IAC-13,A2,5.5

DECLIC, NOW AND TOMORROW

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DECLIC is a multi-user facility to investigate critical fluids behaviour and directional solidification of transparent alloys.

As part of a joint NASA/CNES research program, the facility was launched with 17-A Shuttle flight and has been operated onboard the ISS since October 2009.

The main instrument monitoring is made from the CADMOS (CNES, France).

All the three developed inserts have been tested so far and preliminary results have already been presented during past IACs.

The results obtained with those three inserts have led the NASA and CNES founded scientists to ask for a utilization extension, mainly based on inserts refurbishments and new inserts developments.

As a stepping stone towards the oxidation into supercritical water studies, the cell of the HTI (High Temperature Insert) has been (containing pure water) changed by an identical one containing a dilute aqueous mixture of Na2SO4 – 0.5% w. The so-called HTI-R insert was launched with ATV-4 in June 2013 and first operated in July 2013. The main objective is to study salt precipitation phenomena in a temperature gradient close to the critical temperature of the solvent. The DSI (Directional Solidification Insert) is being refurbished in order to replace the cartridge by a similar one containing a different camphor concentration. Consequently, another parameter (camphor concentration) will be added to the parameters available on-board the payload (furnace's temperatures and cartridge's speed). The so-called DSI-R insert should be launched with ATV5 in 2014.

The upcoming program also includes a refurbishment of the ALI insert, as well as a second set of refurbishments for the DSI and the HTI.

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I. INTRODUCTION

The initial DECLIC operations program, consisting in operating the three developed inserts, is over now. As the experiments have given interesting results, showing the performances and capabilities of the payload, the interest of the community increased, and a complementary program was proposed.

The aim of this paper mainly is to give an overview of the program, including hardware modifications and development, and schedule.

The first part of the paper gives an overview of the payload, the inserts, and the ground segment.

The synthesis of the operations is presented in the second part of the paper.

Then, the complementary program is detailed in the last parts of the paper.

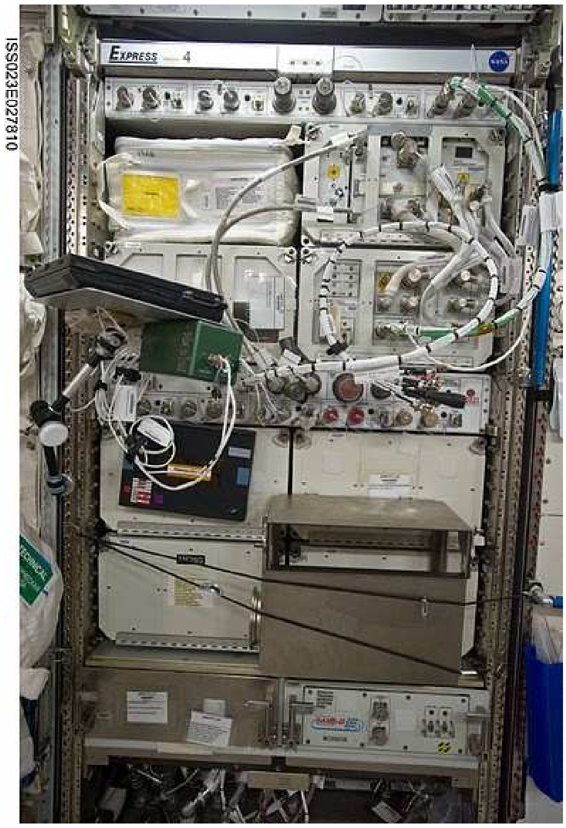


Fig. I: The DECLIC payload fitted in the EXPRESS RACK 4 of the ISS. The two DECLIC lockers are located in the top right quarter of the rack (photo NASA).

II. PAYLOAD, INSERTS AND GROUND SEGMENT

This is a brief overview since those items have already been presented in details during past IACs [1], [2] and [3].

