

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

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  - <sup>5</sup> NCSER ... National Center for Space Exploration Research
  - <sup>6</sup> CEA ... Commissariat à l'Energie Atomique
  - <sup>7</sup> 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

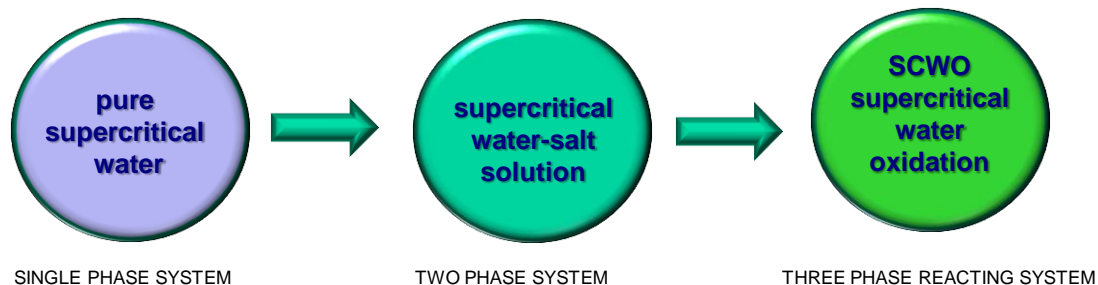
# **Supercritical Water Mixture (SCWM) Experiment**

## ***- Overview -***

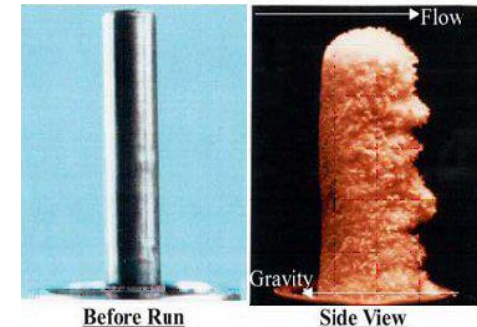
## SCWM Experiment - Background and Motivation

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

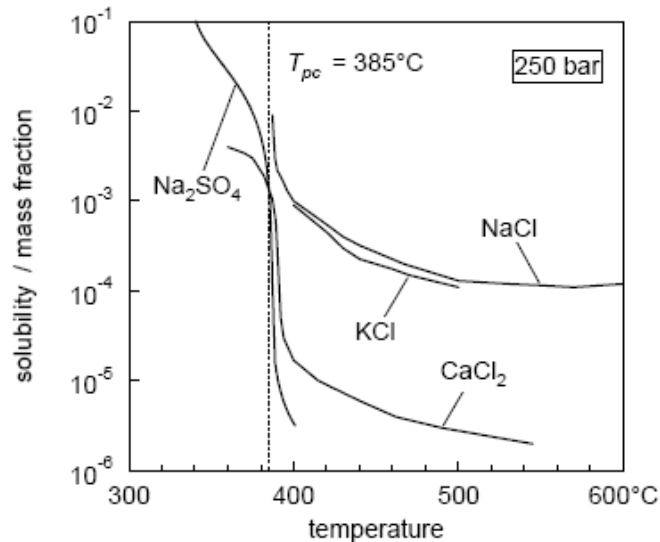


Test in 1-g showing illustrating rapid build-up of salt precipitate;  $\text{Na}_2\text{SO}_4$  aqueous solution 4%-w at ( $T_{\text{BF}} = 356\text{C}$ ,  $P=250$  atm) flowing past unheated rod (left) and heated rod (right) (Hodes, M. '04)

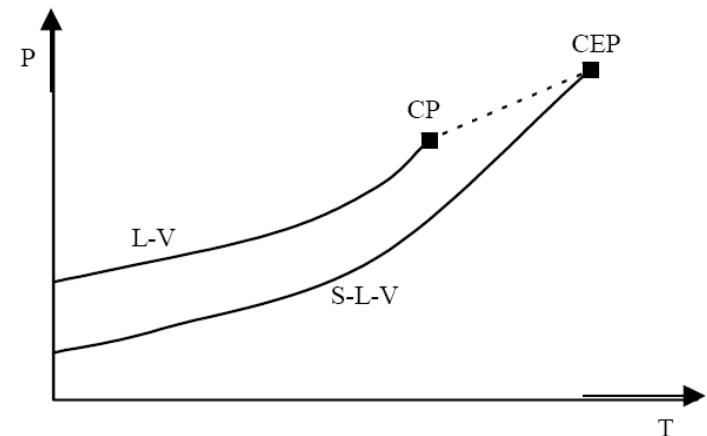
## SCWM Experiment – Objectives

Science Objectives:

- quantify critical point for a specific salt/water mixture (0.5%-w  $\text{Na}_2\text{SO}_4$ )
- 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  $T_c$



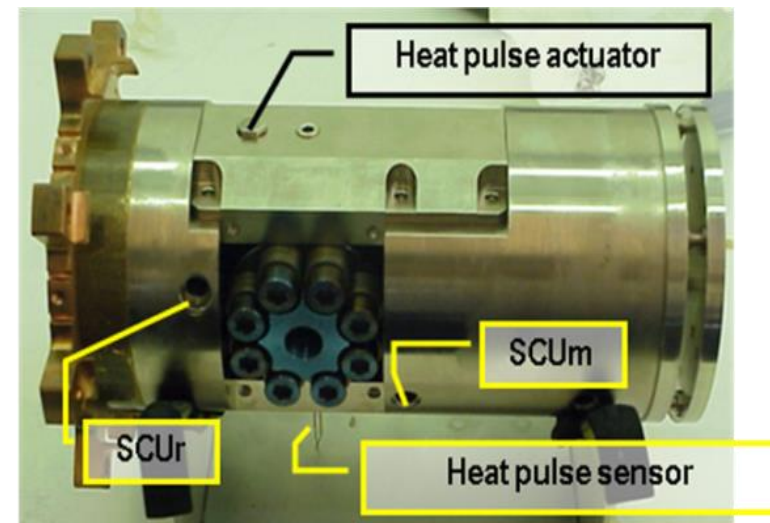
Schematic showing saturation line for pure water and Type 2 (Sodium Sulfate) salt solution ... results in shift of critical end point

## DECLIC Hardware and Diagnostics

- Direct observation: field of view =  $\varnothing$  12 mm w/ a resolution 10  $\mu\text{m}$ .
- Light transmission measurement and grid shadow for turbidity and index gradient
- Light Scattering: small angle or  $90^\circ$  for turbidity measurements
- Small field of view (microscopy) 1 mm w/ a resolution of 5  $\mu\text{m}$
- 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



