Supercritical Water Mixture (SCWM) Experiment

ISS Flight Experiment using the High Temperature Insert – Re-flight (HTI-R) in the DECLIC Facility

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The Supercritical Water Mixture (SCWM) experiment is a follow-on experiment to the pure Supercritical Water HTI experiment conducted on the ISS in 2010.

SCWM will use a modified Sample Cell Unit (SCU) filled with a salt-water solution inserted into the refurbished High Temperature Insert (HTI-R) and returned to ISS, ~ March 2013.
Supercritical Water Mixture (SCWM) Experiment

SCWM experiment time-line:

- HTI returned to ground ULF-6 Mar 2011
- HTI-R refurbishment completed Sep 2012
- HTI-R transfer to KSC Dec 2012
- HTI-R return to ISS Mar 2013
- SCWM ISS testing commences Jul 2013
Outline:

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Background
In a supercritical fluid, molecular cohesion is liquid-like and molecular diffusion is gas-like.

Supercritical water behaves as a dense, non-polar gas.

\[ P_{cr} = 221 \text{ atm} \]

\[ T_{cr} = 374.1 \text{ C} \]
Supercritical Water Mixture (SCWM) Experiment

- Gases and organic substances are completely soluble in supercritical water.
- Inorganic salts are insoluble in supercritical water and precipitate out of solution.
- Oxidizer and hydrocarbon (organic) fuels are brought into intimate single phase contact during reactions.

![Graph showing relative solubility of inorganic salts and organics with temperature.](image)
Between 350 °C and 400 °C (at a pressure of 250 bar)

- density decreases by 70%
- thermal conductivity decreases by 65%
- viscosity decreases by 80%
- mass diffusivity increases by a factor of 4
Motivation
NASA's Advanced Exploration

Overarching Goal: *Develop technologies that promote self sufficiency to enable human exploration beyond low-earth orbit*

**Space Studies Board (2000)**

Solid waste management: “Both systems (incineration and supercritical water oxidation) show promise for future spacecraft design,”

- water reclamation from liquid waste streams
- CO$_2$ recovery for O$_2$ generation and photosynthesis requirements
- N$_2$ recovery from bio-waste streams (plant nutrition recovery for recycling to growth chambers)
- transform to beneficial products such as activated carbon, food production substrate, and fuel (from partial oxidation processes)
**2011 NRC Decadal Survey** - Super Critical Water Oxidation (SCWO) is strategically aligned with many "high priority research recommendations".

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<td><strong>Translation to Space Exploration Systems: Closed Loop Life Support Systems (TSE5)</strong></td>
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Terrestrial Applications of SCWO

SCWO Unit for Bluegrass Army Depot Richmond, KY

SCWO reactor for municipal sludge: City of Orlando, FL (35 metric tons/day)

Hirth, Th., et al., 3rd international symposium on High Pressure Chemical Engineering, Zurich(Switzerland), 1996, p.163
A key technological hurdle is the control of corrosion and fouling caused by deposition of salt precipitates.

This detrimentally impacts operational efficiencies (e.g., heat transfer) and lifetime.

Figure 1 provides a dramatic illustration of the rapid deposition on a heated surface inserted into a flowing water/salt solution and maintained at a temperature just above that of the solubility limit in the bulk fluid ($\text{NaSO}_4$ at 4 wt %, $T_B = 356^\circ \text{C}$, $P = 250$ atm).

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The SCWM experiment fits naturally in the scheme of investigating supercritical water phenomena ... particularly in terms of advancing Supercritical Water Oxidation (SCWO) technology.

One -> two -> three phase reacting system
ISS Rationale

- Sharp changes in density and resulting buoyant flow on Earth impact ability to study unit processes of salt precipitation and transport

- Ground-based reduced-gravity facilities (drop towers, low-g aircraft flights) do not provide sufficient low-g time
SCWM Experiment

Objectives
Science Objectives:

The SCWM experiment is designed to study precipitation and transport phenomena of a solute as it precipitates from solution near the critical point of the salt/water mixture.

