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

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## SCWM - International Research Team

| | |
|---|---|
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| **Uday Hegde** | NCSER[5] (Cleveland, USA) |
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## SCWM – Project Manager

**Gabriel Pont** CNES [4] (Toulouse, France)

[1] ESEME … Equipe commune CEA - CNRS du Supercritique pour l'Environnement, les Matériaux et l'Espace"
[2] ICMCB … 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

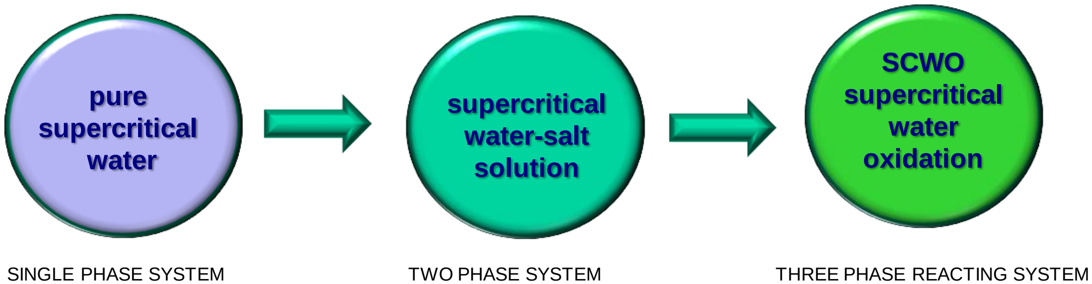
# Supercritical Water Mixture (SCWM) Experiment

## *- Overview -*

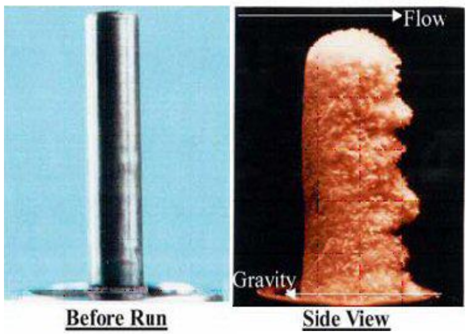
# ***SCWM Experiment - Background and Motivation***

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 trans-critical regions that will require a detailed understanding of near-critical behavior of many thermo-physical processes

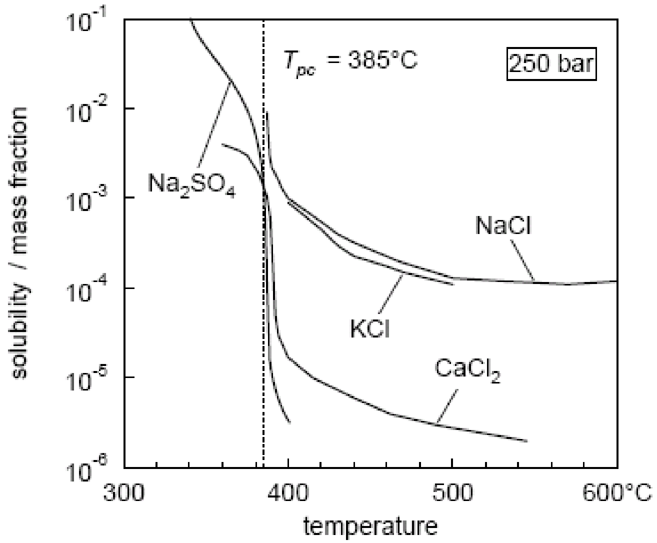



Test in 1-g showing illustrating rapid build-up of salt precipitate; $Na_2SO_4$ aqueous solution 4%-w at ($T_{BF}$ = 356C, P=250 atm) flowing past unheated rod (left) and heated rod (right) (Hodes, M. '04)

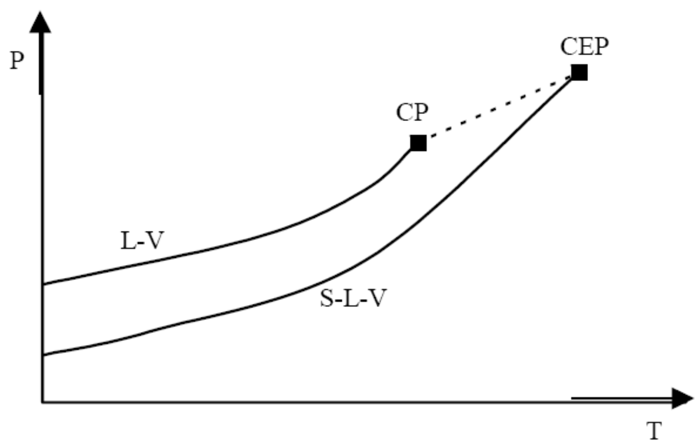
# SCWM Experiment – Objectives

Science Objectives:

- quantify critical point for a specific salt/water mixture (0.5%-w $Na_2SO_4$)
- observe/quantify incipient precipitation and solvation at near critical conditions
- observe/quantify transport processes of the precipitate in the presence of thermal/salinity gradients



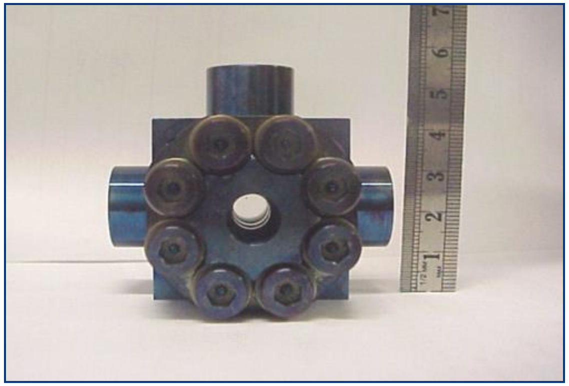

*Solubility profiles of salt in water near Tc*



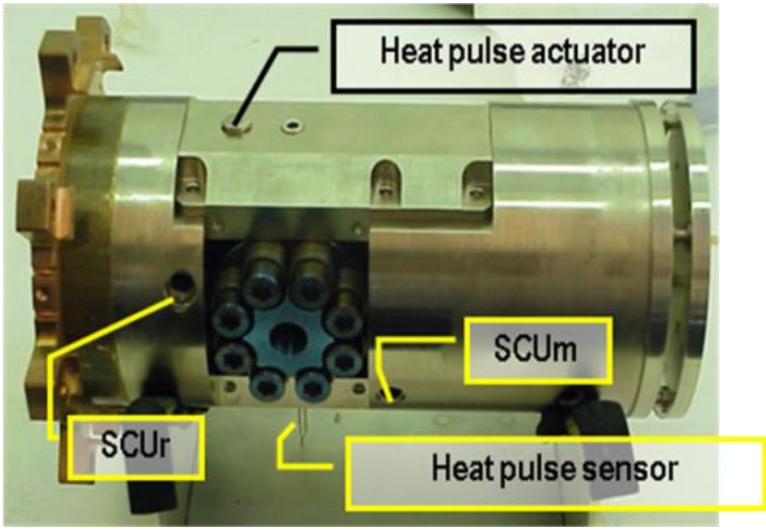

Schematic showing saturation line for pure water and Type 2 (Sodium Sulfate) salt solution … results in shift of critical end point

# DECLIC Hardware and Diagnostics

- Direct observation: field of view = 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



| Optical Axis | ALI | HTI | DSI |
|---|---|---|---|
| O1 | Interferometry | WF and SF imagery, Grid, transmission, Low Angle Scattering | |
| O2 | WF and SF imagery, Grid, transmission, LAS | | Transversal imagery |
| O3 | | | Interferometry |
| O4 | WF and SF imagery, Grid, transmission, Low Angle Scattering | | Transversal imagery |
| O5 | | WF and SF imagery, Grid, transmission, Low Angle Scattering | |
| O6 | Interferometry | | |
| O7 | | | WF and SF imagery (HR) Interferometry |
| O8 | | | Interferometry (reference beam) |



