Design And Operation of a Supercritical Water Oxidation Reactor for Wastewater Reclamation During Long Duration Space Flight

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Supercritical water oxidation (SCWO) has been a topic of immense interest as an effective technique/tool for hazardous aqueous waste disposal. SCWO can be achieved by introducing an oxidizer (e.g., H2O2), or a hydrothermal flame as an internal source of both heat and oxidizer species in an aqueous environment at conditions above the critical point of water (P > 221 bar and T > 374°C). SCWO poses important environmental advantages for the treatment of harmful organic materials contained in waste streams. An SCWO reactor has the potential to be compact in design and therefore can be an ideal alternative to existing technology for wastewater reclamation during long-duration space flight. To understand the key processes involved in SCWO, it is necessary to conduct canonical experiments to obtain fundamental insight into the different coupled processes. A continuous flow SCWO reactor has been designed and fabricated that can operate at a maximum flow rate of 10 mL/min. The SCWO is fabricated out of Hastelloy X to handle the extreme supercritical conditions of water. Two window ports are installed to be able to conduct visualization. Several structure and flow modeling were performed to assess the design integrity. The reactor was tested to achieve supercritical conditions under non-reacting conditions. Schlieren visualization was performed to record the transition from subcritical to supercritical conditions. It is envisioned that the reactor will be used for fundamental experiments.

I. Introduction

Water is a vital resource in space missions due to its many important functions. Despite water conservation efforts, a considerable amount of water is still consumed daily. Each crew member aboard the International Space Station (ISS) typically uses a gallon of water per day for hygiene and consumption. Water is also used for space farming and in oxygen generation systems. In total, a crew of four astronauts on the ISS requires approximately 12 gallons of water each day, with the cost of resupplying water at $83,000 per gallon [1]. Resupplying water becomes even more challenging, and sometimes impossible, for long-duration space missions. Therefore, it is imperative to have a system for recycling wastewater. **S**uper**c**ritical **W**ater **O**xidation (SCWO) is a promising technique for removal of hazardous organic waste from aqueous waste. At pressures and temperatures above water's critical point (P > 221 bar and T > 347 °C), organic compounds become highly soluble in water, facilitating rapid reaction rates when an oxidizer is introduced to the system. Furthermore, the potential for SCWO to be compact is crucial for space vehicles due to their limited size. Improving our understanding of the SCWO process is necessary to determine its effectiveness for water reclamation.

Gotti et al. [2] proposed a SCWO reactor capable of generating hydrothermal flames. This compact reactor, shaped like a cube with 10.5-cm sides has a total working fluid volume of 80 mL. Additionally, it includes two viewing windows to visualize the flow entering through the co-flow nozzle. The simplicity of this design avoids complex manufacturing methods. The reactor's material, Inconel 625, was selected for its excellent tensile properties and

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corrosion resistance. Furthermore, the flange design gives the reactor a lot of versatility in terms of which sensors can be attached to the reactor body. Another common SCWO reactor type features a downflow configuration, favored for its straightforward design and ability to maintain uniform temperature profiles [3]. A downflow-style reactor is essentially a tubular reactor where SCWO processes occur. The oxidizer and fuel are injected from the top of this reactor and reaction processes take place near the inlet region. These reactions are exothermic, increasing the local temperature of the fluid and establishing a uniform temperature distribution. Comparing these two designs reveals that they cater to different experiments, each with its unique advantages and disadvantages. A significant distinction is the absence of a visualization window in the downflow reactor, a requirement outlined in Section III. The first design also allows for a larger variety of sensors to be attached to the reactor due to its use of flanges.

This paper describes the design of a continuous flow reactor that is capable of producing super critical water oxidation conditions with ethanol being the fuel source representing organic compounds present in wastewater. There are many important considerations that must be made when designing an SCWO reactor to ensure that it is capable of completing its function while being safe to use. The design process for this reactor is described in detail starting with identifying the key design-driving requirements.

II. Design Requirements

The primary goal of this reactor is to bring an aqueous fuel solution (ethanol in this instance) to water's supercritical state and introduce an oxidizer to initiate oxidation reactions. The reactor's product fluid can then be analyzed to determine the quantity of water generated during the reaction processes. **Table 1** describes additional requirements and constraints for this system that dictate the design of this reactor.

