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Supercritical Water Oxidation for Wastewater Recovery – Status on Recent Testing of Ersatz Wastewater and a Conceptual Design for Near-Term Lunar Application

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Water is a necessary resource for crewed space exploration missions and the efficient reclamation of aqueous waste streams presents the only long-term viable option for achieving a sustainable extra-terrestrial human presence. Although early Artemis missions are considering water as part of the payload manifest, it would be extremely advantageous if follow-on missions were supplied — either in total or in part — by a water reclamation technology that would operate autonomously between missions. NASA Glenn Research Center (GRC) employs a Supercritical Water Oxidation (SCWO) process that has demonstrated the successful destruction of all organic hydrocarbons found in a typical International Space Station (ISS) aqueous waste stream. SCWO conversion has shown reductions in Total Organic Carbon (TOC) consistently greater than 99% with reactor residence times less than 3 s and an average reaction temperature between 600 °C and 700 °C. Recent efforts have been directed toward developing an autonomous lunar based SCWO water recovery system design based on the current tubular reactor used in the lab for the evaluation of SCWO conversion of wastewater. This conceptual design along with the results of recent SCWO conversion experiments will be presented.

Keywords: *supercritical water oxidation, wastewater, Raman, high pressure, water reclamation*

Nomenclature

BVAD = Baseline Values and Assumptions Document
ESM = Equivalent System Mass
EWW = Ersatz Wastewater
GRC = Glenn Research Center
LSWRS-0C = Lunar SCWO Water Recovery System - 0th Concept
ISS = International Space Station
TOC = Total Organic Carbon
ml = milliliter
mPa = megapascal
nm = nanometer
ppm = parts per million
ppmC = parts per million of carbon
SCWO = Supercritical Water Oxidation

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I. Introduction

As the cost of supplying sources of potable water for crewed space expeditions becomes increasingly intractable as missions venture further from Earth, finding a reliable and cost effective wastewater recovery system becomes increasingly important for the feasibility of long term crewed space missions. This long standing challenge is taking on a new urgency with the advancing NASA Artemis program, as it plans to send astronauts back to the moon. The current system found on the International Space Station (ISS) recovers about 93.5% of its wastewater; a recovery metric that should be improved for the support of long-term space exploration missions. Moreover, the size, volume, and reliability of the current water recovery system suggests opportunities where SCWO technology may be leveraged to create either a completely new wastewater recovery system or one that at least augments a conventional system.

Recent research at NASA Glenn Research Center (GRC) [1–3] , was originally initiated to study fundamental aspects of ignition, stability and control of hydrothermal flames in SCWO applications. This work led to the design of a small scale reactor for the purpose of exploring the efficacy of SCWO conversions of metabolic wastes from contaminated water. Samples of ersatz wastewater (EWW) were supplied to perform these conversion studies and a range of diagnostic metrics (including TOC and Raman analyses) have been employed to evaluate the extent of conversions witha variety of organic concentrations and operating conditions. The EWW that was used represents a typical aqueous waste stream from the ISS. This includes condensate, hygienic wastes (e.g., bathing, showers, laundry, food etc.) and metabolic wastes (e.g., toilets).

Stemming from this activity and using the SCWO lab system as the conceptual basis, a near-term lunar water recovery system was envisioned. The initial concept, referred to as the Lunar SCWO Water Recovery System - “Zeroth” Concept (LSWRS-0C) is presented along with an estimate of the equivalent system mass (ESM). The LSWRS-0C is based entirely on the lab system (hence the “zeroth” reference) and is not optimized for mass, volume and power. The operational concept is that the LSWRS-0C would operate continuously and unattended between crewed lunar missions. The operational capacity of the LSWRS-0C would be sufficiently sized to reclaim all of the wastewater from the preceding crewed mission and would allow for a sizable reduction, if not complete elimination, of the water required to be transported on subsequent crewed Lunar missions. As such, the primary objectives of the work presented in this paper are (i) to establish the efficacy of SCWO in the conversion of metabolic wastewater and (ii) to describe the LSWRS-0C and present a preliminary assessment of the Equivalent System Mass (ESM) for a non-optimized system.