# SCWM Test Sequence 1

***Preliminary Observations***

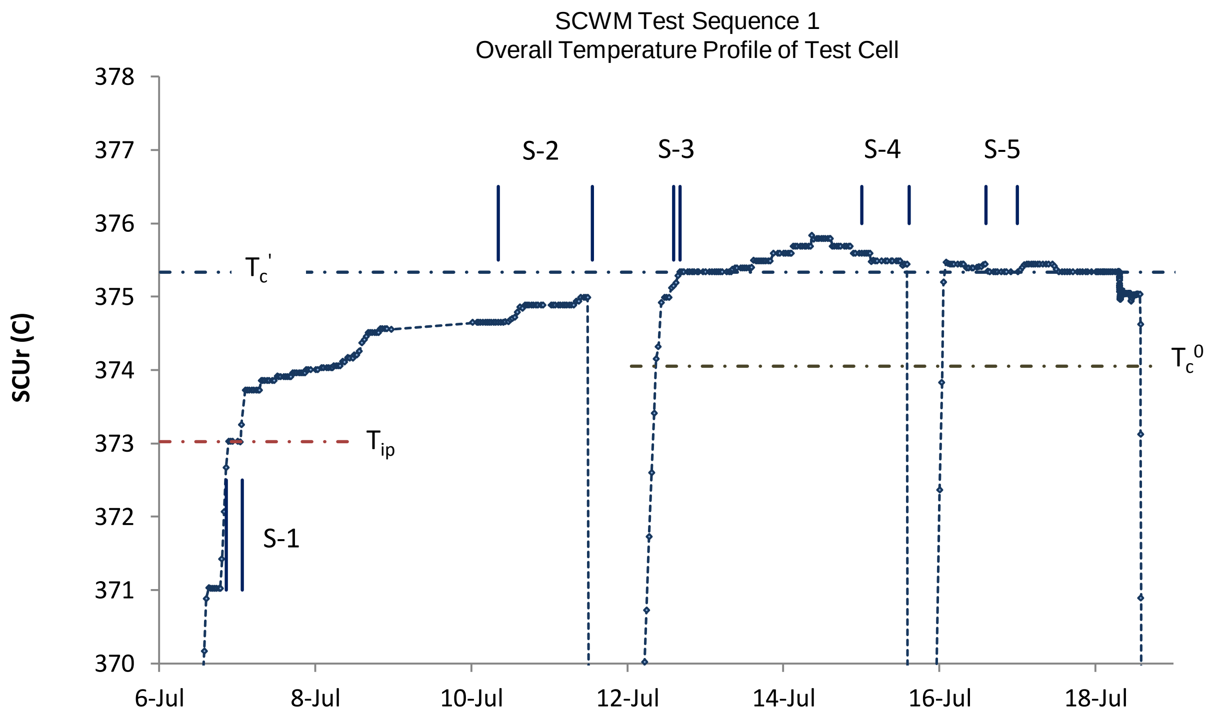
# SCWM Operational Schedule

| SCWM Experiment Schedule - July 2013 to May 2014 | | | | | |
|---|---|---|---|---|---|
| **Sequences** | **Activities** | **Description** | **Duration** | **Start Date (GMT)** | **End Date (GMT)** |
| **SCWM Test Sequence 1** (DECLIC-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 |
| | | **Duration :** | **18 day** | **Delay :** | **66** |
| **SCWM Test Sequence 2** (DECLIC-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 |
| | | **Duration :** | **18 day** | **Delay :** | **66** |
| **SCWM Test Sequence 3** (DECLIC-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 |
| | | **Duration :** | **18 day** | **Delay :** | **31** |
| **SCWM Test Sequence 4** (DECLIC-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 |
| | | **Duration :** | **18 day** | **Delay :** | **24** |
| **SCWM Test Sequence 5** (DECLIC-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 |
| | | **Duration :** | **18 day** | **Delay :** | **24** |
| **SCWM Test Sequence 6** (DECLIC-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 |
| | | **Duration :** | **17 day** | | |

# SCWM Test Sequence 1

Test sequence began on July 1st and ended on July 18th

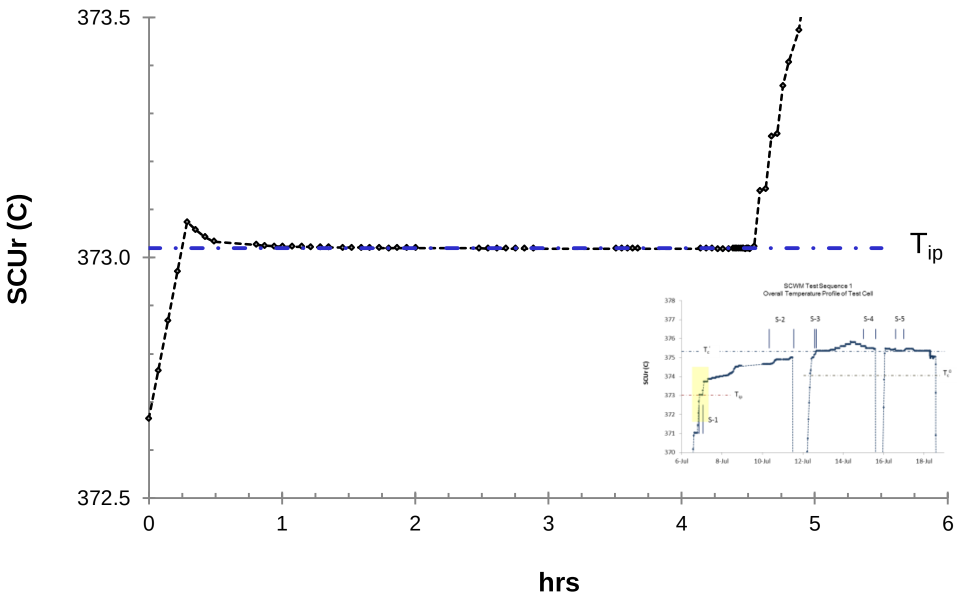
- Primary science objective was to find the shift in critical point
- Three power interruptions occurred near critical point early part of test sequence
- Peltier element, PEB, used in precision temperature control near critical point, exhibited off-nominal behavior
- Time spent on optimizing thermal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



