Supercritical Water Oxidation - Microgravity Research

A Topical White Paper submitted to the Decadal Survey 2023-2032

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Abstract

Closed-loop systems for waste stream processing and resource reclamation (e.g., solid waste management and water reclamation) remain a limiting factor for extended duration space missions contemplated under NASA's exploration initiative. This white paper provides a brief background of Supercritical Water Oxidation (SCWO) technology along with some examples of SCWO's current terrestrial applications. This is then followed by a discussion of NASA's past and current work in the area along with a brief review of topics where focused research is needed in order to advance this technology beyond its current state. The motivation is twofold; (i) to achieve the necessary technology advances to make this relevant for NASA's extended space missions and (ii) to provide a platform for research necessary to extend SCWO's base of terrestrial applications.

1 SCWO Research Significance

1.1 Proposed International Space Station (ISS) Science and Rationale

Supercritical Water Oxidation (SCWO) has long been a technology under consideration by NASA for addressing many of the intractable environmental control and life support challenges associated with extended space duration missions. Because of its relatively low Technology Readiness Level (TRL) for space/extra-terrestrial application, combined with the paucity of successful terrestrial experience, particularly with large scale commercial applications, it has largely remained mired in laboratory venues despite the many enormous advantages the technology offers.

In the last decade there has been a growing community of researchers (somewhat concentrated on the European side of the balance) and a number of technology advances that have combined to change this paradigm. Large scale SCWO facilities are starting to be viewed as attractive alternatives to the more conventional systems for handling a wide range of solid/wet waste streams. In recognition of this, there is a great interest in expanding research in this field and, as such, the ISS is strategically positioned to add to this growing body of research in a way that is uniquely suited to one of SCWO’s key technology thrusts; this being, the area of hydrothermal flames which are now being considered for use in “flame-controlled” SCWO reactors.

As will be discussed in greater detail, SCWO reactors have traditionally been designed for operation with an external heat source and without internal flame combustion. Recent attention has been given to a new reactor concept involving the generation and control of these hydrothermal flames for internal heating to initiate and sustain SCWO operations. There are a number of advantages with this approach, but before it can be widely applied there is a great deal of research that needs to be done on water-flame hydrodynamics, flame ignition, flame stability, and reaction kinetics. The microgravity environment of ISS provides an additional dimension from which to approach this research as well as provides the necessary environmental requisite for advancing the technology’s TRL beyond its current level.

1.2 SCWO Background

SCWO is a technology in which waste water or a “slurry processed” waste stream with entrained solid contaminants is introduced into a reaction vessel at temperatures and pressures above the critical values of water (i.e., 374°C and 221 bar). At levels above water’s critical point, distinctions between liquid and solid phases no longer exist and gases (e.g., O_2 , N_2 , CO_2) and organic material become highly soluble in water. In typical SCWO operating conditions (e.g., from 450°C to 550°C and at pressures of 250 atm) oxidation of carbonaceous waste consistently exceeds 99.99% with reactor residence times often well under one minute.

High destruction efficiencies for a wide range of compounds at relatively low temperatures (400°C to 550°C) has been demonstrated with reactor residence times on the order of seconds. This is largely due to the dramatic changes in the thermophysical properties of water, when transitioning from sub-critical to supercritical, resulting in reductions in diffusive time scales governing thermal, mass and momentum transport within the reactor. At supercritical conditions these diffusive time scales are similar to that of a dense gas. Additionally, because of the depolarization of the water molecule at supercritical conditions inorganic salts (e.g., NaCl , $MgCl_2$, $CaCl_2$) become insoluble and begin to precipitate out as solids. For example, NaCl at ambient conditions (i.e., 25°C and 1.0 atm) has a solubility of approximately 30% by weight, whereas at supercritical conditions (i.e., 600°C and 250 atm) the solubility reduces to less than 0.003% by weight. This technology, when operated in the appropriate regime, has the potential to separate inorganic material, oxidize essentially all organics, and eliminate all microbial contamination. The product stream, depending on the constituents of the feed stream and operating regime, will typically consist of CO_2 , N_2 , water, inorganic precipitate, and mineral acids (from organic sulfur, phosphorous, halogens).