II. Background

SCWO is a method of water reclamation relying on oxidation reactions at temperatures and pressures above the critical point of water; i.e., 374 ˚ C and 22.1 MPa (218.11 atm). When oxygen is introduced at these conditions oxidation reactions occur spotaneously and completely with any organic contaminant creating product streams consisting entirely of CO_2 and H_2O (along with any excess Air). The rapid dissolution and intimate mixing of the reactants occurs because of the loss of water’s polarity at supercritical conditions. Consequently, hydrocarbons which are generally non-polar molecules become highly soluble in supercritical water, which allows for higher wastewater recovery compared with other common reclamation methods (e.g., distillation, filtration, chemical treatment, etc.).

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 650 °C at pressures of 25.35 MPa (250 atm) oxidation of carbonaceous waste consistently exceeds 99.99% with reactor residence times often well under one minute. High destruction efficiencies (often exceeding greater than 90%) for a wide range of organic compounds occurring at relatively low temperatures (400 °C to 550 °C) have 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. [4–6] For example, NaCl at ambient conditions; i.e., 25°C and 0.1014 MPa (1.0 atm), has a solubility of approximately 30% by weight, whereas at supercritical conditions; i.e., at 600°C and 25.35 MPa (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). [7]

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[1] 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.

This work will show that a small scale SCWO reactor is feasible for treating wastewater for lunar missions under the current planned scenario of the Artemis missions. The idea is that wastewater reclamation would take place in the interval between human presence on the moon, relying on dormant power capabilities to recharge the storage system. Currently it is anticipated that the initial set of Artemis missions will have a lunar human presence of up to 3 months at a time with several months interval before the next human mission to the surface. As will be shown even a small scale reactor with a few grams/minute wastewater throughput is more than enough to treat the anticipated volume of wastewater left behind on the lunar surface after a human mission.

A SCWO reactor with a low throughput of a few grams/minute of wastewater is of reasonable size to be accommodated in a laboratory environment. Such a reactor has been designed and is operational in the SCWO lab at GRC. In the following, the design of the lab SCWO reactor is first presented. Results from wastewater reclamation using the lab reactor are then presented which show SCWO is a feasible method for this purpose. A conceptual SCWO design for lunar applications is then presented based on the lab reactor design. Finally, equivalent system mass (ESM) for this design is estimated using NASA standard baseline assumptions and is compared with bringing fresh water supply for each human mission to the lunar surface.

III. Laboratory Reactor Design and Operation

Conditions within the reactor present several design challenges: exothermic reactions generating high thermal loads resulting in localized temperatures that approach the yield limits of most metals at the necessarily high operating pressures. Water itself at near-critical conditions can become acidic, resulting in corrosion of reactor walls and internal components, and fouling from salts that are no longer soluble in water which then begin to agglomerate and stick to interior surfaces. This phenomenon is mostly due to the general insolubility of inorganic salts and can cause significant corrosion and fouling at sensitive locations within the reactor. To protect against these adverse conditions Inconel 625 Grade 1— a high nickel alloy, was chosen. It retains it yield strength at high temperatures and it possesses a relatively high resistance to corrosion. The dimensions of the reactor tube are shown in Figure 1.

A. Reactor Design

A simplified diagram of the tubular SCWO reactor system utilized at NASA GRC is pictured in Figure 2. The system starts at two manually controlled pumps that feed the fuel (waste) solution into the reactor where an oxidant (air) is introduced for both constituents to mix. At this stage, each inlet is preheated to 425 ° C and is pressurized to 27.6 MPa (4000 psia) to bring the phases of each constituent into the supercritical regime. Once mixed, the homogeneous mixture enters the reaction zone where temperatures are raised, for tests reported in this work, to approximately 650 ° C in order to begin oxidizing the organics at a rate sufficient to sustain internal temperatures and reduce power requirements to the external reactor heaters.

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[1] product streams containing inorganic salts may be separated as precipitates prior to cool down when re-dissolution of salts may occur.