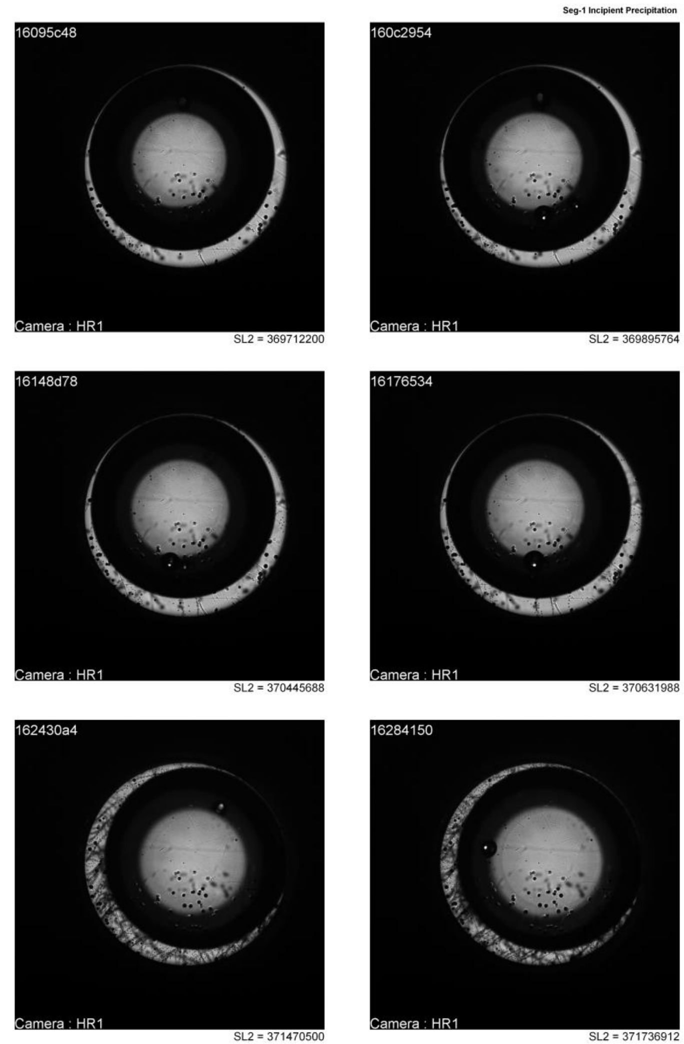
# *Segment 1 – Incipient Precipitation*

First appearance of salt precipitate occurs at $T_{ip}$ ~ 373°C

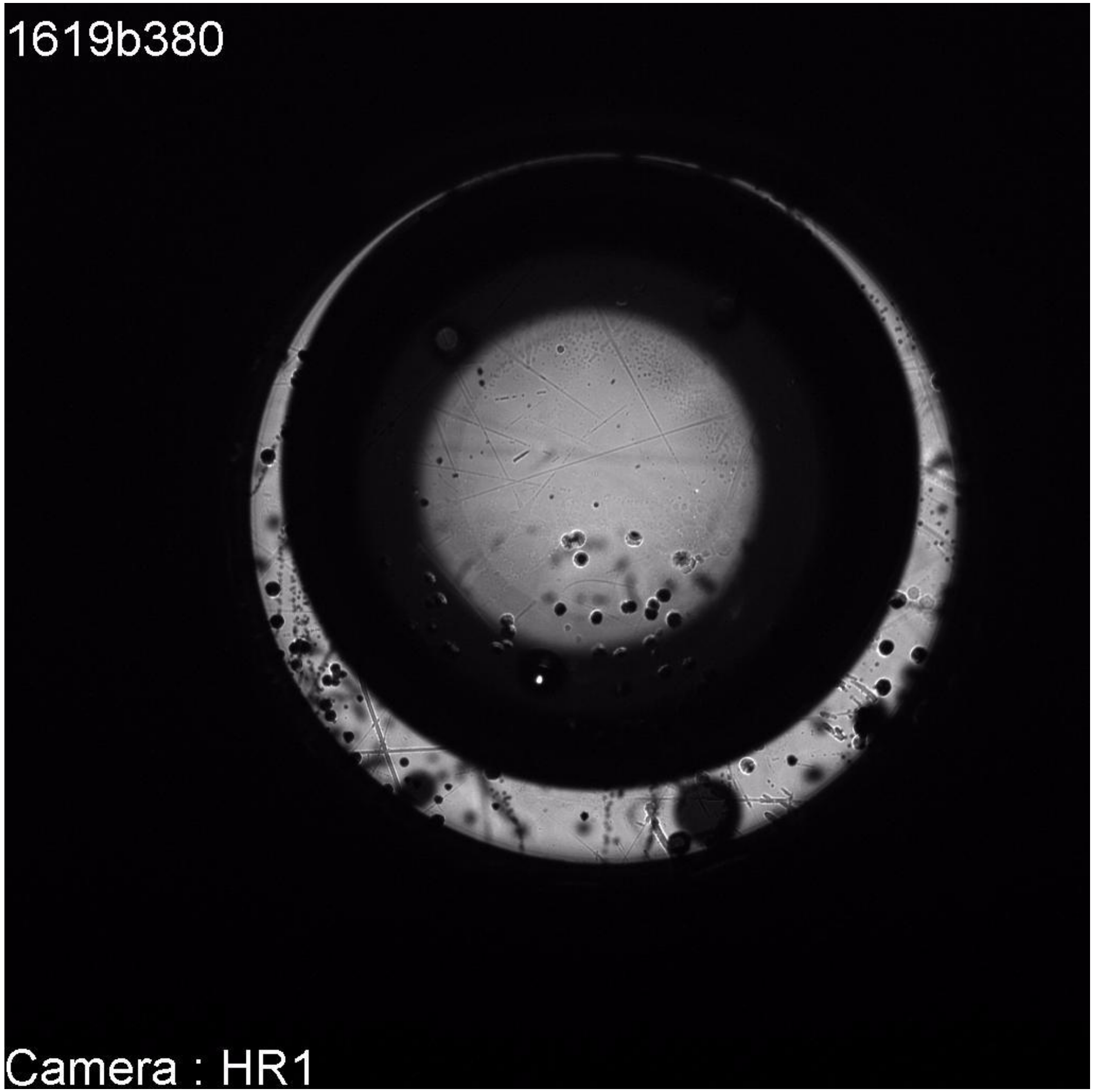
- During isochoric heat-up of test cell localized boiling forms channels of small vapor bubbles which appear to form nucleation sites for salt precipitation




read across then down




**Onset of precipitation**

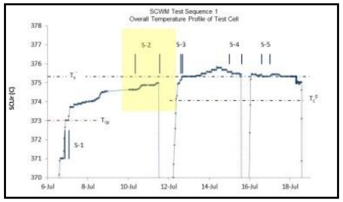

1619b380
Camera : HR1

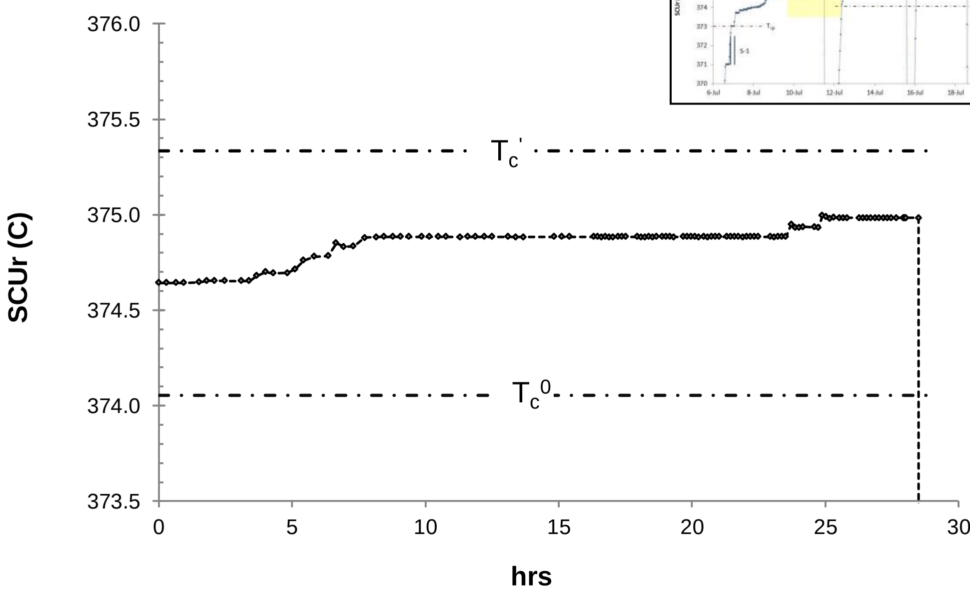
# *Segment 2 – First Approach to $T_c'$*

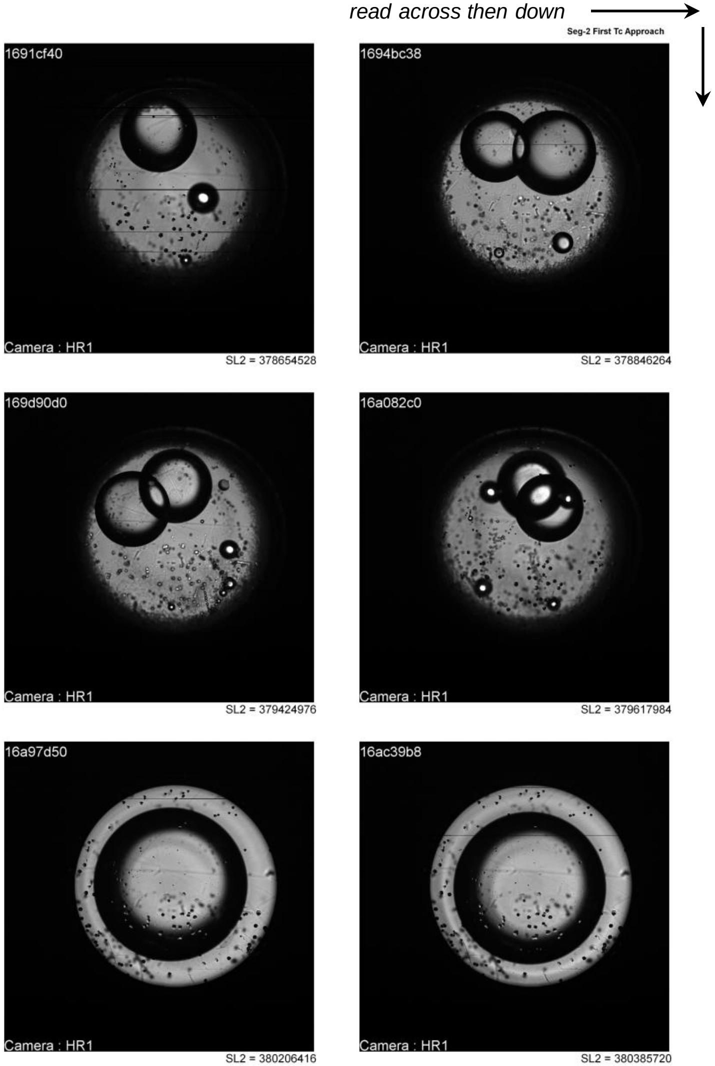
## First approach to Tc' …

- 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 Tc'

