Investigation of Supercritical Water Phenomena for Space and Extraterrestrial Application

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ABSTRACT
The cost of carrying or resupplying life support resources for long duration manned space exploration missions such as a mission to Mars is prohibitive and requires the development of suitable recycling technologies. Supercritical Water Oxidation (SCWO) has been identified as an attractive candidate for these extended missions because (i) pre-drying of wet waste streams is not required, (ii) product streams are relatively benign, microbially inert, and easily reclaimed, (iii) waste conversion is complete and relatively fast, and (iv) with proper design and operation, reactions can be self-sustaining. Initial work in this area at NASA was carried out at the Ames Research Center in the 1990’s with a focus on understanding the linkages between feed stock preparation (i.e., particle size and distribution) of cellulosic based waste streams and destruction rates under a range of operating temperatures and pressures. More recently, work in SCWO research for space and extra-terrestrial application has been performed at NASA’s Glenn Research Center where various investigations, with a particular focus in the gravitational effects on the thermo-physical processes occurring in the bulk medium, have been pursued. In 2010 a collaborative NASA/CNES (the French Space Agency) experiment on the critical transition of pure water was conducted in the long duration microgravity environment on the International Space Station (ISS). A follow-on experiment, to study the precipitation of salt in sub-critical, trans-critical and supercritical water is scheduled to be conducted on the ISS in 2013. This paper provides a brief history of NASA’s earlier work in SCWO, discusses the potential for application of SCWO technology in extended space and extraterrestrial missions, describes related research conducted on the ISS, and provides a list of future research activities to advance this technology in both terrestrial and extra-terrestrial applications.

INTRODUCTION
Even short duration human space missions such as Skylab, Space Shuttle, and the International Space Station (ISS) generate a large amount of waste. The generated waste is usually wet, voluminous, and biologically unstable. Major components of the waste include plastics (about 30% on average) and water (also approximately 30%) [1]. The water in the waste comes from a combination of food residues stuck to food pouches, hygiene wipes, and free liquids remaining in the drink pouches after consumption. It is estimated that each crew member generates about 3 kg of waste per day. Waste accumulation remains a significant problem and will require serious attention in the planning and design for future human space exploration missions such as a Mars transit mission.

Wastes may be stored, discarded, or recycled for recovering resources. For long duration missions, in order to reduce the “system equivalent mass” at launch and to reduce re-supply missions, it is essential to move toward closure of human life support systems. The drive toward effective closure will be enabled by technologies that allow resource reclamation from the air, water, and waste streams. In addition, regenerative systems such as those designed to grow plants for food will require extensive resource reclamation (e.g., carbon dioxide, water and plant nutrients) from bio-waste streams in order to be practicable.

Supercritical Water Oxidation (SCWO) is a process where organic compounds can be efficiently oxidized in water above its critical point at 647.3K (374.1°C) and 22.12 MPa. Under these conditions organic compounds and gases become completely soluble in water leading to extremely high reaction rates between dissolved oxygen and organic
materials. SCWO is considered a “green” technology because of its ability to recover energy and reclaim water from wet waste streams without producing pollutants such as NOx or SOx, which require further scrubbing. The primary products of oxidation are carbon dioxide and water with the inorganic material precipitated out of solution as salt or converted into oxides which can readily be separated from the effluent stream.

SCWO’s primary technical challenge has been the insolubility of inorganic salts in supercritical water. Precipitation occurs in the near-critical and supercritical regimes due to an order of magnitude decrease in the dielectric constant, $\varepsilon$, of water compared to its value under room conditions (i.e., $\varepsilon \approx 80$ at $T = 300$ K compared to $\varepsilon \approx 5.4$ at $T_w$). The Debye ionic screening distance is proportional to $\varepsilon^{1/2}$ so that at near-critical conditions the ionic charges are not well shielded. This leads to a recombination and eventual precipitate agglomeration from dissolved salts. These salts can become concentrated in the effluent stream and develop deposits in flow passages and other internal reactor surfaces leading to clogging, impaired heat transfer, and an overall decrease in operating efficiencies. Additionally if the waste stream contains chlorine or other halogens, supercritical water effluents can become highly acidic leading to corrosion of the reactor vessel.

