

## Preservation Methods of Historical Iron Objects: An Overview

Vimal Kumar\*

(Archaeological Survey Of India, Science Branch, 29 New Cantt Road, Dehradun -248001)

\*Corresponding Author: vimal\_drl@yahoo.in

**Abstract :** This Paper Intends To Expose The Methods Of Preservation Of Historical Iron Objects. Scientific Cleaning Methods For Nails, Cannons, And Bell Are Mentioned. Sodium Hydroxide For Cleaning And Microcrystalline Wax For Protective Layer Are Most Suitable Chemicals For The Treatment Of Iron Objects. Corrosion Processes, Signs And Causes Of Active Corrosion On The Surface Of Iron Objects With Desalination Procedure Are Also Described In This Study.

**Keywords -** Iron Objects, Preservation, Cannons, Cleaning Methods, Desalination.

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### I. INTRODUCTION

Ancient Metallic Objects Are Made Of Many Materials. Some Of Made Of Single Metal, Such As Iron, Gold Copper, Silver, Tin, Or Copper And Its Alloys. There Are Also Some Composite Objects Made Of Several Metals, Like Platted Copper Onto Iron Base. Metallic Artifacts Occur A Major Problem Due To Their Corrosion, Especially If They Have Been Buried In The Ground And They Have Also Difficulty To Protect Against Oxidation While In Storage [1]. Archaeological Metalwork Is The Category Of Objects Made Of Or Containing A Metallic Element. There Are Many Metals, But Only A Small Number Were Regularly Used In The Past To Make Objects. Although Some Metals Such As Gold Are Found In Their Elemental State In Nature, Most Metals Have To Be Produced From Ores, Commonly Metal Oxide Or Sulfide Minerals. An Alloy Is A Mixture Of Two Or More Metals, Used To Manipulate The Properties Of The Material And Reduce The Cost Lowering Precious Metals Content, Such As Gold, While Maintaining Their Appearance. Non-Metallic Elements Such As Carbon Were Deliberately Introduced To Change The Properties Of The Material. Archaeological Science Strives To Constrain The Practices And Motives Of People In Antiquity [2]. Archaeological Metallic Artefacts Buried In Soils Deteriorate By Means Of Various Environmental As Well As Internal Factors And Mechanisms Over Time Such As Change In Composition And Microstructure Of Metal And Corrosive Factors Due To Long-Term Burial Environment. Corrosion In Metals Occurs In Different Morphologies And Results In Different Types Of Corrosion Products Based On Soil Composition. Identification Of Corrosion Mechanisms And Morphology In Archaeological Metals Can Help Conservators To Characterize Deterioration Occurred In Metals And Make Decisions To Protect Artefacts About Preventing Further Deterioration. In Archaeological Bronzes, Different Layers May Form On The Surface Of Artefacts And Their Composition, Depth And Shape Depends On Factors Noted Above [3]. The Present Study Intends To Disclose The Scientific Preservation Methods For Historical Iron Objects.

### II. Iron

Iron Is A Chemical Element With Symbol Fe (Ferrum) And Atomic Number 26. It Is The Metal In The First Transition Series [<https://en.m.wikipedia.org>]. Iron Is Seldom Pure Minor Levels Of Other Constitution Can Introduce Very Different Properties Into Resultant Alloys. The Alloying Elements Of Greater Interest. However Carbon Which In Concentrations Ranging From 0 To 5 Percent Greatly Effects The Properties Of Te Different Alloys Formed. A Description Of The Properties Of Alloys Containing Different Amounts Of Carbon, The Phases Present And Their Nomenclature Is Given In The Table 1 Which Was Described By Cronyn 1990 [4]. If The Percentage Of Carbon Increases In The Composition The Hardness And Strength Of Iron Will Increases.

