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Engineering Modeling of the Pine Bluff Arsenal Supercritical Water Oxidation Reactor

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With management oversight from the U.S. Army Defense Ammunition Center (DAC), and leveraged support from the Environmental Security Technology Certification Program (ESTCP) Office, the U.S. Army Tank-automotive and Armaments Command, Armament Research, Development and Engineering Center (TACOM-ARDEC), in conjunction with Sandia National Laboratories and its contractors, have been developing supercritical water oxidation technology for use in the demilitarization of a variety of military smoke and dye formulations. Results from this work have contributed to the construction and preliminary operation of a prototype supercritical water oxidation system (SCWO) at Pine Bluff Arsenal (PBA) in Arkansas. Over the past year, this unit has been brought on line and will soon be capable of processing complicated feeds slated for demilitarization by the military services. This paper presents an overview of the design strategy, system start-up, and operational performance of this 3500 kg/day (waste feed) reactor.

The design of this system relies on several innovations that permit the reactor to process material with high inorganic content and a wide range of heating values. Specifically, these novel design features are the use of 1) a transpiration-wall design that can significantly mitigate scaling and corrosion as well as limit over-temperature of the reactor pressure wall and 2) a multi-port injector that facilitates the initiation of oxidation reactions with minimum feed preheating. The roles and performance of these two key reactor components are highlighted.

The small-scale design evaluation research performed by Sandia several years ago that guided scale-up to the prototype is illustrated. In addition, this paper presents the initial development and approach to a fluid-dynamical model that describes the operation of the PBA system from an engineering standpoint. The preliminary stages of this work show that the reactor is not a simple plug-flow system as originally thought, but has large recirculation regions that are the result of buoyancy in the dense fluid flow.

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Introduction.

The steady progress of supercritical water oxidation (SCWO) from a laboratory scale endeavor to implementation on a scale suitable for the actual disposal of some difficult-to-treat hazardous wastes is continuing and accelerating. Among the more important recent developments is the construction of two small-footprint units designed independently by General Atomics and Foster Wheeler Development Corporation (FWDC) for disposal of shipboard excess hazardous material. Another significant development is the start-up of a larger facility at Pine Bluff Arsenal (PBA). This project, managed by DAC, is a joint activity of Sandia National Laboratories, TACOM-ARDEC, PBA , and two key private contractors, FWDC and GenCorp Aerojet. This paper reports on the design development methods, construction, and testing of the PBA prototype SCWO system and the initial progress in modeling the flow within the reactor itself. Sandia National Laboratories has collaborated with FWDC and Aerojet GenCorp to use Aerojet's sophisticated platelet transpiration-wall technology[1,2] as a foundation for the system design.

The PBA plant is unique in that it is designed for the disposal of a variety of unusual munition materials that are incompatible with more traditional disposal methods such as open burning or incineration. The transpiration-wall approach improves on earlier SCWO pilot-level systems by integrating corrosion mitigation with a better strategy for preventing scaling and fouling due to solids accumulation. In doing so, this unit, and others that have been developed by this team, represent a different approach to solving these key issues that have, until now, presented significant impediments to the commercialization and acceptance of SCWO as a generally-applicable waste treatment technology.

This overall design strategy has brought to light an additional very important aspect of the practical use of SCWO. This is the issue of heat management in a high-pressure, high-temperature exothermic process. Earlier small-scale systems were essentially simple tubes that relied on an externally heated feed and oxidizer to provide the reactants with a sufficiently high mixture temperature to produce rapid oxidation and high conversion. However, the energy consumption of such a design becomes

prohibitive upon scale-up from a laboratory system. In addition, excessive preheating of feeds to initiate rapid reaction effectively limits the concentration of the waste. This was realized first by the MODAR group[3] a number of years ago and has been the subject of several modeling investigations.[4-6] Their solution was to develop an annular injector and a semi-recirculating vessel reactor that required minimal feed preheat once the reactor had reached steady state. This idea represented a significant improvement on a simple tubular approach, but it relies on internal recirculation patterns to facilitate initiation of rapid oxidation of the incoming waste steam.