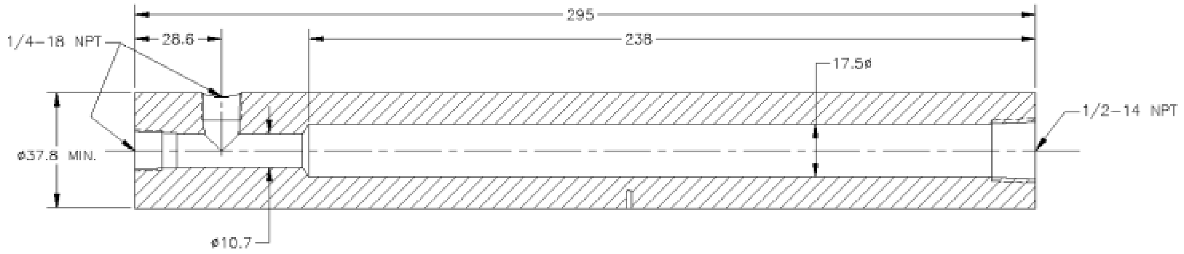


Figure 1: The SCWO Tubular Reactor shown on its side (operational configuration is vertical) made from Inconel 625 Grade I showing (from left to right) the bottom inlet port for the fuel, the side inlet port for the air and the exit (top) port for the outlet product stream (all dimensions are in mm).

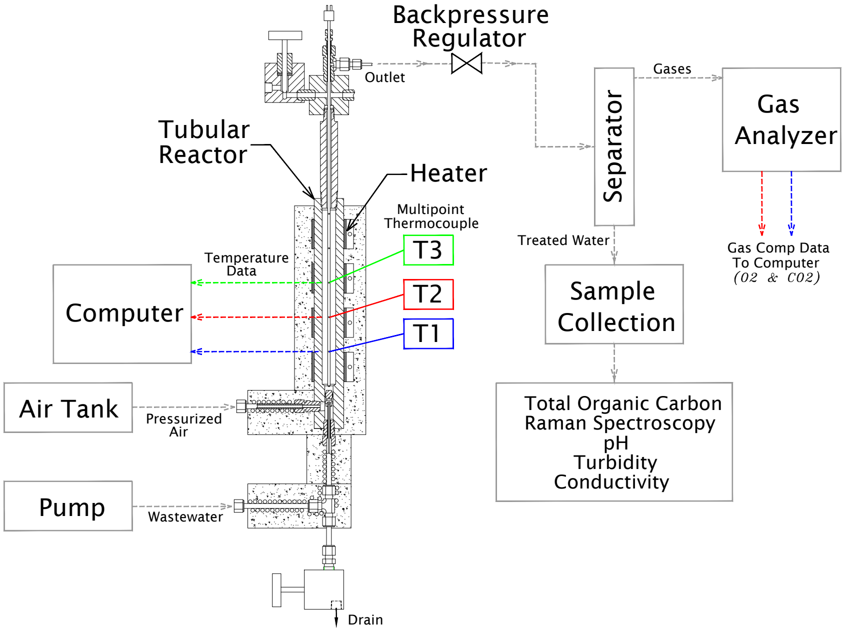


Figure 2: Diagram of the system layout showing the air and wastewater flow path from supply reservoir, through the SCWO Tubular Reactor and separation of the liquid and gas/vapor streams (gray dashed lines). Supporting diagnostics for both liquid and gas/vapor product streams are also shown.

In the reaction zone, a six-point thermocouple probe is present to measure the temperatures at three respective points within the reactor for real-time measurements that are then sent to a computer for record keeping. Once reacted, the resulting product stream passes through an outlet to a gas/liquid separator that diverts the liquid to be sampled for diagnostics and diverts the vapor and non-condensible gases through a gas analyzer to record gas composition data. This measures the gas concentrations in the product stream and provides a real-time indication of the reaction rates. The extracted liquid is diverted from the product stream and is captured in bottles for later analysis.

B. Nozzle-Mixing Chamber

A stainless-steel nozzle was designed to address mixing between both the fuel and oxidant inlet streams. This change was spurred in order to mitigate formations of hot-spots which can be one of the deficiencies present in tubular reactors. Lack of proper mixing leads to the development of a non-homogeneous solution that responds erratically within the reactor: inadvertently, causing an uncontrollable temperature gradient within the reactor. To reduce these effects, the nozzle was implemented to create a space where both the fuel and oxidant streams could mix properly. The nozzle itself features a threaded inlet port at its bottom that attaches to the pre-existing stainless-steel fuel inlet line and has “thru-holes” that spread the flow of