The DECLIC instrument is accommodated in two Single Stowage Lockers (SSL), called the EXperiment Locker (EXL) and the ELectronic Locker (ELL).

The general architecture is given in Fig. II.

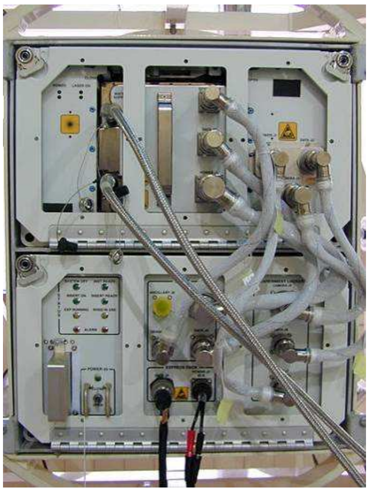


Fig. II: The DECLIC lockers. The ELL is at the bottom while the EXL is at the top and houses the insert. The electrical connections between both component and the water cooling connections (grey “pipes”) to the EXPRESS RACK are also visible. (Photo CNES).

The ELL houses all the power, data handling and high accuracy thermal regulation electronics, and manages the whole system and the scientific experiment execution. It is the interface, for signal and power, with the EXPRESS RACK.

The EXL hosts the optical bench, providing various diagnostics like wide or narrow field of view, grid shadowing, light scattering, interferometers, light transmission measurement etc...). The EXL also receives the experiment container which is called the insert.

Three inserts have been built so far, each of them being dedicated to a science domain:

- Phase transitions near the critical point at room temperature, critical fluids and boiling crisis are studied thanks to the ALI (Alice Like Insert).
- Properties of high temperature supercritical fluid like water are checked thanks to the HTI (High Temperature Insert).

- Microstructures dynamics during the solidification of model materials are studied thanks to the DSI (Directional Solidification Insert).

An insert accommodates a thermostat (ALI, HTI) or a pulling furnace (DSI), containing a sample cell unit (SCU) or a cartridge with the material to be studied, respectively. It also contains most of the electronics associated to the user-dedicated sensors (temperature, pressure...).

The control centre for DECLIC is the CADMOS. The CADMOS is a User Support Operation Centre (USOC) located at the CNES (Centre National d'Etudes Spatiales) centre of Toulouse (France).

As the team is not 24/7 on console, the payload's Health and Status data is also monitored at the POIC (NASA's Marshall Space Flight Center, Huntsville, USA) where Ground Commands Procedures allow to quickly react to non nominal situations.

The real time data is made available to the scientists via a webserver. In addition, an archiving system (to which the scientists can also connect via a web browser) allows storing the exhaustive reference data, which is retrieved via Removable Hard Disks, returned to the ground when full.

RHDD	Up	Down	Up	Down	Up	Down
S/N 001	17A 30/08/2009	19A 05/04/2010	ULF5 24/02/2011	SpX-1 10/11/2012	ATV-4 15/06/2013	
S/N 002	17A 30/08/2009	ULF5 09/03/2011	ULF7 08/07/2011	SpX-1 10/11/2012	ATV-4 15/06/2013	
S/N 003	17A 30/08/2009	ULF5 09/03/2011	ULF7 08/07/2011	SpX-2 02/04/2013		
S/N 004	17A 30/08/2009	ULF6 02/06/2011	46P 26/01/2012	SpX-2 02/04/2013		
S/N 005	17A 30/08/2009	ULF6 02/06/2011	46P 26/01/2012			
S/N 006	17A 30/08/2009	ULF7 21/07/2011	46P 26/01/2012			

Fig. III: RHDDs (Removable Hard Disk Drives) launches and returns. A set of 6 flight RHDDs is available.

The operations are organized in insert-dedicated sequences which typically last 3 weeks and are separated by several weeks (3 at least). That kind of arrangement allows the scientists to perform preliminary data processing of a given sequence in order to set the parameters of the following sequence of the program.

For more details concerning the ground segment and the operations organization, one will refer to [4].