Table 1 Design requirements

	Requirements	Compliant?
1	All systems must withstand an operating pressure of 275 atm	C
2	All systems must withstand an operating temperature of 700 K	C
3	All systems must withstand the operating conditions with a reasonable safety factor	C
4	The system must be controlled remotely	C
5	The reactor must have a maximum continuous flow rate of 10 mL/min	C
6	The flow rates of the working fluids must be controllable	C
7	The reactor must have viewing windows for visualization	C
8	The operating fluid parameters (pressure and temperature) must be recorded	C

Initially, eight requirements were established to govern the SCWO reactor's design. The right column shows each requirement's compliance, all of which the reactor design has met. The first two requirements are set to ensure that the systems can handle the conditions required for supercritical water plus some headroom. This establishes a supercritical water operating pressure range from 220 atm to 275 atm and a temperature range from 650 K to 700 K. The third requirement is necessary because this system operates at extreme conditions and yielding of material can cause serious injury and completely kill this project. To enhance safety, the entire system is designed for remote control, thereby minimizing the risk of injury to operators. Given SCWO's novelty and the exothermic nature of oxidation reactions, careful consideration must be given to the amount of fuel injected into the reactor. Because material tensile properties diminish with temperature, the fifth requirement aims to limit heat generation from the reactions. The remaining three requirements deal with the ability to control the system to gain an understanding of SCWO. Manipulating the flow rates of the oxidizer and fuel will give important insight into SCWO processes. The requirement to have two visualization windows is a major design-driving requirement, as discussed in sub-section III.A.3. These windows will facilitate the use of shadowgraph imaging for flow visualization. Measuring pressure and temperatures at various system points is crucial for control and documentation, as these parameters significantly influence the reactions. All of these requirements work collectively so that the reactor system can satisfy the operating conditions.

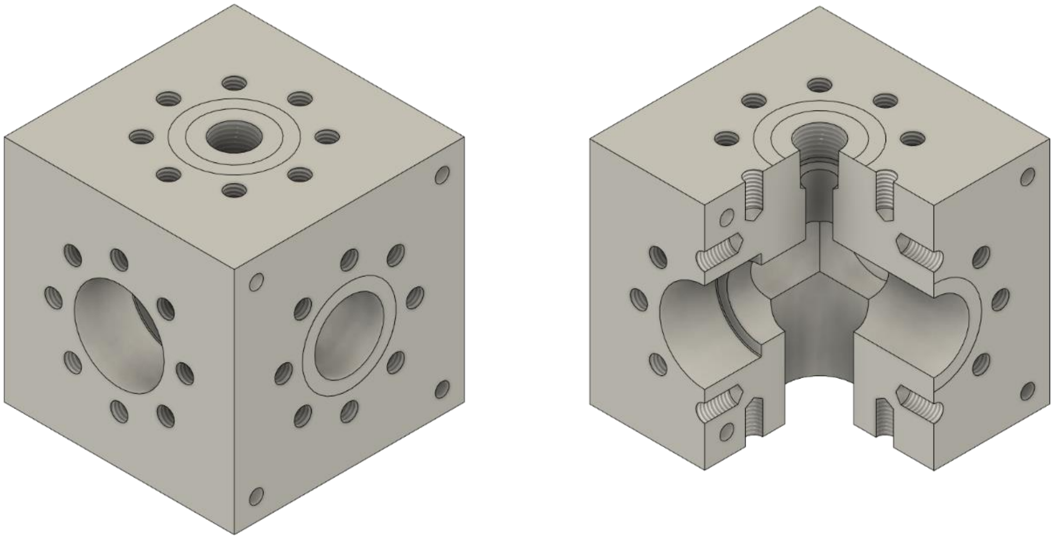
III. System Design

Leveraging insights from the literature search, we designed a custom SCWO reactor and accompanying systems to meet the defined requirements. Each sub-system has been carefully planned to align with and fulfill the project's overarching goals. The primary sub-systems include the main reaction chamber, the flow control system, and the data acquisition system. Each of these sub-systems plays a crucial role: the main reaction chamber is where the SCWO reactions occur, the flow control system regulates the input of reactants to ensure optimal reaction conditions, and the data acquisition system captures vital operational data for analysis and optimization.