**Table. 1. Classification Of Iron According To The Percentage Of Carbon Contents.**

Entry	Carbon Contents	Modern Name		Archaeological Name	Phase Presents		Properties
1	0-0.008	Wrought Iron		Wrought Iron	Ferrite	Mixed With Carbon	Very Malleable
2	0.008-0.07	Dead Mild	Low Carbon				
3	0.07-0.15	Mild	Steel	Carburized	Ferrite+ Pearlite		

4	0.25-0.55	Medium Steel	Carbon	Iron(Steel)		+ Slag In Wrought Iron	
5	0.55-0.85	High Carbon Steel					
6	0.85				Pearlite		
7	0.85-0.9						
8	0.9-1.6	Tool Steel			Cementite + Pearlite		
9	2.5-5	Cast Iron : White Grey		Cast Iron: White Grey	Graphite + Ferrite+Pearlite		Very Brittle: Cannot Be Worked

### III. Nature Of Deteriorated Iron

In The Soil And Underground Environment, Iron Objects And Artifacts Shows Blue, Black Or Brown Oxide Patinas Which Can Be Made Deliberately By Controlled Heating Of Iron, Brown May From Naturally In Relatively Dry Air Without Pollution. This Condition Is The Typical Appearance Of Iron Excavated From Damp Sites. The Mass Is Composed Of Iron Oxides And Carbonates. The Description Of Visible Observation And Symptoms Of Corroded Iron Product Described By Jegdics, 2011 In The Table 4 [5,6,7].

### IV. Signs Of Active Corrosion

Active Post-Excavation Corrosion Has A Number Of Characteristic Visual Symptoms, Given In Table 2 Where Were Described By Loeper-Attia, 2007 [8]. Although Not All Of These Symptoms Will Necessarily Appear Together, They Are Related To Each Other Example: Cracking Is The First Stage, Which May Then Be Followed By Flaking And/OR Delamination, If Corrosion Is Allowed To Continue.

**Table 2. Visual Observations And Symptoms Of Active Iron Corrosion.**

Entry	Active site	Symptoms
1	Surface corrosion	Often orange or brown, fine crystals across surface or larger individual crystals
2	Weeping	Droplets of liquid on surface, often coloured yellow to brown. Dry to form fragile spherical shells
3	Cracking	May be longitudinal, transverse or in networked formations, and of various lengths. May contain fresh corrosion products
4	Blisters and flakes	Rounded pieces of outer corrosion layers lift, forming blisters, which may then flake off completely. The underlying scar may contain bright orange crystals
5	Delamination	Outer corrosion layers lift away from the metal core. Very damaging, can break objects apart completely

**Table 3. Threshold Limits Of Relative Humidity For The Control Of Active Iron Corrosion.**

Entry	Lower Relative Humidity		Moderate Relative Humidity	Higher Relative Humidity	
	Bellow 11%	11% To 19 %	20 % To 30 %	30% To 50 %	Above 50 %
1	No Corrosion Occurs	No Corrosion On For Objects Kept Below 70 % RH Ince Excavation	Corrosion Rate Increases Gradually Up To 30%	Corrosion Increases More Rapidly Above 30%	Rapid Corrosion Occurs (Exact RH Depends On Temperature)
2	-----	Very Slow Corrosion For Those Exposed Above 70%	-----	-----	-----

### V. Causes Of Active Corrosion

Salts From The Burial Environment Are The Principle Cause For Damaging Corrosion Of Iron. The Rate Of Salt-Driven Corrosion Of Iron Is Strongly Correlated To The Relative Humidity (RH). Research Has Been Carried Out To Determine The Effects Of Pollutants On The Corrosion Of Iron, And Suggests That There Is A Complex Interplay Of Factors, Including Pollutant Levels Alone And In Combination With Each Other, The RH And Temperature. Composite Objects That Contain Iron With Copper May Be At Additional Risk. As Well As The Effects Of Galvanic Corrosion, Whereby Copper Corrodes Less At The Expense Of The Iron, Which Corrodes More Rapidly, The Copper Ions Present Increase The Corrosion Susceptibility Of Iron Even Further [42]. Iron Objects From Waterlogged Sites Are Normally Less Susceptible To Corrosion From Chloride Salts And Can Remain In Good Condition [9]. They May Be At Risk From Sulfur-Based Corrosion Owing To Unstable Iron Sulfide Corrosion Products Formed During Burial. Many Iron Objects In Museum Collections

Have Been Previously Treated In A Range Of Ways, From Stripping Of All The Outer Corrosion Layers To Chemical Treatments To Remove Salts And Mechanical Removal Of Outer Corrosion To Reveal The Original Shape Of The Object. As No Treatment Is Guaranteed To Be Completely Successful, All Previously Treated Objects Remain Potentially Susceptible To The Problems Of Active Corrosion.