III. OPERATIONAL SYNTHESIS

As of September 2013, the instrument underwent 480 days of operations smeared among 27 flight sequences, leading to 2.4 TB of data.

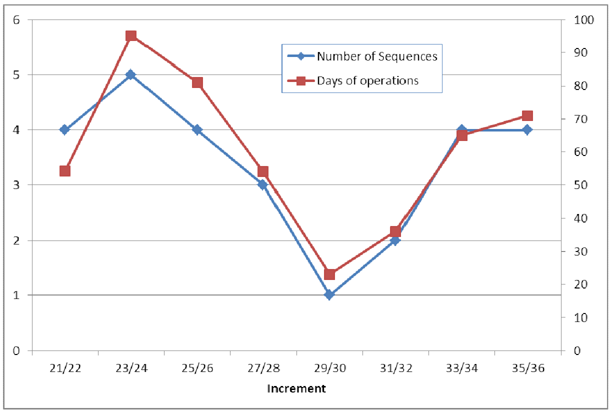


Fig. IV: Number of sequences and days of operations as a function of the ISS' increment number

The main results obtained with the three inserts are briefly summarized hereafter:

- With the **HTI**, the most significant result might be that the relative value of the critical temperature of pure water was obtained with 1 mK resolution and 5 mK reproductibility. The absolute value was measured with a precision of 50 mK

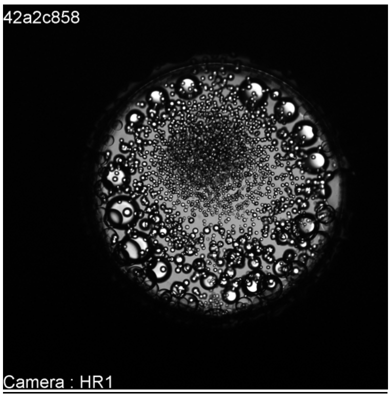


Fig. V: Direct Wide Field Observation at 99mK under Critical Temperature following 8 hours thermal stabilization
External bubbles: boiling at the interface
Central two-phase distribution: nucleation-growth process in the bulk

- With the **DSI**, extended experimental benchmark data in diffusive mode has been obtained. It was also possible to obtain very unique and of major interest observations of some secondary instabilities such as multiplets or oscillating patterns [5].

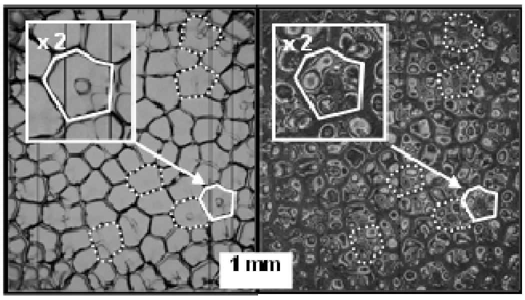


Fig. VI: Direct and interferometric images of multiplets (SCN-0.24wt% camphor; VP = 0.25 µm/s; G = 12 K/cm)

- With the **ALI**, a lot of data is still to be processed but the two main initial objectives have been achieved:
    - Thanks to a dedicated transparent heater deposited on one of the cell's windows, the boiling phenomena, and in particular the triple line behavior, has been studied.
    - The evolution of the turbidity of the SF6 close to its critical point has also been measured.

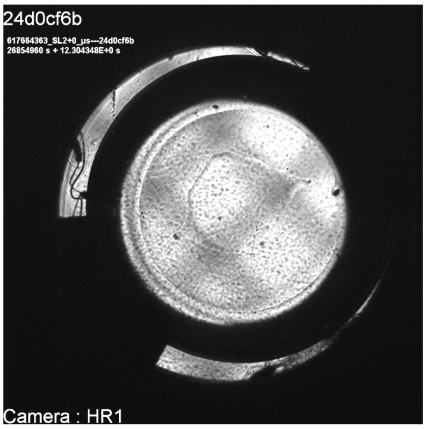


Fig. VII: Transient triple-ligne contact during a heat pulse

IV. COMPLEMENTARY PROGRAM

After the productive first years of operations, the scientific community suggested to proceed with the refurbishment of the inserts in order to extend their use to further studies.

