Optical Cells for Study of Water Properties Near its Liquid-Gas Critical Point

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Abstract

We present a design of an optical cell dedicated to study the water properties near the liquid-gas critical point using the DECLIC-CNES instrument on board the International Space Station. This designed cell satisfies safety requirements for high pressure and high temperature operating conditions of the high temperature insert (HTI). This design is optimized for using high-resolution and high-speed optical diagnostics, local temperature controls and measurements of the DECLIC instrument, in particular to observe and to analyze the thermal and density response of critical water after a transient heating produced by one heat pulse actuator. Illustrations of the high-level performances are provided by the preliminary results obtained during the Earth's tests of the flight model of the HTI insert.

1. Introduction

Supercritical fluids as media for chemical analysis and chemical processing have received strong attention in the past two decades (1). This is especially true for the aqueous solutions (2) which are involved in many promising applications and natural processes. In steam power plants, aqueous electrolytes may be a concern in liquid phases at temperatures up to critical temperature of pure water (T_c = 647 K) and salts may be carried over into superheated vapor that can reach temperatures of 900K. Geothermal brines (some of which contain dissolved methane, i.e., a potential energy source) may reach temperatures around 600 K and pressures above 100 MPa. In the emerging environmental technology of supercritical water oxidation, or in material processing in hydrothermal batches (3), pressure and temperature are typically above the corresponding ones of the critical point of water (T_c = 647 K and p_c = 22 MPa) and it is important to be able to predict the precipitation of various salts species from the complex mixture of water, salts, oxidant gases or liquids, organic solutes, etc. Such high temperatures and pressures, added to the insufficiency of the fundamental knowledge on dissolved compounds in water might produce drastic modifications of the expected chemical behavior of the aqueous media. They have generated new challenges, starting from basic thermodynamic modeling to flow-sheet simulations, etc., in order to reach material design and processing related to technological problems (such as the ones due to corrosion and salt deposition) encountered in plant developments and utilization.

An interesting fundamental problem is that the relevant range of conditions often includes or approaches the critical point of water (4). It becomes then important to know how the properties of the supercritical solvent are modified by the presence of the solute. One of the important issues is the nature of the vapor-liquid criticality of aqueous solutions. Other issues, especially those connected with the large thermal expansion and compressibility of supercritical water, are of crucial importance for understanding the impact of the high fluid compressibility, for example the so-called piston effect which can lead to the interaction of the heat transfer with the chemical processes. These fundamental issues need to be studied, in the wide range of encountered densities (from steam-like to water-like), for compressibility much larger than the one of a perfect gas, for a great diversity of solutes (gases, organics, oxides, etc.), or in presence of various salts which can deposit solids in supercritical water, etc.

In order to address these important issues, we have set up a research program (5) to investigate, by experimental observation under microgravity, what is the underlying mechanisms in the absence of convection that could couple thermo-compressible hydrodynamics with chemical processes in such supercritical aqueous solutions. A first attempt (6) was made by using asymptotic analysis to account for speeding up of heterogeneous reaction in near-critical phases. Recently, the 1D-results of numerical simulations of heating a supercritical binary mixture at one solid wall side have demonstrated that the large compressibility of the fluid is responsible for a coupling between hydrodynamic behavior and critical behavior of the solubility of solid, thanks to the non-local nature of the piston effect, that induces the release of an heterogeneous reaction at the opposite solid surface [(7)-(8)].

Several future experiments [(9)-(10)] are planned to explore these expected new coupling phenomena in supercritical reactive media on the International Space Station. These experiments will fully benefit from the high-level performances of the DECLIC facility [(9)] which has been developed by CNES (Centre National des Etudes Spatiales), in particular for the studies of near critical fluids that require high accuracy temperature control.

One of the DECLIC interchangeable modules (inserts), named High Temperature Insert (HTI), is dedicated to the basic study of pure water to provide the quantitative entry data (from measurements of turbidity, light scattering, piston effect time scale, etc.) and to prepare the future studies in aqueous solutions. The design of this insert is now qualified according to NASA safety standards for experiments at high temperature and high pressure on board the ISS.

We briefly present here the first designed optical cell for experimental observations of critical phenomena at high pressure and high temperature, using the DECLIC instrument on board the International Space Station in the next years 2009-2012. High-resolution and high-speed optical diagnostics are synchronized with temperature measurements and adjusted to the selected monitoring rate of the thermal pulses produced by one heating actuator. Illustrations of the high-level performances are provided by the preliminary results obtained during the Earth's tests of the flight model of the HTI insert, precisely dedicated to the study in weightlessness of water properties near its vapor-liquid critical point.