The primary advantage of SCWO is the ability to carry out oxidative reactions at very high reaction rates on organic contaminants in wet waste streams. This includes waste streams ranging from gray water to slurries heavily loaded with mixtures of organic and inorganic solids. SCWO is an attractive candidate technology for processing solid and liquid wastes for long duration space and extra-terrestrial planetary missions because (i) pre-drying of waste is not required, (ii) product streams are benign, microbially inert, and easily reclaimed, (iii) waste conversion is complete and relatively fast, and (iv) with proper design and operation, reactions can be self-sustaining. In addition, because of the absence of inter-phase reactant transport due to the single phase nature of SCWO reactions, reaction timescales are greatly reduced and many of the complications associated with two-phase transport and processing in reduced gravity environments are eliminated. Since all extraterrestrial applications will operate in a reduced gravity environment, the gravitational influences on (i) reactant mixing, (ii) flame genesis, stability and extinction, (iii) reaction rates, and (iv) waste stream preparation are among some of the issues that need to be thoroughly understood before earth-based experience can be extrapolated and/or refined for the design of extraterrestrial SCWO systems. These effects are, as yet, largely unexplored.

PRIOR NASA RESEARCH ACTIVITIES

Ames Research Center (ARC): Initial efforts by NASA in applying SCWO and wet oxidation to solid waste management were conducted at Ames Research Center starting in the 1980’s in ground-based laboratories. These early tests were designed to look at oxidation rates and destruction efficiencies for cellulose and other waste materials as a function of particle size, mixing, temperature and pressure. Results from these tests provided empirical correlations for use in reactor design.

The studies began in the early 1980’s at ARC when Wydeven studied the oxidation of spacecraft model wastes in a catalytic batch wet oxidation process [2]. The wet oxidation runs were initially conducted in subcritical liquid water at temperatures between 150°C and 300°C and pressures above the boiling point pressure of water. The primary products of oxidation were carbon dioxide, ammonia and nitrogen. Roughly 90% conversion efficiency was achieved for carbon to carbon dioxide and 78% conversion of waste nitrogen to nitrogen gas. The minor products included methane (CH₄); carbon monoxide (CO) and nitrous oxide (N₂O); thus requiring post treatment. In the mid 1980s these studies expanded to supercritical water oxidation [3].

Under a NASA contract (1985-87), Modar, Inc demonstrated the feasibility of processing human feces and urine in a continuous SCWO process with very encouraging results which showed complete conversion of organic carbon to CO₂, of organic nitrogen to N₂ and recovery of major nutrient constituents such as P, K, Na, S, Ca and Mg in usable forms for plant growth systems. Liquid effluents with trace organic carbons of less than 1 ppm required only ion exchange after the process to make it potable. Areas that required further development were identified during the testing. A continuous process requires specialized hardware such as a slurry pump, which can pump the waste slurry at high temperatures and pressures which were prone to plug. Preheated feed lines carrying waste at high temperatures and pressures were prone to ash formation, which was another difficulty. As an alternative to the continuous process, Wydeven conducted research on a SCWO batch process [4]. A batch system is a reasonable alternative for small amounts of human metabolic
wastes (0.12 kg/person-day feces, 1.6 kg/person-day urine). A batch system is easier to automate, and the elimination of some of the continuous flow hardware such as the high-pressure slurry pumps improves the reliability.

After a hiatus of several years, SCWO research at ARC resumed in 1993 with a study by Fisher and Abraham on the kinetics of supercritical water oxidation of solid particulates [5]. Polystyrene beads were used as the model compound because of their well-characterized size distribution and were oxidized in a 2 liter batch SCWO reactor. In 1994 Fisher and Pisharody studied SCWO oxidation of wheat straw particles [6, 7]. A major objective of NASA at the time was the development of a fully regenerative life support system that includes recycling of water, carbon dioxide, and nutrients to grow plants for food. Wheat straw was chosen as representative of the inedible biomass waste from a plant growth system. A series of experiments was conducted to develop reaction rate expressions that can be used to predict the effects of particle size, temperature and pressure. Empirical kinetic expressions were developed that can be used to estimate important process parameters such as reactor size as function of destruction efficiency. The kinetics developed indicated that SCWO is capable of oxidizing solid wastes very rapidly and very completely in small reactors. It was found that a particle size reduction to roughly a few hundred microns is necessary for rapid kinetics.

Figure 1 shows the batch experimental system used for the kinetic studies. The experimental system consisted of a reactant injection system, a water and an air feed system, a 2-L stirred autoclave, and a sampling system. The reactor was a conventional 2L stirred Autoclave Engineers batch reactor constructed of Hastelloy C276. The autoclave was fitted with a six blade magnetically driven agitator.