IV.I SCWM/HTI-R

IV.I.I SCWM/HTI-R Science objectives

The SCWM investigation is a follow-on experiment to the High Temperature Insert (HTI) investigation and serves as a prelude to the study of oxidative processes in a future supercritical water oxidation investigation. The SCWM experiment is the first of two planned re-flight experiments involving the re-flight of a refurbished High Temperature Insert (HTI-R).

These supercritical water re-flight experiments are intended to study unit processes of practical concern that arise in systems using supercritical water for waste management and resource reclamation. Water polarity decreases substantially as the critical point is traversed so that ionic salts, normally soluble in water, begin to precipitate out of solution. These precipitates tend to deposit on heated surfaces, the reactor walls, and inflow and outflow valves which hinder the operation of the supercritical water processor.

The first experiment, SCWM, using a refurbished HTI, the HTI-R, investigates the precipitation and dissolution of a salt (Na_2SO_4) as the ionic solution transitions from sub-critical to supercritical. The investigation focuses on the extent of precipitation, the agglomeration mechanism in 0-g, and the transport of the precipitate under a temperature gradient.

The objective in this investigation is to study the formation of salt precipitation and its transport in the presence of a temperature gradient by filling HTI test cells (originally filled with pure water), with a dilute mixture of salt and water at the critical density of water. This new mixture allows investigators to observe an anticipated shift in the mixtures critical point (i.e., temperature and pressure) along with precipitate formation, mass agglomeration (i.e., clustering), and transport at near such critical conditions (i.e., just above and below the critical point of pure water).

IV.I.II HTI-R Refurbishment

The HTI insert was returned to the ground with the ULF-5 Shuttle flight. The cell, containing pure water, was replaced by a similar cell containing a salt- water mixture. This reflight cell is referred to as the HTI-Reflight (HTI-R).

As stated in [1], an unexpected thermal gradient was seen during the first HTI flight sequences. This thermal gradient was suspected to be linked to a non-linear phenomenon occurring in the regulation loops due to a misfunction of one of the two temperature-sensor Peltier elements (Seebeck effect). During the flight operations, we were able to implement a workaround in order to put the thermal gradient within the cell back at expected values or so ; the faulty Peltier element was replaced, in the regulation loops, by a linear combination of two neighbouring sensors.

As the HTI was being refurbished for the HTI-R program, the Peltier elements have been retrieved and some cracks were find in the alumina plates that accommodates the thermoelectrical material ($FeSI_2$) legs.

Fig. VIII: Peltier element found broken after the HTI returned to the ground

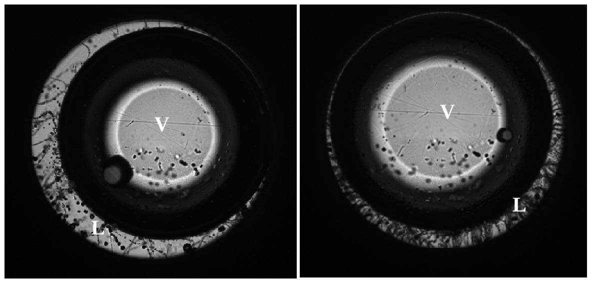
We then had to change the Peltiers assembly. Instead of being wedged in between two rigidly mounted plates, spring washers were introduced in the assembly, so that it could accommodate for the thermoelastic strains.

During the refurbishment, the dismounted screws, the seals and the insulating foils, were also replaced.

VI.I.II HTI-R first operations summary

The HTI-R was launched with the ATV-4 in June 2013 and first operated in July 2013 for a three weeks sequence.

The behaviour of water-salt mixture was observed, and in particular the salt precipitate spatial distribution, as well as a first attempt to measure the mixture critical temperature.