A. Main Reaction Chamber

1. Dimensions

The most important part of this reactor is the main reaction chamber. All other systems are designed around this section, which is the locus of the SCWO processes. Six components need to connect to the main reaction chamber: the inlets, outlet, two viewing windows, a thermocouple, and a pressure transducer. A cubic-shaped reactor, akin to the design in [2], can accommodate all these components on its six sides. Figure 1 illustrates the exterior and a sectional view showing the interior of the reactor, respectively. This reactor design has six orthogonal holes, and the center is where most of the SCWO reactions will take place. Given the reactor's low flow rate requirements, its internal volume is a mere 150 mL, allowing for a compact design that saves on materials and manufacturing costs. The side length of the cube is 10.6 cm, and the orthogonal hole diameters are 4.13 cm for the two window ports, 1.27 cm for the outlet, and 3.18 cm. for the remaining sides which house the inlet nozzle and sensors. A circular hole pattern on each side facilitates the mounting of flanges, connecting the six components to the reactor. Each flange is sealed with a silver metal C-seal, chosen for its oxidation-resistant properties. Sealing performance is improved by adding a circular lay finish around each hole where the metal seals are located. The two window holes do not have this feature for reasons described in sub-section III.A.3. As seen in the images below, the right side of the reactor body has four small holes near the corners. These holes are added to house four heating cartridges which were going to be used to pre-heat the reactor. However, heating cartridges do not provide a uniform temperature distribution, rendering these holes superfluous.



(a) **(b)**

Fig. 1 (a) Reactor chamber orthogonal view and (b) sectional view.

2. Material

Hastelloy X was selected as the reactor material due to its tensile properties at elevated temperatures and superior oxidation resistance. At the operating temperature of 700 K, Hastelloy X has a yield strength of 301 MPa and ultimate tensile strength of 650 MPa [4]. The oxidation resistance of Hastelloy X is outstanding at elevated temperatures, experiencing a metal loss of 0.007 mm per side at a temperature of 980 °C for 1008 hours [5]. Thermal expansion is an important consideration for high temperature applications, so the flanges and bolts are also made out of Hastelloy X, allowing all of the components to expand together. It is especially important to have Hastelloy X bolts due to a risk of diffusion bonding, which can occur between dissimilar metals at high temperatures and forces [6]. Using a different material for the bolts might result in the formation of an unidentified metal near the threads. This poses a significant issue, as the bolts could become permanently fused to the reactor, or the new material might exhibit undesirable tensile properties, potentially leading to material failure at that juncture.

3. *Viewing windows*

The inclusion of viewing windows significantly influenced the reactor's design, notably dictating the choice of a cubic shape for the main reaction chamber. Sapphire, known for its transparency and exceptional high-temperature properties, serves as an ideal material for the reactor's viewing windows [7]. The thickness of the windows was determined using a method outlined in Ref. [8], which proposed Eq. (1) relating the thickness t of a circular window to the unsupported radius r, pressure differential P, clamp constant K, safety factor SF, and modulus of rupture M. A window diameter of 4.08 cm was selected to maximize visibility into the reaction chamber. Based on the metal seal dimensions, the unsupported radius is 1.91 cm. At an operating pressure of 275 bar, a window thickness of 2.54 cm achieves a safety factor of 25. The window will experience other stresses from the seals and thermal expansion and this safety factor accounts for all of the unknowns.

$$t = r \times \sqrt{\frac{P \times K \times SF}{M}} \tag{1}$$

The windows' minimal surface roughness complicates sealing, as a smooth surface necessitates the application of significant force onto the seal. However, since the window is made from a brittle ceramic material, uneven stress distributions can lead to crack formation. Silver C-seals are placed between the reactor and ceramic window due to silver's oxidation resistance and ductile properties. Significant forces exerted on the seal lead to its deformation, ensuring even stress distribution across the window. Although a circular lay finish is commonly applied to surfaces requiring sealing, this technique is unsuitable for the sapphire window. All of the sealing capability is based purely on the force applied on the seal. A copper disk is positioned on the window's opposite side to distribute forces from the Hastelloy flange, thereby reducing stress concentrations. In Fig. 2, the design of the viewing window port is shown.