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*



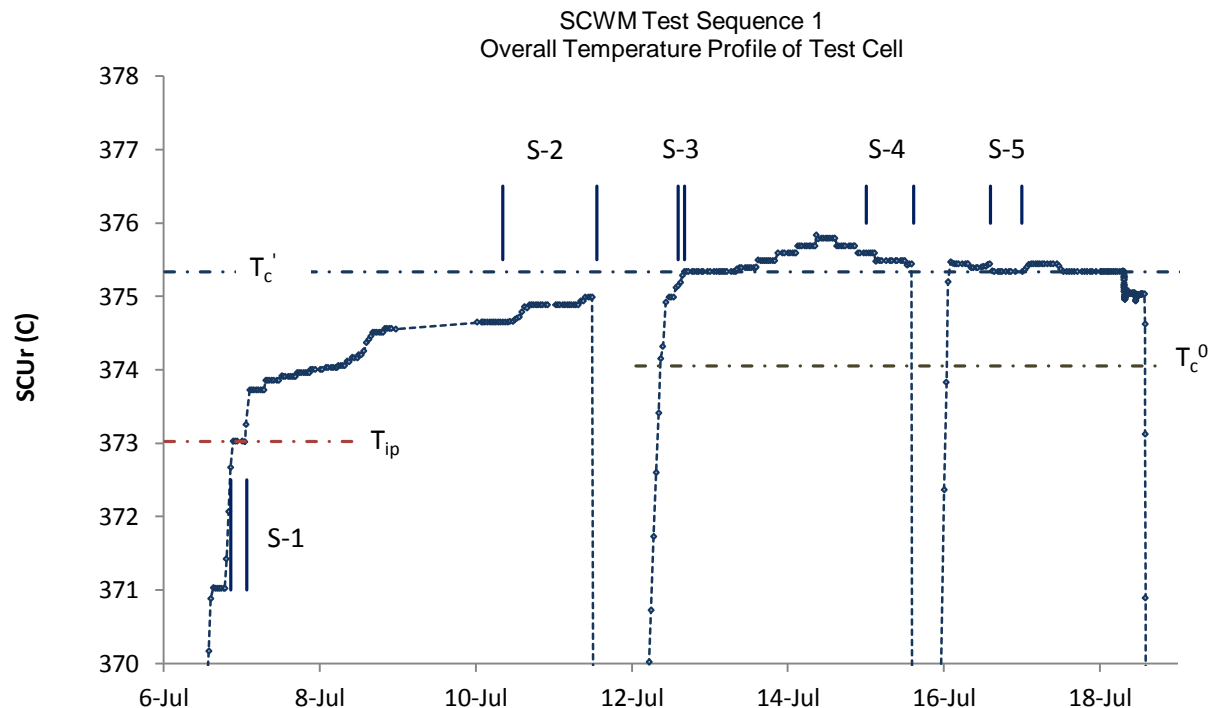
## SCWM Operational Schedule

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 1<sup>st</sup> and ended on July 18<sup>th</sup>

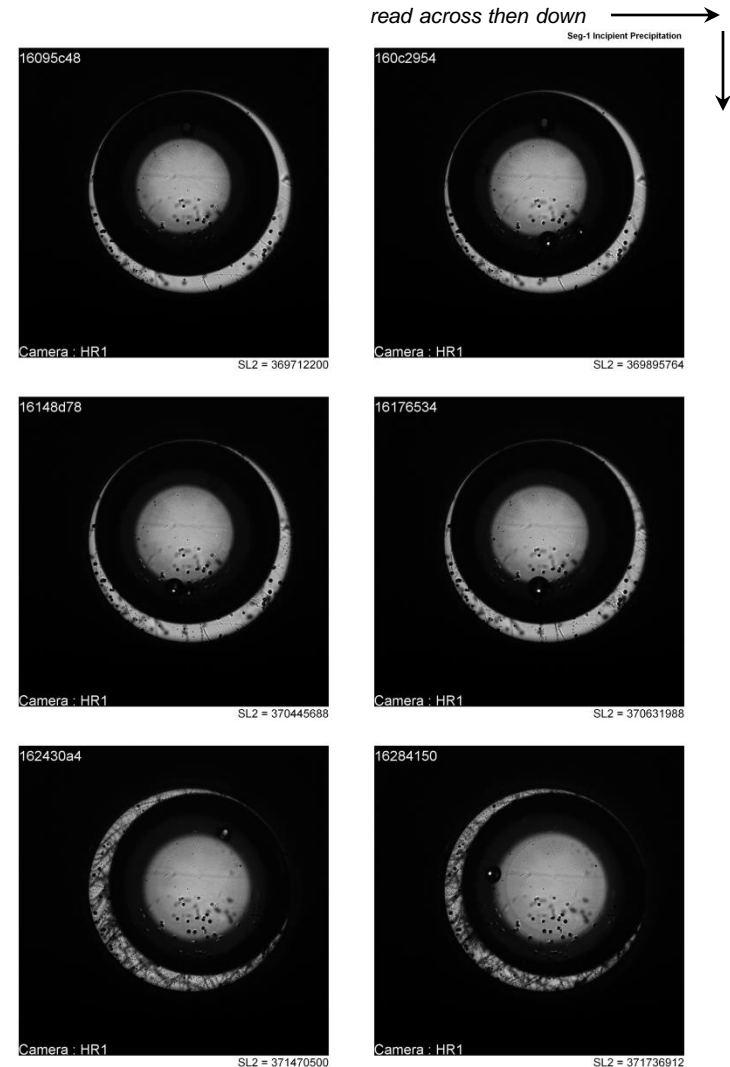
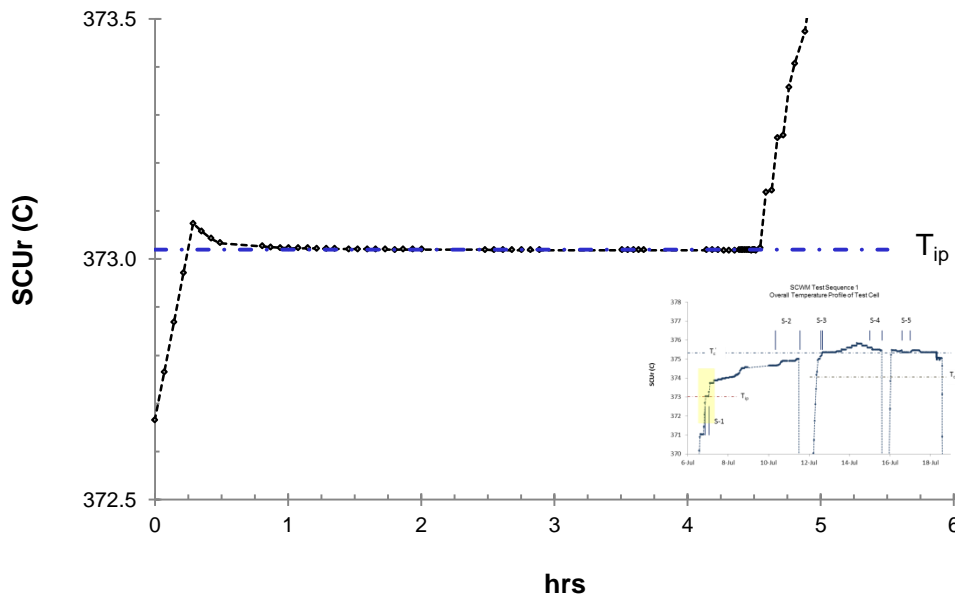
- Primary science objective was to find the shift in critical point
- Three power interruptions occurred near critical point early part of test sequence
- Peltier element, PEB, used in precision temperature control near critical point, exhibited off-nominal behavior
- Time spent on optimizing thermal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



