It has been shown experimentally that γ-FeO.OH reacts with ferrous ion to form magnetite. Such a reaction may account for the very hard adherent layer of magnetite commonly found next to the metal surface (Mark 1981). The oxidation of the Fe^{+2} ions in green complexes and green rust, leads to formation of lepidocrocite (γ-FeOOH) in well-aerated systems and magnetite in oxygen-depleted systems (Balasubramaniam 2003). Fe(III) has a low solubility and tends to precipitate as oxhydroxides. Lepidocrocite seems to be more present in the outer layer (Dillmann 2004).

3.5.6 Goethite is located in the outer corrosion product layers and the yellow-brown goethite occurs in almost all soils and other surface formations (lakes and sea) (Schwertmann and Cornell 2000). The magnetite layer on the metal core is covered by a maghemite layer (γ- Fe2O3), which cannot be separated clearly from the goethite layer. The objects on original surface lie between the magnetite and maghemite layers (Schmutzler and Ebinger-Rist 2008).

3.5.7 Siderite $FeCO_3$

One of the major corrosion products in the waterlogged deposits: it is assumed that this phase is often associated with calcite and sulphides. A layer composed of Ca-containing siderite is directly in contact with the metal (Neff et al., 2004). Siderite is an iron-bearing carbonate common to many diverse sedimentary settings, particularly in marine and lacustrine environments. Substitution of Fe^{+2} by other metallic ions is common in siderite and the mineral is rarely found as pure $FeCO_3$ (Bel 2007).

3.5.8 Iron sulfate: Iron (II) sulfate indicates $FeSO_4$, where the Fe ion has a charge of 2+, rather than the alternative Fe^{3+} (Pollard et al., 2007).

3.5.8 Chloride ion and chlorine containing species

Corrosion is caused by the interaction of oxygen, water and various ions. Chloride ions play a major role in the advance of corrosion and give the metal loss due to corrosion (Ouyang et al., 2009).

3.5.8.1 Akaganeite: β-FeOOH.Cl beta iron hydroxide β−FeOOH, in iron corrosion product (Argo 1981). It is generally considered to play a key role in post corrosion of artifacts (Graaf et al., 1995). The damage caused by akaganeite are mainly of physical character e.g. spalling and cracking, indicated by remaining orange needle shaped crystals (Schmutzler and Ebinger-Rist 2008). Formation of akaganeite (Chloride ions) and cracking of objects are well known phenomenon and can lead to loss of the artifact completely (Degrigny 2006). The formation of akaganeite is generally associated with the rapid aerial oxidation of ferrous ions or green rusts whereas slow oxidation favours the formation the formation of magnetite. Color is yellowish brown (King industries 1984).

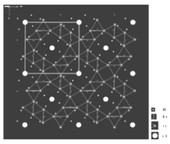


Fig. (3-11) Crystallographic structure of β-FeOOH akaganeite. After: Reguer, et al., 2009

Photo (3-2) Rusty brown coating of akaganeite on rock. After: http://www.webmineral.com/s

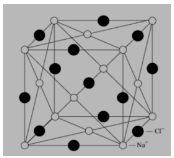


Fig. (3-12) The structure of NaCl. Na+ is FCC (face centered –cubic and Cl- is FCC. After: He 2009

3.5.8.2 Sodium chloride: In the case of iron metal recovered from a marine environment, that chloride ion is present in the corrosion layers as sodium chloride. At sodium chloride concentrations greater than one normal, β-ferric oxhydroxide (β-FeO.OH) is the only iron corrosion product formed. After that, the more common iron corrosion products α-FeO.OH and γ-FeO.OH can also be detected, but little if any sodium chloride. At initial sodium chloride concentrations of less than one normal, all three ferric oxyhydroxides are formed, but again little or no sodium chloride can be detected. It appears therefore that the bulk of the absorbed chloride ion is taken up within the lattice structure of β-FeO.OH prior to the formation of the more common corrosion products, and that β-FeO.OH is the dominant corrosion product while there is an excess of free chloride ions (Mark 1981).

3.5.8.3 Ferrous Chloride (simple chloride) is the compound formed initially when iron metal corrodes in the presence of chloride ions, and it has been identified within corrosion pits where acid conditions prevail. At a pH of less than 3.5, the oxidation rate of ferrous ions in aqueous solution exposed to air is extremely slow (Mark 1981).

3.5.7.4 Ferric chloride has been identified on a number of marine iron artifacts, but only in small concentrations. It is highly unlikely that ferric chloride would be found in proximity to metallic iron, for under such conditions, it is readily reduced to ferrous chloride as it attacks the surface of the iron (Gilberg and Seeley 1982).

3.5.8 Amorphous material

Marine iron corrosion products usually contain a large quantity of amorphous material, which has been shown to have considerable chloride content, much of it present as sodium chloride. This may be microcrystalline, or have a highly disordered lattice, but will certainly carry additional chloride adsorbed on its surface (Mark 1981).

3.5.8.1 Green rust

A compound with the formula $Fe(OH)_2$, 1/4FeO.OH was reported by Uyeda and Yoshioka in 1946, resulting from the rusting of iron in sea-water, and was named by them 'green rust'. It has been shown experimentally that this is a mixed valence compound which precipitates from solution when dissolved ferrous ion is oxidized at neutral to alkaline pH in the presence of chloride ions, is green in colour, and has a typical composition Fe(II), Fe(III), (O,OH,Cl). Green rust has been identified on marine cast iron as well as on mild steel strips immersed in an artificial sea-water solution. It has also been produced as an intermediate corrosion product on steel anodically polarized via an external current (Mark 1981).

3.5.8.2 γ-Ferric Oxyhydroxide

The various ferric oxyhydroxides found on marine iron are known to possess a variable chloride content, and notable among these is β-FeO.OH, which a number of studies suggest is the dominant iron corrosion product in this context. The naturally occurring mineral form of this compound, akaganeite, is completely halide free (Gilberg and Seeley 1982).

3.5.9 Trace of iron oxides

- **Hibbingite γ-$Fe_2(OH)_3Cl$,** a Chlorine-rich corrosion product in meteorites and ancient iron objects. It is colorless to pale green, weathering red and appears to have cleavage. It is also very soluble in water (Bernhardt et al., 1994).

3.5.10 Calcium carbonate and magnesium hydroxide

Calcium carbonate and magnesium hydroxide are two major *corrosion compounds of iron* associated with objects (Hamilton 2000).The corrosion rate of cast iron in seawater was lower than would have been predicted solely on the basis of chlorinity due to effects such as the activity of carbonate ions in the seawater (Heldtberg et al., 2004).

3.6 Post-excavation changes in iron antiquities (wet artifacts)

As result of excavation an iron object, its surrounding climate is changed into higher oxygen and less water containing conditions. This causes the oxidation of iron and ferrous species just as drying of the find which causes complex physical and chemical changes. If there is still a metal core inside the object, electrochemical corrosion caused by humidity is still possible. Additionally, if there is a chloride contamination, post-excavation corrosion becomes much more probable because of hydrolysis and oxidation of ferrous chloride solution. The most destructive post-excavation product is the akaganeite phase. The destructive effect of akaganeite consists of its potential to release chloride ions and of its increased volume during crystallization, which can also be applied for other ferric oxyhydroxides (Schmutzler and Ebinger-Rist 2008). An object, which has been immersed for a long period in saltwater and is recovered from the seabed, risks to deteriorate rapidly if brought in contact with air prior to being treated (Protection of underwater cultural heritage, 2001), because the artifact is removed from its burial environment, it is subjected to certain physical and chemical changes. The equilibrium the artifact has achieved with its surroundings is upset (Singley 1981). On-going corrosion problems occur on iron objects after excavation if they still contain an iron core and are contaminated with salts, especially an acidic iron (II) chloride solution. When a freshly excavated iron object is exposed to a new environment above the ground, it generally experiences a lower relative humidity (RH) and a higher O_2 concentration relative to the burial environment. As the iron dries, the contaminating solution of acidic $FeCl_2$ plus other salts concentrate and the corrosion layers crack, allowing overview of archaeological iron: the corrosion problem, key factors affecting treatment (Selwyn 2004).

3.7 Iron artifacts after drying out

. Plenderleith and Wernner (1971) explained these problems of objects that have been excavated from damp environment are dried quickly instead of being allowed to adapt themselves gradually to the new environment above ground (Plenderleith and Wernner 1971). For iron materials lying above or on the seabed, the primary cathodic reaction is the reduction of dissolved oxygen (Ruppé and Barstad 2002). Graaf (1995) also have shown that two problems are encountered in the conservation of iron archaeological artifacts. The first problem concerns encrustation, a hard agglomerate layer that covers the artifact, consisting of soil and migrated oxides. The second is to prohibit any further corrosion (Graaf 1995).

Cast iron shouldn't be allowed to dry out before or during treatment (although it may be exposed to the air for short periods when only surface water is evaporated). This in principle only applies to objects that have been chemically and /or physically allow corrosion to extend to the inner layers, but as it is impossible to be certain of the condition prior to cleaning, all cast iron must be assumed to be unstable (Rees-Jones 1972).

The initial iron corrosion products are iron II chlorides, which are subject to further oxidation on aerobic sites to the characteristic red-brown iron III oxy-hydroxides. Under the covering of marine concretion on the wreck site, anaerobic conditions can develop and precipitate corrosion products such as FeS pyrrhotite and FeS_2 pyrite within the wood structure (Macleod 1990).

All recovered iron artifacts are actively corroding. While it is true that they are corroding at different speeds and some may be dry or have electrically passive coatings or come from a reducing environment-recovery change everything. Dry site recovered artifacts; left to dry even further, will be thrown artificially into a dry cycle. Acid inside the concretion will build up, concretions will begin to crack, and the artifacts itself may begin to spall and flake. Even those objects that show no active corrosion and are kept in low relative humidity have acquired anions from their stay in the soil. These anions such as chloride will initiate the corrosion process from within, perhaps years after recovery. This corrosion will show up in the form of weeping brown droplets that appear on the artifacts. Concreted artifacts recovered from the oceans are also actively corroding and it need of stabilization (Rodgers 2004). The corrosion of archaeological iron objects after excavation can be rapid and severe. This is due to the presence of chloride ions, which accelerate corrosion and can lead to the complete destruction of objects in a short space of time. Although it is possible to stop this process using dry storage conditions, these are difficult to maintain and require significant resources. (http://www.britishmuseum.org/research/research_projects/archaeological_iron.aspx).

The deliquescent bead-like corrosion spots, often found on iron artifacts and described as 'sweating', are normally stated to be ferric chloride. These features frequently occur when artifacts with high chloride ion concentrations are allowed to dry out rapidly or are subjected to conditions of fluctuating relative humidity. Ferric chloride is unstable to hydrolysis, being converted to β-FeO.OH, which may account for the rather small quantities detected in practice, as well as the presence of β-FeO.OH at the sites of active corrosion on an The presence of ferrous chloride pockets in pits at the metal-oxide interface has been demonstrated, and ferric chloride has also been detected although not in significant quantities. Both iron chlorides no doubt exist in their hydrated forms, $FeCl_2.4H_2O$ and $FeC1_3.6H_2O$ respectively, which are rapidly converted by liquid ammonia to iron oxides and ammonium chloride. The iron oxides formed have a variable chloride content, in which chloride is probably adsorbed by electrostatic attraction onto the oxide surface as well as bound interstitially within the crystal structure (Gilberg and Seeley 1982). If the object cleaned from their marine crust and left to dry out the iron objects are exposed to a rapid oxidation. Corrosion layers crack allowing more oxygen to reach the metal surface. According to Turgoose (Turgoose 1982) this oxidation causes the formation of solid iron oxyhydroxides and can be described by the reaction: this oxidation causes the formation of solid iron oxyhydroxides and can be described by the reaction

$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4FeOOH + 8H^+$ (Degrigny and Spiteri 2004).

The difference between some cannonballs artifacts is shown in the following photos (3-1).

	
An early 18th-century 33-pound cast iron cannonball found in the mouth of Portsmouth Harbour (England) and allowed to dry without any conservation.	*This is a civil war heated fired cannonball used in the St. Lawrence waterway, Massena, new York. This type of artifact was used to shoot at wooden sailing ships. The heat would cause fires to start on the ships. This old fireball cannonball appears to be made of a hard heavy pitted stone. This type cannonball would be heated in a furnace at a fort to about 1000 degrees.*

photos (3-1) Some samples of the cast iron cannon balls,

(http://www.landthrip4usa.com/ciwarhecafis.html)

CHAPTER 4

DIFFERENTE METHODS OF DECHLORINATION OF EXCAVATED IRON ARTIFCATS FROM SEAWATER

The literature on the desalination methods of iron artifacts from the marine environment contains detailed information about the effect of these methods and the best conditions.

Nordgren said that minimizing post-excavation iron corrosion and removal of chlorides are particular concerns for the monitor conservators who have collaborated with other conservators, conservation scientists, chemists, physicists, and corrosion engineers to better understand the current condition of the monitor artifacts and develop strategies for their stabilization and conservation (Nordgren 2006). In the selection of conservation treatment for iron, it is important to understand the process responsible for the deterioration of artifacts that must be conserved, and the ways which may be related to the structure and composition of the artifacts. Conservation in an archaeological context means the investigation, stabilization and, in some cases, reconstruction of the entire spectrum of archaeological materials (Pollar et al., 2007). *Conservation of underwater archaeological objects involves a number of different steps as follows:*

4.1 The definition of desalination

Desalination is the process of removing soluble salts from an artifact, typically through repeated baths in distilled or deionized water. Certain salts, such as some nitrates and sulphates, are easily soluble in water and can be absorbed into porous metal. In drier conditions, these same salts lose water and crystallize to solids. As they crystallize, their volume increases and they can cause physical damage to the fabric of an artifact. For this reason, it is often essential to remove soluble salts if they are present.

Desalination is usually necessary when artifacts have come from environments known to have a high level of soluble salts, such as marine contexts, privies, areas of brackish water and certain terrestrial sites. If metals require desalination, it may be necessary to use chemical baths other than water, since water can stimulate rapid corrosion. Desalination is typically accomplished by soaking an artifact in successive baths of good-quality water. Through this process, water-soluble salts diffuse from the artifact into the less salty water. The salt content of the water baths must be measured regularly in order to check the progress of the desalination (Dixon 2006).

4.2 Chemical desalination treatment

The chemical solution is used as a cheap and easy method for the treatment of the archaeological objects in situ of the excavation and the labs of the conservation. Chemical solutions are considered to be dangerous in the concentrated solution to the archaeological objects. Water as a relatively non-volatile cleaning fluid and as polar solvents which dissolves ionic substances presents its own problems (Moncrieff 2005). One method of removing chlorides involves washing them out in successive baths of strongly alkaline water. However, this may not be appropriate for certain objects, especially if the metal is attached to non-metallic material. The condition of the metal is also relevant. For example, soaking may not be an appropriate treatment for crumbling, friable metal. In any case, treatment should only be attempted under the direction of a conservator (Riss 1993).

The factors which have to be taken into consideration in order to remove the chloride from the crust are the following, the efficiency of washing method:

The wide variations which occur in the diffusion coefficients, depth of corrosion and initial chloride concentrations between different artifacts, and even different sections of the same artifact, make it very difficult to obtain valid comparisons of the efficiencies of different washing techniques (North and Pearson 1978).

The material transport across the crust either way is promoted by a wash liquid which is capable of waiting optimally all cracks, pores and capillaries. The best in this respect is steam; the second best is hot water (80°C) and then follows cold water containing 2% surfactant (wetting agent).

pH-values of the wash liquid allying between 12 and 13.5, facilitate the dissolution of all chloride salts present in the crust. North and Pearson tested the efficiency of different wash solutions in the pH range 8.3-14. In this range they found no evidence that pH, per se, had any significant effect on the chloride extraction process (North and Pearson 1978).

Heating of the wash liquid increases the rate of dissolution, whereas contrary to expectation acetone methanol and ethanol are useless as accelerators of the dissolution and extraction of chlorides from rusted iron. On the other hand, pH values have no bearing on the rate of chloride ion extraction from the crust.

As *the diffusion of the chloride ions in pure water is very slow, no significant improvement in the chloride extraction rate can be expected by frequent change of the wash liquid, or otherwise lowering its chloride content*. Reductive interstate in the process of washing reduces the iron (II) compounds to magnetite in porosity and diffusion coefficients. On account of the greater density of salt solutions compared with pure water, the extracted chloride settles in the lower portion of the wash liquid. The washing is no doubt, improved if the corroded objects are positioned above the bottom of the wash-basin (Stambolov 1985). Most low temperature "stabilisation" treatments are described as chloride removal methods although the preceding discussion indicates that ferrous ion removal is equally, if not more, important. However, removal of cations implies anion removal. This desalination treatment can be attempted in various ways, of which a simple immersion treatment is the commonest (Hjelm-Hansen et al. 1993).

North and Pearson (1978) said that the washing method provide extraction of chlorides by immersing an object in an appropriate solution and the heat treatment methods provide the volatilization of chlorides at a temperature over 400°C. Heat treatment can cause serious damage to iron objects so its application should be limited. Washing methods could be divided into aqueous and non-aqueous methods. Since the latter have been shown to be ineffective (North and Pearson 1978).

Conservation treatments for archaeological iron are designed to remove as much of the salt contamination (especially Cl^- ions) as possible. If enough Cl^- ions are removed, then these objects can resist corrosion when stored or displayed in a controlled museum environment without special storage conditions. In general, immersion treatments involve placing iron in an aqueous solution, usually a near-neutral or alkaline one, and waiting for the Cl^- ions to diffuse out. One advantage of using alkaline treatment solutions is that they promote the desorption of Cl^- ions because of the net negative charge induced on the surface of iron oxyhydroxides by excess OH^- ions. Another advantage is iron passivation (Selwyn 2004).

4.2.1 Water diffusion

In any archaeological excavation of the artifacts, there will always be some artifacts that can not be conserved by any the treatments. The chlorides can be removed by a process referred to as water diffusion.

From a standpoint of coefficients of thermal expansion, however, the alternate heating and cooling probably changes the diffusion gradient of the solution rather than significantly changing the size of the metal capillaries. In some instances this will decrease the time required to remove the soluble chlorides, but found that there was no significant difference between the time required to wash similar objects at room temperature and at 50°C. The alternated heating/cooling cycle may facilitate the treatment, however, when significant levels of chloride are present and months to years are required to remove them. After the soluble chlorides have been eliminated, the artifacts need to be carried through the same final steps as iron treated by other methods (Hamilton 2000).

Alkaline cleaners are effective for both organic and inorganic dirt removal. They saponify and hydrolyze, that is, break down the organic constituents of the dirt to shorter, soluble or dispersible fragments. Alkaline solutions also swill clay and dissolve many inorganic salts and they neutralize any acidic components of the dirt (Stambolove 1985). Laboratory studies have shown that iron objects can be passivated in alkaline solutions such as sodium borate ($Na_2B_4O_7$, pH 9.2), sodium sesquicarbonate (equimolar Na_2CO_3 and $NaHCO_3$, pH 10), sodium carbonate (Na_2CO_3, pH 11.2), and sodium hydroxide (NaOH, pH 12.6–13.5) (Selwyn 2004).

4.2.2 Chemical desalination treatment

4.2.2.1 Liquid Ammonia*

It is shown that not only does liquid ammonia act in a solvent capacity, but it also converts insoluble chloride-containing iron corrosion products into chloride-free iron compounds and ammonium chloride, the latter being readily removed by washing with water under anaerobic conditions. Pre-treatment with liquid ammonia, followed by aqueous washing, has been shown to be both rapid and effective in the stabilization of marine cast iron artifacts with initial high chloride content (Gilberg and Seeley 1982). Hydrogen peroxide (H_2O_2) and ammonia solution ($NH_3 + H_2O$) with mechanical treatment are very effective. Concentrated hydrogen peroxide is unstable and especially in alkaline solutions it disintegrates to oxygen and water. Metals salts accelerate this mixture, once having entered the pores rust, generates a strong oxygen gas evolution, which leads to eventual collapse of the structure (Stambolov 1985).

4.2.2.2 Sodium sulphite (The alkaline sulphite Na_2SO_3)

The alkaline sulfite treatment was developed by North and Pearson (1975) to stabilize marine cast iron, but is also used on wrought iron (Hamilton 2000). The alkaline sodium sulphite technique is one of the most successful for the treatment of archaeological iron but the mechanism by which it operates is rather different from that which has been assumed up to now (Gilberg and Seeley 1996) and it is considered better aqueous chloride extraction due to alkali and deaerated environment, but normally less than 90% chloride removed., caustic solution., impractical on scale required. The washing procedure takes a long time – requiring months on average for a complete treatment. However, not even such as prolonged treatment can guarantee entire long-time stability of desalination finds. The elimination of corrosive chloride ions was effective with this solution (Schmutzler and Ebinger-Rist 2008). Washing of the chloride salts is due to the property of sodium sulfite to reduce the chlorides to magnetite, and magnetite is considered to be stable (Stambolov 1985).

The procedure is as follows:

1. Once the objects have been mechanically cleaned, they are immersed in a solution of 0.5 M (20 g. per liter of water) of sodium hydroxide and 0.5 M (126 g. per liter of water) of technical grade sodium sulfite. Tap water can be used for the first one or two baths but deionized or distilled water should be used in the final baths. The container should be filled as full as possible and sealed to prevent any access to air. The solution is mixed and the object placed in it as quickly as possible to avoid any oxidation of the solution. The container is placed in an oven and kept heated to a temperature of 60º C. The object is processed through several baths until chlorides are eliminated; this may take from a week to several months and numerous baths. The solution does not attack any residual metal so there is no danger of too many baths.

When a marine iron object is immersed in this hot reducing solution, the iron corrosion compounds are converted to magnetite and the chlorides are transferred to the solution where they are discarded with each bath change. The objects come out of the treatment with a very black surface coloration. Since the solution is strongly alkaline, contact with the skin should be avoided.

2. Once the alkaline sulfite stabilization treatment is completed, the objects are washed for one or more hours in several baths of deionized water and then placed in a 0.1 M solution of barium hydroxide (32 g. per liter of water). Barium hydroxide is slightly poisonous, so contact with the skin should be avoided. If the object is intensely rinsed in several baths of deionized water following the alkaline sulfite stabilization, the barium hydroxide baths can be eliminated - thus it is optional.

The alkaline treatment has been very effective for conserving iron recovered from a marine environment. The main drawbacks of the treatment are that it has to be carried out in an air tight container and the solution should be kept heated (Hamilton

2000). The alkaline sulphite solutions have pH values of approximately 14 and need to be neutralized using concentrated HNO_3. A 50ml alkaline sulphite solution needs approximately 0.5 * 50/16 = 1.5ml of acid to bring it to pH7 provided 16M HNO_3 (concentrated, 67%). It should be mentioned that the pH could change after the addition of H_2O_2 and therefore the pH needs to be monitored and adjusted if necessary to make sure it falls in the range of 1-12. Desalination was terminated for the alkaline sulphite treatment after wash 5 (Wang and others 2010).

4.3 Reduction methods

Recent years have seen an increase in the conservation of objects. The conservators have many methods to choose the best one, according to the state of the object. The problems, characteristics and needs of each object must be considered individually. Consolidation is essential to conserve the objects without damage to their form and texture and without risk of stain and discoloration. This technique is used to consolidate the inscription contains. Reduction methods are considered one of the consolidation methods for iron archaeology. There are many methods to consolidate metallic artifacts as follow:

Tap water continues to be used for electrolytes until the chloride level is less than that of the tap water. Using rain water in electrolytes between tap water and D.I. water will considerably reduce cost. Following this procedure will result in great financial savings when a large number of chloride-contaminated materials are to be processed. Occasionally just deionized or distilled water is recommended as a storage solution for metal artifacts. Unaltered deionized or distilled water should never be used. They are generally slightly acidic and hence highly corrosive. Likewise, when used for rinsing or as a bath for detecting chlorides, the duration should be kept to minimum and adequate precautions taken (Hamilton 2000).

4.3.1 Electrochemistry reduction

Before electrochemical methods can be applied, conservators must first assess the condition of a marine artifact. Electrochemical techniques are mainly known in conservation and restoration of metallic heritage as a tool for treatment of the objects involving the reduction of the corrosion products or the electrochemically aided removal of chlorides (Arnaud 2007). The use of electrochemistry is for facilitating mechanical cleaning. Often, marine artifacts are encased in a "concretion" layer that is a mixture of corrosion products and biological and mineral deposits. Turning up the current density causes a vigorous evolution of hydrogen bubbles, which can knock off the encrustation. This approach works for wrought not cast iron because the engraving in the delicate graphitized layer on cast iron would be lost in the process (Arnaud 2007).

Electro-chemical method, hot solution of *sodium sulphite* is used which is quick and similar to electrolytic reduction. An expert should only employ this method since in case of highly corroded objects nothing will be left after employing electrolytic reduction and electrochemical method of cleaning. Hence before applying this method, a thorough investigation of the condition of the metal objects received for treatment should be conducted so that its fusibility could be decided (Yadav 2009). All metals, however, when reduced to very small particles appear dark of black in color, and during electrochemical reduction this debris tends to settle in cavities and crevices along the surface of the metal that is being cleaned (Stambolove 1985).

Therefore these experiments suggested that rapid electrochemical processes are taking place during immersion in alkaline solution. These processes are likely to cause irreversible changes in the corrosion product layers, which should be realized when considering the use of these solutions. On the other hand the effectiveness of the stabilization may be associated with these changes (Degrigny and Spiteri 2004).

4.3.2 Electrolytic reduction

Electrolysis basically reverses the electrochemical reaction which created the rust in the first place. It does not restore the oxidized iron to its original state, but rather removes the rust from the surface of the un-rusted metal below. The iron that rusted in the first place was an anode in the electrochemical cell. Electrolysis reverses the reaction by making the rusted object into the cathode and some other piece of metal into the anode. An electromotive difference is created between the cathode and anode with the use of a direct electric current. Just as in the original reaction which created the rust, the anode and cathode must be bridged with an electrolyte. The anode is the positive terminal of the electrolytic cell, to which electrons, negatively charged ions, travel when an electric current is passed through the cell. Oxidation occurs at the anode and oxygen is evolved. The cathode is the negative terminal of the electrolytic cell to which positively charged metallic ions travel. At the cathode, reduction takes place and hydrogen is evolved. Full immersion is required and rust is more effectively removed from the cathode when the surface is in a direct "line of sight" with the anode (http://ecologicarchitecture.com/SoloHobbit/rust/index.htm#types).

Electrolysis of cast iron artifacts in alkaline solution is a method of conservation of shipwreck material. Basically, this function as an electrolytic cell, consists of a receptacle with a treatment solution, a cathode (the iron object), and an anode (mild steel or stainless steel). The purpose of electrochemical treatment is to extract chloride ions by applying an electrical field between the objects (Ouyang et al., 2009). Electrolysis, which produces an oxygen-reduction reaction, is the most common and earliest way to stabilize them. The conservator can treat only one type of metal at a time, and needs anode, a tank to hold the artifact and anode, a power source, and an electrolyte solution. The tank should be large enough for the solution to cover the artifact completely (Singer 1998).

Electrolytic reduction may be the standard treatment method for marine artifacts, but it's a painfully slow process. *Cast-iron artifacts can take three years on average to conserve and wrought iron about half that time* (Arnaud 2007). General time frames, based on artifact size, are actually more useful than attempting a graph of chloride ion concentration versus time for every artifact. Small artifacts of pin, or buckle size receive one to two weeks of electrolysis. Larger artifacts, of spike or plate size, should undergo reduction for about a month. Renewed corrosion in storage (very rare) is the best indicator that the artifact has not been thoroughly rinsed (Rodgers 2004). These methods are generally applied in such cases where the corrosion product is so hard that it can neither be removed mechanically or chemically (Yadav 2009). Electrolytic reduction as described for iron will work well for most of these miscellaneous metals provided, of course, there is a core of sound metal to make the electrolytic connection. This is a large presumption, and the process will actually become destructive if there is no sound metal within the artifact. Electrolytic action will remove the concretion surrounding an artifact. This process can be destructive if the archaeological surface needs to be saved but is not metallic. Therefore, included below are hints for each of these metals undergoing electrolysis (Rodgers 2004).

In electrolytic reduction method the object is made cathode and the electrolyte is a solution of sodium hydroxide, the most common electrolyte, and sodium carbonate (Yadav 2009). The current is carried away from the iron by negative ions through an electrolytic solution to the anode, where they are oxidized (Buys and Oakley 1996). The lack of rotation of cast iron cannon from marine environment during electrolysis treatment resulted in post excavation problems. Areas of original surface cracked because the cradle and insulating supports has minimized the outward diffusion of chloride ions (Macloed 1987).

The reactions at the cathode are:

$$M^+ + e \rightarrow M \quad or \quad H^+ + 2e \rightarrow H_2$$

At the anode the following oxidations occur:

$$M \rightarrow M^+ + e \quad or \quad 4OH \rightarrow 4OH + 4e \quad and \quad 4OH \rightarrow 2H_2O + O_2$$

During electrolysis, then, there is competition at the cathode between hydrogen and metal ions for the procurement of electrode. The light metals, e.g. sodium, potassium, magnesium, calcium, barium, aluminum, etc. are never deposited on the cathode because their positions are more stable in the oxidized state than in metals. Electrolytic cleaning of antiquities may take place in containers made of one of the following materials: mild steel, ceramics or glass of polythene. The gas bubbles liberated at both electrodes during electrolysis release sodium hydroxide into the atmosphere, which is unhygienic and also a waste of reagent (Stambolov 1985). Sodium hydroxide is the standard electrolyte used in electrolytic cleaning, it is the only electrolyte used when the objective is to maximize the reduction of ferrous corrosion products and chlorides (http://nautarch.tamu.edu/class/anth605/File10b.htm#Sodium).

The object is made the cathode in a solution of 2% sodium hydroxide, and a piece of mild steel sheet (Anode). The applied DC current density is 10 A/m^2 (higher current densities cause blistering of the surface layers of the object by the hydrogen gas involved there. Lower density values merely prolong both the time required to remove the chloride salts, and the reduction of the rust). The electrolysis continues with weekly change of the bath (2% W/V) sodium hydroxide) and tests of its chloride. For this purpose distilled water is used to which 0.1% sodium chromate is added as corrosion inhibitor. As soon as the pH of the wash water is reduced to 8.5, the washing is considered finished (Stambolov 1985).

If iron reduction is the objective, the specimen should be started off at a low current density. It is followed by a medium current density for the long chloride removal stage. A continuation of low current density would only lengthen the process of chloride removal, while the vigorous production and evolution of hydrogen at high current density interferes with the efficient removal of chloride from the metal and its corrosion products. At both low and medium current density, the marine encrustation and some corrosion products are slowly removed from the object by the mechanical action of the evolved hydrogen. For maximum efficiency, however, the artifact should be finished at a high current density. This ensures the complete removal of any remaining marine encrustation and loose corrosion layers, as well as any remaining chlorides. When high current densities are used only in the last stage of electrolysis, the metal corrosion products that are capable of being reduced have already been reduced, and it is less likely that they will be removed by vigorous hydrogen evolution. While the current density recommendations serve as useful guidelines, they cannot be adhered to rigidly. The conservator should take into consideration the individual peculiarities of the objects being treated and the facilities available to treat the objects. In the case of very large objects, for example, the above current density recommendations may require current in excess of the maximum capacity of an available or practical power supply (Hamilton 1999).

This is most easily accomplished by electrolytic reduction techniques, but if the artifact is very badly oxidized, and the overall form and dimensions of the object are to remain intact, the only alternative is to remove the soluble chlorides in the much slower process of water diffusion. The artifact is placed into a container filled with water, and the water is changed frequently as the soluble chlorides diffuse out of the metal into the solution. The water should be changed weekly or as often as necessary as determined by a qualitative or quantitative chloride test. However, for all intent and purpose, water diffusion is not an option when it comes to treating iron recovered from a marine environment. It just does not remove the chlorides within in any accepted time frame when any other option is available. It is only a consideration, when one is attempting to conserve an artifact that is so badly corroded that it chances of being destroyed if it were cleared by electrolytic reduction or by the alkaline sulfite treatment discussed elsewhere. Since water diffusion requires a long time, the water must be inhibited to prevent the metal from rusting (Hamilton 2000).

Current density

Hamilton said that the current density used in electrolytic reduction is expressed as the number of amperes per unit of square area, introduced in the electrolytic cell by external D.C. power supply, such as one ampere per square centimeter (1 amp/cm^2).

Plenderleith and Werner suggested approximately 10 amps per square decimeter (1 amp/cm2) of cathode area so as to give a steady, vigorous evolution of hydrogen. They say, however, that this density is not critical for iron and steel artifacts. This statement is misleading. If the artifact is solid, well-consolidated metal, or has only ferric corrosion compounds, the current rate is not critical. If the object has ferrous corrosion compounds, an initial high current density will quickly flake off the corrosion layer and significantly alter the shape of the specimen. In addition, an initial high current density can disfigure the surface of iron and also seal off the object, preventing the removal of deeply seated chlorides.

In Hamilton (1976) proposed the following current densities and objectives:

1. Low current density .001-.005 amp/cm2 attempts to approximate the reduction range of ferrous corrosion compounds.

2. Moderate current density, .05 amp/cm2 attempts to approximate the optimum conditions for chloride removal without undue evolution of hydrogen.

3. High current density of 0.1amp/cm^2 has as its major goal the vigorous evolution of hydrogen for mechanical cleaning. These were recommended as rough guidelines for treating most iron artifacts from under the sea. These current densities were established by measuring the electrode potential established first on the surface of a rectangular bar of steel and then verified on a number of small artifacts. The high level of chloride (2,000 to 18,000 ppm) and lack of external circulation can cause the anode (the metal vat) to corrode extensively through anodic dissolution (Hamilton 2000).

5% sodium carbonate electrolyte with a pH of 11.5 will suffice for the electrolytic cleaning of most iron artifacts if maximum reduction is not the objective. In terms of safety, it is much less caustic than sodium hydroxide and is much safer to handle. It is less conductive than sodium hydroxide and has to be used in stronger concentrations, 5 to 10% versus 2 to 5%. It is less soluble, which makes it more difficult to mix, but it does not generate the extreme heat of sodium hydroxide when mixed in concentrated solutions. The most important disadvantage of Na_2CO_3 relates to its pH and cathode reduction potentials (Hamilton 2000).

4.3.3 Thermal reduction

An alternative processing method is heating up the corroded ironwork (≤ 350°C) in a plasma chamber or oven inside an inert or reduced atmosphere. As a result the corrosion crust becomes crumbly due to micro cracks (Dickmann1 2006). Heated in a furnace with gas supply equipment at temperatures up to 800°C, excavated ironwork is desalinated because at those temperatures the chlorides evaporate. Notwithstanding the thermal treatment, the object is kept well in shape provided the atmosphere in the furnace is reductive or at least neutral.

The furnace is heated by electric heaters. To obtain the gas, anhydrous liquid ammonia is heated to 850°C and the resultant gas is passed over a porous nickel catalyst which, is held at this temperature. The ammonia is completely dissociated into hydrogen and nitrogen and fed as "cracker gas". Temperature used during the aforementioned thermal treatment is bound to change the crystalline structure of heated iron (Stambolov 1985). Rosenberg had applied the annealing method at 800ºC for the iron-containing artifacts, then boiled in a saturated solution of sodium carbonate, that is finally soaked in water for a week or two, and dried stabilized in microcrystalline wax. The maximum temperature of 800ºC was typically maintained for 30-60 minutes, while the objects, wrapped in asbestos paper, were placed in a ceramic furnace with a normal atmosphere (Buchwald 2005). Briks and Meier said when iron is heated in air it forms multi-layered oxide scale comparing wüstite (FeO), magnetite and hematite, the precise composition of which is temperature dependant (Fell 2004).

Atmospheric reduction

Hamilton said that Barkman and Franzen have demonstrated that annealing iron at a temperature of 1060˚C in a reducing atmosphere successfully stabilizes and preserves it, returns it to the metallic state, and eliminates by sublimation the corrosive chloride compounds. The iron to be treated is placed in a hydrogen furnace and heated in the presence of hydrogen gas. The temperature is slowly elevated to 1060˚C over a period of one week. At this elevated temperature, all the moisture is driven off and all the chloride corrosion compounds are volatilized. The hydrogen reduces the iron corrosion compounds back to a metallic state and combines with oxygen in the corrosion products, forming water which is driven off by the heat (Hamilton 2000).

4.4 The history of dechlorination treatment methods of iron artifacts

The conservation of the metal objects has developed significantly in the last few years. Nowadays, the most of conservation treatment aim to remove the chlorides in order to stabilize the artifacts. Cronyn (1990) said that most techniques of stabilization of iron from marine sites in the past have aimed at the removal of chlorides, but none has been particularly successful (Cronyn 1990).

Before 40 years ago, many works of dechlorination are accomplished by using acids as citric acids, EDTA and sulfuric acid, but the acidic solutions haven't the good results to remove the chloride ions. They have the good effect to remove the earthy and corrosion compounds (Stambolov 1989). There is little reason to use the chemical treatment by acids for dechlorination, caused by the strong of acids on the surface of the metal objects. Hydrogen plasma was added to the field of conservation and restoration of the artifacts as a dechlorination method for 40 year ago.

The history of the use of electrochemistry for the treatment of metallic cultural heritage started when Friedrich Rathgen began to apply electrolytic reduction for the treatment of active corrosion problems in archaeological irons using a potassium cyanide electrolyte and three Daniell solid state electrochemical cells in series. He was also a pioneer in the use of zinc granules for electrochemical reduction (Cano 2009). Finkener (1886) advocates electrolytic reduction in potassium cyanide (Cyankalium) baths and stripping by hydrogen evolution before thorough washing. After brushing with wire brush objects are coated with nitrocellulose lacquer in order to ‘give back a metallic look as shown in Figure (4-1).

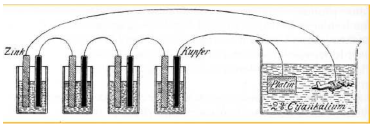


Fig. (4-1) shows electrolytic reduction technique

After: The Metals Conservation Summer Institute 2006)

Axel Krefting (1883), suggests to remove all corrosion layers and to prevent further rusting. Bronzes are stripped for 24hrs by immersion in sodium hydroxide with zinc granules without external electrical source. Other obscure methods exist at the time, such as dipping coins in liquid lead (Pb), followed by quenching in cold water and leaving over night in milk in as indicated in Figure (4-2).

Rosenberg advocates a localized stabilization method by using aluminum foil and an Agar / Glycerol electrolyte to electro-chemically reduce chlorides into stable mineral as shown in Figure 4-3.

	
Fig. (4-2) shows the immersion of bronze objects in sodium hydroxide with zinc granules without external electrical source	*Fig. (4-3) shows electro-chemically reduction of copper object by using aluminum foil and an Agar / Glycerol electrolyte*

After: The Metals Conservation Summer Institute 2006

In 1904 William Flinders Petrie used on-site the washing of iron in water, then oven drying, waxing. In 1905 Rathgen and Finkener proposed boiling iron in molten potassium cyanide.

In 1917 Rosenberg suggested heating iron up to 800ºC, quenching in potassium carbonate. Subsequent boiling in frequent changes of distilled water until no more chlorides. Vigorous chemical cleaning methods are still used such as electrochemical cleaning, boiling in sodium phosphate, Alkaline Rochelle salt and citric and sulphuric acid.

In 1956, Plenderleith recommended the use of electrolytic reduction in sodium hydroxide as shown in Figure 4-4.

After 2nd World War, mineralized silver is also converted into metallic particles by electrolytic reduction. In 1964 Hydrogen reduction is first used for the conservation of iron finds from the Vasa. This heat treatment involves temperatures of up to 850°C. Successful for stabilization of cast iron artifacts, but much metallurgical information is destroyed as shown in Figure 4-5.

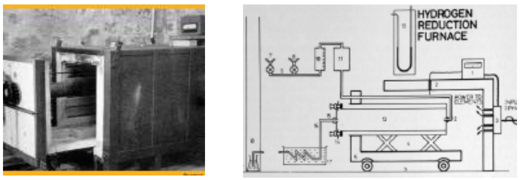


Fig. (4-4) Hydrogen reduction
After: The Metals Conservation Summer Institute 2006

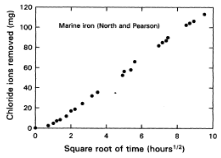
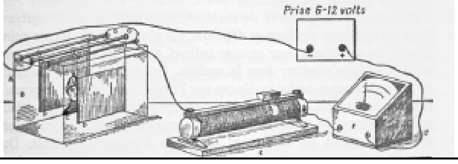


Fig. (4-5) Graph of the amount of chloride ions removed (mg) against the square root of time (hours) for a piece of graphitized cast iron (marine) from a partially corroded cannonball. The data points are from North and Pearson.
After: Selwyn, et al., 2001

In the 70ies France-Lanord proposed electrolytic reduction with low current low current. Increases removal of chlorides without stripping corrosion products. EDF pushes technique further for treating marine bronzes under cathodic protection in sodium sesquicarbonate. This treatment has been adapted as standard treatment for marine bronzes. The measurement of the corrosion potential of the object with a reference electrode reference electrode allows a precise and controlled reduction of only un-wanted corrosion products (chlorides).

A new desalination method using alkaline sulfite baths was introduced in the late 70ies and has been widely adapted for chloride contaminated archaeological iron. This method breaks down insoluble chloride containing products, such as akaganeite as shown in photo (4-1).

	
Photo (4-1) shows desalination method using alkaline sulfite baths	*Fig. (4-6) shows the electrochemical cleaning*

Electrochemical cleaning follows preliminary hand cleaning. The electrolysis unit consists of a power generator and a stainless steel tank containing a 5% to 10% sodium hydroxide solution that is shown in figure 4-6. Leads connect the generator with a brass rod from which the artifacts are suspended within the solution by means of wire and alligator clips. The electrical current, in passing from the artifact (cathode) to the walls of the tank (anode), breaks down the solution into hydrogen and oxygen. The reduced hydrogen ion in turn effects the reduction of the surface corrosion products (Ford 1981).

In 1978, North and Pearson published a detailed study of the diffusion of C1^{-} ions out of layers of corrosion products from marine cast iron. They assumed that the C1^{-} ions were uniformly distributed in the corrosion layer at the moment that the layer was immersed in the treatment solution. Under this assumption, the diffusion equation predicts that the total amount of chloride removed from the sample varies linearly with the square root of the treatment time, as they observed in their work (Selwyn, et al., 2001).

Pearson 1972 cleaned Captain Cook's cannons by exposure to anode surface. He used a single mild steel anode along one side of the vat and used immovable wooden support cradles on the cannons (Hamilton 1964). Recovered iron fragments are accordingly oven heated at 1060°C in hydrogen gas. This restores the iron to its original state and eliminates the injurious chloride compounds (Barkman and Franzen 1972).

Boiling the objects in successive baths of distilled water is continued till all the chloride is removed. After many times of washings the objects are assumed to be desalinated. Cast iron objects cannot be desalted in this manner (Rees-Jones 1972).

Today it is still used in some labs as a pre-treatment before desalination and mechanical cleaning. Hydrogen gas plasma emerges in the 80ies as the ideal treatment for large amounts of artifacts. The created hydrogen plasma is highly reactive and reduces iron oxides as indicated in photo (4-2).

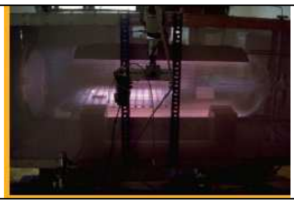


photo (4-2) shows hydrogen gas plasma equipment

In 1984, EDF setted up a research programme advocating electrolytic techniques. Cast and wrought iron is treated, but also non-conducting materials such as leather, wood, paper or porcelain (The Metals Conservation Summer Institute 2006).