T = 372.02 K T = 373.72 K

Fig. IX: Backlit images showing the incipient precipitation point of the Na_2SO_4 salt in the liquid region (L) of the Sample Cell Unit (SCU). Image at left shows streams of small vapor bubbles generated from nucleate boiling, appearing as tendrils travelling approximately radially from the SCU wall to the vapor (V) region in the center. Image at right shows a coarsening of these tendrils, after a temperature increase of 700 mK and a time lapse of 696 minutes, indicating the onset of salt precipitation along the channels created by the vapor bubbles. This observation suggests an interesting linkage between localized boiling and precipitation.

Five remaining sequences are planned until spring 2014.

IV.II DSI-R

IV.II.I DSI-R Science objectives

The new set of experiments in the DSI-R will focus on the investigation of the formation of well-developed dendritic array structures that are of direct technological relevance for the solidification and casting industry. The experiments will focus on elucidating:

- the fundamental mechanism of sidebranch formation
- the interaction of primary array and the secondary sidebranch structures
- the mechanism of the cell to dendrite transition
- the dependence of cell and dendrite tip shapes on growth conditions.

Experiments already performed in the DSI have yielded interesting observations of dendritic array structures (Fig. X), which suggest the existence of possible coherent modes of dendritic sidebranching. However, for the SCN-0.24wt% camphor alloy, dendrites were only observed in a high velocity regime where the solidification front developed significant curvature due to the combination of the rejection of latent heat and the much lower thermal conductivity of the alloy than its quartz container wall. In addition, dendrite tip radii are too small to be accurately resolved at those high velocities. The new set of experiments in the DSI-R will be conducted for a higher composition

(SCN-0.5wt% camphor alloy) where dendritic arrays form at a lower pulling velocity where the front curvature is minimized. Fig. 1(b-e) shows the results of preliminary ground based experiments and phase-field simulations, which demonstrate that well-developed dendritic array structures form for a lower pulling speed VP = 10 µm/s for a thermal gradient G = 23 K/cm. The ground based experiments and phase-field simulations are in excellent agreement for theses growth conditions. In addition, those simulations predict a dendrite tip radius of 14 µm, which should be sufficiently large to be accurately resolved by interferometry in the DSI-R. Additional simulations and ground based experiments are in progress to develop the flight matrix of growth conditions.

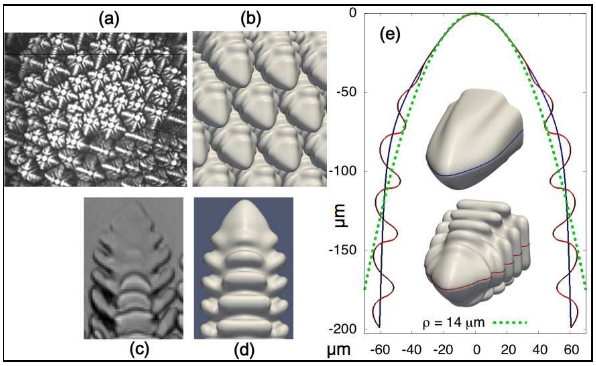


Fig. X. Experimental and simulated dendritic array structures. (a) experiment in the DSI for a SCN-0.24wt% camphor alloy with VP = 30 µm/s and G = 12 K/cm. (b-e) Preliminary results for SCN-0.5wt% camphor alloy to be used in the DSI-R with VP = 10 µm/s and G = 23 K/cm: (b) phase-field simulations of dendritic array, (c-d) comparison of dendrite observed in thin-sample ground-based experiments (c) and simulated (d), and (e) longitudinal sections of the simulated dendrites without (blue curve) and with (red curve) thermal fluctuations; parabolic fit of tip region (green dashed line) yields a tip radius of 14 µm.