## Segment 1 – Incipient Precipitation

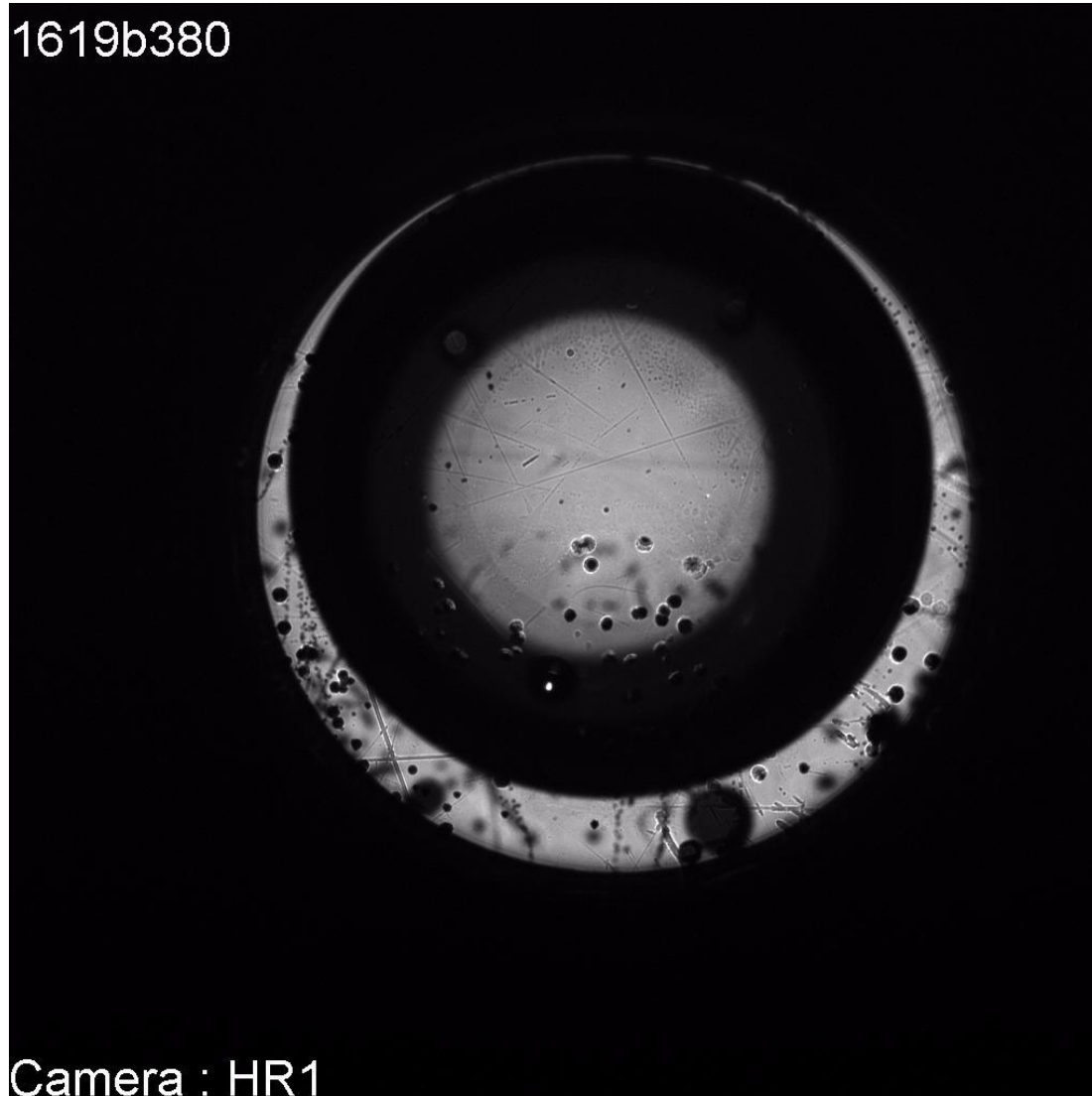
First appearance of salt precipitate occurs at  $T_{ip} \sim 373^\circ\text{C}$

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



Onset of precipitation

1619b380



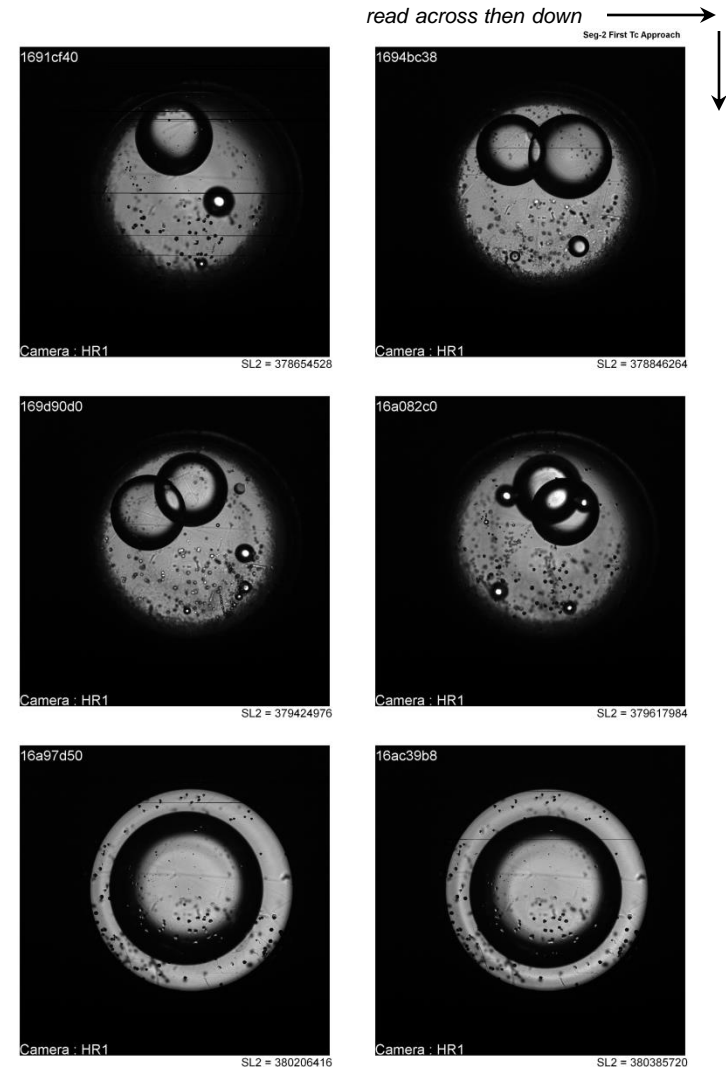
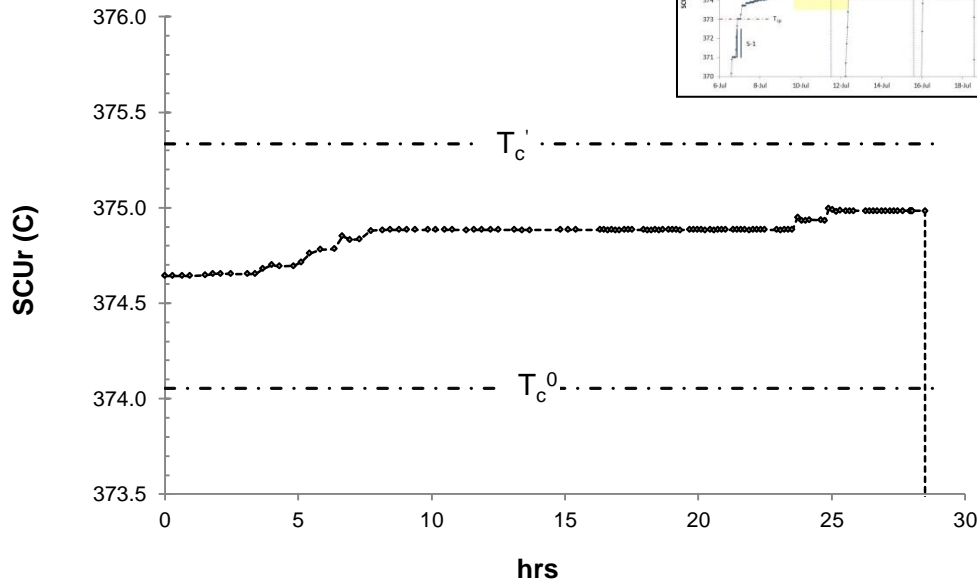
Camera : HR1