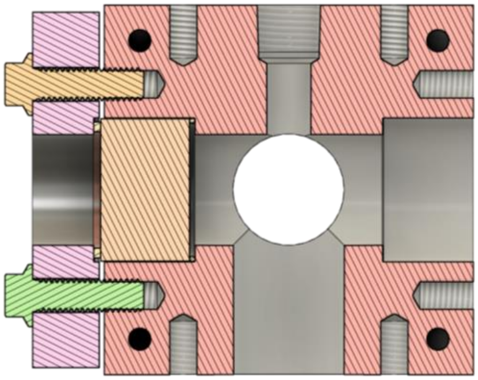


Fig. 2 Design for the viewing window port

4. *Flanges and Bolts*

The flanges and bolts are used to seal the reactor operating at extreme conditions. Constructed from Hastelloy X, as detailed in Section III.A.2, they offer exceptional durability and resistance. All of the flanges are cylindrical with a thickness of 1.91 cm and an outer diameter of 10.16 cm. The inlet flange will be connected to the bottom of the reactor and has a 1/2 in. female ISO parallel threaded hole in the center for mounting the co-flow nozzle. The flanges for the outlet, thermocouple, and pressure transducer have a 1/4 in. female ISO parallel thread hole for mounting their components. The window flanges have a 3.18 cm diameter hole in the center for visualization of the reaction chamber.

Given that bolts are often failure points in high-pressure systems due to intense shear stresses on the threads, a meticulous analysis is crucial for designing a safe system. The main forces that the bolts experience are the preload and the force from the internal pressure which acts on the flanges. The bolt preload is related to the force applied to the seals which is specified by the seal manufacturer. The window seals require a seating load of 23,202 N and the non-window flanges require a seating load of 33,686 N. Forces on the bolts from the internal pressure on the window and non-window sides are 36,449 N and 39,816 N, respectively. For this analysis, the bolts on the non-window sides will be evaluated since they will experience greater stress than the bolts on the window flanges. Upon pressurization, each side flange withstands a total force of 73,502 N, equivalent to approximately 1 metric ton per bolt. Stress is simply force divided by the area, which in the case of thread shear is equal to the circumference of bolt minimum diameter time the length of engaged thread. This calculation results in a shear stress of 50 MPa. The yield strength of materials in shear is half of what it is for tensile stress, so the shear yield strength of Hastelloy X at 700 K is 150 MPa. With a safety factor of three, these eight bolts can adequately withstand the reactor's forces.

5. *Concentric Flow Nozzle*

The final component of the main reaction chamber is the concentric flow nozzle. The purpose of this assembly is to direct the fuel and oxidizer flows to be injected into the reactor concentrically. This design facilitates the initiation of SCWO reactions near the fluid inlets, aiding in visualization. Figures 3 and 4 show the co-flow nozzle assembly and the cross-sectional view of the assembly mounted to the inlet flange, respectively. The fuel is injected through the core tube and the oxidizer is injected through the annular tube. The fluids remain separate until exiting the nozzle within the reactor (located on the left side in the figures). All of the individual tube fittings can be purchased off-the-shelf from fitting companies such as Swagelok. A significant advantage of a low flow-rate reactor is the availability of small tubing capable of withstanding extreme conditions. These fittings are made from 316 stainless steel and can withstand the high pressure and temperature required for the reactor.

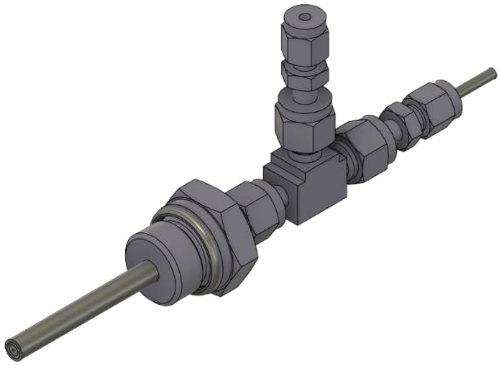


Fig. 3 Co-flow nozzle assembly.