The transpiration-wall reactor design, pictured in Figure 1, is intended to take advantage of a multiport injector to minimize preheat while simultaneously maintaining a turbulent plug flow to assure high conversion and greater simplicity for effluent management. By combining this feed method with a transpiration-lined vessel, low corrosion and minimal scaling can be achieved in a simple flow system with a well-defined residence time. As stated above, the PBA system is based on these two major design ideas. However, new results from fluid dynamical modeling of this system suggest that the flow in this reactor may be more complicated than originally postulated.

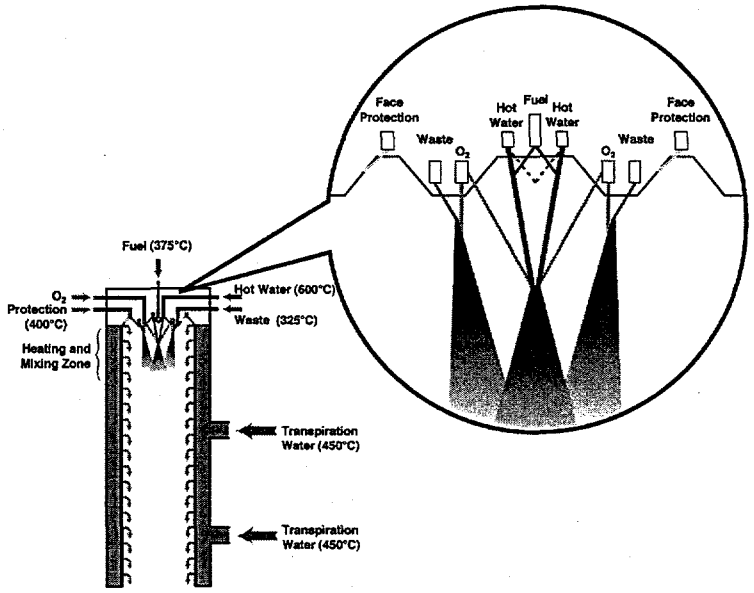

Figure 1. Illustration of transpiration-wall design concept and the autothermal feed injector.

This paper describes the design and operation of the PBA SCWO plant, illustrates the operating parameter range, and cites an example of a portion of a typical test run. The results of the initial stages of plant operation have demonstrated a need for a more sophisticated view of the reacting flow in this system. An overview of progress to date on the model development of the exothermic, high-density flow is included.

Design Background

Sandia's Engineering Evaluation Reactor (EER) demonstrated the successful operation of this design concept in 1995-1996.[7,8] The system consisted of a 2.79 cm (1.1 inch) internal diameter, 91 cm (3.0 ft) long turbulent flow reactor with a nominal flow capacity of 10 g/s. A number of tests were conducted focusing on two major aspects of the system: mitigation of inorganic deposits and ease of autothermal operation. These small-scale tests showed that the transpiration-wall design was effective at reducing deposits of sodium sulfate in the feed, but indicated that transpiration flows greater than those that could be obtained in the laboratory-scale system would be necessary to fully eliminate the problem. Aerojet's experience in this technology combined with these tests led to the final flow rates used in the detailed design of the transpiration-wall platelet for PBA.

Because of the considerable transpiration flow rate required in the full-scale system, every effort was made to reduce the amount of water needed in preheating the feeds. This constraint led to the development of a feed injector that uses a small amount of auxiliary fuel and a small amount of 600 °C supercritical water to provide the heat needed to sustain the oxidation of the waste. Isopropanol is chosen as the fuel because it is reactive at a low temperature and has a well understood oxidation kinetics at these conditions.[9] Successful testing of the feed injector, illustrated in Figure 1, at the 1.1 inch diameter scale was demonstrated for a number of waste feeds.