The paper is organized as follows. Section 2 gives the design of the HTI cell which will be used during the first increment planned for DECLIC utilization on board the US module of ISS. Section 3 shows some results obtained during preliminary tests performed on Earth's with the HTI Insert.

2. Cell design

The cell design satisfies several scientific and safety requirements. Since the cell is intended to study water in the vicinity of its critical point using the optical diagnoses of the DECLIC instrument [(9)], its optical design permits the observation by (incoherent) light transmission and grid shadowscopy of the complete cell volume, the turbidity measurements by laser light attenuation and static diffusion measurements by small angle and 90° laser light scattering. Since this optical cell will be operated at high temperature and high pressure under the safety requirements of NASA on board the ISS, the cell design is conform to a maximum operating temperature of 450 °C and pressure of 55 MPa, and to leak before burst safety constraint. Moreover, both the cell body and the transparent materials are resistant to corrosion at high temperature, especially corrosion within supercritical water and aqueous media.

The transmission observation of the fluid volume can be made through a 8 mm observable cell diameter. As an illustrative example, in cell picture of **Fig. 1** made at room temperature, we can observe a curved meniscus which separates a water vapor bubble surrounded by water liquid wetting the cell body. In addition, 90° light scattering is measured by a photodiode through a 1.6 mm diameter hole and a diamond window. Several Pt sensors (25 Ω or 100 Ω resistance value) located in the cell body and its sample cell housing (SCH) are used to monitor temperature and/or to generate heat flux close to the fluid (see below).

Fig. 2(a) shows the cross section of the fully assembled sample cell whose typical external dimensions are: ~ 42.6 mm length, ~ 55 mm height, and ~ 47 mm depth. The cell body and transmission flanges are made of Inconel 718 (a nickel based super- alloy from Aubert & Duval, France). The optical windows chosen for transmission observation are made of sapphire (18 mm diameter – 9 mm thickness), while the one for 90° light scattering measurements is made of synthetic bulk polycrystalline diamond (5.5 mm diameter - 1.2 mm thickness). The thermal differential dilatation between different materials is accounted for by using an appropriate number of elastic washers made of Inconel 718 (from Ressorts Masselin, France). After filling at a near critical density of water (quality Ultrex ® II, Ultrapure Reagent, from J. T. Baker, USA), the cell is closed by a "blind window" made of Inconel 718 (5.5 mm diameter - 2.5 mm thickness), using a similar design as the 90° light scattering part. The tightening is achieved using gold sealing.

The main volume (280 mm^3) of the fluid sample observed by transmission is a cylinder (≈ 8 mm diameter - ≈ 5 mm thickness) as shown in Figure 2(b). The dead volumes are limited to the small scattering and filling channels [1.6 (1) mm diameter - ≈ 7 mm length, respectively]. When filled at the critical density of water

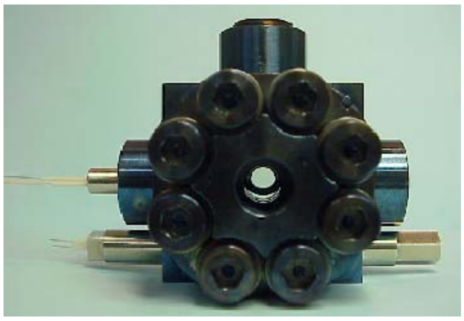


Fig. 1 Experimental cell for experiments on near critical pure water, in the High Temperature Insert inside the DECLIC CNES facility.

(ρ_c = 322 kg.m^{-3}), the typical mass of water is ≈ 90 mg.

The opposite side to scattering observation is equipped with a Pt 100 sensor (see **Fig. 2**(b)).

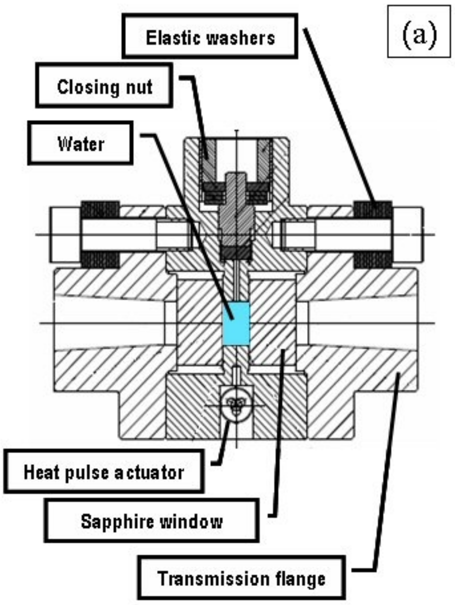
The lower part of the cell body houses a specific heating system made of a serial of three Pt100 resistive sensors, which allows local heat pulse source monitored by DECLIC software. A detailed picture of this actuator is given in **Fig. 3**, while next Section provides a typical heat pulse timeline and its related temperature responses.