**Table. 4. Description Of Corrosion Products, Minerals With Chemical Name And Formula.**

Entry	Colour	Mineral	Chemical name	Chemical formula
1	Black	Magnetite	Iron(II,III) oxide	Fe <sub>3</sub> O <sub>4</sub>
2	Red or black	Hematite	Iron(III) oxide	α-Fe <sub>2</sub> O <sub>3</sub>
3	Yellow-brown	Goethite	Iron oxy-hydroxide	α-FeOOH
4	Red-brown	Akaganeite	Iron oxy-hydroxide	β-FeOOH
5	Orange	Lepidocrocite	Iron oxy-hydroxide	γ-FeOOH
6	Yellow-brown	Siderite	Iron carbonate	FeCO <sub>3</sub>
7	White	-	Iron(II) chloride	FeCl <sub>2</sub>
8	Green	-	Iron(III) chloride	FeCl <sub>3</sub>
9	Dark blue (or white)	Vivianite	Iron phosphate octahydrate	Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> 8H <sub>2</sub> O
10	Pink	Strengite	Iron phosphate dihydrate	FePO <sub>4</sub> 2H <sub>2</sub> O
11	Yellow-brown	Pyrrhotite	Iron sulphide	Fe <sub>1-x</sub> S (x=0-0.2)
12	Yellow-brown	Mackinawite	Iron sulphide	Fe <sub>1-x</sub> S (x=0.01-0.08)
13	Yellow	Pyrite	Iron sulphide	FeS <sub>2</sub>
14	Blue-black	Greigite	Iron sulphide	Fe <sub>3</sub> S <sub>4</sub>
15	Green	Rozenite	Iron sulphate tetrahydrate	FeSO <sub>4</sub> 4H <sub>2</sub> O
16	Blue-green	Melanterite	Iron sulphate heptahydrate	FeSO <sub>4</sub> 7H <sub>2</sub> O
17	Orange	Butlerite	Iron hydroxide sulphate dehydrate	Fe(OH)SO <sub>4</sub> 2H <sub>2</sub> O
18	Yellow-brown	Jarosite	Iron potassium hydroxide sulphate	Fe <sub>3</sub> K(OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>
19	Yellow-brown	Natrojarosite	Iron sodium hydroxide sulphate	Fe <sub>3</sub> Na(OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>

### 1.1. RELATIVE HUMIDITY AND ITS ROLE IN CORROSION

Many Corrosion Reactions Involve Water. In The Burial Environment, Objects Are Damp From The Surrounding Soil. In The Atmosphere, The Moisture Content Of The Object Is Controlled By The Water Content Of The Air. The Amount Of Water Vapour That Air Can Hold Is Dependent On Temperature, And Is Normally Expressed As Relative Humidity (RH). RH Is The Percentage Of The Total Amount Of Water Vapour Air Can Hold At A Given Temperature. Warm Air Holds More Water Than Cold Air Therefore, In A Closed Space, When The Temperature Decreases, The Relative Humidity Increases. If The Amount Of Water Vapour Exceeds The Maximum Amount That The Air Can. The Role Of Relative Humidity Describe In The Table Described By Costa, 2001 And Several Researchers [10, 11, 12, 13, 14].

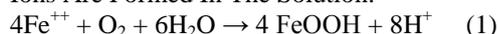
### 1.2. POLLUTANTS AND ITS ROLE IN CORROSION

Pollutants Are Airborne Compounds That Cause Or Enhance Corrosion Of Metals. The Source Of Pollutants May Be External (Eg. Car Exhaust Emissions And Industrial Processes) Or Internal (Eg. Emissions From The Materials Immediately Surrounding The Object In The Building, Showcase Or Storage Environment). Of These, The Most Common Source Of Problems For Archaeological Metals Is The Effect Of Organic Pollutant Gases From Inside Showcase Environments [15].

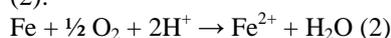
## VI. Corrosion Process In The Iron

It Is A Basic Principle That All Metals (Excluding The Noble Ones) Are Chemically Unstable In Ordinary Air But This Can Hardly Be Said To Be Part Of Common Knowledge. When Metal Comes In Contact With Oxygen A Chemically Unstable State Is Metal Oxide. A Metal Can, For Obvious Geometrical Reasons, Only React With Oxygen Where It Is In Contact With The Metal's Surface. So All Non Metal Are Covered

