National Aeronautic Space Administration
Ames Research Center

Supercritical Water Oxidation (SCWO) Trade Study and 2021 Final Report

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Summary

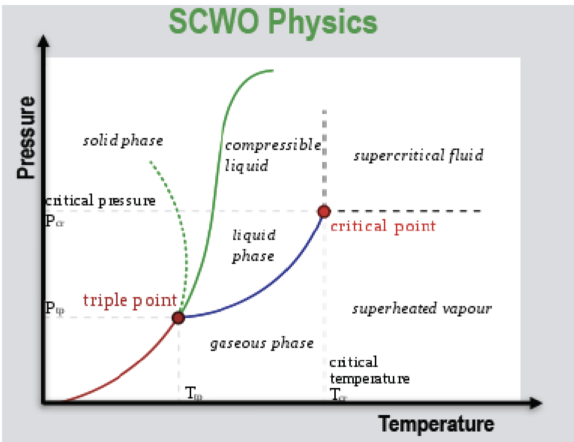
SCWO is a promising technology whose main benefits is that it is capable of completely mineralizing organic compounds in wastewater and separating inorganic salts. This means that SCWO can theoretically function as a single step water treatment system. It performs the functions of both the primary treatment system and the secondary brine drying function to achieve near 100% water recovery. It can also handle solids so no pretreatment of the feed is required. A preliminary trade study indicates that SCWO could be competitive with the ISS state of the art if its power consumption could be reduced. Thermal and mechanical energy recovery system exist that could reduce SCWO energy consumption to a level that is competitive with the state of the art. In addition, increasing the feed wastewaters organic content by including other wastes, such as feces, could produce a reactor that is thermally self-sustaining.

There are 5 different types of SCWO reactors. They are; tubular, tank, impingement, transpiring wall reactors (TWR) and super critical water mixing (SCWM) reactors. Of these the best suited for NASA missions are the impingement and SCWM reactors. The impingement reactor is best suited for near term missions because it can treat the low organic content wastewaters such as are expected for initial Lunar and Mars missions and has the ability to remove precipitated inorganic solids. The SCWM reactor is best suited for longer duration CELSS type missions where high organic content wastewater is available and will resolve solids fouling and corrosion issues. In addition, these two reactors have a long NASA heritage and have been developed specifically for space flight application. Tubular reactors suffer from plugging issues which is a safety concern. Tank reactors will increase in size inversely with gravity, which will trade poorly in Lunar and Mars environments where gravity is reduced. TWR reactors require high organic content wastewater feed and the SCWM reactor is an optimized version of the TWR for NASA applications.

It is recommended that in FY 2022 NASA continue to fully evaluate the ability of SCWO to produce potable water and remove inorganics as a solid byproduct. This should be done using the impingement reactor for near term missions and SCWM for longer duration missions. NASA should also develop optimized recuperative heat exchangers and pressure recovery devices to reduce power consumption and investigate inclusion of feces and other organic wastes into the wastewater model to increase its organic content and further reduce thermal energy requirements.

Introduction

SCWO technology is a high temperature and pressure process that can potentially produce potable water in a single step and achieve near 100% water recovery. SCWO works by using high temperatures and pressures to turn water into a plazma.[1] Under normal conditions, water exists in either of its three states: solid (ice), liquid, or gas. However, if water is exposed to high enough temperatures and pressures an additional phase that is neither a gas, solid or a liquid will emerge. This forth phase is called a plasma and only exists above the supercritical point (374.1 °C and 22.12 MPa). This state of water is known as supercritical water (SCW).[2] Figure 1 provides a pressure temperature diagram that shows the critical point of water. When this state is achieved water exhibits some unique characteristics such as a reduced hydrogen bonding, high diffusivity, zero surface tension, small dielectric constant, low viscosity, controllable dissociation constant, and excellent transport properties.[3] Moreover, under these critical conditions water begins to lose its polarity and starts to behave more like an organic molecule, becoming an excellent nonpolar solvent that is miscible for organics, gases, and other ionically attracted molecules. At SCW conditions salts, become non-soluble and will fall out of solution.[1,3,4] Figure 2 shows a solubility versus temperature diagram for some common salts found in wastewater at SCW conditions.



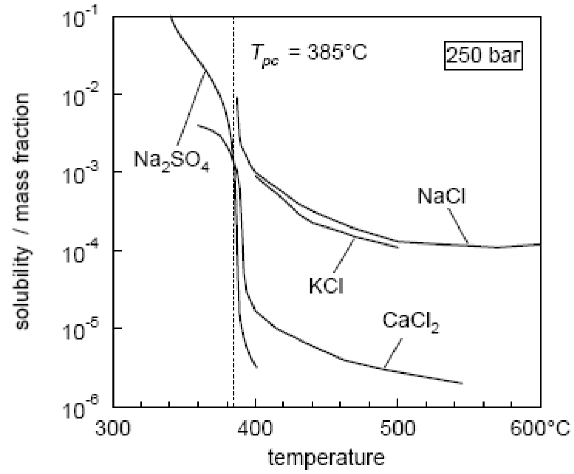


Figure 1. Pressure verse temperature diagram. Figure 2. Solubility verse temperature diagram

Oxygen is most commonly used as the oxidizing agent in SCWO and the reaction is considered homogeneous. The elevated temperature and pressures and unrestricted mass transfer possible at SCW conditions allows oxidation reactions to be carried out quickly in an aqueous medium and be complete (over 99%) in only a few minutes.[6] Some of the products found in SCWO are carbon dioxide, nitrogen, water, mineral acids, inorganic salts, oxidized ash, and heat. Typically, NO_x, SO_x, and dioxins are low.[3,7] In 1982 Timberlake S., et al, showed that when urea is exposed to temperature above 650°C at SCW conditions, the primary byproducts are carbon dioxide, N_2, water and a precipitated salt.

SCWO doesn't require pre-drying of waste streams, the reaction is fast, salts can be removed as a solid byproduct, the product is sterile, potable and near 100% water recovery is possible.[1] Although SCWO has never been tested using the current life support wastewater load model, Modar has tested SCWO using a mixed feed of feces, urine and wipes. [10] Some key results of this testing are provided in Table 1

I. Background information

SCWO was invented in 1982 by pioneer Dr. Michael Modell at the Massachusetts Institute of Technology. In the patent (4,338,199), he describes SCWO as a useful method that permits the use of a vast range of organic materials as a fuel in the desalination of seawater and brine or for the removal of specific inorganic salts from water. Since Modell's development countries like United States, Japan, Spain, France, Sweden, Ireland and Germany have all have active SCWO development programs. Through the last 3 decades there have been numerous companies and research institutions that have gotten involved in the business of developing and commercializing SCWO.

Table 1. Modar SCWO testing with NASA solid waste model feed [10]

Analysis (mg/L)	SCWO Product Water from 2.5% feces solids in H2O feed	SCWO Product Water from 2.5% feces solids in urine feed	SCWO Product Water from 3% feces solids with wipes in urine feed	SCWO Product Water from 4% feces solids with wipes in urine feed
Gas (mol%)				
O2	6.43	7.30	5.19	6.15
CO2	7.47	9.79	10.49	9.59
N2	-	0.17	-	0.12
N2O	-	0.03	-	0.11
Liquid (ppm)				
TOC	0.4	0.8	0.7	1.3
NH3	<1	8.2	1.9	3.5
Na	0.9	4.3	6.3	6.9
K	0.1	8.2	6.8	11
Ca	<0.1	<0.1	0.2	<0.1
Mg	<0.008	<0.008	<0.008	0.02
Cl	10	48	85	46
SO4	10	10	7	6
P	0.3	0.3	0.3	0.2
Cr	14	4.3	11	3.6
Ni	0.65	-	0.7	1.2
pH	2.8	3.1	2.8	3.3
Solids (wt%)				
Na	1.2	22.20	27.4	18.89
K	5	24.20	21.92	24.28
Ca	0.4	2.00	3.01	2.70
Mg	0.70	1.65	1.26	1.35
Cl	2.00	26.23	38.36	28.76
SO4	5.15	2.77	9.32	5.40
P	7.68	7.87	0.41	2.56
Cr	0.60	0.24	0.41	0.03
Ni	0.20	0.95	0.22	0.81
Fe	-	0.20	0.10	0.13
TIC	-	0.04	0.03	0.01
C	-	0.19	0.4	3.11
H	-	0.00	0.00	0.19
N	-	0.00	0.00	0.17
Density (g/cc)	-	1	1	1.2