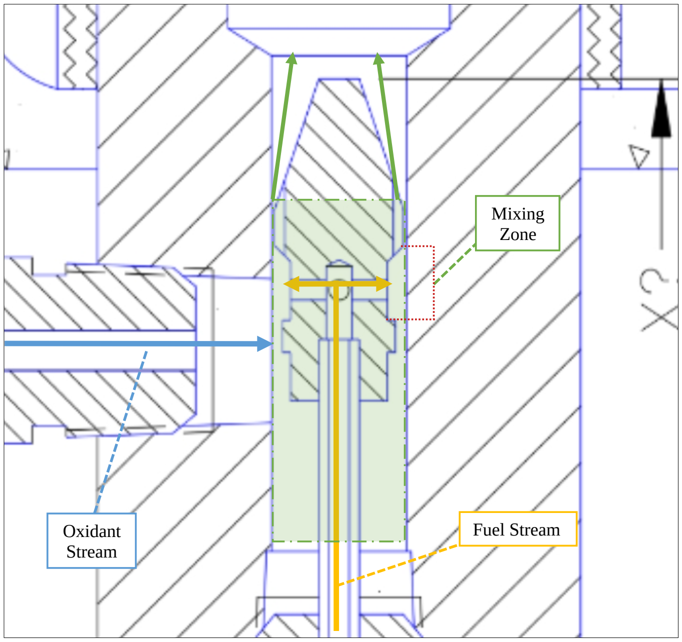


Figure 3: Schematic of Nozzle-Mixing Chamber Schematic of Nozzle-Mixing Chamber

the fuel flow radially into the oxidant stream.. Here, both reactants mix and escape the mixing chamber by means of grooves that lead further into the reactor. An example of this flow can be seen in Figure 3 and images of the nozzle are shown in Figure 4.

Figure 4: Images showing stainless steel nozzle-mixing chamber with six radial holes located just above the circumferential collar, which serve as the ejection ports for fuel entering from the steel fuel supply tube attached at the base.

C. SCWO Conversion - EWW and Urea Solutions

SCWO conversion of a "diluted" mixture of EWW is presented in Table 1. The EWW sample is formulated to be representative of a typical waste stream from the ISS and consists of wash water, formulated urine, condensate from the habitable environment and other sources of moisture. [8] It is received from the supply source as a concentrate; in this case, forty times the concentration of a typical waste stream and when prepared for the tests shown in this work, it is then diluted to a 1:10 solution; i.e., 1 part EWW concentrate, as received, to 10 parts pure water. This results in a test solution approximately 3.6 times the concentration typically generated in the ISS.

It should be noted that these test results were obtained from a continuous flow maintained for an operational period lasting over six hours. This was accomplished by operating two high-pressure piston pumps in tandem, with each pump containing approximately 250 ml of test solution. Each of the test samples listed in Table 1 were collected in 100 ml sample bottles at a flow rate of approximately 3 ml/min. Each

Table 1: SCWO of EWW at 1:10 Dilution

Sample Number	TOC (ppm)	pH	Turbidity (NTU)	Conductivity ($\mu S/cm$)
untreated	947.62	6.77	192	1410.0
1	5.36	2.56	1.92	1759.0
2	4.40	2.60	0.38	1481.0
3	3.62	2.68	0.35	1199.0
4	3.33	2.73	0.58	1070.0
5	4.41	2.75	0.95	974.2

time a sample bottle was filled the alternating piston pumps were cycled, by idling one and activating the alternate pump. This operational sequencing of the two high pressure pumps was done to demonstrate that a continuous flow stream, using two alternating pumps, would allow for a continuous flow stream that could be supplied indefinitely. It was successfully demonstrated that transitions between pumps caused minimal disturbance; i.e., reactor conditions were maintained and processing proceeded uninterrupted.

After treatment, each sample was tested for the extent of oxidation by using a Raman diagnostic technique that detects the presence of any contaminant that is "Raman active". Raman has been shown to be an effective diagnostic for measuring SCWO conversion efficacies for a range of typical organic contaminants. [9–12] This was done using the IsoPlane81 (previously known as FERGIE) from Teledyne Princeton; a compact imaging spectrograph encompassing UV-NIR wavelengths using a 532 nm excitation laser for initiating the Raman shift of any remaining contaminant. Each sample was also measured for the reduction in Total Organic Carbon (TOC) using a Teledyne Tekmar Lotix Combustion Analyzer. Additional diagnostics included measurements of pH, turbidity, conductivity. The results of these measurements are shown in Table 1.

