Supercritical Water Mixture (SCWM) Experiment in the High Temperature Insert-Reflight (HTI-R)

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Supercritical Water Mixture (SCWM) Experiment in the High Temperature Insert-Refight (HTI-R)

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SCWM – Project Manager

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\(^3\) CNRS … Centre national de la recherche scientifique
\(^4\) CNES … Centre National d’Etudes Spatiales
\(^5\) NCSER … National Center for Space Exploration Research
\(^6\) CEA … Commissariat à l’Energie Atomique
\(^7\) NASA-GRC … NASA – Glenn Research Center
Presentation Outline

• SCWM Experiment Overview
  - Background and Motivation
  - Hardware and DECLIC diagnostics
  - SCWM science objectives

• Test Sequence 1 – July, 2013
  - Test Sequence operation profile
  - Preliminary observations

• Summary and Future Work
  - Upcoming SCWM Test Sequences - Baseline schedule
Supercritical Water Mixture (SCWM) Experiment
- Overview -
SCWM Experiment - Background and Motivation

SCWM was conceived as a *precursor* experiment for eventual SCWO experiments:

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

- key technological hurdle limiting application of SCWO technology is the control of corrosion and fouling caused by deposition of salt precipitates
- new SCWO reactor designs (internal heating) will have transcritical regions that will require a detailed understanding of near-critical behavior of many thermo-physical processes

Test in 1-g showing illustrating rapid build-up of salt precipitate: Na$_2$SO$_4$ aqueous solution 4%-w at (T$_{BF}$ = 356°C, P=250 atm) flowing past unheated rod (left) and heated rod (right) (Hodes, M. ’04)
**SCWM Experiment – Objectives**

Science Objectives:

- quantify critical point for a specific salt/water mixture (0.5%-w Na$_2$SO$_4$)
- observe/quantify incipient precipitation and solvation at near critical conditions
- observe/quantify transport processes of the precipitate in the presence of thermal/salinity gradients

![Solubility profiles of salt in water near $T_c$](image)

Schematic showing saturation line for pure water and Type 2 (Sodium Sulfate) salt solution … results in shift of critical end point
DECLIC Hardware and Diagnostics

- Direct observation: field of view = $\varnothing$ 12 mm w/ a resolution 10 $\mu$m.
- Light transmission measurement and grid shadow for turbidity and index gradient
- Light Scattering: small angle or 90° for turbidity measurements
- Small field of view (microscopy) 1 mm w/ a resolution of 5 $\mu$m
- Cameras: 2 High resolution (HR) and 1 high speed (HS) cameras
- Light Sources: 2 mW He-Ne 633 nm laser with various attenuation filters; several 670 nm LED's

<table>
<thead>
<tr>
<th>Optical Axis</th>
<th>ALI</th>
<th>HTI</th>
<th>DSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>Interferometry</td>
<td>WF and SF imagery, Grid, transmission, LAS</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>WF and SF imagery, Grid, transmission, LAS</td>
<td>Transversal imagery</td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>Interferometry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>WF and SF imagery, Grid, transmission, Low Angle Scattering</td>
<td>Transversal imagery</td>
<td></td>
</tr>
<tr>
<td>O5</td>
<td>Interferometry</td>
<td>WF and SF imagery, Grid, transmission, Low Angle Scattering</td>
<td></td>
</tr>
<tr>
<td>O6</td>
<td>Interferometry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O7</td>
<td>Interferometry</td>
<td>WF and SF imagery (HR)</td>
<td></td>
</tr>
<tr>
<td>O8</td>
<td>Interferometry</td>
<td></td>
<td>(reference beam)</td>
</tr>
</tbody>
</table>
SCWM Test Sequence 1

Preliminary Observations
## SCWM Operational Schedule

### SCWM Experiment Schedule - July 2013 to May 2014

<table>
<thead>
<tr>
<th>Sequences</th>
<th>Activities</th>
<th>Description</th>
<th>Duration</th>
<th>Start Date (GMT)</th>
<th>End Date (GMT)</th>
</tr>
</thead>
</table>
| SCWM Test Sequence 1  
(DELCIC-HTI-SEQ8) | DECLIC-HTI-SC7 | Science HTI | 16/00:00 | 1-Jul-13 | 17-Jul-13 |
|  |  | Margins | 01/00:00 | 17-Jul-13 | 18-Jul-13 |
|  |  |  |  | 18 day | 66 |
| SCWM Test Sequence 2  
(DELCIC-HTI-SEQ8) | DECLIC-HTI-SC8 | Thermal Regulation improvement + Science HTI | 16/00:00 | 9-Sep-13 | 25-Sep-13 |
|  |  | Margins | 01/00:00 | 25-Sep-13 | 26-Sep-13 |
|  |  |  |  | 18 day | 66 |
| SCWM Test Sequence 3  
(DELCIC-HTI-SEQ9) | DECLIC-HTI-SC9 | Science HTI | 17/00:00 | 2-Dec-13 | 19-Dec-13 |
|  |  | Margins | 01/00:00 | 19-Dec-13 | 20-Dec-13 |
|  |  |  |  | 18 day | 66 |
| SCWM Test Sequence 4  
(DELCIC-HTI-SEQ10) | DECLIC-HTI-SC10 | Science HTI | 16/00:00 | 20-Jan-14 | 5-Feb-14 |
|  |  | Margins | 01/00:00 | 5-Feb-14 | 6-Feb-14 |
|  |  |  |  | 18 day | 66 |
| SCWM Test Sequence 5  
(DELCIC-HTI-SEQ11) | DECLIC-HTI-SC11 | Science HTI | 16/00:00 | 3-Mar-14 | 19-Mar-14 |
|  |  | Margins | 01/00:00 | 19-Mar-14 | 20-Mar-14 |
|  |  |  |  | 18 day | 24 |
| SCWM Test Sequence 6  
(DELCIC-HTI-SEQ12) | DECLIC-HTI-SC12 | Science HTI | 16/00:00 | 14-Apr-14 | 30-Apr-14 |
|  |  | Margins | 01/00:00 | 30-Apr-14 | 1-May-14 |
|  |  |  |  | 17 day |
SCWM Test Sequence 1