The first ever commercial SCWO company, Modar Inc., was established in 1980 by Modell. His company focused on the destruction of hazardous organic waste.[10] In 1994 Modar Inc. delivered a SCWO system to NASA as part of a Phase II SBIR. Later, in 1996, Modell's company was bought by General Atomics, which has become the oldest active SCWO company as of today. There are also six other active entities that have their own SCWO plants. These are: SRI International, SuperWater Solutions, SuperCritical Fluids International, Innoveox, Aquarden Technologie and ENN Envirotech Co., Ltd. The last company, ENN Envirotech Co., Ltd, is the youngest active company to have been formed (2011) and has built one of the largest SCWO systems, 240 ton/day. In a 2020 review, X. Tang et al states that the University of Valladolid, University of Cádiz, Xi'an Jiaotong University and Shandong University are the four known research colleges capable of conducting detailed studies of SCWO. Table 2 summarizes the commercial and non-commercial SCWO plants recently active. [9]

Table 2. Recently active commercial and non-commercial SCWO plants.

Commercial Companies and Non-commercial Groups (recently Active)	Country	Year established	References
General Atomics	USA	1990	[11–13]
SRI INternational	USA	1990	[14,15]
Aquarden Technologies	Denmark	2005	[9,16,17]
SuperWater Solutions	USA	2006	[18,19]
SuperCritical Fluids International (SCFI)	Ireland	2007	[20,21]
ENN Envirotech Co., Ltd	China	2011	[22,23]
University of Valladolid	Spain	2006	[24–26]
University of Cádiz	Spain	2008	[27–30]
Shandong University	China	2011	[31–35]
Xi 'an Jiaotong University	China	2010	[36–39]
Japan Industrial Technology Research Institute	Japan	2007	[40]
University of Toronto	Canada	2008	[41]
University of Missouri Duke University	USA	2015	[42]

II. SCWO Process

In a Journal Review by Bermejo and Cocero, titled Supercritical Water Oxidation: A Technical Review it is explained that a general SCWO process consists of 4 main steps. These four main steps are: (1) feed pressurization, (2) reaction, (3) salt separation, (4) depressurization and heat recovery. Each of them is described below and shown in Figure 3.[43]

1. <u>Feed pressurization:</u> In a SCWO reactor, the feed consists of the wastewater and the oxidant. Usually, the oxidant is either pure oxygen or air. The wastewater feed and oxidant are pressurized separately to 22.1 MPa or more and then mixed together at the entrance or in the SCWO reactor. In some cases, where the organic content of the feed is high, a third input of pure water is also pressurized separately and used to control the reactor temperature by diluting the feed (not shown in Figure 3)

2. <u>Reaction:</u> An exothermic reaction occurs when the oxidant and the organic waste streams are mixed in the heated reactor at 700-750ºC and 22 MPa. Because the water exists as a plasma at these conditions, oxygen is fully soluble and inorganics are not. The high solubility of oxygen and the high temperatures drive the oxidation reactions quickly to

fill mineralization. The insolubility of inorganics causes their precipitation into a solid phase.

3. Salt separation: In the reactor, precipitated sticky and non-sticky salts are produced. These solids can be removed using filtration, hydro-cyclones or impingement canisters. If the salts are sticky, impingement canisters are typically used. If the salts are not sticky, filtration or cyclones are used. If the salts are not removed in the SCWO reactor they will eventually redissolve when the product is reduced below SCW point and will be present in the product water where they can be removed by reverse osmosis (RO) or other desalinization approaches.

4. Depressurization and heat recovery: At the reactor outlet liquid and gaseous products need to be cooled, depressurized to room conditions and separated into two phases. The product can be cooled by preheating the feed using a heat exchanger.[48] Pressure can similarly be recycled using a pressure recovery device to pre-pressurize the feed (not shown in Figure 3). If the organic content of the feed is high enough the SCWO will produce more energy than it consumes and electricity can be produced using a steam turbine (not shown in Figure 3).

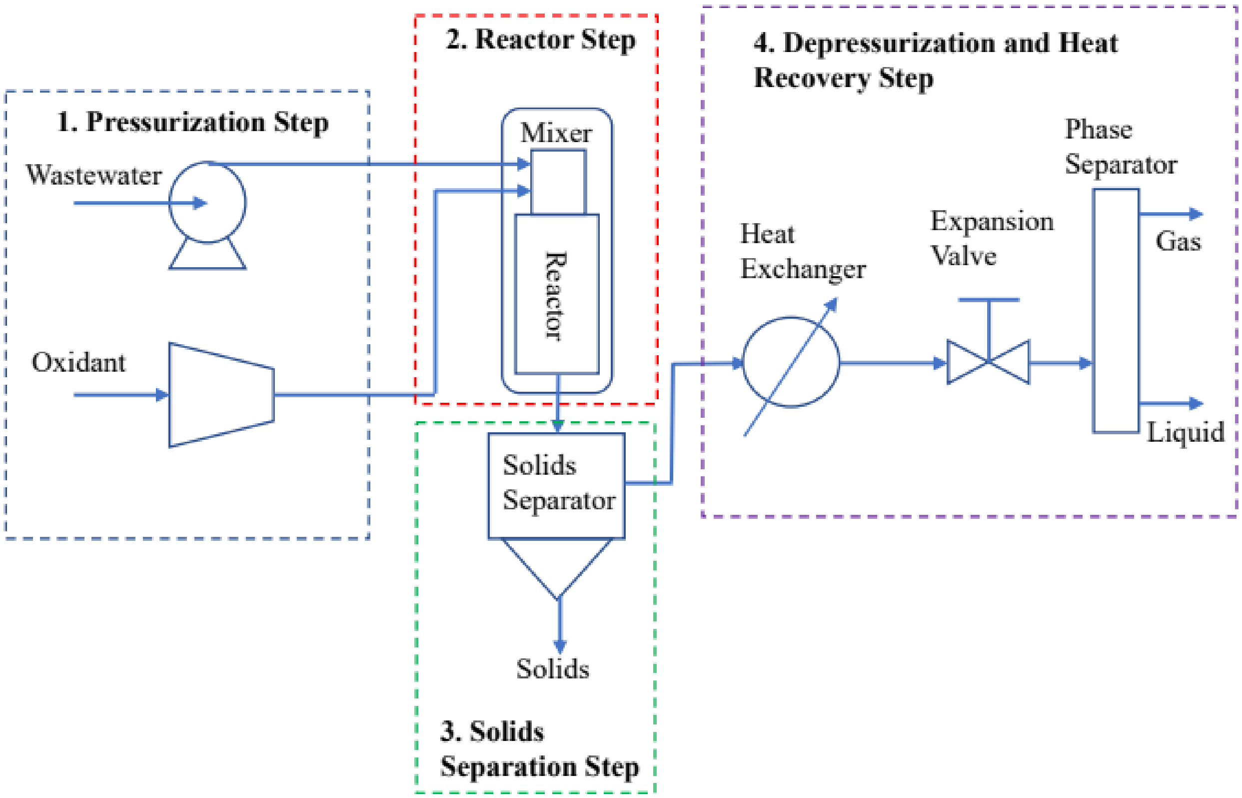


Figure 3. Diagram of four steps in typical SCWO system

A review of the relevant literature provides operating data that can be used to estimate the chericteristics of a theoretical SCWO treating a NASA model wastewater. Table 3 provides a description of the primary process variables, their impact and relevant references.

Main Operation Parameters	Details	References
Reaction temperature	Increasing the reaction temperature causes the reaction efficiency of the process to increases and the residence time to shorten. Typically, the oxidation of nitrogen compounds to N2 gas sets the upper temperature limit required for complete conversion. Reaction temperature around 650°C, require a residence time of <50 s for complete conversion.	44
Residence time	Vary from a few seconds to many minutes. It depends on the reaction temp and wastewater charicteristics.	43
Concentration of oxidant	Typically, an orders of magnitude excess in oxidant concentration over stochiometric requirements are used to insure complete oxidation .	45,88
Operation pressure	If the pressure is above the critical pressure of water (22.1 MPa) the plasma phase will be formed. Pressures much above this level do not appreciably improve reaction kinetics.	46,47

Table 3. Description of main SCWO operational parameters.

