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

Michael C. Hicks¹, Uday G. Hegde², Yves Garrabos³, Carole Lecoutre³, Bernard Zappoli ⁴

¹ NASA - Glenn Research Center (NASA - GRC)
² National Center for Space Exploration Research (NCSER)
³ Institute of Condensed Matter Chemistry of Bordeaux (ICMCB)
⁴ Centre National d'Etudes Spatiales (CNES)
Supercritical Water Mixture (SCWM) Experiment in the High Temperature Insert-Refight (HTI-R)

**SCWM - International Research Team**

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yves Garrabos</td>
<td>ESEME¹/IMCMB²/ CNRS³ (Bordeaux, France)</td>
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<tr>
<td>Bernard Zappoli</td>
<td>CNES ⁴ (Toulouse, France)</td>
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<tr>
<td>Carole Lecoutre</td>
<td>ESEME¹/IMCMB²/ CNRS³ (Bordeaux, France)</td>
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<tr>
<td>Daniel Beysens</td>
<td>ESEME¹/CEA⁶/ESPCI-PMMH (Paris, France)</td>
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<tr>
<td>Uday Hegde</td>
<td>NCSER⁵ (Cleveland, USA)</td>
<td></td>
</tr>
<tr>
<td>Michael Hicks</td>
<td>NASA-GRC⁷ (Cleveland, USA)</td>
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</tbody>
</table>

**SCWM – Project Manager**

<table>
<thead>
<tr>
<th>Name</th>
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<tbody>
<tr>
<td>Gabriel Pont</td>
<td>CNES ⁴ (Toulouse, France)</td>
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</tr>
</tbody>
</table>

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1 ESEME … Equipe commune CEA - CNRS du Supercritique pour l’Environnement, les Matériaux et l’Espace
2 IMCMB … Institut de Chimie de la matière condensée de Bordeaux
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 in the High Temperature Insert-Reflight (HTI-R)

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; Na₂SO₄ 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
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DECLIC Hardware and Diagnostics

- Direct observation: field of view = ø 12 mm w/ a resolution 10 μm.
- 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 μm
- 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>
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<tbody>
<tr>
<td>O1</td>
<td>Interferometry</td>
<td>WF and SF imagery, Grid, transmission, Low Angle Scattering</td>
<td>Transversal imagery</td>
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<tr>
<td>O2</td>
<td>WF and SF imagery, Grid, transmission, LAS</td>
<td>Interferometry</td>
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<td>O3</td>
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<td>Transversal imagery</td>
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<tr>
<td>O4</td>
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<td>O5</td>
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<td>WF and SF imagery (HR) Interferometry</td>
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<td>O6</td>
<td>Interferometry</td>
<td>Interferometry (reference beam)</td>
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</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>
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<td>DECLIC-HTI-SC7</td>
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<td>18 day</td>
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<td>Thermal Regulation improvement + Science HTI</td>
<td>18 day</td>
<td>9-Sep-13</td>
<td>25-Sep-13</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>01/ 00:00</td>
<td>25-Sep-13</td>
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<td></td>
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<td>SCWM Test Sequence 3</td>
<td>DECLIC-HTI-SC9</td>
<td>Science HTI</td>
<td>18 day</td>
<td>2-Dec-13</td>
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<td>Delay : 31</td>
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<td>SCWM Test Sequence 4</td>
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<td>18 day</td>
<td>20-Jan-14</td>
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<td>5-Feb-14</td>
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<td>Delay : 24</td>
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<td>SCWM Test Sequence 5</td>
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**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

![Overall Temperature Profile of Test Cell](chart.png)
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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>
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<tbody>
<tr>
<td>378.654528</td>
<td>374.693</td>
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<tr>
<td>378.846264</td>
<td>374.832</td>
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<td>379.424976</td>
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<td>374.884</td>
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<tr>
<td>380.385720</td>
<td>374.984</td>
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First approach to $T_c'$:

SCUr : ranges from 374.693 °C to 374.984 °C
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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

<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>
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<td>382 813 464</td>
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<tr>
<td>382 816 272</td>
<td>375.295</td>
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<td>382 844 604</td>
<td>375.341</td>
</tr>
<tr>
<td>382 816 272</td>
<td>375.295</td>
</tr>
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</table>

First critical transition: SCUr ranges from 375.312 °C to 375.295 °C
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Segment 5 – Quench Transition

Transition from supercritical to sub-critical

• average quench rate ~ 591 mK/hr

\[ \text{SCUr} = \frac{375.364 \, \text{°C}}{375.298 \, \text{°C}} \]

\[ \text{Quench transition: SCUr ranges from 375.364 °C to 375.298 °C} \]
Supercritical Water Mixture (SCWM) Experiment in the High Temperature Insert-Reflight (HTI-R)

Camera: HR1

17497e30
Summary

Test Sequence 1 provided preliminary value for critical point of solution

- $T_c' = 375.335 \, ^\circ C$ (indicated) for $Na_2SO_4 \, 0.5\%$-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
Test Sequence 1

Salt Precipitation During Temperature Increase

$\Delta T_1$ $\Delta T_2$

$T_c$ $T_c + (\Delta T)_{2}$

$T_c - (\Delta T)_{1}$

Time
Test Sequence 2

Salt Solvation During Temperature Decrease

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

\[ T_c \]

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

Time
Test Sequence 3

Salt Agglomeration

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

\[ T_c \]

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

Time

Temperature
Test Sequence 4

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

Temperature

Tc

Time

T1 (control point A)

T2 (control point B)

T3 (temperature control point 1)

T4 (temperature control point 2)
Analysis (cont)

Shadow-graphic Configuration

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

\[ n = 1 + K\rho \]

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

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