The cell is integrated within a nickelled copper alloy housing (labeled SCH for Sample Cell Housing), to form the HTI-Sample Cell Unit (SCU), as shown in **Fig. 4**. The two Pt25 sensors used for temperature regulation (SCUr) and temperature measurements (SCUm) are located inside the copper alloy housing, while the Pt100 sensor used for temperature measurements (DOCs) inside the cell body is located in the opposite channel to the 90° light scattering one (See Fig. 2 for details).

3. Preliminary typical results.

We report here only three significant results obtained during the performance tests of the HTI-insert.

First result given in **Fig. 5** concerns ±5 mK thermal quenches performed at a regulated temperature of 375 °C. The local temperatures measured by the two Pt25 sensors (labeled SCUr and SCUm) and one Pt100 sensor (labeled DOCs) indicate the high-level performances of this cell thermal monitoring especially required for critical temperature determination from turbidity measurements, and for the study of the liquid-gas phase separation process (from direct observation of the growing domains) [11].



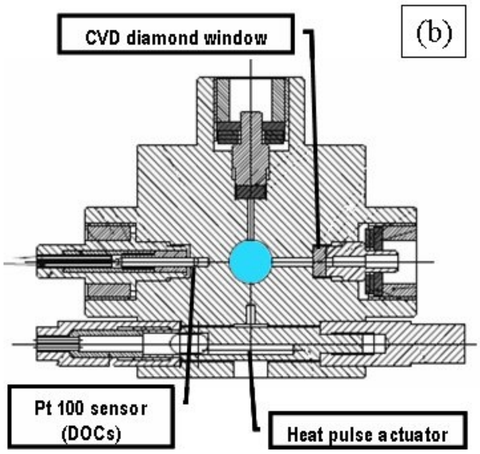


Fig. 2 (a) Cross section of the optical cell showing the optical channel for light transmission observation and de- tails of the mechanical assembly; (b) Cross-section showing the optical channel for 90° light scattering measurements through a CVD diamond window, and the details of the Pt100 temperature sensor (DOCs) and heat pulse actuator.

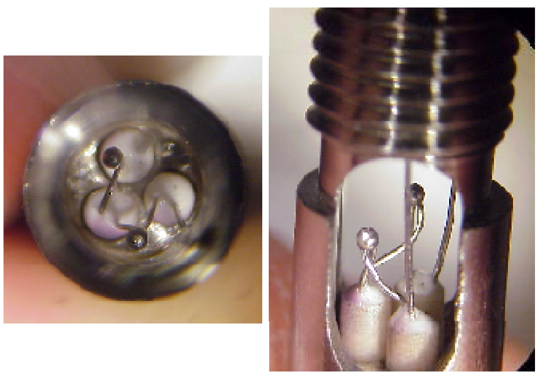


Fig. 3 Detail of the heat pulse actuator, showing the serial assembly of three Pt100 sensors.

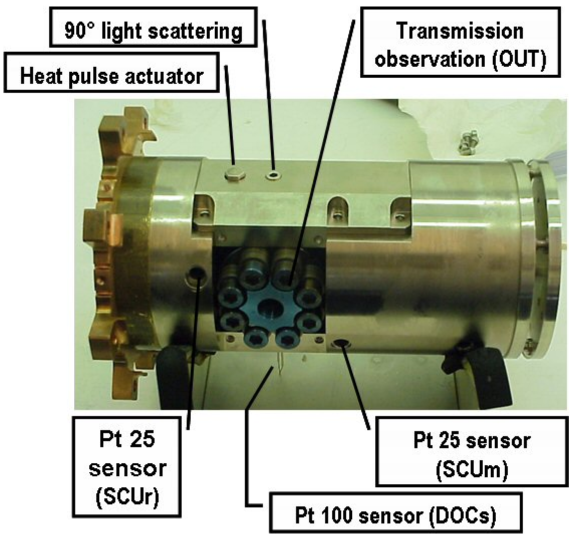


Fig. 4 Partial integration of the optical cell in the sample cell housing (SCH) made of copper alloy with nickel layering. The locations of the heat pulse actuator, the Pt25 sensors for the SCU temperature regulation (SCUr) and SCU temperature measurement (SCUm), and the Pt100 sensor for the cell temperature measurement (DOCs) are shown.