Interest in using SCWO to process larger amounts of waste materials led to further consideration of continuous SCWO systems. Larger amounts of waste are produced by regenerative life support systems that include plant growth systems for producing food. A continuous SCWO breadboard unit was developed by MODAR, Inc., via a Small Business Innovative Research grant and delivered to ARC in January 1996 [8]. This system has unique
features such as an impingement canister reactor and computer controlled remote operation and data acquisition. An experimental program was conducted to evaluate the ability of this SCWO system to treat life support system solid wastes. The experimental program at ARC covered a range of model organics such as iso-propanol, acetic acid, ammonium acetate, urea, ground corn flakes, and urine. The results obtained were promising in terms of the completeness of reaction and the absence of undesirable byproducts. Difficulties encountered included the delivery of solid wastes to the continuous SCWO reactor, sticky salts in the reactor, and energy recovery. A diagram and picture of this SCWO reactor are shown in Figures 2 and 3.

In the early 2000s NASA began focusing on more near term and shorter missions that have less need for fully regenerative life support systems. Development of fully regenerative life support systems that include plant growth for food has abated, and consequently development of the continuous SCWO system also abated. However, handling of human metabolic wastes remains an issue. SCWO continues as one of a number of technologies with potential for application to treatment of human metabolic waste on near-term space missions.

Glenn Research Center (GRC): In 2004, research commenced at NASA’s Glenn Research Center (GRC) as part of its microgravity combustion program to investigate the role gravity plays in some of the fundamental thermo-physical processes that take place in a typical SCWO reactor. An investigation was launched to assess the establishment of temperature and concentration gradients in the absence of gravity in a near-critical and supercritical bulk fluid as a function of different injector designs. A SCWO Test Facility, shown in Figure 4, with a 480 ml reactor was designed and built for use in the Zero Gravity Facility (ZGF, a.k.a., the
5.2 Second Drop Tower) [9]. The chamber was filled to a predetermined level with the organic substance of interest (10% methanol in water). A test was initiated once the reactor fluid temperature was stabilized at 723 °K with the reactor pressure held constant at a nominal 250 atm. At this time, heated and pressurized air was injected into the reactor through a 1 mm diameter nozzle. Diagnostics included a rake of four thermocouples placed inside the reactor at different axial distances from the nozzle. A limited number of ZGF tests were conducted before the project was put on hold due to shift in funding priorities.

Figures 5(a), and 5(b) show temperature profiles from a test with an injection air velocity of 45 cm/s. The 1-g oxidation reaction is presented in Figure 5(a) and is characterized by a rather narrow temperature range. The temperature spread is less than 6 °K at the point of peak temperature between the upper three thermocouples (i.e., TC-B, TC-C, TC-D) and the average rate of temperature rise is approximately 2.1 °K/s. Since thermocouple TC-A is immediately following axial injection of oxidizer; (a) in 1-g temperature profiles show high degree of buoyant driven thermal mixing for locations above injector and (b) in 0-g temperature profiles show significant thermal stratification with a hot zone (TC-B) established between two cooler regions suggesting poor thermal mixing in 0-g.
located near the exit plane of the injector it is upstream of the exothermic reaction zone and consequently lags behind the other TC’s. These temperature profiles are compared with the 0-g reaction shown in Figure 5(b) where the temperature spread between the upper three thermocouples suddenly grows, from 5 °K in 1-g, to over three times that by the end of the 5.2 s 0-g period (i.e., 17 °C between TC-C and TC-D). Additionally, the average rate of temperature rise in 0-g is 5.1 °K/s, over twice that observed in 1-g. It is apparent that sudden changes in the hydrodynamic flow field occur with the transition to 0-g. Even though there is probably some residual convective flow well into the 5.18 second microgravity period it is interesting that there is such a significant localized temperature effect associated with the absence of any buoyant forces.

The observed effect on internal temperature profiles may be illustrated by considering the combined buoyant/forced flow field of a non-reacting axisymmetric jet. Figure 6 shows the velocity vectors and temperature map for a supercritical water jet, at 800 K, injected into a reactor filled with supercritical water at 700 K for both normal gravity and zero gravity cases. The computation includes time dependence and the figure depicts conditions at the same time following injection. The entrainment and higher velocities near the central axis in normal gravity are clearly seen. The zone of temperature spread is significantly narrower in normal gravity because of buoyancy. The zero gravity simulation shows the impact of no buoyant forces and a radial spread of the heated jet results. It is only in the immediate neighborhood of the injection, where inertial forces dominate, that the normal gravity and zero gravity behavior are similar.