Test sequence began on July 1\textsuperscript{st} and ended on July 18\textsuperscript{th}

- Primary science objective was to find the shift in critical point
- Three power interruptions occurred near critical point early part of test sequence
- Peltier element, PEB, used in precision temperature control near critical point, exhibited off-nominal behavior
- Time spent on optimizing thermal regulation system ... attempted to minimize temperature gradients
Segment 1 – Incipient Precipitation

First appearance of salt precipitate occurs at $T_{ip} \sim 373^\circ$C

- During isochoric heat-up of test cell, localized boiling forms channels of small vapor bubbles which appear to form nucleation sites for salt precipitation
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Camera: HR1
Segment 2 – First Approach to $T_c'$

First approach to $T_c'$ …

- Very slow approach in steps of 10 mK at an average rate of 14 mK/hr near critical
- Precipitate appears to re-dissolve just below $T_c'$

<table>
<thead>
<tr>
<th>SL2</th>
<th>SCUr (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>378 654 528</td>
<td>374.693</td>
</tr>
<tr>
<td>378 846 264</td>
<td>374.832</td>
</tr>
<tr>
<td>379 424 976</td>
<td>374.883</td>
</tr>
<tr>
<td>379 617 984</td>
<td>374.884</td>
</tr>
<tr>
<td>380 206 416</td>
<td>374.884</td>
</tr>
<tr>
<td>380 385 720</td>
<td>374.984</td>
</tr>
</tbody>
</table>

First approach to $T_c'$:

SCUr: ranges from 374.693 °C to 374.984 °C
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Camera: HR1
Segment 3 – First Critical Transition

First transition form sub-critical to supercritical at $T_c' = 375.335 \, ^\circ C$

- Approach to $T_c'$ faster than Segment 1, at an average rate of 134 mK/hr near critical (between D - E in plot)
- Precipitate does **not re-dissolve** prior to transition

First critical transition:

<table>
<thead>
<tr>
<th>SL2</th>
<th>SCUr (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>382 803 210</td>
<td>375.312</td>
</tr>
<tr>
<td>382 805 712</td>
<td>375.319</td>
</tr>
<tr>
<td>382 813 464</td>
<td>375.308</td>
</tr>
<tr>
<td>382 816 272</td>
<td>375.295</td>
</tr>
<tr>
<td>382 844 604</td>
<td>375.341</td>
</tr>
<tr>
<td>382 816 272</td>
<td>375.295</td>
</tr>
</tbody>
</table>

SCUr : ranges from 375.312 °C to 375.295 °C
Supercritical Water Mixture (SCWM) Experiment in the High Temperature Insert-Reflight (HTI-R)

Camera: HR1
Segment 5 – Quench Transition

Transition from supercritical to sub-critical

- average quench rate ~ 591 mK/hr

\[ \text{Quench transition: } \text{SCU}\text{r : ranges from } 375.364^\circ \text{C to 375.298 }^\circ \text{C} \]

\[ \text{table:} \\
\begin{array}{|c|c|}
\hline
\text{SL2} & \text{SCU}\text{r (°C)} \\
\hline
390 692 880 & 375.36395 \\
390 693 456 & 375.36023 \\
390 695 712 & 375.34375 \\
391 433 784 & 375.29800 \\
391 433 958 & 375.29800 \\
391 434 390 & 375.29800 \\
\hline
\end{array} \]
17497e30

Camera : HR1
Summary

Summary

• Test Sequence 1 provided preliminary value for critical point of solution
  - $T_c' = 375.335 \, ^\circ C$ (indicated) for $\text{Na}_2\text{SO}_4 \, 0.5\%\text{-w aqueous solution}$
  - Precipitation phenomena appears to be dependent upon near critical “approach rate”
  - Salt dissolution / precipitation appears to be highly reversible … surface effects are minimal

Future Work

• Thermal regulation system needs to be optimized for operation w/o one of the Peltier elements (PEB)
• Temperature “offset” needs to be defined

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1 indicated value of SCUr will need to be verified once the actual “offset” has been determined
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Test Sequence 1

Salt Precipitation During Temperature Increase

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

\[ T_c \]

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

Time

Temperature
Supercritical Water Mixture Experiment (SCWM) in the High Temperature Insert – Reflight (HTI-R)

Test Sequence 2

Salt Solvation During Temperature Decrease

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

\[ T_c \]

\[ T_c - (\Delta T)_3 \]

Time
Supercritical Water Mixture Experiment (SCWM) in the High Temperature Insert – Reflight (HTI-R)

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

- $T_1$ (control point A)
- $T_2$ (control point B)
- $T_3$ (temperature control point 1)
- $T_4$ (temperature control point 2)

Temperature vs. Time graph showing the progression of temperature control points over time.
**Analysis (cont)**

**Shadow-Graphic Configuration**

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

\[ n = 1 + K\rho \]

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

\[ \psi, K \text{ are constants} \]