IV.II.II DSI-R Refurbishment

The DSI insert has been returned with the ULF-6 Shuttle flight. After two post-flight sequences in October 2011 and January 2012, the cartridge is being replaced by another cartridge containing a different camphor concentration. Consequently, another parameter (camphor concentration) will be added to the parameters available onboard the payload (furnace's temperatures and cartridge's speed). The so-called DSI-R insert will be launched as soon as possible, likely by mid-2014.

As for the HTI refurbishment, the dismounted screws, the seals and the insulating foils, were also replaced.

IV.III ALI-R

IV.III.I ALI-R Science objectives

Latest operations of ALI have shown that the turbidity measurements can take benefit from the high-quality thermal and optical environment of the insert and the microgravity environment of the ISS, allowing these measurements performed very close to the critical point. The preliminary analysis of the different theoretical formulation of the Ising-like equation-of-state models has also shown that the measurements of the singular properties at off-critical density (~1.7 % off from the critical density) can still be an accurate probe for testing the recent classical-to-critical crossover models. However, only a test cell exactly filled at critical density can be useful to discriminate the contribution of the Green-Fisher critical exponent and to evaluate the fluid-dependent parameters when experimental data are covering the 1 mK temperature distance to Tc only attainable using DECLIC facility on board the ISS. Despite the importance of the exponent, η, to describe how the correlation function behaves asymptotically close to Tc, only a few theoretical works have been accumulated over the past few decades. To our knowledge, there is no precise experimental determination of the exponent in the liquid-gas critical point system to date. The difficulties in the experimental tests are originated from the smallness of the exponent, between 0 and 0.05, the gravity effects, and non-negligible influence of confluent singularities.

The ALI-R will measure experimentally the effects of the non-zero value of the Green-Fisher exponent in the liquid-gas critical point for the first time. By analyzing the theoretical predictions, a measurement of the turbidity of the SF6 sample with a precision better than 0.3% near the critical temperature (~ 1mK above the Tc) in microgravity condition could test the theoretical predictions. In order to achieve this goal, a new sample cell has to be prepared such that the average density is closer to the critical density (< 0.1%) than the current ALI sample cell.

IV.III.II ALI-R Refurbishment

The main objective of the refurbishment is to replace the direct observation cell by an identical cell filled with SF6, as close as possible to the critical density.

To do so, ten new cells are being manufactures and integrated. They will be filled and tested on the ground, and the best (i.e. SF6 density closest to the critical density) will be selected and integrated in the ALI insert.

As the ALI is going to return with SPx3 in January 2014, and as a post-flight ground sequence is being required, the refurbishment is likely to start in March 2014 and the insert should then be available for launch by the end of 2014.

V. THE "R2" PROGRAM

While the complementary program has just started to give the first results, with the first HTI-R sequence completed in July 2013, the scientific community suggested proceeding with another set of refurbishments for the HTI and the DSI.

V.I DSI-R2

The DSI flight campaign was carried out on a succinonitrile – 0.24 wt% camphor alloy. This composition was very adequate to explore the largest range of possible microstructure from the planar front to fully dendritic structures. In the dendritic regime, the very interesting observations on DSI led us to choose a higher composition for the DSI-R sample, as previously explained. In the DSI, very striking observations of secondary instabilities (multiplets, oscillating patterns) were also performed for the very first time in extended 3D patterns close to the critical pulling rate that corresponds to the transition between planar and cellular growth. Both thin-sample experimental studies ([6], [7], [8]) and 2D computer modeling studies ([9], [10]) have shown that the stability domain of multiplets or oscillatory structures is usually limited to 1 to 4 times the critical rate and in DSI, these critical velocities were very low (below 0.5 µm/s for the applied thermal gradients), so that those structures appeared only in very narrow range of pulling rates. The set of experiments in the DSI-R2 will focus on investigating those secondary instabilities of the cellular regime, using a lower composition such as for example SCN- 0.1wt% camphor. There are two primary reasons for this choice. Firstly, the increase of onset velocity of the primary morphological instability resulting from a reduced composition leads to an extension of the stability domain in terms of pulling rate. Therefore, those secondary instabilities can be more easily studied experimentally over a wider range of parameters. Secondly, the lower composition will allow us to precisely measure this onset velocity and to deduce from this measurement the thermal gradient in the vicinity of the interface, which has been so far difficult to precisely determine.