1.2.1 *Current Terrestrial SCWO Applications*

The enormous advantages associated with SCWO processing over conventional systems have long been established and have been well documented in literature; however, the extensive application of this technology has been limited by three significant technical challenges; these being, (i) the corrosive nature of supercritical water in the presence of an oxidant and certain inorganics typically found in waste streams, (ii) the heavy loading of precipitated salts on heat transfer surfaces and narrow flow passages, and (iii) the attendant increases in design and operating costs necessary to address these challenges. As a result, large scale SCWO systems have traditionally been the technology of last resort for most common waste streams. However, with a combination of growing environmental concerns along with significant technological advances that have been made in the past decade there is a growing interest in SCWO processing. This has been true for waste streams ranging from the most problematic (e.g., highly toxic wastes from military weapons stockpiles, radioactive wastes from nuclear power facilities, naval ship wastes, pharmaceutical wastes) to some of the more benign and ubiquitous municipal waste streams. Some examples include (i) the recent commissioning of a SCWO facility for the demilitarization of the chemical weapons stockpile stored at the U.S. Army's Blue Grass Chemical Activity in Richmond, KY, (ii) a SCWO facility for the safe destruction of hazardous by-products from demilitarization processes at the U.S. Army's Pine Bluff Arsenal and more recently and (iii) a proposed SCWO facility designed to handle the municipal sludge disposal demands in Orange County, California.

1.2.2 *Microgravity Relevancy*

Direct Benefit to NASA's Mission: In order to extend the reach of this technology into space and beyond, a significant re-design of SCWO reactors will likely be required. 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 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.

An example of the gravitational influence on SCWO processes is found in the determination of whether flames appear when a stream of reactants is introduced into the reactor. Traditionally

SCWO has been considered a low temperature “flameless” oxidation process; however, the presence and persistence of diffusion flames, long known to exist in SCWO reactors, have recently been studied. It was found that these flames are spontaneous and, under certain operating conditions, may be unavoidable. It was also observed that flame stability was highly dependent on buoyant forces at air/fuel ratios greater than 1.8. The presence of these flames in the reaction vessel, if not properly controlled, will result in excessive local temperatures (i.e., temperatures exceeding 3,000°C have been observed) that could damage unprotected component surfaces such as reactor walls, fluid injection nozzles, etc.

Earth Benefits: Recent work has promoted the concept that these hydrothermal flames, when properly controlled, could serve as a “pilot” for initiating and controlling reactions internally rather than by heating externally through the massive 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 the internal reactor surfaces at temperatures below the point where salts precipitate from solution and potentially eliminate corrosion and fouling problems. This new reactor design may be the pivotal technology breakthrough needed to establish the technology as an economically competitive contender for a much broader array of applications. However, in order for this to happen, 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.

The investigation of hydrothermal flames in microgravity, entirely similar to the rationale used for the study of traditional flames in microgravity, allows for the development of a fundamental understanding of SCWO combustion phenomena that could not otherwise be obtained. As an example of the masking influences of gravity on fundamental mechanisms one can look at the manner in which salts are transported once they fall out of solution and begin to agglomerate. Salts will readily precipitate, oftentime suddenly and within a very narrow temperature band, from solution in a SCW medium and begin to aggregate and attach to surfaces. The transport mechanisms of salt in SCW are poorly understood, particularly in the presence of hydrothermal flames and the extreme thermal gradients that occur. Transport of salt precipitates in 1-g will be from a combination of diffusive and convective processes (i.e., buoyantly induced and forced). In a 0-g environment the diffusive processes (e.g., thermal, thermophoretic, concentration) can be readily isolated and quantified providing information that can ultimately be used to develop mitigation schemes for 1-g systems. As with the study of traditional flames, reduced gravity environments provide an ideal test bed for the direct observation of fundamental phenomena in hydrothermal flames that is not possible in a gravitational environment.

1.2.3 *Previous NASA SCWO Research*

A number of years ago a significant research effort was undertaken by NASA Ames Research Center (ARC) to investigate the feasibility of SCWO for handling solid bio-waste as a competing technology for extra-terrestrial based waste management systems. Work in this area was effectively suspended (circa ’98), due to competing priorities, but not before a series of investigations concluded that this technology held considerable promise because of distinct advantages not shared by other technologies. These advantages, some of which were noted earlier, include (i) very high conversion rates (e.g. residence times on the order of seconds or less), (ii) minimal pre-processing of waste feed streams, (iii) conversion efficiencies often approaching 99.99%, (iv) clean and well characterized product streams consisting of CO_2, N_2, water and, to the extent inorganic material is included in the feed stream, some residual precipitates (salts) and metal oxides, and (v) probably the most significant advantage, the technology’s “duality of purpose” allowing SCWO to be used for both waste management and water reclamation.