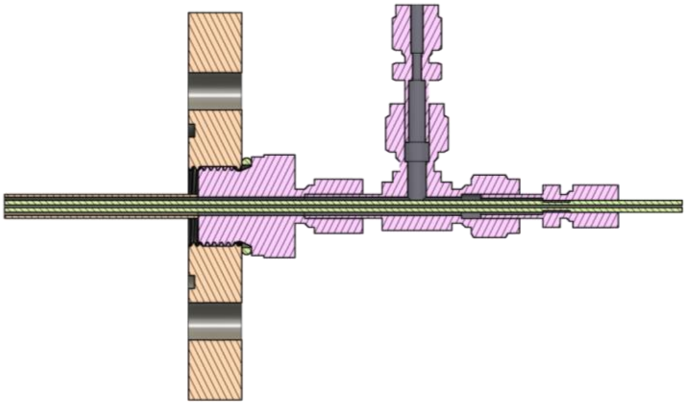


Fig. 4 Co-flow nozzle cross-sectional view in the inlet flange.

6. *SCWO Reactor Assembly*

Following the design of all reactor components, the system was assembled to illustrate the completed setup. Figure 5 depicts the full assembly. As shown below, the inlet co-flow nozzle is located at the bottom and the outlet tube is at the top. If necessary, the positions of the flanges can be altered to accommodate alternative configurations.

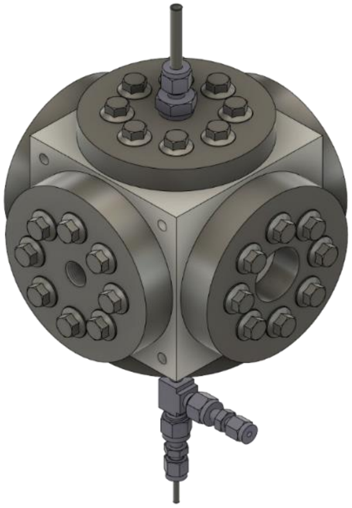


Fig. 5 SCWO reactor assembly.

7. *Finite Element Analysis*

Conducting a finite element analysis (FEA) is crucial to verify that the reactor's structural integrity meets operating conditions with an adequate safety factor. The primary concern is the main reaction chamber since there are multiple points of potential failure. The structural analysis, utilizing Ansys [9], assesses the reactor model against forces anticipated during normal operation. The main considerations are the thermal strain from thermal expansions, the internal pressure, and the forces on the reactor from the bolts. The analysis applies loading in two steps: initially heating the reactor to 700 K, followed by applying an internal pressure of 275 atm along with the bolt forces. Bolt forces applied to bolt locations equal the sum of the bolt preload and forces from the internal pressure acting on the flanges; the bolts on the window and non-window sides experience a combined force of 59651 N and 73502 N, respectively. Displacement boundary conditions at the main reaction chamber's corners permit thermal expansion. The results of this analysis are shown in Fig. 6. High stress concentrations occur near the reactor center where the orthogonal holes intersect. The maximum stress is 169.5 MPa and the yield stress of the material at a temperature of 700 K is 301 MPa, meaning that the reactor has a safety factor of 1.78. While the safety factor is not optimal, it is deemed acceptable with the implementation of additional safety measures. Such measures include housing the reactor within a sand-filled protective enclosure and remote system control.

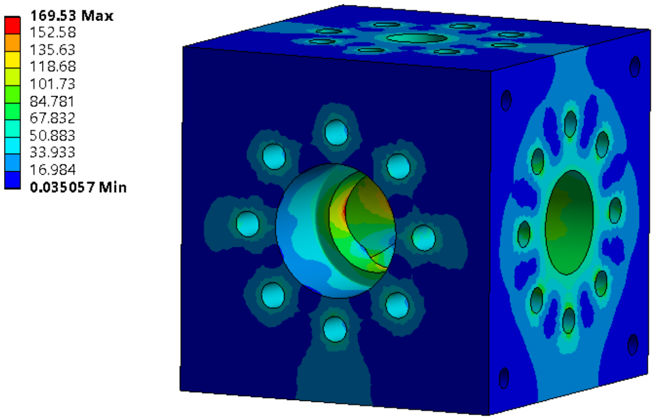


Fig. 6 Predicted equivalent Von-Mises stress (MPa) distribution in the main reactor chamber.