V.II HTI-R2

An additional re-flight of the High Temperature Insert (HTI-R2) is proposed in order to study unit processes of practical issues arising from the supercritical water processing of waste streams produced during long duration space missions. There are two primary investigation proposals that are of interest and the ultimate definition of the follow-on experiment for HTI-R2 will depend on the findings of ongoing ground based research.

Option 1: Precipitation and Dissolution of Inorganic in a Binary or Tertiary System

As previously noted in the discussion of the HTI-R experiment, water polarity decreases substantially as the critical point is traversed causing the precipitation of ionic salts, which are normally highly soluble in water at sub-critical temperatures. These precipitates tend to deposit on heated surfaces, the reactor walls, and inflow and outflow valves which hinder the operation of the supercritical water processor. The first reflight, the HTI-R experiment, investigated the precipitation and dissolution of a dilute Type-II saltwater (Na_2SO_4) mixture transitioned from sub-critical to supercritical (as well as the reverse phase transition) and the transport of the precipitate under a temperature gradient.

The proposed experiment under this option would repeat the objectives of HTI-R and, depending on the results of that experiment and further ground based research, will use either the same salt-water mixture in a tertiary system incorporating CO_2 or a binary system with a different salt-water, potentially a Type-I salt. The tertiary system, with CO_2 , has the added benefit of replicating the behavior of salt formation and transport in a SCWO system, which has CO_2 as a major product constituent.

Option 2: Dissolution of Organic Material Hydrogen bonding between water molecules, which is very strong at ambient conditions, decreases significantly as water approaches its critical point. The result is that organic compounds become highly soluble in supercritical water. This experimental option proposes the use of a non-soluble (i.e., in water) organic material whose solubility undergoes a reversal in near critical water. The intent would be to study the mechanisms of organic solubility as water transitions from sub-critical to supercritical.

The proposed experiment under this option would observe and understand the phenomena associated with the dissolution and transport of an organic substance in water at near critical conditions. The investigation will determine the shift in critical point and will provide detailed observations of the dissolution and transport processes. This investigation will provide observations that can enhance the fundamental understanding of the mechanisms that govern the dissolution, transport and mixing of organic compounds in supercritical fluids. This experiment serves as an excellent precursor to supercritical water oxidation (SCWO) experiments in that it provides experimental observation of the organic dissolution mechanism, the rate of dissolution, and the primary transport processes of a reaction system prior to the reaction occurring.

VI. CONCLUSION

DECLIC has been operated onboard the ISS for 4 years now and the first set of experiments, using the 3 inserts, is over now.

One after the other, the inserts are returned to the ground in order to be refurbished. The first refurbished insert, the HTI, has already been re-launched to the ISS and operated for a first sequence.

It is foreseen that, at least 2 out of the 3 inserts will be refurbished a second time, extending the DECLIC utilization for a few more years.

ACKNOWLEDGMENTS

The authors would like to thank all the companies involved in the development of DECLIC. ASTRIUM-ST (France), which was the prime contractor, but also SODERN (France), University of Amsterdam (The Netherlands), COMAT (France), EREMS (France), the Thermoelectric materials laboratory from Ecole des Mines de Nancy (France)...

The science teams were also involved in the development phases, not only by expressing their needs, but also by developing the cells (ALI and HTI cells were built by ICMCB-CNRS, France), or filling the DSI cartridges (IM2NP-CNRS, France). Thanks to them for their involvement and constant inspiration.

ICMCB team gratefully thank Eric Georgin for his assistance during the cell integration, ARCOFLUID company for it numerical simulation support and Jean Pierre Manaud, Iyad Saadedin, and Guy Campet for development and processing of the thin resistive layer made of Sn alloy oxide.

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