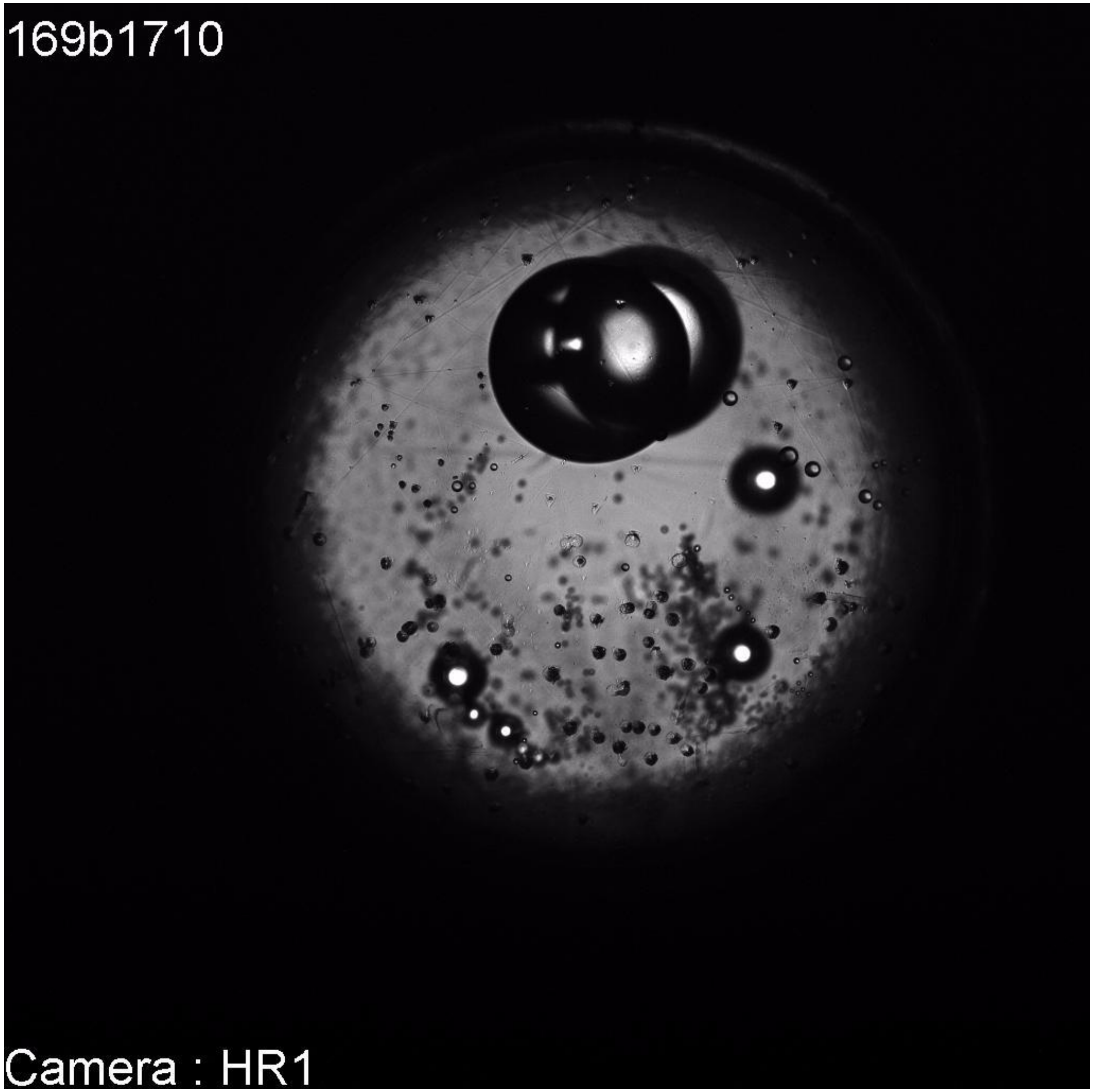
| SL2 | SCUr (°C) |
|---|---|
| 378 654 528 | 374.693 |
| 378 846 264 | 374.832 |
| 379 424 976 | 374.883 |
| 379 617 984 | 374.884 |
| 380 206 416 | 374.884 |
| 380 385 720 | 374.984 |




**First approach to Tc' :**
SCUr : ranges from 374.693 ºC to 374.984 ºC

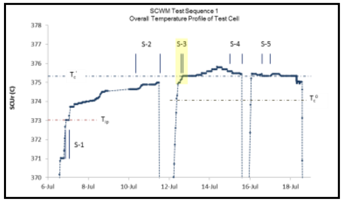

169b1710
Camera : HR1

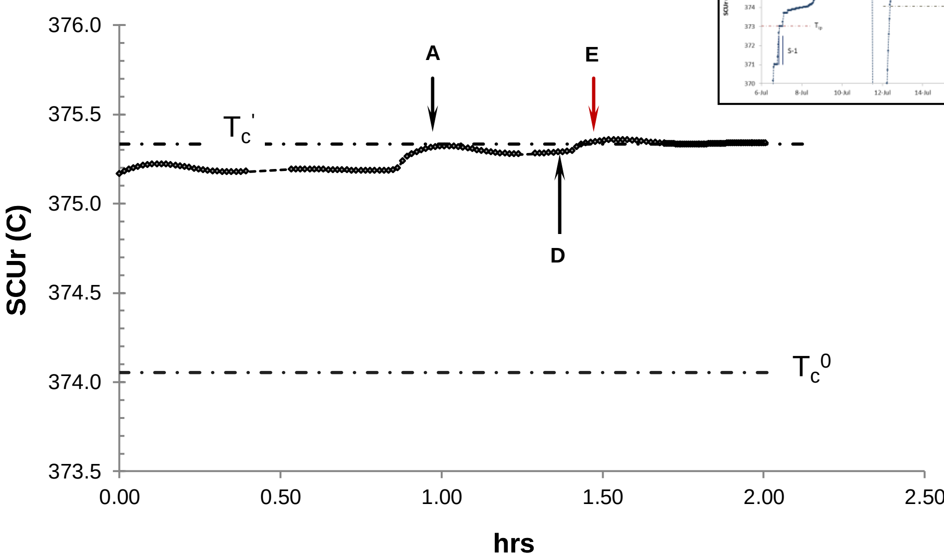
# *Segment 3 – First Critical Transition*

First transition form sub-critical to supercritical at Tc' = 375.335 ºC

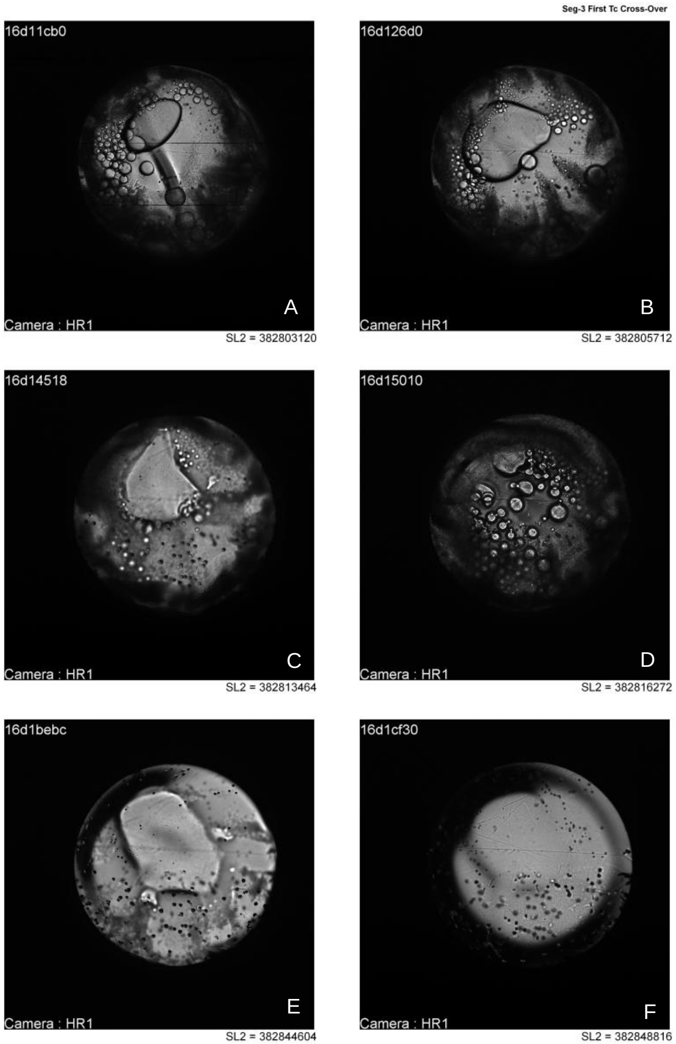
- Approach to Tc' faster than Segment 1, at an average rate of 134 mK/hr near critical (between D - E in plot)
- precipitate does **not re-dissolve** prior to transition