B. Flow Control System

The flow control system is designed to supply the main reaction chamber with continuously pre-heated fuel and oxidizer. Pre-heating the fluids ensures that reactions commence instantly upon the contact of fuel and oxidizer. An aqueous ethanol solution serves as the fuel, delivered into the reactor via a syringe pump. The syringe pump allows for setting a specific volumetric flow rate to ensure continuous fluid supply. After the pump, the fuel tubing is coiled in a sand bath heater to bring the fluid to supercritical water conditions before entering the reactor. The fuel line connects to the core flow tube of the inlet nozzle as previously discussed. Oxidizer flow control is more intricate due to the compressible nature of the gaseous phase working fluid, synthetic air. A tank of synthetic air connects to an air-powered gas booster pump, which pressurizes the air to the desired pressure. This pump, however, pressurizes the gas in bursts rather than continuously. A continuous flow is achieved by directing the oxidizer into a reservoir connected to a mass flow controller. The reservoir's size must ensure that the pressure drop during pump bursts is minimal. The mass flow controller is used to limit the oxidizer flow rate and for control of equivalence ratio, which is the ratio of the actual fuel/oxidizer ratio to the stoichiometric fuel/oxidizer ratio. After the mass flow controller, the oxidizer flows through tubing in a sand bath heater, heating it to the operating temperature. Another benefit of a low flow rate reactor is that the working fluids move slowly through the tubing and heating them to high temperatures does not require an exceptionally powerful heater. The inlet flows are primarily controlled by solenoid valves and pumps, which are controlled electronically with a relay module.

Post-reaction, the product fluid is cooled to room temperature by flowing through tubing immersed in an ice bath before it proceeds to the back-pressure regulator. The back-pressure regulator maintains constant reactor pressure by permitting fluid exit only upon reaching the desired pressure. Accounting for pressure drop, this regulator can be set to only allow fluid through once it reaches a specific pressure. Subsequently, analyzing the product fluid with a gas analyzer provides insights into the SCWO processes that transpired.

C. Data Acquisition System

The primary goal of the data acquisition system is to record essential data to deepen our understanding of SCWO and to monitor the system's flow, ensuring its optimal operation Given the combustion processes' strong dependence on the system's pressure and temperature, recording this information is crucial for the experiments. In the reactor system itself, temperatures and pressures are recorded at different locations. Pressure is recorded before the fluids enter the heater and inside the main reaction chamber. The temperatures of the fluids are recorded after the heater, inside the main reaction chamber, and before the back-pressure regulator to ensure that the product fluid is cooled down to a safe temperature. The system's sensors transmit data to National Instruments Data Acquisition (DAQ) cards, which are then connected to a computer running LabVIEW software. The entire reactor system is controlled with LabVIEW, allowing the operator to use the system remotely in a different room. The SCWO processes can be analyzed in various ways, such as by employing a gas analyzer to measure the carbon monoxide (CO) concentration in the product fluid. CO is a common compound in combustion processes and its concentration can tell us a lot about how much water was formed in the reactor.

IV. Conclusion

SCWO, an exciting technology, holds significant promise in hazardous waste removal, particularly in managing waste during space missions. A continuous-flow SCWO reactor is designed to gain a detailed understanding of the physicochemical processes inherent in SCWO. The design is versatile and can be configured in different ways, such as injecting the fuel and oxidizer from the top to turn the reactor into a downflow style reactor. The two viewing windows allow for shadowgraph or Schlieren visualization of the mixing patterns present in the high-reaction zone near the inlet. The system's design incorporates safety factors and enables remote control from a separate room to minimize operational risks. Currently under testing, the system will soon move into the experimentation phase. While designed for ethanol, the reactor can accommodate other organic fuels and oxidizers.

Acknowledgments

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