Since metabolic wastes will inlcude significant amounts of urea (i.e., carbamide, $CO(NH_2)_2$) it was of interest to run a series of SCWO tests that isolated this particular compound. Complete oxidation of urea will lead to N_2, CO_2, and H_2O and if strategically circumvented with intervening electrocatalysis, may serve as a source of H_2. Urea is generally one of the more difficult species found in metabolic waste streams to oxidize and requires temperatures in excess of 650 °C, which coincidentally is the limiting temperature of the lab reactor used in this testing. In order to raise the internal reactor temperature without exceeding the maximum allowable reactor wall temperatures ethanol was injected into the test solution. Two tests were run with an aqueous urea solution at 50,000 ppm; one with a 10% ethanol concentration (C_2H_5OH (aq) 5%-v) and the second with a 5% ethanol concentration (C_2H_5OH (aq) 5%-v).

D. SCWO Conversion - Results

The plot shown in Figure 5 shows the Raman scans for the SCWO-EWW conversion tests discussed in the preceding section. The three curves shown are the Raman shifts of all of the Raman active contaminants (yellow curve) along with the treated sample that lies directly on the curve showing the profile for the Raman shifts of pure water.

In Figure 6 plots of the Raman shift of the SCWO of urea are shown,with Figure 6 (a) showing results of a urea solution (50,000 ppm) in 10% ethanol solution and Figure 6 (b) showing results of the same urea solution in 5% ethanol. As noted earlier the purpose of the addition of ethanol was to raise the internal bulk fluid temperature to temperatures above the threshold temperature for urea oxidation, approximately 650 ºC. These plots show the nearly complete oxidation of urea for the higher ethanol concentration, with an average bulk fluid temperature of T °C as compared with the incomplete urea oxidation for the 50,000 ppm ethanol solution shown in Figure 6 (b).

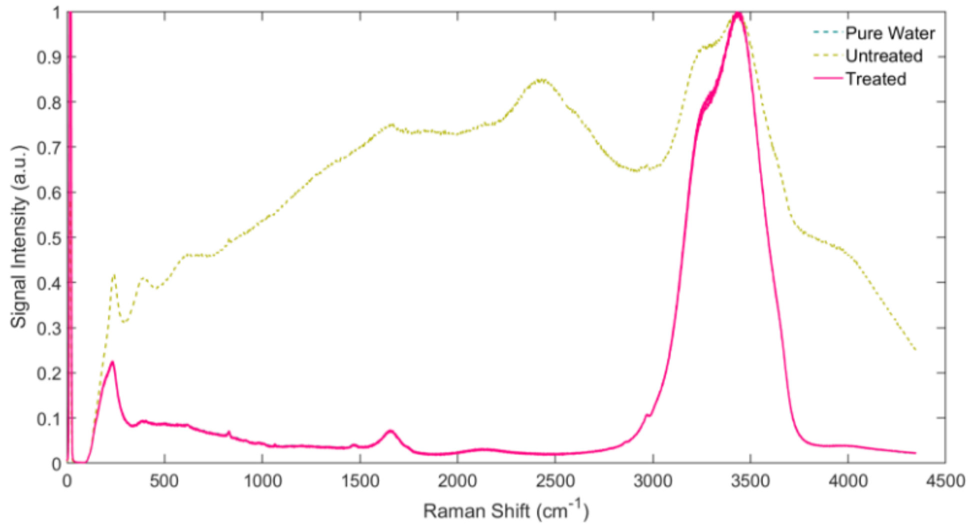
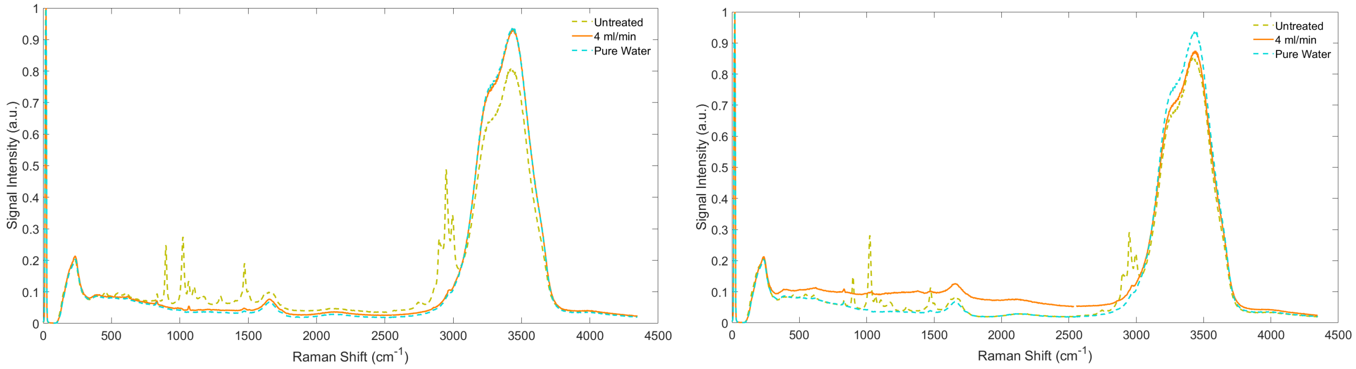


