Metal Artifact Preservation Using the Subcritical Water Extraction Technique

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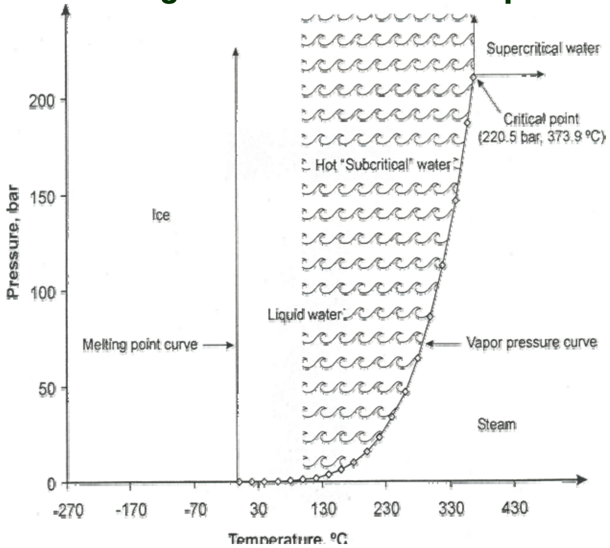
Abstract

The dielectric constant, viscosity and surface tension of water are reduced significantly when temperatures are increased above the boiling point. These characteristics have proven beneficial in the chemistry of metallic artifact preservation.

Metallic artifacts that have been exposed to salt water environments are typically severely corroded. The standard method of treating corroded metallic artifacts is the electrolytic reduction method. This technique is time consuming and can cause destruction of delicate details in cast iron specimens.

This poster describes the use and benefits of subcritical water as a rapid alternative to the electrolytic reduction process. Examples of the subcritical water extraction technique are presented and a discussion of the chemistry of the salt water corrosion process of metallic objects is included.

Phase Diagram of Water with Vapor – Liquid Equilibrium Phase Boundary



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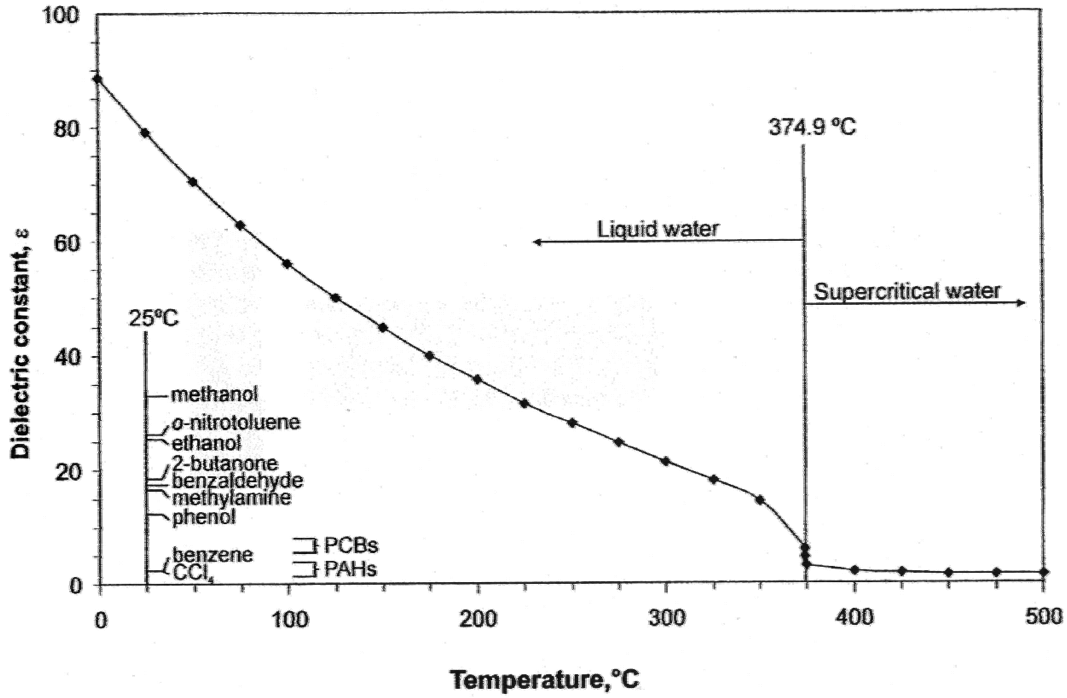
Variation of Dielectric Constant with Temperature for H_2O



Conventional Treatment- Metals

- Primary Cause of Damage
  - Electrochemistry of oxygen ....oxidation of metals
- Treatment
  - Soak in high-pH solutions
  - Perform electrolytic reduction in high-pH solutions

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Mardikian attaches an anode to the interior of the *Hunley*

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Electrolytic Process

- **Electrolytic reduction - standard treatment**
- **Slow process**
    - Convert corrosion products back to a metallic state.
        - Reduction is critical for preserving surface
        - Electrochemical methods cannot reverse corrosion of metals.
- **3 years on average to conserve**

Dual SCF/Subcritical H_2O

Subcritical Water Treatment

Faster

- improved transport properties of the subcritical fluid.
- subcritical water has a higher diffusion rate
- lower viscosity than water under ambient conditions

"The corrosion goes deep into the pores. Surface tension and viscosity and transport properties become limiting factors,"

“Subcritical extraction is causing significant changes in corrosion products that may be accelerating the removal of chlorides and protecting the artifacts against further corrosion.”

Michael Drews, Professor Emeritus
School of Materials Science &
Engineering,

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Trapped Inclusions

- Location of chlorides promoting corrosion.
- Inclusions - variable chemistry primarily iron silicates and phosphates
- Inclusions reaching surface provide conduits for chlorides to penetrate the metal,
  - accelerates corrosion
  - ß-FeOOH
- Inclusions trap chlorides
  - removal difficult
  - further corrosion, even after treatment.
- Subcritical water technique
  developed at Clemson is
  able to remove trapped chlorides
  - Convert ß-FeOOH to other oxides

Subcritical Water Treatment Results

- Removed very high levels of Cl- from the samples in very short periods of time.
- Dramatically shorter treatment time
  - Subcritical water - 5 days
  - Conventional - over 6 months
  - NaOH or Na2CO3 alone sometimes not effective
- Resulted in the apparent transformation of ß-FeOOH into other iron oxides.
- Specimens maintained their physical appearance, mechanical properties
- Maintained their apparent corrosion resistance (even those stored in a saturated water vapor chamber for at least 2 years)

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Results: Before and After

Before treatment

After Treatment

James W. Hunter, III, Friends of the Hunley, Inc

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