**CURRENT NASA RESEARCH**

This earlier work at GRC was instrumental in development of a collaborative effort between NASA and the French space agency CNES, which was initiated in 2008. The objective of this ISS flight investigation, referred to as the Salt Water Mixture Experiment (SCWM), is to investigate the behavior of salt precipitate formation and transport in supercritical water with and without the presence of a temperature gradient. In SCWO systems, removal of precipitated salts may be facilitated by transporting precipitates from a supercritical zone to a sub-critical region where they may be re-dissolved. This requires the transport of salts through a temperature gradient. However, in order to understand these complicated processes in a salt-water mixture it is necessary to first establish a baseline understanding of the thermal transport processes with pure water in a bi-phasic system as it transitions into its supercritical phase. Thus, the first phase of this collaborative study consists of baseline experiments on the formation of temperature gradients in pure water near the critical point.

These experiments were conducted in the High Temperature Insert (HTI) of the DECLIC facility on board the ISS in 2010. DECLIC\(^1\) is a joint CNES/NASA multi-user facility dedicated to the study of physical and chemical phenomena in transparent materials under microgravity conditions, and under accurately controlled temperature conditions [10]. The experimental arrangement has an optical bench that receives an experiment specific insert. The experiment insert for the near-critical observations of water is called the High Temperature Insert (HTI), see

\(^1\) Dispositif pour l’Etude de la Croissance et des Liquides Critiques (i.e., Device for the Study of Critical Liquids and Crystalization) an ISS facility designed and built by the French Space Agency for studies of fundamental phenomena of supercritical fluid phenomena.
Figure 7(a). The dimensions of the insert are approximately 200 x 200 x 400 mm. The HTI contains a fluid cell holder which has a mass of about 25 kg including the 0.8 kg mass of the fluid cell. The fluid cell (Fig. 7(b)), housed in a fluid cell holder, consists of an Inconel 718 housing fitted with opposed sapphire windows (18 mm dia) for direct observation. It also has a 5.5 mm dia polycrystalline CVD diamond window for 90 degree light scattering measurements which will be described in a separate paper. The windows utilize gold seals for leak tightness. The cell is rated to a maximum temperature of 678 K (405°C) and a maximum design pressure of 35 MPa. The fluid cell has an internal volume of 0.3 cc in the shape of two intersecting cylindrical disks. It is filled prior to launch, via an inlet port, with pure water at an average density (i.e., vapor/liquid average) of 322 kg/m$^3$, which is the critical density.

The ISS experiments utilized distortions in images of an optical grid inserted in the imaging path of the fluid cell, which provided a shadowgraphy diagnostic capability. The locations of the reference grid intersection points were tracked using imaging software. It was found that during imposition of a temperature gradient, the temperature and density gradients first form near the boundary during the transition to steady conditions. There is a substantial time lag before temperature and density gradients form in the central region of the cell. However, temperature measurements indicate that the bulk fluid temperature is raised uniformly to the average of the boundary values of the temperature during the initial transient phase which is not consistent with a purely diffusive process. These observations may be explained by considering the temperature field in a stationary fluid in microgravity near its critical point. This may be described by the following equation under conditions of uniform pressure [11]:

$$\frac{\partial T}{\partial t} + c V \frac{\partial T}{\partial y} = \left[ 1 - \frac{1}{\gamma} \right] \frac{\partial < T >}{\partial t}$$  \hspace{1cm} (1)

The term on the right hand side arises from the compressible nature of the fluid and becomes important when the ratio of specific heats, $\gamma$, is large as is the case near the critical point. When heat is added at the boundary of the fluid domain, detailed analysis has shown that fluid expansion in the developing thermal boundary layer compresses the fluid in the interior with an attendant temperature rise. This phenomenon has been termed the “piston effect” and is caused by acoustic motion [12]. The net result is that the fluid in the interior rapidly attains, approximately, the average temperature of the boundary by compressive heating of the highly compressible supercritical fluid rather than by diffusive transport. As the thermal boundary layer increases in size, the piston effect diminishes in strength, and the final thermal equilibration is by diffusion.

The ISS test sequence in 2010 was designed to investigate the formation and stability of a temperature gradient in water in its supercritical state. The follow-on SCWM experiment will utilize a low concentration solution of sodium
sulfate and is scheduled to be performed on the ISS in 2013. Supporting experiments on the ground have shown that while salt is present in the vapor phase below the critical temperature, precipitation occurs mainly in the liquid phase with nucleation on the surfaces (e.g., windows) in contact with the liquid, and possibly with smaller particulates (less than 15 microns) in the liquid phase.