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

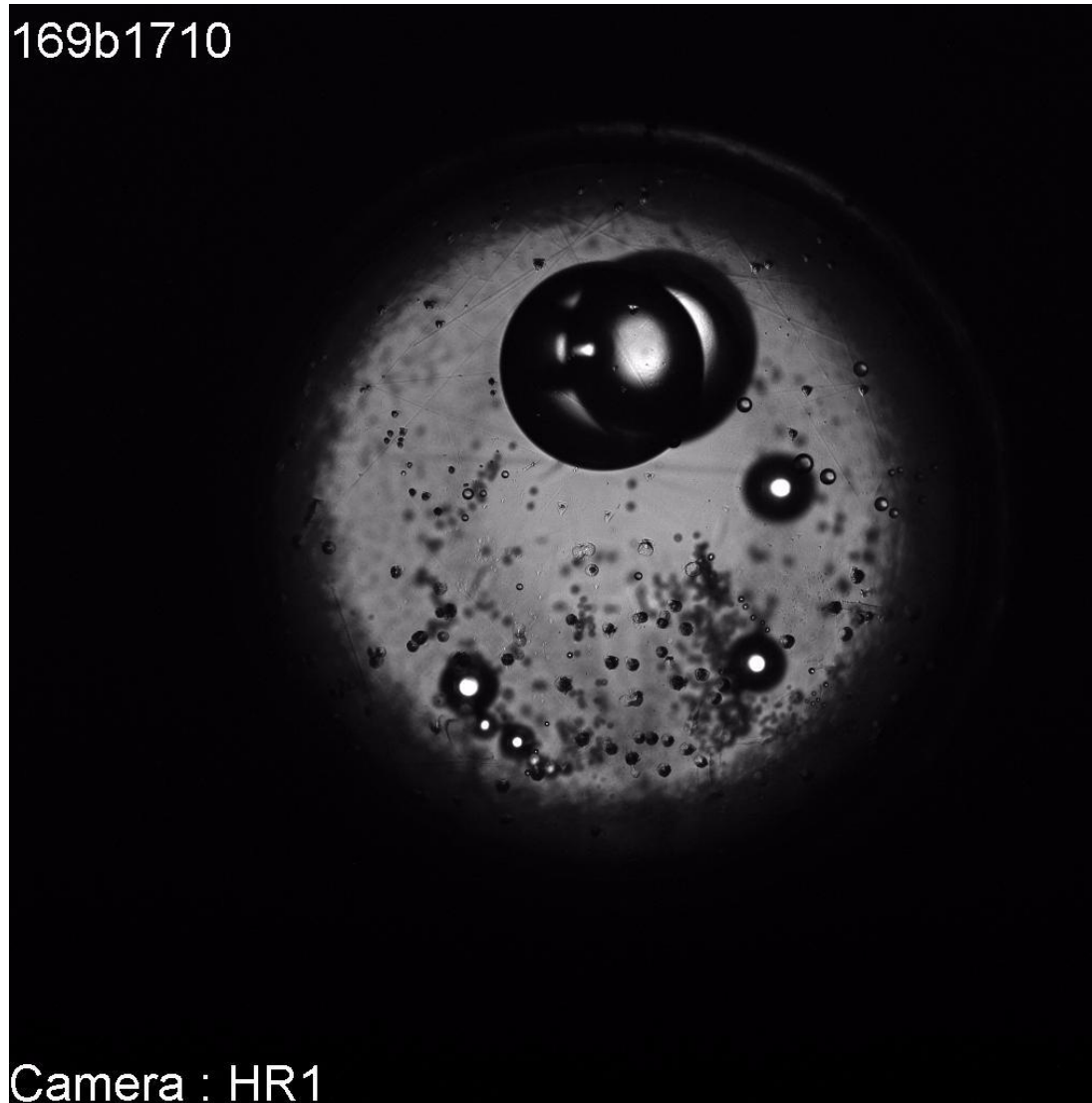
First approach to  $T_c'$  ...

- 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  $T_c'$

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  $T_c'$  :  
SCUr : ranges from 374.693 °C to 374.984 °C

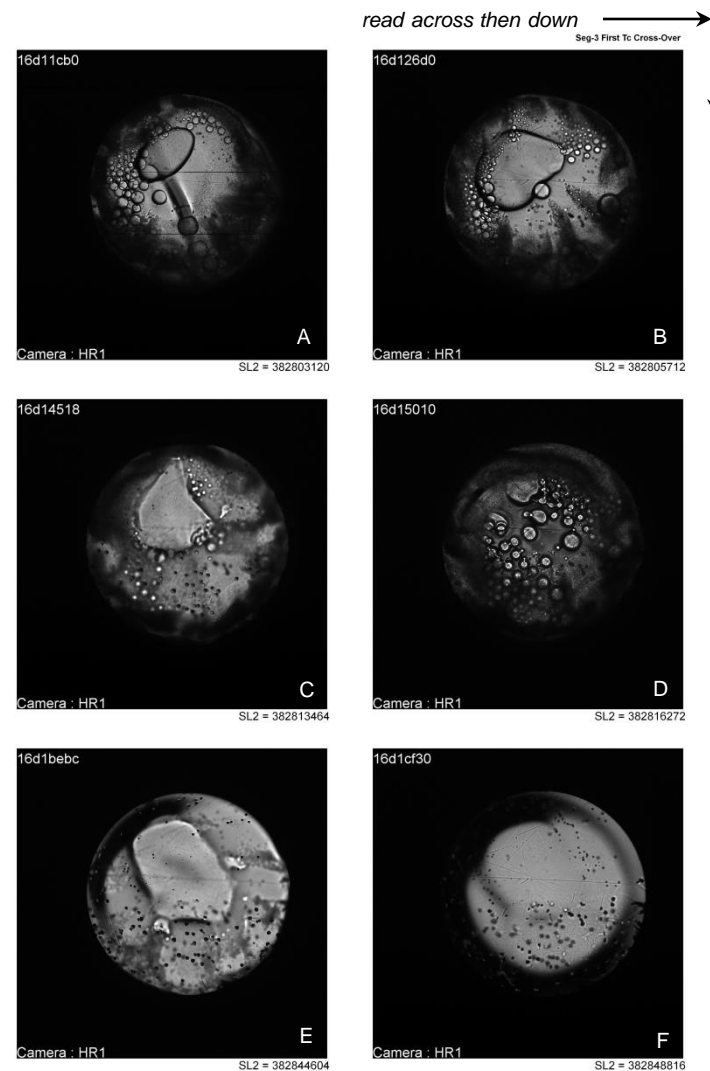
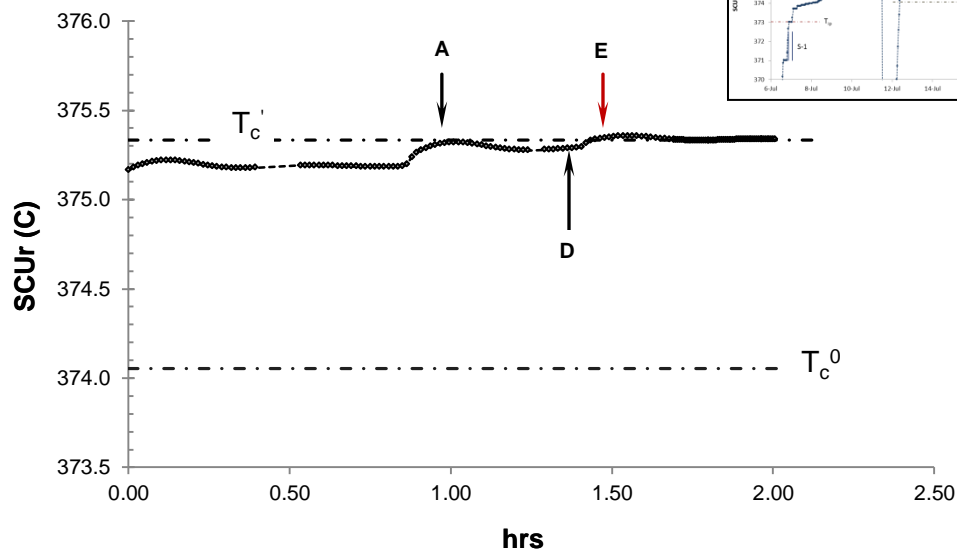