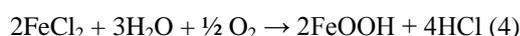
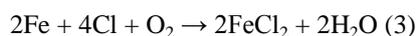
With A Layer Of Metal Oxide [16]. The Facilitates Access Of Oxygen Causes Rapid Iron Oxidation And  $\text{Fe}^{++}$  Ions Are Formed In The Solution:



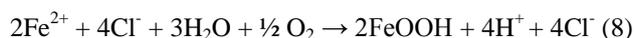
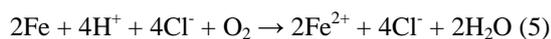
The Deposition Of Iron Oxy-Hydroxide ( $\text{FeOOH}$ ) Occurs As It Can Be Seen From Reaction (1), The Deposition Of Iron Oxy-Hydroxide ( $\text{FeOOH}$ ) Occurs With Hydrogen Ions Formation. It Is Important To Notice That The Presence Of An Acid Solution Allows Further Corrosion Of The Remaining Iron In Accordance With Reaction (2):



The Presence Of Chloride And Sulphate Anions In Corrosion Products Has An Important Effect As Well. Due To Charge Balance To The Present Positive Ions Close To The Surface Of Iron, Chloride Ions Accumulate In The Corrosion Product Layer Due To Their High Mobility And Their Dominance In The Surrounding Environment. Askey Et. Al., 1993 Have Proposed A Corrosion Cycle ("Acid Regeneration Cycle" ) Because The Hydrochloric Acid Consumed In The First Reaction Regenerates In The Second One. This Cycle Shows That Chloride Ions Play A Direct Role In The Process Of Corrosion.



Turgoose Et. Al., 1985 [18] Believe That Chloride Ions Play An Indirect Role In The Process Of Corrosion, Increasing The Solution Conductivity. In Addition, Due To Its High Hygroscopic Ability, The Presence Of  $\text{FeCl}_2$  Provides Moisture Necessary For The Evaluation Of Electrochemical Reactions. Their Point Of View Can Be Easily Seen, As Selwyn Et. Al., 1999 [19] Demonstrated, When The Previous Two Reactions Are Displayed As A Complete Dissociates:



Chloride Ions Are Not Involved In The Mechanism Of Electrochemical Reactions; They Are Present Only To Equalize The Charge In Reactions. It Is Known That These Ions Accelerate The Corrosion Of Iron, Because Of Their Difficulty To Establish And Maintain A Passive Film On The Iron Surface And Because Of Their Ability To Form Soluble Compounds To Be Incorporated Into A Passive Film Due To Their High Charge Density [19]. Graedel Et. Al., 1990 [20] Proposed A Similar Corrosion Cycle, But The Regeneration Of The Sulphuric Acid And Accelerate The Corrosion Process. Instead Of Forming  $\text{FeCl}_2$  In The Reaction With Sulphuric Acid, Iron Initially Forms  $\text{FeSO}_4$ , A Soluble Salt (Analogous To Reaction 4). The Oxidation Of  $\text{Fe}^{2+}$  Ions To The  $\text{FeOOH}$ , Releasing  $\text{H}_2\text{SO}_4$  (Similar To The Release Of  $\text{HCl}$ ), Then Leads To Further Corrosion. In Contrast To Chloride Ions, Sulphate Ions Are Gradually Separated From The Corrosion Cycle Since They Form Insoluble Iron (III) Hydroxyl Sulphates [19, 20]. The Oxidation Of The  $\text{Fe}^{2+}$  Ions In The Solution (Equations 4 And 6) Leads To The Deposition Of Several Types Of Oxyhydroxides, Such As Goethite,  $\alpha$ - $\text{FeOOH}$ , Lepidocrocite,  $\gamma$ - $\text{FeOOH}$  And Akagaenite,  $\beta$ - $\text{FeOOH}$ . The Third Form Of Oxyhydroxide, Akagaenite, Is Often Detected On Untreated Archaeological Artefacts Exposed To Air. The Formula Of Akagaenite, Stabilized By Chloride Ions, Often Found In The Literature, Is  $\text{FeO}_{0.833}(\text{OH})_{1.167}\text{Cl}_{0.167}$  [21, 22, 24]. As Indicated Above, Except Akagaenite,  $\beta$ - $\text{FeOOH}$ , Other Types Of Oxy-Hydroxides ( $\alpha$ - $\text{FeOOH}$  And  $\gamma$ - $\text{FeOOH}$ ) Can Be Formed, But In A Lesser Degree, According To Equations 4 And 6, If The Content Of Chloride Ions Is Low Enough. The Presence Of Akagaenite In Corrosion Products Is A Sign Of Active Corrosion Of Iron, Under A Layer Of Corrosion Products. A Higher Molar Volume Of The Precipitated Types Of Iron Oxy-Hydroxides Under (Or Inside) A Layer Of Corrosion Products Causes Stress, Occurrence Of Cracks And Other Defects In The Layer, Which Facilitates The Access To Oxygen And Moisture And Faster Progress Of Corrosion Processes. The Volume Of One Mole Oxy-Hydroxide Is Approximately Three Times Higher Than The Volume Of One Mole Of Iron, And Is  $20.9\text{ cm}^3$  For  $\alpha$ - $\text{FeOOH}$ ,  $21.7\text{ cm}^3$  For  $\gamma$ - $\text{FeOOH}$  And  $26.7\text{ cm}^3$  For  $\beta$ - $\text{FeOOH}$ . The Volume Of One Mole Of  $\text{Fe}_3\text{O}_4$  Is  $14.9\text{ cm}^3$  [22]. Another Symptom Of Corrosion Problems On Excavated Artefacts Is The Formation Of Either Wet Droplets Of Acidic Liquid (Known As The Formation Of Tears), Or Dry, Hollow And Red Spherical Membranes On The Object Surface, Visible Under The Microscope At Low Magnifications. The Formation Of Tears Is Associated With The Hygroscopic Nature Of Iron Chloride Salts. When Humidity Is Relatively High And Salt Absorbs Water, Wet Orange Paints Dissolve And Form Liquid Droplets. Iron Oxy-Hydroxides ( $\text{FeOOH}$ ) Are Deposited Along The Edges Of Drops {Because Iron (II) Ions In The Solution Are Subject To Oxidation And Hydrolysis} And Form A Frame For A Spherical Shell [19, 21, 22, 25]. Visually, By The Appearance Of An Artefact Covered With A Layer Of Corrosion Products, It Is Not Possible To Estimate