| SL2 | SCUr (°C) |
|---|---|
| 382 803 210 | 375.312 |
| 382 805 712 | 375.319 |
| 382 813 464 | 375.308 |
| 382 816 272 | 375.295 |
| 382 844 604 | 375.341 |
| 382 816 272 | 375.295 |

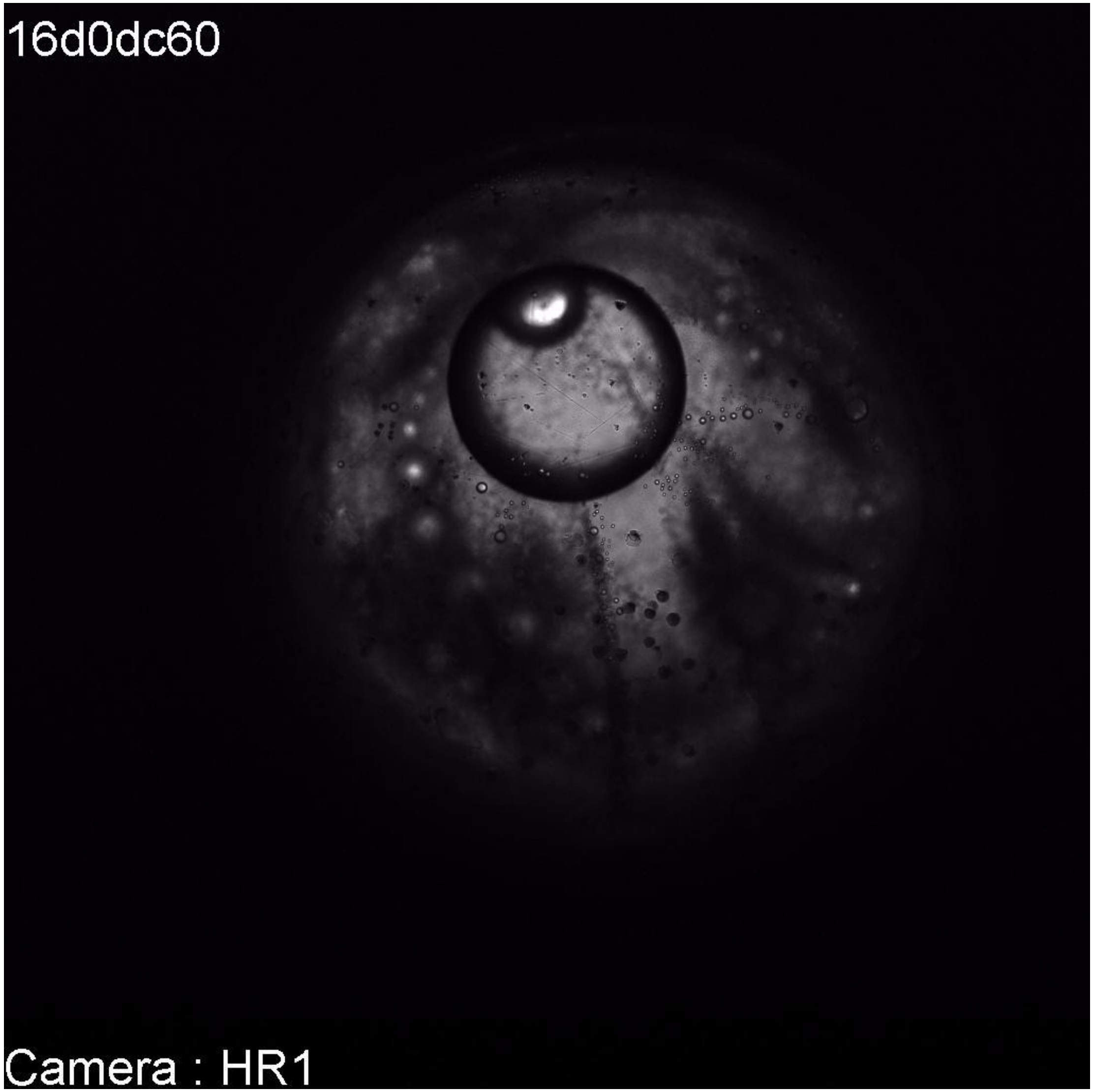



*read across then down*




**First critical transition :**
SCUr : ranges from 375.312 ºC to 375.295 ºC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Camera : HR1

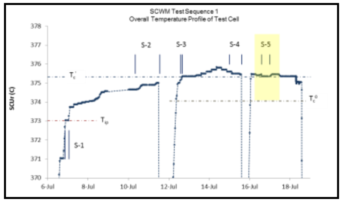
# *Segment 5 – Quench Transition*

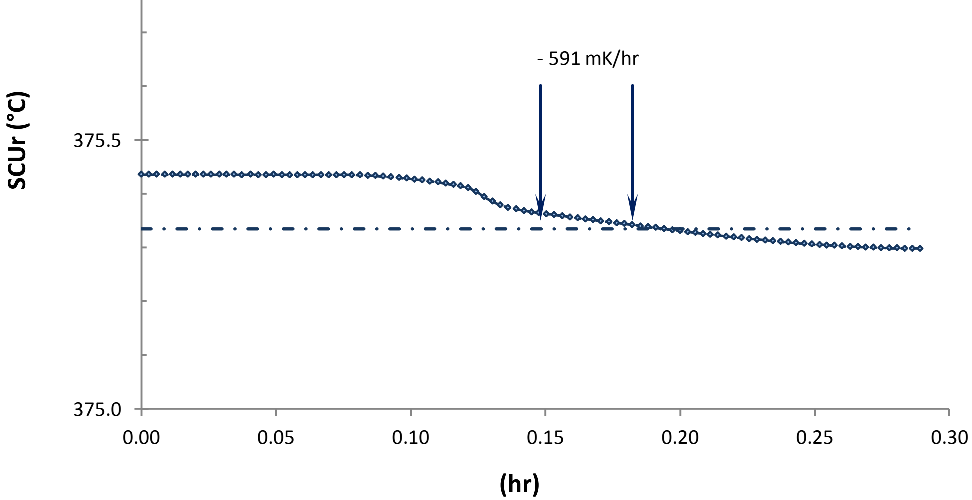
Transition from supercritical to sub-critical