## Segment 3 – First Critical Transition

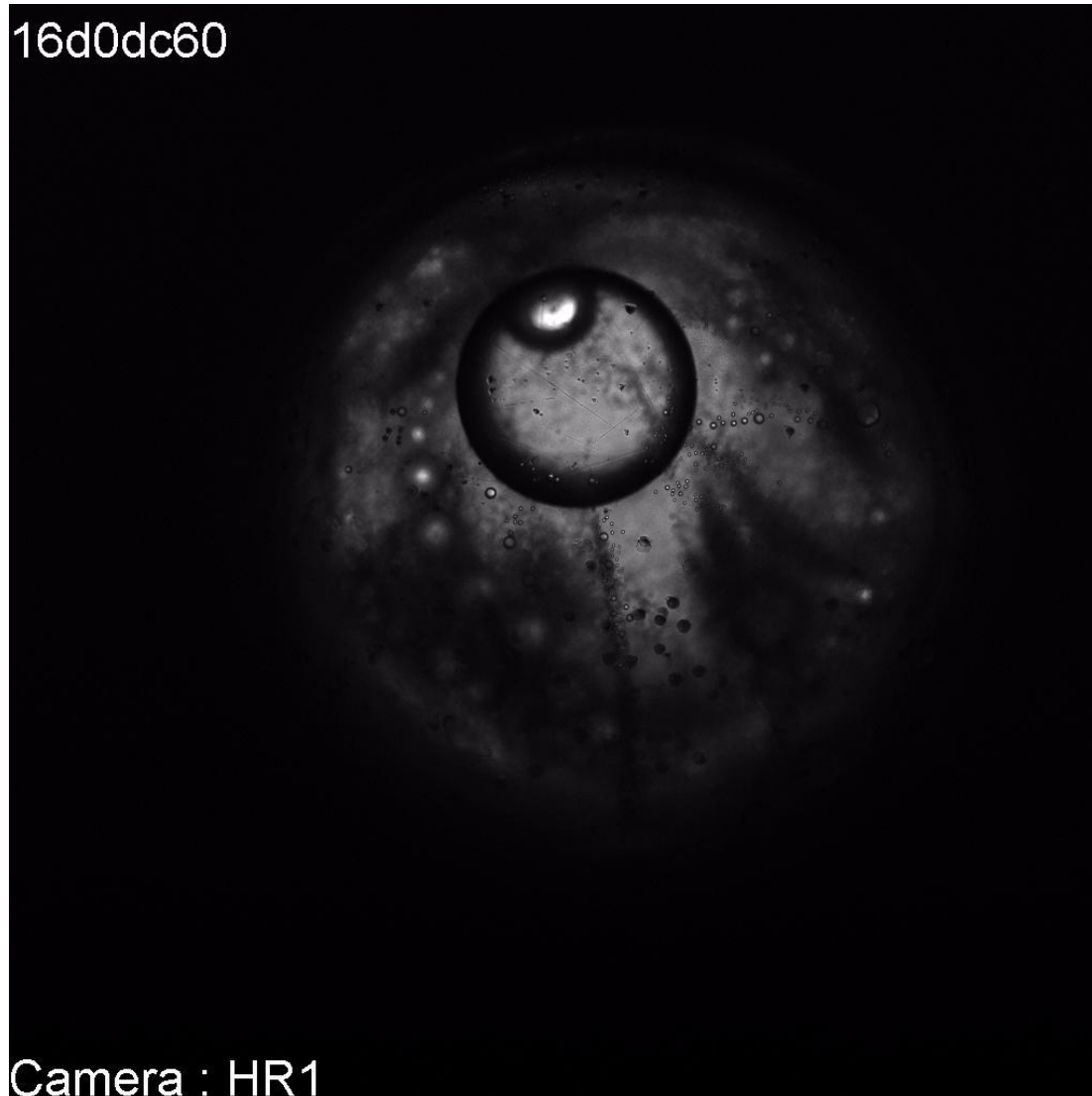
First transition from sub-critical to supercritical at  $T_c' = 375.335 \text{ }^\circ\text{C}$

- 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

SL2	SCUr ( $^\circ\text{C}$ )
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



First critical transition :  
SCUr : ranges from 375.312  $^\circ\text{C}$  to 375.295  $^\circ\text{C}$





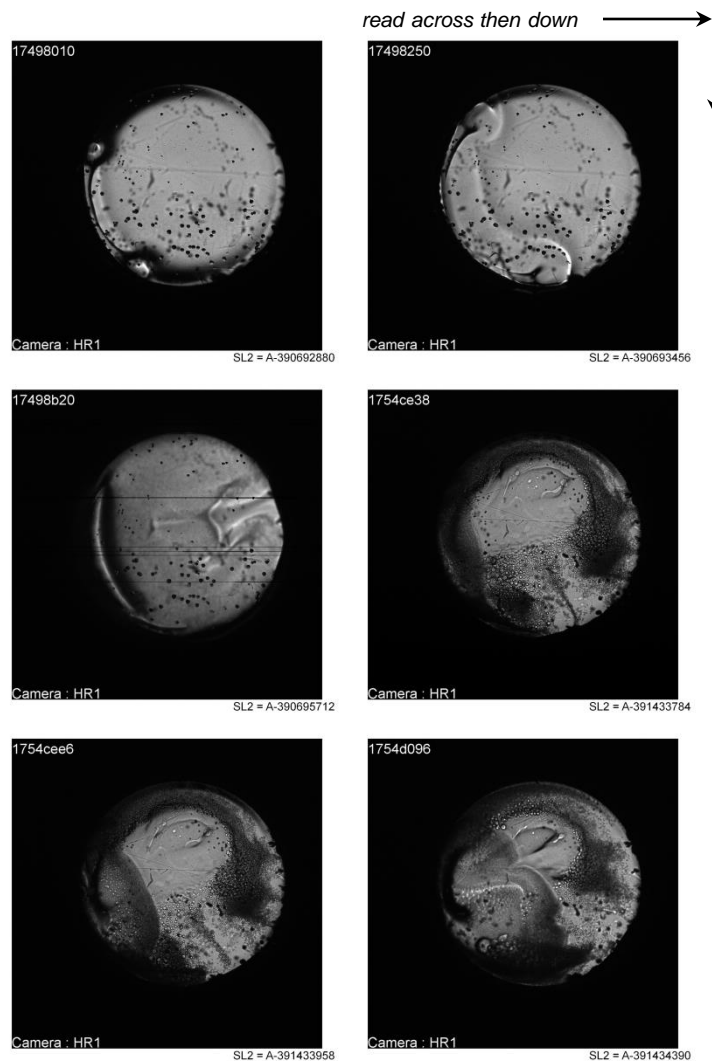
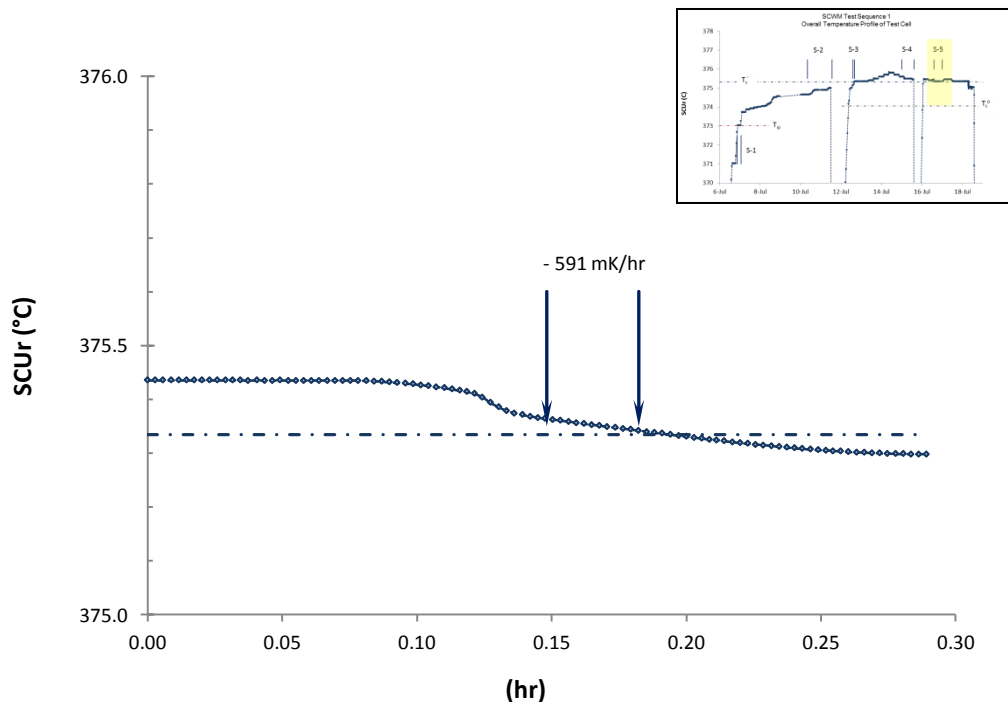
## Segment 5 – Quench Transition