How Much Of Iron Core Is Left And Whether There Is A Presence Of Cracks And Other Defects In The Material. Watkinson Et. Al., 1983 [26] Suggested One Of Such Determination Procedures, Based On Measuring The Ratio Of The Artifact Mass (Determined On The Analytical Balance) And Its Volume (Based On The Amount Of Fluid Displaced After Immersion In An Appropriate Solution). The Ratios Lower Than 2.9 Indicate That The Artefact Is Fully Mineralized. Another Method, Proposed By Thickett Et. Al., 2008 [27] Is Based On The Measuring Of The Amount Of Oxygen Consumed Along Time. The Consumption Of Oxygen Is Related To The Development Of The Corrosion Process Under A Layer Of Corrosion Products. The Majority Of Authors [7, 27, 28] Consider The Most Reliable Method To Be The Radiographic Method For Estimating The Amount Of Iron Core And The Types And Forms Of Damage.

## **VII. Cleaning Of The Iron Objects**

The Antique Metal Objects Should Be Examined To Make Sure It Is Strong Enough To With Stand The Amount Of Handling Needed For Cracks , Weak Areas , Old Repairs , And Loose Or Missing Parts. Plating Is A Coating Of One Metal Over Another Metal, And Tin Or Zinc Plating May Be Found On Some Objects Crated With Thin Sheets Of Iron. Zinc Plating Is Generally Referred To As Galvanizing. Patina Is A Thin Chemically Induced Layer Of Relatively Stable Corrosion On The Surface Of An Objects. Many Iron Alloy Artifacts, Particularly Weapons, May Have Original Patinated Surfaces Of Dark Brown Or Dark Blue [29]. The Clean Well-Ventilated Work Area Are Required For The Cleaning And Waxing Process. Place A Clean Piece Of Muslin Or Other Soft Cotton On The Table As A Work Surface. Materials Required To The Cleaning And Waxing Of The Iron Objects [29]: Clean Cotton Padding Placed Over A Stable Work Surface; Heavy Polythene Sheeting To Protect The Padded Work Surface; Cotton Swabs; Gloves: Latex, Vinyl Or Polyethylene; Mineral Sprits; Ultra Fine (4/0) Steel Wool; A Penetrating Lubricant That Displaces Moisture; Soft Clean Natural Bristle Brushes, Such As Hake, Watch, Or Paint Brushes; Stiff Natural Bristle Brushes And Bamboo Skewers; Apron Or Smock To Protect Clothing; Clear Microcrystalline Paste Wax; Clean Natural Bristle Stipping Or Stencil Brushes Or Shoe Buffing Brushes, For Waxing And Buffing.