III. SCWO Problems

The SCWO technology is commercially available and as a result many of the technical hurdles to it utilization have been resolved. However, there are several inherent problems with the SCWO process that always need to be addressed, such as corrosion and salt precipitation. The insolubility of the inorganic salts in supercritical water remains a major technical challenge. The precipitate that forms can become concentrated in the systems reactor and plumbing, potentially leading to clogging, impaired heat transfer, and corrosion. Other significant problems are metal creep and corrosion.[3,8] Corrosion is particularly problematic and can be complicated by solids fouling. In 2017, S. Zhang et al. stated that of 15 commercial SCWO plants commissioned to treat a range of wastes, all had been shut down due to numerous mechanical, operational, and economic problems related to corrosion and salts.[3,49,50] Metal creep ultimately limits the maximum temperature that can be achieved for continuous operation.

Corrosion

Intense temperatures and high concentrations of dissolved oxygen, in the company of extreme pH values, elevated concentrations of ionic species (at subcritical conditions), and sharp pressure changes all make SCWO systems susceptible to corrosion.[43,51] The corrosion rate depends on the feed and materials of constructions used.[52] At SCW conditions metals suffer various alterations in morphology, color, and weight; also changes like pits, cracks, faceted grains, oxide dissolution, and spallation can to occur.[53,54] Marrone and Hong, 2009, Somerday et al., 2006, identified that the regions where the most severe corrosion develop are those where reactants/products are at the conditions just below the SCW point and solubilized ionic species are present. For example, piping used for preheating, cooling, and heat exchangers just before the SCWO reactor inlet and right at the inlet are susceptible to accelerated corrosion. Once in the supercritical sections the limited dissociation of ionic species reduces electrochemical corrosion but other types of corrosion persist.[52,55]

There are 4 dominant types of corrosion in SCWO applications: general corrosion, pitting corrosion, intergranular corrosion, and stress corrosion cracking (SCC); all of which are discussed in Table 4.

Table 4. Types of corrosion in SCWO

GENERAL CORROSION	PITTING CORROSION	INTERGRANULAR CORROSION (IC)	STRESS CORROSION CRACKING (SCC)
Attributed to a general instability of the oxide film causing corrosion to attack the entire metal surface. Occurs when a proctective layer is unable to be formed by the alloy components. In this type of corrosion, the aboslute material loss tends to be high. corrosion rate is lineal, can be considered in the wall thickness calculations.	Localized form of corrosion, occurs in the passive state of the metal. It is produced by aggresive anions (e.g. Cl and Br) that penetrate into the protective oxide film and locally destroy it. Generally, pit growths happen in high rates. High temepratures favor pitting corrosion, weakens the oxide film.	Not as critical as the other forms of corrosion. Enrichment or segregation of trace elements at the grain boundaries can posibly lead to harmful conditions. IC can be observed under nearly all conditions, especially when the penetration depth and amount of dissolved materials is low. May lead to SCC	Extremely dangerous form of corrosion. Nature and occurances are stochastic, thus the failures produces can be catastrophic. SCC is observed in high temp. water in the presence of H or O anions. Other harmful anions are CL, Br, and Sulfide. May lead to failure of the entire reactor that arises from leakage.

Salt precipitation

As mentioned earlier, aqueous inorganic salts in solution under SCW conditions are insoluble. These precipitated solids can cause problems of fouling, plugging and corrosion if not properly managed. Even in the presence of high velocity flows, precipitated salts can agglomerate and cover an equipment's internal surface hindering heat transfer. If the deposited salts are unable to be controlled, they can accumulate to the point of blocking flow paths such as the reactor, heat exchanger, transport lines, etc.[56,57] In the long term, the deposition of these salts may lead to failure/shutdown or even cause over pressurization. For this reason, it is extremely important to control precipitated salts to maintain safe operation.[37]

IV. Reactor Design

Numerous SCWO reactor designs have been developed over the years. In 1999, Schmieder and Abeln studied and divided these into different reactor concepts, the most commonly used are: tubular reactor, tank reactor and transpiring wall reactor (TWR). Table 5 provides a history of SCWO designs.

Table 5. Summary of SCWO companies and Research Institutes

Commercial Companies and Non-commercial Groups (recently Active*)	Countries	Reactor type	References
General Atomics	USA	Tank, doble tank	52,70,76,77
Aquarden Technologies	Denmark	Tubular	9,78
SuperWater Solutions	USA	Tubular	78,79
SuperCritical Fluids International (SCFI)	Ireland	tubular	2,21,78,80
Innovex		Multi-oxidant injection tubular	81,82
University of Valladolid	Spain	Transpiring wall and filmed cooled	83,84
University of Cádiz	Spain	Tubular	50,85
Xi 'an Jiaotong University	China	Transpiring Wall Reactor	37,39,86,87
University of British Columbia	Canada	Tubular	78,88

Tubular Reactor

Tubular reactors are the most widely used SCWO reactors. This type of reactor is used in several industrial SCWO plants.[58] Tubular reactors are also used in small laboratories dedicated to studying the viability of new SCWO applications.[59–66] SCWO reaction kinetics are pseudo first order with regard to the waste concentration. Hence, tubular reactors tend to be favorable since plug flow reactors are capable of achieving high conversions in short residence times. An example of a simple tube reactor is shown in Figure 4. In this configuration wastewater enters through the left side at pressure, is mixed with the oxidant and is heated in the tube using an external electrical mantle. The reactor shown is a batch process but continuous flow tube reactors do exist. Product exits through the right side as a two-flow mixture

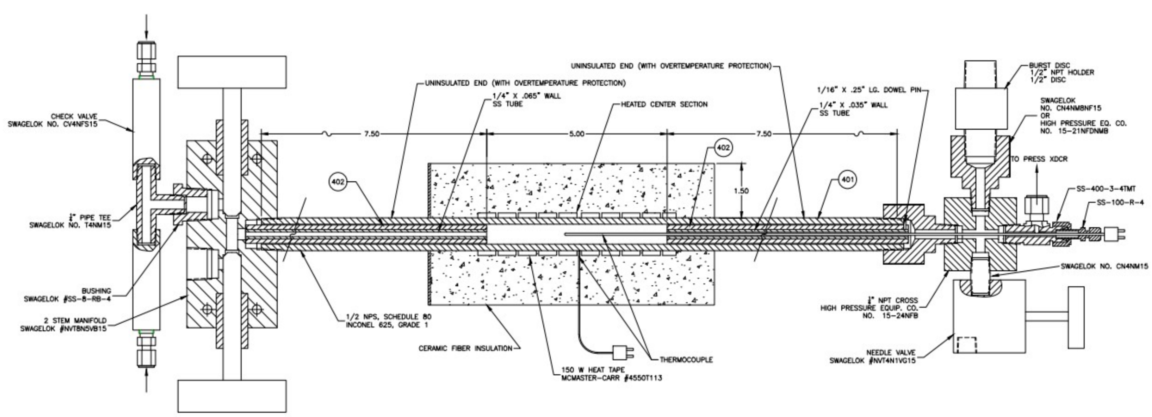


Figure 4. Diagram of Glen Research Center (GRC) Tube reactor

In a review by S. Zhang et al., several evident shortcomings of tubular reactors are pointed out, such as: (i) they possess a form factor that often results in a reactor size that is very long. (ii) the tube tends to plug as a result of salt precipitation and therefor they must be limited to low salt concentration wastewater, (iii) due to fast exothermic reactions, uncontrollable hot spots inside the reactor are produced, thus local overheating may occur causing safety concerns. (iv) the reactor design doesn't permit the pressure effect to be separated from the temperature effect, resulting in difficult control of temperature and pressure. (v) They require thick tube walls to accommodate high pressures, which increases the reactor's weight and cost.[3,43]

In order to address the above problems and optimize the tubular reactor design several new techniques have been developed in recent years. For example, tubular reactors have begun to be designed with smaller diameters to increase fluid velocity in order to try to prevent salt precipitation. Another approach is the use of two alternating reactors to manage the plugging issue. While one is being used the other one can be cleaned and vice versa.