Keene and Orton (1985) used steaming procedure as a desalination method. The objects were placed above water level in a domestic pressure-cooker containing de- ionized water and steamed at 15lb pressure during working hours. At the end of each day, the deionized water used was tested for chloride, and the objects were removed and dried. The basis of the method was that steam would penetrate the pores of the corrosion, and the constant supply of freshly condensing water would rapidly remove soluble chloride as it ran out, but after two months chloride levels were still high, and the objects were flaking and visibly corroding. The treatment was discontinued.

Also, Keene and Orton (1985) used soaking procedure as a desalination method. Groups of objects were placed in sealed polyethylene boxes, containing 5% sodium benzoate in deionized water, and kept at 50ºC. The solution was changed every 3-4 weeks, and tested for chloride. The treatment of the objects had started in the circulating bath but it still took two months for chloride levels to fall to undetectable levels. The sodium benzoate appeared to dissolve away surface corrosion in places where there was only a thin layer over the metal (Keene and Orton 1985). 1987 The Titanic is discovered and 1800 items are conserved at EDF using innovative electrolytic techniques as shown in photo (4-3).

Electrolytic techniques have greatly improved and the use of reference electrodes has given us safe tools to work with. They are currently also used in situ to monitor and stabilize submerged iron artifacts as indicated in photo (4-4).

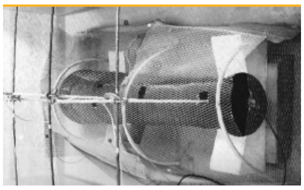


Photo (4-3) shows the electrolytic techniques of an object from Titanic shipwreck

Photo (4-4) shows the electrolytic techniques in situ of excavation

After: The Metals Conservation Summer Institute 2006.

Hjelm-Hansen et al. (1993) said that numerous solutions have been used, including sodium hydroxide, alkaline sulphite, sodium sesquicarbonate and alcoholic hydroxides. At present, there is no consensus as to the optimum treatment and one reason for this appears to be that there is no reliable method of assessing the ongoing processes during treatment or the stability of treated artifacts, except the potentially destructive exposure to high humidity (Hjelm-Hansen et al. 1993).

In 1998, Wunderlich and Neubacher presented the desalination of archaeological iron objects with hydroxylamine as reducing agent. They saw a lot of advantages compared with other methods, which made the desalination treatment really promising: Apart from a short treatment time (about 2-4 weeks), a hydroxylamine solution has inhibitive properties during the desalination and drying process. Moreover a post-treatment is not necessary, because hydroxylamine decays after several weeks into the volatile compounds ammonia, nitrogen and nitrous oxide. So far, the suitability of this method has been proven only with few objects, experience was mixed (Degrigny 2006).

Basic methods of conserving underwater archaeological material culture, Hamilton 1997, this is one of the best references of artifact dechlorination.

Cano said that similar procedures were recommended for many restoration treatments for different metals were very radical and removed all the corrosion products leaving only the clean metal surface. Since the conservation–restoration criteria evolved and the importance of the corrosion products was recognized as part of the history of the object and, in many cases, the only remaining of the original surface or decorations. Many conservators–restorers detest electrochemical techniques for the use that was made of them in those times. In this field, it is usually distinguished between “electrolytic reduction”, when the source of energy is an external source (a battery or generator) and “electrochemical reduction”, when the source of energy is the formation of a galvanic cell between the object acting as cathode and a less noble metal, usually zinc or aluminum, acting as anode (Cano et al., 2009).

In recent years a number of refinements in the actual practice of artifact electrolysis have been introduced. The electrolysis cells were made from 12.7cm lengths of 3.8cm diameter clear Plexiglas pipe, solvent- welded to square flat bases of the same material. The volume of electrolyte in each cell was measured and maintained as indicated in figure 4-7 (Carlin et al., 2001).

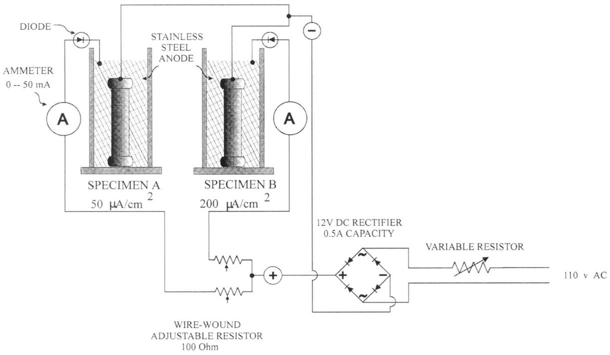


Fig. (4-7) Schematic diagram of the electrical circuit

After: Carlin et al., 2001

The electrochemical stabilization of archaeological cast iron, currently used in restoration and conservation, is designed to extract chlorides by applying an electrical field between the metal (object containing a metal core), which is cathodically polarized, and a stainless steel cage, which is anodically polarized. However, stabilization of artifacts in potentiostatic mode is a relatively long procedure and weakens the artifacts because of the hydrogen evolution when the applied voltage is too negative. In an effort to reduce the secondary effects caused by hydrogen, we decided to study the use of pulsating currents. The aim is to be selective with respect to the reactions produced and to increase the rate of dechlorination treatment (Dalard et al., 2002)

Degrignya and Spiteri (2004) used sodium carbonate and sodium hydroxide in the desalination treatment of swivel gun. After been mechanically cleaned from its crust the gun was conserved in a sodium carbonate solution that was changed every 2 months. The artifact was brought to the Malta Centre for Restoration for stabilization and was immediately immersed in a 1% (w/v) NaOH solution (NaOH was used instead of KOH because of the presence of large quantities of chlorides in the KOH brand available in Malta.

The quantity of chlorides released during the early stage of washing is after some time proportional to the square root of the total washing time as shown in Figure 4-8). Plots of the chloride concentration versus the square root of time are then useful tools to monitor the stabilization process. Deviations from linearity occurs only when the amount of chlorides extracted is equal to the chloride concentration of the iron corrosion products and the remaining metal (Degrignya and Spiteri 2004)

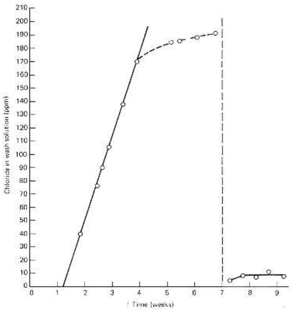


Figure (4-8) A typical plot of C_{Cl^-} *=(√t, t in weeks) for a cast iron artifact pretreated by hydrogen reduction (North 198)*

After: *Degrignya and Spiteri (2004)*

In 2004, Groot and Degrigny said that due to the extensive corrosion of the cast iron elements, the electrical contact was made on the copper based rim. The wire was attached on a pre-polished area with "Araldite" rapid set epoxy adhesive. Stainless steel grids were placed in and outside the porthole. Through a bridge a good connection was made between the inner and the outside anode. The object together with the anode was placed in a plastic tank. To limit the volume of electrolyte to the minimum (to be able to better follow up the extraction of chlorides) spare containers were placed in the tank. The porthole was connected to the negative (-) terminal of the power supply and the stainless steel anode to the positive (+) terminal. The 1% (w/v) NaNO3 solution was prepared with deionized water and to avoid its evaporation and pollution a plastic sheet covered the tank. The pH of the electrolyte at the beginning of the stabilization treatment was 6.2 (the device is shown in photo 4-5 (Groot and Degrigny 2004).

In 2004, Smart plasma project setup by the Hogeschool Antwerpen was to develop a prototype capable of cleaning such pieces by using atmospheric plasma (Storme 2004). Schmidt-Ott (2006) said that the desalination of iron artifacts performs in alkaline sulfite solutions with satisfactory results. They use 1 molar solution in stainless steel containers (Schmidt-Ott 2006).

In 2009, electrolysis is used to clean concretions from cannons, anchors and other large archaeological objects, and to remove chlorides. Use of an electric current will either cause hydrogen micro-bubbling on the object's original surface, which helps remove concretions, or trigger chemical changes in corrosion products (reduction), thus speeding up the extraction of chloride ions. Electrolysis also serves to remove chlorides and surface corrosion from nonconductive organic materials and occasionally ceramics. In the case of glass, salt removal is followed by controlled drying in the air or, depending on the object’s conservation condition, consolidation treatments entailing, inter alia, a series of immersions in ethyl lactate followed by very gradual, controlled drying (Memet 2009).

In the frame of the French research program ODeFA, which was mainly dedicated to the understanding of dechlorination mechanisms of corrosion layers during treatments, some Roman ingots were treated. Cathodic polarization in a KOH bath and immersion in a 2% NaOH bath were applied. The analysis of ingots at the end of treatments revealed the presence of remaining iron/sulphur containing compounds. (Remazeilles 2010).

Metal objects are placed in a desalination bath and undergo the first steps of electrolysis, a process that removes negative ions and salt from the artifact (Teature's guide 2010).

CHAPTER 5

THE DECHLORINATION TREATMENT OF IRON ARTIFACTS BY H_2 PLASMA, AND/OR SODIUM HYDROXIDE SOLUTION

This chapter presents a review of literature published on the desalination treatment of the iron objects from the marine environment by sodium hydroxide and/or hydrogen plasma. Riss said that conservation treatment attempts to stabilize iron objects by removing the contaminating chlorides (Riss 1993). The only way, an iron artifact recovered from the sea can be stabilized is to remove the chlorides from the metal (Hamilton 2000).

5.1 The dechlorination treatment of the iron artifacts by NaOH

Sodium hydroxide is the desalinating agent by ion exchange according to Cl-OH.

5.1.1 Chemical diffusion

Following any conservation treatment - electrochemical, electrolytic, chemical, or water diffusion - it is necessary to remove insoluble oxide sludge, metallic powder, residual chlorides, and all the chemical residues through an intensive rinsing. In water diffusion the artifact is removed after establishing that the chloride count in the solution has leveled off and ceases to rise when it is changed. The artifact is then removed and rinsed thoroughly in several changes of alternate boiling and cold deionized water to get rid of any residual electrolyte and chlorides. By rinsing in boiling water the surface of the metal oxidizes to a flat black color that provides a pleasing appearance. Since large objects may require two to four weeks of rinsing, the iron may rust in the deionized water. This can be prevented by adding gluconic acid, sodium gluconate or sodium glucoheptanate, the gluconates act as rust inhibitors during any washing and continue to serve in this capacity during solvent dehydration, heat-drying or air drying (Hamilton 2000). Migrations of atoms or molecules are the mechanism of kinetic processes in materials for their synthesis and processing as well as for their structural evolutions (Philibert 2005). The inter diffusion coefficient as function of temperature and time is obtained by applying Fick's diffusion laws. Tracking the time dependence of the mean square penetration depth of the mixing process allows to detect changes in the mass transport caused by convective flow (Griesche 2010).

Because absolute temperature does not change much for environmental applications, this is the least variable characterization of equation. The viscosity of a liquid is highly dependent on temperature. In general, large molecules (with a larger equivalent diameter) will have a lower diffusion coefficient than small molecules.

The basic physico-chemical properties of water are dependent upon the temperature. As is well known, water can be kept in the liquid phase even above 100°C by the application of pressure. Thus, high temperature water (say at 27S°C) implicitly means that it is also under high pressure. If it is in a boiling condition, it will be a two phase system. Being under pressure also means that water or a steam-water mixture at high temperatures will always be a closed system (Venkateswariu 1996).

5.1.2 Sodium hydroxide

Chloride removal is diffusion controlled, slow, and is unlikely to be 100% efficient, although efficiency can be improved using chemical additives. The quantity of chlorides released during the early stage of washing is after some time proportional to the square root of the total washing time (Figure 5-1). Plots of the chloride concentration versus the square root of time are then useful tools to monitor the stabilization process. A deviation from linearity occurs only when the amount of chlorides extracted is equal to the chloride concentration of the iron corrosion products and the remaining metal (Degrigny and Spiteri 2004).

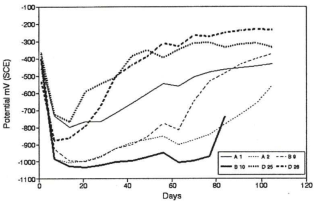


Figure (5-1) Ecorr (SCE) vs. time for iron archaeological artifacts immersed in 0.5 M sodium hydroxide (Hjelm-Hansen 1992).

After: Degrigny and Spiteri 2004.

The iron artifact recovered from the sea can be stabilized by removing the chlorides from the metal. Alkaline chemicals, such as a 2% sodium hydroxide solution, serve only as inhibitors to prevent rusting; it is the water that removes the soluble chlorides (Hamilton 2000).

Sodium hydroxide is the desalinating agent by ion exchange according to ClOH. Iron oxychloride FeOCl was the Fe (III) compound containing most chloride and therefore the most important one to be removed (Schmutzler and Ebinger-Rist 2008). Desalination is the process of removing soluble salts from an artifact, typically through repeated baths in distilled or deionized water. Certain salts, such as some chlorides, nitrates, and sulphates, are easily soluble in water and can be absorbed into porous materials burial environment. In drier conditions, these same salts lose water and crystallize to solids. As they crystallize, their volume increases and they can cause physical damage to the fabric of an artifact. For this reason, it is often essential to remove soluble salts if they are present (http://www.sha.org/research_resources/conservation_faqs/process.cfm). The chemical treatment with this solution begins by completely immersing of the heavily or partly mineralized iron artifacts in 2-5% (w/v) (Argyropoulos et al., 1997). When marine cast iron artifacts are soaked in a treatment solution, the hydroxide ions diffuse into the corrosion product reacting with chloride ions containing compound to produce free chloride ions, and then chloride ions diffuse out from the pores of high chloride ion concentration into the treatment solution (Ouyang et al., 2009).

Sodium hydroxide is more soluble in solution than sodium carbonate; however, it will generate extreme heat when mixed in concentrated solutions. With its higher pH (12.9), sodium hydroxide is much more caustic than sodium carbonate and presents a potential hazard to those working with it (http://nautarch.tamu.edu/class/anth605/File10b.htm#Sodium). Selwyn and others said that results are presented on the effectiveness of treating archaeological iron by immersion in an aqueous sodium hydroxide (NaOH) solution (2% w/v, pH 13.5, room temperature) followed by immersion in an aqueous 1,2- diaminoethane (ethylenediamine, EN) solution (5% v/v, pH 11.5, 50°C). Conservators favour aqueous NaOH solutions (0.1M to 0.5M, pH 13–14) for treating archaeological iron because they are relatively cheap, readily available, and have a high pH. Furthermore, many studies have demonstrated the effectiveness of NaOH solutions in removing Cl^- ions from archaeological iron. A contributing factor to its success as a treatment solution is its high pH, giving it the ability to stop corrosion by passivating iron, even archaeological iron. Helm-Hansen et al. monitored the corrosion potential of archaeological wrought iron in a 0.5M solution of NaOH. After several months, they observed that the iron objects had not passivated in sodium sesquicarbonate, but those in NaOH had passivated. This observation supports the assumption that it takes time for the OH^- ions to diffuse to the metal surface and increase the pH from acidic to alkaline, and that the time to passivate gets longer when a less alkaline treatment solution (one with a lower pH) is used compared to a more alkaline (higher pH) one (Selwyn 2004) and it's important that all metal objects should be kept submerged in tap water with an inhibitor added to prevent further corrosion. For long term storage, excellent results have been achieved using a 1 (v/v) % oxidizing solution of potassium dichromate with sufficient sodium hydroxide added to create a pH of 9 to 9.5. Alkaline inhibitive solutions such as a 5% solution of sodium carbonate or 2% sodium hydroxide can also be used, but they are not satisfactory for long term storage. As mentioned above, any adhering encrustation or corrosion layers should be left intact until the objects are treated since they form a protective coating which retards corrosion (Hamilton 1997). Sodium hydroxide (NaOH) can actually burn the skin on contact with an artifact after weeks of rinsing (Rodgers 2004), so we should start with low concentration.

The pH of the solution in which the metal is immersed is another important parameter affecting E_{corr}. Pourbaix E/pH diagrams can be used to predict the behavior of the metal (either immunity (no corrosion, corrosion or passivation). Since the metal considered is rarely pure and the potential is not measured at standard conditions, such diagrams have to be used with care, and E_{corr} time plots are still needed to verify the actual behaviour of the metal in the solution considered. For obvious reasons, conservation professionals choose a solution with a pH favoring the passivation of the metal surface (Degrigny 2010).

In alkaline environments (pH = 10-13.5), the corrosion rate of iron is expected to be negligibly low due to the ease with which a protective passive film is formed. The influence of pH on the corrosion behaviour of a passive alloy in a chloride containing environment is presented schematically. In general, passivity of metallic materials decreases with increasing acidity of the environment: the polarization curves move to higher current densities in the passive range (I_{pass}) with decreasing pH, indicating an increase in corrosion rate if an environment establishes potentials in the passive range; as the pH drops, the passive potential range becomes smaller making it much more difficult to maintain passivity and finally passivity is completely destroyed. It has been found that the pH can play a major role on the initiation process of pitting corrosion: a decrease in pH is usually accompanied by a displacement of the pitting potential, in the active direction (Kursten 2003).

5.1.3 Sodium hydroxide on the heating condition

At a higher temperature, atoms and molecules move faster. Because they are moving faster, chemical reactions occur more quickly. Thus, a higher temperature increases the rate of decay, and chemical reaction. Chemical reaction rates increase with higher temperature, increased concentration of reactants and increased pressure. Water is a reactant in many decay processes (Alten 2008).

5.1.4 Sodium hydroxide and Sodium Sulfate

Marine cast iron artifacts were treated by immersion in 0.5N NaOH/0.5 Na_2SO_4 solution at 60°C for a period of up to about three months in sealed containers. The treatment of a freshly excavated material is most effective, the reason for the failure of the technique when artifacts have been allowed to dry out (Gilberg and Seeley 1996).

Wang said that experiments in desalination using sodium hydroxide and alkaline sulphite revealed little difference in the efficiency of chloride removal as judged by the chloride extraction rates and the amount of residual chloride on the surface of the objects treated. Solutions of lower concentration and less frequent changes of desalination solutions were proven to be equally as efficient as the solutions of 0.5M with weekly changes. The efficiency of the treatment is also being evaluated by monitoring changes in condition of the treated objects in storage. It is hoped that alkaline sulphite solutions can be replaced by sodium hydroxide alone, with the benefits of lower cost, reduced damage to the environment, and easier monitoring of extracted chloride ion concentration.

It is reported by Watkinson (1996) in his assessment of the chloride extracted as a function of total chloride contained in the object that sodium hydroxide, alone, was a less efficient chloride extractor than alkaline sulphite. In his study the absolute measurement of residual chloride in the object was obtained by post-treatment digestion of the whole object. However, this is obviously not possible for objects in a museum collection. Since sodium sulphite in the alkaline sulphite solution acts as an oxygen scavenger rather than a reducing agent, recent research carried out by Watkinson and Al-Zahrani (2008) suggests that deaerated sodium hydroxide could be a more effective desalination solution than alkaline sulphite (Wang and others 2010).

5.2 The dechlorination treatment of iron artifacts by plasma

Plasma reduction is considered the most important way that can be used to extract chlorides and remove the encrustation layers of earth compounds and rusted layers on the surface of an archaeological artifact.

In the recent 30 years of research on the use of plasma reduction to remove the chloride, to facilitate the mechanical treatment and to passivate the surface of the metal objects. North and Pearson (1977) said that thermal decomposition reactions of prepared FeOCl and natural marine cast iron corrosion products in inert, oxidizing and reducing atmospheres were determined for temperatures up to 1000°C. The results were used to discuss thermal stabilization treatment of marine iron. Pure dry hydrogen was shown to be the best atmosphere to use in thermal stabilization treatments but even in this case, to achieve complete chloride removal would require treatment temperatures above the limit of metallurgical (North and Pearson 1977). Daniels and others (1979) used hydrogen + argon on the treatment of tarnished silver and corroded lead object. Also they used oxygen + argon (oxidizing plasmas) on the treatment for removing the organic layer at 50ºC (Daniels, et al., 1979).

Tylecote and Black (1980) gave some recommendations for concerning types of ferrous artifacts which should never be subjected to elevated temperatures because this may cause changes in their metallurgical structures (Tylecote and Black 1980).

Buchwald (2005) said that Rosenberg (1917) had applied the annealing method at 800ºC for the iron-containing artifacts, then boiled in a saturated solution of sodium carbonate, which is to be finally soaked in water for a week or two, and dried stabilized in microcrystalline wax (Buchwald 2005).

Daneil (1989) used hydrogen plasma to treat silver objects. The temperature didn't exceed 40ºC. They have been complete removal of the tarnish, but some small black spots remain (Daneil 1989). Patscheider and Veprek (1986) argued that a new method based on the application of low pressure hydrogen plasma has been developed for the restoration of iron artifacts. It efficiently removes chlorides and by preventing any significant post-corrosion. The treatment temperatures of less than 400˚C do not introduce any irreversible changes in the wrought iron, preserving its original composition, structure inclusions and morphology, which contain important information on the origin and manufacturing methods of the artifact (Patscheider and Veprek 1986).

Sjogren and Buchwald (1991) confirmed that no sputtering and no reduction to free iron took place under the test conditions, operating at or below 120˚C and at pressures of 0.4-1mb hydrogen. The objects acted as cathodes in a 600-1600V d.c. electrical field. While the chlorine-containing β-FeOOH, akaganeite, was present in all objects before the test, no akaganeite and no chlorides were present afterwards. The objects, including one meteorite which had been exposed for more than 5000 years to seawater, were found to be stable after the glow discharge treatment. The major mineral after treatment was identified as magnetite, and the objects generally assumed an iron-grey surface color (Sjogren & Buchwald 1991). Graaf and others (1995) stated that it is an effective and fast way of restoration and preservation of archaeological artifacts. In this method high intensity atomic hydrogen source plasma is used, which expands in a low pressure treatment vessel. It proves that both hydrogen atom reduction and thermal decomposition are important. The removal of the dirt crust of the excavated artifacts was greatly facilitated in the treatment (Graaf 1995). Kotzamanidi and others (2002) explained the effect of plasma cleaning and conservation treatment on the corrosion layer, and the reduction of iron oxides to the stable iron oxide, magnetite, was observed for all the samples (Kotzamanidi et. al., 2002). Sjogren and Buchwald (1991) restored the objects, including one meteorite which had been exposed for more than 5000 years to seawater, were found to be stable after the glow discharge treatment. The major mineral after treatment was identified as magnetite, and the objects generally assumed an iron-grey surface color (Sjogren and Buchwald 1991). Schmidt-Otta (2004) added that the pure hydrogen plasma originally is considered to be less effective than a mixture of hydrogen and argon proved to be at least as efficient. This is of special interest, since pure hydrogen plasma at low pressure causes a reduction of the iron artifact’s temperature to about 80°C during plasma treatment (Schmidt-Otta 2004). Krcma said that the principle of plasma chemical treatment is based on the removal of the oxide and chloride molecules in low-temperature and low-pressure hydrogen plasma (Krcma, et. al.). Favre-Quattropani and others (2000) succeeded in depositing plasma-polymerized coatings on a variety of metallic substrates-stainless steel, iron, silver, copper, and even some archaeological iron nails (Favre-Quattropani et al., 2000). Moncrieff and others (2005) said that both oxygen and hydrogen are gases but under ordinary conditions react only slowly with objects or their dirt. As alternative approach has received attention from research workers during recent years (Moncrieff 2005).

5.2.1 Definition of plasma

A plasma is an ionized gas consisting of positively and negatively charged particles with approximately equal charge densities. Plasmas can be produced by heating an ordinary gas to such a high temperature that the random kinetic energy of the molecules exceeds the ionization energy. Collisions then strip some of the electrons from the atoms, forming a mixture of electrons and ions (Gurnett and Bhattacharjee 2005). Plasma is an attractive medium for particle acceleration (Bngham 2006). It has been said that 99% of the matter in the universe is in the plasma state, that is, in the form of an electrified gas with atoms dissociated into positive ions and negative electrons. This estimate may not be very accurate, but it is certainly a reasonable one in view of the fact that stellar interiors and atmospheres, gaseous nebulae, and much of the interstellar hydrogen are plasmas (Chen 1984).

Plasma is based on a simple physical principle. By supplying energy the states of matter change: from solid to liquid and from liquid to gas. If further energy is added to a gas it becomes ionized and passes over into the plasma state – a fourth state of matter. Through contact with the surfaces of materials utilizing Plasmatreat’s technology the added energy of the plasma state can be transferred to the material surface and made available for subsequent reactions on those surfaces (http://www.plasmatreat.com/plasma_technology/fourth_aggregate_state_of_matter.html)

Plasma can be defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles. Some scientists have dubbed plasma the "fourth state of matter" because while plasma is neither gas nor liquid, its properties are similar to those of both gases and liquids (http://www.astp.com/plasma/pl_examples.html).

Plasma is an electrical conducting-gas that is a gas which contains a noticeable many charged particles (electrons and ions) (Shawki 1992). This ionized gas mixture burns at the plasma is ignited by induced microwave heating, hence the name "inductively-coupled plasma." The carrier gas is inert argon (Ar) 6000-8000°K (Herz & Garrison 1998). Plasma is a substance in which many of the atoms or molecules are effectively ionized. Depending on the energy level of electrons, plasmas are usually classified as thermal and cold. Marcus said that glow discharge (GD) is a general term for low-power electrical discharge in reduced pressure systems. GD device consists of a vacuum vessel, with two physically separated surfaces inside that form a cathode and anode. The geometrical shape of the vessel and electrodes can be varied almost infinitely. The vacuum vessels evacuated and filled with a discharge gas to pressure ranging from about 10 to 1000 Pa. Noble gases, most commonly argon, are used in analytical GDs in order to avoid chemical reactions inside the device. The current is low to moderate, varying between approximately 0.1mA to a few amperes. The GD plasma is physically divided into more or less distinct regions. Depending on the voltage-current characteristics, a GD classified as normal or abnormal. The discharge changes characteristics from a GD to what is known as an Arc discharge (Marcus 2005). Plasma created by radio-frequencies is characterized by ions that move by diffusion and scattering and thus arrive at the object with relatively small velocities. Plasma is a substance in which many of the atoms or molecules are effectively ionized. Depending on the energy level, plasmas are usually classified as high temperature, thermal and cold plasmas. The plasma method includes impregnation, treatment, calcinations and reduction (Zou et al., 2007). Filament cathode low pressure gas discharges are used as ion sources for plasma chemistry. The plasma density obtained as a function of total discharge power (some of the power supply voltages multiplied by collected currents) (Jones 1987).

Plasma as the fourth state of matter

A plasma can be produced by raising temperature of a gas until a reasonably high fractional ionization is obtained. A plasma is essentially a gas consisting of neutral and charged particles, ions and electrons, rather than of neutral atoms and molecules. In general a plasma is electrically neutral overall, but the presence of charged particles means that a plasma can support electric currents with electric and magnetic fields. It is important to be aware that a plasma can not be treated simply as an ordinary gas which is electrically conducting. There is a fundamental difference between a neutral gas and a plasma that results from the different nature of the inter-particle forces. In a neutral gas the forces are very strong and short range, so that the dynamics of neutral gas is dominated by two-body billiard-ball-like collisions. In a plasma, the inter-particles forces between charged particles are electromagnetic forces. In addition, a moving charged particle creates a magnetic field which produces a force on the other charged particles. The electromagnetic forces are comparatively weak and long-range. Due to the long range of the inter-particle forces each charged particle in a plasma interacts with a large number of other charged particles resulting in collective plasma behavior. Hence the fact that plasma is referred to as the fourth state of matter. A plasma is a macroscopically electricity neutral substance containing many interacting free electrons and ions which exhibit collective behavior due to the long-range coulomb forces (Goossens 2003).

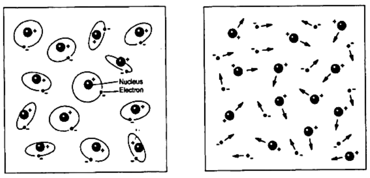


Fig.(5-2) Schematic representation of a gas in the left figure and a plasma in the right figure. After: Goossens 2003

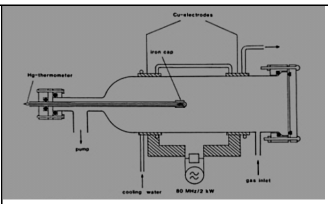


Fig.(5-3) Plasma machine
After: Patscheider and Veprek 1986

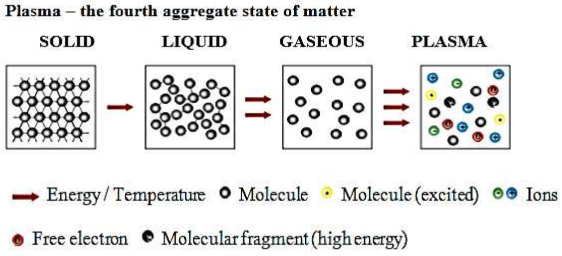


Fig. (5-4) Plasma- the fourth aggregate state of matter

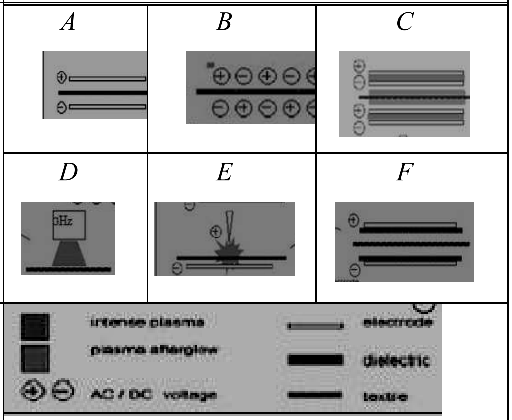


Fig. (5-5) The different ways of producing plasma

After: Senthilkumar and Gopalakrishnan 2009

Plasma arc light doesn’t emit distinct frequencies but continues frequency bands. However, these bands are much narrower than those of incandescent lights. Therefore, less radiation of undesired frequencies must be filtered (Hanfmann et al., 2000).

Ways to induce the ionization of gas

Glow-Discharge: It is produced at reduced pressure and assures the highest possible uniformity and flexibility of any plasma treatment. It is formed by applying a

1. Direct current, microwave, low frequency (50 Hz) or radio frequency (40 kHz, 13.56 MHz) voltage over a pair or a series of electrodes (Figures A, B, C). Alternatively, a vacuum glow discharge can be made by using microwave (GHz) power supply (Figure D).

2. **Corona Discharge**: It is formed at atmospheric pressure by applying a low frequency or pulsed high voltage over an electrode pair, the configuration of which can be one of many types. Typically, both electrodes have a large difference in size (Figure E). The corona consists of small lightning-type discharges, there in homogeneity and the high local energy levels make the classical corona treatment.

3. **Dielectric-Barrier Discharge**: It is formed by applying a pulsed voltage over an electrode pair of which at least one is covered by a dielectric material (Figure F).

What are plasma arc heaters?

All electric arcs are plasmas. Plasma simply refers to the presence of ionized gases. Plasma arc heaters are electrical resistance heaters where the resistive element is the electrically conductive partially ionized gas between two electrodes. Whereas plasma arcs occur in nature as sudden lightning discharges, plasma arc heaters provide a continuously controlled electrical arc discharge. Although the arc discharge can be controlled by magnetic and mechanical means, the key design feature of plasma arc heaters is the controlled feed of gas to the arc environment. The gas can be reduced (e.g., hydrogen), oxidizing (oxygen) or inert (argon). Heaters can be designed for both low and high gas-flow rates. The gas can be used to convey fine solids, liquids, or additional gases into the arc-heated zone for physical transformations and chemical reactions. This controlled flow of various gases enhances the versatility of plasma arc heaters when compared to conventional electric arc furnaces with "free burning arcs" and no gas control features. The core temperature of the plasma arc may range from 4,000 to 20,000°C (7,200° to 36,000°F)$\frac{c}{100}=\frac{f-32}{180}$. The working temperature of the bulk gas, depending on the gas flow rates and the heater design, is about 2,000 - 3,000°C (The Epri center for materials production 1992).

5.2.2 Plasma reduction *(Physical-chemical-mechanical treatment)*

Recently, plasma has been employed in the treatment of archeometallurgy. The plasma experiments on the object have revealed promising results in the restoring of the metallic properties, as well as the removal of the chloride impurities and corrosion products. The plasma is a very interesting issue nowadays due to direct relation with the thermonuclear fusion. But in the current work significant is the 'plasma interaction with solid surfaces' through with the cleaning of artifacts is curried out. Over the past 40 years, engineers worldwide have developed many materials processing applications using plasma arc heaters (Kirkland & Armitage 2007). This method is considered a novel one for reducing corrosion compounds. The treatment occurs by placing the object in a quartz discharge tube surrounded by hydrogen gas under low pressure. Iron is in the center of the hydrogen plasma, and the magnetite and ferric oxide on the surface of the iron are converted to metallic iron. Because the treatment is carried out at a temperature of less than 400°C, there is no change in the metallic structure of the iron (Hamilton 1999).

Kotzamanidi said that the plasma method is considered to be better than conventional methods of conservation such as the mechanical removal of corrosion products, or treatment with liquids, since on the one hand it is more effective and poses no danger to the objects providing that the treatment temperature is not too high, and on the other it does not remove surface details (Kotzamanidi et al., 1999), so we can hardly advocate the use of this method.

5.2.3 The kind of the plasma

There are many types of plasma as follow

5.2.3.1 High temperature and low temperature

A good example of naturally occurring high temperature plasma is lightning. This type of plasma can be artificially generated using a high voltage, high temperature arc, which is the basis for the corona discharge process and for the plasma torch used to vaporize and redeposit metals. At high temperatures the bonds between electrons in outer shells and nuclei of gaseous atoms are broken providing admixture of positively charged ions and electrons (Shawki 1992)

Low temperature plasmas, used in surface modification and organic cleaning, are ionized gases generated at pressures between 0.1 and 2 torr. These types of plasmas work within a vacuum chamber where atmospheric gases have been evacuated typically below 0.1 torr. Low pressure allows for a relatively long free path of accelerated electrons and ions. Since the ions and neutral particles are at or near ambient temperatures and the long free path of electrons, which are at high temperature or electron volt levels, have relatively few collisions with molecules at this pressure the reaction remains at low temperature (http://www.astp.com/plasma/pl_examples.html).

5.2.3.2 The kind of the plasma gases

At low pressure the electrons, ions and neutral gas atoms (and molecules) can each attain different average energies arising from their mean free path and the discharge excitation. Thus, it is systems which can be characterized by several different internal temperatures and in which the prime gas remains relatively cool (Daniels 1979).

Hydrogen plasma

The use of hydrogen plasma has proven to be the favorable tool, since the sputtering effect and connected temperature rise of the object’s surface in hydrogen plasma is smaller than in argon, or argon-hydrogen mixtures (Schmidt-Ott and Hug 2007). As recently as 1978, objects undergoing hydrogen reduction were placed in a special furnace with 100% dry hydrogen gas, or a mixture of hydrogen and nitrogen, and heated to a temperature of 300°C and over a period of days taken to 100°C (Hamilton 2000).

Iron artifacts have been conserved by placing the artifacts in a quartz discharge tube surrounded by hydrogen gas under a low pressure which is ionized into plasma by the introduction of high frequency radio waves. In the process iron is in the center of the hydrogen plasma and the magnetite and ferric oxide on the piece are converted to metallic iron. Because the treatment is carried out at a temperature of less than 400°C there is no change in the metallic structure of the iron (Hamilton 2000).

During the treatment, all the moisture is driven out of the artifact and the chloride corrosion compounds are volatilized. The hydrogen reduces the iron corrosion compounds back to a lower oxidation state or metal. Hydrogen also combines with oxygen in the corrosion products, forming water which is driven off by the heat. This treatment, while successful, has several drawbacks. First it requires rather expensive and sophisticated equipment that is outside the financial capabilities of most laboratories. Second, there is the problem of the changes in the metallurgical characteristics in the metal when heated to high temperatures. The loss of information by the treatment of totally rusted marine cast iron at 800°C will not be great and there seems to be little objection to the use of the hydrogen reduction process at 800°C for this purpose. The reduction of rust on wrought iron is a different matter. The main problem is knowing whether the residual metal contains, either intentionally or unintentionally, enough carbon to give useful information to the archaeometallurgist. If Carbon is absent then treatment at 380°C is acceptable although some change will occur. The slag inclusions will suffer very little microscopic change and no macroscopic change. To ensure the removal of chlorides at 380°C the treatment time must exceed 60 hours. As long as the conservator follows the recommendations cited above, annealing in a reducing atmosphere of hydrogen, the major objections are overcome. The main limiting factor is the high cost of this type of furnace, which also limits the size one can afford to purchase and the inherent safety concerns and potential danger of heating hydrogen to these temperatures. The treatment does result in stable, chloride free artifacts (Hamilton 2000).

Mode hydrogen plasma is suitable as a standard conservation method for highly chlorinated archaeological iron, plasma treatment under a high chemically reducing atmosphere by using hydrogen. The use of low pressure hydrogen plasma in order to reduce oxides on corroded objects was first, and this method was first developed for ferrous artifacts in the eighties at Zürich University by Veprek et al. A short exposure (about 10 min) to hydrogen plasma loosens the encrustation from the artifact and it can be removed with a simple tool like a scalpel (Graaf et al., 1995).

Hydrogen and argon plasma

A discharge was produced in 1:1 hydrogen and argon using 1.6 kV, 50 Hz using the horizontal rod electrodes, when a current of 23 mA was produced at a pressure of 13 Pa as measured on a Pirani gauge. A thermocouple immersed in the plasma did not register a temperature of more than 50°C. Surfaces of materials were examined before and after immersion in the plasma (Daniels et al 1979). It is shown that pure hydrogen plasma treatments with relatively low gas flow increase the radical concentration as compared to hydrogen-argon plasmas consisting of ten parts hydrogen to one part argon. These results lead to new standard parameters for archaeological iron objects. The new hydrogen plasmas being at least as efficient as those previously applied but with reduced object temperatures (about 90 °C) during treatment (Schmidt-Ott 2010).

Oxygen and argon plasma

Using the horizontal rod electrodes a discharge was produced in 1:1 oxygen/argon mixture using 1.6kV 50 Hz a.c., a current of 23 mA was produced at a pressure of 17 Pa as measured on a Pirani gauge. In the plasma, near immersed objects, a thermocouple did not register a temperature of more than 50°C (Daniels et al 1979).

The treatment of the archaeological iron artifacts by oxygen plasma reduction

Oxygen plasma treatment is a safe and environmentally friendly alternative to traditional cleaning methods. A wide variety of industries utilize gas plasma treatment to remove organic surface contamination from materials that require critical cleaning. The active species in the oxygen combined with VUV energy creates a chemical reaction with the surface contaminants, resulting in their volatilization and removal from the reaction chamber. Plasma uses in removal of organic contamination from glass slides and flat panels, and other materials such as various metals and ceramics (http://www.astp.com/plasma/pl_examples.html).

During heat treatment, exposure of steel or cast iron to an oxygen-rich atmosphere for a long time and at a high temperature can cause oxygen to penetrate austenite grain boundaries and react with carbon and other elements, such as silicon, manganese, and aluminum that are contained in the steel or cast iron (Bramfitt and Benscoter 2002).

5.2.4 Chloride extraction by plasma reduction

A definite description of the corrosion layer including all compounds in which chlorine can be bound and processes that result in chlorine removal is not available at present. However, akaganeite or β-$FeOOH.Cl_{0.02\text{-}0.05}$ is generally considered to play a key role in post-corrosion of artifacts. The reduction of akaganeite in hydrogen plasma can involve a number of reactions:

$FeOOH.Cl_{0.05} \rightarrow Fe_2O_3.CI_{x<0.05}$ (thermic)

$Fe_2O_3 . CI_{x < 0.05} \rightarrow Fe_3O_4. CI_{y< x\ 0.05}$ (exothermic)

$Fe_2O_3. CI_{x < 0.05} \rightarrow Fe_3O_4 .CI_{y < x\ 0.05}$ (endothermic)

$Fe_3O_4.CI_y \rightarrow Fe$ (exothermic)

$Fe_3O_4.CI_y \rightarrow Fe$ (endothermic)

With possible intermediate compounds

$FeOCl \rightarrow Fe$ (Thermic)

$FeCl_3 \rightarrow FeCl_2 + Cl$

$FeCl_2 \rightarrow Fe + 2Cl$

As there is no definite answer to which structures are obtained after dehydration of akaganeite, various options are given. The reduction of $FeC1_3$ to FeCI is exothermic for both atomic and molecular hydrogen. The reduction of $FeC1_2$ is strongly endothermic with molecular hydrogen and therefore requires atomic hydrogen. In addition to reducing reactions involving hydrogen, thermal decomposition of chlorides is also possible. FeOC1, a possible intermediate product in the decay of akaganeite, decomposes thermally to $FeC1_3$. At temperatures above 350°C $FeC1_3$ evaporates. The reduction of chloride from a corrosion layer can therefore occur both thermally and by chemical process (Graaf et al., 1995). In general, the objects acted as cathodes in a 600-1600V d.c. electrical field (Sjogren & Buchwald 1991).

Heating below 570˚C, a two-layered scale develops consisting of magnetite next to the metal and hematite on the surface. Above 570˚C, wustite forms below the other two iron oxides, next to the metal, giving the sequence: metal, FeO, Fe3O4, Fe2O3 - the ratio of which are roughly 95:4:1 at 1000˚C (Fell 2004).

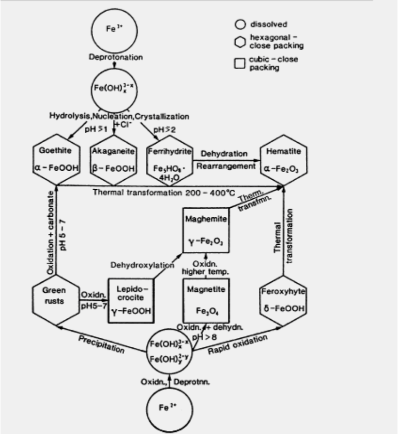


Fig. (5-6) Schematic representation of major Formation and transformation Pathway of common iron oxides

After: (Schwertmann and Cornel 2000).

5.2.5 Advantage and disadvantage of plasma treatment

- The main advantage of this method is the fact that it is possible to treat the artifact of small, big size, the hollow artifacts or artifacts with broken relief.

-The gradual removing of the marine sediments minerals and the chlorine compounds from the outer layer to be in stable state and sometimes even the complete reduction back to iron metal is proportional to the duration of the plasma treatment and the temperature degree (Rašková and Krčma 2007).

- The positive effect of the facilitation of mechanical cleaning and the speeding-up of the subsequent desalination in alkaline sulphite for archaeological iron artifacts continues to be a major advantage of plasma reduction for pure hydrogen plasmas as well as proceedings of metal (Schmidt-Otta 2004, Schmidt-Ott and Boissonnas 2002).

-Daniel (1979) noted that the hydrogen penetrates to a significant depth under the gross surface, as documented by the transformation of iron oxides in cracks and fissures, 5mm under the surface. Iron erosion (physical sputtering) was not observed. Also all edges on cut samples were as sharp after two weeks' glow discharge as before, and reduction to free iron was not observed (Daniel 1979).

- Objects that have a residual metallic core, the method can be quite effective. This is because repetitive initial treatments can help the conservator to remove the softened agglomerates (Kotzamanidi 2002).

- The effects of plasma activated chemical reactive gases can be utilized. The treatment time can be reduced to several minutes. Moreover, the construction of the plasma pencil is adapted to a fine hand work (Klima et al., 1999).

-The reduction of iron oxides and removal of chlorine (Arnould-Pernot 1994, Novakovic et al., 2009) was effective to depths of 5mm below the surface, and somewhat more where the cracks were millimeters wide. The corrosion products located in internal fissures and along crystals were transformed into magnetite and had lost part of their coherence, so that the fissures had become more open.

-No changes were observed in the metallic structural elements, and the micro hardness remained unaltered on the tested samples in the range 200-250HV (Sjøgren and Buchwald 1991).

Plasma can reduce the iron oxide layer to magnetite and remove chloride ions from the reduced layer becomes more porous as the result of transformations and reductions. (Sjøgren and Buchwald 1991, Kotzamanidi and others 1999).