Transition from supercritical to sub-critical

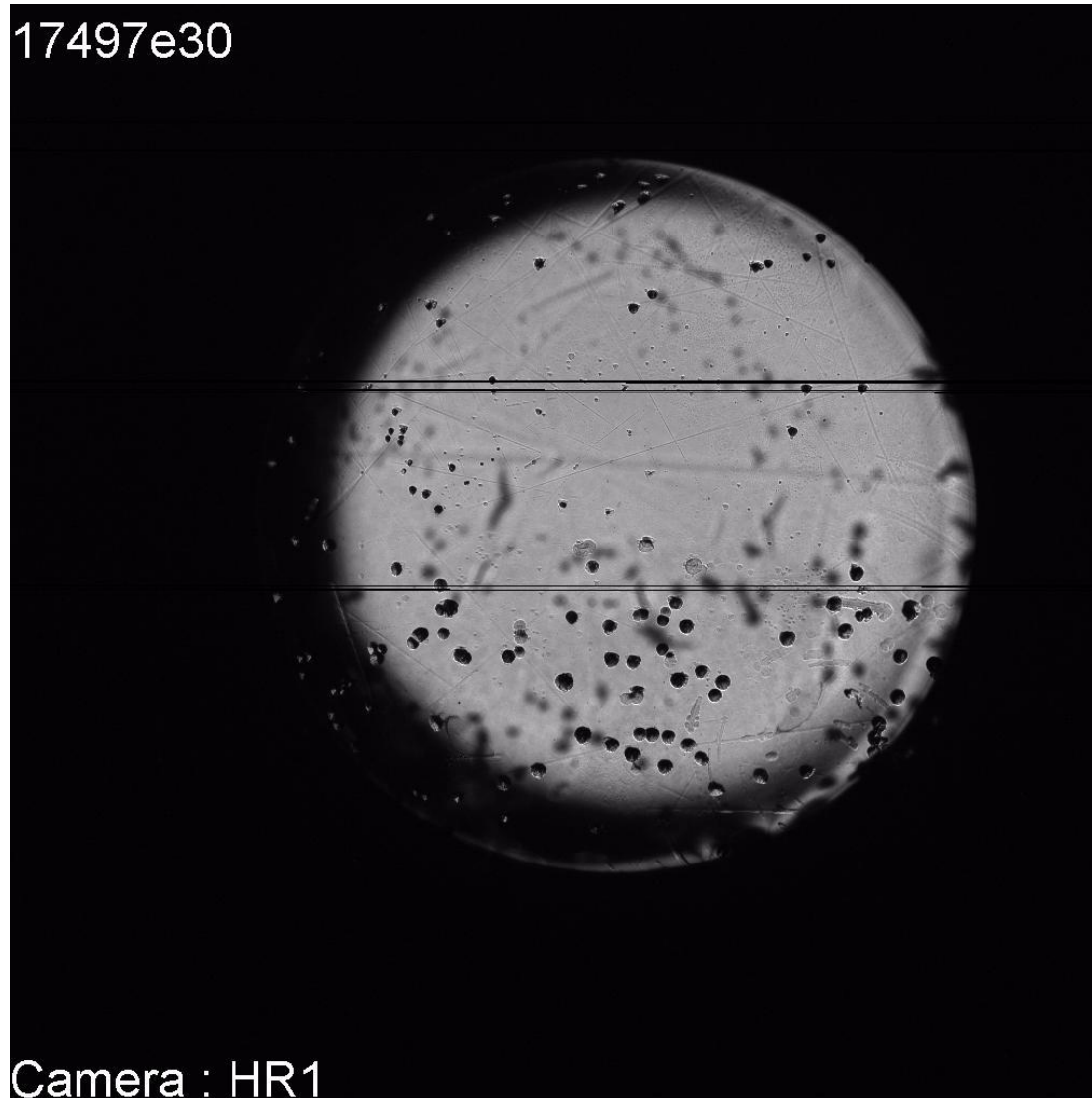
- average quench rate ~ 591 mK/hr<sup>1</sup>

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

<sup>1</sup> from SL2 = 390695712 to SL2 = 390692880



**Quench transition :**  
SCUr : ranges from 375.364 °C to 375.298 °C



## Summary

### Summary

- Test Sequence 1 provided preliminary value for critical point of solution
  - $T_c' = 375.335 \text{ }^\circ\text{C}$  (indicated)<sup>1</sup> for  $\text{Na}_2\text{SO}_4$  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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<sup>1</sup> indicated value of SCUr will need to be verified once the actual “offset” has been determined



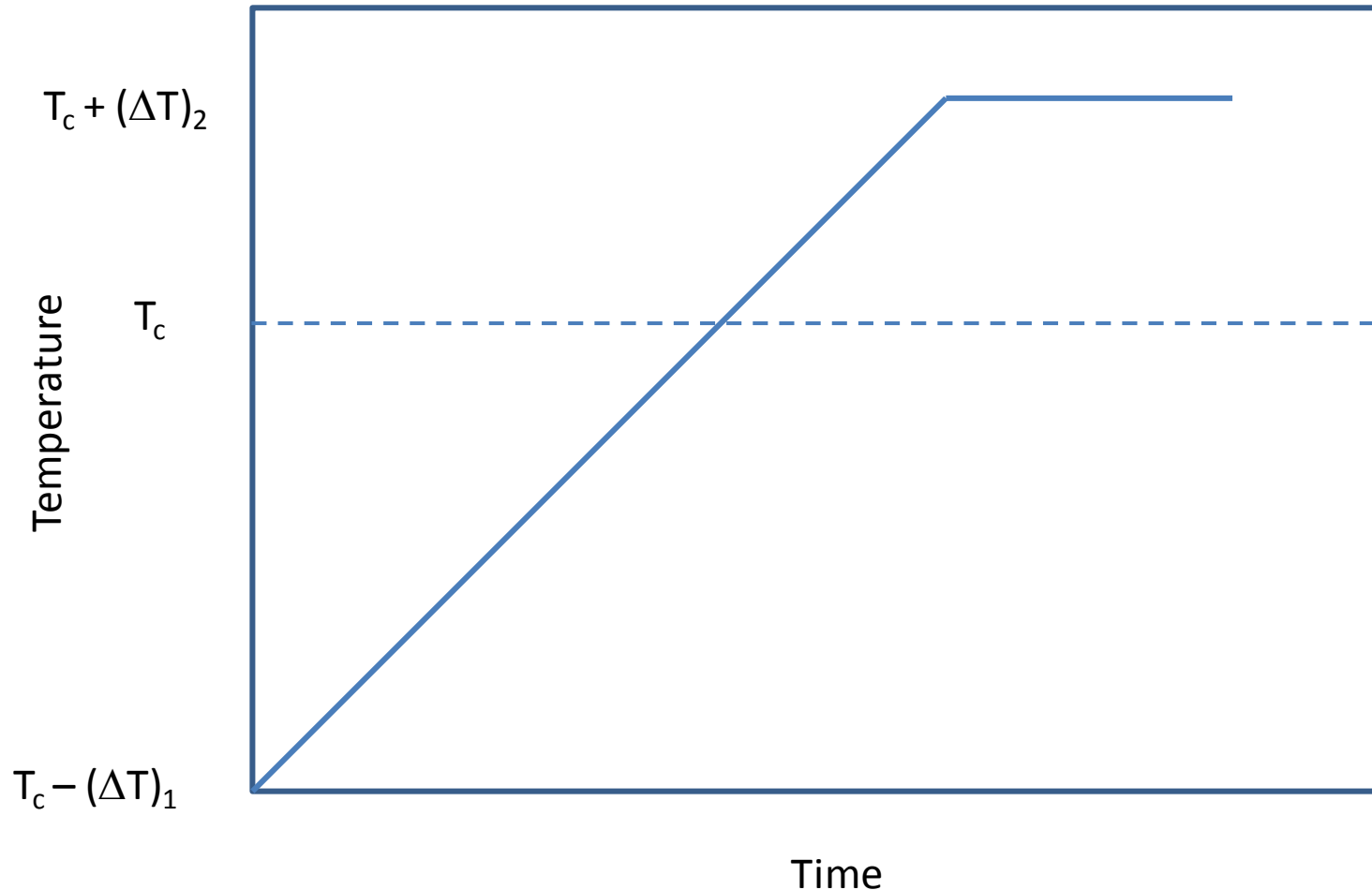
# *Supercritical Water Mixture Experiment (SCWM) in the High Temperature Insert – Reflight (HTI-R)*