A recent variation on the tube reactor is the multi-injection tube reactor shown in Figure 5. In this strategy, the use of sequential multi-dosing of feed, oxidant or quenching water can effectively eliminate the local overheating of traditional tubular reactor. Plus, this method can help enhance certain aspects of the reactors, like: energy integration, salt precipitation, creation of diverse reaction pathways, and overall efficiency improvement.

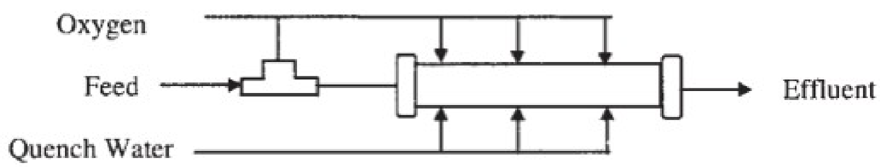


Figure 5. Scheme of multi-injection tubular reactor

Another modified tube design recently introduced is reverse flow tubular reactors as shown in Figure 6. This configuration has a single tube separated into two symmetric thermal zones. This design allows the process feed to be fed in either direction, thus making it possible to redissolve salt layers formed in one flow direction while the reactor is operating in the opposite direction. For this approach to work requires that the precipitated salts are soluble which is often not the case for life support wastewater.

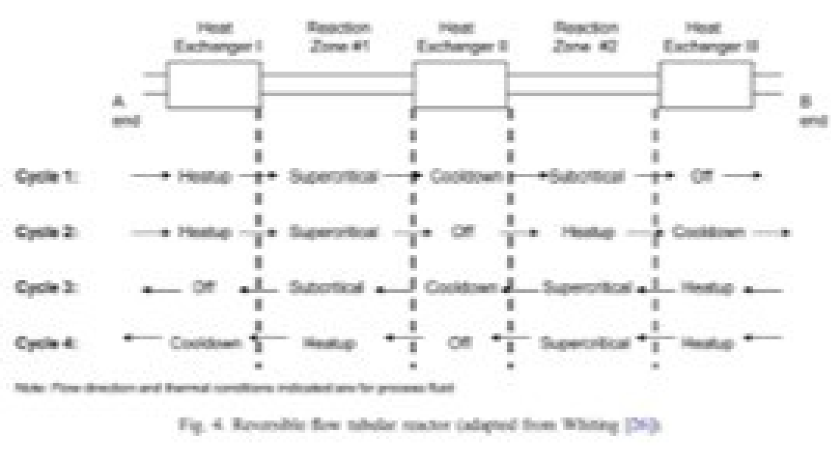


Figure 6. Operational scheme of reversible tubular reactor (adapted from Whiting [26])

Tank Reactor

The first reverse flow tank reactor was developed by Modar Inc. and is shown in Figure 7.[67] A Tank reactor consists of a cylindric vertical pressure vessel (elongated and hollow), capped at both ends so as to create an interior reaction chamber that has two distinct thermal zones.[68] The upper region of the reactor vessel is kept at supercritical temperature and the lower region of the vessel is kept at subcritical temperature. The feed enters the vessel through a nozzle jet that extends into the vessel from the top. This provides an agitation that permits the vessel to functions as a continuous stirred tank reactor (CSTR) in the supercritical zone.[69] Dense materials (e.g. salts) precipitate in the supercritical zone and fall by gravity, inertia, and forced conviction into the liquid phase at the bottom of the vessel. Here, in the subcritical zone the salts are redissolved forming a dense brine that is removed from the reactor.[70] In the commercial plant of Nittetsu (Japan) this reactor design is used for the destruction semiconductor-manufactured waste (treatment capacity of 63 kg/h). Also, in 1998 the Defense Advanced Research Projects Agency and the Office of Naval Research contracted Stone and Webster, to design a compact, automated shipboard unit using this reactor design.[43,70,71]

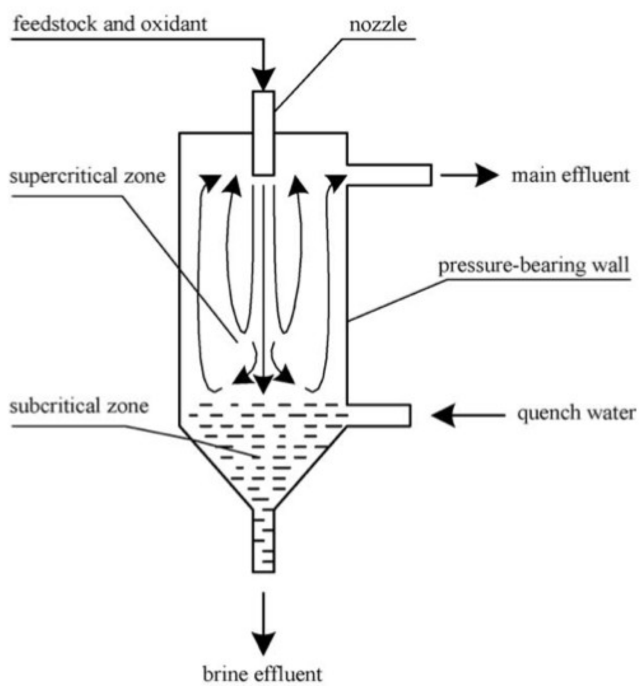


Figure 7. Schematic diagram of reverse flow tank reactor (adopted form E.L. Daman, Process and apparatus for supercritical water oxidation, U.S. Patent #5571423 (1996).

Transpiring Wall Reactor

Transpiring Wall Reactor (TWR) is a reactor designed to address the problems of corrosion and salt precipitation.[72] Currently, this reactor design is considered to be the most corrosion resistant configuration and is preferred when handling very hazardous or high salt contaminants.[37,73] The overall concept of this reactor is to keep salt and corrosive particles away from the reactor wall by introducing a flow of subcritical water through a porous reactor liner that creates a subcritical sheath of water that isolated the SCW from the reactor walls, see Figure 8.

In 2004, P.A. Marrone et al. published a SCWO article where they described an example of a TWR reactor design that was developed by Foster Wheeler Development Corp. in collaboration with Aerojet-General Corp. and Sandia National Laboratories.[74] Aerojet-General Corp. designed a cylindrical liner using technology developed for cooling of high-pressure rocket engines. This liner, capable of fitting within a tubular pressure housing, is composed of numerous thin metal layers or platelets bonded together; each of the platelets is engraved with a specific pattern of indentations.[75] When the platelets are combined to create the liner, a three-dimensional network of channels is formed. The channels are established to measure and distribute clean water through the liner into its inner surface, thus forming the outer subcritical boundary of the reaction chamber. This configuration is shown in Figure 9.

In this design the continuous film of water prohibits precipitated salts from adhering on to the reactor wall surface. This is done by sweeping away the solid particles in the flow from the internal surface of the reactor and/or by redissolving the salts if the temperature of the water is subcritical. Also, the uninterrupted flow of clean water that passes through the porous wall helps cool the wall and minimizes corrosive species from getting to the metal surface of the liner.[70] However, since the hot products are cooled and diluted when mixing with the cool transpiring water less energy is available for preheating the feed. In order to avoid any plugging problems, the salts need to exit the reactor as a subcritical solution, making the heat recovery less efficient.[43,70]

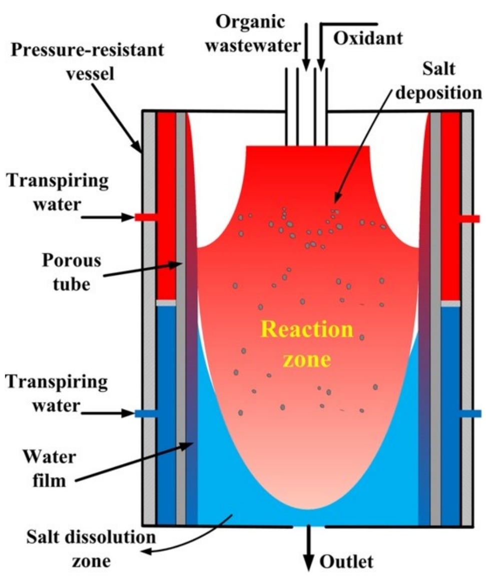


Figure 8. Diagram of generic transpiring wall reactor.