-The microstructure of wrought iron appears not to be affected by plasma treatment (Kotzamanidi and others 1999).

-One year after the treatment, the result is very positive, no further corrosion having developed, even storing the section outside desiccators (Sjøgren and Buchwald 1991).

-The influence of the plasma treatment on frequently occurring iron corrosion products could be made apparent in surface layers. Investigations of surface regions of archaeological iron samples also showed that a reduction, for example of hematite to magnetite, did take place. Examination of the stratigraphical samples showed that the effect of hydrogen plasma in the deeper lying layers, namely the loosening between layers, is not related to a chemical reduction but to the high frequency field (Schmidt-Ott 2010)

- Hydrogen plasma has the ability to regenerate lead, copper and silver from some of their corrosion products, and to reduce hematite to magnetite (Daniel, et al., 1979).

-Plasma treatment has the advantage of being environmentally friendly compared to other methods (Kirkland and Armitage 2007).

-Iron hasn't shown any significant color and metallurgical changes (Schmidt-Ott & Boissonnas 2002).

-Plasma treatment is still successful in decreasing the density of corrosion products. However a complete removal of chlorides through plasma becomes impossible, a subsequent desalination procedure becomes necessary (Schmidt-Ott & Boissonnas 2002, Grassini et al., 2008).

The primary disadvantage of this conservation technique is the high cost of the equipment and the small size of the artifacts that can be treated in all but the most expensive units. Thus far, the technique has not seen use in most conservation laboratories (Hamilton 2000).

Objects that are completely oxidized, the plasma treatment can turn them, dangerously brittle (Kotzamanidi 2002). Plasma atoms are stopped at the surface of the object, so plasma can not penetrate under the surface of the object.

CHAPTER 6

CONSERVATION STEPS

This chapter discusses the conservation steps of the iron artifacts from the marine environment. A number of sequential steps in the conservation of metals as follows:

Preliminary steps as storage prior to treatment, mechanical cleaning and preliminary evaluation follow by treatment methods and the final steps are rinse after wet treatment, drying, sealant, storage and periodic inspection (Hamilton 2000).

The conservation of archaeological artifacts from marine environments has been the focus of considerable controversy in recent years because of the failure of standard methods to stabilize such objects against further corrosion (Gilberg and Seeley 1982).

6.1 Storage prior to treatment

Post-excavation corrosion of archaeological iron artifacts still remains one of the major problems in metal conservation. No stabilization treatment has proven 100% effective in the removal of chlorides. Also treatments are often problematic as they can be followed by color changes in the artifact, changes in the corrosion layers or loss of important information contained within the object. While searching for better stabilization procedures we need good storage conditions:

Hamilton said that all storage solutions are prepared with distilled or deionized water. The exception to this general rule occurs when the material contains more chloride than is present in the local tap or well water. In this case there is no advantage to mixing up a solution with expensive distilled or deionized water only to have it contaminated with chloride well in excess of the local water supply (Hamilton 2000). Prior treatment of the metal artifacts are stored wet to prevent them from drying out (Burns 2002), and Peachey (2001) began the treatment desalination (salt removal) by immersion the objects in deionized water and chemical treatment to help archaeologists to identify an object after excavation (peachy 2001).

The difference between the distilled, de-ionized, rainwater and tap water

De-ionized water (DI water) is very low in ions.

Distillation is used to remove all of the dissolved solids from water.

Rainwater is considered a low chloride water source and it tends to contain some chlorides (in coastal areas), but not nearly the amount found in most tap water. Rainwater is free, and acts as a good intermediate phase rinse solution between tap water, deionized and distilled water (Rodgers 2004).

The metal objects recovered from salt water sites can be kept in sea water initially, if no fresh water is available. Keep the objects wet at all times. They should not be allowed to dry. If objects are dried out before treatment, especially those made of iron, the metal can corrode, pieces can flake off, and salt contamination can become difficult to remove. Spray the objects with sea water, or wrap them in damp rags until they can be placed in a tank (Riss 1993).

Waterlogged artifacts are returned to fresh water storage. While the artifact is undergoing mechanical cleaning its storage container should be checked for biological growth, dirt and other detritus, scrubbed clean and its storage solution replaced (Rodgers 2004). Studies have now shown that immersion of archaeological iron in water (at room temperature, warm, or boiling) is generally not effective in removing Cl^- ions. One contributing factor may be that in neutral solutions, some fraction of the Cl^- ions remains adsorbed on the surface of the iron corrosion products (Selwyn 2004). The storage solution should start with rainwater, deionized water, or distilled water. Tap water contains chloride anions that will encourage corrosion in iron. Since there are no worries concerning osmotic collapse, there is no problem in placing iron artifacts directly into the alkaline storage water. Non-concreted artifacts and dry recovered artifacts, even those covered in earth concretions will almost immediately gain the benefits of the storage solution as it will easily penetrate to the artifacts surface and neutralize much of the acid there while the foil will begin a beneficial ion exchange with the artifacts (Rodgers 2004). After excavation the iron finds are stored in deep-freeze containers at -30°C. This prevents further corrosion of the objects during the intermission prior to desalination (Stambolov 1985). *The researcher doesn’t agree with this method of storage, because the side effect of the low temperature.*

Tap-water contains above 2.5 g/litre sodium chloride at concentrations (www.who.int/water_sanitation_health/dwq/chloride.pdf). The water should be changed weekly or as often as necessary as determined by a qualitative or quantitative chloride test. However, for all intent and purpose, water diffusion is not an option when it comes to treating iron recovered from a marine environment. Since water diffusion requires a long time, the water must be inhibited to prevent the metal from rusting.

In some instances this will decrease the time required to remove the soluble chlorides, but Oddy and Hughes (1970) found that there was no significant difference between the time required to wash similar objects at room temperature and at 50°C for both iron. The alternated heating/cooling cycle may facilitate the treatment, however, when significant levels of chloride are present and months to years are required to remove them. After the soluble chlorides have been eliminated, the artifacts need to be carried through the same final steps as iron treated by other methods (Hamilon 2000).

Keene and Orton (1985) said that the object was mechanically cleaned and then boiled in changes of distilled or deionized water. It was dried out at the end of each day. Boiling had serious disadvantages. The former is a drastic treatment, and can only be used for lightly corroded objects in which the corrosion layers contain no important detail. Boiling was very time-consuming and objects were easily damaged during the process, both physically and by fresh corrosion (Keene and Orton 1985). Iron artifacts are always storage in chromate solution after removal from the encrustation (Hamilton 1976). Big tanks or rubber tanks with fresh water are used to contain the artifacts for a number of days. Then the water can be checked by the solution of $AgNO_3$, HNO_3 and the desalinated equipment (Chien, http://www.unescobkk.org/fileadmin/user_upload). Rees-Jones said that the simplest and cheapest container is a wooden box with polyethylene sheets for immersion the large objects to suit the shape of the object (Rees-Jones 1972).

Wall used stainless steel tanks supported on wooden blocks to prevent scratching and movement. The cannon were kept submerged in fresh water on the research. The bores were flushed with a water hose to remove loose sand and debris (Walle 2010). Keene and Orton (1985) showed that the water became well oxygenated as a result of the circulation process, and 'flash rusting' was a serious problem, frequently clogging up the circulating system. The objects were kept in paper or polyethylene bags grouped inside cardboard boxes. The most fragile ones were packed individually in plastic or card- board boxes. Packaging was not acid-free (Keene and Orton 1985).

6.2 Mechanical cleaning restoration (traditional method)

Removing the artifacts from this tough mass is analogous to remove objects from inside concrete blocks (Hamilton 2000). The first stage in the cleaning involves the removal of encrustations and is carried out mechanically, except in case of fragile objects or objects with a loose corrosion layer, where chemical and physical methods are used (Rees-Jones 1972). Tools and machines are used in mechanical cleaning or during the use of other methods, which increase the effectiveness of these methods. Cleaning by using small dental tools and chisels was performed to remove any adhering marine growth (Burns 2002) and corrosion products are carefully removed with the help of sharp blade or scalpel. This is a very useful method since there is no danger of any chemical reaction but it requires a lot of patience and skill otherwise the objects may be spoilt (Yadav 2009). The cancerous incrustation is removed with light hammer while still wet (Thomson 1968). The cleaning process efficiency depends on three parameters groups: equipment, particles and process (Degrigny 2006). Wrong cleaning can destroy not only decorative detail of the object within the corrosion layers, but also organic and environmental evidence preserved by the corrosion, so that the object must be investigated before starting any process for conservation and restoration. The manual cleaning play a good role in helping conservation professionals in their work but it is inefficient in sometimes. Mechanical cleaning is arduous but the removal of the corrosion or protection film by flowing sand slurry has been shown to raise corrosion rates 10-fold to 10 mm year^{-1} (Pierre et al., 1984). Fouling can be removed from any surface by mechanical cleaning. Initial proteinaceous and bacterial films can be removed by simply wiping or brushing, whereas hard-shelled organisms require vigorous scraping to dislodge them from many surfaces. Smooth and simple surface contours lend themselves to easy cleaning, whereas complex contours with re-entrant angles, etc., are more difficult to clean (Jenkins 1978). Encrustations on large substantial objects are removed by careful use of a small hammer and fine chisel, or on smaller objects with an electrical or compressed-air vibrator (Rees-Jones 1972). Vibro-tools or sand blasting with various abrasive materials may be more effective, but the problem remains intractable. Nevertheless, where the iron can sustain the shock, the crust is readily removed with light hammer-blows (Thomson 1968). Mechanical cleaning is a painstaking process that requires a great deal of patience to prevent damage to an object. It will likely be the most important step in uncovering the details of an artifact's wear, usage, and fabrication, and is the first step in the micro-excavation of an artifact (Rodgers 2004).

6.3 The dechlorination methods

Dechlorination treatment methods was discussed in the previous chapters.

6.4 Immersion in distilled water after chemical desalination treatment

Following any conservation treatment - electrochemical, electrolytic, chemical, or water diffusion - it is necessary to remove insoluble oxide sludge, metallic powder, residual chlorides, and all the chemical residues through an intensive rinsing. In electrolytic reduction or water diffusion the artifact is removed after establishing that the chloride count in the solution has leveled off and ceases to rise when it is changed. The artifact is then removed and rinsed thoroughly in several changes of alternate boiling and cold deionized water to get rid of any residual electrolyte and chlorides. By rinsing in boiling water the surface of the metal oxidizes to a flat black color that provides a pleasing appearance. Since large objects may require two to four weeks of rinsing, the iron may rust in the deionized water. This can be prevented by adding gluconic acid, sodium gluconate or sodium glucoheptanate, The gluconates act as rust inhibitors during any washing and continue to serve in this capacity during solvent dehydration, heat-drying or air drying. Still, in practice, these are not commonly used unless there is some problem. Pearson prevented Captain Cook's cannons from rusting during the rinse process by washing with a potassium chromate solution (1000 ppm chromate) with a pH not lower than 8.5. But the strict disposal requirement of chromate solutions prevents their being used on a large scale. Neither the gluconates or chromate solutions are used widely, and satisfactory results are achieved without them. The artifact is allowed to stand in the last vat of rinse water for a minimum of 24 hours. A sample of the bath water is taken and acidified with nitric acid and tested with silver nitrate for the presence of chloride.

Distilled and deionized water are virtually interchangeable in many rinse processes since they both contain very few chloride ions. Both can be manufactured with elaborate scientific equipment or by fairly simple arrangements. Deionized water is produced by filtering tap water through a deionizing unit that consists of a plastic cartridge in which tap water is introduced at one end and deionized water emerges from the other. These units are cheap, simple to operate, and are available through scientific equipment catalogues. Another low chloride water source is rainwater. Rainwater tends to contain some chlorides (in coastal areas), but not nearly the amount found in most tap water. Rainwater is free, and acts as a good intermediate phase rinse solution between tap water and deionized and distilled water (Hamilton 2000).

6.5 Drying the objects after wet chemical treatment

After chloride extraction is often neglected, but in fact, it is one of the most important factors. Sufficient drying takes place only if the flaw of the liquid from the inside toward the surface of the crust is continuous (Stambolov 1985). After rinsing, the moisture absorbed by the artifact must be removed before any sealant, except certain waxes which are heated above the boiling point of water, can be applied. When specimens can be immersed in any wax heated above the boiling point of water, drying is an optional step. Artifact drying can be accomplished by heat, vacuum desiccation, or dehydration in water-miscible alcohol or acetone.

After treating iron, the metal surfaces are in a reactive state and quickly rust on exposure to air. Contact with air should be minimized until tannic acid can be applied to the surface, if the black coloration is desired, or the final sealant or insulating coating is applied to the artifact in order to prevent superficial rust that quickly forms. Some exposure to air is inevitable and it is particularly troublesome when drying by heat (ovens or infra-red lamps) or vacuum desiccation. (Using gluconate rinses could be helpful here

to prevent rust). Also, infra-red lamps are not very effective on dense objects and it is expensive to obtain ovens or vacuum chambers to accommodate very large specimens.

An alternative is to use a water-miscible solvent, ethanol, methanol, isopropanol, or acetone. Isopropanol is recommended because it is nontoxic, has a higher flash point, and does not have an obnoxious odor. Ethanol, and acetone are as effective, or even more effective, but suffer from one or more of the above disadvantages. Each of these solvents surmounts the problems of rusting when exposed to air and can be used on objects of any size. For objects with little metal remaining, drying in an oxygen-free environment, such as provided by alcohols, is necessary to prevent the remaining metal from rusting and ferrous compounds from oxidizing to a ferric state. Both reactions will cause artifacts to expand and slough off the oxide layers. Alcohols also have the advantage of enhancing the removal of any remaining soluble chlorides and water in the specimens. In addition, all stains and undesirable features can be removed by brushing while the objects are still in the alcohol. Upon completion of the water-rinsing, an artifact is removed while the water is hot and wiped with rags. This allows most of the water to evaporate before giving it a preliminary rinse in alcohol that has been previously used for drying wet objects to remove the bulk of the remaining surface water. It is then submerged in the water free isopropanol to dehydrate for a minimum of 24 hours. By taking these precautions the water content of the alcohol bath is kept low and it can be used for long periods. When the water content becomes sufficiently high it is used for the preliminary rinse and fresh alcohol is used for the dehydration bath. This efficiency procedure is important during periods of shortages and high prices (Hamilton 2000).

The heating in the furnace to dry the objects after chemical treatment was applied from many conservators in the literatures as Rees-Jones at 850°C (Rees-Jones 1972).

6.6 Final conservation steps

6.6.1 Corrosion inhibitors

Selwyn (1993) stated that corrosion inhibitor protects a clean metal surface may not have an effect on corroded archaeological metal because the corrosion layer may prevent the inhibitor from reaching the metal surface (Selwyn 1993). On the other hand, Hamilton (1999) said that the tannin solution is successfully treated for porous cast-iron cannon balls, wrought iron or steel by this method after the chlorides were removed by water diffusion (Hamilton 1999). Tannic acid was used for protecting cast iron because it can be removed easier than wax or paraloid.

Inhibitor selection begins with the choice of physical properties. It must be the first step of the inhibitor evaluation for any new system. These physical measurements are those routinely done as part of minimal quality acceptance testing (Buck1995).

Corrosion inhibitors has been known for years that certain substances can reduce and sometimes stop attack by acids, salts and organic materials on metals, an effect known as inhibition. Many compounds are able to inhibit corrosion in metals, but they vary in their mode of action and in their effectiveness in different media. It may be possible to use corrosion inhibitors to slow the corrosion rate of archaeological iron. Anodic inhibitors slow the anodic reaction (e.g. iron corrosion), and cathodic inhibitors slow the cathodic reaction (e.g. oxygen reduction). For an inhibitor to be effective, it must reach the region where either the anodic or cathodic reactions occur. Corrosion inhibitors have been developed for use on clean metal surfaces (typically covered by only a thin air-formed oxide film) and, because of the thickness of corrosion products on excavated material, it is difficult to determine how effective such corrosion inhibitors might be when used on archaeological iron (Selwyn 2004). The use of inhibitors can also improve the protective properties of primers or oxide (magnetite) coatings. In many systems, where only water-soluble inhibitors were used recently, much better results can be obtained with more hydrophobic analogs. They prevent surface corrosion and simultaneously remove deposits as the water-supply system is used (Kuznetsov 1994).

6.6.1.1 Tannic acid

The tannin solution reacts with the iron or iron oxide to form a ferrous tannate, which oxidizes to a mechanically strong, compact, blue -to black-colored ferric tannate. In order to ensure a continuous tannate film. Knowles and White (1958) recommend that all iron oxide products can be removed from the surface of the artifact, otherwise there is a possibility that corrosion may start at the junctures of the cathodic iron oxide and the tannate film. Tannin solutions react directly with the metal base and with the rust if the solution is sufficiently acidic (pH 2 to 3). In addition to forming a corrosion-resistant film, tannin solutions can be used to impart an aesthetically pleasing black color to iron. If the tannic acid mixture has to high of a pH, phosphoric acid should be added to bring it down to a pH of 2.4. A phosphate film is formed on iron objects by impregnating them with a 20 percent solution of phosphoric acid (H_3PO_4). Impregnation under a vacuum is recommended in order to ensure complete penetration of the acid into all porous areas of the metal. The acid complexes with the iron to form an inert film of ferric phosphate film on the surface of the metal.

Solutions of hydrolysable tannins such as chestnut, myroblans, or valonea extracts with a pH of 2 to 2.5 provide the most weather-resistant protection. Tannic acid solutions (Baker reagent tannic acid, $C_{76}H_{52}O_{46}$) are a standard part of the conservation of all iron artifacts in most conservation laboratories.

For maximum protection, several coats of tannin solution (200 g. tannin, 1 liter water, 150 ml ethanol) are applied with a stiff brush. A brushed-on film provides better protection than a dipped or sprayed application because the brushing assures that the solution has access to the metal in areas of loose rust and eliminates the polarization have been successfully treated by vacuum-impregnating with a tannin solution. After applying, the object is allowed to completely air-oxidize between each application of the tannic acid. Allow it to dry one to two days after the final application. The tannin solution reacts with the iron or iron oxide to form a ferrous tannate with oxidizes to a mechanically strong, compact blue-black colored ferric tannate in order to assure a continuous film. Knowles and White (1958) recommend that all the iron oxide be removed, otherwise, they contend, there is a possibility that corrosion may start at the junctures of the cathodic iron oxide and the tannate film (Hamilton 1999).

It has been demonstrated that rusted iron objects are well stabilized with tannins or the condensation products of salicylic acid. The tannins exist as two distinctive groups: the hydrolysable tannins consist of carbohydrate core and several phenolic units attached to each other by ester linkage. The phenolic nuclei detected in tannins extracted from various plants, generally belong to the series of ortho-di and trihydric phenols (Stambolv 1985). Tannic acid is applied to the exterior of artifacts for two reasons:

First, it is an acid and a corrosion inhibitor. This acid forms complex organic compounds that help stabilize the surface of the artifact being treated. The second reason for using tannic acid is that it restores the artifact to a more historically corrects black color. The object should wash in distilled water for 24h, boiled in fresh distilled water and dried in an oven set at 150˚C for two hours. While still too hot to touch, the object is then coated with the acid. The surplus tannin acid is removed by soaking in hot water for two hours (Thomson 1968). The phosphoric acid –tannin based rust transformer becomes also protective to rust which contains chloride and sulfate salts. The tannin treatment reduces in the first stage the iron (III) - ions to iron (II) ions. Iron (II) ions produce then ferrous tannate, which is soluble. Subsequent oxidation turns this compound into water-resistant, blue, presumably epitaxially orientated with respect to the metallic substratum, ferric tannate (Stambolov 1985).

6.6.2 Coating materials

One of the final conservation steps is the sealant. The formation of a protective coating on the surface of a metal can resist corrosion and support our work. Schweitzer (1989) recommended that before applying any type of surface protection, it essential that the surface of the object be properly prepared. If not properly prepared, it is possible for corrosion cells to develop under the protective coating and result in the coating delaminating and flaking off (Schweitzer 1989). Brüggerhoff said that molten wax, cosmoloid 80H, vegetable pitch and lead white that they have been used for thousands of years as a surface coating (Brüggerhoff 2007).

Coatings used for conservation and restoration treatments should meet a number of special requirements, mainly transparency, a good aesthetic appearance, long term stability and reversibility. The latter is a vital condition for restoration products, since the treatment applied to an object intended to last for centuries will eventually need to be renewed (Degrignyet al., 2007). Coating iron and steel surfaces is the thickness of the layers of the conservation material. Thin coating layers are not sufficient to provide an effective protection from corrosion on steel samples e.g. in the case of a single coating of wax (this is also standard with other materials), but also in coatings of only ~ 10 μm, as achieved by a single application of spray or a manual application with a paint brush of low viscous ORMOCERs (Brüggerhoff 2007). The effectiveness of treatment and conservation are achieved by the protection systems. Measuring techniques for coatings can be regarded as pillar supporting modern coating technology (Brock et al., 2000).

Evans (1963) said that metal coatings are often applied to improve the corrosion life of the underlying metal and the several mechanisms by which this improvement is achieved. Coatings are also applied for several reasons, e.g. (a) for increased wear resistance. (b) for consistent low electrical contact resistant reflectivity (d) oxidation resistance to mention by only a few (Evans 1963). Turgoose (1982) suggested that the ideal storage environment would be damp and oxygen-free. The corrosion processes can occur at relative humilities as low as 20% (Turgoose 1982).

Polymers are often used to protect iron, but they all have in common the drawback that they are vulnerable to weathering particularly outdoors (Stamboov 1985).

6.6.2.1 Paraloid

There are many types of paralloid. Acryloid B-72, (Paraloid B-72 in Britain) is an Acrylic resin that is a good, all-purpose consolidant. It is a colorless, durable, stable resin that achieves good penetration and if applied properly, should not appreciably alter the appearance of the material to which it has been applied. It is soluble in acetone and toluene and is readily reversible. It has good aging properties and miscibility with several types of solvent).

Paraloid B44 retains a stable pH over time, whereas Paraloid B72 tends to become more acidic. Furthermore, paraloid B44 has been successfully used as a protective coating for mineralized organic remains during desalination treatments with alkaline sulphite solutions. Because of its lower glass transition in baths heated to a temperature of 50 °C. The glossy appearance of Paraloid B44 can be reduced by using methylbenzene (toluene) as a solvent (Schmidt-Ott and Boissonnas 2002).

Incralac is the trade name of a lacquer manufactured using acryloid B-44 (methyl methacrylate copolymer), which can be solubilized readily in acetone, toluene, xylene, dimethyl benzene and dichloromethane, as well as in a number of solvents less commonly used in the conservation field (Moffett 1996).

Acryloid B-72 is unique in possessing a high tolerance for ethanol, e.g., after being dissolved in acetone or toluene, up to 40 percent ethanol can be added to the solution to control the working time. This property allows its use in applications, where strong solvents cannot be tolerated. The alcohol dispersion may be cloudy or milky; however, clear, coherent films are formed upon drying. Friable surfaces of porous, salt-contaminated objects can be stabilized with Acryloid B-72 while the salts are being diffused out in water baths without the adverse effects resulting from the use of soluble nylon discussed below (Hamilton 1999). Acryloid B-72 (referred to as Paraloid B-72 in Europe) is a thermoplastic acrylic resin manufactured by Rohm and Haas, which has replaced PVA in many applications, and is preferred by many conservators over PVA. Durable and non-yellowing, Acryloid B-72 dries to a clear transparency, with less gloss than PVA, and is resistant to discoloration even at high temperatures. It is very durable, and has excellent resistance to water, alcohol, alkalis, acid, mineral oil, vegetable oils, and grease, and it retains excellent flexibility. Acryloid B-72 can be applied in either clear or pigmented coatings by a variety of application methods and can be air dried or baked. In stronger concentrations, Acryloid B-72 can be used as glue (Hamilton 1999).

Krylon Clear Acrylic 1301 is a formulation of 20 percent Acryloid B-66 in non-water miscible toluene that is easily obtained and is excellent for consolidating or sealing off the surfaces of a wide range of material. It is ethyl methacrylate resin that is harder than Acryloid B-72, and can be used in place of it in most instances (Hamilton 1999).

6.6.2.2 Waxes

Paraffin and microcrystalline waxes are the most important in preservation of the iron objects, although, according to an old tradition, the beeswax is unsurpassed, as preservative especially when applied on iron which has been heated prior to wax.

The paraffin waxes are white, translucent, waxy, odorless, solids containing large crystals. They are soluble in benzene, ligroin, warm alcohol, chloroform, turpentine, carbon disulfide and olive oil, but insoluble in water and acids. They are therefore water for water pellet, and already as relatively thin. They are good water-damp barriers. Melting point is 50-60°C (Cronyn 1990).

Microcrystalline waxes are derived from petroleum, which have a fine crystalline structure and are white, amber or black solids, which usually have odors. They are tasteless and chemically inert. As far as solubility is concerned they behave like the paraffin waxes, and are impermeable to water vapor. The melting point is 60-100°C (Stambolov 1985). The microcrystalline wax coatings formerly applied have been discontinued as they didn't provide the desired long-term protection against post-treatment corrosion, and are not easily reversible. The prevailing custom in the final stage of corrosion prevention with regard to desalted objects is to impregnate them with microcrystalline wax. The objects still, hot from being dried under infrared lamps, are immersed in a bath of melted microcrystalline (or even better paraffin) wax over a heat source. A mass of air bubbles will be driven out of the pores of the objects and will be driven out of the pores of the objects and will be replaced by wax. An optional addition to the above finishing is to brush graphite powder over the still melted wax surface, using a stiff-bristle brush; the wax is, in this way worked into the hollows and interstices as thoroughly as possible. After drying under the infrared lamps the hot modeled concentrations are impregnated with melted microcrystalline wax (Stambolov 1985). In the Mediterranean countries tend to prefer the use of waxes for archaeological iron objects as opposed to other coatings used in Greece or the rest of Europe (Argyropoulos et al., 2007)

The anticorrosive waxes are just as effective in protecting metals as transparent lacquers. Indeed, a few of them are even somewhat superior. This statement must be qualified because there have been no simulations of exposure to sunlight or continual rainfall. Both these realistic factors might lead to different evaluations. When comparing wax to lacquer, results have shown that the optical appearance of wax – a matt, unobtrusive surface – is superior. It is not possible to establish a pecking order in the case of anticorrosive waxes (waxes with added corrosion inhibitors), since the differences in quality are so slight, and are dependent on the test and the type of substrata. If we compare ORMOCERs with standard preferred lacquers (polyurethane systems), there are scarcely any differences (Brüggerhoff 2007).

Removal of the microcrystalline-polyethylene wax blend coating would not be as straightforward. Although the natural waxes were used early on in conservation treatments, the synthetic waxes are now more favored by the field; they are generally more neutral and stable and are unfettered with free fatty acids. Of the synthetic variety, microcrystalline and polyethylene waxes are most commonly employed. Polyethylene waxes are made from the polymerization of ethylene gas derived from petroleum. Wax like coatings have a "hard-soft" structure, so they can protect precision surfaces from mechanical wear or post-corrosion. They are resistant to solar radiation, and have good water-repellant properties and quick-acting protection. When their cost is relatively low, they also give "secondary" protection. Volatile inhibitors are used not only by themselves, but also in combination with other anti-corrosion materials (oils, lubricants, lacquers, etc.), which creates additional possibilities for reliable protection of enclosed volumes (Kuznetsov 1994).

Cosmolloid 80H by immersion in the molten wax at 120°C until bubbles ceased to rise. After this the assembly was lifted out on to supports above the molten wax and allowed to drain whilst still in the hot oven (Organ 1963). The results showed that very poor protection was afforded by the tested polyurethane and ketonic resins (Brüggerhoff 2001).

6.7 Storage and show processes *(Final conservation steps)*

For safe storage and display, it is necessary to reduce the chloride concentration as much as possible in the corroded artifacts. After the treatment and coating the iron objects they will go to the museums. It has to be kept dry at less than 15% RH to prevent rusting. Active corrosion is indicated by bright orange powdery crystals or little droplets of weeping iron. Orange iron-stained tissue paper is a common sight and indicates an urgent need for dry storage (http://www.finds.org.uk/conservation/note3.php). Pure iron (II) chloride (the inevitable product from the interaction of chloride ions during rusting of archaeological iron) is a stable and solid substance below 44% relative humidity, a content between iron (II) chloride and iron pore depresses this threshold of stability to 20% relative humidity (Stambolov 1985).

Many materials used for the storage and display of artifacts will degrade, slowly releasing gaseous compounds such as carbonyl sulphide or ethanoic (acetic) acid. In an enclosed area such as a display case, the concentration of such compounds can reach appreciable levels and accelerate the deterioration of certain artifacts, particularly those made of metal. The fact that certain types of wood can lead to corrosion in a museum environment has long been known, but it was not until the early 1970s that other materials were recognized as the cause of active corrosion in storage or on display (Green and Thickett 1995). However, past attempts to develop display cases or storage units that used a nitrogen atmosphere and a controlled relative humidity either were extremely expensive or required considerable maintenance or monitoring of gas-flow equipment. Additional problems have always arisen when mechanical or electrical devices were attached to a case for humidity control. The design and construction of a thermatically sealed case that could be filled with nitrogen or another inert gas and left unattended for an extended period. In the inert microenvironment of such a case, freedom from the possibility of aerobic biological harm to an artifact could be achieved. The cases should not be dependent on any mechanical or electrical systems. They should require little maintenance, no more often than every two years (Maekaw 1998).

This process need to the periodic conservation (Strati 1995). Iron objects are particularly vulnerable. If the object left untreated, they can be stabilized only by putting them into a very dry environment of below 30% RH. Storage systems may be designed to facilitate access to the objects by researchers and public, or they may favor the safeguarding of objects from overexposure to handling. Allowances should be made for accessing and retrieving objects for exhibition, loan, conservation, or research. Storage should be planned with adequate security from theft, fire, natural disasters, and other hazards. Environmental factors are critical to the safe storage of collections. Heating, ventilation, and air conditioning should maintain a stable environment including, most importantly, relative humidity levels appropriate to the particular types of materials in each storage space. Other environmental factors include dust and other pollutants, light, biological pests, vibration, and exposure to accidents. Storage systems may be selected to achieve a careful balance between protection and accessibility (Karp 1979).

Part (2) Experimental procedures

Chapter (7) The Preparation of iron coupons and the methods of accelerated aging

Chapter (8) Methods of diagnoses of the iron corroded coupons and iron objects

Chapter (9) Diagnoses of iron coupons before desalination by investigating and analyzing

Chapter (10) Diagnoses of the iron objects from Syros museum and Paros Island by investigating and analyzing before the treatment

Chapter (11) The methodologies of the dechlorination treatment methods of iron corroded coupons

Chapter (12) Results of treatment monitoring of the iron coupons

Chapter (13) Results of treatment monitoring of iron artifacts

Chapter (14) Condition of the coupons and artefacts after the treatment

CHAPTER 7

THE PREPARATION OF IRON COUPONS AND THE METHODS OF ACCELERATED AGING

Accelerated corrosion tests have been used in conservation since 1972 by Werner (Robinet and Thickett 2003). The experimental treatments are an essential step before beginning of the treatment methods. The experimental part plays a critical role in the conservator's work, in applying the results of these experiments to the artifacts and to evaluate these methods. The coupons were corroded artificially to simulate the marine finds (wrought and cast iron).

The scientific experiments were performed by using sodium hydroxide and/or hydrogen plasma to know the best dechlorination method. The iron coupons were used to prove the results of the treatment method of the iron artifacts.

Although these experiments have several advantages, there are also significant problems as the difference between the coupons and the artifacts in size, the chloride level, and the form of corrosion compounds.

7.1 The Production of iron coupons

The coupons were fabricated from iron, produced by Halyvourgiki Inc., Athens, Greece.

Chemical cleaning of the iron coupons

After production and before artificial aging of the coupons, they have been cleaned by using a dilute nitric acid (2% HNO_3), or Decon 90 'Acid Rinse' detergent.

7.2 The methods of accelerated aging

The experiments were carried out on Demokritos. The coupons are flat with dimension (10 × 10 × 0.2 cm^3). The chemical composition of the iron coupons are iron 97.6%, carbon 1.74% and manganese 0.66% wt. by SEM. Unfortunately, we have not any cast iron coupons.

For these experiments, we used more than 50 artificial samples. Depending on the method of preparation of the coupons, they were divided into 4 groups. The coupons were aged by three methods. The result of the X-ray diffraction has shown the presence of akaganeite as a corrosion compounds after the accelerated ageing. The experimental conditions were chosen based on the conditions of the original environment of the objects and the kind of corrosion.

Group	**The environment of artificial aging**	**The goal**	**The type and shape of metal (iron coupons)**
A	The coupons were exposed to salt spray	To check the effect of the difference of the treatment methods as chemical treatment, plasma reduction or the combination of the two methods	Iron metal coupons Flat coupons The coupons are flat with dimension 5 x 5 x 0.2 cm^3 Coupon dimensions must be identical from one coupon to the next.
A1	Was desalinated by using NaOH		
A2	Was desalinated by using H_2 plasma		
A3	Was desalinated by using NaOH followed by H_2 plasma		
A4	Was desalinated by using H_2 plasma followed by NaOH		
B	3.5% Sodium chlorides		
B1	Was desalinated by using H_2 plasma		
C	The coupons were exposed to iron (III) chloride – hexahydrate	To determine the impact of the chlorides on the iron surface and the behavior of iron chloride in hydrogen plasma.	Iron metal coupons were exposed to iron chloride Flat coupons The size is 2.5x 2.5 x 0.2 cm3. The experiments was applied on
D	Iron (III) chloride – hexahydrate	The effect of plasma on the iron chlorides	

			the iron chlorides

Table (7-1) The condition of accelerated aging

Three types of environments were used in coupons testing for applying the dechlorination treatment.

7.2.1 Salt Spray (Group A)

Salt spray is a standardized test method used to check the difference of the desalination treatment methods. 5% Neutral salt spray tests were carried out as per Brouillard salin, ASTM B-117 test.

Accelerated aging conditions were performed by using 5% NaCl and the temperature test chamber was kept at 30°C) at NTUA. That means, the corrosive medium consist of water and sodium chloride in the ratio of 95:5 by weight. Specimens were exposed to the salt sprayed with sodium chloride solutions *(corrosive environment)* then exposed to an atmosphere of 100% relative humidity; it has initially retained the salt within their corrosion layer for 12 days. A solution containing 5% sodium chloride was atomized by compressed air in the chamber. This method provides a means of evaluating and comparing desalination treatment, after exposure to a corrosive environment. After exposure to the solutions (salt spray), the coupons were cut into four parts of approximately 5 x 5 x 0.2 cm^3.

7.2.2 Sodium chlorides (Group B)

20 iron coupons were exposed to 3.5% sodium chloride i.e. a solution with the same concentration of NaCl as the marine one. These coupons were prepared in chemical laboratory, NTUA. Before exposure to the solution of sodium chloride, the coupons were cut into four parts of approximately 5 x 5 x 0.2 cm^3. The exposed surface of each coupon was totally immersed in the solution of acquired accelerated aging on slanting position in the bath for 21 days at room temperature. After that, *the coupons were* removed gently and the other methods of treatment were applied.

7.2.3 The ageing by iron (III) chloride –hexahydrate ($FeCl_3.6H_2O$) (group C)

10 iron coupons of dimensions 2.5×2.5×0.2 cm^3 were exposed to iron (III) chloride –hexahydrate (pure chloride) $FeCl_3.6H_2O$ for one month (M=270, 30g/mol).

7.2.4 Iron (III) chloride –hexahydrate ($FeCl_3.6H_2O$)

Iron (III) chloride –hexahydrate contains the iron in the +3 oxidation state. It appears to have hygroscopic properties.

7.3 Reasons of using these artificial aging

The main goal of our experiments is to introduce a comparison study of the different dechlorination treatment methods by using NaOH and/or hydrogen plasma reduction. Artificial aging by salt spray was the main important procedure of our experiments. High level of chloride after exposure to 5% sodium chloride in salt spray cabinet was to simulate the behavior of real iron artifacts from marine environment and it provided more reliable data. This is the most important test in evaluating the results of the experiments.

Artificial aging by 3.5% sodium chloride was also to simulate the same level of sodium chloride in natural sea water (Aylor 1995 and Cater 2002). Iron chloride was used to study the effectiveness of hydrogen plasma as a desalination method. The previous corrosive conditions, to which the iron coupons were exposed, can be classified as mild, moderate and severe. Accelerated aging by salt spray was done for 12 days which is equivalent to about 100 years natural aging in seawater.

CHAPTER 8

THE METHODS OF DIAGNOSES OF THE COUPONS AND THE IRON ARTIFACTS

The effect of coefficient of desalination treatment was assessed by several investigations and analyses methods such as stereo and metallographic microscope, silver nitrate, XRD, scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). These analyses methods have successfully demonstrated the suitable method of desalination treatment and to identify the major and minor minerals of the marine compounds before the desalination treatment. The efficiency of dechlorination treatment is often compared by determining the amount of chlorides ions before each stage of desalination treatment.

8.1 The investigation methods

X-ray radiography and the examination by the microscopes are very essential for evaluate the deterioration of the objects.

8.1.1 The investigation by X-ray radiography

Takayasu and Takayasu said that this process helps to obtain the information that we need to clean and restore the objects (Takayasu and Takayasu 2005).

The degree of penetration the rays depends on the composition, density of the rays and thickness of the object to be studied, and the energy of X-ray. The non-destructive radiography testing laboratory (NDRTL) was carried out in the Institute of Materials Science (IMS), of NCSR (Demokritos). In this lab, Radiographic tests with Ir-192, Se-75, as well as portable X-rays; NDRTL has the unique advantage to perform radiography tests by using cobalt (Co-60) X-rays. Also, this work was performed in Technological Educational Institute (TEI) of Athens, Department of Conservation of Antiquities and Works of Art.

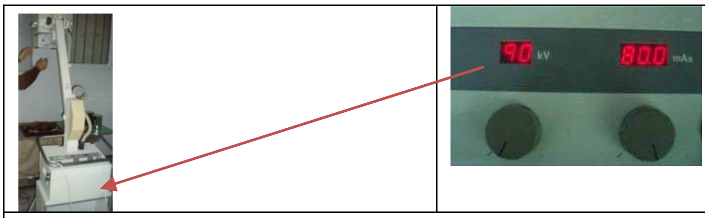


Photo (8-1) X-ray radiography in TEI and the condition of the work

X-ray radiography has become the popular method for investigation the inside of objects, and this method is very important for underwater archaeology to excavate the investigation into the inner structure (Hamilton 2000).

8.1.2 Stereo and optical microscope

Stereo microscope is allowing for an in-depth, 3-D view of the sample. These microscopes usually have both a top and bottom light and can be used for performing both reflected and transmitted light observations. While reflected light is required for looking at opaque objects, transmitted light is ideal for transparent objects (http://www.amscope.com/LowPower.html?gclid=CPvhsKKWk6ECFQcx3wod20RtOQ).

The optical microscope, often referred to as the "light microscope", is a type of microscope which uses visible light and a system of lenses to magnify images of small samples. Optical microscopes are the oldest and simplest of the microscopes. Digital microscopes are now available which use a CCD camera to examine a sample, and the image is shown directly on a computer screen without the need for optics such as eye-pieces. ZEISS 745022-9902 was used to investigate the sample in Demokritos before, during and after the treatment.

8.1.3 Metallographic microscope

Indeed, often it is a key tool in the examination of iron objects and fragments. The analyses of the samples allow knowing the possible condition and deterioration of the archaeological materials. Metallographic **examination** allows us to recognize important features of the samples. For that reason we will focus our investigation on the corrosion layer, the color of corrosion compound, and the effect of the heating by plasma on the metallurgical properties. The selected the sample to observe, can modify the image magnification, by the combination of the objective lenses and eyepieces, so that it can have different global magnifications: 50X, 100X, 200X, 500X and in some occasions until 1000X. This will do necessary to have so many images as sample magnifications we want to show. This is justified by the very high resolution to be attained in higher magnification.

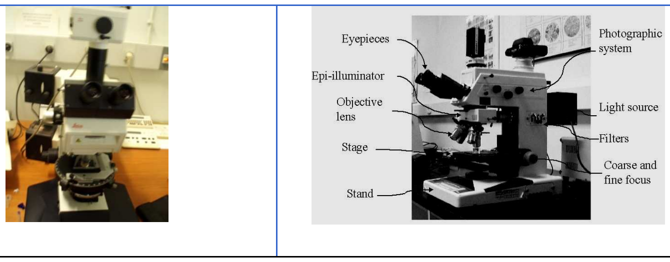


Photo (8-2) The metallographic microscope in Demokritos

Buchwald and Clarke (1989) studied the major corrosion products of iron artifacts are Cl^- containing akaganiete, and goethite with minor amounts of lepidocrocite and maghemite by metallographic examination (Buchwald and Clarke 1989).

The preparation of the samples for investigation and analysis by metallographic microscope and scanning electron microscope

Samples were prepared for the investigation and analysis before each stage of desalination treatment. Each method needed to prepare the samples for scientific study in different ways. The metal samples were cut from the edges by manual and electronic hacksaw. Firstly, the samples were mounted into cross sections in SERFIX Kit epoxy resin; code FIXMO with SERFIX hardener at room temperature. They were polished with SiC (Silicon Carbide) abrasive papers (grades 80 to 4000) then using the soft cloth (final polishing) in order to avoid any phase transformation during preparation.

8.2 Analytical technique

The identification of the level of chlorides is the key to our work in the conservation and restoration. The stage of preparation of the samples is by cutting, mounting, grinding and polishing the samples. Structural evidence for the desalination of akaganeite in the preservation of iron archaeological objects was by using silver nitrate test, X-ray powder diffraction, absorption spectroscopy, EDS, and ion chromatography.

8.2.1 Chloride test by silver nitrate

The chloride ion concentration was determined by titration with a silver nitrate solution (the simplest method). The sample from the solution treatment was analyzed quantitatively.

This test, coupled with the color tests (the formation of the clouds when the sample has chlorides) are usually performed as preliminary analyses for any unknown sample, followed by more reliable instrumental techniques to confirm the results. After the discussion about the problem of measuring the level of the chloride by using silver nitrate of the object before the chemical treatment or during the dry treatment (mechanical and plasma treatment), we used 5% nitric acid to dissolve the oxidized layer.

Silver nitrate (Volhard's Method) at NTUA

Before and during chemical cleaning, the chloride level should be calculated. This method uses a back titration with potassium thiocyanate to determine the concentration of chloride ions in a solution. Before the titration an excess volume of a silver nitrate solution is added to the solution containing chloride ions, forming a precipitate of silver chloride.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

The indicator Fe^{3+} (ferric ion) is then added and the solution is titrated with the potassium thiocyanate solution. The titrate remains pale yellow as the excess (unreacted) silver ions react with the thiocyanate ions to form a silver thiocyanate precipitate.

$$Ag^{+}_{(aq)} + SCN^{-}_{(aq)} \rightarrow AgSCN_{(s)}$$

Once all the silver ions have reacted, the slightest excess of thiocyanate reacts with Fe^{3+} to form a dark red complex. $Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightarrow [FeSCN]^{2+}_{(aq)}$.

The concentration of chloride ions is determined by subtracting the titration findings of the moles of silver ions that reacted with the thiocyanate from the total moles of silver nitrate added to the solution.

This method is used when the pH of the solution after the sample has been prepared is acidic.

Concentrated nitric acid (6 mol L^{-1})

Silver nitrate solution: (0.1 mol L^{-1}). If possible, dry 5 g of $AgNO_3$ for 2 hours at 100°C and allow to cool. Accurately weigh about 4.25 g of solid $AgNO_3$ and dissolve it in 250 mL of distilled water in a conical flask. Store the solution in a brown bottle.

Potassium thiocyanate solution: (0.1 mol L^{-1}). Weigh 2.43 g of solid KSCN and dissolve it in 250 mL of distilled water in a volumetric flask.