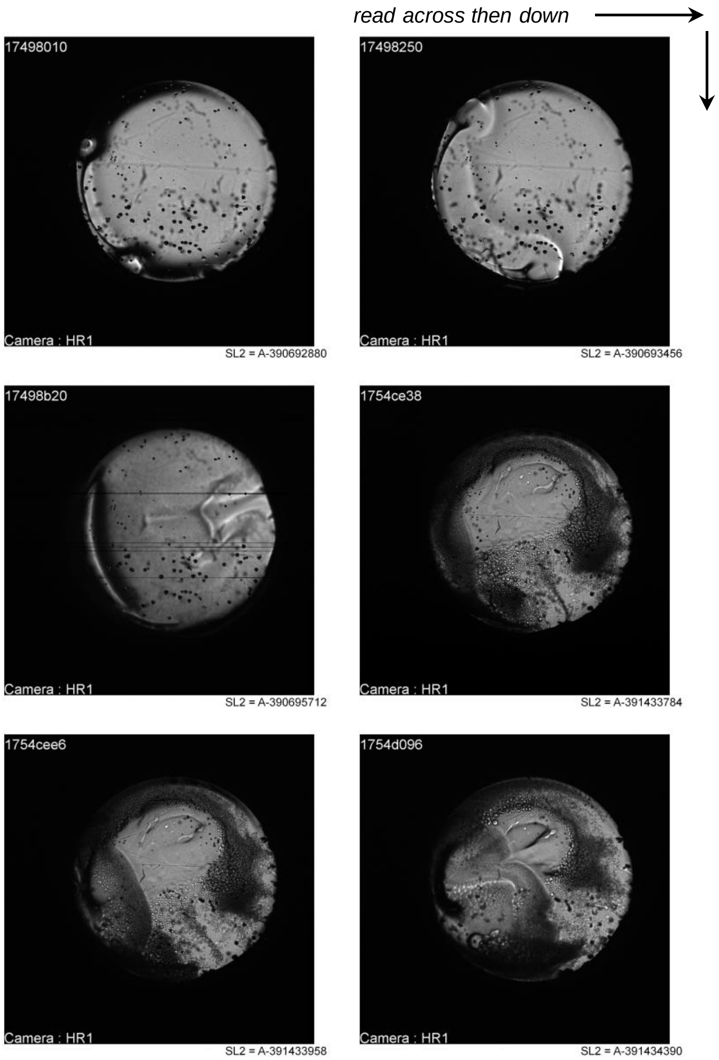
- average quench rate ~ 591 mK/hr [1]

[1] from SL2 = 390695712 to SL2 = 390692880

| SL2 | SCUr (°C) |
|---|---|
| 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 |

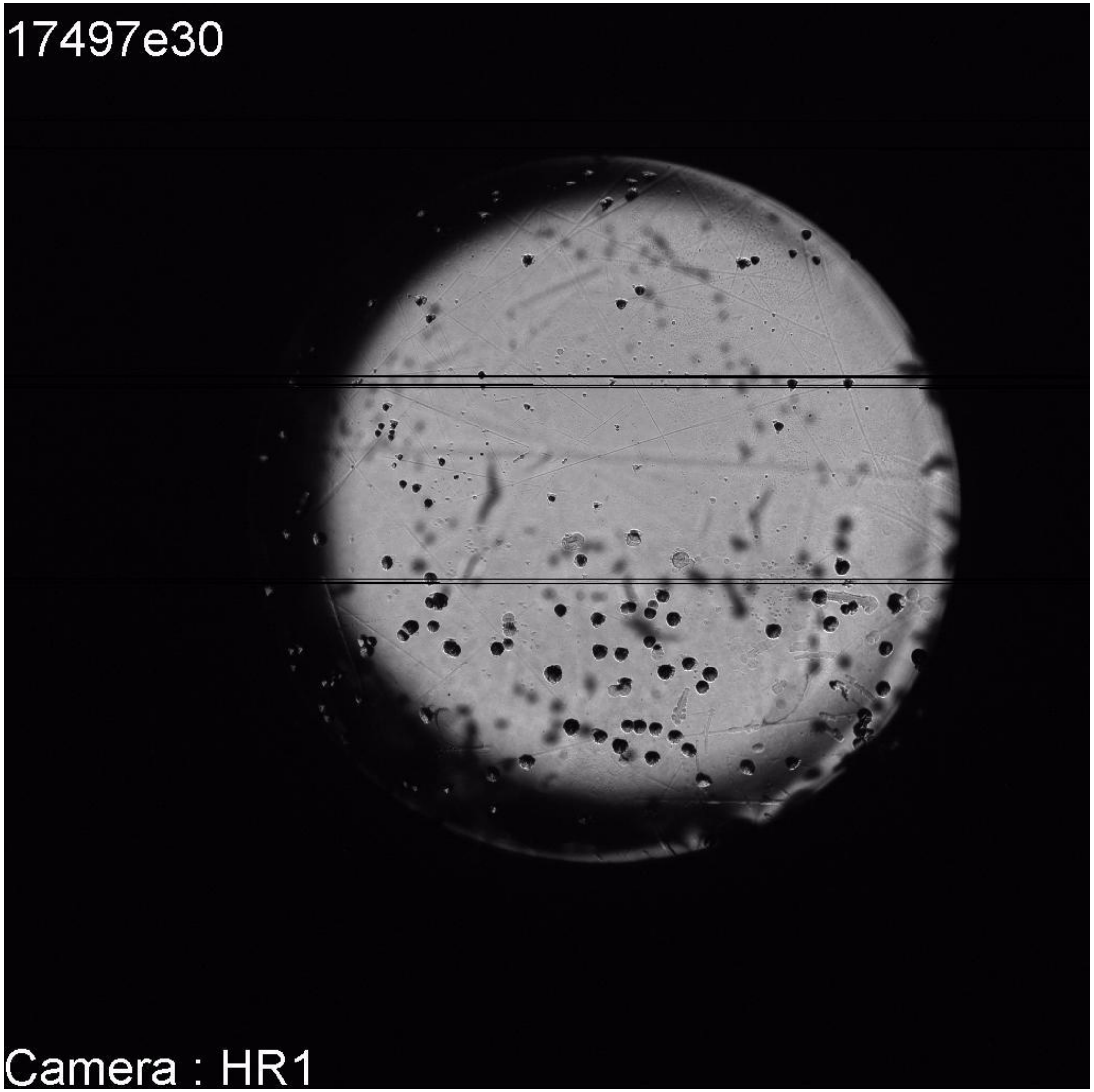



**Quench transition :**
SCUr : ranges from 375.364 ºC to 375.298 ºC

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



# Summary

Summary

- Test Sequence 1 provided preliminary value for critical point of solution
  - Tc' = 375.335 ºC (indicated)[1] 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

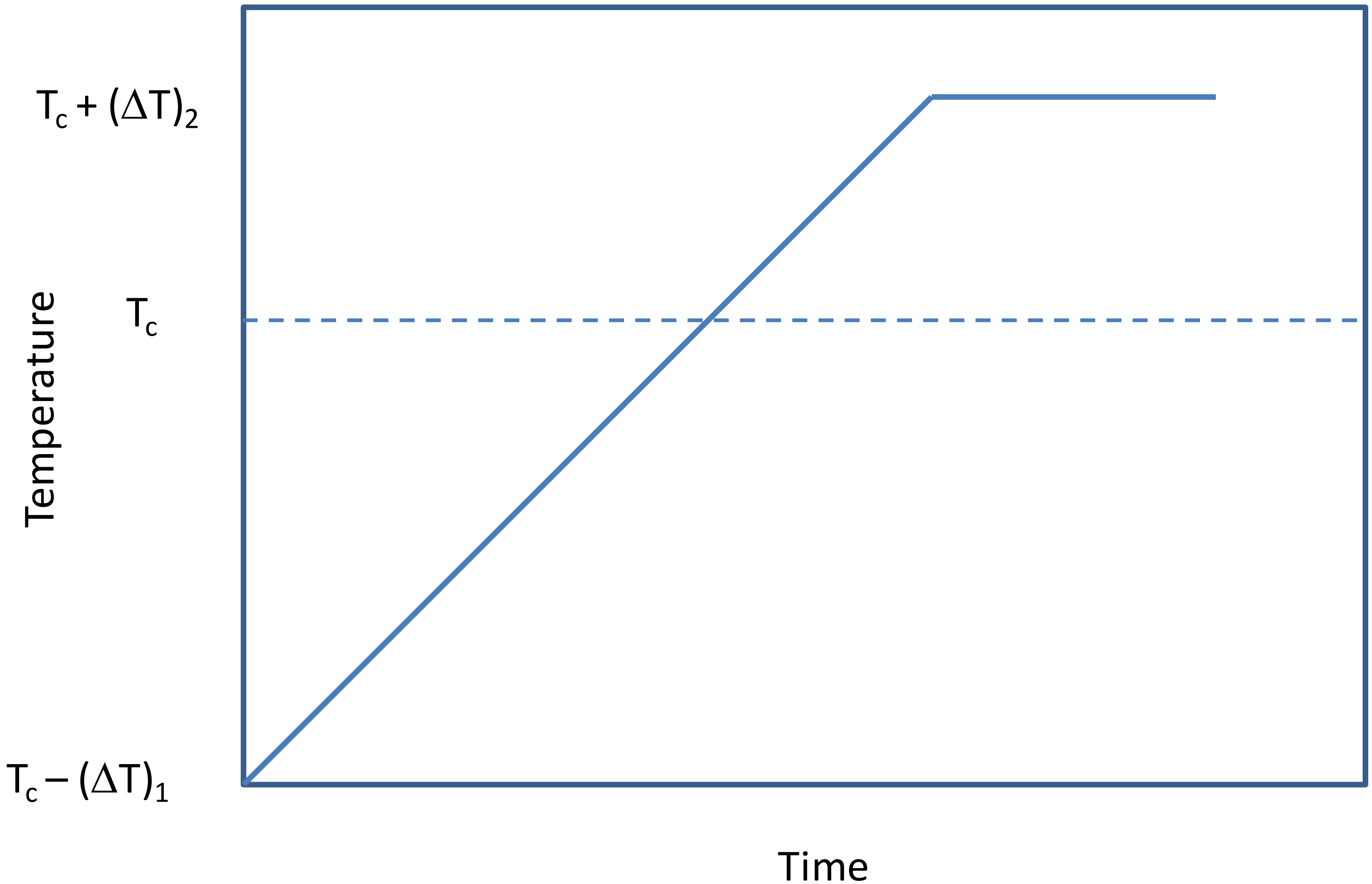
- Thermal regulation system needs to be optimized for operation w/o one of the Peltier elements (PEB)
- Temperature “offset” needs to be defined