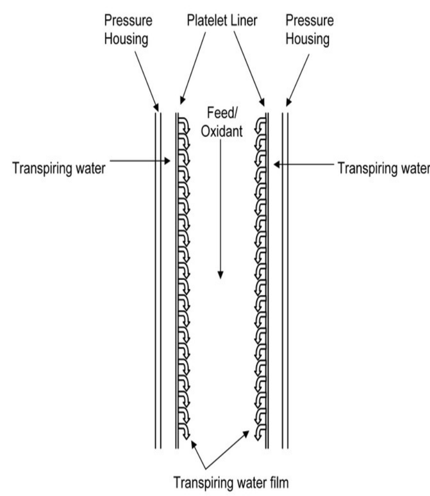


Figure 9. Foster Wheeler TWR reactor composed of numerous thin metal platelets bonded together.

There have been alternate designs of TWRs developed that involve different techniques and characteristics. For example, Xu et al. (2010) set forth to optimize the conventional TWR design by proposing a novel "TWM" reactor that combines the properties of TWR and MODAR reverse flow tank reactor. This novel concept reactor was designed and manufactured to treat sewage sludge by SCWO and it served as the core equipment for the first SCWO pilot plant in

China. This TWM reactor, see Figure 10, is divided into two zones, the supercritical above and subcritical below. Just like the Modar tank reactor, the precipitated salts found in the supercritical zone tend to fall towards the subcritical region where they redissolve. After salt removal, clean fluid flows toward the reactor top outlet and the equipped valves are used to regulate this flow rate. Also, the bottom outlet permits the dirty fluid (which contains a lot of salt and solids) to flow out of the reactor. This TWM flow pattern helps eliminate natural convention effect. A porous transpiring wall is combined with the pressure-bearing wall in this type of TWM reactor. Similar to the TWR, the clean and cool transpiration water pumped forms a protective film on the internal surface of transpiring wall to help decrease salt deposition and corrosion.[3,37]

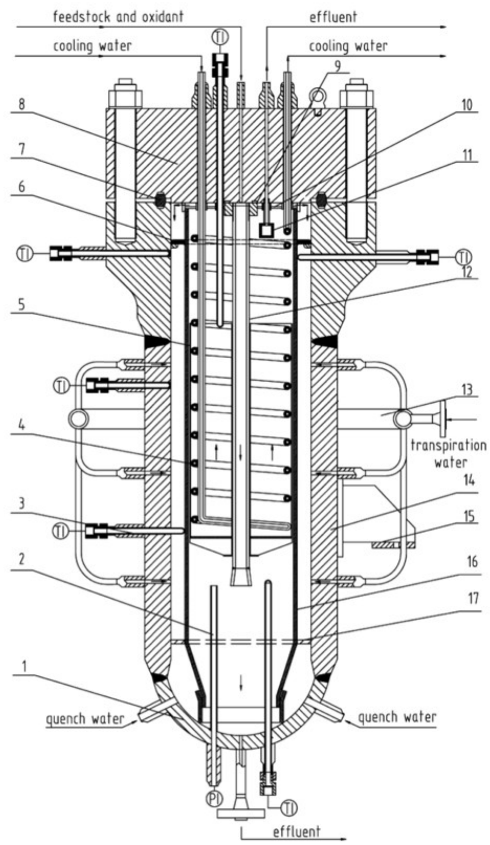


Figure 10. Schematic diagram of TWM reactor

V. SCWO design developments for space application

There have been two types of SCWO reactors developed by NASA over the last 3 decades. These are an impingement reactor, which is similar to a Tank reactor, developed by Modar Inc. and an supercritical water mixing (SCWM) reactor, similar to a TWR reactor, developed inhouse by Glen Research Center.

Modar/NASA Impingement Reactor.

Under a series of NASA contract in the late 1980s and early 1990s, Modar Inc., demonstrated the viability of processing human feces, wipes and urine in a continuous flow SCWO process.[5, 6 & 10] The results demonstrated near complete conversion of organic materials to CO_2 and organic nitrogen to N_2. In 1986 Modar demonstrated that the inorganic solids produced from treatment of human wastes are sticky salts (e.g. sodium chloride). Modar used this information to design a solid removal system for space application that used this “sticky” characteristic to remove salts. In 1995 Modar delivered to NASA an impingement canister SCWO reactor sized for an 8 person crew. The use of an impingement canister inside a tank reactor allows the SCWO reactor to exploit the stickiness of the solids that precipitate in supercritical water. A diagram of this impingement reactor is provided in Figure 11.

The NASA Modar reactor uses the impingement canister integrated into a 2 stage SCWO reactor that is shown in Figure 12 and 13. In this approach, the feed flows down from the top of the reactor and inorganic solids impinge on the bottom and side walls of a liner in the first stage impingement reactor. The plasma flow is reverses when it gets to the bottom of the impingement canister and flows back up though the reactor and out of the top reactor in the opposite direction that it entered. The plasma then flows into a second stage tubular reactor where full oxidation occurs. After an adequate collection period the Impingement canister liner fills up with solids and the system is shut down and the impingement canister liner is removed and replaced or cleaned. This is done by removing the head of the reactor pressure vessel and removing the internal reactor liner.[6] The removal of the impingement canister typically needs to occur in time frames from months to years, depending on wastewater feed inorganic concntrations.

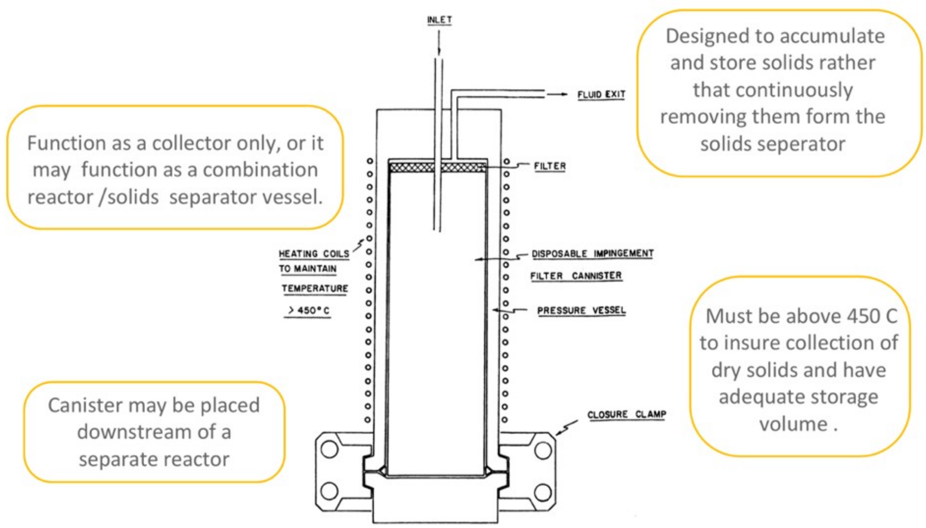


Figure 10. Schematic representation of an impingement canister

The NASA Modar SCWO reactor was delivered to NASA in 1995 and is currently located at Ames Research Center. This system is being upgraded to meet current pressure safety standards. Although the reactor was tested by NASA back in 1995 no data from these tests has been published. The testing in 1995 was focused on treating solid wastes such as inedible biomass in a CELSS life support system and the pumping system never successfully pumped these high solids wastewater to the required pressures.

Figure 12. Modar NASA Impingement SCWO

The flow path of the Modar Impingement reactor is shown in Figure 13. It is composed of two reactors, a first stage impingement reactor and a second stage tubular oxidation reactor. The first stage reactor separates out solids, mixes the feed with oxidant and heats the feed to a uniform temperature and the second stage tube reactor ensures the oxidation reaction proceeds to completion. The Modar SCWO also incorporated two recuperative heat exchangers to preheat the feed which are also shown in Figure 13.