Result Calculations

1. Determine the average volume of potassium thiocyanate used from your concordant titres.
2. Calculate the moles of potassium thiocyanate used. As shown in the following equation of the reaction between silver ions and thiocyanate ions

$$Ag^{+}_{(aq)} + SCN^{-}_{(aq)} \rightarrow AgSCN_{(s)}$$

To calculate the moles of unreacted silver nitrate in 100 mL of sample of solution extract, and multiply the figure by five to determine the total moles of unreacted silver nitrate (the excess) in the 500 mL volumetric flask.

3. Calculate the moles of silver nitrate in the 50 mL of solution that were added during the sample preparation of the solution of the treatment.
4. Calculate the total moles of silver nitrate that reacted with the salt from the sample of the solution by subtracting the moles of unreacted silver nitrate (the excess) from the total moles of silver nitrate added to the sample of the solution.
5. Use the equation of the reaction between the silver ions and the chloride ions to calculate the moles of sodium chloride in the sample of solution of the treatment.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

6. Calculate the concentration of solution of the sample.

Other method which we used in the lab in Demokritos

1.7 grams of silver nitrate crystals was dissolved into 98 milliliters of distilled water. The solution was stored in a dropper in a dark place, because it is somewhat light sensitive (The solution can be transformed for dark color). The sample of the alkaline bath water (10 to 30 ml) was placed in the clean test tube. Two drops were added of dilute nitric acid. The formation of a white precipitate (i.e., cloudiness) indicates the presence of chlorides. If the cloudiness is so weak as to raise doubts as to its presence, compare it with an untested sample of the rinse water.

Accuracy check

Use the standard additions method to find if the sample has interference. Use the standard solution method to make sure that the user has followed the test correctly and that the reagents are good.

Standard additions method (sample spike) required for accuracy check:

- Chloride voluette ampoule standard, 12,500-mg/L as Cl^-.

Standard solution method

A silver nitrate standard solution will slowly decompose with exposure to light. Complete the following test to make sure the concentration is accurate.

Required for accuracy check:

- Sodium Chloride Standard Solution, 1000^- mg/L as Cl^-. 100^- mL class a volumetric flask (for use with 0.0141 N titrates only).

Silver nitrate is used as the titrate and potassium chromate as the indicator. Silver nitrate first reacts selectively with the chloride in the sample to produce insoluble white silver chloride. After all the chloride has been precipitated, the silver nitrate reacts with the chromate to form an orange or red-brown silver chromate precipitate. The test by silver nitrate was accomplished at room temperature.

8.2.2 Scanning electron microscope

Scanning electron microscopy is a valuable tool for the examination and analyses of iron archaeological objects because of the possibility of high magnification and depth of analysis. The examination of samples in high magnifications allows identification of structural characteristics of the metal artifacts and corrosion compounds. The coupons and objects were examined under the SEM and were analyzed by ESD. Microstructure and surface characterization with chemical analysis capability (EDAX-EELS). EDAX, Model (200/400,132-10), lined up around 20-25keV.

Photo (8-3) The SEM equipment in Demokritos

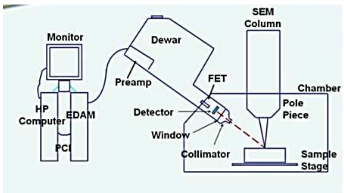


Fig.(8-4) The schematic diagram of the SEM

The sample must be located at a working distance of approximately 10mm. The EDS detector is positioned so that 9.8 to 9.9 mm is the optimal position. If the sample is above or below this position the number of x-rays hitting the detector will be greatly reduced. As in the case of scanning electron microscopy, qualitative and quantitative analysis based on the detection and treatment of X-rays emitted after excitation of the sample ray energy is characteristic of the person from which emitted intensity (the number Event-counts) characteristic of the concentration of the sample in the following table.

Tilt	*0*
Duration	*1 minute- 2 minutes*
Magnification	*40-4000*
Resolution	*1024×800 (The most)*

Table (8-1) The condition of investigation and analysis by SEM- EDS

8.2.3 XRF

XRF is one of the most non-destructive analyses of archaeological materials. The objects were analyzed by XRF, when we had a problem in SEM. The portable XRF results were also useful in the evaluation of the chlorides level. The XRF has some basic limitations such as inability to detect elements with low atomic number (Z) and the difficulty in determining the depth from which X-rays. A portable XRF spectrometer assembled at our laboratory was used for the in-situ non-destructive examination of the cannonballs.

		
XRF in plasma laboratory	*The condition of the analyses*	*The object after immersing in the distilled*

Photo (8-5) the analyses by XRF

8.2.4 XRD analyses

The Siemens D500 X-ray diffractometer was used for powdered samples and thin films from the corrosion layer or from solid metal analysis (Bragg-Brentano geometry), (Cukα radiation, 40kV, 35mA) automatic diffractometer was used for this work. X-ray techniques have been used to analyze the effects of desalination treatment methods on corroded iron coupons and iron artifacts, where chlorides form a substantial part (akaganeite) of the corrosion. For analysis of samples, the device of the Institute of Materials Science, NCSR "Demokritos". For reliable quantitative results require the use of standard samples. Each archaeological sample obtained two measurements for each point: first, the device operates under 15 kV and 100 μA was used to verify the concentrations of major elements (Major elements) and second (at 40 kV - 300 mA) for detection of trace elements. The timing of each spectrum was maintained in all cases constant (1:49 minutes) while the rate of occurrence ranged between 370 and 480 cps.

Photo (8-6) Siemens D500 in Demokritos and Siemens D5000 in NTUA

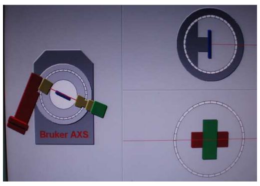


Fig. (8-5) Schematic during the analysis by XRD

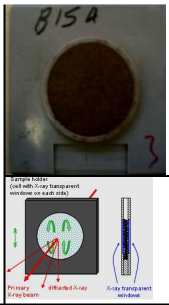


Fig. (8-5) Schematic diagram of a sample holder
After: Sarrazin et al., 2005

Photo (8-7) The machine of grinding

The distinction between maghemite γ-Fe_2O_3 and magnetite Fe_3O_4 in the diffraction pattern is difficult, because the corresponding 2θ Bragg diffraction angles of their peaks are almost the same, since the structure of both oxides are closely related.

8.2.4 AAA (Atomic absorption analyses

Atomic absorption analyses (Petkin element 3300) was used in evaluation the elements in the solution samples of several marine environments in Greece, while analyzing the structure.

Photo (8-6) Atomic absorption analyses in NTUA *(Petki*n element 3300*)*

8.2.5 Ion chromatography

Ion chromatography was used to measure the chlorides but the result was not accurate. The separations of the samples from the residues were so difficult, and it was accomplished by filtration as shown in figure (8-8).

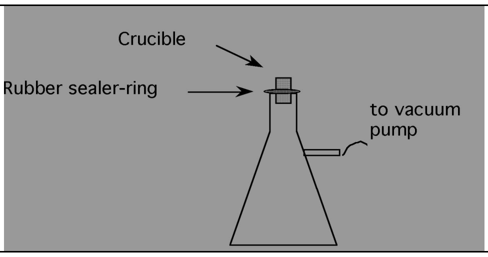


Fig.. (8-8) Apparatus for filtration using a crucible filter

8.2.6 The pH

The change in the value of pH for distilled water (prior treatment) and the solutions before the treatment, during and the end point of the wet treatment is a measure of the effect of the method.

8.2.7 The gravimetric method using weighing and length

Already, we are using this method to know the rate of corrosion. Measurements and weighing of the coupons and the objects indicated that the post-treatment length of the objects remained equal to its wet length, but the weight changed during and after the desalination treatment. Each coupon, fragment and the objects (traditional balance) was weighed before, during and after the treatment by *using* an electronic *weighing* balance.

8.2.8 Hardness test

The use of hardness test is a mean of estimating the effect of plasma's temperature. In particular, by means of the combined use of surface and bulk techniques micro hardness test specimens must have a polished surface whereas it's usually sufficient that specimens for macro/regular hardness testing have a ground or clean surface only.

The Vickers Hardness (HV) is calculated by measuring the diagonal lengths of an indent left by introducing a diamond pyramid indenter with a given load into the sample material. The loads used range from 10 g (1 g) up to 100 kg.

The full load is normally applied for 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured by using a microscope and their average calculated. The area of the sloping surface of the indentation is calculated (http://www.struers.com)

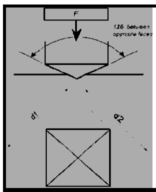


Fig. (8-7) Vickers test scheme *xF= Load in kgf* *d = Arithmetic mean of the two diagonals, d1 and* *HV = Vickers hardness*	*APhoto (8-7) The equipment of Vicker hardness test in NTU* $HV = \frac{2F\sin\frac{136^o}{2}}{d^2}$ $HV = 1.854\frac{F}{d^2}$ approximately

The goal of this method was to know the effect of the temperature during the reduction by hydrogen plasma.

CHAPTER 9

DIAGNOSIS OF THE CORRODED IRON COUPONS BY INVESTIGATION AND ANALYSIS BEFORE THE DECHLORINATION TREATMENT

This study focuses mainly on the best methods that have an effect on the removal of chlorides. The coupons were developed under long-term artificial ageing. We noted that the corrosion compounds and the chlorides level on the coupons were different after exposure to salt spray, sodium chloride and iron chloride accelerated aging procedures. The coupons are flat with dimension of 10 × 10 × 0.2 cm^3.

Photo (9-1) the iron coupons after accelerated aging and before dividing into four parts

Photo (9-2) the coupons before the desalination treatment and after dividing for four parts

Red rust (iron oxides) appeared on the surface of these coupons

The coupons are flat with dimension (5 × 5× 0.2 cm^3), after dividing into 4 parts.

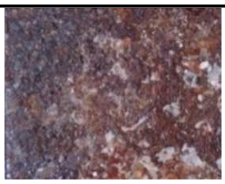


Photo (9-3) The coupon that was exposed to sodium chlorides before any treatment	*Photo (9-4) The iron coupon after exposing to Iron (III) chloride – hexahydrate* $FeCl_3.6H_2O$	*Photo (9-5) iron (III) chloride – hexahydrate before exposing to hydrogen plasma*

9.1 The investigation by optical microscope

Results obtained by using optical microscopy investigations confirm the effect of treatment methods.

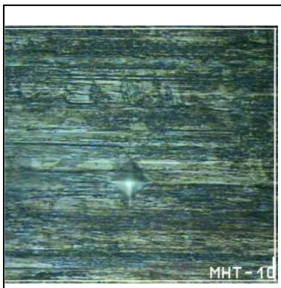
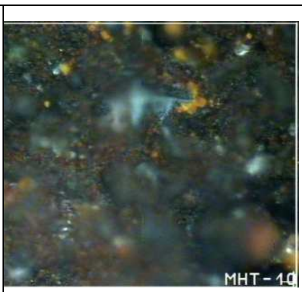
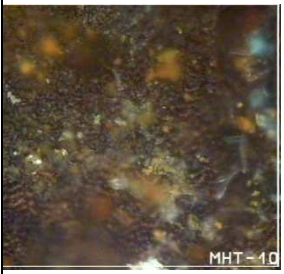
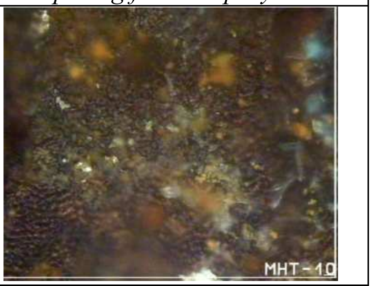
		
AC before accelerated Ageing X500	*AC1 by optical microscope mag. X500, Gr. A*	*AC1-X500, this photo shows the higher percentage of hematite that was present in the bulk oxide before the treatment and after exposing for salt spray. Gr. A*
		
AC4-X500, the different of iron oxides after accelerated aging by sodium chloride		*AC1 - X500 before the desalination treatment*

Table (9-1) The result of the examination by optical microscope

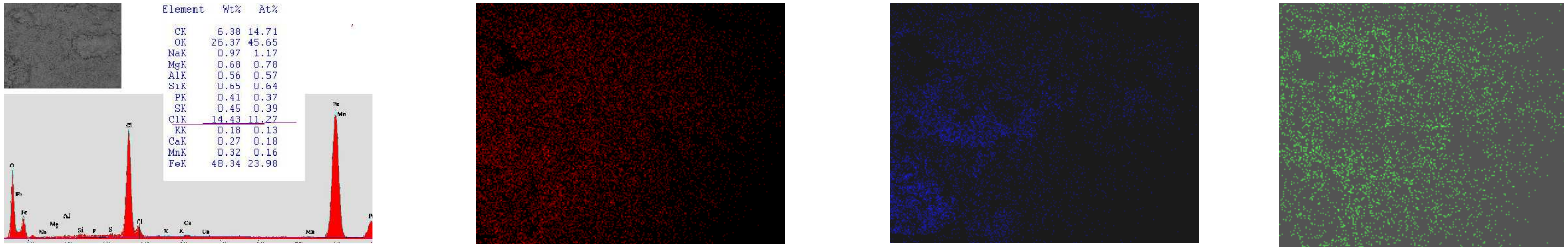
9.2 Results of analysis by SEM, EDS and XRD

9.2.1 Diagnoses of the iron corroded compounds on the surface by XRD

Most of the SEM pictures from all groups we obtained showed presence of high percentage of the chlorides.

The method of accelera	***Cl%***
Gro. A (Salt spr	*0.9-1.5*
Gro. B (Sodium chl	*0.45-0.85*
Gro. C (Iron chlo	*10-14*

Table (9-2) The level of chlorides before the desalination

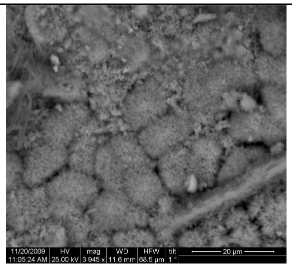


Element	Wt%	At%
CK	6.38	14.71
OK	26.37	45.65
NaK	0.97	1.17
MgK	0.68	0.78
AlK	0.56	0.57
SiK	0.65	0.64
PK	0.41	0.37
SK	0.45	0.39
ClK	14.43	11.27
KK	0.18	0.13
CaK	0.27	0.18
MnK	0.32	0.16
FeK	48.34	23.98

Bulk of the sample — *Bulk-Fe before the treatment* — *Bulk-Cl* — *Bulk-O*

Table (9-3) Element mapping by EDS of coupons, after exposing for iron chlorides. The sample has high percentage by weight of chloride.

```
----------------------------------------------------
  C K    2.08    5.90   0.0044   1.1246   0.1869   1.0006
  O K   22.07   47.00   0.0952   1.1072   0.3885   1.0030
  NaK    0.27    0.41   0.0004   1.0379   0.1308   1.0001
  MgK    0.09    0.12   0.0002   1.0645   0.1897   1.0001
  AlK    0.07    0.09   0.0002   1.0336   0.2721   1.0010
  SiK    0.13    0.16   0.0005   1.0641   0.3780   1.0018
  P K    0.06    0.06   0.0003   1.0292   0.4971   1.0034
  S K    0.13    0.13   0.0008   1.0561   0.6146   1.0061
  ClK    0.65    0.63   0.0048   1.0163   0.7171   1.0102
  K K    0.17    0.15   0.0015   1.0204   0.8606   1.0298
  CaK    0.11    0.09   0.0011   1.0432   0.9072   1.0493
  MnK    0.42    0.26   0.0039   0.9370   1.0019   1.0000
  FeK   73.75   44.99   0.7099   0.9558   1.0071   1.0000
```



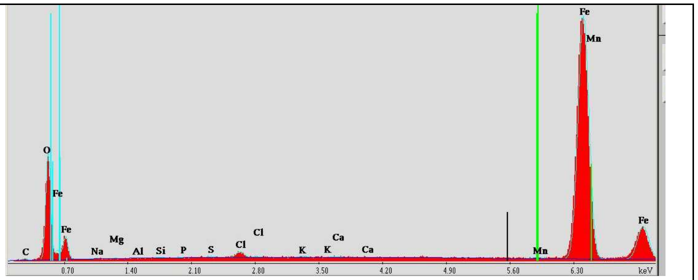
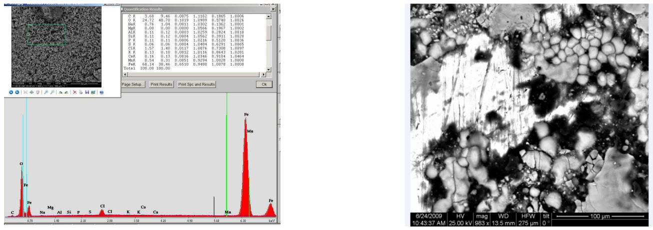


Table (9-4) The result of bulk analyses by SEM and EDS of the coupons after exposure to sodium chloride (Group B), and this table shows the chemical composition of the iron coupons after accelerated aging by 3.5% sodium chloride.



SEM image, Magnification X 983

Table (9-5) the characteristic of the coupon surface after accelerated aging by salt spray.

Right SEM photograph shows the holes that contains chlorides.

9.2.2 Diagnoses of the iron corroded compounds on the surface by XRD

The powdered samples were analyzed by using XRD that was accelerated by salt spray.

Name of sample	***AC1***
Magnetite	++
Aka ganeite (42-1315)	++
Lepidocricite	++
Goethite	+
Hematite	+

Table (9-6) Shows the comparison between the iron oxide and oxi-hydroxides (Group A)

This table shows most of iron corrosion compounds that were found in the iron coupons. Also, it shows most of the results of analyzed samples. Sometimes the other samples were different in the percentage of corrosion compounds. The solid samples of 3×3×2 mm^3 in size were cut from the edge of the iron coupons and were collected in a powder form from the oxidized surface for XRD analyses.

9.2.3 Ion chromatography

This method was used to evaluate the level of chlorides before the desalination. Most of the results were accomplished and confirmed by atomic absorption, because the use of nitric acid led to a fault in the results of ion chromatography.

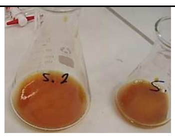
	*Gro. A*	*Cl^- (mg/l)*
The sample after dissolving the oxidized layer and filtration	*Before the treatment*	*4052*

Table (9-7) the chloride level before the desalination

9.2.4 The results of Vicker hardness test

Vicker hardness was measured after preparation of the samples and exposure to the accelerated aging method.

The sample	**The outer layer/hv**	**The interior layer/hv**
AC before exposing for any accelerated aging	194	194
AC (salt spray)	175.5	189.2-198.7

Table (9-8) Vickers hardness test of the iron coupon before the desalination treatment

CHAPTER 10

DIAGNOSES OF IRON ARTIFACTS FROM SYROS MUSEUM AND PAROS ISLAND BY INVESTIGATING AND ANALYZING BEFORE THE DECHLORINATION TREATMENT

Generally, iron objects are considered the most excavated artifacts from the marine environment, although oxidation is one of their most important activities leading to corrosion. From two different archaeological excavated sites, thirty two iron artifacts were coming from Paros and Syros Islands in different forms and sizes. The iron artifacts were diagnosed by combination methods to know the effect of the desalination treatment methods for removing the chlorides. The primary purpose of these combination methods is to determine the proportion of different elements (chlorides) and minerals present (akaganeite) in a material before the treatment, and it is generally used for characterizing the efficiency of the treatment methods for decreasing the chlorides level, removing the corrosion layers and marine compounds. Each artifact was analyzed prior to determine the best conservation procedure for that specimen.

Samples of the seawater, the marine encrustation and the corrosion products of the cast and the wrought iron artifacts were diagnosed. The samples were taken randomly from the objects for investigation and analysis. The samples were cut from the metal and the oxidized layers (interior and exterior).

The cast iron cannonballs artifacts

About 3-4 samples were taken randomly from the oxidized surface from loose layer of objects that were removed before, during and after the desalination. The evaluation was performed for the interior and exterior layers.

The wrought iron objects

One sample was cut from the edge of the core metal beside some sample were cut from the exterior oxidized layers.

10.1 Diagnosis with the naked eye

Diagnosis with the naked eye is a first step in the artifacts dechlorination treatment. The thickness of the corrosion layer of the wrought iron is about 0.3-2 cm (visible to the *naked eye*), but the thickness of the corrosion layer of the cast iron is about 0.1-0.5cm. Most of the objects are in good state, but about 6 objects are completely corroded. The artifacts were covered by an outer agglomerated crust, containing iron oxides with high concentration of chlorides associated with low amount of marine compounds such as quartz sands grains, calcite and clay minerals.

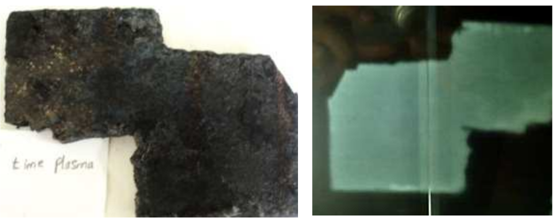
10.2 Results of the investigation methods

The primary aim of the archaeological investigation of the objects is to get a clear understanding of the state of the artifacts.

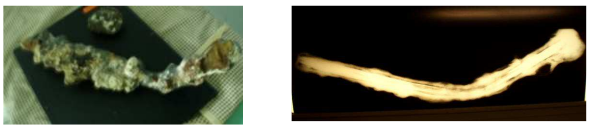
10.2.1 X-ray radiography

X-ray radiography is a non-destructive scientific method employed for evaluating the state of artifacts before the treatment. This technique is a main stage of the investigation of the metal objects from the seawater because they can be wrapped rapidly during the use of the desalination methods. Also, it can find out the original size and shape of the artifacts which are different as indicate by the following pictures:

The thin section from the fragments of completely corroded



This object is in a good state



This object isn't completely corroded, but most of the encru
cotnains marine compounds.

This object has a residual metallic core, but has at
time a thickness layer from the iron corrosion layer
calcareous compounds

X-ray radiography of the fragment

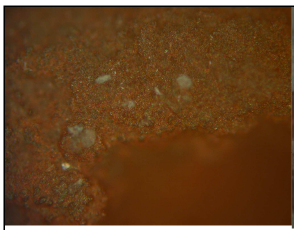
The completely corroded object

Photo (10-1) X-ray radiography for the objects

Five of the fragments were investigated by X- ray radiography that provides additional information about the initial structure.

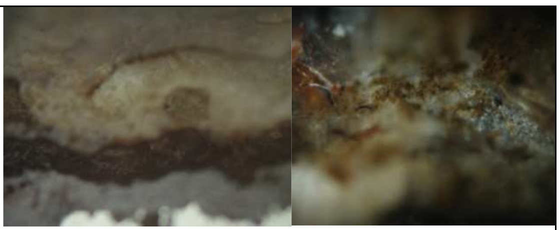
10.2.2 Results of the examination by metallographic microscope

The metallographic examination of artifacts revealed the corrosion layers before the treatment.



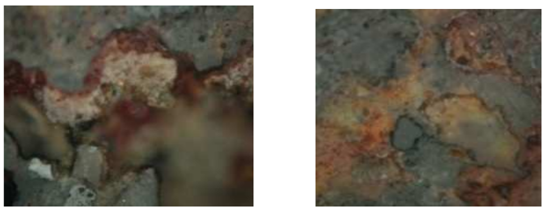
US 7 Before the treatment
photo shows the earthy co
X500

US11 before the treatment T
shows the marine compounds
the treatment. X500

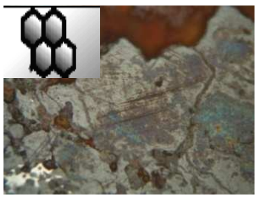


US12 before the desalination treatment
X500

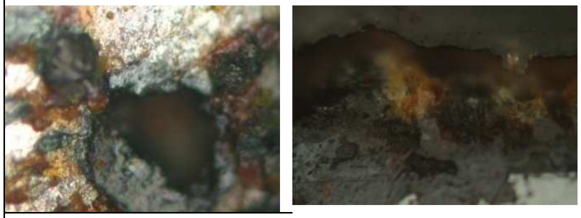
The layers of oxides of US



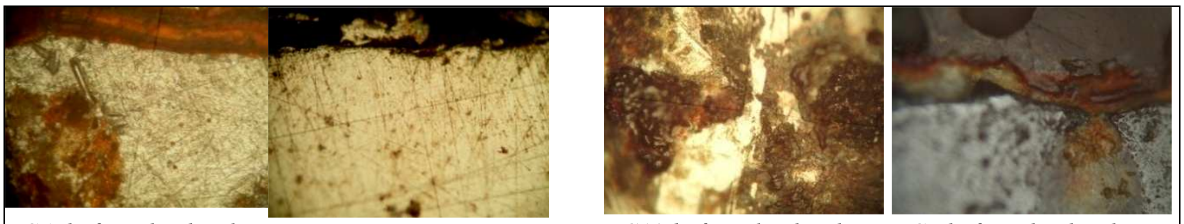
US8, The exterior layer of the marine compounds whi
with the iron oxides. X500



US8, the intergranuler cor
X500



US1 the thickness of the corrosion layers combined with
marine compounds. X500



US6, before the desalination treatment

US10 before the desalinati treatment

US5 before the desalinatio treatment

US4 before the reduction treatment of the corrosion lay

US2 before the desalination treatment

Photo (10-2) The results of examination by metallographic microscope

10.3 Results of the analysis methods

10.3.1 The results of analysis of sea water in Greece (mg/l)

The study of the marine environment is to evaluate the effect of the chemical elements on the iron objects. The seawater samples were analyzed by atomic absorption analysis for (Na, Ca, Si, Mg, Fe, Mn, K, and Al), silver nitrate for evaluating (Cl) and pH of the samples were tested.

The samples	***Na***	***Cl***	***Ca***	***Si***	***Mg***	***Fe***	***Mn***	***K***	***Al***	***pH***
Crete	+++	*22245*	*295*	*1.41*	*990*	*0.18*	*0.05*	*116*	*0.49*	*8.5*
Paros	++++	*25205*	*412*	*0.68*	*1530*	*0.19*	*0.03*	*535*	*0.61*	*8.5*
Rodeos	++++	*23075*	*385*	*0.56*	*1230*	*0.17*	*0.4*	*510*	*0.61*	*8.5*

+ The sample had a high level of sodium that could not be measured.

Table (10-1) Results of sea water environment by atomic absorption analysis

Generally, the pH of seawater is (4.5-8.5). The results showed that the sea elements in Paros Island are higher and more critical than the other environments. Paros Island has the highest level of chlorides and the most corrosive environment, but Crete has a less aggressive environment.

10.3.2 Results of XRD

Before the treatment of the artifact, the results showed that magnetite was detected in the corrosion layer with a very low quantity, but the oxi-hydroxide compounds as akaganeite, lepodocrocite and goethite were detected in the corroded layers with a very high level.

The objects which were reduced by pure hydrogen plasma at 200ºC, Group F2, *(US7, US8, US9, US11, US12)* from Paros Island

Samples of items were analyzed from the outer and inner crust, so the spectra showed large amounts of minerals from the marine environment and have created a solid encrustation with iron oxide corrosion. Four objects from this group are flat, which were covered by hard aggregations consisting of minerals as sodium chloride NaCl, quartz SiO_2, calcium carbonate $CaCO_3$, albite $NaAlSi_3O_8$, anorthite $CaAl_2Si_2O_8$, orthoclase and sulfur compounds such as gypsum which mixed with metal oxides.

Duration	*Magnetite*	*Aka.*	*Geo.*	*Lepi.*	*Hem.*	*Iron sulfate*	*Orthoclase*	*Quartz*
US8	++	+++	+	+	+	+	++	++
US9	++	++		++	+	+	+++	+++

Table (10-2) Diffraction patterns of objects of US8 and US9

The results showed that the chlorine-containing β-FeOOH(akaganeite) were present in all objects before analysis.

US2 (Group F1) was reduced at 300ºC

This object had a substantial proportion of oxy-hydroxides on the external corrosion layer before treatment. This layer has a high content of akaganiete.

Mineral	***Before treatment***
Magnetite	+
Akaganeite	++
Hematite	+
Goethite	+
Lepidocrocite	++
SiO_2	+++
Orthoclase	+++

Table (10-3) The results of the analysis by XRD of US2

US5 (Group F1)

The following table shows the minerals before the reduction treatment. Magnetite was detected before the treatment in the low concentration, but akaganeite was identified before the treatment as the major mineral. Results of X-ray diffraction analysis showed that the marine encrustation compounds such as the red brown clay and calcareous compounds in exterior layer. This layer was not easily removable for many times of the reduction treatment by hydrogen plasma reduction.

Dura.	Mag.	Aka.	Geo.	Lepi.	Hem.	Orthoclase	Quartz	Iron sulfate
before	++	+++	+	+	+	++	+++	+

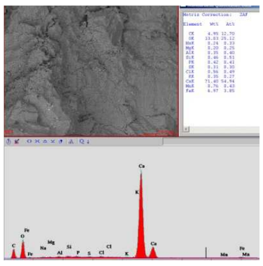
Table (10-4) Results of analyses by XRD of US5 (Gr.F1)

10.3.3 Results of SEM and EDS

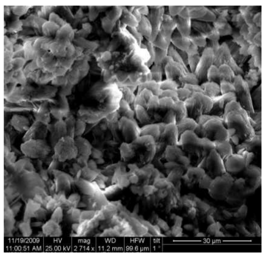
Most of the objects had a thick layer of the encrustation of the marine encrustation compounds (reddish brown clay from the iron oxides in the seabed) mixed with the corrosion layer. After and before each stage, SEM and EDS were the main method for evaluation the chloride level and the effect of desalination methods. EDS was used to measure the elementary composition and state of the artifacts.

The results of seabed analysis

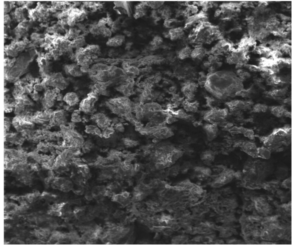
The chlorides ions diffuse through the encrustation back into the surrounding sea water.

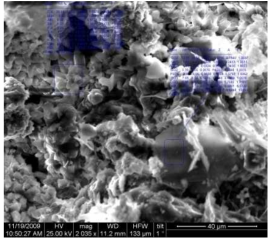


The seabed analysis, White minerals



The photomicrograph of white mineral





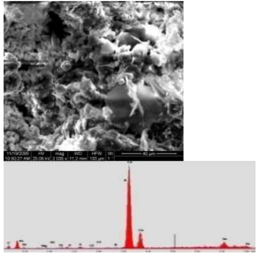
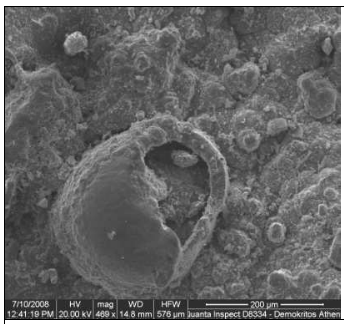


Table (10-5) SEM of red-brown clay

The results show that Paros Island has the highest level of chlorides and the most corrosive environment. Crete has a less aggressive environment.

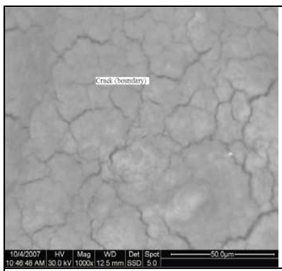
The results of SEM and EDS of the iron objects from Paros Island



```
Elem     Wt %  Mol % K-Ratio    Z       A       F
------------------------------------------------------------
 Na2O    9.43  15.45  0.0126  1.0021  0.1797  1.0011
Al2O3    7.41   7.39  0.0135  0.9981  0.3424   1.0032
 SiO2   15.01  25.38  0.0318  1.0277  0.4395   1.0025
 P2O5    3.60   2.58  0.0080  0.9941  0.5114   1.0034
 Cl2O    3.14   3.67  0.0181  0.9757  0.7196   1.0076
  CaO    5.48   9.94  0.0362  1.0030  0.8999    1.0241
Fe2O3   55.93  35.59  0.3592  0.9195  0.9985  1.0000
kV: 25.00  Tilt: 0.00  Take-off: 35.00  AmpT: 51.2
Det Type:SUTW, Sapphire   Res: 131.59  Lsec: 246
```

Table (10-6) US7, Gro. F2, morphology of the object surface before the treatment that show the clay mineral and

US9, Group F2



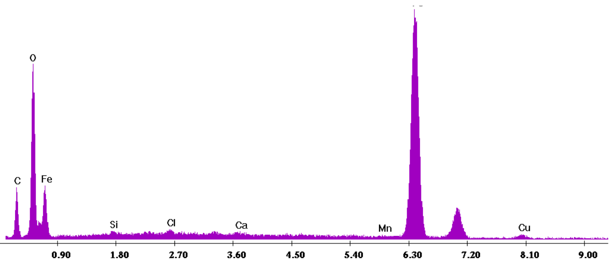
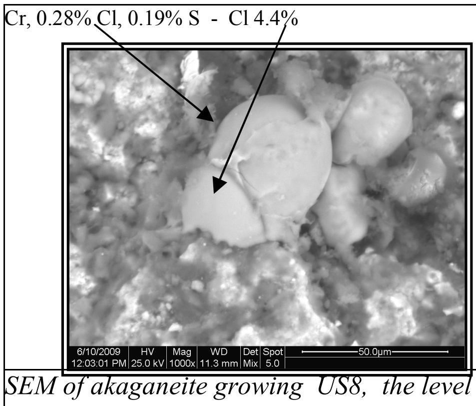
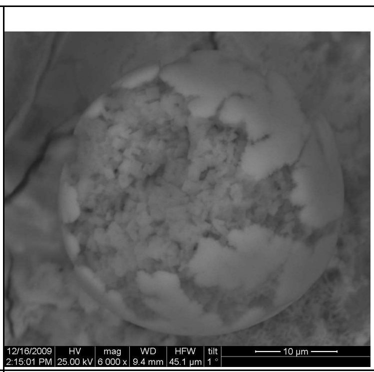


Table (10-7) US9 before plasma reduction treatment and SEM photograph shows the marine encrustati surface of the object

US8, Group F2

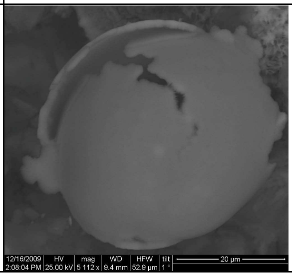


SEM of akaganeite growing US8, the level of chlorides is 4.4% Cl



The form of the chloride granular

```
Elem    Wt %  At % K-Ratio    Z       A       F
------------------------------------------------------------
 O K   25.78  52.38  0.1009  1.0994  0.3551  1.0024
 NaK    1.08   1.53  0.0016  1.0307  0.1407  1.0004
 MgK    0.66   0.88  0.0014  1.0571  0.2026  1.0006
 AlK    0.64   0.77  0.0019  1.0264  0.2882  1.0017
 SiK    0.39   0.45  0.0016  1.0567  0.3956  1.0030
 P K    0.38   0.40  0.0020  1.0221  0.5148  1.0053
 ClK    6.63   6.08  0.0493  1.0079  0.7317  1.0085
 MnK    0.30   0.18  0.0028  0.9298  0.9954  1.0000
 FeK   64.13  37.33  0.6094  0.9484  1.0019  1.0000
Total  100.00 100.00
```



EDS-SEM for other form of chloride granular

Table (10-8) US8 before hydrogen plasma treatment that revealed the large amounts of chlorine *in the exterior layer of this object*

US12, Group F2

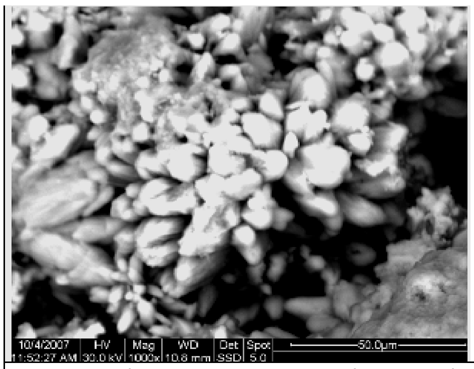
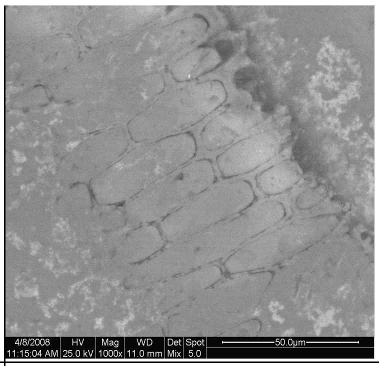
	
Scanning electron microscope photographs of marine encrustation before desalination treatment	*US12 before the desalination treatment, and this picture shows intergranualar corrosion*

Table (10-9) The surface feature of US12

US4, This object was divided into 3 parts before desalination treatment methods

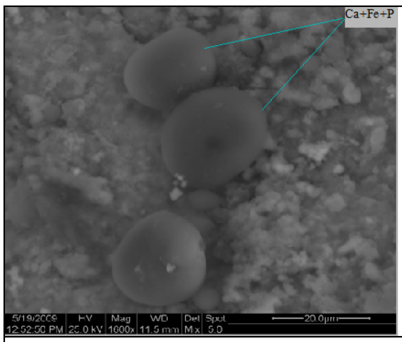
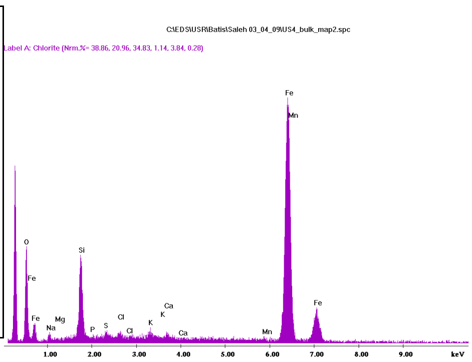
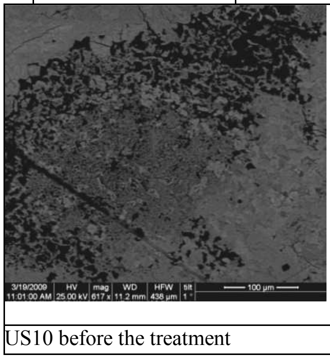
	
US4 before the treatment	

Table (10-10) SEM and EDS of US4 before the treatment

US10, Group F3

Us10	Ca	S	Mg	K	Si	Mn	Cl	O	Na	Fe
Before the treatme	0.36	1.14	0.57	0.64	2.06	----	4.08	25.48	1.43	64.24



US10 before the treatment

```
Elem    Wt %  At % K-Ratio   Z      A      F
----------------------------------------------------------
 O K   31.06  59.60  0.1266  1.0923  0.3722  1.0022
 NaK    0.40   0.54  0.0006  1.0240  0.1412  1.0002
 SiK    0.23   0.26  0.0010  1.0499  0.4070  1.0029
 S K    1.16   1.11  0.0079  1.0422  0.6464  1.0082
 ClK    4.42   3.82  0.0329  1.0006  0.7370  1.0090
 K K    0.63   0.50  0.0055  1.0047  0.8502  1.0241
 CaK    0.19   0.15  0.0018  1.0277  0.8955  1.0391
 FeK   61.90  34.03  0.5853  0.9418  1.0040  1.0000
Total  100.00 100.00
```

Grey spot EDS of US10

```
Elem    Wt %  At % K-Ratio   Z      A      F
----------------------------------------------------------
 O K   24.15  50.05  0.0890  1.1007  0.3340  1.002
 NaK    1.89   2.73  0.0027  1.0319  0.1405  1.000
 SiK    0.57   0.67  0.0024  1.0580  0.3985  1.0033
 S K    1.54   1.59  0.0103  1.0501  0.6345  1.0093
 ClK    5.83   5.45  0.0430  1.0094  0.7232  1.0092
 K K    0.89   0.75  0.0077  1.0134  0.8320  1.023
 CaK    0.37   0.31  0.0035  1.0364  0.8791  1.038
 FeK   64.77  38.45  0.6147  0.9496  0.9995  1.00
Total  100.00 100.00
```

Black spot EDS of US10

Table (10-11) SEM and EDS US10, before hydrogen plasma treatment and it shows the exterior layer of this object

US20, Group F6

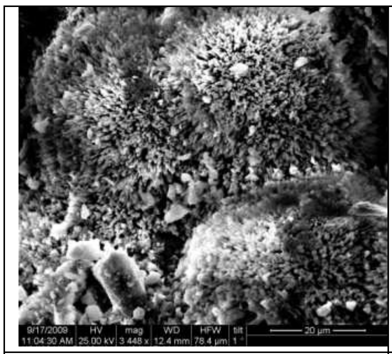
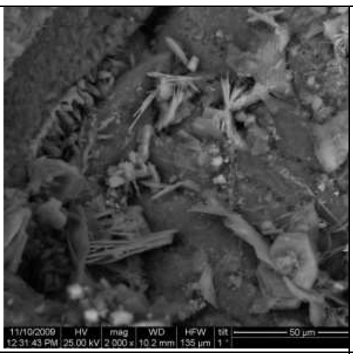
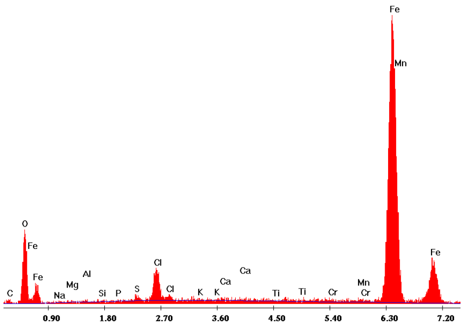
		
US20 before the treatment and the collection of the chlorides	*The red clay with corrosion products*	*US20 before the treatment and the collection of the chlorides.*

Table (10-12) SEM-EDS of US20

The results of analyses of cast iron artifacts

Cast iron objects had a high percentage of chlorides.