In the early 2000's work at NASA Glenn Research Center (GRC) was initiated to study the influences of gravity on spontaneous flame ignition and diffusive processes. An experimental test rig was built to investigate a number of these issues in both 1-g and 0-g, using GRC's Zero Gravity Facility (providing 5.2 seconds of 0-g). However, these studies were cut short again due to competing priorities.

1.2.4 *Current International Collaborative Research*

The earlier SCWO work at NASA-GRC provided the foundation for proposing a new collaborative flight investigation on the ISS. NASA has partnered with scientists from the Centre National d'Etudes Spatiales (CNES, the French Space Agency) and Institute of Condensed Matter Chemistry of Bordeaux (ICMCB), a research group affiliated with the Centre National de la Recherche Scientifique (CNRS), in an ISS investigation entitled the Supercritical Water Mixture (SCWM) experiment. This experiment is designed to study transport phenomena, in 0-g, of salt precipitate in water at near-critical and supercritical conditions. The work is motivated by the need to address fouling and corrosion associated with salt precipitation in supercritical water. An initial set of experiments was completed in 2018 and a second round is scheduled for 2022.

Additionally, since 2011, NASA has established an on-going collaboration in SCWO research with research teams at York University, Waterloo University and presently at Lakehead University in Canada, through International Letters of Agreement. Various SCWO experiments have been jointly carried out to investigate ignition limits of various alcohol-water blends under supercritical conditions.

1.2.5 *Alignment w/ National Academy of Sciences Earlier Recommendations*

In a recent publication by the National Academy of Sciences, *Recapturing a Future for Space Exploration*, the current SCWM investigation was highlighted as an example of international ISS collaboration that should be aggressively pursued by NASA. A table was presented that highlighted the relative merits of the proposed SCWO research activities. Scoring was based on the relevancy of SCWO research to five key NASA "Program Elements"; these being, (i) Fundamental Physics – Condensed Matter and Critical Phenomena, (ii) Fundamental Fluid Physics – Multiphase Flow, (iii) Fundamental Fluid Physics – Critical Point Phenomena, (iv) Fundamental Combustion Research and (v) Translation to Space Exploration – Closed Loop Life Support Systems. The relevancy to each of the above program elements was based on a scoring of "Low", "Medium", "High" and included the following six "prioritization criteria"; (i) impact on exploration missions, (ii) research value of using 0-g, (iii) ability to translate results to terrestrial use, (iv) impact within research field, (v) ability to address unique needs of NASA and (vi) research that could be dual-use. Particularly noteworthy were the assessments provided for the Fundamental Fluid Physics and Fundamental Combustion Research Program Elements, where a rating of "High" is given to four out of the six Prioritization Criteria and a ranking of "Medium" is given to the rest.

2 Science Definition and ISS Utilization

2.1 Potential ISS SCWO Research Topics

The preceding discussion suggests the following broad research areas in SCWO for consideration in a comprehensive and robust microgravity science program:

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 being performed on ISS. These research topics would include:

- 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., CO_2, N_2)
- the physical mechanisms of the dynamics of salt deposition on thermal control surfaces
- effects of variations in mass/thermal diffusivities
- the role of thermophoretic forces on particles in the presence of large temperature gradients
- 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, are proposed experiments involving hydrothermal flames. In the same vein as the current suite of experiments in the ISS combustion science program, a 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:

   - flame inception, stability and propagation,
   - flame combustion in diffusion-limited and pre-mixed regimes
   - reduced chemistry models for key reaction mechanisms
   - numerical and analytical modeling schemes for hydrothermal flames

3. Research focusing on building a database 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_2 containing waste streams (e.g., urea, ammonia, acetic acid); and NOx 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.

5. Research focusing on synergistic work related to transcritical phenomena associated with hydrocarbon combustion at supercritical pressures. This includes mapping thermophysical properties for multi-component fuel and gas mixtures and near-critical phase transitions of relevant multi-phase hydrocarbon/water/gas systems serving to extend SCWO research into other related high pressure combustion systems.

3 Conclusion

The proposed SCWO research, particularly in light of the recent emphasis on 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.

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