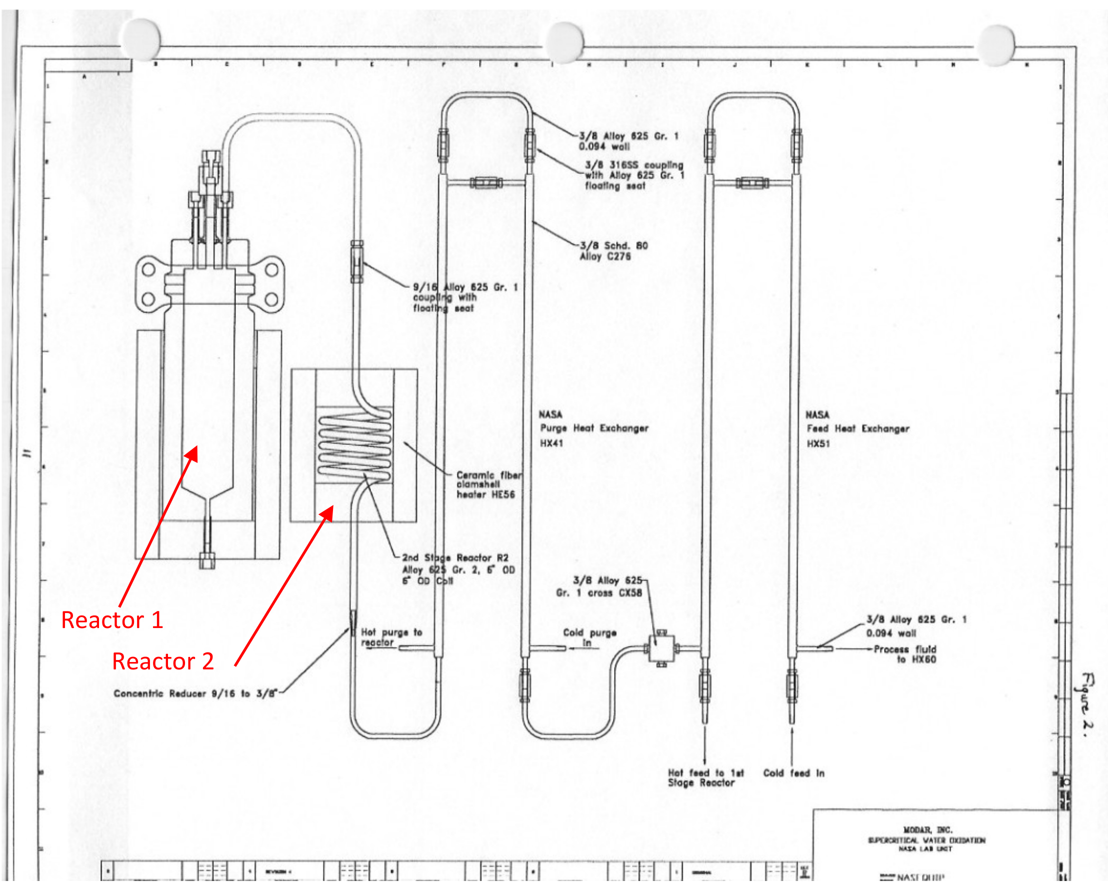


Figure 13. Modar NASA Impingement reactor flow diagram.

NASA Glenn Research Center, super critical water mixture (SCWM) reactor

NASA Glen Research Center has also developed a SCWO reactor that is similar to a TWR but uses parallel flow water sheaths to achieve the separation of SCW from the reactor wall. This system uses a hydrothermal flame to produce a self-sustaining SCWO reaction in a constrained region in the center of a plug flow of sub-critical water.

The conceptual design is shown in Figure 14. Figure 14 (left) shows the flow through a conventional tubular reactor and Figure 14 (right) shows the flow through the GRC SCWM reactor. The SCWM reactor uses a thermal flame to heat the internal core of a flowing plug of water. This heated super critical core is surrounded by a cooler sub critical sheath of water. This sheath of water protects the walls of the reactor from super critical conditions and redissolves any solids that pass from the supercritical region to the subcritical reagion. Eventually the core and sheath mix and all the fluid becomes subcritical causing most solids to redissolve.

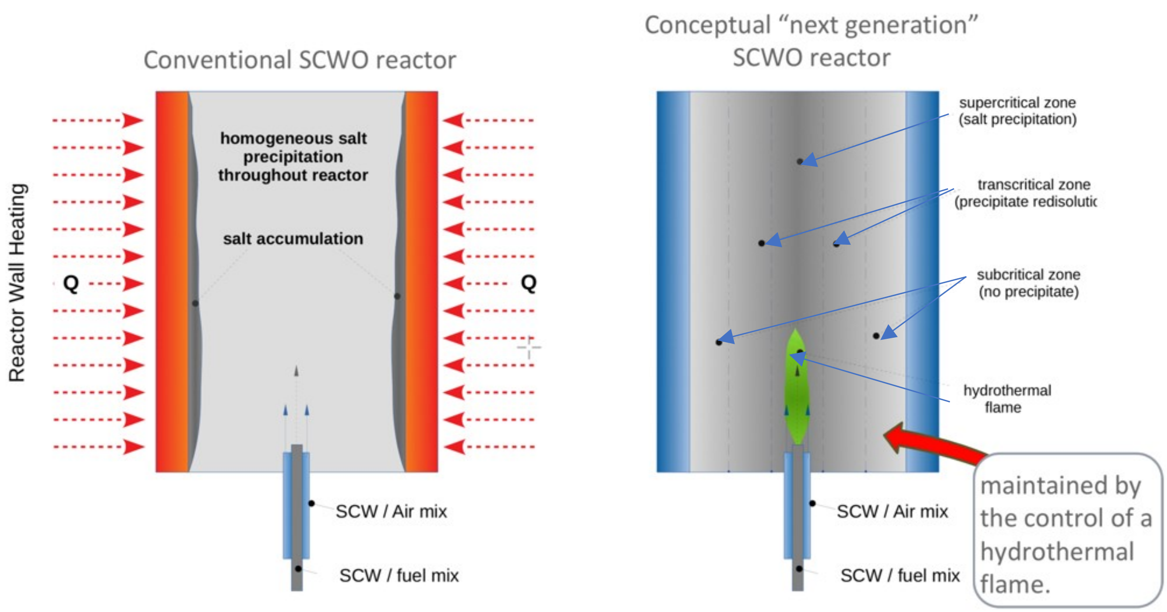


Figure 14. Conceptual design for GRC SCWM flow reactor. (Left) shows the flow through a conventional tubular reactor and (right) shows the flow through the GRC SCWM reactor.

The SCWM is heated by the organic content in the waste stream oxidizing exothermally to produce a hydrothermal flame. Hydrothermal flames were first described in 1985 by E.U. Franck.[89] These flames occur when the organic content of the feed is high enough (2.5 to 5%) that the oxidation process provides enough energy to make a self-sustaining thermal reaction. Throughout the years, many SCWO technologies have been proposed that use hydrothermal flames such as TWRs. Most salts that precipitate in the super critical region will be redissolve when they come in contact with the subcritical fluid. This minimizes the solids plugging and corrosive effects related to supercritical fluids.[1,90] t

The GRC SCWM reactor is flight qualified and has been flown to ISS as part of the NASA Microgravity Combustion Program in a payload known as the Supercritical Water Mixture Experiments (SCWM-series). This experiment was first launched in 2010 and is still onboard. SCWM-Series is an international set of investigations using the DECLIC facility, built and operated by CNES. Two SCWM-Series payloads were developed and tested on ISS. The objective of SCWM-1 was to observe SCW and determine onset of salt precipitation. The objective of SCWM-2 was to obtain phase transition points and transport properties of a tertiary CO_2, Na_2SO_4 and H_2O fluid. The SCWM reactor and flight payload assembly are shown in Figure 14 and 15.