B1, Group (E), high level of chloride before the desalination

```
 Elem     Wt %  At % K-Ratio   Z      A      F
-------------------------------------------------------------
 O K   32.27  60.47  0.1285  1.0892  0.3650  1.0020
 AlK    0.35   0.39  0.0011  1.0169  0.3034  1.0019
 SiK    1.25   1.33  0.0055  1.0470  0.4163  1.0031
 P K    0.79   0.76  0.0043  1.0127  0.5312  1.0051
 S K    0.31   0.29  0.0021  1.0393  0.6423  1.0087
 ClK    5.63   4.76  0.0419  0.9973  0.7405  1.0083
 K K    0.11   0.08  0.0009  1.0014  0.8448  1.0231
 CaK    0.40   0.30  0.0038  1.0244  0.8945  1.0372
 MnK    0.89   0.48  0.0081  0.9205  0.9973  1.0000
 FeK   58.02  31.14  0.5466  0.9388  1.0035
```

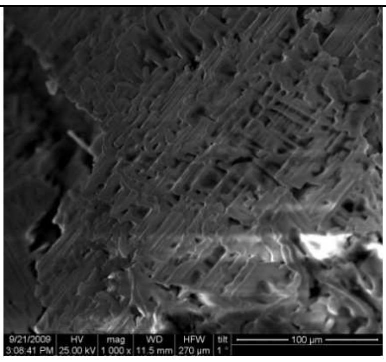
Table (10-13) The interior layer before the treatment

Ti	***P***	***Ni***	***O***
0.25	*0.15*	*1.82*	*35.56*
Si	***S***	***Mn***	***Mg***
0.30	*0.21*	*0.41*	*0.22*
Fe	***Cl***	***Ca***	
52.77	*8.16*	*0.15*	

Table (10-14) The interior layer of B1

B2, Group E, the crystallization of NaCl on the object

```
 Elem     Wt %  At % K-Ratio   Z      A
-----------------------------------------------
 O K   18.75  30.85  0.0393  1.0703  0.1954
 NaK   28.67  32.82  0.0882  1.0036  0.305
 MgK    1.67   1.81  0.0045  1.0294  0.2631
 AlK    0.71   0.69  0.0025  0.9997  0.3555
 SiK    0.51   0.47  0.0025  1.0293  0.4736
 P K    0.52   0.44  0.0031  0.9957  0.5957
 S K    4.83   3.96  0.0356  1.0220  0.7044
 ClK   29.97  22.25  0.2200  0.9751  0.7516
 K K    0.25   0.17  0.0018  0.9792  0.7098
 CaK    0.21   0.13  0.0016  1.0030  0.7800
 MnK    0.11   0.05  0.0009  0.9021  0.9598
 FeK   12.19   5.75  0.1094  0.9196  0.9739
 CuK    0.38   0.16  0.0033  0.8911  0.9753
 AsK    1.25   0.44  0.0105  0.8447  0.9960
Total 100.00 100.00
```



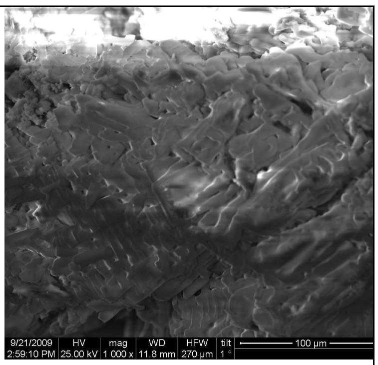


Table (10-14) Spot EDS and SEM of the interior layer that revealed the high amount of NaCl

B3, high level of chlorides

Elem	Wt % The outer layer before the treatment	Element Wt % of The inner layer before the treatment
O K	*23.63*	*19.86*
SiK	*2.11*	*0.25*
P K	*0.25*	*1.30*
S K	*0.33*	*0.42*
ClK	*6.22*	*5.08*
CaK	*0.50*	*0.57*
MnK	*0.42*	*1.40*
FeK	*65.77*	*70.58*
Nak	*0.35*	-----
K K	*0.27*	*0.34*
AlK	------	*0.19*

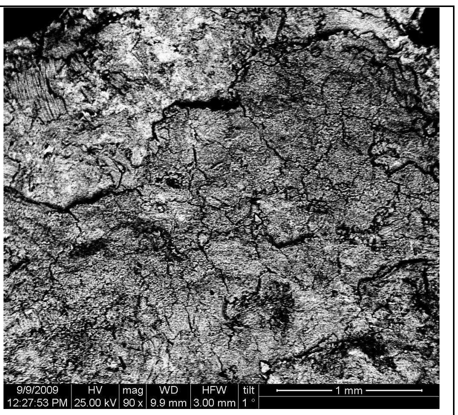
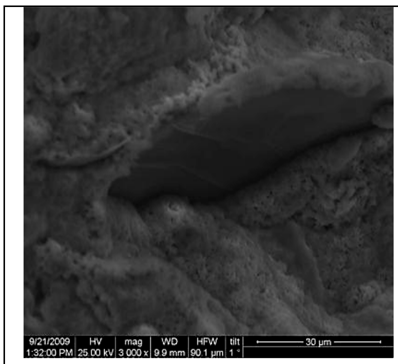
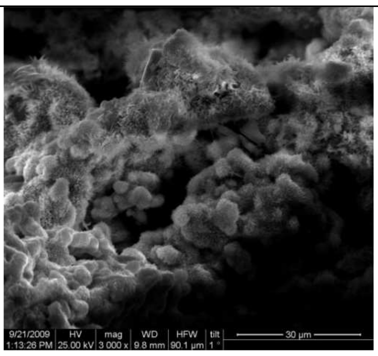


Table (10-15) EDS and SEM and of B3 (high level of chlorides)

B4, before the treatment

		
The crystal of carbon in the exterior layer (the graphite flakes)	*B4 before the desalination treatment*	*Bulk- analyses of B4, and the high level of chlorides*

Bulk- analyses of B4, and the high level of chlorides

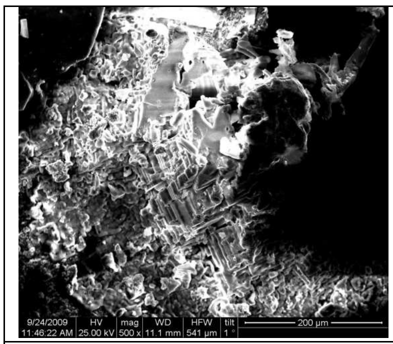
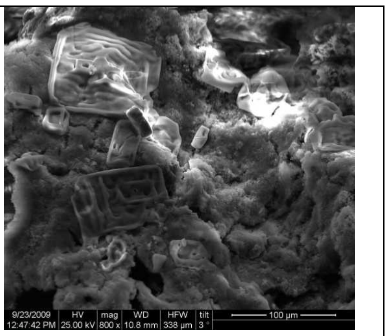
```
 Elem    Wt %  At % K-Ratio   Z      A      F
-------------------------------------------------------
 O K  38.76  62.65  0.1209  1.0681  0.2917  1.0011
 NaK   3.67   4.12  0.0067  1.0015  0.1818  1.0011
 MgK   0.48   0.51  0.0012  1.0272  0.2528  1.0021
 AlK   0.26   0.24  0.0009  0.9975  0.3577  1.0043
 SiK   2.12   1.95  0.0106  1.0271  0.4821  1.0068
 P K   9.69   8.09  0.0571  0.9935  0.5904  1.0051
 S K   1.90   1.53  0.0121  1.0197  0.6221  1.0067
 ClK   3.87   2.83  0.0269  0.9752  0.7081  1.0070
 K K   0.50   0.33  0.0041  0.9792  0.8327  1.0150
 SnL   2.29   0.50  0.0191  0.8019  1.0236  1.0160
 CaK   1.91   1.23  0.0172  1.0024  0.8821  1.0197
 MnK   1.25   0.59  0.0110  0.9013  0.9826  1.0000
 FeK  33.31  15.43  0.3036  0.9190  0.9918  1.0000
           Total  100.00 100.00
```

Table (10-16) SEM- EDS before the treatment of B4

The completely corroded artifacts

The completely corroded object has the highest percentage of chlorides.

US18 (Compleytly corroded object)

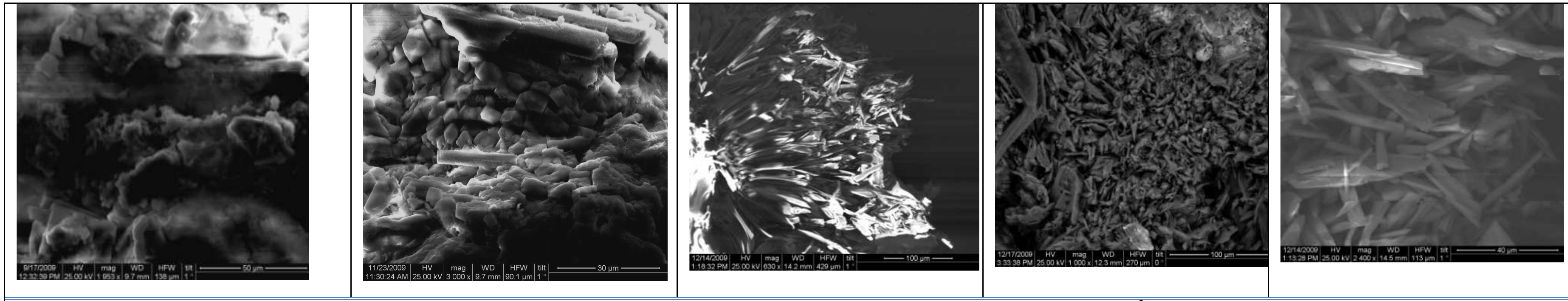
		
The interior layer US18	*The interior layer*	*The organic material inside the object*

The interior layer

```
 Elem    Wt %  At % K-Ratio   Z      A      F
-------------------------------------------------------
  O K  45.40  66.86  0.1017  1.0468  0.2139  1.0006
  NaK   4.06   4.16  0.0082  0.9816  0.2047  1.0012
  MgK   1.80   1.74  0.0051  1.0068  0.2808  1.0020
  AlK   0.64   0.56  0.0024  0.9778  0.3874  1.0039
  SiK   1.45   1.21  0.0075  1.0068  0.5143  1.0064
  P K   0.17   0.13  0.0011  0.9739  0.6288  1.0113
  S K   7.94   5.84  0.0593  0.9996  0.7390  1.0105
  ClK   3.91   2.60  0.0283  0.9535  0.7521  1.0119
  K K   0.60   0.36  0.0051  0.9575  0.8620  1.0298
  CaK  13.56   7.97  0.1216  0.9808  0.9049  1.0107
  MnK   0.19   0.08  0.0016  0.8822  0.9684  1.0018
  FeK  18.89   7.97  0.1670  0.8993  0.9805  1.0027
  NiK   0.33   0.13  0.0028  0.9143  0.9556  1.0031
  ZnK   1.06   0.38  0.0090  0.8727  0.9757  1.0000
   Total  100.00 100.00
```

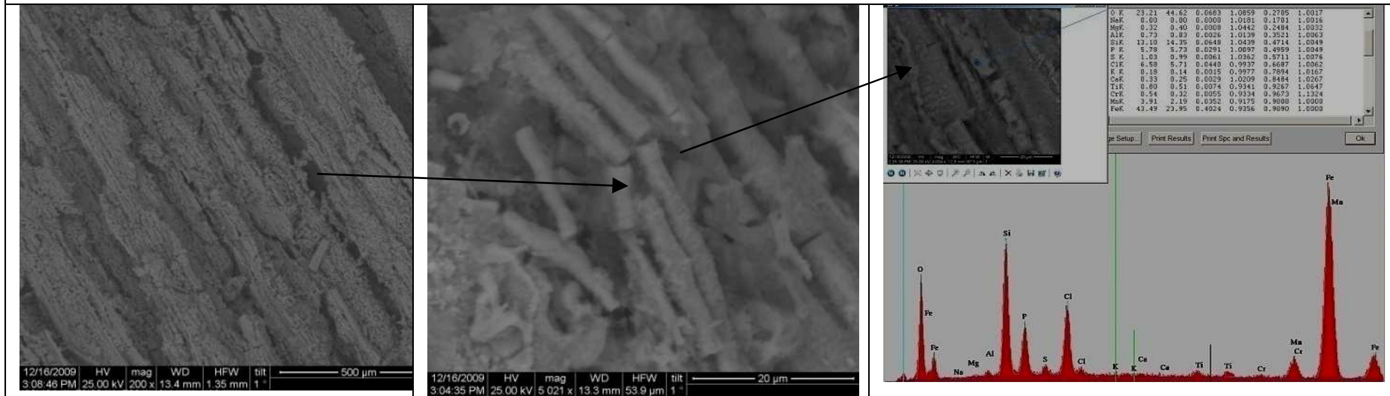
(10-17) Results of analyses by SEM and EDS of completely corroded object US18

US19, Group G



Elem	Wt %	At %	K-Ratio	Z	A
NaK	41.05	51.69	0.2029	1.0130	0.4866
MgK	0.24	0.29	0.0007	1.0390	0.2752
AlK	0.14	0.16	0.0006	1.0090	0.3882
SiK	0.04	0.04	0.0002	1.0389	0.5169
P K	0.23	0.21	0.0015	1.0050	0.6432
S K	2.87	2.59	0.0232	1.0315	0.7496
ClK	53.13	43.39	0.4217	0.9842	0.8056
K K	0.40	0.30	0.0025	0.9884	0.6232
CaK	1.75	1.26	0.0124	1.0124	0.7022
MnK	0.00	0.00	0.0000	0.9105	0.9261
FeK	0.15	0.08	0.0013	0.9281	0.9467
Total	100.00	100.00			

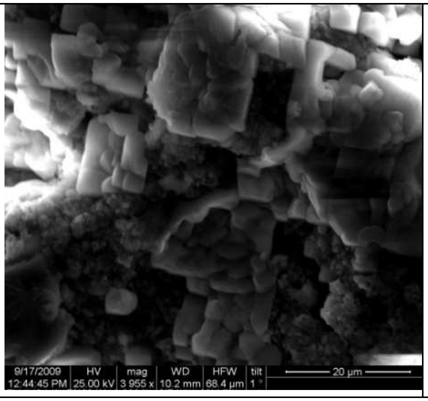
Photo (10-18) The forms of sodium chlorides on the completely corroded objects. The cubic granular in picture one (3.6µm^2) and dendritic-form of sodium chloride in picture no. three.



O K	23.21	44.62	0.0683	1.0859	0.2705	1.0017
NaK	0.00	0.00	0.0000	1.0181	0.1701	1.0016
MgK	0.32	0.40	0.0008	1.0442	0.2484	1.0032
AlK	0.73	0.83	0.0026	1.0139	0.3521	1.0063
SiK	13.10	14.35	0.0648	1.0439	0.4714	1.0049
P K	5.78	5.73	0.0291	1.0097	0.4959	1.0049
S K	1.03	0.99	0.0061	1.0362	0.5711	1.0076
ClK	6.58	5.71	0.0440	0.9937	0.6687	1.0062
K K	0.18	0.14	0.0015	0.9977	0.7894	1.0167
CaK	0.33	0.25	0.0029	1.0209	0.8484	1.0267
TiK	0.80	0.51	0.0074	0.9341	0.9267	1.0647
CrK	0.54	0.32	0.0055	0.9334	0.9673	1.1324
MnK	3.91	2.19	0.0352	0.9175	0.9000	1.0000
FeK	43.49	23.95	0.4024	0.9356	0.9890	1.0000

US25 is completely corroded object

The magnification of spot shows the line corrosion



Elem	Wt %	At %	K-Ratio	Z	A	F
O K	18.66	31.29	0.0359	1.0705	0.1797	1.0008
NaK	22.42	26.17	0.0840	1.0016	0.3733	1.0019
MgK	2.37	2.62	0.0090	1.0267	0.3671	1.0030
AlK	0.70	0.70	0.0034	0.9964	0.4870	1.0057
SiK	0.83	0.79	0.0053	1.0253	0.6146	1.0103
P K	0.59	0.51	0.0043	0.9909	0.7225	1.0182
S K	3.97	3.33	0.0335	1.0146	0.8088	1.0273
ClK	30.34	22.96	0.2508	0.9698	0.8473	1.0059
K K	0.32	0.22	0.0026	0.9750	0.8038	1.0126
CaK	10.08	6.75	0.0864	0.9977	0.8555	1.0033
MnK	0.27	0.13	0.0023	0.8912	0.9614	1.0004
FeK	9.18	4.41	0.0812	0.9077	0.9733	1.0006
NiK	0.24	0.11	0.0022	0.9211	0.9759	1.0000
Total	100.00	100.00				

SEM photo for pure crystal of sodium chlorides

Photo (10-19) Results of investigation by SEM and analysis by EDS of US2 (completely corroded object)

CHAPTER 11

THE METHODOLOGIES OF THE DESALINATION TREATMENTS OF THE IRON CORRODED COUPONS AND IRON ARTEFACTS

This study began in 2006. At the first time, we had some problems to find the iron artifacts from marine environments to apply the plan and the best results from the experimental parts. After transformation the iron artifacts into the Demokritos, we started to take the photos. Modern wrought and cast iron artifacts were investigated by unrestrictive methods as microscopes, X-ray radiography and by cutting some samples from the metal and samples from the oxidized layers. The desalination treatment is to make stable iron artifacts for a long term after excavation by using chemical treatment and/or pure hydrogen plasma. This approach provides an effective methodology for the chloride removal techniques that can be used to desalinate the iron artifacts from the marine environment. In our work, desalination treatment was carried out on batches of iron objects. The state of object or the level of the chlorides determines the technique that can be used.

11. 1 Description of the dechlorination treatment method

Desalination was accomplished by the chemical treatment and/or pure hydrogen plasma for removing the chlorides ions.

11.1.1 Sodium hydroxide (Stabilization storage after excavation of the objects)

It is considered the most effective solution and a widely-used method to desalinate the chlorides from the iron objects after removing from the marine environments. Sodium hydroxide contains (>99% of NaOH), (<1% Na_2CO_3), (0.0005% Cl) and other trace elements. NaOH is a non-volatile substance; the solution was changed every 2 weeks to reactivate this solution. The chloride level was measured by using silver nitrate and SEM. The standard of the chemical treatment of our experiments on the coupons and modern iron artifacts was according to Selwyn (2004). This method was used by completely immersing the object in 1.5-2% (w/v) sodium hydroxide (pH 13.5, at room temperature), and every 2 weeks the sodium hydroxide bath was renewed. Sodium hydroxide treatment was used until the chloride level decreases; followed by immersion in distilled water in order to remove the residue of chemical treatment (Selwyn 2004). In this case, sodium hydroxide used for chemical treatment with NaOH solution in 2% (dilute solution) which consists of 2 grams of NaOH dissolved in 98 grams of water by completely immersing the coupons in this solution.

During the desalination treatment, the loose layer was removed mechanically. After finishing from the treatment by the chemicals, we immersed the objects in the distilled water to remove the residue of these solutions. That means the immersion in distilled water after the chemical treatment with tested pH of the water and chemical analyses by silver nitrate, is the main stage before drying and coating to give the final appearance of the object. Periodically, the rinsing bath must be changed and monitored for evaluation of the chlorides level by using the analytical method of EDS and silver nitrate. The drying of the objects after the chemical treatment is a necessary stage before the coating.

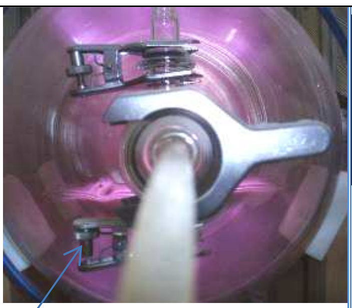
11.1.2 Sodium hydroxide in heating condition

The coupon was desalinated by 2% sodium hydroxide at the heating condition to remove completely the chlorides in short time, at 50ºC, according the previous work. The chloride extraction rate is increased by raising the temperature.

11.1.3 Plasma reduction desalination treatment

Plasma reduction was applied since 1979 (Daniels et al., 1979, Patscheider and Vepřek 1986). RF glow discharge plasma device made by Vacotec is similar to Veprek's (Veprek *et al.*, 1988). The technique is based on the reductive action of cold hydrogen atoms, which react chemically, mechanically and physically with the products of oxidation of the metal surface object. Those procedures were recently adopted by the Plasma Laboratory of N.C.S.R "Demokritos" with the purpose of cleaning and restoring archaeological artifacts. For the past ten years intensive studies have been undertaken in our Laboratory. We did not use methane in our work because the side effect on our health and the environment but Argon was used to clean the oven after the treatment. We have studied the plasma-surface interaction theoretically, by taking into consideration a number of experimental conditions. In this way, we described the plasma sheath parameters (ion- electron velocity, ion- electron density, sheath potential). We enforced firstly an external d.c. potential on the treatment object, in order to affect the plasma sheath potential and the reduction rate. Expanding our conception, we passed a d.c. current between objects and plasma, and led into some important results on the cleaning and restoring rate. By present work, we extended these procedures on iron objects removed from marine environments, and resulted in very interested inferences, as the presence of the chloride compounds containing iron corrosion products.

pho. (11-1) Plasma thermometer and the Pyrex tube during reduction. This picture shows the iron objects in the Pyrex tube during reduction by 100% hydrogen gas with orange color and the thermometer.



The bright orange light resulted from the hydrogen atoms

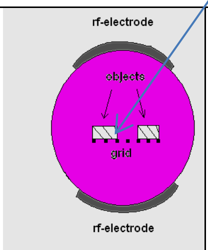
Pho. (11-2) The machine of plasma in Demokritos

Power supply

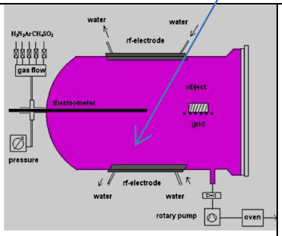
The gases tubes

The Pyrex tube and the objects

Cooling syste



Pho. (11-3) the furnace temperature measurement



1at=760 Torr

1at=105 pa

Fig.(11-1) Schematic diagram of the Demokritos plasma reactor

The reactor consists of a Pyrex glass longitudinal cylinder (discharge tube) of 40cm inner diameter and 130cm in length. The reactor cylinder was evacuated to 10Torr by means of a mechanical Alcatel vacuum pump. Gases (Ar, H_2, CH_4, N_2) were introduced through needle valves and flow meters that are attached to the reactor. Methane was not used in our work because of the side effect on our health and the environment, but Argon was used to clean the oven after the reduction treatment. Temperature was measured with a mercury thermometer inserted along the axis of the discharge in a silica-glass case. The power from RF generator (27.12MHz, 4kW) is coupled through two copper electrodes, 34cm × 90cm, placed externally along the reactor. Both the generator and the electrodes are cooled by water. The artifacts are placed in Pyrex grids along the long axis of the reactor cylinder. It has also been successfully applied to the conservation of different iron artifacts. The technique is based on the reductive action of hydrogen atoms, which react chemically with the oxidized products of the metal object. In low pressure glow discharge plasmas, the electrons have sufficient energy to enable them to break the hydrogen molecules in subjects at low temperature and pressure.

Hydrogen plasma generated 100% H_2 gas in the tube (furnace) for *reduction* of the chlorides and oxides and to burn out the surface contaminations (soluble salts). Hydrogen reduction treatment utilizes a furnace heated with hydrogen gas to essentially burn out the soluble salts embedded in the iron object over a period of 6-7 days. *It was focused in the middle of the reactor from outside, through a quartz glass port in the Pyrex tube.* Before starting the treatment process, the small machine needs 30-40 minutes for heating the furnace, but the large one needs 90-120 minutes for heating the furnace at 600ºC as indicated in figure (11-1). The object that was undergoing hydrogen reduction was placed in the hydrogen furnace and slowly raised from 20 to 300˚C. The temperature depends on the amount of power forwarded, gas percentage, and power reflected (the lesser amounts). Iron coupons and artifacts were reduced at different ranges of temperature 150, 200, 300ºC (Aged by salt spray and sodium chlorides).

11.1.3 Plasma reduction treatment combined with chemical treatment

Iron coupons, two cast cannonball and some modern wrought iron objects were desalinated by using hydrogen plasma reduction combination of NaOH desalination.

11.1.4 Chemical treatment combined with hydrogen plasma

Iron coupons, two cast cannonball and some modern wrought iron objects were desalinated by using NaOH combination of hydrogen plasma reduction desalination.

11.1.5 Sodium hydroxide at the heating condition combined with H_2 Plasma

10 coupons were desalinated by immersing in NaOH, at 50˚C (heating condition). In this case, the treatments increases the chlorides transport rate. After that, the coupons were treated by low hydrogen plasma at 100ºC.

11.2 The drying process

When the desalination treatment of the object was finished, artifacts were dried. After that, the each artifact was put in a separate nylon bag with a silica gel.

The drying by solvents: For the smooth objects, the solvents were sufficient to dry the surface of the coupons and objects.

Air blast at room temperature (was not effective on the porous metal objects as cast iron), but it was effective on the smooth surface metal.

Oven drying: The objects were put in the *oven* at 50ºC for 20 hours.

The drying by plasma: Heating at low temperature by plasma is the best method because it can be passivated at the surface before the protection process.

Silica gel: Is an important material that control humidity during the storage of the iron.

11.3 The protection methods of the objects

The *main* goal of the protection process is to prolong the age of the objects as long as we can and to decrease the risks of transformation and to improve the appearance of the objects. After applying the protection materials the objects are in good condition, without cracks in the surface.

11.3.1 Tannic acid

The artifact was successfully sealed, when it was dehydrated in a solvent such as acetone or ethanol and/or was dried by oven heating to dry the objects after wet treatment. Tannic acid works well as an oxide inhibiter because it forms a barrier of corrosion resistant tannate film on the iron object. The pH of tannic acid should be at least 2.4; if a higher pH is recognized, the addition of phosphoric acid can be used to lower the pH of the solution. The object should be coated several times with brushed on layers of the solution allowing the object to dry between coatings.

Logan recommends a tannic acid solution consisting of:

(a) 100g tannic acid
(b) 50ml ethanol
(c) 900ml deionized water

11.3.2 Paraloid B72 (2-3%)

We used the paraloid B72 with acetone to protect wrought iron objects. Paraloid B-72 general-purpose thermoplastic acrylic resin is similar to Paraloid B-66 acrylic resin, but capable of forming softer films. Paraloid B-72 acrylic resin is unique in possessing a high tolerance for ethanol (Chapman and Mason 2003).

11.4 The storage of the objects

After protection, each artifact was put in a separate nylon bag with a silica-gel in a metallic case. Silica gel is a crystal that absorbs a certain amount of moisture. Once it has absorbed that amount of moisture, it has to be dried out again to keep working.

11.5 The desalination treatment of the iron corroded coupons

The goal of this experiment was to assess, the effect of the treatment methods on the iron coupons, which is better to compare the results because they have the same state and size. Depending on the way of preparation of the coupons, we divided them into 8 groups, each group has 5 coupons. The different substrates, with a total number of iron coupons, were divided into the following categories. The samples were desalinated for 20-30 hrs at 100 –300°C, at 0.65 kW power and 0.6-1 Torr pressure. The following table shows the condition of reduction treatment.

ΟΜΑΔΑ ΠΛΑΣΜΑΤΟΣ				Salt spray		ΗΜΕΡΟΜΗΝΙΑ	16/1/2008
ΑΝΤΙΚΕΙΜΕΝΑ			AC2 a	AC3a			
ΩΡΑ	ΑΕΡΙΑ		P	T	Power	IR	ΠΑΡΑΤΗΡΗΣΕΙΣ
	H2	N2	(Torr)	(C)	(w)	(C)	
12:52	0,9		0,96	60	0,6	0,01	
13:15	0,9		0,96	80	0,6	0,02	
13:30	0,9		0,95	200	0,6	0,04	plasma start
13:50	0,9		0,95	200	0,6	0,04	
14:10	0,9		0,95	200	0,6	0,04	
14:30	0,9		0,95	210	0,6	0,04	
15:20	0,9		0,95	210	0,56	0	
15:40	0,9		0,95	210	0,56	0	
16:55	0,9		0,95	210	0,56	0	
16:15	0,9		0,95	210	0,56	0	plasma off

Table (11-2) the model of recording the information of desalination of the coupons by pure hydrogen plasma

Also, the samples were desalinated by using 2% sodium hydroxide for 2 weeks, and/or low temperature hydrogen plasma for 20 hours.

11.6 The treatment of the selected iron artifacts

Greece is a country in the southern Mediterranean with a total shore length of 16,575Km (Garrod and Wilson 2003). Greece has many islands (Chlorinated environment) and is blessed with an extensive and abundant marine environment.

Firstly, the iron artifacts were desalinated using the following methods:-

Group	The objects	The goal
F	Iron objects in good state, from Paros island	To check the effect of the difference treatment methods (chemical treatment, plasma reduction and the combination between the two methods)
F1	H_2 Plasma (250-300ºC)	
F2	H_2 Plasma (150-200 ºC)	
F3	H_2 Plasma (100-130 ºC)	
F4	H_2 Plasma followed by NaOH	
F5	NaOH followed by hydrogen plasma	
F6	NaOH	
G	Completely corroded-Paros island	The effect of low temperature of plasma treatment
H	Cast iron cannonball	To check the effect of the difference treatment methods (chemical treatment and/or plasma reduction.

Table (11-3) the groups of iron artifacts

Only 30% of all the objects were unstable, but most of them were badly or completely corroded, and they had a thick layer from the marine encrustation associated with corrosion compounds. The objects of the present study are made of wrought and cast iron in different condition, dimensions, weights, and forms that were investigated, analyzed, treated and protected. Some objects were washed with distilled water to remove residues of chemicals, followed by drying and protection by inhibitors or protection materials.

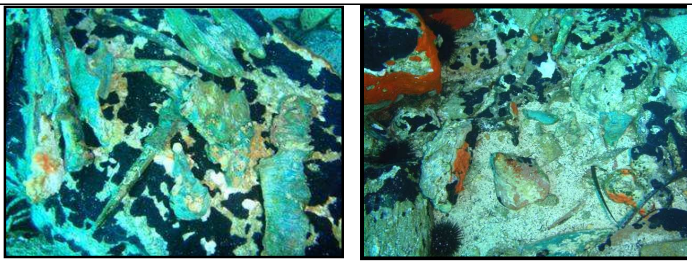
11.6.1 The desalination of the wrought iron artifacts from Paros Island

Most of the artifacts have 2-4 heavily encrusted layers from marine and corrosion products with thickness of 0.2-4cm, resulting from the condition of the marine environment. The completely corroded objects are porous consisting of mainly calcium and iron corrosion compounds. The iron objects have been **mechanically cleaned** firstly by hammer, scalpel, brushes and dental tools or air blast, before and during the treatment by hydrogen plasma and/or chemical treatment, to remove the marine and corrosion products. This process included removing marine encrustations and corrosion compounds (loose deposits). The documentation of the object before the treatment by Photographs, weighing, geometry and scale drawings was recorded. 36 Modern iron objects from Paros Island, most of which are in good state, but 4 objects are completely corroded. When they were transferred to the conservation laboratory the artifacts were covered with corrosion crusts and marine encrustation. Most of these objects are chains, because they are used in lifting the objects from the ships. A chain is a series of connected links which are typically made of metal. The objects were brought from Paros in large tank with enough seawater. The artifacts were completely covered by water.

The iron artifacts from Paros Island are considered modern artifacts or were aged 'naturally' in the seawater for long-term. The following photos show the changes in state, appearance and size of the iron artifacts.

The Calcareous clay stone

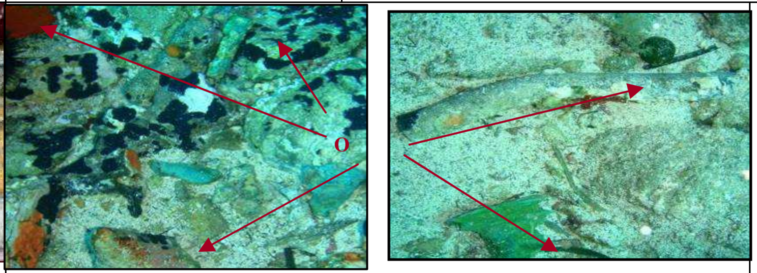
The marine plants in Paros



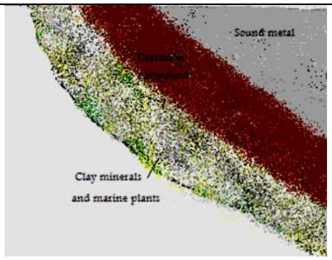
Long time-of-wetness, Low oxygen, High level of chlorides

The objects in the first environment

The objects after excavation



The first environment of the objects in Paros island



The corrosion layers of the marine iron objects

Reddish brown iron oxide

US2o

US5

US6

US10

US4

US2

US8

US9

US7

US11

US12

Group (F3) which treated by hydrogen plasma at 130ºC

Group F2 which treated by pure H2 plasma at 200 ºC

Photos (11-4) *Samples of the iron artifacts from Paros Island*

The prior treatment (Immediate treatment after excavation)

Some artifacts from Paros Island were stored in distilled water to prevent them from drying out and to prevent further decay by the osmotic effect of the salts (mainly chlorides salts and active corrosion). The iron objects and fragments were carefully removed from the original environment. The divers in Paros Island have good conservation strategies on the site and after the excavation, the objects were immersed in 50% fresh water and 50% sea water, after that the objects were immersed in 100% fresh water.

Artifacts removed from marine conditions are usually found encrusted and enclosed by other item in one mass as shown in photo (11-4). These collections have more than 32 modern iron objects (according to the Greek law) which were divided into eight groups. The big or large objects were cut to small pieces and they were treated by different methods. Iron oxides, calcareous, and marine compounds were the most common material found in encrustations, so the most common conservation solutions chosen are those that will render passive chemical reactions of iron (sodium hydroxide), and yet keep other possible associated materials safe. We collected some iron oxides from the objects before the treatment as indicated in photo (11-4). Experimentation should be carried out on the modern objects due to the structural and competitive heterogeneity.

Group F1

The treatment was conducted by using 100% hydrogen plasma which was at temperature of (280-300°C) and the pressure of 1.50-1.60 Torr. The objects in this group were first treated in plasma for long duration of time, in the range of 1 to 5 hours (initial treatment), followed by 120 hours. In order to determine which transformations at the corrosion layer were due to the effect of heating, and which occurred under the action of H_2 atoms, one sample was simply heated in an oven at a temperature of 300°C.

		
Photo (11-5) Group F1 in plasma machine	*Photo (11-6) US4 before and after desalination treatment*	

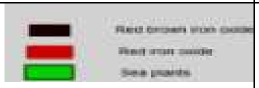
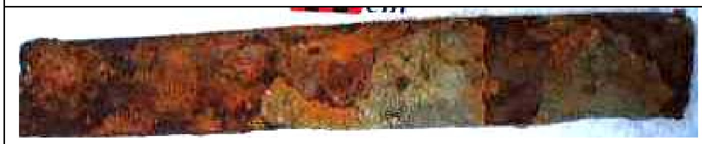
This object was cut into 3 parts. The first and the second were treated by hydrogen plasma reduction in different conditions and the third was treated by sodium hydroxide. Some objects were divided into two or three parts to compare the different treatment methods.

Group F2 (250ºC)

This group has 5 modern objects (US7, US8, US9, US11, US12) in different shapes treated with pure hydrogen plasma for over one week (long durations) but this duration was not enough to remove completely the chlorides. The exterior layer became more easily to be removed mechanically during the treatment by using plasma reduction.

Group F2 (US11)

The dimensions of this object (46.7×7.5 cm^2), the calcareous, marine compounds and iron oxides deposited over the surface.

	*Before the treatment*	
		
		*A drawing of the corrosion layers*
	*During the treatment by hydrogen plasma at*	
	*After the treatment by hydrogen plasma*	

Photos (11-8) shows the state of object before and after the treatment and coating by paraloid B72

US8 (Group F2)

The object was covered with the calcareous encrustations combined with the iron oxides. The object was treated by plasma reduction. This object was treated on the oven of plasma at 200ºC for one week. During the reduction treatment, the mechanical treatment was used to remove all accessible corrosion.

				
Before the treatment	*After mechanical treatment*	*After 3hrs plasma reduction*	*After finishing the treatment method and protecting by paraloid B72*	

Photos (11-9) the stages of the treatment of the object by hydrogen plasma

US7 (Group F2)

In this case, ordinary object was brought from Paros in plastic or net bag with seawater.

	*The length of the object was 23.6cm before desalinating*
	*After12hrs, plasma reduction, and changing in the thick. The object lost 0.5cm for cutting the sample for analysis.*

Photos (11-10) The stages of the treatment by hydrogen plasma of US7

US9 (Gr. F2)

The dimension of this object 27.5×8.5cm^2

				
Before the treatment		*After 3hrs plasma*	*After 100hrs plasma*	*After finishing the treatment*

Photos (11-11) the stages of the treatment by hydrogen plasma reduction treatment

US12 (Group F2)

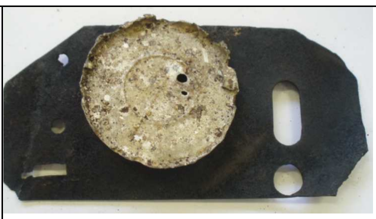
The thick encrustation of the corrosion layer and the marine encrustation compounds was of 0.2cm which was removed mechanically, but the problem was to remove or decrease the concentration of the chlorides. The dimension is of 15×9.3×0.5cm^3. This produced no sensible change in weight,

					
Before the treatment and exterior layer	*The interior layer after removing*	*During the reduction treatment by plasma* *Pho. (11-12) The stages of the treatment of the object (US8)*			*After the treatment*

From these photos, the colour gradually changed through the reduction treatment.

Group F3 ***(130°*C)**

100% hydrogen plasma was used in low temperatures (100-130°C) and the pressure was 0.55-0.65 Torr.

	
Pho. (11-12) The object inside the furnace of plasma. The right photo shows the appearance of the surface after desalination by plasma	

US6*:* This object was treated for long durations in the range of 1 to 100 hours.

			
Before the treatment	*During the treatment*	*The final treatment by using the plasma reduction*	*After protection the objects by paraloid*

Photo (11-13) the stages of the treatment of US6 by hydrogen plasma at low temperature

The treatment by chemical solutions with mechanical treatment

Objects were first immersed in seawater for two weeks followed by seawater + fresh water for another two weeks and after that the objects were lifted from the bath to start the treatment method. Then the object was treated for long duration of time in sodium hydroxide for four months.

Group 4, 5: Some objects are desalinated by NaOH and/or hydrogen plasma.

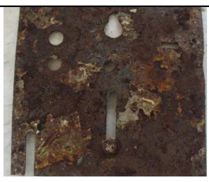
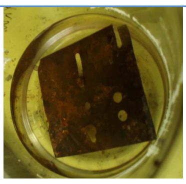
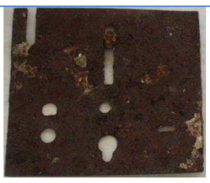
Group F6

The following object was treated by 2% sodium hydroxide for 5 month and was protected by paraloid B27. This object was closed with wire 25cm in length.

				
The object before the treatment	*The exterior layer of corrosion*	*After the treatment*		*After protection*

Pho. (11-14)The object before and after the treatment

US4 object was divided into 3 parts

				
US4-Before dividing and desalinating. The photo shows the calcareous compounds on the surface.		*During the treatment by using sodium hydroxide that hadn't any effect the surface encrustation*		*After desalination for 14 weeks, but 2% NaOH removed some points from the outer layer*
		Photo (11-15) The stages of the treatment of US4		

The treatment of the completely corroded object (Group G)

The completely corroded object suffers from the high level of chloride as Akaganeite.

The first object

Photos (11-16) A part from the ship

The maximum length of 56.6 centimeters, the oxides was closed to the metallic core.

The second object

This object is completely corroded (according to the investigation by X-ray radiography).

			
Line corrosion like old wood structur due to the marine environment or internal corrosion and the high percentage of chlorides		🟥 Iron oxides ▨ Seabed sediments *Documentation by draw*	*The length is 15cm and the diameter is 2.5cm. It is completely corroded and fragil. The object was treated in a reducing plasma glow discharge of 100% H2 at pressure of 0.80Torr to 1Torr, and at a temperature range of 40°C to 80°C.*

Photo (11-17) shows the completely corroded object

The third object

The length is 24.7cm

	
The object after removing immediately from fresh water (An active corrosion situation)	
	
After drying the object and efflorescence of salts	*photos (11-18) The corroded objects a thick layer of concretion*

The fragments

		
Shells inside the iron fragment	*The exterior surface of the object*	*The section from inside the fragments*

Photos (11-19) the fragments of iron oxides

11.6.2 The treatment of the cast cannon-balls (*Group H)*

The passenger steamer "Patrice" was one of the ships of the Greek steamboat company, which was the first ferry company founded in Greece. It was a luxury ship, constructed by iron, 217 feet in length, 28 feet in width, 787 tons in weight, and 180 horsepower by speed. Divers do remove metal artifacts from the sea without any conservation planning. They do move the objects away from Port to Museum and create an exhibition place to protect them.

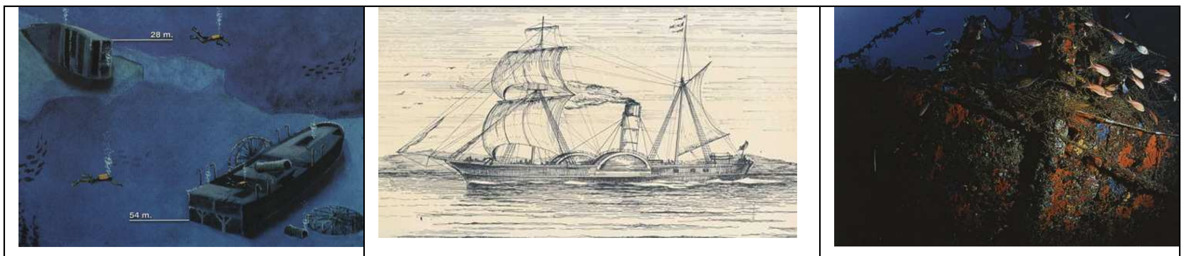


Photo (11-20) Patrice shipwreck, One of the largest shipwrecks of its kind in the Mediterranean region After: http://www.ketepo.gr/en/temporary-exhibitions/

During filming, one of the two steamship wheels, weighing 14-16 tons and lying 52 meters underwater, as well as a number of other finds, were salvaged and placed in a special, purpose-build wing at the Industrial Museum in Syros.

The selected excavated cast iron artifacts retrieved from the wreck, south west from the island of Kea in the Aegean Sea, which sank in 1868 (February 23), when paddle wheel steamer was on it's way from Piraeus to it's home port Syros, when it hit a reef and sank (Great crash). In 2006 the collection of objects was brought up, which were transferred to the Industrial Museum of Syros. They were delivered to the Metals conservation laboratory of the Department of Conservation of Antiquities and Works of Art, at TEI of Athens. Finally, the 4 cast iron cannonballs were transferred to Demokritos.

Four cannon balls made of cast iron from Syros Island were treated by using either hydrogen plasma reduction or chemical treatment using NaOH solution, and a combination of them for a comparison study. These methods have been employed to remove the chloride content which is the main problem in the corrosion process and to passivate the iron objects.

The success and the duration of the treatment by using 100% hydrogen plasma (60-170 hours) depended on the state of the object (cast iron is very hard but remains brittle due to its micro-crystalline structure) and the temperature range of 200-250˚C. The duration of the treatment by sodium hydroxide for 4-5 months depended on the state of the object and the concentration of the solution (1.5-2% w/v); and a contributing factor to it's success as a treatment solution was it's high pH of 13.5 at room temperature, giving it the ability to stop corrosion by passivation of iron artifacts. Every two weeks the sodium hydroxide bath was renewed. Before and after each stage of treatment, the removal of chloride and the marine encrustation materials were evaluated by SEM, EDS and silver nitrate methods.

The treatment of the first cannon ball (Group H)

This object was treated by a combination of chemical treatment by completely immersing it in NaOH, followed by using pure hydrogen plasma. Firstly, the treatment started by immersing the object in 1.5% (w/v) sodium hydroxide (pH 13.5, at room temperature), for four months. And the object was immersed in distilled water for one month. The solution was changed every two weeks. The chlorides were measured by silver nitrate. After that, it was treated by hydrogen plasma at 200-220ºC for 60 hours. During that process, chloride was measured by means of EDS, and we concluded whether an additional elimination of the chloride was to take place. After immersion in sodium hydroxide, the object was desalinated by hydrogen plasma.

<table>
<tr><td></td><td></td><td></td></tr>
<tr><td>B1 before the treatment</td><td colspan="2">Photos show the collection of chlorides during immersion in 2% sodium hydroxide, and the quantity of chlorides released during the early stage of washing. The cracks and exfoliation which occurred during the chemical treatment</td></tr>
</table>

<table>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td>This photo show the submerged corrosion during the extraction of the chlorides by sodium hydroxide</td><td>The object had thickly covered with iron oxides, chlorides and calcareous encrustation</td><td>During the immersion in distilled water. The cracks in the exterior layer that it is 0.3-0.5cm in the thickness</td><td>After finishing the chemical desalination</td></tr>
</table>

Photos (11-21) The stages of the desalination treatment of B1 by sodium hydroxide, and shows the migration of the chlorides to the surface.

<table>
<tr><td></td><td></td><td></td></tr>
<tr><td>B1 after 3hrs plasma</td><td colspan="2">B1 during the reduction treatment by hydrogen plasma and revealed some pitting</td></tr>
</table>

<table>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td colspan="2">B1 after 30 hours plasma reduction, The holes caused by collection of chlorides</td><td colspan="2">After coating by tannic acid</td></tr>
</table>

Photos (11-22) the stages of the treatment by plasma reduction, the migration of the chlorides to the surface

The weight of the cannon was about 16.6kg before the desalination, but after the desalination treatment the weight was about 16kg.

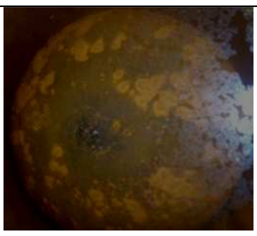
The dechlorinaion treatment of the second cannonball

The object was unstable in the post-excavation because it had active chlorides. The marine environment contains varying amounts of salt concentration on the surface. The object was treated by using plasma reduction at a temperature range of 200-250˚C for 170hrs. *After desalination treatment* the metal was protected with tannic acid. *Geometry of this object is* 11kg in weight, 13cm in diameter, and 46cm in circumference.