**BACKUP**



Test Sequence 1

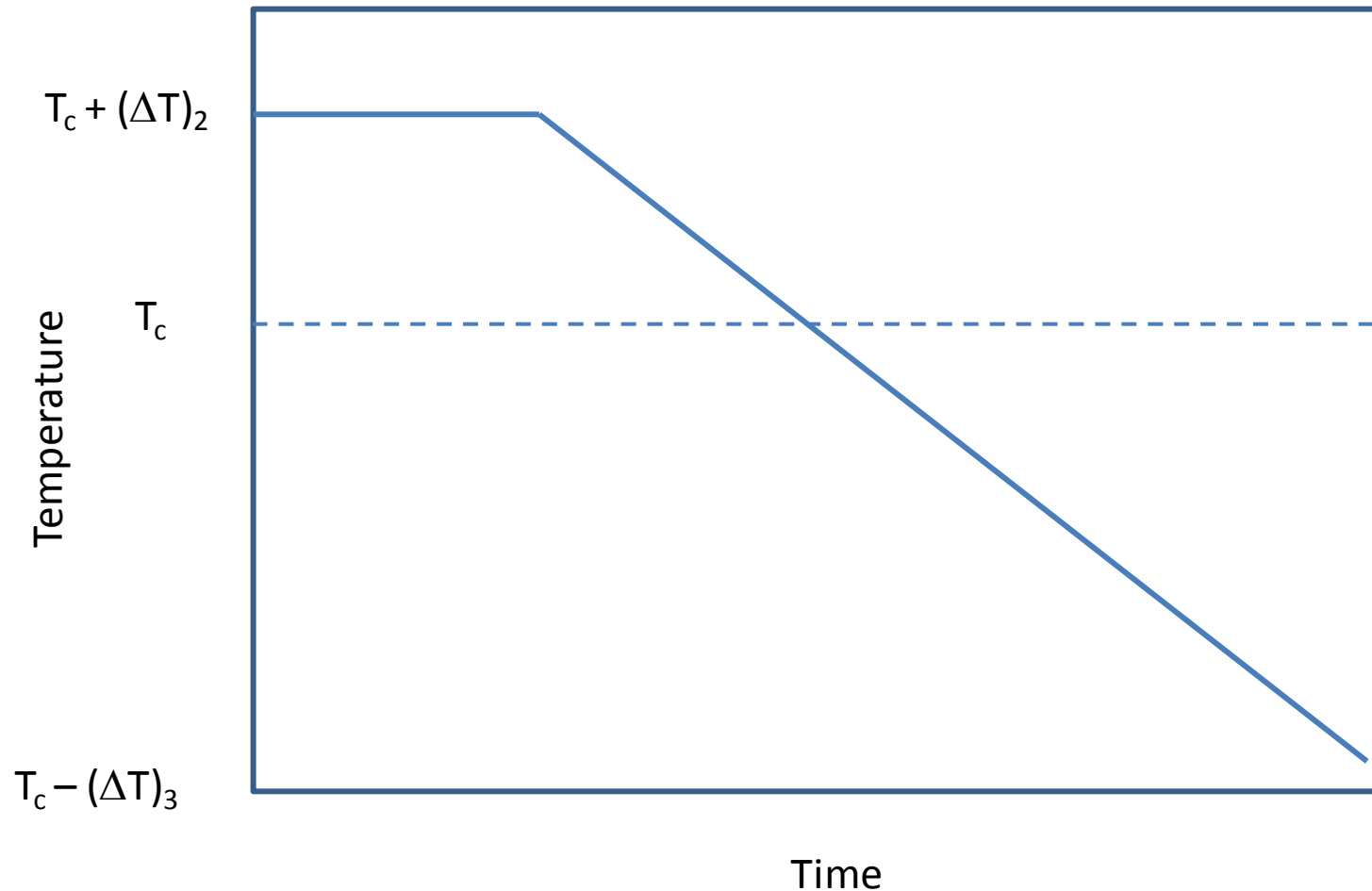
Salt Precipitation During Temperature Increase





## Test Sequence 2

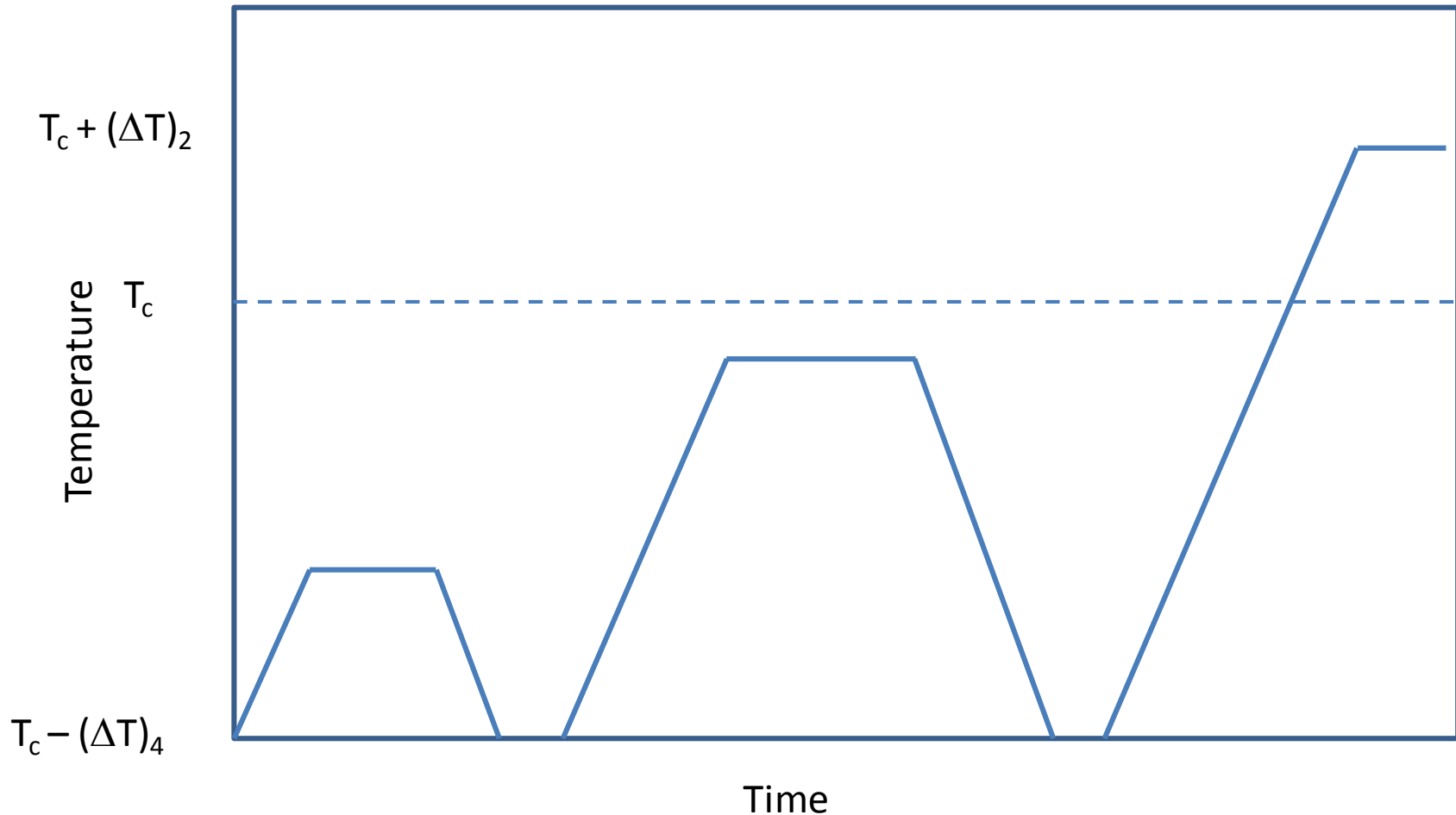
### Salt Solvation During Temperature Decrease