Figure 14. SCWM SCWO reactor

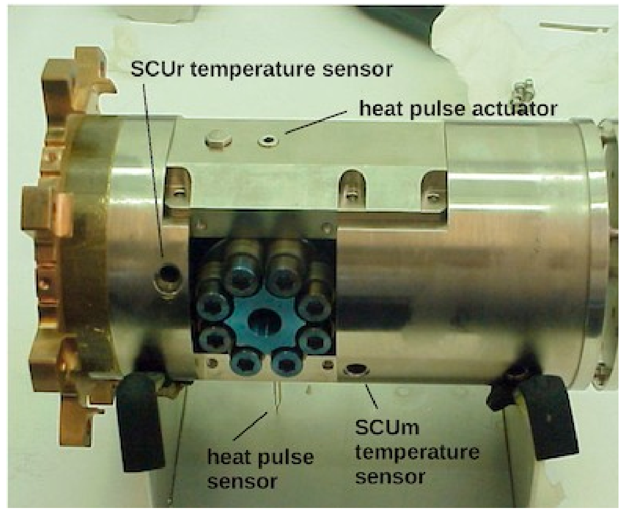


Figure 15. SCWM Sample Cell Unit (SCU) comprising the experimental cell in its housing

Glen has also recently patented an evolution of the SCWM that would be more applicable to NASA planetary missions. This reactor is called the Supercritical Flame-Piloted Vortex Reactor (SCFPV). The SCFPV reactor is shown in Figure 16. Some of the important features of the SCFPV Reactor are that corrosion and fouling of heat transfer surfaces are largely eliminated since the primary heat source, the hydrothermal flame, is internal to the reactor. Walls are only exposed to subcritical conditions. This is accomplished by maintaining an annular co-flow stream where the mass flow rate is modulated to ensure a sufficient outer layer of sub-critical fluid. Once a supercritical core region is established, mixing between the core region and the outer subcritical flow region is largely eliminated due to the large differences in density and viscosity. Depending on the hydrocarbon content of the feed stream (require ~ 5%) the flame will be used to sustain supercritical temperatures in the core region or will be used as a pilot to initiate supercritical temperatures and subsequently turned off once energy release from the reactants is sufficient to sustain the supercritical temperatures. The flow configuration is further stabilized by generating a vortex using helical vanes placed on the inside of the reactor wall. This will serve a dual role as a (i) flow stabilizer to prevent bulk mixing between the much denser subcritical liquid and the supercritical core region and as a (ii) mechanism for phase separation where precipitates will migrate to the subcritical fluid region.

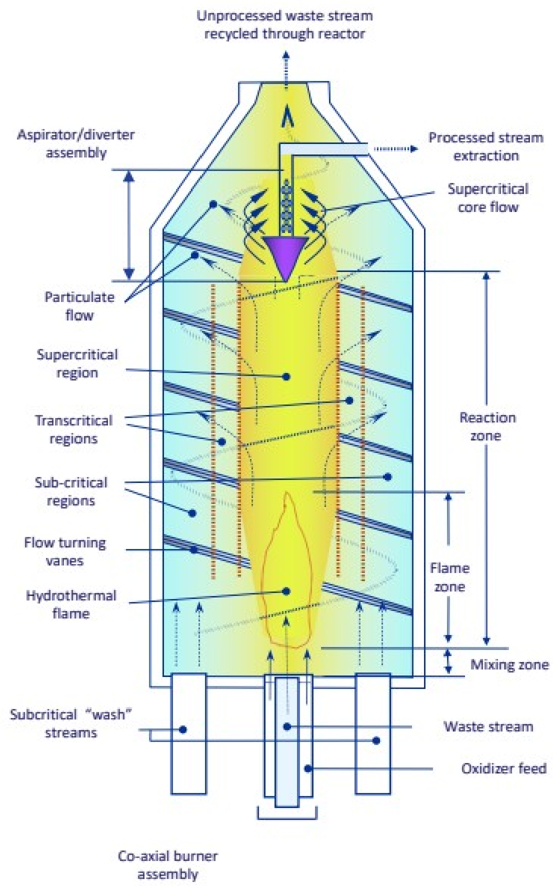


Figure 16. Schematic of Supercritical Flame-Piloted Vortex Reactor (Patent No. 10954152).

VI. Energy Recovery

Regardless of the SCWO reactor design used, getting the feed to its SCW point takes a lot of energy. For NASA applications, where the feed wastewater is relatively low in organic content, there is not enough energy in the feed to provide a self-sustaining reaction. Energy needs to be provide in the form of thermal and mechanical pumping. This requirement can be reduced though the use of regenerative heat exchangers to preheat the feed and pressure recovery devices that pre-pressurize the feed and oxidant streams. The NASA Modar SCWO at Ames utilizes multiple regenerative heat exchangers to preheat the feed.

In some cases the feed is sufficiently high in organic content the process can be sustainable and even a net energy producer. Many recent studies have evaluated energy recovery in SCWO.[91] The majority of these studies have evaluated SCWO as a prospective source for energy by exploiting the exothermic behavior of the oxidation reactions of very high organic content feeds. In 2002 Cocero et al. conducted a SCWO energy study utilizing the software Aspen Plus®.[48] Two years later Bermejo et al. looked at energy recovery of SCWO treatment of a coal slurry using a steam turbine to produce electricity.[92] In 2008 Marias et al. proposed using an auxiliary fluid to run a steam turbine. Marias et al. claimed that it is feasible to recover approximately 627 kW from a stream at 650 °C and 30 MPa processing 900 kg/h of high strength wastewater.[93] In research done by Svanstrom et al. SCWO energy recovery was simulated from sewage sludge (10% weight) using Aspen Plus® software. The results indicated that the reactor effluent could be used to both produce electricity and heat a municipal water stream.[94] A more recent study conducted by Jimenez-Espadafor et al, indicated that SCWO treatment costs could be decreased by recovering energy using a steam generator and feed preheating.[95 54]

VII. Discussion

SCWO reactors are primary of four types: Tubular, Tank, Impingement and TWR (or SCWM). Of these three, the TWR has recently become the most popular. This is because the TWR reduces corrosion and addresses the precipitation of salts. However, a TWR reactor requires the use of a hydrothermal flame for heating and this requires a higher organic content feed than the current life support wastewater Model [6, 5, 10.] Tubular, Impingement and Tank reactors can treat low organic feeds and theoretically can remove inorganic salts but have other drawbacks. Table 6 provides a comparison of each of the reactors studied for each of the key SCWO performance parameters. An “x” entry is a negative determination.

Table 6. A comparison of the 5 studied SCWO reactor designs to key performance parameters for NASA missions. Note that an “x” entry is a negative determination.

Reactor Type	Water Quality	Corrosion	Solids Fouling	Solids Separation	Plugging Potential	High Organic Feed	Complexity	Ease of Automation	Gravity Dependance	weight	Pumping	volume	Safety
Tubular		x	x		x			x					x
Tank		x	x				x		x	x		x	x
Impingement (Modar)		x	x					x		x		x	
TWR				x		x	x				x		
SCFPV (GRC)				x		x	x				x		

Table 6 demonstrates that all of the SCWO reactor designs have different strengths and weaknesses. For the Tubular reactor the “Plugging Potential” category is a show stopper. This is a safety issue and there is no simple solution to this problem. Tubular reactors can be expected have short lives, high maintenance requirements and safety will always be a concern.

Another potential show stopper category in Table 6 is “High Organic Feed”. The current Life Support wastewater model, for either planetary or spacecraft applications, does not have a high organic feed. At least not high enough to support a self-sustaining reaction or a hydrothermal flame. Either additional organic wastes, such as feces, or some sort of resupplied fuel would be required.[6] This is a problem for both the TWR and SCFPV reactors. These reactors use self-sustaining reactions such as hydrothermal flames. These types of rectors are more applicable for long duration missions where larger quantities of organic wastes from food production are available.

Another problematic category in Table 6 is “Gravity Dependence”. Current NASA missions are Lunar and Mars which both have reduced gravity. The Tank reactor uses gravity to separate out salts. Although the approach will still work in reduced gravity, residence times and reactor volumes will scale inversely with gravity. In reduced gravity, Tank reactors could get very big. Big reactors at high pressures and temperature can get dangerous.

For early planetary missions the impingement reactor offers the most advantages. This is not unexpected because it was designed by Modar specifically for NASA Life Support applications.[5, 6 & 10] For example, NASA has previously funded Modar to conduct urea destruction [5], solids treatment [6], the fate of metals [97] and trade studies designed to optimize the SCWO design. [10]. The cumulative results of these studies is the Modar impingement reactor.

The Modar reactor is externally heated with an electrical jacket around each reactor so it is able to treat low organic wastewater like the current life support planetary wastewater model. [10] It is not subject to plugging because it is designed specifically to precipitate and separate inorganic solids in a reactor liner. The Modar reactor also does not need gravity to function. It uses a change in velocity direction rather that a directional field defined by gravity to separate salts.

The main drawback of the Impingement reactor is that the impingement liner needs to be replaced. This is not an easy task and will require human interaction or a complicated automation approach. The impingement reactor will also always have higher mass and volume than the Tube or TWR reactors because it requires a larger dead volume at SCW conditions.