### **1.3. METHOD FOR CLEANING OF THE IRON OBJECTS**

1. Remove Any Loose Dirt Or Dust By Brushing Lightly With A Soft Brush Or Camel Hair Paint Brush. If Brushes Have Metal Ferrules, Cover Them With Tape To Prevent Them From Scratching The Objects. Do Not Use Dusting Cloths, As They Will Not Get Into Small Crevices, And Can Scratch Artifacts If Trapped Grit Is Rubbed Over Surface. If The Artifacts Has Soil That Is Firmly Attached, A Stiff Paint Brush Or Stripping Brush May Be Needed. Vacuum Away Any Residues, Brushing The Dust Towards The Vacuum Nozzle.
2. Remove Any Waxy Or Oily Accretions By Light Brushing The Area With A Natural Bristle Brush Or Cotton Swabs Dampened With Mineral Spirit. Rinse The Brush In A Small Container Of Mineral Spirits Or Replace The Cotton Swabs As They Become Soiled. Cleaned The Brush Or Replace The Swabs Regularly To Avoids Scratching The Surface With Loosened Rust And Accumulated Grime.
3. To Remove Minor Rust Deposits, Wet Small Wads Of 4/0 Ultra Fine Steel Wool With The Penetrating Lubricant With A Brush And Allow It To Penetrate For Up To 8 Hours, Keeping It Covered With Polyethylene Sheeting To Reduce Evaporating. After A Sufficient Amount Time Has Elapsed, The Rust Should Be Easier To The Rub Away. Do Not Use Bronze Or Tin Wool In A Mistaken Attempt To Reduced Potential Abrasion. These Materials Will Actually Leave A Thin Layer Of Copper Alloy Or Tin On The Surface That Will Increase The Rate Of Corrosion Through A Process Called Galvanic Interaction. Never Immerse An Iron Object In A Bath Of Water, As It Will Begin Rusting Almost Immobility. Old Wax Can Be Pushed With The Blunt End Of A Bamboo Skewer. Wax Residues May Be Removed With Mineral Spirits.
4. Once The Corrosion Has Been Reduced Clear Any Residue With Clean Mineral Spirits On Swabs Or Brushes Or Clean Pieces Of Soft Cotton Rags. A Clean Soft Brush May Be Used To Remove Any Remaining Residue From Crevices Or Recessed Design Elements. Allow The Artifacts To Air Dry. Finally, Remove The Protective Wrap Applied To Non-Metallic Components.
5. Procedure For Waxing : Apply A Small Amount Of The Paste Wax To Clean Stencil Brush And Rub Thinly Over The Entire Surface Of The Object, Being Careful To Get Complete Coverage. Do Not Apply Too Much –A Little Wax Goes A Long Away.

### **1.4. REMOVAL OF CALCAREOUS AND IRON CONCRETIONS**

The Chemical Method For Marine Finds Was Described By Zhang Zhiguo [30] The Calcareous Concretions Are Usually Composed Of Two Layers, An Outer And Inner Layer. The Outer White Layer Consisted Of Calcite ( $Mg_{0.1}Ca_{0.9}CO_3$ ) And Aragonite( $CaCO_3$ ) And Inner White Layer Consisted Of Kutnahorite  $Ca_{1.11}Mn_{0.89}(CO_3)_2$  And  $CaCO_3$ . The Iron Objects Was Soaked In A 10% EDTA Disodium Salt Solution (EDTA-

2Na) With Ph Value 10. The Concretion Was Completely Dissolved After 102 Hours. The Zhang Zhiguo [30] Again Demonstrated That 10% EDTA-2Na Can Remove These Types Of White Calcareous Concretions Presents On The Marine Iron Objects. 9.35% Mercaptoacetic Acid Salt Was The Best Solution To Dissolve The Iron Concretions.