Figure 5: The three curves (two curves effectively lying on top of each other) shown in Figure 5 are the Raman shifts of all of the Raman active contaminants (yellow curve) along with the treated sample that lies directly on the profile for pure water.



(a) **(b)**

Figure 6: Normalized Raman spectra of aqueous urea solution (concentration at 50,000ppm) + 10% ethanol **(a)** and the same aqueous urea solution + 5% ethanol **(b)**. Plot was normalized with peak intensity (in a.b.u.) at excitation laser wavelength of 532 nm.

IV. SCWO Lunar Water Reclamation

A. Conceptual Design

Using the GRC SCWO reactor as a starting point, a concept of the system was generated in the form of a piping and instrumentation diagram (PID). This diagram is shown in Figure 7 and highlights five subsystems included for basic operation of the system. Starting at the heart of the entire system, is the tubular reactor. For purposes of this work, the reactor design considered for the ESM calculation is made according to the same specifications proposed for the design of the GRC lab reactor. Next, is the heating system that will also theoretically be similar in part selection to the GRC's reactor. The next three subsystems that were broken up into the air (oxidant), fuel (wastewater), and outlet systems. These three were simplified from their GRC counterparts to be streamlined for lunar applications as the GRC reactor has components deemed unnecessary for space travel. All five subsystems were then used to formulate a part selection for use in the next section. This section discusses the conceptualization a lunar-based SCWO reactor made for the sole purpose of supplying an early-stage lunar base with a reliable method for reclaiming wastewater.