The Modar impingement reactor was sized for an eight person planetary mission. This has allowed us to disassemble and weight the key reactor components and measure volumes. In addition, previous Modar testing using a prototype of the delivered system, can be used to estimates power consumption. [10] Using this data, a preliminary comparison between the Modar SCWO and the current ISS state of the art was prepared. The results of this trade study are provided in Table 7. The SCWO data in Table 7 is ½ of the measured mass and volume of the actual Modar system.[10] This was done in order to provide a scaled comparison to the 4 person ISS systems. SCWO mass and volumes used include only the critical reactor components. It does not include the feed pump, air compressor or control electronics. The SCWO components included in the trade study are shown in Figures 13 and 17. ISS WRS data is from Flynn, et al, 2015 [98] and brine data is from Shaw, et al, 2015 [99]. The SCWO reactor takes the place of both the ISS WRS and brine drying functions.

Table 7. Modar Inc. SCWO trade study comparison to ISS water recovery system (WRS) and brine drying state of the art

Technology	**Mass**	**Vol**	**Power**	**Heat**	**S&E Mass**
Units	Kg	M^3	W	W	Kg/90days
ISS WRS	744	1	320	320	22
Brine Dry	65	0.1	165	165	?
SCWO	118	0.6	811	930	5
SCWO Savings	85%	45%	-67%	-67%	>77%

As shown in Table 7, the Modar Impingement SCWO reactor is competitive with the current state of the art in mass and volume but considerably higher in power and heat. The integration of energy recovery approaches could reduce SCWO power. Increasing the feed organic content to the point that the SCWO reaction is self-sustaining would also help to reduce thermal energy consumption. The results of this initial trade study shows that energy is a key development tall pole for the future of SCWO.

Figure 17. SCWO components used in trade study. Shown are both reactors and all heat exchangers, heaters high pressure plumbing and phase separators.

VIII. Conclusion

SCWO is a promising technology whose main benefits is that it is capable of completely destroying organic compounds and precipitating out inorganic salts. This means that SCWO can theoretically function as a single step water treatment system. It performs the functions of both the primary treatment system and the secondary brine drying system to achieve near 100% water recovery. It can also handle solids, so no pretreatment of the feed is required. The SCWO product water should meet NASA potable standards, with the exception of pH. This technology has been under development for decades and operating commercial system exists.

Most of the commercial SCWO operations, past and present, are using high organic content wastewaters. This is because if the organic content of the feed is high enough the SCWO reaction is self-sustaining. If it is two low then more electrical energy is required to maintain temperature. If organic content of the feed is low, energy use can be offset by integrating energy recovery approaches, both thermal and mechanical.

Reactors that require the use of a hydrothermal flame will only trade well as the feed organic content increases. As a result, there are two scenarios that are of interest to NASA. The first is the current Life Support wastewater model which includes urine, flush, humidity, hygiene and cloth wash and a second longer term planetary CELSS based wastewater model that has higher organic content due to food production and the inclusion of feces in the wastewater.

For the low organic content waste scenario, the Modar impingement reactor seems to be the best approach. It can be heated with electrical energy and adapted to use energy recovery approaches. In fact, the NASA Modar reactor already includes thermal energy regeneration. The Modar Impingement reactor also demonstrated a competitive, but preliminary, trade with the existing ISS state of the art and exists as a near operational prototype.

For the CELSS scenarios the TWR and SCFPV reactors seem to be the best. They offer a solution to the corrosion and solids plugging issues and should be lower mass and volume than the Modar approach. The fact that they do not sperate out the salts can be resolved by integrating a down-stream reverse osmosis system. This will increase mass and volume slightly and reduce the maximum water recovery ratio possible but it offers a more stable, automatable and reliable design approach.

Regardless of the SCWO reactor system design selected both thermal and mechanical energy recovery will be important. The preliminary trade study presented in Table 6 demonstrates that the impingement reactor design is competitive with the state of the art except in power. The best way to reduce this is to implement advanced energy recovery approaches both thermal and mechanical and to increases the organic content of the feed.

Another key concern with SCWO is safety. The question is, could a SCWO system ever be approved for flight by NASA? This question has already been answered by the GRC SCWM reactors that are approved for flight and currently on ISS. In addition, ongoing work with the Modar reactor at Ames has demonstrated that ASME Codes and NASA pressure safety standards allow SCWO conditions and materials exist that can be used to qualify a reactor for continuous operation.

IX. Recommendation

The first step in the development of SCWO is to verify that it can reliably produce potable water using a representative planetary life support wastewater model. This was actually a FY 21 task but due to Center access restrictions, as a result to COVID, it will only be partially completed this year when GRC tests 2L of planetary simulated wastewater, provided by TTU, in the GRC tubular reactor, shown in Figure 4. These tests have not yet been complete at time of writing this report. Regardless of the results of this test, more testing will be required next year in order generate a more statistically valid body of data and allow for optimization of reactor conditions. This will require utilization of larger, more representative quantities of wastewater tested under a wider range of operational conditions. Specifically, we need to perform tests using the Modar reactor and the current planetary life support wastewater model in a mode that simulates a continuously operating SCWO system. This will insure that SCWO can reliably meets NASA potable standards under realistic mission conditions.

Assuming that this testing demonstrates that the SCWO is capable of producing potable water, the next question is what type of SCWO reactor should NASA be developing. NASA currently has an operational version of the Modar Impingement reactor and a flight version of the GRC SCWM reactor. The Modar reactor is at Ames and is a full-size (8 person) continuous duty system. The SCWM reactor is research scale and is currently on the ISS. Plans are underway to develop a next generation SCWM in collaboration with the European Space Agency (ESA) and fly it by 2024. Glen has also recently patent the next generation of a SCWM reactor which is more appropriate for an operational NASA life support applications called the SCFPV reactor. These two reactor designs, the Modar Impingement and SCFPV reactors, represent ideal candidates for both near and long-term NASA missions. They also represent examples of the two broad categories of SCWO reactors. The Impingement reactor is an evolution of the Tubular and Tank reactors that remove solids in the reactor itself. The SCFPV is an evolution of the TWR reactor that allows solids to pass though the reactor for down-stream separation. These two reactors allow NASA to conduct tests with both high and low organic content wastewater and allows the testing of the two principal methods of solids separation.

NASA should also address energy consumption for either of these reactors by develop higher efficiency thermal energy recovery exchangers and pressure recovery systems. The thermal heat exchangers used in the Modar reactor use a thick-walled shell and tube design where each tube is thick enough to withstand total pressure under SCW conditions. This drastically reduces the heat transfer coefficient of the exchanger because of the thickness of the heat transfer surface. It is also not needed because the pressure difference between both sides of the exchanger is much lower than the total SCW pressure. An inner, thinner wall heat transfer tube could be used in the heat exchangers and as long as the outer shell tube is still thick enough to withstand SCWO pressures it would meet NASA and ASME pressure safety code requirements. It is therefore recommended that NASA developed heat exchangers designed specifically for this unique application. It is expected that such a heat exchanger exchange could drop thermal energy requirements by 30% for the Modar impingement reactor.

Pressure recovery system have been widely used in the reverse osmosis industry and although they are design to operate at lower pressures, 2000 psi versus 4000 psi, the design concepts should carry over to the higher pressure operation. NASA should develop a version of a pressure recovery devices that is rated to SCWO pressures. It is expected that such a pressure recovery system could drop mechanical energy requirements by 75% for both the Modar and SCFPV reactors. Implementation of these two energy recovery approaches could drop the SCWO energy requirement to levels competitive with the current ISS state of the art and would have a positive impact on any trade future study comparison.

X. Acronyms

CELSS	closed environment life support system
CENS	National Centre for Space Studies
DECLIC	Device for the Study of Critical Liquids and Crystallization
GRC	Glen Research Center
ISS	International Space Station
RO	reverse osmosis
SCC	stress corrosion cracking
SCFPV	Supercritical Flame-Piloted Vortex
SCW	supercritical water
SCWM	supercritical water mixing
SCWM-series	Supercritical Water Mixture Experiments
SCWO	supercritical water oxidation
TWM	transpiring wall mixing
TWR	transpiring wall reactor

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