- Observe/quantify the critical point of a liquid-gas phase transition for a salt/water mixture
- Observe/quantify the onset of precipitation in a supercritical homogeneous phase as a function of temperature
- Observe/quantify the transport processes of the precipitate in the presence of temperature and/or salinity gradients
SCWM Experiment
Salt Selection Criteria
- Substantial decrease in solubility near critical conditions and below the DECLIC temperature limit (~ 405°C);
- Compatible with HTI-R SCU material (Inconel 718)
- Available solubility data in water near critical conditions
SCWM Experiment
Proposed Test Sequences
Test Sequence 1

Salt Precipitation During Temperature Increase

\[ T_c + (\Delta T)_2 \]

\[ T_c - (\Delta T)_1 \]

Time

Temperature

\[ T_c \]
Test Sequence 2

Salt Solvation During Temperature Decrease

\[
T_c + (\Delta T)_2
\]

\[
T_c
\]

\[
T_c - (\Delta T)_3
\]
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Test Sequence 3
Salt Agglomeration

Temperature

\[ T_c + (\Delta T)_2 \]

\[ T_c \]

\[ T_c - (\Delta T)_4 \]

Time
Test Sequence 4

Salt Transport in Near (Sub)-Critical and Supercritical Water

\[ T_1 \text{ (control point A) } \]
\[ T_2 \text{ (control point B) } \]
\[ T_3 \text{ (temperature control point 1) } \]
\[ T_4 \text{ (temperature control point 2) } \]
Previous ISS Results
Supercritical Pure Water Studies
Phase Distribution Below the Critical Point

1-g

ISS

T = 624 K

Dark region between liquid and vapor regions is the meniscus
Analysis

Imposed gradient at $\Delta T \approx -300 \text{ mK}$ (with $T \approx T_c + 1 \text{ K}$)
Analysis (cont)

Shadow-Graphic Configuration

\[ \delta = \frac{\psi}{n} \frac{dn}{dy} \]

\[ n = 1 + K\rho \]

\[ n = \text{refractive index} \]

\[ \psi, K \text{ are constants} \]
T = 648.2 K (~ 1 K above critical point)
Note that there is no vapor/liquid phase difference
Points N, C, W, E, and S are chosen as reference points for tracking the grid displacement under imposed temperature gradients.
Shift Tracking

The shift $\delta$, is expressed as the sum of a spatially uniform component and a local component

$$\delta = <\delta> + \delta'$$

with

$$<\delta> = \delta(C)$$

The shifts in the reference points at different times during the temperature gradient timeline are tracked using ImageJ. (Abramoff et al., Biophotonics International, 2004)
The shift in the y-direction is much greater than the shift in the x-direction. Shift near the center is delayed compared to near-boundary points. This is a consequence of reduced thermal diffusivity near the critical point.
Grid Shift for Negative Temperature Gradient

Shifts in the grid first appear near the boundary as already noted.

The grid shifts in the direction of lower temperature, i.e., larger density.
The shift in the center region is uniform for both positive and negative temperature gradients. Hence the experiment provides a uniform density gradient in the bulk fluid (interior region).
Modeling
**Numerical Results**

Configuration: 1 cm dia fluid cell in an inconel block  
Initial Condition: $T = 648$ K  
Temperature Gradient: Decrease temperature of top surface by 0.1 K in 400 seconds

Cell block temperature equilibrates quickly
Numerical Results (contd.) : Temperature Field in the Fluid

(a) 400 seconds
Diffusive boundary layer + piston effect in bulk fluid

(b) 1000 seconds
Diffusive boundary layer extending into bulk; piston effect diminished

(c) 2500 seconds
Diffusive equilibration underway in entire cell

(d) 5000 seconds
Diffusive equilibration complete

The temperature gradient in the bulk fluid is negligible at the early stages. When diffusive equilibration is complete there is a uniform temperature (and density) gradient in the central region (nearly linear temperature profile). At equilibration, temperature gradient in the y-direction is greater than the gradient in the x-direction.
Ground Based Testing
SCWM Lab Test Cell 1
Liquid water-vapor regions near the critical temperature

Liquid water-vapor regions during heat-up for a 10% Na2SO4-water solution
Stratification during cool-down

**Summary - Preliminary Observations**

- The precipitated salt particulates/agglomerates are on the order of a 10-20 microns.

- Stratification/banding, suggesting a salinity concentration “inversion”, occurs during quenching
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