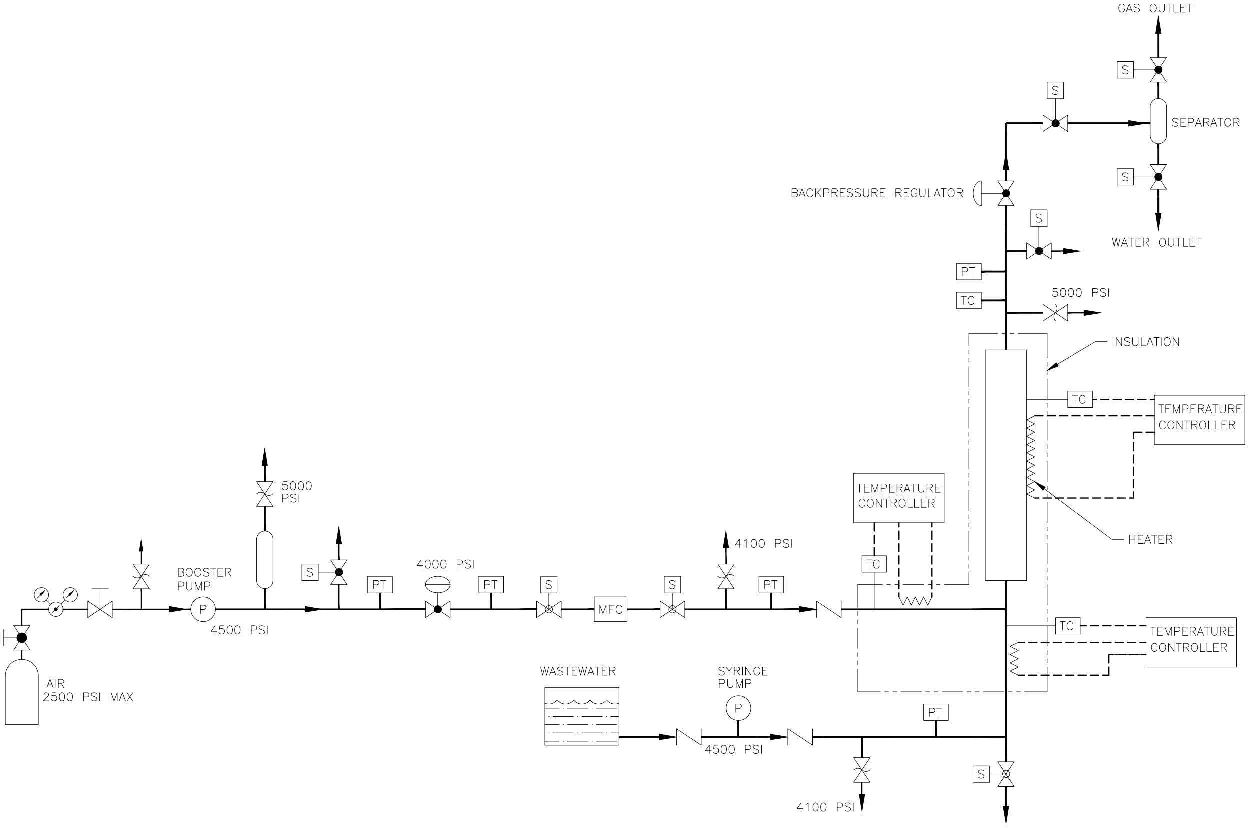


Figure 7: Conceptual Piping and Instrumentation Diagram (PID) for a Lunar SCWO Water Recovery System - Zeroth Concept (LSWRS-L0C) patterned after the lab-based system used in this study to perform SCWO water conversion tests.

B. Equivalent System Mass (ESM)

Validation of any system proposed for space travel must be done in terms of a cost analysis on a mission-to-mission basis and among similar systems that perform comparably to its desired function. Utilizing the most current Life Support Baseline Values and Assumptions Document (BVAD) [13] developed by NASA in 2015, it is possible to convert each component, its size constraints and energy requirements into an equivalent system mass (ESM) that can be used as a comparative basis with other options. Table 2 shows a very rudimentary analysis based on the lab reactor design and supporting infrastructure assuming hardware that is currently commercially available. A summation of the derived masses for each of the subsystems of the LWRS-LOC results in an equivalent system mass of about 174 kg. This total could be substantially reduced with a design that has been optimized for volume, mass and power requirement.

The 174 kg of mass of the LSWRS-L0C has no relevant meaning on its own and must be given context. This is done by assuming a mission profile of 30 days on an early-lunar base with a total of 4 crew members. Based on ratios provided in the 2015 BVAD, a total of 537.60 kg of water would be necessary to supply each astronaut for the duration of the mission. The LSWRS-L0C would not be designed to meet demand but instead would operate during dormant periods in between crewed missions. The goal would be to design the system to operate unattended and continuously such that the amount of water that has been recovered during the dormant period would be sufficient to meet the needs of crew for the subsequent mission.

Table 2: Equivalent System Mass of the Lunar SCWO Water Recovery System - Zeroth Concept (LWRS-0C) SCWO Water Recovery System

System Component	Equivalent Mass (kg)
Mass	64.14
Volume	11.06
Power	54.00
Thermal	44.62
Total	**173.85**

V. Conclusion

The tubular reactor developed at GRC appears to be suitable for applications in water reclamation and has been validated by means of Raman characterizations and TOC measurements that show conversion rates above 99% across multiple samples and diagnostics. Further iteration and research can generate higher yield and efficiencies within SCWO as knowledge of the technique matures. Using the data thus far, a conceptual design was created to perform a preliminary ESM analysis for a water reclamation system that is both reliable and cost efficient. Additionally, as the development of the concept continues , efficiencies in cost will be realized.

Acknowledgments

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