## Test Sequence 3

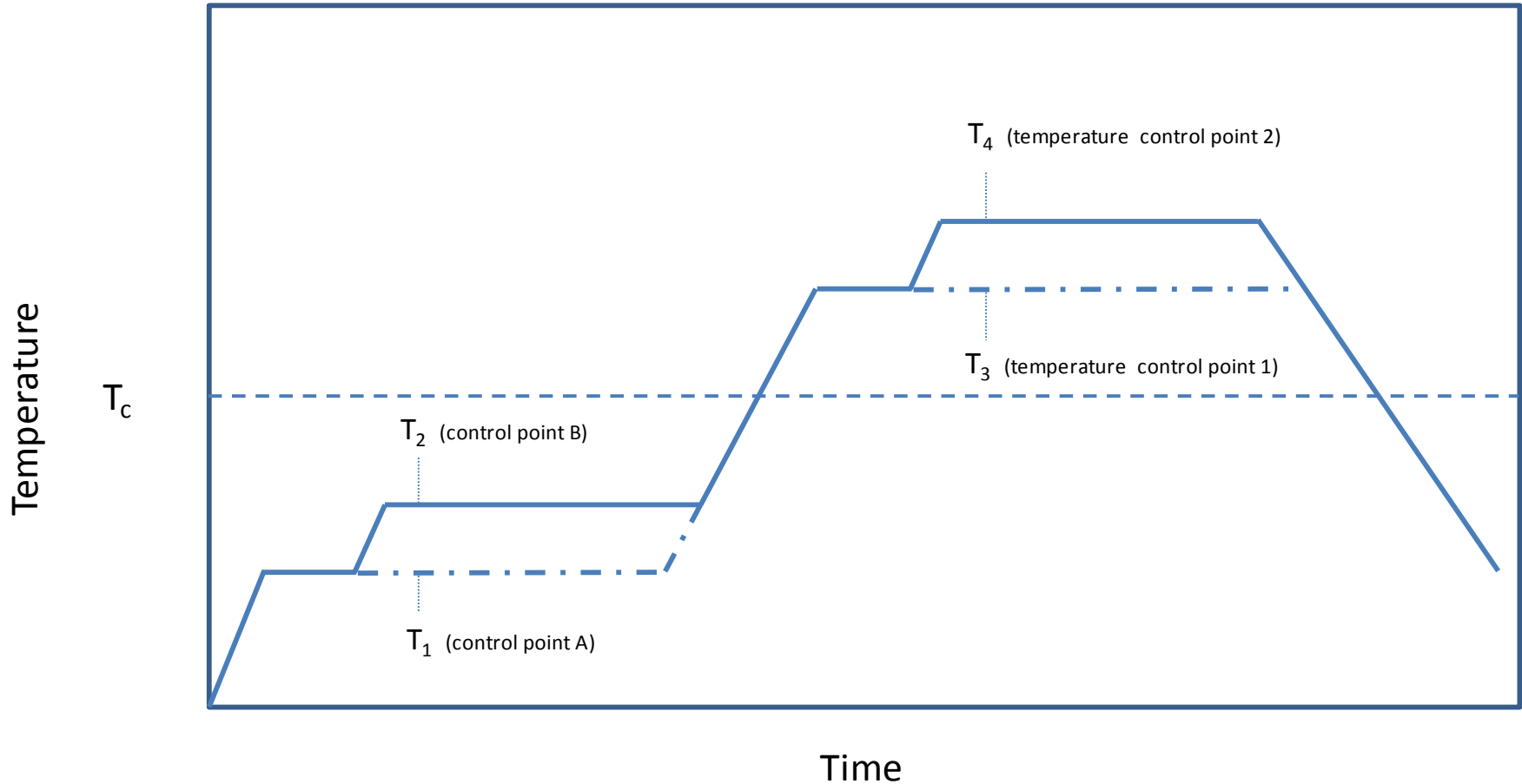
### Salt Agglomeration





## Test Sequence 4

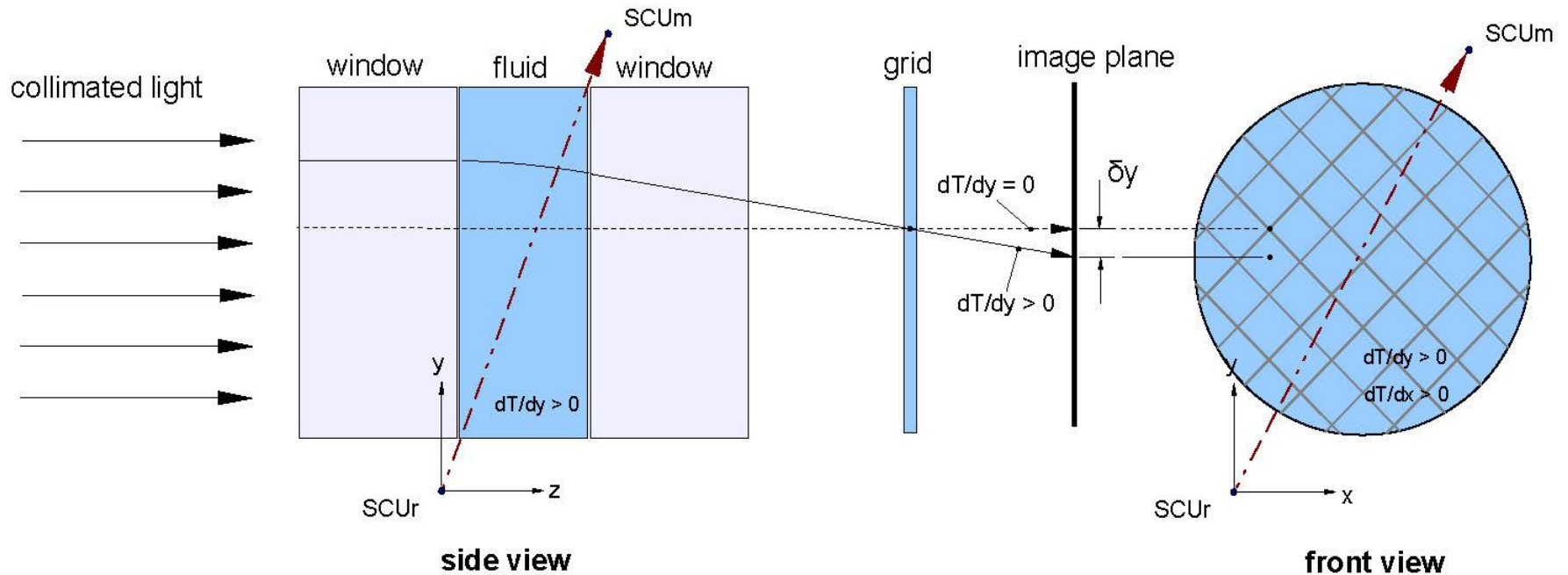
### Salt Transport in Near (Sub)-Critical and Supercritical Water





## Analysis (cont)

### Shadow-graphic Configuration



$$\delta = \frac{\psi}{n} \frac{dn}{dy}$$

$$n = 1 + K\rho$$

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