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

# BACKUP

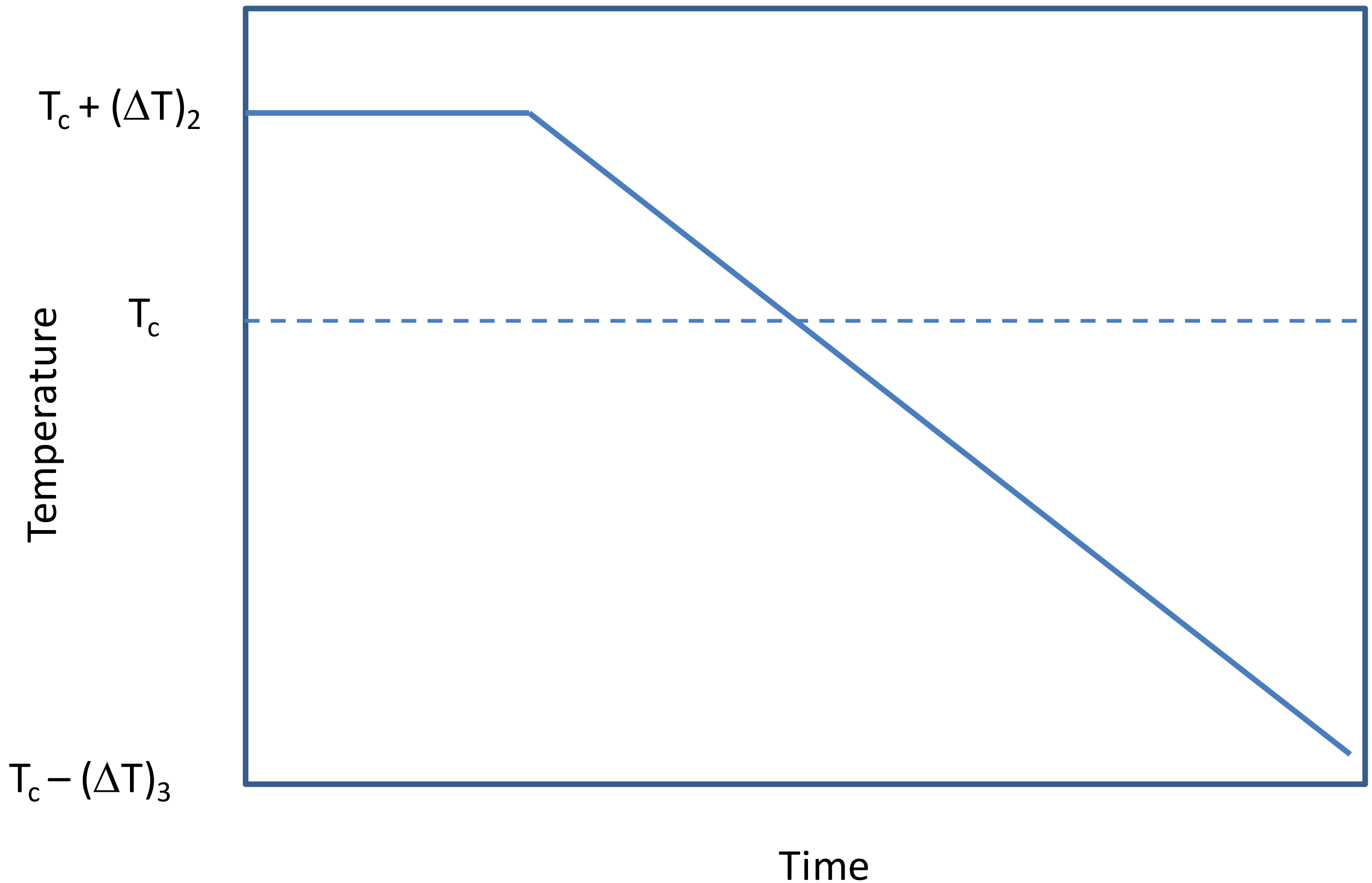
## Test Sequence 1

### Salt Precipitation During Temperature Increase

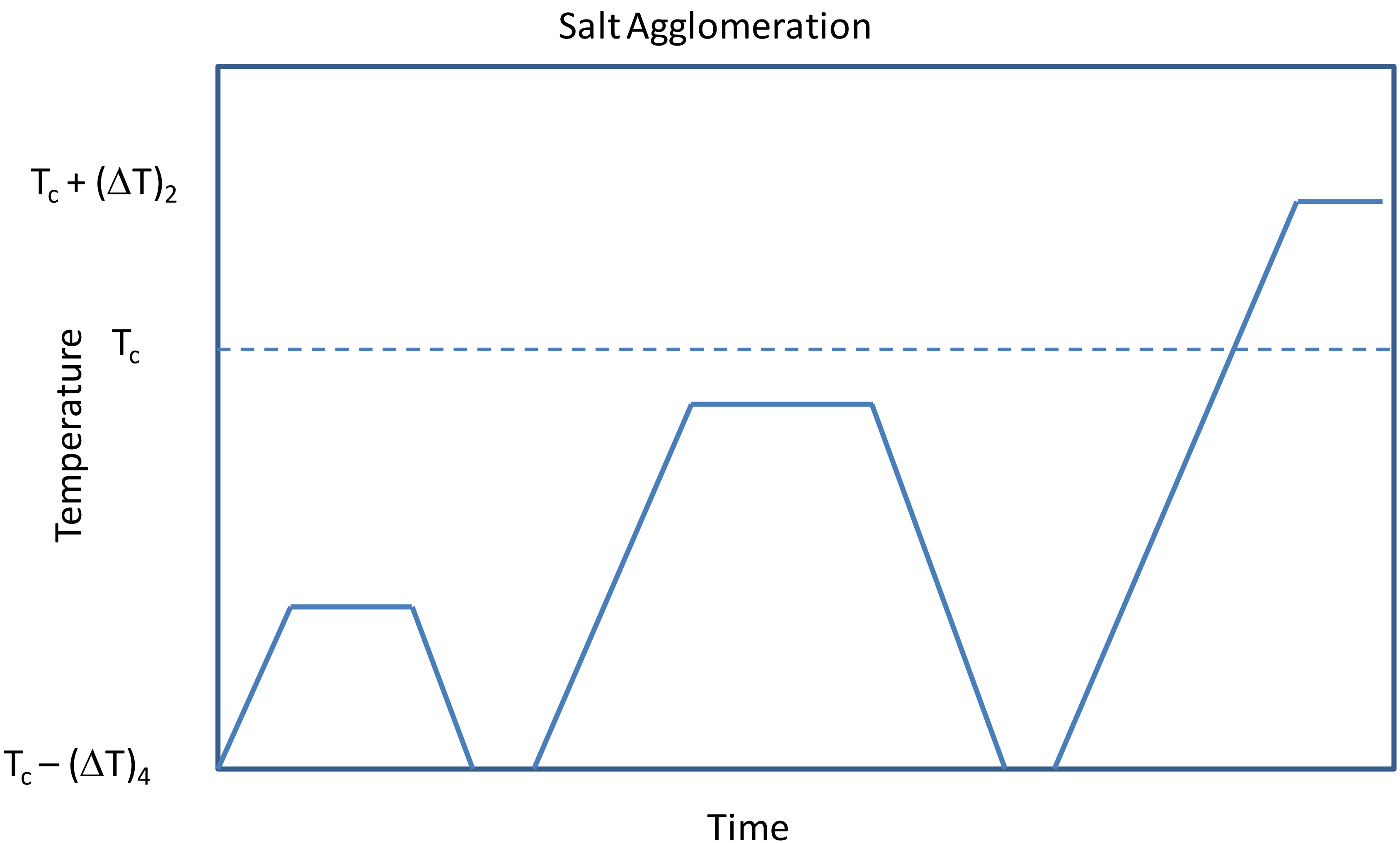


## Test Sequence 2

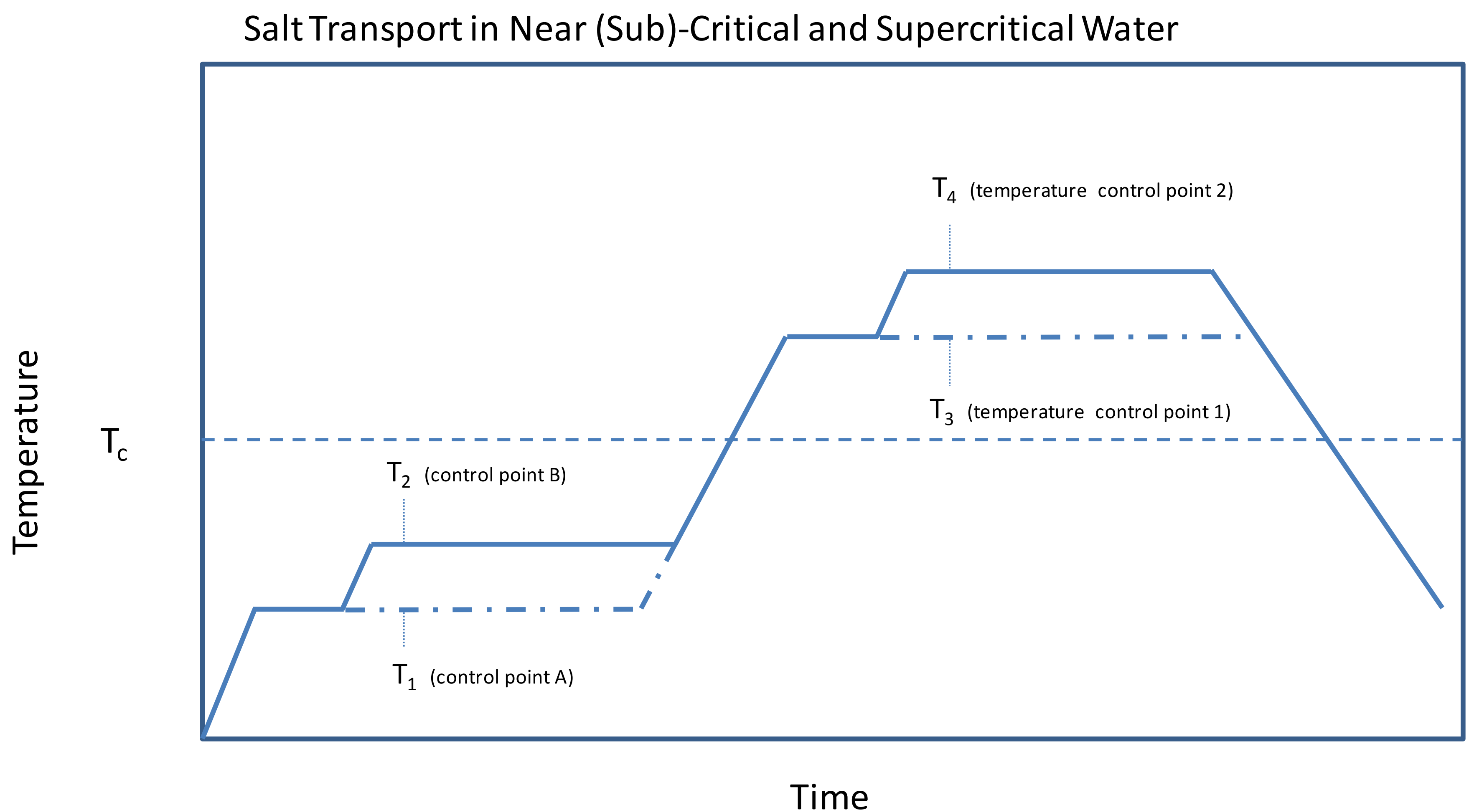