At supercritical temperatures salt deposits form on all of the surfaces in contact with the fluid, including those which were previously in contact with the vapor alone in the sub-critical regime. Experiments to observe the re-dissolution of the salt were also conducted by cooling the fluid cell [13]. An interesting stratification pattern, shown in Figure 8, was seen in the liquid during the cool-down period that is not observed in the pure water tests. Shortly after the cessation of the buoyant convection, due to the heat-up period, a dark band just below the meniscus appears which sits above a lighter region. This stratification pattern of alternating dark and light regions might be explained by the thermal gradient that begins to develop upon cooling. As the test cell cools a thermal gradient, from high temperature fluid at the meniscus to lower temperature fluid at the base of the cell begins to develop. The downward drift of the salt-laden fluid (i.e., the darker fluid) is momentarily retarded by the fact that it is at a higher temperature, and consequently less dense, than the cooler, less saline but denser fluid. This creates a salinity inversion that gradually diminishes as salt diffuses out of this dark band.

**FUTURE PLANS**

In order to extend the reach of SCWO technology for practical space based application, a significant re-design of the conventional SCWO reactor may be required. It has recently been suggested [14] that hydrothermal flames could serve as a pilot for the initiation and control of reactant heating rather than by heating externally through the reactor walls. This concept envisions a cylindrical reactor with an internal supercritical core region surrounded by a sub-critical annular flow. This approach would keep internal reactor surfaces at temperatures below the point where salts precipitate from solution and potentially eliminate many of the corrosion and fouling problems that currently plague present reactors. This new reactor design concept may be useful in reducing the mass and volume of space based SCWO reactors, allowing this technology to take its place as an attractive alternative to other waste management and/or resource reclamation technologies.

To date, there has been little in the way of detailed analysis, modeling and testing, either on a component or system level, where the absence of, or significant reduction in, gravitational forces has been evaluated. Most of the necessary work in this area lies in the realm of thermal and fluid physics where phase separation, heat transfer, reactant transport, reaction kinetics, spontaneous flame onset and reaction propagation, will present unique challenges in a microgravity environment. Additionally, there is a large gap in the fundamental understanding of hydrothermal flames (e.g., flame inception, stability, radiative effects, diffusive mechanisms, chemical kinetics, etc.), that must first be bridged before this can be designed into a space-based application.

In order to bring SCWO technology to the level it needs for future space application a wide range of research topics are presented for consideration:

1. Research focusing on transport phenomena and solvation mechanisms in both near critical and supercritical water regimes. These areas of research would be a significant extension of the current SCWM investigation slated to be performed on ISS in CY 2013. These research topics would include:
   
   (a) solubility mechanisms for binary phase aqueous mixtures of Type I and Type II salts and ternary phase aqueous mixtures (i.e., liquid-solid-gas) with soluble gases (e.g., CO2, N2),
(b) the physical mechanisms of the dynamics of salt deposition on thermal control surfaces,
(c) effects of variations in mass/thermal diffusivities,
(d) the role of thermophoretic forces on particles in the presence of large temperature gradients,
(e) the thermo-compressible effects on precipitate formation and transport.

2. Research focusing on hydrothermal flames is of particular interest to NASA, and in direct alignment with GRC’s resident expertise in microgravity combustion science. In the same vein as the current suite of experiments in the ISS combustion science program, the 0-g environment provides an ideal experimental platform for studying hydrothermal flames without the attendant complexities of buoyant forces. To date, very little work on hydrothermal flames has been performed in the following areas:

(a) flame inception, stability and propagation,
(b) flame combustion in diffusion-limited and pre-mixed regimes,
(c) reduced chemistry models for key reaction mechanisms,
(d) numerical and analytical modeling schemes for hydrothermal flames.

3. Research focusing on building a data base for reaction kinetics in near-critical and supercritical regimes. This includes the reaction kinetics and destruction efficiencies of the typical constituents of bio-waste streams, N\textsubscript{2} containing waste streams (e.g., urea, ammonia, acetic acid), and NO\textsubscript{x} mitigating schemes in high temperature reactions (flame combustion).

4. Research focusing on the hydrodynamics of injecting disparate fluid phases (i.e., sub-critical, trans-critical, supercritical) into a quiescent or non-quiescent bulk fluid at supercritical conditions.

The proposed SCWO research, particularly in light of some of the proposed new reactor designs relying on hydrothermal flames, is a highly relevant area for both terrestrial and extra-terrestrial systems. A largely untapped, but critical, nexus exists between traditional combustion research and its potential for making significant advances in SCWO technology. Growth in this research field provides an exciting opportunity for increased international ISS collaboration and would align NASA’s microgravity research program with many of our ISS partners; many of whom are heavily invested in SCWO technology research.

REFERENCES