		
Photo shows the object that had some cracks before starting the reduction treatment by plasma.	*The object after reduction for 3hrs.*	*After 30hrs plasma reduction*
		
The loss of the most of external layer during the treatment by plasma reduction for 80hrs	*The exfoliation of the oxidize layer for 100hrs*	*High level of chlorides under the exterior layers after reduction for 130hrs.*
	Photos (11-23) The stages of the treatment by pure plasma reduction	

The treatment of the third object

This object was treated by simply and completely soaking in 1.5 % W/V sodium hydroxide and a pH of 13.5 at room temperature. Distilled water was used to remove the chemical residues of sodium hydroxide, at that time distilled water changing was carried out every two weeks, preceded by tests for chloride ions by silver nitrate and EDS. The cannonball was dried in the hydrogen plasma at low temperature of 80ºC. The weight of B3 before the desalination was 11.75Kg and after the treatment was 11.5Kg.

			
The red rust of the object before beginning the desalination		*The state of the cast iron object after immersing in sodium chlorides for 2 weeks*	
			
After immersion in sodium hydroxide for five months	*After rinsing in distilled water for removing the chemical residues*	*Exterior layer after drying the object*	*The object after applying for tannic acid*

Photos (11-24) The stages of the treatment by sodium hydroxide of the third cannonball

The treatment of B4

After cleaning the object by hydrogen plasma reduction for (24h) at 200-220ºC and decreasing the concentration of chlorides, the object was lifted up from the oven after cooling for 24 hours, and it was immersed in 1.5% W/V sodium hydroxide NaOH of pH 13.5 for 4 months. The solution was changed every two weeks to be more reactive in order to remove the chlorides. The pH was 13.5 during the whole period of the treatment till the endpoint of this process. The object was immersed in distilled water for removing the residues of sodium hydroxide. Tannic acid was used after drying the object on the oven of plasma at 80ºC. Before the treatment, the weight of the object was 12.23Kg, but it weighed 12Kg after finishing the treatment, and during the chemical treatment it weighed 13Kg.

		
The object before the treatment	*The first stage of the treatment by hydrogen plasma*	*During the desalination treatment by sodium hydroxide*

		
After immersing in distilled water	*After heating by hydrogen plasma for drying*	*After finishing the desalination treatment and protection of the object*

Photos (11-25) the stages of the treatment by pure hydrogen plasma followed by sodium hydroxide

After finishing the desalination treatment the cannonball artifacts will be returned to storage or display in a suitable place in the museum of Syros.

CHAPTER 12

RESULTS OF TREATMENT MONITORING OF THE IRON COUPONS

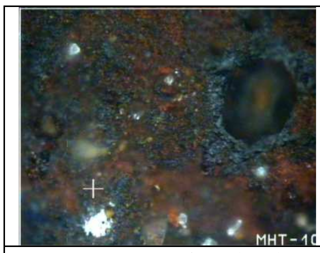
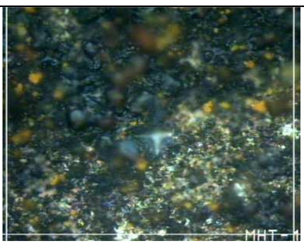
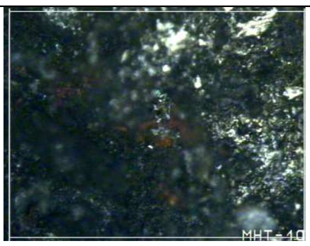
This chapter aims to compare the effectiveness of the different desalination treatment methods to remove the chlorides from the coupons. Many methods of examination and analysis have been carried out in order to have good results on the effectiveness of these dechlorination methods. Three types of iron coupons were used for the experimental application of the desalination methods.

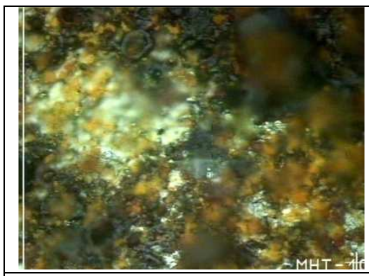
The corrosion compounds on the surface of the coupons which were exposed to sodium chlorides were not in adherence, so as to be cleaned easily. Iron oxides compounds on the surface of the iron coupons which were corroded in the salt spray cabinet were in adherence. So, they were used in the chemical treatment and/or plasma reduction. The coupons were oxidized by sodium and iron chlorides that were used in plasma reduction.

The corrosion layer on the surface of the coupons was desalinated rapidly and easily by plasma reduction and/or by chemical treatment in most of the coupons.

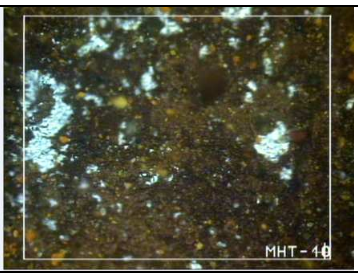
12.1 Results of investigation by microscopy

Examination of the iron surface coupons was performed by using stereo and metallographic microscope.

		
AC1a - X500 After the desalination treatment for 3hours by stereo microscope, (Gro.A).	*AC4a-X500, after the reduction treatment for 3hours by stereo microscope, (Gro.A).*	*This photo shows AC3a - X200, magnetite layer after reduction the coupon by plasma for 3hours (stereo microscope), (Gro.A).*



This photo shows the transformation on the coupons surface after reduction for 3hrs- X500 by stereo microscope (Gro.A)



This photo shows AC3a by stereo microscope-X500 after reduction for 3hrs. Maghemite was the main compound (stereo microscope), (Gro.A)

The Photos of the iron chlorides after reduction for 9hrs under metallographic microscope (Gro. D)

Photo (12-1) The results of investigation under stereo and metallographic microscope

12.2 Results of analyses methods

Several analysis methods were performed to assess treatment methods of iron coupons simulating the condition of the iron artifacts.

12.2.1 Results of X-ray diffraction (XRD)

The analysis by XRD is one of the best evaluation methods for identification of the corrosion compounds after desalination. Powdered samples from the coupons were analyzed during and after the desalination treatment. The results were obtained from analysis of most of the coupons during each stage of desalination. The Peaks of the major, minor and trace elements revealed the effect of different desalination treatment methods.

AC1 (Aged by Salt spray, Group A)

Table (12-1) shows the effect of plasma on the iron coupons. This coupon was oxidized by salt spray. At the same time, the phase of magnetite had a minor peak with hematite, after reduction by hydrogen plasma for 3 hours. Detection of magnetite (black mineral) is obviously after reduction at low temperature for 18 hours.

Minerals	**After 3hrs**	**After 9hrs**	**12hrs**	**15hrs**	**18hrs**
Magnetite	++	+++	++++	++++	++++
Maghemite	++				
Akaganeite	+++	+++	++	+	
Lepidocricite	+	+			
Goethite					
Hematite	+				

(*)The no. card of akaganeite is 42-1315, the chemical structure is $Fe(O, OH)_{16}$

Table (12-1) The effect of plasma on the iron corrosion at low temperature of AC1, at 100-130°C

Lepodicrocite was transformed into magnetite after 9 hours, but goethite was removed completely after 3 hours.

AC2 (Aged by Salt spray, Group A)

After 3 hours reduction of the coupons at a temperature of 300ºC, a phase analysis of them gave the following main constituents: the phase of maghemite γ-Fe_2O_3 was the major compound, a phase that was visible, because it has brown color and can be formed by the dehydration of lepidocrocite in high percentage.

Mineral	**After 3hrs**	**6hrs**	**9hrs**	**12hrs**
Magnetite	+++	++++	++++	++++
Maghemite	+	+	+	
Akaganeite	++			
Hematite	+	+		
Goethite				
Lepidocrocite	+	+		

Table (12-2) Results of analyses by XRD for the coupons

Akaganeite, lepidocrocite and goethite were markedly reduced as shown by table 12-2. *Despite, the akaganeite was reduced, but we found about 0.25% chlorides by EDS.* X-ray diffraction shows that the oxide reduction is completed after 12 hours of treatment in hydrogen plasma at a temperature of 300°C.

Samples	**Gas/Pressure**	**Temp.**	**Dura.**	**Magnetite (Major)**	**Akaganeite (completely removed)**	**Geothite (completely removed)**	**Lepidocrocite (completely removed)**	**Hematite (completely removed)**
AC1	H_2 0.55-60 Torr	100-130°C	21hrs	After 21hrs	After 21hrs	After 3hrs	After 21hrs	After 15hrs
AC2	H_2 1.12-1.26 Torr	250-300°C	15hrs	After 12hrs	After 15hrs	After 3hrs	After 12hrs	After 3hrs
AC3	H_2 0.90-0.95 Torr	150-200°C	21hrs	After 15hrs	After 18hrs	After 3hrs	After 21hrs	After 6hrs

Table (12-3) the results by XRD of the analysis of the powdered samples.

12.2.2 Ion chromatography

Before the desalination, the level of chloride was 1796.8 ppm.

The type of the desalination	Chloride level
2% NaOH at room temperature for 2 weeks	132 ppm
2% NaOH (heating condition) for 10hrs, at 50ºC	695 ppm
Hydrogen plasma reduction for 20hrs, at 300ºC	30 ppm

Table (12-4) the results of analysis by ion chromatography for the iron coupons

The above table indicates that hydrogen plasma was the fastest in decreasing chloride level within a short time. High temperature condition of the plasma decreased the duration of desalination treatment.

Photo (12.2) The coupon after reduction by plasma for 20hrs at 200ºC, Magnetite is the major mineral. The oxide layer was removed by nitric acid

12.2.3 Results of SEM and EDS

SEM analysis of iron coupons were carried out to confirm the results of the desalination methods. Each stage of the treatment was assessed by SEM and EDS until the stabilization of the treatment to determine the best desalination procedure for that specimen.

Results of SEM and EDS from each category of samples, before and after each stage of treatment are shown as follows.

<u>AC1 (120-130 ºC)</u> (Aged by Salt spray, Group A)

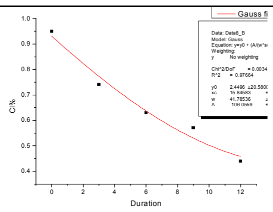


Fig. (12-1) Concentration of Cl- as determined by EDS of AC1that was desalinated at 120-130ºC (Aged by Salt spray). After desalination for12 hours, the chloride level was 0.48%, (Group A).

<u>AC2 (250-300 ºC)</u> (Aged by Salt spray, Group A)

Chlorides were completely removed after desalination by hydrogen plasma at 270-300ºC for 15 hours, not in favor of using high temperature.

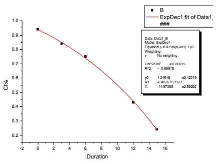
<table>
<tr><th>Elements</th><th>Fe</th><th>O</th><th>Cl</th><td rowspan="5"> </td></tr>
<tr><td>3hrs plasma</td><td>67.13</td><td>31.60</td><td>1.27</td></tr>
<tr><td>6hrs plasma</td><td>85.65</td><td>14.54</td><td>0.91</td></tr>
<tr><td>9hrs plasma</td><td>93.38</td><td>6.45</td><td>0.17</td></tr>
<tr><td>12hrs plasma</td><td>87.78</td><td>12.34</td><td>0.28</td></tr>
<tr><td colspan="5">*AC2 was desalinated at 250-300ºC (Aged by salt spray). After desalination for12hours, the chloride level was 0.28%, (Group A).*</td></tr>
</table>

Table (12-3) The desalination of AC2 by hydrogen plasma, (Group A).

AC3 at 150-200ºC

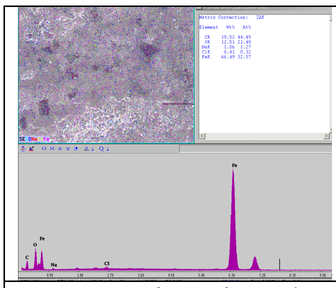
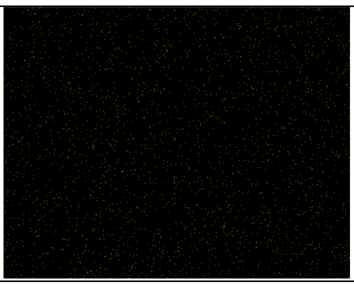
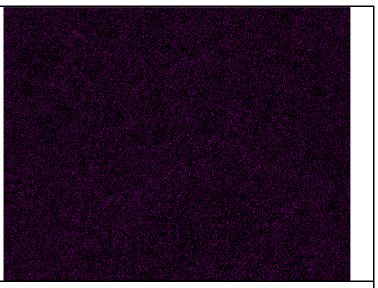
The coupons were desalinated at 150-200ºC; Group A (Salt spray, Group A)

The 1st gr.	**Fe**	**O**	**Cl**
Before plasma	78.57	20.58	0.85
3hrs plasma	79.23	19.84	0.93
6hrs plasma	83.55	15.67	0.78
9hrs plasma	84.45	13.93	0.62
12hrs plasma	84.85	14.68	0.47

Table (12-4) the desalination of AC3 by hydrogen plasma, (Group A)

Depending on the desalination treatment duration, H_2 plasma was able to significantly reduce the thickness of corrosion layer and chloride level. At this state, chloride removal was so slowly.

SEM/ EDS results of AC at temperature of 210-220ºC during reduction condition by hydrogen plasma

		
Map-SEM of AC after reduction at 210-220ºC for 12 hours	*Cl*	*Fe*

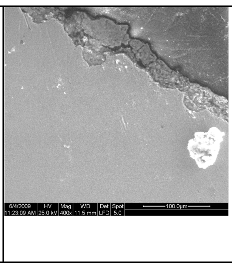
```
Matrix Correction:   ZAF

Element    Wt%   At%

  CK     19.52 44.45
  OK     12.51 21.40
 NaK      1.06  1.27
 ClK      0.41  0.32
 FeK     66.49 32.57
```

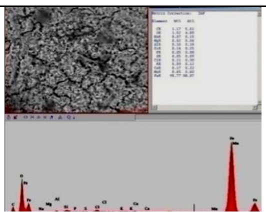
Fig. (12-2) Map-SEM of the coupon for 12hrs at 210-220ºC

Cl concentration was 0.43% after reduction by hydrogen plasma for 12hrs

2% NaOH combined with plasma reduction (Group A)

```
Elem     Wt %  At % K-Ratio    Z       A       F
---------------------------------------------------------------
 O K   16.61  40.30  0.0734  1.1203  0.3929  1.0037
 NaK    1.14   1.92  0.0015  1.0501  0.1257  1.0000
 AlK    0.00   0.00  0.0000  1.0456  0.2591  1.0010
 ClK    0.42   0.46  0.0030  1.0300  0.6947  1.0104
 MnK    0.66   0.46  0.0062  0.9489  0.9988  1.0000
 FeK   80.30  55.80  0.7809  0.9680  1.0046  1.0000
Total  100.00 100.00
```





The thickness of corrosion layer is about 69.6 μm, After one week imn sodium hydroxide combined with hydrogen plasma at 200 ºC for 15hrs

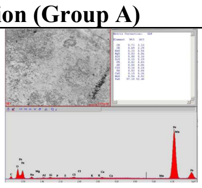
After the treatment by sodium hydroxide for one week combined with 20hrs hydrogen plasma. Chloride level is 0.23%

Elements	**Fe**	**O**	**Na**	**Mn**	**Cl**
Before sodium hydroxide	74.36	23.55	----	-----	1.04
After NaOH treatment for 2 weeks	77.43	20.73	----	1.06	0.88
5hrs plasma	76.12	19.63	1.82	0.66	0.53
10hrs plasma	75.23	18.15	2.44	0.64	0.59
15hrs plasma	80.30	16.61	1.14	0.66	0.42
20hrs plasma	85.10	13.74	0.40	0.53	0.23

Table (12-5) the desalination of coupons by sodium hydroxide combined with hydrogen plasma, (Group A)

2% NaOH in hot condition combined with plasma reduction (Group A)

```
Elem     Wt %  At % K-Ratio    Z       A       F
---------------------------------------------------------------
 O K   28.56  57.84  0.1339  1.1001  0.4250  1.0026
NaK     0.14   0.20  0.0002  1.0313  0.1331  1.0001
ClK     0.15   0.13  0.0011  1.0089  0.7246  1.0100
 MnK    0.85   0.50  0.0079  0.9306  1.0033  1.0000
FeK   69.07  40.08  0.6610
```



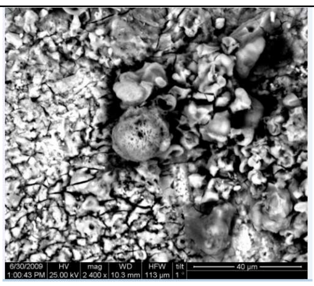
After the treatment by sodium hydroxide combined with 12hrs hydrogen plasma

Fig. (12-3) Map of SEM that shows the desalination by using sodium hydroxide for 10hrs in hot condition Combined with hydrogen plasma for12hrs at 200 ºC, the chloride level was 0.16%, (Group A).

Plasma reduction combined with sodium hydroxide (Group A)

These coupons were desalinated for 15 hours at temperature of 200ºC, combined with 2% sodium hydroxide. The chloride level was 0.15%.

```
Elem     Wt %  At % K-Ratio    Z       A       F
---------------------------------------------------------------
 O K   28.46  55.42  0.1248  1.0937  0.4000  1.0024
 NaK    1.55   2.09  0.0023  1.0253  0.1420  1.0004
 MgK    0.45   0.57  0.0010  1.0516  0.2034  1.0007
 AlK    1.31   1.51  0.0039  1.0211  0.2902  1.0017
 SiK    3.81   4.23  0.0158  1.0513  0.3945  1.0015
 S K    0.07   0.07  0.0005  1.0435  0.6083  1.0051
 ClK    0.15   0.13  0.0010  1.0021  0.7117  1.0089
 K K    0.22   0.18  0.0020  1.0061  0.8601  1.0261
 CaK    0.34   0.26  0.0033  1.0291  0.9066  1.0423
 TiK    0.21   0.14  0.0021  0.9414  0.9642  1.1081
 MnK    0.55   0.31  0.0051  0.9247  1.0009  1.0000
 FeK   62.88  35.08  0.5968  0.9431  1.0063  1.0000
Total  100.00 100.00
```



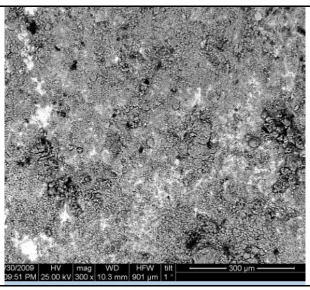


Table (12-4) EDS/SEM of desalination of coupons by hydrogen plasma combined with sodium hydroxide

Desalination by hydrogen plasma at temperature of 270-300ºC (oxidized by sodium chloride) (Group B)

5 coupons were desalinated by H_2 plasma for 20 hours at temperature of 270-300ºC

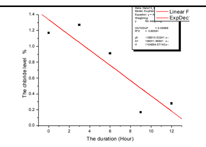
The 1st gr.	Fe	Cl	AC	
Before plasma	78.21	0.85	Elem Wt % At % K-Ratio Z A F -- C K 11.78 36.42 0.0251 1.1408 0.1865 1.0005 O K 2.92 6.78 0.0098 1.1231 0.2973 1.0044 ClK 0.21 0.22 0.0015 1.0330 0.7050 1.0112 MnK 0.68 0.46 0.0065 0.9515 1.0006 1.0000 FeK 84.41 56.12 0.8243 0.9707 1.0060 1.0000	
3hrs plasma	80.16	0.48		
6hrs plasma	82.98	0.38		
12hrs plasma	76.94	0.46		
15hrs plasma	84.54	0.21		
20hrs plasma	86.67	-----		*Diagram shows the effect of plasma reduction on removing the chlorides from the coupons*

Table (12-5) shows the EDS of desalination of coupons by hydrogen plasma at temperature of 270-300ºC

After 20 hours reaction in the furnace, the chlorides were removed completely because the corroded surface was so easy to be removed.

Desalination by hydrogen plasma at temperature of 200ºC (oxidized by Sodium chloride, Group .B)

Coupons were desalinated by H_2 plasma for 20 hours.

Duration	Fe%	Cl%
5hrs plasma	71.93	1.65
20hrs plasma	68.63	0.49

Table (12-6) EDS analysis of desalination of iron coupons by hydrogen plasma at temperature of 200ºC

The results of SEM/EDS of desalination by sodium hydroxide in hot condition (Group A)

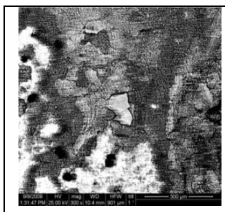
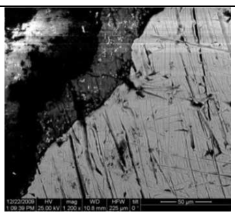
	Elem Wt % At % K-Ratio Z A F O K 29.83 59.30 0.1389 1.0975 0.4231 ClK 0.31 0.28 0.0023 1.0062 0.7258 MnK 0.66 0.38 0.0062 0.9282 1.0033 FeK 67.64 38.52 0.6456 0.9468 1.0082 Total 100.00 100.00	
The feature of the coupons after desalination by sodium hydroxide in hot condition for 10hrs	*EDS result after using heated sodium hydroxide treatment for 10hrs after one day followed by 3hrs plasma.*	*Heated sodium hydroxide treatment after desalination for 10hrs followed by 9hrs plasma at 200ºC. The thick of the corrosion layer is 1.6µm.*

Table (12-7) The results of SEM/EDS o f desalination by sodium hydroxide at hot condition (Group A)

At room temperature, desalination by classical method as sodium hydroxide needed a long time to reduce the high level of chlorides, but in the heating condition was more efficient for decreasing chloride level in a short period of time.

12.2.4 Results of the chemical analysis by silver nitrate (quick test)

This method was used to have accurate results; the study highlighted the presence of chlorides (Actively corroded). *Nitric acid* was used to dissolve the oxidize layer to measure the level of chlorides before starting the desalination method.

AC(Group A)	**Cl^- (mg/l)**
After immersion in sodium hydroxide for 2 weeks	465
plasma for 9hrs	17

Table (12-9) Results of desalination of coupons by sodium hydroxide
For 2 weeks combined with plasma for 9 hours

12.2.5 The results of Vicker hardness test

The main purpose of the hardness test is to determine the effect of heating on the properties of the iron objects after the reduction treatment.

The sample	**The outer layer/hv**	**The inner layer/hv**
After 3hrs, after plasma reduction - 200°C and 250°C, Aged by NaCl	183	158.7-218
After 6hrs, Aged by sodium chloride after plasma reduction - 200°C and 250°C	166	173.5-216
AC2 (Aged by salt spray after plasma reduction - 200°C and 250°C)	175	198-200.4
After 3hrs plasma reduction	180-200	190-220
AC3a (Aged by salt spray after plasma reduction - 280° C and 290°C)	188.7	198.5-203
AC3a2 (Aged by salt spray after plasma reduction - 280° C and 290°C	218	214
AC4 (Aged by sodium Chloride before plasma reduction)	197	176.7-202

Table (12-10) the effect of heating on the hardness of coupons at different temperatures

The different temperatures of the reduction by hydrogen plasma on the coupons did not change the hardness of the iron metal. Results of treatment monitoring of the iron coupons were obtained by examination and analyses methods for determining Cl^- ion concentrations during and after the desalination.

CHAPTER 13

RESULTS OF TREATMENT MONITORING OF THE IRON ARTIFACTS

Several experiments were performed on iron coupons simulating the condition of the iron artifacts from the marine environment. This chapter presents results of treatment monitoring of the behavior of archaeological iron artifacts during and after the desalination by immersion in sodium hydroxide and/or hydrogen plasma. The excavated objects from the marine environment had a thick layer from seabed which was removed by the mechanical cleaning before or during the desalination treatment. This layer is a protective crust of marine encrustation and corrosion compounds that was adherent to inhibit the diffusion of oxygen to the corroded surface. Monitoring is necessary to prevent re-growth of chlorides to artifacts caused by incomplete dechlorination. The results were assessed and characterized by means of the combined use of different analytical techniques such as X-ray radiography, scanning electron microscopy + energy dispersive spectrometry (SEM+EDS) and X-ray diffraction (XRD). Before and after each stage of treatment chloride was evaluated by these methods. Also, the fragments (completely corroded) were examined and analyzed. The loose particles from the oxidized layers were used in investigation and analysis methods.

On plasma, the movement of electron action of hydrogen atoms removes the concretion surrounding (the softened agglomerates) and the oxides layers of the artifact (mechanical effect) which became more porous and (therefore) less hard by transformations and reduction after the final treatment (more than 150 hrs of plasma reduction for wrought iron from Paros and cast iron objects from Syros).

<u>The iron artifacts were divided into four groups as follows:</u>

The iron artifacts were divided according to the type of iron and their condition, that they are heavily or partly mineralized iron artifacts as shown in the following table:

The type of iron	Light corrosion	Moderate corrosion	Heavy corrosion	Completely corroded
Cast iron	B3, B4	B2	B1	
Wrought iron	US1, US2, US3	US4,US5, US6, US7, US22	US8, US9, US11, US12	US15,US16, US19, US20, US21, US24, and others

Table (13-1) State of the iron corrosion of the artifacts

The marine encrustation layer was not easily removable for many times of the reduction treatment by hydrogen plasma reduction. Mechanical cleaning is very important method for the iron objects during reduction process. This method requires high skill and knowledge. This method is very important for achieving success in the process of treatment. It aims to remove marine encrustation, loose corrosion and accretions. These have recently become cheaper and more sophisticated and would be useful tools to the other methods. The soft metal surface can easily be scratched by the mechanical tools, which is irreversible. This method was less damaging during the mechanical cleaning.

13.1 Results of the desalination methods of the iron objects from Paros Island

Hydrogen plasma is one of the best condition to reduce the chlorides percentage, because of the artifacts could not be exposed to oxygen and could not be renewed the corrosion. The temperature range of 100 –300°C was selected, and based on the phase diagram of iron and the previous work.

The most of these objects contain about 4 layers of marine encrustation and corrosion compounds and at the same time, they have different color and thickness. The exterior layer mostly is a red layer of iron oxyhydroxides. The internal layer was characterized using a scanning electron.

When we started to treat wrought-iron objects coming directly from the sea, they were kept wet firstly for 2 weeks. If the object was allowed to dry out before treatment, it would undergo further oxidation, and any conservation attempt may be worse. H_2 plasma reduction using different ranges of temperature, pressure and duration as follows in table 13-2.

Group	Gas/Pressure	Temperature	Dura.	Cl% after the treatment
F1	H2 0.95-1 Torr	150-200°C	168 hrs	0.13-0.20
F2	H2 1.50-1.60Torr	280-300°C	140 hrs	026-0.30
F3	H2 0.55-0.65 Torr	100-130°C	120 hrs	0.43 -0.54

Table (13-2) shows the condition of pure hydrogen plasma in removing the chlorides at low temperature and low pressure

The above table shows the results of the effect of hydrogen plasma. The higher the temperature, the higher the chloride removal and the longer the duration, the higher the concentration of the removed chlorides. The level of chlorides decreased faster after desalination by plasma during the first time within the range of 3- 5 hours. The artifacts were desalinated by plasma condition for several durations, at the range of 100 to 180 hours.

Chemical washing of the iron artifacts by sodium hydroxide was to diffuse the chlorides compound. The dechlorination methods by hydrogen plasma and/or sodium hydroxide started after the prior treatment. After finishing these methods the surface color appeared differently.

The removal of chlorides is very essential for long-term stability of archaeological iron artifacts removed from marine environment by formation passivated surface on the iron object.

The completely corroded objects were desalinated in this method. Firstly, the object was immersed in 1-1.5% sodium hydroxide followed by hydrogen plasma at low temperatures, in order to avoid any change in their initial shape (brittle compounds). Removal of the chlorides completely by using this method was too difficult to save the objects without destroying.

13.2 Results of the desalination methods of the cast iron artifacts from Syros museum

During the desalination treatment, the cast iron artifacts were characterized into two layers:

- The exterior layer contains iron hydroxides with high level of carbon and chlorides (Chlorine is recycled to form more iron chlorides, akaganiete is the most one) associated with low amount of soil elements (quartz and calcite). Sometime, this layer has some metallic components, and the exterior layer is the thickest on the cat iron objects. The exterior layer of the objects hasn't thick marine adhering encrustations.
- An irregular metallic iron core combined with free carbon.

Desalination of cast iron artifacts was more difficult than wrought iron. Chloride ions were diffusing faster into alkaline solution, especially in porous cast iron. Finally, tannic acid is used to inhibit the cast cannonball. Cast iron objects as a porous material needed many times to protect it. Tannic acid is the best in good condition for storage or show. The effects of desalination treatment on chloride removal of the iron cannonball artifacts during and after the desalination is shown in the following table

Object	*The treatment method*	*The condition of the treatment*	*Cl^- concentration Evaluation by EDS and silver nitrate*	*Duration*	*The Weight before and after*	*Photo before desalination*	**Photo after desalination**
B1	*Completely immersing in NaOH*	*1.5% (w/v) sodium hydroxide (pH 13.5, at room temperature for 4months, after that the object was immersed in distilled water for one month*	*5.63% before the treatment by bulk compound using EDS.* *1870.09 Cl^- (mg/l) after immersion for one week in sodium hydroxide. Chloride level after finishing the immersion in NaOH was 35 Cl^- mg/l*	*4 onths immersion in sodium hydroxide + 60 hrs pure hydrogen plasma*	*Bef. 17kg After 16.6Kg*		
	Followed by using H_2 plasma or 60hrs. After treatment the object was protected with tannic acid	*Plasma 200-220ºC for 60 hrs*	*After finishing the desalination by hydrogen plasma, the chloride level was 0.35 % by EDS*				
B2	*Using plasma reduction for 120hrs.*	*at a temperature range of 200-250˚C*	*Before the desalination, the chloride level was 2.75% in the exterior layer, 12.4% in the interior layer and About 4% after 80hrs plasma reduction*	*120 hrs*	*Bef. 11.200*		
B3	*NaOH* *After treatment the object was protected with tannic acid*	*1.5% (w/v) sodium hydroxide (pH 13.5, at room temperature.*	*Before the treatment 5.08%,and after 5 months immersion in NaOH* *63 Cl^- (mg/l)*	*5 months NaOH*	*Before 11.55 After 11.35Kg*		
			21.3 Cl^- (mg/l)	*2months in destilled water*			
B4	*H_2 plasma*	*200-220ºC*	*Before the treatment , the concentration of Cl^- was 6.35%, and after reduction the percent of chloride was 2%*	*24hrs plasma*	*Before 12.23Kg After 12Kg*		
	NaOH after finishing the desalination the object was protected with tannic acid	*1.5% (pH 13.5), at room temperature*	*56 Cl^- (mg/l) in NaOH for 5 months*	*5 months*			
			38 Cl^- (mg/l) in distilled water for one month	*One month*			

Table (13-3) the condition of desalination methods of the iron artifacts

13.3 Results of the desalination treatment methods of the iron objects

The degree of success of our desalination treatment was determine by decreasing the rate of chlorides removal and the corrosion layers as well as the final appearance of the object were the factors of evaluating the treatment methods.

13.3.1 Results of the prior treatment

We know that the distilled water had no any effect on removing the iron chlorides, because water diffusion did not remove insoluble salts from the artifacts. Water has a good effect on removing most of the salts and clay minerals. Most of the salts are hygroscopic, so the water can affect the salt concentration and osmotic pressure.

13.3.2 Chemical treatment

The chemical desalination treatment of iron artifacts from the marine environment is the most common, well-known and efficient method. The artifact was desalinated with a weak alkaline (1.5-2% sodium hydroxide), which was better for initial treatment. Each object in case of the chemical treatment was desalinated separately, by sodium hydroxide, to avoid the effect of other object. The iron artifacts were immersed in distilled water after chemical treatment to remove the residue of the chemical solution. Thus, even the smaller residual amount of them can cause serious damage in the long - term.

13.3.3 Desalination by hydrogen plasma reduction

Hydrogen plasma that showed that hydrogen plasma is the fastest method for dechlorinaion treatment, according to our results and the literature work. This method is considered as a dechlorination technique of the metal artifacts. The gradual removal of the marine sediments minerals and the chloride compounds from the outer layer to be in a stable state. The complete reduction back to iron metal depends on the duration of the plasma treatment and the degree of temperature. The marine encrustations on the object surface became brittle and can easily be removed by the mechanical tools to discover the original surface, which is the source of information. Hydrogen reacts with carbon in cast iron (graphitization phenomenon) to form *methane by* chemical effects. During the hydrogen-plasma treatment, the oxidized layer was incompletely reduced, but they were easier to remove. Hydrogen plasma is a method of drying and passivation and saves time for dechlorination treatment.

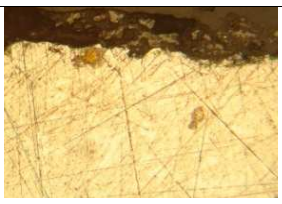
The quite stable behavior of the objects and its black appearance (magnetite) after removing the marine compounds and the iron oxides for most of the object was performed by hydrogen plasma reduction. But the completely corroded objects did not change the surface color because the temperature was low.

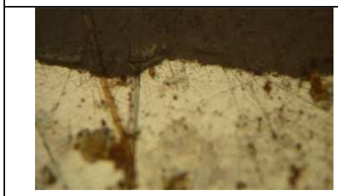
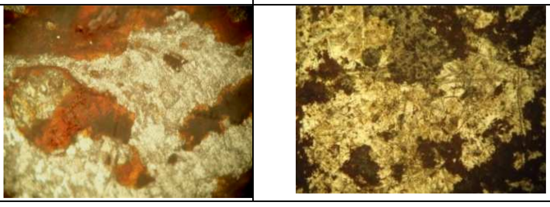
The treatment temperature is limited to a maximum of about 300°C, to avoid any effect on the metallurgical properties. The higher the temperature, the higher the chloride removal and the longer the duration, the higher the concentration of the removed chlorides.

This method has no effect on the metallurgical properties and the surface decoration. Low treatment temperatures of around 80- 120˚Cdid not remove substantial amounts of chlorides in short time. It was proved that plasma had no effect on the metal properties (not exceeding 300ºC).

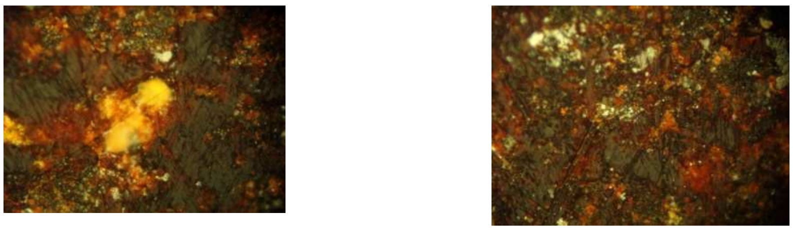
The dechlorination of the objects was for each group by plasma. The completely corroded iron artifacts were desalinated separately, because they have high level of chlorides.

13.4 Results of investigation by metallurgical microscope

<table>
<tr><td></td><td></td><td></td></tr>
<tr><td colspan="2">*US12, shows the thickness of corrosion layer after desalination by plasma reduction. The oxyhydroxide oxides were not completely transformed for magnetite after three hours plasma*</td><td>*US5 after the treatment and reduction the oxides layers to one (magnetite*</td></tr>
</table>

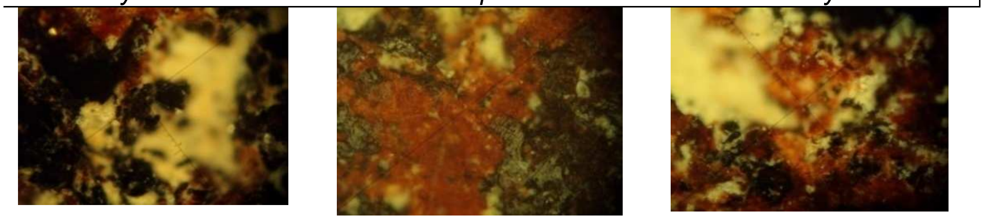
 *US8, the final stage of the desalination treatment*	 *US6 transformation of iron hydroxides to magnetite*	 *US1, The transformation of the iron oxy-hydroide into magnetite after desalination*	
			
US4 (300ºC) after the treatment and reduction corrosion layers	*US10 during and after the treatment*		*US2 after the treatment*

Examination of cast iron artifacts

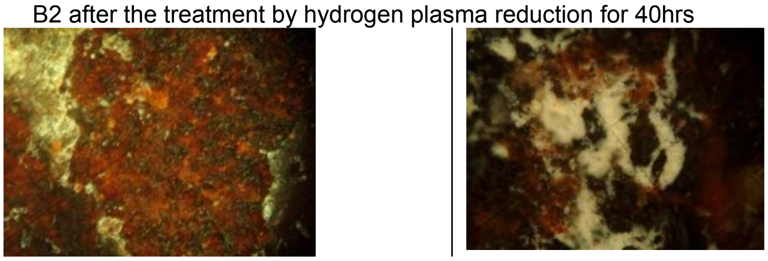


B1, After 4months immersing in sodium hydroxide combined by plasma reduction

B3 after 24hrs reducing by hydrogen plasma followed by immersing in sodium hydroxide for 5 months. These photos are from the inside layer



B2 after the treatment by hydrogen plasma reduction for 40hrs



B4 after 24hrs followed by immersing in sodium hydroxide for 5 months

Photo (13-1) results of investigation by metallographic microscope

13.5 Results of XRD

The X-ray diffraction patterns have shown the corrosion compounds and marine materials on the surface of the objects. Most of the objects are flat, which were covered by hard aggregations consisting of minerals such as sodium chloride NaCl, quartz SiO_2, calcium carbonate $CaCO_3$, albite $NaAlSi_3O_8$, anorthite $CaAl_2Si_2O_8$, orthoclase and sulfur compounds such as gypsum which mixed with metal oxides.

XRD results of US1

After desalination by plasma reduction for 3 hours, magnetite was detected with a high quantity. The following table shows the result of XRD of the object before and after each stage of plasma treatment.

Duration	Magnetite	Aka.	Geo.	Lepi.	Hem.
3hrs	+++	++		+	+
9hrs	+++	++		+	+
12hrs	+++	+			
21hrs	+++				
33hrs	++++				

Table (13-4) results of analysis by XRD of US1

The level of chlorides decreased after desalination treatment. Also, table 13-4 shows that the akaganeite, goethite and lepidocrocite were decreased gradually. Magnetite was increased during the treatment. The deposits on the surface became very brittle and easily to be removed by conservator-restorer to discover the original surface. Maghemite can be formed firstly by combining with magnetite, after a short reduction time. That means, magnetite and maghemite can be difficult to distinguish in the chart of XRD. Magnetite was the main compound in the surface after reduction treatment by plasma reduction, but maghemite was present obviously after reduction for 3 hours.

XRD results of US2

The oxy-hydroxide compounds were not completely transformed into magnetite after reduction for 3 hours in a plasma environment.

Mineral	**After 3hrs**	**After 6hrs**	**9hrs**	**12hrs**	**15hrs**	**20hrs**
Magnetite	++	+++	+++	+++	+++	++++
Aka.(42-1315)	++	+	+			
Hematite	+	+	+	+	+	
Goethite						
Lepidocrocite	+	+	+	+		
SiO_2	+	++	+	+		
Orthoclase	+++	++	++	+		

Table (13-5) the results of the analyses by XRD of US2

The excavated iron artifacts from the marine environment had a thick layer from marine encrustation which was removed mechanically. The presence of hematite after 30 hours by plasma treatment at a temperature of 200˚C indicated the need for long treatment to achieve complete reduction of external corrosion layer of the objects. Goethite was removed after reduction by hydrogen plasma for 3 hours.

Results of X-ray diffraction analyses showed that the marine compounds (especially the red brown clay) in exterior layer were not easily removed after many times of the treatment by hydrogen plasma reduction. The main residues of the iron oxides after the treatment by using plasma reduction for duration of 15-20 hours was only hematite content, but the iron oxides were removed after treatment by pure hydrogen plasma for 10 hours. However, after the final stage of desalination by plasma reduction for one week, most of the residues were removed. Maghemite was the main mineral after 3 hours hydrogen plasma.

XRD results of US5

During the reduction treatment, magnetite was increased gradually, and akaganeite was removed after the treatment for 9 hours at temperature of 300ºC.

Dura.	Mag	Aka	Geo	lepi	Hem
3hrs	+++	++		+	+
9hrs	+++	++		+	
12hrs	+++				
21hrs	+++				
33hrs	+++				
80hrs	++++				

Table (13-6) results of XRD analysis of US5 (Group F1)

Gr. F2 Temperature degree 250-300°C, H2 0.95-0.1 Torr

The name of the sample	US9	US9	US9a	US9a2	US9a3	US9a4	US9a5	US9a6	US9a7	US9a8	US9a69	US910	US911	US9a12	US9a13	US9a14
	k1874	K2215	k2942	k3065	k3228	k3383	k3482	k3514	k3514	k3514						
Magnetite	++	++	++	++	++	++	++	++	++	+++	+++	+++	+++	++++	++++	++++
Aka.(42-1315)	++	+				++	++	++	+							
Aka.(13-0157)-(34-1266)	++	+	+	+	++	++	++	++	++							
Lepidocricite	++	+				+	+	+			+	+				
Goethite	+	+							+	+	+	+			+	
Ferihydrite 29-0712	+++	+++	+++	+++	+++	+++	+++	+++					+			
Fe2(So4)3 42-0225	+	+	+	+	+	+										
Siderite(FeCO3)		+								+	++	+++				
Hematite	+								+	+	++	++			++	
Orthoclase	+++	++	+	+	+		+	+	+	+						
Quartz	++	+	+		+		+	+	+	+						

Table (13-7) the results of analyses by XRD analyses of US9 before each stage of the treatment (Gr.F2)

The presence of hematite after 30 hours treatment by plasma at a temperature of 200°C indicates the need for long treatment duration to achieve complete reduction of external corrosion layer objects.

Samples	Gas/Pressure	Temp.	Dura.	Magnetite (Major)	Akaganeite (completely removed)	Geothite(completely removed)	Lepidocrocite (completely removed)	Hematite(completely removed)
Group F2	H2 0.95 - 1 Torr	180-200°C	168hrs	After 25hrs	After 18hrs plasma	After 6hrss	After 9hrs	After 9hrs
Group F3	H2 0.55-0.65 Torr	100-130°C	100hrs	After 35hrs	After 30hrs	After 12hrs	After 15hrs	After 20hrs
Group F1	H2 1.50-1.60Torr	250-300°C	100h	After 20hrs	After 20hrs	After 3hrs	After 9hrs	After 3hrs

Table (13-8) The condition of the treatments and analyses by XRD of the wrought iron artifacts

Results of US10 (Group G)

Hematite was detected at a low concentration after the treatment by plasma for duration of 100 hours, and at the same time the proportion of magnetite contained in the sample has a high percentage (as shown in the peaks).

US12 after reduction by plasma for 12hrs *US11 after reduction for 15hrs*

M- magnetite, Mg- maghemite, H-hematite, A- akaganeite, G-goethite.

Us9 after reduction for 9hrs *US8 After reduction for 15hrs*

Table (13-1) shows XRD patterns of the iron corrosion products, during the reduction treatment, (Group F2)

13.6 Results of SEM and EDS

The data of SEM/EDS analyses are shown in the following figures and photographs that provide evidence that the chlorides enrichment was indicated before, during and after the dechlorination treatment. The chemical analysis by using this method was to show the surface structure and morphology of the treated artifacts. These photographs show the thickness of the corrosion layer, the morphology and the degree of corrosion on the surface of the samples, which are important for the understanding of the state of the objects before and after the desalination treatment. EDS analysis has shown the level of chlorides in most of the objects after finishing the dechlorination treatment. SEM-EDS examination and analysis of the active corrosion layers showed a range of 2.0-3.80% Cl before treatment of the objects, but only 0.17-0.45% after dechlorination treatment.