Salt Solvation During Temperature Decrease



## Test Sequence 3

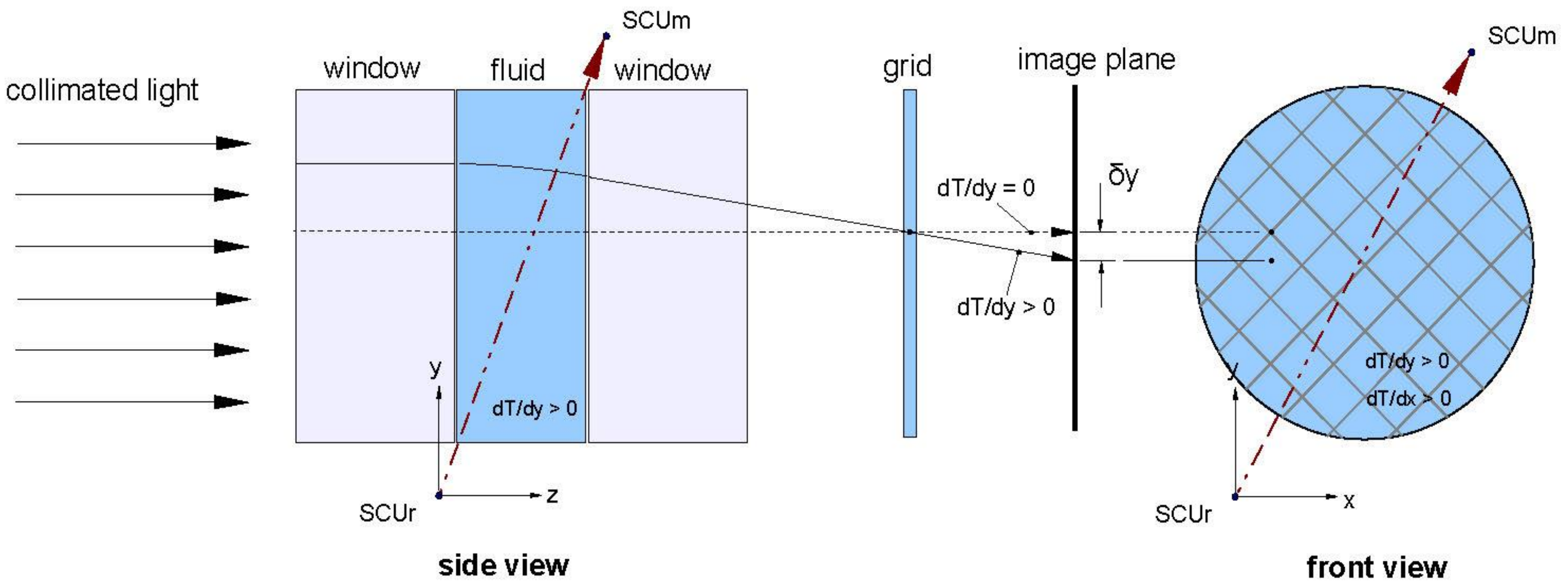


## Test Sequence 4



# Analysis (cont)

## *Shadow-graphic Configuration*




$$\delta = \frac{\psi}{n}\frac{dn}{dy} \qquad n = 1 + K\rho$$

*n = refractive index*
*$\psi$, K are constants*