### **VIII. Desalination Solutions And Procedure**

This Method Were Described By [31] And Experimented By Britta Schmutzler Et. Al., 2010 [32]. Alkaline Sulphite, 0.5 Mol/L Sodium Hydroxide (NaOH) And 0.5 Mol/L ( $\text{Na}_2\text{SO}_3$ ) (North And Pearson 1975); Diluted Alkaline Sulphite, 0.1 Mol/L NaOH And 0.05 Mol/L  $\text{Na}_2\text{SO}_3$  [33] And NaOH 0.1 And 0.5 Mol/L. One Liter Of Solution Was Used For Each 100g Set Of Metal To Ensure Comparability Of Results. After 60 Days, The Chloride Content Of The Solutions Was Determined. At A Concentration Of 0 To 2mg/L Chloride The Desalination Was Considered To Be Complete. After Treatment, The Objects Were Soaked In The Warm De-Ionized Water Until The Ph Was Neutral, Followed By Drying. The Containers With The Metal And The Desalination Solutions Were Placed In The Oven Purged With  $\text{N}_2$  In 99.999 % Mol Quality. Before Running The Experiments, The Oven Was Evacuated Twice And Flushed With Nitrogen Gas. The Experiments Were Conducted At Room Temperature ( $20 \pm 1$  °C). Pure Sodium Hydroxide Without The Addition Of Sulphite Extract Slightly More Chloride In A Nitrogen Atmosphere, But The Difference In The Concentration Does Not Seem To Play A Significant Role.

### **IX. Scientific Treatments Of Cast Iron Bells**

This Method Was Described By Storch, 2006 [34]. The Bell Surface Was Cleaned With A Rotator Wire Brush; Removed Flaking Corrosion, Dirt, Organic Accretions, And Paint Splatter. Wiped With A Cotton Cloth To Remove Powdered Rust. Treated With Tannic Acid Based Rust Converter {Tannic Acid And An Ethylene Vinyl Acetate (Evac) Resin Emulsion} Applied Two Coats By Brushing. Coating With Tinted Canauba Wax And Buffed With Cotton Buffing Pad On Drill And By Hand. The Tannic Acid Combines With The Rust On The Cast Iron Surfaces And Forms Ferric Tannate [35, 36]. The Ferric Tannate Forms A Passivation Layer On The Surface Which Slows Down Galvanic Corrosion. The Evac Resin Forms Over The Tannate Layer As The Water In The Emulsion Evaporates. Once The Stabilizer Has Cured Overnight, The Surfaces Are Ready For The Application Of A Final Wax Coating. The Wax Coating Can Be Maintained Annually Or As Needed, And Makes Dusting Easier.

### **X. Preservation Method For Cleaning Of Nails**

This Method Was Described By Mcchonchie, 2012 [37]. The First Step Was Remove The Clips, Staples And Release The Objects Carefully From The Wooden Box. The Surface Of The Iron Nails Were Prepared For Treatment By Carefully Mechanically Cleaning With Steel Brushes, Scaples, Proes And Washing With Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). A Tannic Solution (2.5 Percent W/V) Was Prepared From Tannic, Distilled Water And Ethanol. They Applied Numerous Thin Coats Of The Solutions With Acrylic Brushes, Brushing Continuously As The Acid Dried To Help Distributed The Solution Evenly And To Remove Flaky Areas Of Iron Tannate. A Protective Microcrystalline Wax Was Applied To The Dried Nails To Acts As A Vapour Barrier. However The Objects Will Need To Be Stored In The Display Case With A Stable Relative Humidity At A Low Level. According To Studies Of Corrosion Potential For Chloride-Containing Archaeological Iron At Different Levels Of Relative Humidity That 12 Percent Should Be The Maximum Allowable Relative Humidity For Long Term Storage And Display [38, 41].

### **XI. Preservation Methods For Iron Cannon Under The Sea**

This Method Was Described By The Pearson, 1970 [39]. The Transits Of The Six Cannon 7600 Kg Irons Ballast And 760 Kg Stone Ballast, To The Mainland From The Reef Was Carried Out In The Large Tanks Filled With Sea Water. This Wars To Ensure That The Relics Were Not Exposed To The Atmosphere In The Which Rapid Drying Out And Subsequent Oxidation And Spalling Of The Metals Surface Would Take Place. The Jetsam Was Ten Transported To Melbourne Packed In Wet Sawdust Impregnated With A 10% Solution Of Formalin (To Destroy Harmful Bacteria During Transit) Contained In The Large Fiberglass-Lined Wooden Tanks.