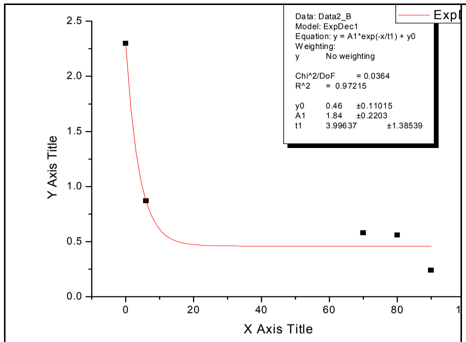
	Elem Wt % At % K-Ratio Z A F --- O K 41.58 67.99 0.1824 1.0712 0.4090 1.0016 NaK 2.55 2.90 0.0040 1.0044 0.1571 1.0004 MgK 0.79 0.85 0.0018 1.0302 0.2229 1.0007 AlK 1.20 1.16 0.0038 1.0004 0.3163 1.0015 SiK 2.44 2.28 0.0108 1.0300 0.4274 1.0017 S K 0.48 0.39 0.0032 1.0226 0.6518 1.0052 ClK 0.56 0.41 0.0041 0.9786 0.7477 1.0085 K K 0.72 0.48 0.0064 0.9826 0.8828 1.0231 CaK 1.42 0.93 0.0136 1.0058 0.9214 1.0338 MnK 0.34 0.16 0.0031 0.9042 1.0035 1.0000 FeK 47.92 22.45 0.4455 0.9220 1.0084 1.0000 Total 100.00 100.00	Elem Wt % At % K-Ratio Z A F --- O K 41.58 67.99 0.1824 1.0712 0.4090 1.0016 NaK 2.55 2.90 0.0040 1.0044 0.1571 1.0004 MgK 0.79 0.85 0.0018 1.0302 0.2229 1.0007 AlK 1.20 1.16 0.0038 1.0004 0.3163 1.0015 SiK 2.44 2.28 0.0108 1.0300 0.4274 1.0017 S K 0.48 0.39 0.0032 1.0226 0.6518 1.0052 ClK 0.56 0.41 0.0041 0.9786 0.7477 1.0085 K K 0.72 0.48 0.0064 0.9826 0.8828 1.0231 CaK 1.42 0.93 0.0136 1.0058 0.9214 1.0338 MnK 0.34 0.16 0.0031 0.9042 1.0035 1.0000 FeK 47.92 22.45 0.4455 0.9220 1.0084 1.0000 Total 100.00 100.0	lemWt % At % K-Ratio Z A F --- O K 2.46 8.03 0.0146 1.1777 0.5013 1.0050 NaK 0.13 0.30 0.0003 1.0972 0.2155 1.0000 SiK 0.21 0.39 0.0014 1.1386 0.5713 1.0010 S K 0.15 0.24 0.0013 1.1173 0.7731 1.0036 ClK 0.24 0.36 0.0022 1.0651 0.8410 1.0066 K K 0.16 0.21 0.0016 1.0676 0.9257 1.0212 CaK 0.19 0.25 0.0020 1.0917 0.9503 1.0365 MnK 0.47 0.44 0.0046 0.9751 0.9975 1.0000 FeK 95.99 89.78 0.9534 0.9932 1.0000 1.0000 Total 100.00 100.00
The diagram of reduction chloride ions	*After 20hrs reduction by plasma*	*After 70 hrs reduction by plasma*	*After 90 hour and the earthy compounds were reduced*

Table (13-9) The behavior of Us4 during the treatment at high temperature of 300°C.

Desalination of US4

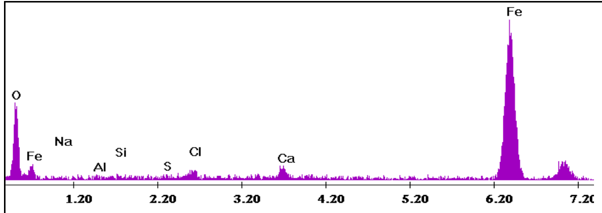
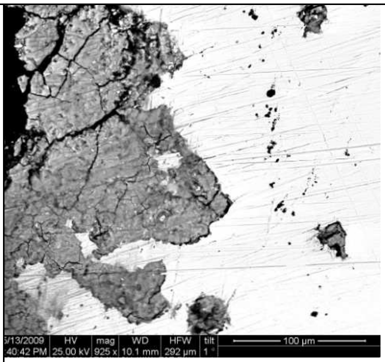
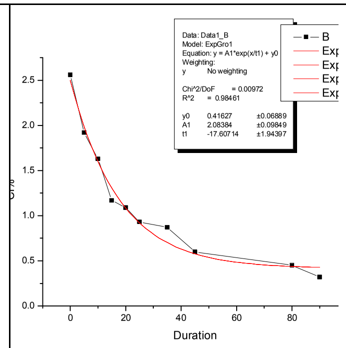
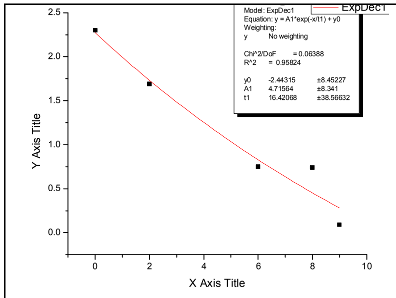
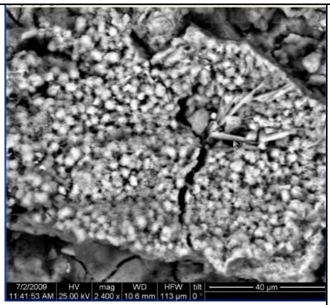
	Elem Wt % At % K-Ratio Z A F --- O K 21.22 46.61 0.0900 1.1083 0.3816 1.0030 NaK 1.33 2.04 0.0018 1.0390 0.1333 1.0002 MgK 0.71 1.03 0.0015 1.0655 0.1912 1.0004 AlK 0.70 0.92 0.0020 1.0346 0.2720 1.0013 SiK 0.58 0.72 0.0023 1.0651 0.3748 1.0022 P K 0.55 0.62 0.0028 1.0302 0.4904 1.0038 S K 1.16 1.28 0.0075 1.0572 0.6043 1.0059 ClK 0.58 0.58 0.0042 1.0174 0.6994 1.0098 K K 0.28 0.25 0.0025 1.0215 0.8483 1.0283 CaK 0.33 0.29 0.0032 1.0443 0.8965 1.0460 MnK 0.54 0.34 0.0050 0.9380 0.9982 1.0000 FeK 72.01 45.32 0.6918 0.9568 1.0041 1.0000 Total 100.00 100.00		
After treatment for 20hrs	*After treatment for 20hrs*	*After 35hrs plasma reduction at low temperature*	*The diagram of the desalination of this object*

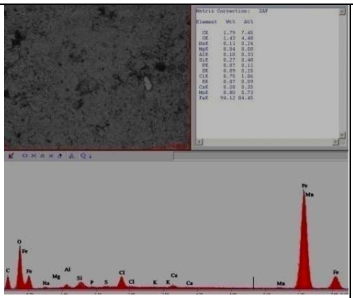
Table (13-10) The behavior of Us4 during the treatment at low temperature by hydrogen plasma



The diagram of desalination by immersing in NaOH



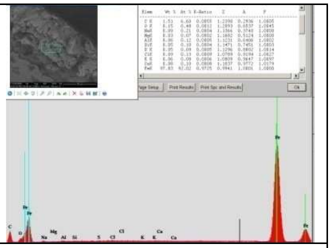
After desalination treatment by NaOH for 2 weeks



After desalination treatment for 6 weeks

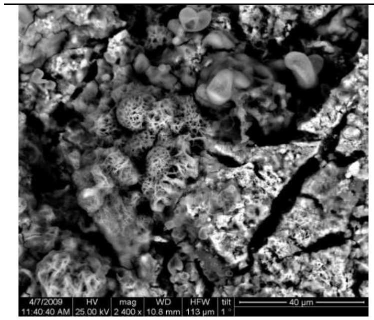
Elem	Wt %	At %	K-Ratio	Z	A	F
O K	18.61	40.09	0.0759	1.1056	0.3680	1.0030
NaK	5.68	8.51	0.0083	1.0364	0.1415	1.0005
MgK	2.16	3.07	0.0045	1.0629	0.1937	1.0006
AlK	0.98	1.25	0.0027	1.0321	0.2706	1.0015
SiK	2.27	2.79	0.0090	1.0625	0.3715	1.0019
P K	0.53	0.59	0.0026	1.0277	0.4759	1.0033
S K	0.46	0.50	0.0029	1.0546	0.5897	1.0056
ClK	0.64	0.63	0.0046	1.0142	0.6915	1.0092
K K	0.38	0.33	0.0033	1.0183	0.8424	1.0262
CaK	0.41	0.35	0.0039	1.0412	0.8912	1.0422
MnK	0.37	0.23	0.0034	0.9353	0.9966	1.0000
FeK	67.51	41.67	0.6459	0.9540	1.0029	1.0000
Total	100.00	100.00				

After desalination treatment for 2 months by immersion in NaOH



The lowest level of chlorides (0.09%) after treatment the objects but some parts of the original surface was removed.

Table (13-11) Results of analyses by SEM of US4 by using sodium hydroxide

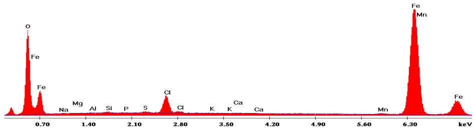


After 10hrs reducing by hydrogen plasma

Elem	Wt %	At %	K-Ratio	Z	A	
O K	28.65	55.19	0.1126	1.0919	0.3593	1.0021
NaK	1.99	2.67	0.0030	1.0237	0.1460	1.0004
AlK	0.43	0.49	0.0013	1.0195	0.2988	1.0021
SiK	3.32	3.64	0.0143	1.0496	0.4101	1.0026
P K	0.33	0.33	0.0017	1.0152	0.5097	1.0044
S K	0.94	0.90	0.0061	1.0419	0.6248	1.0071
ClK	3.05	2.65	0.0222	1.0001	0.7195	1.0088
K K	0.54	0.43	0.0047	1.0042	0.8468	1.0241
CaK	0.70	0.53	0.0066	1.0272	0.8935	1.0378
MnK	2.27	1.27	0.0208	0.9230	0.9964	1.0000
FeK	57.79	31.90	0.5455	0.9414	1.0027	1.0000

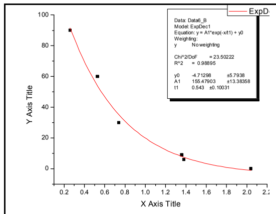
The object after treatment for 6hrs

Elem	Wt %	Mol %	K-Ratio	Z	A	F
Na2O	2.14	5.12	0.0022	1.0272	0.1370	1.0001
SiO2	0.41	1.02	0.0008	1.0532	0.3913	1.0019
SO3	1.20	2.22	0.0032	1.0454	0.6299	1.0059
Cl2O	1.21	2.07	0.0073	1.0042	0.7282	1.0093
K2O	0.09	0.15	0.0007	1.0083	0.8664	1.0275
CaO	0.30	0.79	0.0021	1.0313	0.9125	1.0452
MnO	0.64	1.33	0.0046	0.9265	1.0035	1.0000
Fe2O3	94.01	87.32	0.6266	0.9450	1.0083	1.000

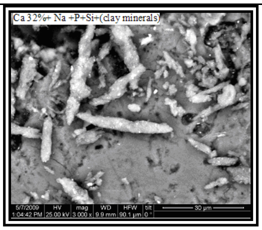


The object after treatment for 60hrs

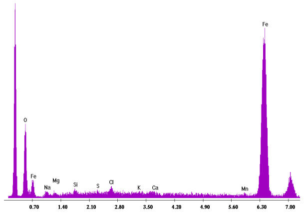
Table (13-12) results of analyses by SEM of US2 at high temperature treatment



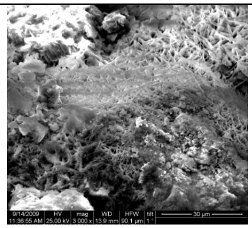
The diagram of the dechlorination



LUS2 after 10hrs (1.31% chlorides)



LUS2 after 10hrs



LUs3

Table (13-13) Results of analyses by SEM/ EDS of US2 at low temperature. In this case, the chlorides levels were reduced most of chlorids at the first 40 hours.

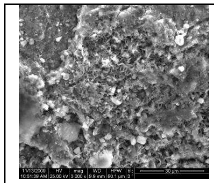
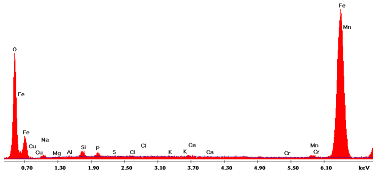
	
After 6 weeks treatment by sodium hydroxide and the picture showed the low level of chlorides	

Table (13-14) Results of analyses by SEM-EDS of US20 after desalination treatment by NaOH

SEM results of US5

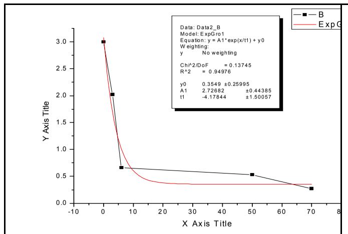
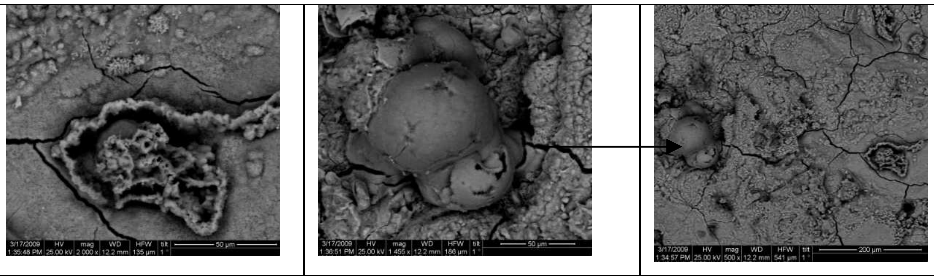
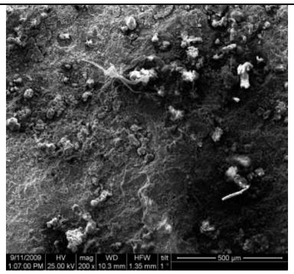
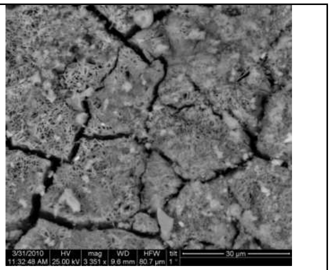
					
The diagram shows the level of chlorides before each stage of reduction treatment	*LUS5 after reduction for 3hrs and shows the forms of chloride*			*After treatment reduction for 40hrs*	*After 70hrs treatment by plasma reduction*

Table (13-15) results of analyses by SEM of US5 during the treatment by using plasma reduction at low temperature

US5 at 300ºC

```
Elem    Wt %  At % K-Ratio   Z      A      F
----------------------------------------------------------
  O K   17.66  42.07  0.0759  1.1178  0.3830  1.0035
NaK    0.25   0.41  0.0003  1.0478  0.1269  1.0001
MgK    0.27   0.42  0.0005  1.0746  0.1838  1.0002
AlK    0.49   0.69  0.0013  1.0434  0.2629  1.0011
SiK    0.42   0.57  0.0016  1.0741  0.3641  1.0020
  S K    0.42   0.50  0.0027  1.0660  0.5971  1.0063
ClK    0.54   0.58  0.0039  1.0274  0.6986  1.0107
  K K    0.39   0.38  0.0035  1.0315  0.8481  1.0306
CaK    0.28   0.27  0.0028  1.0542  0.8956  1.0499
MnK    0.54   0.37  0.0051  0.9466  0.9978  1.0000
FeK   78.74  53.73  0.7633  0.9657  1.0038  1.0000
Total  100.00 100.00
```

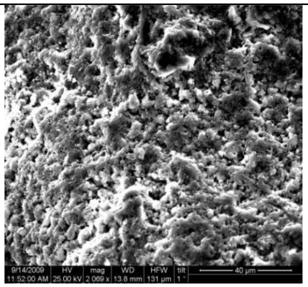
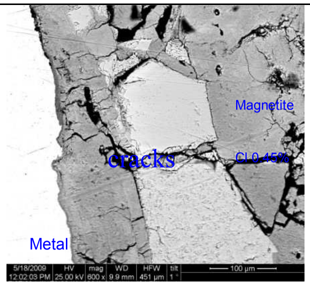
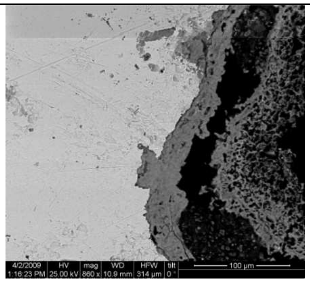
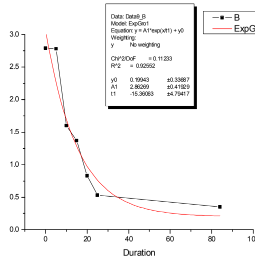
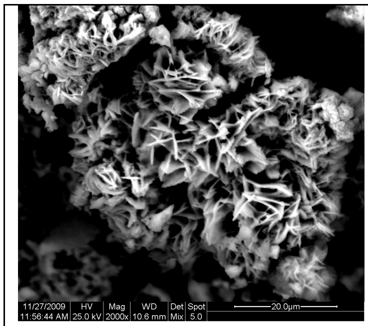
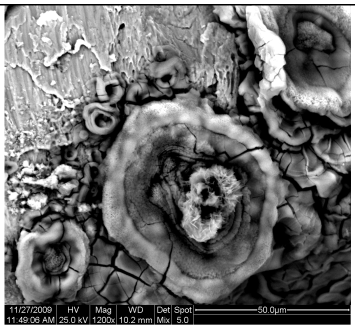
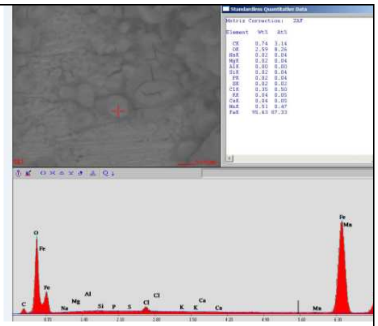
				
After 60hrs reduction by hydrogen plasma	*After 3hrs reduction by hydrogen plasma*	*US5 the large crack in the corrosion layer.*	*US5 before the treatment and photo shows the layers of corrosion mixed with clay minerals*	*The diagram of desalination*

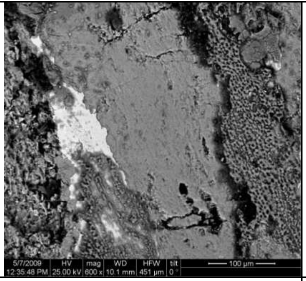
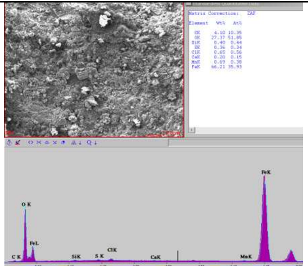
Table (13-16) Results of analyses by SEM of US5 during the treatment by using plasma reduction at 300ºC

		
US1 after reduction for 18hrs by hydrogen plasma at low temperature		*US1 after desalination by sodium hydroxide for 2 weeks*

Standardless Quantitative Data

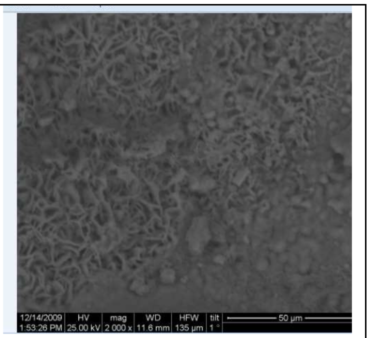
```
Matrix Correction:   ZAF

Element   Wt%   At%

  CK     0.74   3.14
  OK     2.59   8.26
 NaK     0.02   0.04
 MgK     0.02   0.04
 AlK     0.00   0.00
 SiK     0.02   0.04
  PK     0.02   0.04
  SK     0.02   0.02
 ClK     0.35   0.50
  KK     0.04   0.05
 CaK     0.04   0.05
 MnK     0.51   0.47
 FeK    95.63  87.33
```

Table (13-17) SEM-EDS results of desalination treatment of US1 by sodium hydroxide and hydrogen plasma

Elem Wt % At % K-Ratio Z A F O K 20.88 47.51 0.1062 1.1220 0.4519 1.0031 SiK 0.65 0.85 0.0033 1.0735 0.4735 1.0015 ClK 1.33 1.36 0.0108 1.0246 0.7876 1.0081 MnK 0.61 0.40 0.0057 0.9398 1.0001 1.0000 FeK 76.54 49.88 0.7358 0.9579 1.0037 1.0000 Total 100.00 100.00		
After 5 hrs plasma treatment on the outer corrosion layer	*After 10hrs plasma, the marine encrustation that was covered the metal surface*	*After 2 weeks immersing in NaOH (0.65% Cl)*

```
Matrix Correction:   ZAF

Element   Wt%   At%

  CK     4.10  10.35
  OK    27.37  51.85
 SiK     0.40   0.44
  SK     0.36   0.34
 ClK     0.65   0.56
 CaK     0.20   0.15
 MnK     0.69   0.38
 FeK    66.21  35.93
```

Table (13-18) Results of analyses by EDS-SEM of US1 during the treatment by using plasma reduction at temperature of 300ºC combined with sodium hydroxide

Elem Wt % At % K-Ratio Z A F --- C K 7.31 25.07 0.0147 1.1488 0.1754 1.0006 O K 2.53 6.51 0.0091 1.1309 0.3153 1.0048 NaK 0.55 0.99 0.0007 1.0600 0.1239 1.0001 MgK 0.48 0.81 0.0009 1.0871 0.1786 1.0001 AlK 0.38 0.58 0.0010 1.0554 0.2545 1.0011 SiK 0.50 0.73 0.0019 1.0865 0.3533 1.0019 P K 0.21 0.28 0.0010 1.0508 0.4662 1.0035 ClK 0.16 0.18 0.0011 1.0411 0.6874 1.0111 CaK 0.09 0.09 0.0009 1.0678 0.8931 1.0547 MnK 0.61 0.46 0.0058 0.9585 0.9974 1.0000 FeK 87.19 64.31 0.8556 0.9780 1.0034 1.0000 Total 100.00 100.00	
Table (13-19) US23 after reduction by hydrogen plasma for 10 hours combined with NaOH for 5 months	

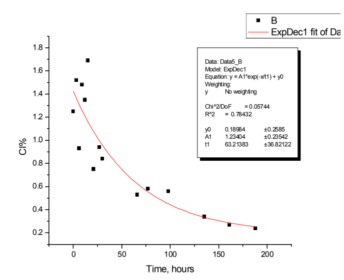
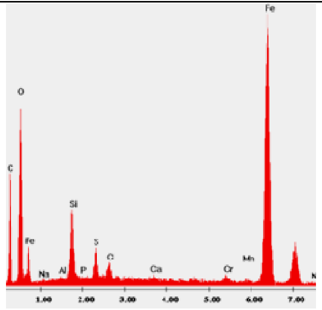
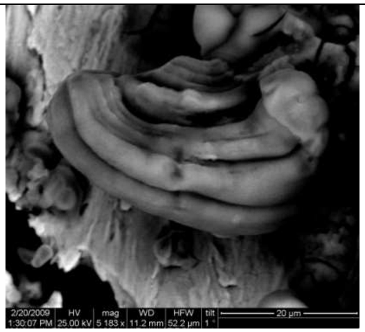
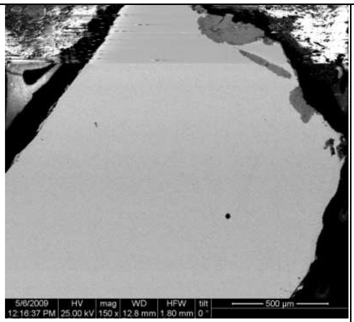
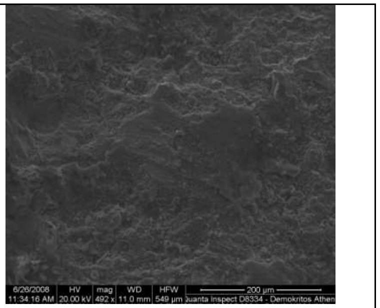
				
The diagram of desalination of US7	*Picture no.4 for the US7object reduced for 3 hour at 200℃ from white spot*	*US7a12 -The chloride in the pit (from the edge of the object).*	*US7a14 After reduction the chlorides level. The corrosion layer is 12.5µm*	*US7a14 after finishing the reduction treatment for 180hrs*

Table (13-20) The behavior of chlorides during and after each stage of the desalination treatment (US7)

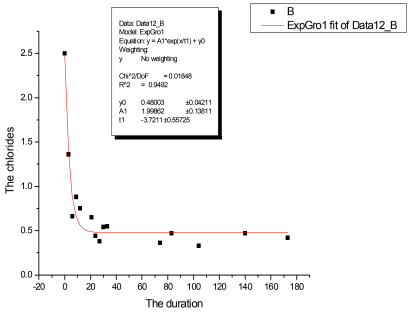
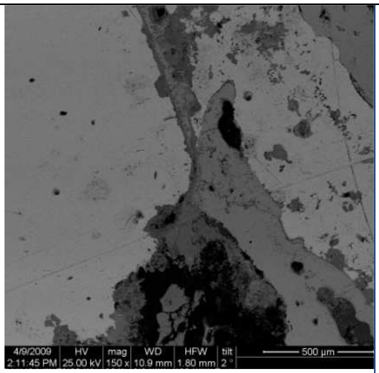
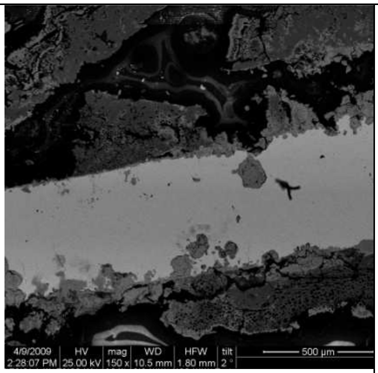
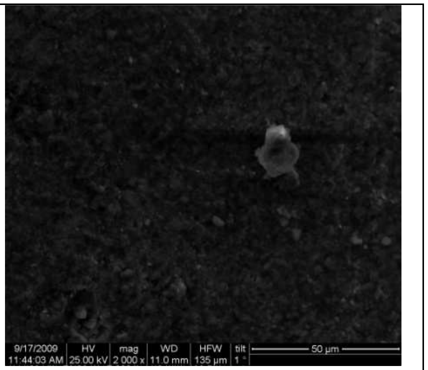
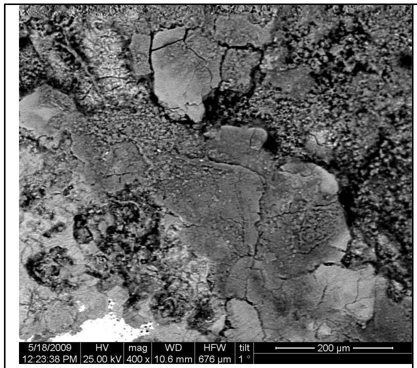
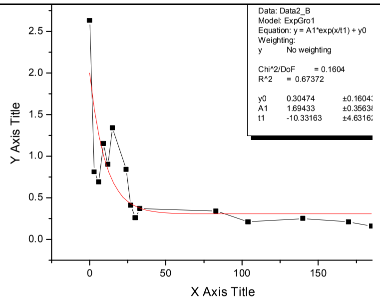
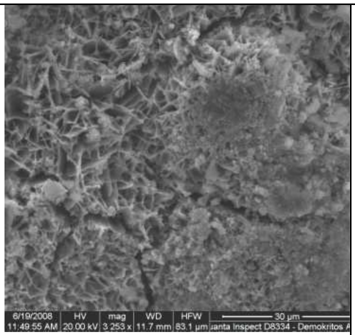
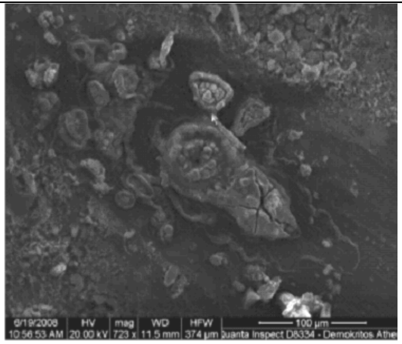
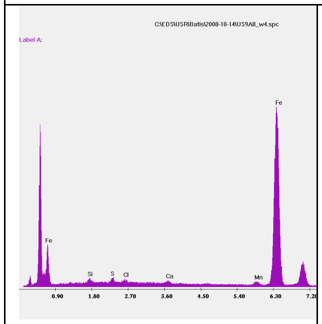
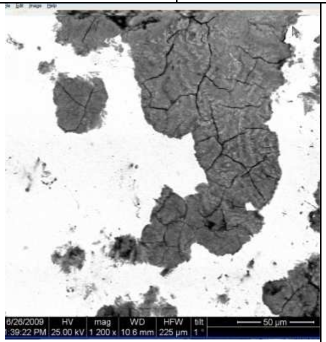
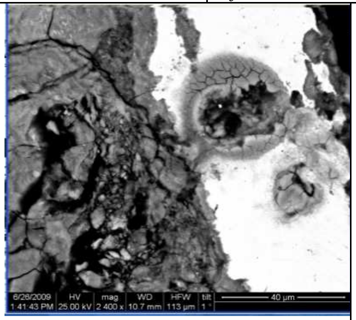
			
The diagram of reduction the chlorides	*After 3hrs reduction by plasma*	*After 12hrs reduction by plasma*	*After 5 days of reduction*

Table (13-21) SEM/EDS results of the desalination stages of US8

<table>
<tr>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td>Elem Wt % At % K-Ratio Z A

O K 20.01 45.74 0.0869 1.1132 0.3887
NaK 0.64 1.02 0.0009 1.0435 0.1288
MgK 0.24 0.36 0.0005 1.0702 0.1860
AlK 0.11 0.16 0.0003 1.0391 0.2661
SiK 0.66 0.85 0.0026 1.0697 0.3700
▼ S K 0.52 0.59 0.0033 1.0617 0.6025
ClK 0.34 0.36 0.0025 1.0226 0.7029
K K 0.28 0.26 0.0025 1.0266 0.8524
CaK 0.48 0.44 0.0048 1.0495 0.8999
MnK 0.51 0.34 0.0048 0.9425 0.9987
FeK 76.21 49.89 0.7360</td>
</tr>
<tr>
<td>US9a2 before plasma reduction, earth minerals in the surface. shows the thick of the clay minerals</td>
<td>The diagram of the desalination of this objects</td>
<td>US9a3 the form of chlorides with sulfur products (dendritic form)</td>
<td>US9a10. SEM photomicrographs of the surface after plasma reduction shows clays and calcareous deposits. The level of chlorides is 1.61%</td>
<td>US9a3 the form of chlorides with sulfur products The crystal of chloride , results from</td>
</tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td>Elem Wt % At % K-Ratio

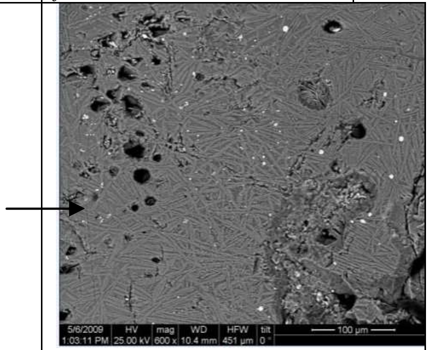
O K 16.09 37.45 0.0446
AlK 1.04 1.44 0.0042
SiK 5.01 6.64 0.0271
P K 0.57 0.69 0.0036
S K 0.19 0.22 0.0014
ClK 0.28 0.29 0.0022
K K 0.83 0.79 0.0079
CaK 1.33 1.24 0.0136
TiK 12.79 9.94 0.1272
CrK 0.32 0.23 0.0033
MnK 5.13 3.47 0.0470
FeK 56.42 37.61 0.5317
Total 100.00 100.00</td>
<td> </td>
</tr>
<tr>
<td>After 33hrs plasma reduction</td>
<td>US9a9 (220 X magnification and 20 KV), spot on akaganeite</td>
<td>Microscopic observation of the sample after 69hrs plasma reduction</td>
<td>Scanning electron micrograph of the sample after 78hrs plasma reduction</td>
<td colspan="2">US9a14 Slag in the object Layered structure is shown with short arrow and slag by long arrow on the metal surface</td>
</tr>
</table>

Table (13-22) SEM/EDS results of the desalination stages of US8

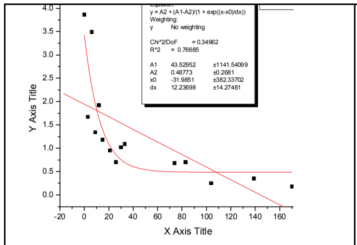
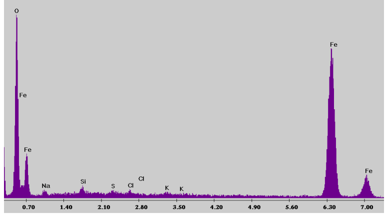
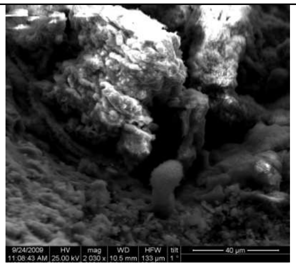
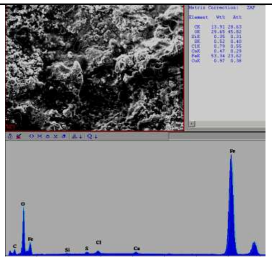
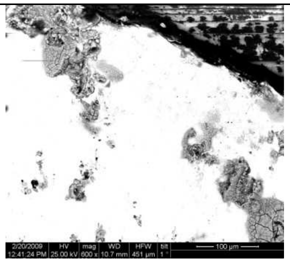
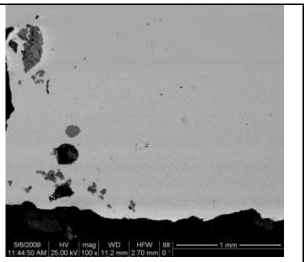
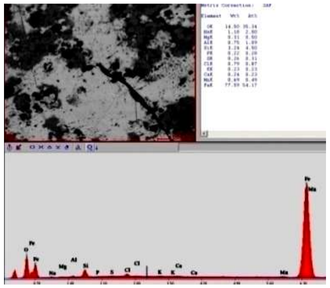
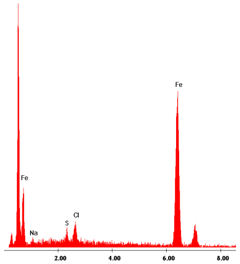
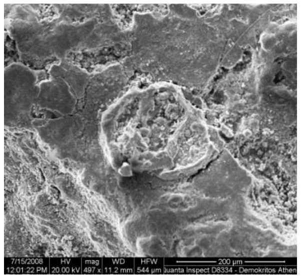
 					

Diagram of the desalination	*US11a3 – The chloride level is about 0.75*	*US11a2*	*US1a6*	*US11a11*	*US11a14*

Table (13-23) shows SEM/EDS of the US11, the stages of dechlorination

		
US12 after reduction for 3hrs	*After 6hrs plasma reduction shows corrosion layers with clay minerals and chlorides*	

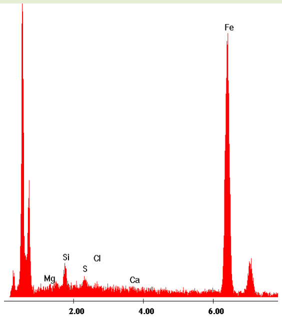
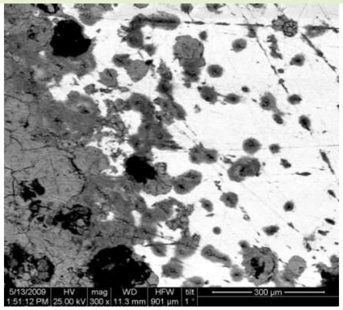
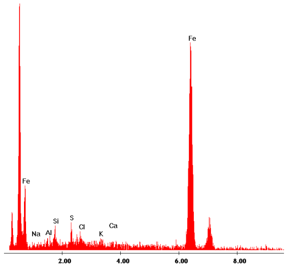
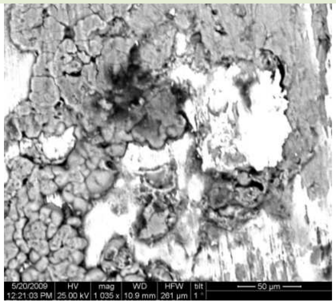
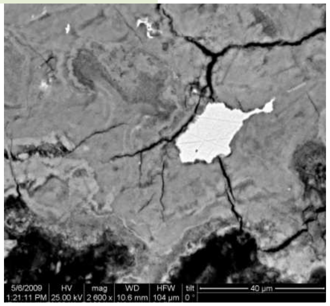
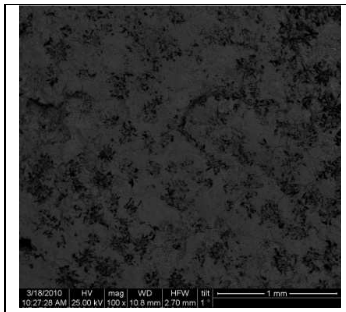
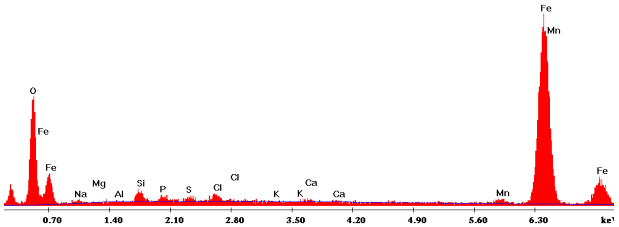
				
US12a3 after 9hrs plasma reduction	*US12a4 After 12hrs hydrogen plasma reduction*	*EDS for the sample for the object after reduction for 30hrs*	*US12a12 after treatment for 160hrs*	*After reduction the chlorides*

Table (13-24) the behavior of US12 during desalination by plasma reduction

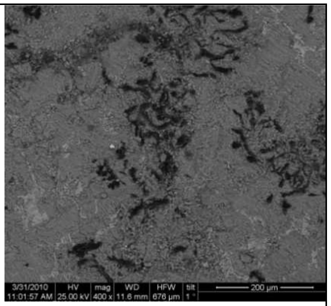
B1 (the first cast-iron object)





B1 after finishing the wet chemical treatment followed by 8hrs hydrogen plasma (Binary texture image of graphite morphology)

```
Elem    Wt %  At % K-Ratio   Z      A      F
------------------------------------------------------------
C K   19.75  38.09  0.0463  1.0823  0.2164  1.0005
  O K   26.29  38.07  0.0779  1.0657  0.2776  1.0016
NaK    0.16   0.16  0.0003  0.9993  0.1637  1.0002
MgK    0.14   0.13  0.0003  1.0250  0.2391  1.0004
AlK    0.15   0.13  0.0005  0.9953  0.3412  1.0014
SiK    1.19   0.98  0.0057  1.0248  0.4636  1.0020
P K    1.07   0.80  0.0062  0.9913  0.5804  1.0030
S K    0.29   0.21  0.0021  1.0175  0.6859  1.0051
ClK    0.81   0.53  0.0062  0.9729  0.7788  1.0081
 K K    0.15   0.09  0.0013  0.9769  0.9012  1.0239
CaK    0.32   0.18  0.0031  1.0001  0.9396  1.0389
MnK    1.23   0.52  0.0112  0.8993  1.0113  1.0000
FeK   48.45  20.10  0.4507  0.9169  1.0145  1.0000
Total  100.00 100.00
```



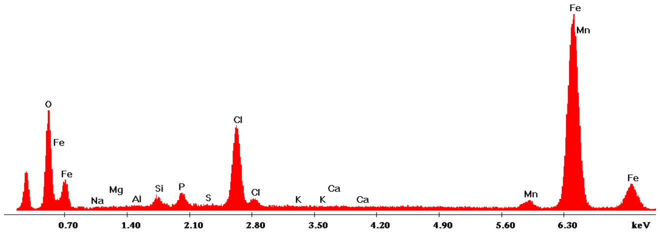
The first ball after desalinating by sodium hydroxide for four months combined with hydrogen plasma for 20hrs

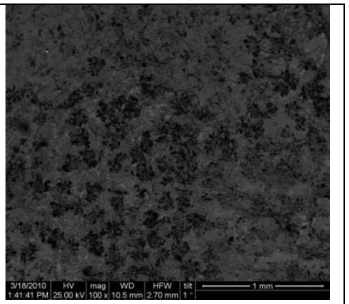
Table (13-25) shows results of analyses by SEM and EDS, after the treatment of this object by plasma condition.