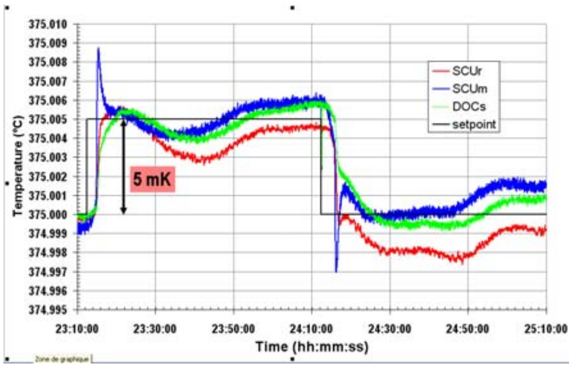


Fig. 5 Temperature (in °C) - Time (in hh:mm:ss) responses of the Pt25 SCUm and SCUr located in the SCH and temperature response of the Pt100 DOCs located in the sample cell body (see Fig. 4, for details), after heating (cooling) quenches of 5mK amplitude (as shown by the temperature profile labeled set-point) around T = 375°C.

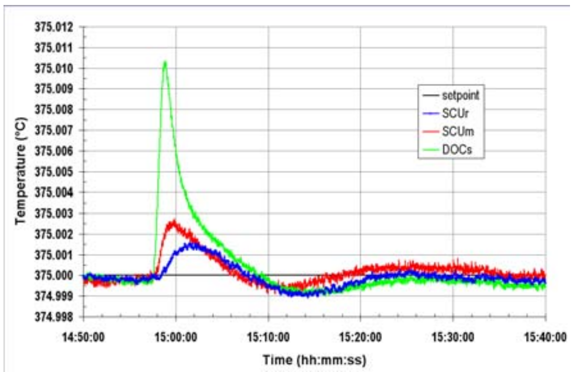


Fig. 6 Temperature (in °C) - Time (in hh:mm:ss) responses of the two Pt25 SCUm and SCUr located in the SCH, and the Pt100 DOCs located in the sample cell body (see Fig. 4 for details), after a heat-pulse of 0.6mW during 60s performed at constant set temperature T = 375°C (see the temperature profile labeled set-point).

Second result is given in **Fig. 6** where is illustrated the local temperature responses of the above sensors, during and after a heat pulse of 0.6 mW power and 60 s duration, produced by the (3x) Pt100 resistive source (see above Fig. 3). Such a required stimuli is appropriate to study the adiabatic response of the fluid sample (the so-called Piston effect), in weightlessness conditions [12].

Third result is given in **Fig. 7** where we show two pictures of a two-phase cell at normal boiling temperature [T ≈ 100 °C, see **Fig. 7**(a)] and just below the critical temperature of water [T_c -T ≈ 2 mK, see **Fig. 7(**b)]. In this latter case of a "near critical" non-homogenous domain, the meniscus is very thin and no curvature is noticed because the surface tension vanishes at the critical temperature of any one component fluid. Moreover, as expected from the

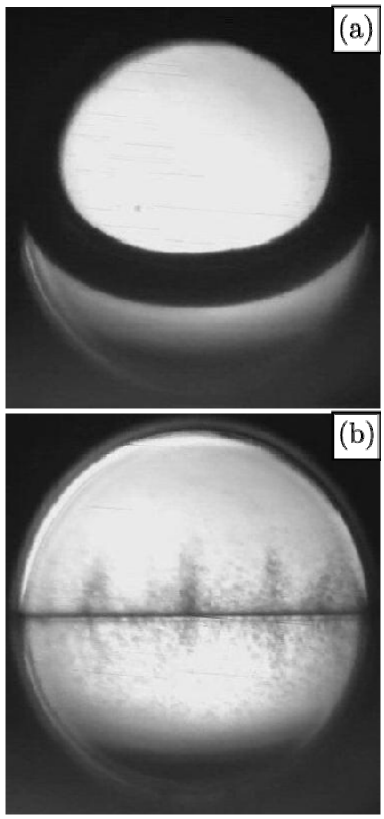


Fig. 7 Two coexisting (vapor-liquid) phases in the optical cell filled with pure water at critical density: (a) at thermodynamic equilibrium close to the normal boiling temperature (T = 100 °C), where the shape and position of the meniscus are governed by a balance between the wetting driven forces (due to a large value of the liquid-vapor interfacial tension) and the gravity driven forces (due to the large density difference between liquid and vapor); (b) after a negative temperature quench from the homogeneous domain just below the critical temperature T_c. A thin meniscus forms at the middle position of the video picture, with equal gas and liquid volumes, probing that the density of the cell is at the exact water critical density. The horizontally flat meniscus is only due to the gravity driven forces, since the surface tension vanishes at the critical temperature.

symmetrical sample fluid volume, the meniscus appears exactly on the middle of the cell, which reflects a sample cell filled exactly at water critical density.

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