The First Step Of The Preservation Process Was To Remove The Coral Encrustations. The Coral Was Removed By Striking Firmly With A Hammer At Right Angles To The Coral Surface. This Caused The Coral To Crack In Large Pieces. Exposing The Cannon Surface Which Was Covered With A Wet Layer Of Black Corrosion Products, The Aqueous Components Of Which Had A pH Of 8, Close To That For Natural Sea Water Of pH 8.2. It Was Found That Coral Removal Was Easier And Less Messy In The Dry State. I.E Water Was Not Direct On The Cannon Due To The Large Amount Chloride Presents On The Cannon Surface. After Removal Of Corals, The Cannon Were Placed On The Wooden Cradles In The Fiberglass-Lined Wooden Tanks

(Used Throughout The Preservation Process) Under A 2% Solution Of The Sodium Hydroxide Of pH 12.6 Prior To The Next Stage Of The Preservation Process. In This Solution The Cannon Will Not Corrode Due To The Passive Film Formation On The Cannon Surface [40]. Within The Minutes Of The Cannon Being Placed In The Sodium Hydroxide Solution, Gas Bubbles Were Seen To Envolve From The Cannon Surface At An Initial Rate Of Approximately 11/H Which Continued, Slowly Decreasing, For About 7 Days.

The Porous Corroded Surface Layers Of The Cannon Were Heavily Impregnated With Salts From The Sea Water. The Next Stage Of The Preservation Process Was To Remove These Salts And Also Reduce The Corrosion Products Already There, So That Prolonged Exposure To The Atmosphere Would Not Cause Continued And Rapid Corrosion With The Subsequent Spalling Of The Surface Layers. The Salts (Essentially Chlorides) Were Removed By Electrolysis Making The Cannon The Cathode In In A 900/L Solution Of 2% Sodium Hydroxide In Th Fiberglass-Lined Wooden Tanks. The Anode Was 1-83 By 0.91 M Mild Steel Sheet On The Opposite Side Of The Tank, With An Insulated Iron Bar Interested In The Bore Of The Cannon As An Auxiliary Electrode To Provide Good Current Distribution. The Strength Of The Sodium Hydroxide Solution Was Chosen So That There Would Be No Corrosion Of The Mild Steel Anodes During Electrolysis [40].

### 1.5. WASHING PROCEDURE OF CANNONS

According The Experiences Of Pearson, 1970 [39] After Electrolysis, The Cannon Were Subjected To The Prolonged Washing Procedure To Remove The Sodium Hydroxide, Final Traces Of Chloride And Any Soluble Product Of Reduction From The Electrolysis Stage Of The Preservation Process. Chromate-Inhibited Distilled Water Was Chosen As The Wash Solution With A Chromate Ion Concentration Of  $8.7 \times 10^{-3}$  M (1000 PPM) And A pH Of Not Less Than 8.5 To Ensure Inhibition. The Presence Of A Plentiful Supply Of Oxygen Promotes The Inhibitor Film Formation By The Chromate Ion, So The Solution Was Stirred By Bubbling Air Through It, This Also Improved Its Washing Efficiency. A Side Advantage With The Use Of Chromate Is That It Acts As A Deterrent To Fungal Growth On The Wax Which Is Used For The Final Surface Coating. The Initial Chorded Level Of The Wash Solution Was Approximately  $5 \times 10^{-4}$  M (20 PPM). Washing Was Continued For Up To Five Months With Fortnightly Changing Of The Distilled Water Until No Increase In The Chloride Content Of A Fresh Solution, Initially Between  $3.6 \times 10^{-5}$  And  $1.1 \times 10^{-4}$  M (1 To 3 Ppm) Was Observed Over A Two-Week Washing Period, Also, The pH Of The Solution Was Reduced From An Initial Value At The Commencement Of Washing Of 10.5 Down To The 8.5. Washing Was Then Considered Finished. The Wet Cannon Were Dried By Placing Infrared Heaters Around Them. A Microcrystalline Wax Is Probably The Best Form Of Protective Coating For Graphitized Cast Iron, Especially When It Is Proposed To Exhibit The Item Inside A Museum. This Wax Imparts A Moisture-Impervious And Relatively Hard Surface To The Cannon, Ideal For Indoor Exhibition.

## XII. Conclusions

This Study Described The Methods For The Preservation Of Iron Objects According To The Experiences Of The Conservator. Sodium Hydroxide And Microcrystalline Wax Were Most Suitable For Cleaning And Protective Coating Respectively. Twelve Percent RH Should Be Standard Maximum Limit For Display The Iron Objects.

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