B2 (the second cast iron object)

	Al_2O_3	SiO_2	P_2O_5	Cl_2O	MnO	Fe_2O_3
Bulk 1, 200x	2,48	1,72	2,1	11,28	2,7	80
Bulk 2, 400x	0,74	1,42	1,3	10,26	2,69	83,61
Bulk 3, 200x	1,5	2,67	2,45	13,09	3,55	76,75
Bulk 4, 800x	0,24	0,95	2,46	8,03	2,5	85,83
Bulk 5, 3000x	0,13	0,38	0,46	7,9	2,37	88,76
Average	1,018	1,428	1,754	10,112	2,762	82,99

The outer layer after 40hrs plasma reduction

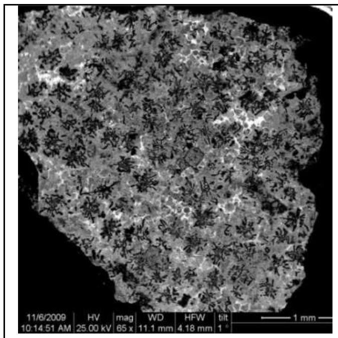
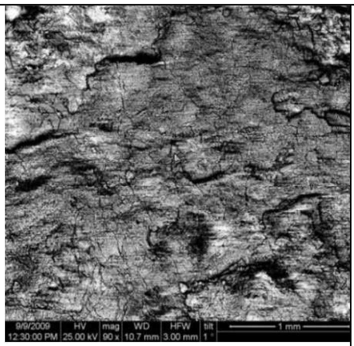
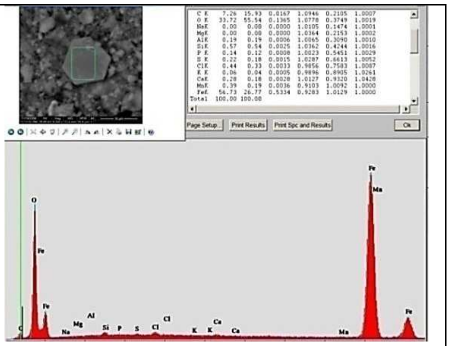




The exterior layer after plasma reduction for 30hrs , cast iron elements were heavily graphitized

Table (13-26) The results of analyses by SEM and EDS of the second ball by plasma reduction at temperature of 220ºC

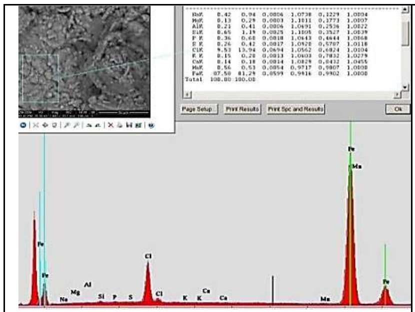
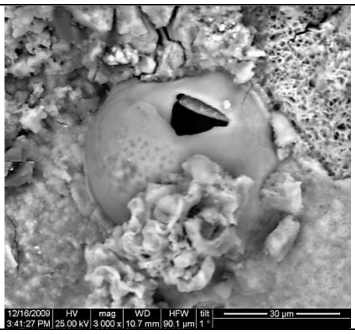
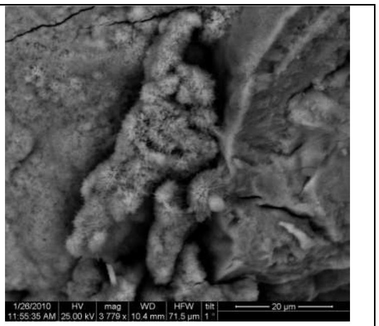
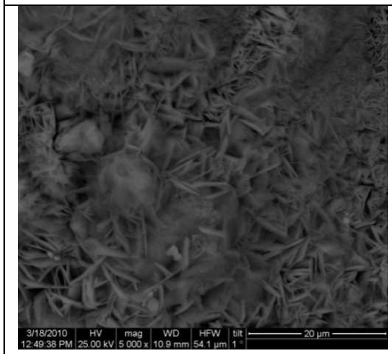
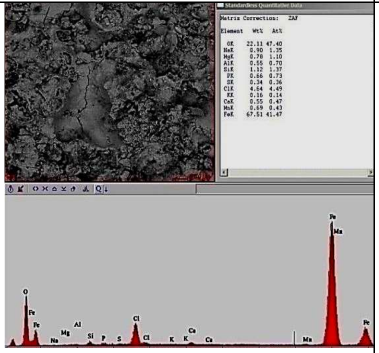
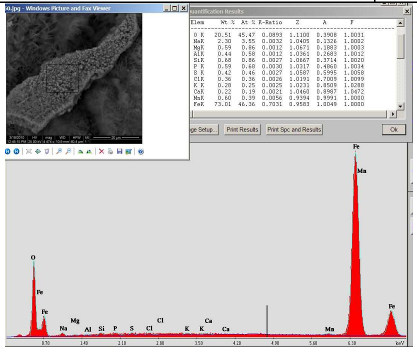
B3 (the third cast iron object)

		
B3S3(the flower form of the object5 causing of the collection of carbon	*After desalination by sodium hydroxide for 2months*	*After the treatment by sodium hydroxide and during immersion in distilled water (Cl 0.44%)*

```
  C K    7.26  15.93  0.0167  1.0946  0.2105  1.0007
  O K   33.72  55.54  0.1365  1.0778  0.3749  1.0019
  NaK    0.00   0.00  0.0000  1.0105  0.1474  1.0001
  MgK    0.00   0.00  0.0000  1.0364  0.2153  1.0002
  AlK    0.19   0.19  0.0006  1.0065  0.3090  1.0010
  SiK    0.57   0.54  0.0025  1.0362  0.4244  1.0016
  P K    0.14   0.12  0.0008  1.0023  0.5451  1.0029
  S K    0.22   0.18  0.0015  1.0287  0.6613  1.0052
  ClK    0.44   0.33  0.0033  0.9856  0.7583  1.0087
  K K    0.06   0.04  0.0005  0.9896  0.8905  1.0261
  CaK    0.28   0.18  0.0028  1.0127  0.9320  1.0428
  MnK    0.39   0.19  0.0036  0.9103  1.0092  1.0000
  FeK   56.73  26.77  0.5334  0.9283  1.0129  1.0000
Total  100.00 100.00
```

Table (13-27) shows the results of analyses by SEM and EDS of 3rd ball by sodium hydroxide

B4 (the fourth cannon ball cast iron object)

		
After reduction by plasma reduction for 5hrs, chloride level was 5.53%	*After exposing for plasma condition for 5hrs*	*After plasma reduction for 15hrs*
		
After immersion in sodium hydroxide for one month (the level of chlorides was 4.64%		*After immersion for 4 months in sodium hydroxide. The chloride level was 0.36%*

```
Matrix Correction:   ZAF

Element    Wt%   At%

  OK     22.11 47.40
 NaK      0.90  1.35
 MgK      0.78  1.10
 AlK      0.55  0.70
 SiK      1.12  1.37
  PK      0.66  0.73
  SK      0.34  0.36
 ClK      4.64  4.49
  KK      0.16  0.14
 CaK      0.55  0.47
 MnK      0.69  0.43
 FeK     67.51 41.47
```

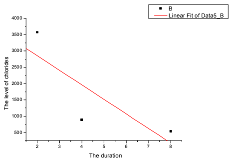
```
Elem     Wt %   At % K-Ratio    Z        A        F
------------------------------------------------------------
 O K    20.51  45.47  0.0893  1.1100  0.3908  1.0031
 NaK     2.30   3.55  0.0032  1.0405  0.1326  1.0002
 MgK     0.59   0.86  0.0012  1.0671  0.1883  1.0003
 AlK     0.44   0.58  0.0012  1.0361  0.2683  1.0012
 SiK     0.68   0.86  0.0027  1.0667  0.3714  1.0020
 P K     0.59   0.68  0.0030  1.0317  0.4860  1.0034
 S K     0.42   0.46  0.0027  1.0587  0.5995  1.0058
 ClK     0.36   0.36  0.0026  1.0191  0.7009  1.0099
 K K     0.28   0.25  0.0025  1.0231  0.8509  1.0288
 CaK     0.22   0.19  0.0021  1.0460  0.8987  1.0472
 MnK     0.60   0.39  0.0056  0.9394  0.9991  1.0000
 FeK    73.01  46.36  0.7031  0.9583  1.0049  1.0000
```

Table (13-28) shows the results of analyses by SEM and EDS of fourth cannon ball by combination methods. Firstly, plasma reduction combined by sodium hydroxide

The previous SEM investigation indicates the surface form of the objects has an important role on the phenomenon of graphitization and reduction of iron oxide to iron metal.

13.7 Testing for chlorides with silver nitrate

Results of the US1 after chemical cleaning by 4% sodium hydroxide

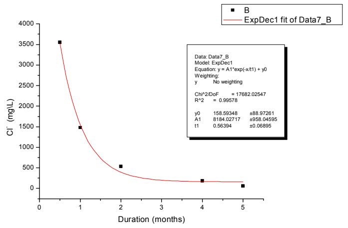


The diagram of the desalination by sodium hydroxide

The sample	Cl^- (mg/l)
After 2weeks	3570
One month	889
2 months	536
4 months	215

Table (13-29) the results of the US4 after chemical cleaning

Results of the US5 after chemical cleaning by 4% sodium hydroxide



The treatment by high concentration of sodium hydroxide

The sample	*Cl^- (mg/l)*
US4 (2 weeks)	*3550*
US (One month)	*1478*
US4 (2 months)	*532.5*
US4S (4 months)	*182*
US4 (5 months)	*56*

Table (13-29) the results of the US5 after chemical cleaning by wet-chemistry methods

The parts of this object were closed by corrosion compounds, that were removed mechanically.Chlorides were removed completely on this object by firstly using plasma combined with sodium hydroxide.

The results of the US15 and US5 during and after chemical treatment

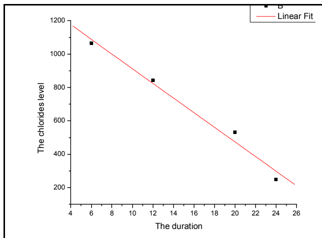
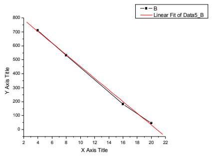


Fig.(13-2) The diagram of desalination of US15

The sample	*Cl- (mg/l)*	*The sample*	*Cl- (mg/l)*
US5S4	*95.09*	*US5a2S2*	*50*
U85S8	*38*	*US5a2S4*	*-------*

Table (13-30) shows the effect of sodium hydroxide in combination with plasma

The results of the US20 after chemical cleaning

 	**The sample**	**Cl$^-$ (mg/l)**
	US20 after desalinating for one month	710
	US20 after desalinating for 2 months	532.5
	US20S after desalinating for 4 months	182
Table (13-30) Diagram of sodium hydroxide on dechlorination of US20	US20S after desalinating for 5 months	43

The results of the US23 and US10 during and after chemical cleaning

The sample	Cl- (mg/l)	The sample	Cl- (mg/l)
US23 (2 weeks)	710	US10 (6hrs plasma + 2weeks)	380.357
US23 (2 months)	355	US10 (6hrs plasma + 2months)	153
US23 (4 months)	26	US10a (6hrs plasma + 4months)	16

Table (13-31) The comparison between the treatments by using sodium hydroxide combination in the reduction by hydrogen plasma for 6hours at (200ºC).

Results of chemical treatment of cast iron objects

The first cannon ball

Sodium hydroxide of concentration 1.5% and a pH of 13.5 was used to reduce the chlorides compounds in this object for 5 months. *The solution was changed every 2 weeks to reactivate the efficiency of the solution. Chloride ions were decreased fastly after the first stage.*

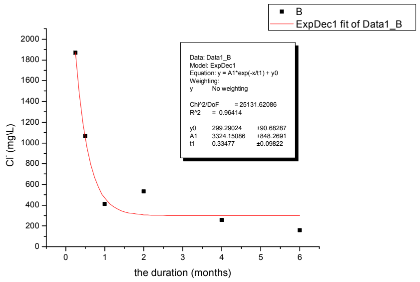
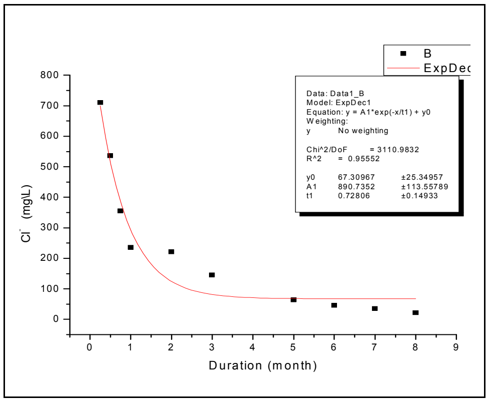


Table (13-32) The behavior of the chlorides during the treatment by sodium chlorides

The sample	Cl$^-$ (mg/l)
B1 (one week)	1870.09
B1 (two weeks)	1065
B1 (one month)	412.05
B1(2 months)	532
B1 (4months)	256
AB1, after immersion in distilled water for one month	158.5
After immersion in distilled water for 2 months	35

The second cannon ball was treated by pure hydrogen plasma

This object was treated by 1.5% sodium hydroxide of pH 13.5 for five months which was changed every two weeks. This object was in a good condition before the treatment.



The effect of sodium hydroxide on cast iron objects

The sample	Cl^- (mg/l)
B3 (one week)	710
B3 (2 weeks)	536
B3 (3 weeks)	355
B3 (one month)	236
B3 (2 months)	221
B3 (3 months)	146
B3 (5 months)	63
After immersion in distilled water for one month	46
After immersion in distilled water for one months	35
After immersion in distilled water for 2 months	21.30

Table (13-33) shows the effect of sodium hydroxide on iron objects

The treatment of the fourth cannon ball

This object had no high chloride level at the first stage of dechlorination.

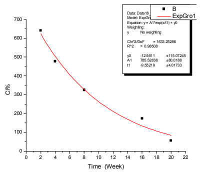


Table (13-34) diagram of the desalination

The sample	Cl^- (mg/l)
2 weeks	642
5 weeks	478
2 months	326
4 months	173
5 months	56
One months in distilled water	38

13.7 Vicker hardness test

Desalination treatment of iron artifacts has been studied in hydrogen plasma. The treatment duration, pressure and temperature have been varied. The following tables show the effect of plasma on the hardness of the objects after reduction treatment by using different temperature. No changes in the property of the surface during and after the treatment.The vicker hardness test of US12 after reduction for 3hours was 290 hv in the interior and 280 in the exterior layer.

Sample	**The exterior layer/hv**	**The interior layer/hv**
US2 before the reduction	**150-169.6**	**178-200**
After 5hrs reduction	**200-247.5**	**250**
After 25hrs reduction	**179**	**197.3-230**
After 30hrsreduction	**185**	**227.3-250**

Table (13-35) The effect of heating by plasma on US2 Vicker hardness test of US8

Sample	The outer later/hv	The interior layer/hv
Before the treatment	195	216
After 3hrs	214	234.5
After 21hrs	175	222.5
After 156hrs	189	235
After 183hrs	224	244

Table (13-36) Vickers hardness test before and after the treatment of US8

As indicated in (Table 13-37), results of the different methods were based on the conversion of the corroded coupons and the metallic iron objects; also the removal of chlorides prevents the pressure inside (osmotic pressure) the objects and prevents the formation of cracks on the surface of the object, because the object withstand a high level of chlorides. The disadvantage of the dechlorination by hydrogen plasma was for the reduction of chloride level from the pits, because the effect of plasma is on the surface, but on the other hand, sodium hydroxide can penetrate inside the metal artifacts (chemical diffusion).

Treatment method	**Total iron item**	**Percentage of efficiency***	**Treatment time (hrs)**	**Remarks**
Dry mechanical cleaning by using manual tools as scalpels, needle, chisel, various brushes and hammer	most of the objects	15%	200hrs	To remove the deterioration phenomena of the loose corrosion layers and marine compounds
Dry mechanical treatment by blasting and dental cleaning machine	3 objects	10%	20hrs	More effective on removing the calcareous, marine encrustation and iron oxides.
Chloride extraction by water for the objects from Paros Island	13 objects	40%	After excavation till coming to the Demokritos	This method was so important to protect them, and at the same time water hadn't any effect on the iron chloride removal, but water can dissolve the marine encrustation and the soluble salts.
Water extraction (distilled water)	2 objects	20%	300hrs	Prior to treatment, artifacts were stored wet to prevent them from drying out. These forms stay with the artifact through the wet treatment
Pure hydrogen plasma reduction	30 coupons+25 objects at different temperature	97%	12-21 hrs for coupons, 60- 190 hrs for objects	The effect of plasma based on the metal surface (0.5 cm inside the object)
Hydrogen plasma followed by NaOH (1-2%)	5 coupons + 2 objects	95%	24hrs hydrogen plasma + 2 months sodium hydroxide	The combination methods (hydrogen plasma and sodium hydroxide) were collected between more advantages, but it was a disadvantage that most of the formation of the exterior layer couldn't be magnetite.
Sodium hydroxide followed by H_2 Plasma	5 coupons & 3 objects	98%	4 months sodium hydroxide + 4 days H2 Plasma	This method was the best way to remove the chlorides. The stabilization of iron objects after the treatment by this method was the main advantage by passivation. The objects were now fully restored and supported by sodium hydroxide and hydrogen plasma.
1-2% Sodium hydroxide	5coupons+ 5 wrought iron	95%	2 weeks for the coupons	Chlorides and rust were decreased by this process. The object was left in the bath for 2 weeks.
Sodium hydroxide (Heating condition)	5 coupons	95%	12hrs	The solution was used at a low temperature (50ºC) for a long time, and it was better for chlorides removal.
Hot sodium hydroxide followed by H2 Plasma	5 coupons	99%	24 hrs sodium hydroxide + 12hrs H2 Plasma	The stabilization of iron objects after the treatment by this method was the main advantage. The objects were now fully restored and supported by sodium hydroxide and hydrogen plasma.

Table (13-37) Efficiency of the iron treatments form the marine environments and reports the results that can be compared with other.

The efficiency of the desalination was assessed by t he final appearance and the level of chloride removal

Part (3) Discussion and conclusion

Chapter (15) Discussion

Chapter (16) Conclusion

CHAPTER 15

DISCUSSION

After doing literature search and a series of experiments in different conditions and diagnostic tests, monitoring results and the condition of the iron coupons and artifacts after desalination, the discussion came as follows:

Every object has a different state of corrosion, level of the chlorides and the thickness of marine agglomerated crust that was 1mm to 5mm by dimension. Generally, the oxidized layer and the marine encrustation associated with chloride compounds were on the surface of the marine iron artifacts. The state of the object is related to earlier work of Watkinson and Al-Zahrani (2008) found chlorides can also be associated with solid corrosion products. Following excavation reaction of iron with atmospheric oxygen and moisture which readily forms β-FeOOH (akaganeite) in low pH and Fe^{2+}/ Cl^- rich environment, formed at the metal surface when iron dries out (Watkinson and Al-Zahrani 2008).

During the desalination treatment of the iron coupons, goethite was removed after heating for 3 hours, lepidocrocite was removed after reduction for 6 hours and akaganeite needed a longer time of about 18-20 hours to be removed by plasma reduction. Hydrogen plasma has a slightly faster chlorides reduction rate than sodium hydroxide. The black appearance of the coupons and artifacts surface resulted from the ovens at high temperature. Low temperature plasma-chemical treatment and/or low concentration of sodium hydroxide were experimented in removing the chloride ions.

Most of the wrought objects were covered by marine protective layer from adherent calcareous (marine encrustation) and corrosion compounds that prevented these artifacts from being completely corroded. The iron artifacts removed from the marine environment, (highly chloride environment), have stable compounds from the marine and corrosion compounds as a protective layer.

Surface properties were examined by metallurgical microscopes after the dechlorination treatment by pure hydrogen plasma that resulted in no changes below 300˚C. According to Schmidt-Otta (2004) that has been shown the same result that no observable changes in the metallographic features of the objects were identified, but the duration of reduction was prolonged (Schmidt-Otta 2004).

Iron artifacts were desalinated by using plasma reduction at temperature ranges of 80-300˚C (low-temperature) and pressure for different durations. Also, marine encrustations and chemical residues after the chemical desalination were removed by the good drying for 10 hours at 80˚C by hydrogen plasma. During the heat shock treatment, the temperature of the hydrogen plasma did not change the metallurgical properties, if it has *not* exceeded 300° C.

From our findings, 100% hydrogen plasma reduction can certainly decrease corrosion layer and chloride ions gradually. By evaluating the results from scanning electron microscope and X-ray diffraction, we therefore found out, that higher temperatures lead to a more efficient desalination of the objects in a shorter period of plasma treatment. The removal of chloride ions from the oxidized layer covering the artifacts depended on the level of chloride, the state of the objects, the temperature degree of hydrogen plasma and the treatment duration. Chemical hydrogen plasma affected many compounds like akaganeite, calcite and phosphate. This method is a destructive method at high temperature. Earlier findings by Rašková and Krčma (2007) reported on the gradual removing of the marine sediments minerals and the chlorine compounds from the outer layer to be in stable state and sometimes even the complete reduction back to iron metal which was proportional to the duration of the plasma treatment and the temperature degree.

Our result also indicates that akaganeite was removed completely from the coupons after reduction by hydrogen plasma for 15 hours at 300ºC. The chloride level on the coupon was 0.15% wt. by EDS after desalination treatment by sodium hydroxide in hot condition for two weeks combined with hydrogen plasma for 15-20 hours. Graaf et al., (1995) has also reported that the reduction of chloride from a corrosion layer can occur both thermally and by chemical process.

Desalination treatment appears to be the most important stage in conservation of marine iron artifacts. The application of dechlorination methods had been applied to iron artifacts only. Desalination of iron artifacts is important for the treatment and stability of these objects by preventing re-corrosion. Also, after the desalination treatment by plasma, the magnetic properties increased by the formation of magnetite on the surface of the iron objects through long periods of plasma reduction and preserved surface details.

One of the objects contains an aluminum part which has a low melting point, but the object did not undergo any changes in the surface details, and its properties. Also the examination by metallographic microscope or Vicker hardness test proved that plasma did not have any side effects on the metallurgical properties below 300ºC. On the contrary, the disadvantage of the plasma was the black appearance of the surface (the formation of stable magnetite) and this appearance depended on the kind of iron, its contents and the temperature degree. To remove the chemical residues after immersion in distilled water, the objects can be heated on plasma condition. Also, plasma did not affect the interior layer or the metal core because the maximum depth of the chemical effect of plasma on the metal surface did not exceed 5mm. Results indicated that temperature of plasma did not have any effect on the cast iron at the temperature ranges of (200-230ºC). The area of plasma bright light surrounding the iron objects significantly increases the rate of desalination in the iron surface artifacts, because of the effect of hydrogen atoms. This process can be destructive if the surface of the object has organic decorative.

Patscheider and Veprek (1986) argued that a new method based on the application of low pressure hydrogen plasma has been developed for the restoration of iron artifacts. It efficiently removes chlorides and by preventing any significant post-corrosion. The treatment temperatures of less than 400ºC do not introduce any irreversible changes in the wrought iron, preserving its original composition, structural inclusions and morphology, which contain important information on the origin and manufacturing methods of the artifact.

Most of the objects had a different amount of chlorides before treatment, because the long term the object spent in marine environment allowed growth on the metal objects. The duration of desalination depends on the state of the iron object, the rate of corrosion, and the condition of treatment.

The magnetite layer thickness after desalination was about 25-100 µm, evaluation by SEM. Unfortunately, the weight of the cast iron objects were changed after desalination treatment by -0.1 to – 2.0% and dimensions of -0.2 to -0.5 % in diameter. The wrought iron changed in weight by 100- 600gm according to the size of the object and its state. The dimension was changed by 5- 10mm. Generally, the changes in wrought were less than the cast iron. Sjogren and Buchwald (1991) have reported that the major mineral after treatment was identified as magnetite, and the objects generally assumed an iron-grey surface color.

After finishing the dechlorination treatment for one year, the coupons and iron artifacts were not protected, and they resisted the oxidation and relative humidity in our laboratory in Demokritos. No further corrosion developed, the micro hardness remained unaltered on the tested samples (the range of 200-250HV), when the chloride level was below 0.3% (EDS evaluation). Stabilization of iron coupon and artifacts has occurred for most of the objects (about 70%) by these dechlorination methods. After finishing dechlorination treatment, the wrought iron artifacts were covered by paraloid B72 for protection. Only tannic acid was used as inhibitor for sealing cast iron cannonball. North and Pearson (1977) said that thermal decomposition reactions of prepared FeOCl and natural marine cast iron corrosion products in inert, oxidizing and reducing atmospheres were determined for temperatures up to 1000°C. Rodgers (2004) explained that the cast iron artifact will retain its shape but the outer layer may only be very soft graphite. Conserving the archaeological surface in this case may mean

The C1 < 0.3% is not sufficient to create new corrosion attacks under normal indoor conditions and after protection in Demokritos lab. This level of Cl < 0.3% was so difficult to be achieved by hydrogen plasma reduction and/or immersion in sodium hydroxide in most of the objects.

The reduction of iron oxides and the removal of chloride were effective to the depths of 2mm below the surface of the wrought iron, but for 5mm below the surface of the cast iron because of the effect of cracks and pores that were under the surface. This method is efficient for removing chlorides from the non-porous metal artifacts and the object containing a metal core. This is in agreement with earlier findings by Daniel (1979) who noted that the hydrogen penetrates to a significant depth under the gross surface, as documented by the transformation of iron oxides in cracks and fissures, 5mm under the surface. Iron erosion (physical sputtering) was not observed. Also all edges on cut samples were as sharp after two weeks' glow discharge as before, and reduction to free iron was not observed.

From literature as found by earlier researchers like Degrigny and Spiteri (2004) on desalination by chemical solution such as sodium hydroxide is the most effective in the treatment of iron archaeological objects. It is very effective for removing the chloride ions. Complete dechlorination of most of the objects was not accomplished.

Even a dilute solution is the best to protect the natural passivaed layer of magnetite. If the solution is changed after short regular time, the chlorides will not need much time to be removed. The dechlorination treatment durations of the cast iron objects were longer than the wrought iron objects based on the initial structure. The disadvantage of this method based on washing out the chlorides in sodium hydroxide solution is the re-corrosion. Missing parts in magnetite layer has occurred for one object after finishing the chemical desalination treatment. This is related to findings by Argyropoulos et al., (1997) that the chemical treatment with sodium hydroxide solution begins by completely immersing of the heavily or partly mineralized iron artifacts in 2-5% (w/v).

According to Sjogren and Buchwald (1991) and Schimit (2002) on the treatment by plasma reduction combined with sodium hydroxide, the method which we also used. Some conservators start with the treatment by plasma to remove the encrustation of marine and corrosion compounds by thermal expansion. Sodium hydroxide (the most famous solution) is the strongest base solution in removing the chlorides and passivating the object.

The object which was desalinated with chemical solution can re-rust very rapidly and we can find some new compounds after desalination. The dechlorination treatment to remove the salts leads to an internal explosion by osmotic pressure, if the condensation of salts after drying without immersion immediately in distilled water, after excavation. This phenomenon was shown clearly in cast iron artifacts.

The desalination by sodium hydroxide in the hot condition combined with plasma reduction is the best method for the encrusted artifact for the following reasons:

This desalination treatment method is an efficient to decrease the chlorides and improve the surface appearance by passivation and formation of magnetite. The combination between sodium hydroxide in the hot condition and plasma reduction speeds the duration of desalination. Chloride level after finishing the desalination of the coupons by the two methods was 0.16% (Wt.) in short time.

This method can be used, because of the use of plasma helps to avoid exposing the metal artifacts to oxygen and prevent re-corrosion. Reactivation corrosion after immersion in sodium hydroxide solution was very rare during the treatment by chemical solution, so these methods can be used.

The encrusted objects could not be treated immediately after the excavation with any dry methods as plasma without immersion in wet chemical treatment because the rapid drying or faulty dehydration tends to destroy this object by formation of abnormal encrustation and cracks.

Sodium hydroxide did not affect the marine and calcareous materials so the combination method supported cleaning these materials were the best method. The new technology (plasma reduction) had a good role for removing the residue of the washing solutions on the surface, but it was incompletely removed. Cast and wrought iron artifacts needed long term for removing the moisture inside the objects in order to dry completely. This method suits the fragment or completely corroded artifacts at low concentration of NaOH combined with plasma reduction at a low temperature after recovering from the seawater. Desalination by sodium hydroxide is the most effective in the treatment of iron archaeological objects.

After the first treatment of the objects for 21 hours, akaganeite presence was evident in most of the objects, and at the same time, goethite and hematite have already appeared at low levels. This result is in agreement with earlier findings by Kotzamanidi et al., (1999),

Temperature reduction of the cast iron artifacts that was less than 250˚C did not introduce any changes on the initial structure (iron 95% and carbon > 3%). The temperature was selected according to the melting point of the iron and its alloys (iron 2750˚F, cast iron 2350˚F and steel 2500˚F) and the diagram phase of the iron and its alloys. This result is also agreement with earlier findings by Ståhl and others (1998) that It was demonstrated that heating could cause the release of the chlorine (but only when heated above 200°C which transforms akaganéite to hematite (α-Fe_2O_3), and that the chlorine could not be removed from inside the tunnels of akaganéite by washing with water (Selwyn 2004).

Chemical residues left on the artifact after chemical desalination can cause long-term problems; but the immersion in the distilled water followed by heating in the plasma oven at 80˚C for 24 hours effectively removed most of this residue.

Chemical desalination treatment by using (sodium hydroxide) and/or physical treatment by plasma reduction were compared and the results showed that plasma reduction is the fastest desalination method, where sodium hydroxide is the strongest solution to decrease the level of chlorides. These methods did not completely remove the chlorides.

Cast iron objects needed more time than wrought iron to desalinate by chemical treatment (sodium hydroxide) and/or plasma because their initial structure and porous surface.

This study shows that it is possible to have the lowest level of chlorides by (plasma reduction in low pressure and low temperature (100-300ºC) and/or sodium hydroxide (1-2% and pH 13.5) in hot condition. It should be taken into consideration that partial reduction for oxidized objects may be re-corroded.

Finally, we can say that these methods are aspects of the desalination and passivation method; so it rescues corroded artifacts which would otherwise be totally destroyed. Longer duration of desalination can be more effective than increasing the condition for removing the chloride ions.

The main disadvantages of using sodium hydroxide is that firstly, the salt movement is slow from the metal removed from the marine environment after the first stage. The removal rate of chloride on wrought iron was faster than cast iron artifacts. Although, sodium hydroxide has a slight force for removing the chlorides from the initial layer. Most of the cast iron objects, after the treatment, became porous in different forms.

At the same time, the methods of investigation and analyses of ***wrought iron*** shows that the deposits before the treatment consisted of three layers, sometimes the objects had four layers; this phenomenon was shown on metallographic microscope and SEM. An external zone of marine compounds (red-brown clay) and calcareous compounds (Calcite- is the main constituent of sea shells and other calcareous materials, which is insoluble in water) with low amount of iron corrosion.

There was a direct relationship between high temperature and the fastness of chlorides removal during the desalination method. At the same time, plasma was used to dehydrate the objects after any wet chemical treatment and it had a good efficiencies. The results demonstrate that chloride ions were more effectively removed from archaeological iron by immersion in NaOH than immersion in the other solutions.

Plasma is a new technology used in the reduction and protection of the metal surface. This treatment duration depends on temperature, pressure and the time of reduction.

The corrosion oxides were hardened more than before with marine compounds for the objects that were dried firstly by plasma. After desalination, some marine compounds (red clay) were transformed into new compounds. Plasma reduction was used at temperature range of 100-300ºC.

The efficiency of chemical treatment depended on the concentration of the chemical solution, the pH, the temperature and the treatment’s duration. Immersion the object in the solution is more effect than swapping by using mechanical tools.

Comparison of the advantages and disadvantages of the desalination methods was the evaluation of the efficiency of these methods. It was found out that objects which have been desalinated by using sodium hydroxide and/or hydrogen plasma were less likely to re-corrode after passivation of the surface. Chloride saturated water was more corrosive than the other environments, so re-corrosion in storage was the best indicator of success of reductive dechlorinstion methods. The efficiency and success of these desalination methods of iron artifacts are systems to monitor quantitatively the chloride concentration after each stage.

The completely corroded artifacts were in a brittle interior layer as powder because of the high concentration of the chlorides. There is a risk of disintegration, if treatment using the plasma conditioning and/or chemical treatment. However, the treatment of the completely corroded objects was reduced by plasma reduction at low temperatures of 80-100ºC.

15.2 Recommendations

Cooperation between **the conservator** and archaeologist after excavation from the marine environment immediately is so important to preserve all the marine finds. The metal iron finds must be separated into each group (similar objects) during the treatment. Gilberg and Seeley recommended that the removal of the chloride ions is absolutely essential for preservation and conservation of the iron artifact (Gilberg and Seeley 1981).

X-ray radiography is used to assess the state of ancient objects, the original size, and the effect of plasma on the decorative surface.

The solution of silver nitrate should be stored in a dropper in a dark place, because it is somewhat light sensitive and the solution can be transformed for dark color. Depending upon the structural strength of the object, and the compounds of the environment, iron objects or fragments may be lifted out of the marine environment for setting up a marine archeology museum.

Cast and wrought iron should be carefully dried, because waiting for the objects to dry after the excavation tend to make it crack with possible damage. To avoid any damage of the objects to be fragile, we recommend starting the desalination treatment of the iron artifacts immediately (in situ) after the excavation or during the transportation to desalinate artifacts by immersion in distilled, fresh or de-ionized water follow by immersion in dilute NaOH (1.5-2%).

Degrignya and Spiteri (2004) recommended that 1% (w/v) NaOH solution is used instead of KOH because of the presence of large quantities of chlorides in the KOH brand available in Malta (Degrignya and Spiteri 2004).

Generally, objects shouldn't be allowed to dry out after excavation, before or during the chemical treatment without desalination the chlorides and removing the clay and calcareous deposited along the objects and removing concrete formation of these materials. Objects should be treated on-site (after the excavation) till bringing them back to the lab or to be stable enough that the decision of conservation can be known (the suitable method).

The solutions are regularly changed, which encourages further diffusion of salts until almost all of the soluble salts are removed (with the test of chlorides level). All the samples and objects require long time for treatments by any way to remove the chlorides. After the excavation, and finishing treatment stages of the metal archaeological objects, they need a special display cases that should be designed for metal objects (RH-less than 20% and temperature degree between 15-25ºC), especially when the iron artifacts from underwater excavations because of the remain traces of chloride ion. The first warning is that an artifact can be treated by unsuitable method as the chemical solution can cause corrosion of iron or the high temperature from plasma can destroy the metallurgical properties.

At relative humidity levels ≥ 56% (Common problems), the chloride containing solution can occur on the objects surface as yellow droplets, called 'weeping' iron. It is shown that iron objects are corroding in ambient conditions during treatment by chemical treatment or plasma reduction, because the chlorides can renew the corrosion process.

The combination of different pretreatment methods (investigation and analyses) and treatment methods improved the applicability and the results. The iron objects undergo stabilization and conservation if long-term preservation is to be accomplished. So we should intend to evaluate the material of inhibitor and coating materials again after 3–5 years, to highlight heterogeneities on the coatings if present on the artifact. Before applying the coating materials or inhibitors, surface should be cleaned. Also, all open holes or micro cracks it should be covered in the surface.

Rust must be converted to magnetite, the most stable iron oxide after desalination treatment. Upon arrival at the laboratory, the cast can be stored in 1-2 percent solution of sodium hydroxide. After excavation, objects should be gently washed in clean running water to remove salt deposits from their surfaces, and then immediately dried in air. The removal of rust by using phosphoric acid had an effective role on the removal of the chlorides, but the disadvantage of this solution which changed the surface color of the objects during the long time of immersion.

After excavation and during immersing the objects in distilled water, we showed that some object can re-rust, so we recommend to add an inhibitor (dilute concentration) to the rinse solution thus inhibiting further oxidation and allow them to dry out slowly.

Some chemical solutions (acids in high concentrations or sulfuric acid) are negligible as its harmful effects for the metal artifacts. The objects shouldn't be exposed to air (during the chemical treatment or plasma reduction) until the chlorides have been removed from the metal to inhibit the reactivate or re-rust. We recommend that the temperature of the treatment by using plasma reduction is not above 300°C, and at the same time plasma encourages conservator to treat many objects to save the time. If the chemical residues left on the artifact can cause long-term problems on the stable of the protection material, so after any chemical treatment, the object must immerse completely in distilled water.

The badly corroded and friable archaeological specimens, the only treatment for them will be by consolidating with wax and reducing of some mineralized metals in the future. Vacuum apparatus is the main machine in the all of the stages of the chemical treatment and the preparation of the investigated and analyzed sample.

Coupons, objects and the samples of examination and analyses should pack in sealed containers with silica gel. Conservators should know most of the treatment methods which have side effects on the skin and breathing and we recommend wearing (safety glasses and gloves) and not opening the door of Plasma machine during the treatment because the effect of radiation. Rees-Jones (1972) used wax for protecting cast-iron artifacts and it was effective for cast iron, but we don't to use it, because the cast iron is considered a porous material.

After finishing the desalination treatment, the metal should be appropriately coated or painted by the inhibitors. Porous objects, such as cast iron required multiple applications of lacquer of tannic acid in order to build up a base that will prevent absorption of the humidity. The completely corroded object couldn't be desalinated, but they can be preserved in good storage with silica gel crystals.

We recommend to use tannic acid that can be removed by soaking in hot water for two hours and paraloid that can be removed or dissolved by soaking in acetone. However there are no inhibitors or protection materials that can completely prevent the post – corrosion, if the objects contains chloride ion in high level.

The iron objects from the marine environments required an immediate treatment to prevent any deterioration. We should clean the oven of plasma after each stage of the treatment, to remove the residual of the chemical gases as (HCl). Before opening the door of the oven after finishing the reduction treatment, the use of argon gas is so important to clean the toxic atmosphere.

15.3 Future studies

We propose the following points which can be subject of future:

- The effect of hydrogen plasma and (hydrogen +argon) on the other metal object from the marine environment. The use the plasma on protection by polymer the metal objects after the treatment.
- The treatment of the cast iron in the open environment and the retreatment of some cast iron object which dried without removing the chlorides.
- Laser cleaning will be one of our goals to use it after the chemical treatment to remove the calcareous and earthy compounds.
- Studying the effect of enzymes and oxygen plasma (comparison study) on removing the old coating material, this will be the best method because they don't affect the metal objects.
- Studying the present environmental control techniques for exhibition cases, especially the relative humidity and temperature.

- Further studies are needed to better understand the effectiveness of different methods of dechlorination treatments.

CHAPTER 16

CONCLUSIONS

The combination of the investigations and analyses methods play a means of evaluating the desalination methods. These allow visualizing the effectiveness of the desalination treatment by using sodium hydroxide and/or hydrogen plasma.

Plasma treatment has mechanical, physical and chemical effects during the desalination treatment. Sodium hydroxide did not affect the marine encrustation, but it has a good effect on the chloride extraction rates from marine iron artifacts. The storage prior treatment by immersion in distilled water was to remove the soluble salts.

Sodium hydroxide in hot condition combined with hydrogen plasma is considered the most effective desalination method and it resisted the re-rust of the object after reduction the chlorides because of the good effect of this treatment by passivation of the surface. Also, the desalination methods succeeded in the transformation of the corrosion layers associated with chloride compounds into a natural protection layer of the magnetite. In comparison to other established marine iron artifacts desalination treatment, the use of sodium hydroxide followed by hydrogen plasma reduction presents many advantages:

Plasma reduction speeded the reduction of the chloride level, the corrosion compounds and the marine encrustations adherence. Insoluble chlorides were decreased slowly by sodium hydroxide.

Transformations of the chlorides and corrosion layer into magnetite were performed and were observed for all the iron coupons, but in the case of iron objects, the reduction of akaganeite into magnetite did not occur easily because of the high level of chlorides. All of the acids did not affect the chloride levels of the iron objects, but some of them like phosphoric and citric acid were used before. So, the selection of the alkaline solution as sodium hydroxide attributed to the high removal effect of the chloride ions.

The higher temperatures led to more efficient desalination of the objects in a shorter period. Also, the longer duration led to the higher removal of chlorides by using the desalination methods. But, concentrated sodium hydroxide can cause burns of the skin of the object (natural protective layer) that is often superficial by missing some parts in this layer. Also, the high temperature plasma ≥ 400ºC can cause burns in the object surface and can change the metallurgical properties or irreversible changes in the wrought iron.

In conclusion based on our findings in this doctoral research, heated sodium hydroxide, followed by hydrogen plasma reduction is the best method of desalination treatment of the marine iron artifacts. The final appearance and the level of the chlorides are the most important factors of evaluation the best treatment methods.

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GLOSSARY

Alloy	A mixture or compound of two or more elements, at least one of which is metallic.
Annealing	Is a softening process of heating and cooling sheet metal, which has become work-hardened by hammering, spinning, or stamping, in order to relieve stress and to return the metal to a malleable state.
Brittleness	Could therefore be defined as lack of ductility.
Casting	An object created by pouring molten metal into a mold.
Cast iron	Is a generic term that identifies a large family of ferrous alloys. Cast irons are primarily alloys of iron that contain more than 2 percent carbon and 1 percent or more silicon.
Chlorides	Salt of chloride that is generally soluble. High concentrations contribute to corrosion problems.
Coating	a protective barrier, usually a synthetic resin or a wax, applied to a metal surface
Conservation	Is the profession responsible for the preservation of material culture.
Consolidant	A liquid solution of a resin (normally a synthetic polymer) used to impregnate a fragile object in order to strengthen its structure.
Corrosion	the electrochemical degradation of a metal, due primarily to the loss of electrons and the recombination of metal ions with other electro-negative elements such as oxygen, carbon, sulfur, chloride, and nitrogen
Corrosion products	The results of interaction between a metal and its environment. They normally take the form of a disfiguring film or crust but are sometimes valued, as in the case of a patina.
De-ionized water	Water that has been purified by being passed through an activated resin to remove dissolved salts and other impurities.
De-passivation	Destruction of the protective oxide layer due to carbonation and chloride attack.
Desalination	Is the process of removing salt, other minerals and contaminants from the object.
Electrolyte	A nonmetallic substance that carries an electric current, or a substance which, when dissolve in water, separates into ions which can carry an electric current.
Environmental	A general term which includes the study of ancient plants, animals, insects and soils.

archaeology	
Etching	The production of patterns on a surface by the use of a corrosive chemical agent. Chemical etching is the oldest and most commonly applied technique for production microstructural contrast. In this technique, the etchant reacts with the specimen surface without the use of an external current supply. Etching proceeds by selective dissolution according to the electrochemical characteristic of the component areas.
Galvanic series	A list of metals and alloys arranged according to their relative corrosion potentials in a given environment.
Hardness	Hardness is the property of a material that enables it to resist plastic deformation, usually by penetration. However, the term hardness may also refer to resistance to bending, scratching, abrasion or cutting.
Inhibitor	A chemical substance or combination f substances that, when present in the proper concentration and forms in the environment, prevents or reduces corrosion.
Investigative conservation	The process of uncovering information about an object through actions such as examination under a microscope, radiography and corrosion removal.
Iron tannate	A dark-coloured layer on the surface of iron objects produced deliberately as part of a conservation treatment with tannic acid to provide a measure of protection against corrosion.
Localized corrosion	Corrosion at discrete sites, for example, pitting, crevice and stress corrosion
Mechanical cleaning	The selective removal of dirt, corrosion and concretion from the surface of artifacts using hand-held tools (such as a scalpel) or small power tools (such as the air abrasive).
Metallic bonding	Bond formed by positive ions surrounded by a sea of valence electrons.
Mineral	A term applied to inorganic substances such as rocks and similar matter found in the earth strata, as opposed to organic substances such as plant and animal matter. Minerals normally have definite chemical composition and crystal structure.
Noble metal	A metal with a standard electrode potential that is more noble (positive) than that of hydrogen.
Osmosis	A process of diffusion of a solvent such as water through a semipermeable membrane which will transmit the solvent but impede most dissolved substances. The normal flow of solvent is from the dilute solution to the concentrated solution in attempt to bring the solution on both sides of the membrane to equilibrium.
Oxidation	Loss of electrons by a constituent of chemical reaction. Also refers to the corrosion of a metal that is exposed to an oxidizing gas at elevated temperatures.

Porosity	Measures of the volume of internal pores, or voids, in ion exchanges and filter media; sometimes expressed as ratio to the total volume of the medium.
Paraloid B72	A reversible synthetic resin used in archaeological conservation as an adhesive and consolidant.
Passivity	The state of a metal surface characterized by low corrosion rates.
pH	A measure of the degree of acidity or alkalinity (basicity) of a solution; the negative logarithm of the hydrogen –ion activity. At 25˚C, 7.0 is the natural value. Decreasing value below 7.0 indicates increasing acidity; increasing values above 7.0, increasing basicity.
Pitting	Corrosion of a metal surface, confined to a point or small area that takes the form of cavities.
Preservation	Is the specific effort to not merely stop but reverse the various negative and unwanted effects of destructive chemical and other agents that can destroy the objects. Preventative conservation is the most direct and uncomplicated way of caring for works of art or artifacts.
Reduction	Is the movement of anions (chlorides and sulphides) to rise and remove them from the surface of the objects.
Replacement corrosion	The corrosion that forms on and below the original surface of a metal object, effectively replacing these parts and often replicating surface detail.
Rust	A corrosion product consisting of hydrated iron oxide. This term is properly applied only to ferrous alloys.
Salinity	A measure of the amount of dissolved salt in water.
Saline water	Water containing an excessive amount of dissolved salts, usually over 5000mg/L.
Smelting	A melting process that causes materials to separate into two of more layers.
Solution	A homogeneous dispersion of two or more kinds of molecular or ionic species. Solutions may be composed of any combination of liquids, solids, or gases, but they always consist of a signal phase. A liquid, such as boiler water, containing dissolved substances.
Tempering	Is the process of heating the hardened iron enough to allow some crystals to reform, but still retains some of the amorphous structure. Tempered iron has more spring than the hardened iron.
Tannic acid	A pale brown powder which, in solution, is sometimes used in conservation of iron to form a protective black surface film.
Titration	An analytical process in which a standard solution in a calibrated vessel is added to a measure volume of sample until an endpoint, such as a color change, is reached. From the volume of the sample and the

	volume of standard solution used, the concentration of a specific material may be calculated.
Hardness of a material	The resistance the material exhibits to permanent deformation by penetration of another harder material. Hardness is not a fundamental property of a material and hardness values are thus arbitrary.
X- ray radiography	A non-destructive imaging technique used widely in archaeology to produce images on film which show the details beneath the surface of badly corroded metalwork for example.
XRF analysis	X-ray fluorescence analysis, a non-destructive technique used in archaeological research to identify the elemental composition of a material.

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