COMPLEXING AGENTS AND ELECTROLYSIS
RESTORE SOME ARTEFACTS FROM THE TITANIC, PROVIDING INSIGHTS
FOR RESEARCH IN DEEP-SEA AREAS

• chemistry has played a central role in restoring artefacts
• on the ocean bed at the wreck site, there is a complete absence of light, a temperature of
  around 0 °C, and very little oxygen
• metallic objects undergo corrosion, the effect of an electrochemical process
• aspects of the geochemistry of iron and other metals had been accidentally introduced
  into the deep-sea environment

The Effect of Bacteria on the Titanic
• bacteria plays a major role in promoting corrosion, resulting in fast-growing structures
  such as rust flows and rusticles on the Titanic
• bacteria on the seabed feed on metals, especially iron, producing black sulfides that
degrade and stain many artefacts
• a variety of bacteria are present in rusticles and these are predominantly sulfate-reducing
  species that multiply quickly in anaerobic conditions
• rusticles have a brittle hydrous iron oxide shell with a dark red outer surface and an
  orange inner surface. The core of the rusticle and the inner surface of the shell consist of
  spherical aggregates of needle-like crystals of goethite [αFeO(OH)]. The outer surface of
  the shell has the crystal structure of lepidocrocite [γFeO(OH)]
• rust flakes contain a mixture of goethite, lepidocrocite and other minerals. They consist of
  a well-crystallised iron mineral, possibly hematite (Fe₂O₃), associated with a silicon-rich
  iron mineral. Black patches of siderite (FeCO₃) and iron-rich cubes, possibly magnetite,
  are also present. They have a thin coat of PbCO₃ and small cubes of galena (PbS) are also
  present
• it is suggested that the source of the lead is the paint on the hull of the Titanic

The Effect of Exposing Artefacts to Air
• objects from the wreck absorb chlorides and sulfates from the seawater, becoming
  weakened, stained and encrusted so, when they are raised to the surface, they must be
  kept wet
• ceramic and glass items can lose surface layers if salts are allowed to crystallise
• leather can harden, crack and shrink as it dries out if salts in the pores are not removed
  before drying
• metal objects undergo accelerated corrosion if exposed to air

Treatment of Artefacts at the Surface
• as soon as the objects are brought to the surface, the acidic silt is washed off
• artefacts are packed in foam according to material type. Foam is used instead of water to
  reduce damage during transportation
• at the laboratory, the objects are washed in fresh water and, if they are not too fragile, are
  brushed to remove corrosion objects
• artefacts are stored in water with biocide to remove troublesome fungi and bacterial
  growth
• salts trapped in an object are removed by electrolysis or treatment with complexing-
  reducing agents
• corrosion of iron objects is reduced using an alkaline dithionite bath
• sesquicarbonate (hydrated Na$_2$CO$_3$ and NaHCO$_3$) is used for the desalination of copper objects
• removal of chloride is essential since it promotes corrosion and depolymerises organics. For example, copper-based materials corrode to form copper hydroxychlorides
• hydrolysis of metal ions formed by the oxidation of iron

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\begin{align*}
Fe & \rightarrow Fe^{2+} + 2e^- \\
Fe^{2+} + 2H_2O & \rightarrow Fe(OH)_2 + 2H^+
\end{align*}
\]

can lower the pH of water around the artefact to as low as 4.2, resulting in chloride ions from the surrounding seawater diffusing onto the metal surface
• electrolysis is used to clean and stabilise strong metal artefacts, including most bronze objects. It stops further corrosion and it removes the chloride from within the objects. The cell consists of the object itself (cathode), a stainless steel anode, and an alkaline electrolyte such as dilute NaOH$_{(aq)}$ or Na$_2$CO$_3(aq)$. The passage of a weak electrical current draws out the chloride ions from the metal. When a stronger potential is applied, the hydrogen bubbles produced at the cathode loosed corrosion products and any calcareous deposits at the surface
• ceramics and organic materials are cleaned using electrophoresis. The object is placed between a positive and a negative electrode, and a potential is applied. Salts, dirt and other particles located within the electric field break up and their charged components migrate through the solution to the electrodes
• an electric pen is also used to remove stains from thick ceramic objects. The pen is a miniature electrolytic cell. The object to be cleaned is either dipped into an electrolyte or the stained section is placed under an electrolyte drip. The pen is moved around on the object to clean areas
• a complexing agent in neutral solution (eg. a neutral citrate solution containing sodium dithionate) is used to remove iron stains from delicate textiles or newspapers by reducing the oxidation state of the rust lattice or iron corrosion product from iron(III) to iron (II), destabilising the lattices so that it falls apart. The neutral solution buffers the citrate ion present, resulting in the formation of a hydrous iron oxide citrate complex which is very stable
• oxalic acid is used as a complexing agent to remove corrosion products by complexing with the iron oxide to form iron oxalate, which is removed by rinsing in water
• the main problem with glass is surface iridescence caused by hydrolysis of the silica network
• deep-penetrating iron corrosion stains are removed by electrolysis or a neutral solution of complexing agent
• leather and wood need a consolidant to replace the material consumed by micro-organisms, minimising cell collapse
• storage of bronze- and silver-plated objects in damp environments can cause corrosion to recur
• the study of shipwrecks in a range of sites and conditions allows greater understanding about long-term deterioration rates of materials. This is useful for the monitoring and maintenance of underwater constructions

REFERENCES
Freemantle, Michael, 1994, Chemical Techniques Help Conserve Artefacts Raised From Titanic Wreck; Chemical & Engineering News (17th October); pages 49 - 52