Figure 2 shows a typical test sequence in which a thermocouple located 10 cm downstream of the injector, inside the reactor, was used to detect reaction initiation and extinction for various flow conditions. The results from these tests set the flow and

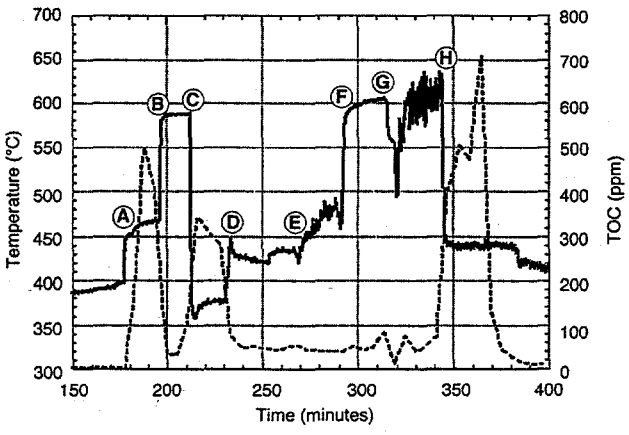

Figure 2. Experimental traces of the internal reactor temperature (solid curve) and TOC (dotted curve) during operation of the EER at a variety of feed conditions. See Table 1 for a description of the key operation events.

preheating parameters for the full-scale system. A key aspect of the of the bench-scale testing pointed to the possibility that the full-scale system could be operated with no preheating of the waste feed stream while still achieving high conversion. Note that the tests using the EER presented in Figure 2 were conducted using air as the oxidizer and n-propanol and the auxiliary fuel.

Table 1 - Events on Figure 2 Records

Index	Action
A	Reactor operating with preheated water and oxidizer (air). At "A" a preheated 10% solution of n-propanol and water was introduced.
B	Air was introduced and oxidation of the n-propanol initiation fuel raised the temperature. TOC dropped.[a]
C	Pure water with no organic content was introduced through the waste injector ports. The initiation reaction was quenched. TOC increased.
D	5% methanol was added to the waste feed line. Oxidation restarted. TOC dropped.
E	Methanol concentration was increased to 10%. TOC remained low, temperature increased slowly.
F	Methanol concentration was rapidly increased to 15% TOC remains low, temperature increased abruptly.
G	Waste line was switched from 15% methanol to a 7% mixture of JP-5 jet fuel and water.
H	Air was turned off. Oxidation stopped.

a - The TOC instrument was on a 0-1000 scale such that the quantitative accuracy at the lower readings is suspect, however, oxidation was probably not complete and the ~50 ppm values close. Residence time in this reactor was only several seconds, depending on feed rates.

Full-scale design over view

The PBA plant consists of a number of subsystems. These are: 1) feed preparation and supply; 2) oxygen supply 3) feed preheater; 4) transpiration-wall reactor; 5) quench and heat exchange; 6) pressure let-down and effluent release. A schematic of these subsystems are illustrated in Figure 3. The entire system is controlled by a distributed control system (DCS) that monitors and/or controls over one hundred process variables. The operator interacts with the plant remotely by way of a graphical user interface from a control room in a building adjacent to the main reactor structure.

Feed preparation and supply. The waste feed system is designed to provide 150 kg/hr (320 lbs/hr) of up to 25 wt% colored smoke or dye slurry to the high pressure slurry feed pump. The waste feed system consists of a dump tank, steam-injection hot water system, grinding equipment and two 1000-gallon feed storage tanks with continuous mixers. A monorail hoist assists operations personnel in lifting and dumping the waste drums into the dump tank. An auger located at the bottom of the tank moves the slurry into a two-stage grinding system. The first stage coarsely grinds the pyrotechnic slugs into 1-cm pieces. A colloid mill is used in the second stage grinding which reduces the particle size of the slurry down to 100 microns. The slurry is then pumped into the series of holding tanks that are continuously stirred to prevent settling. A slip stream of the slurry is drawn off from a steam traced recirculation loop to provide feed to the suction side of the high pressure slurry pump.

Oxygen system. The oxidizer is 100% high-pressure oxygen. It is supplied by a PRAXAIR LOX system that consists of a liquid storage tank, a liquid oxygen pump, an evaporator, and a high-pressure gas reservoir that is maintained at 34.5 MPa (5000 psig)

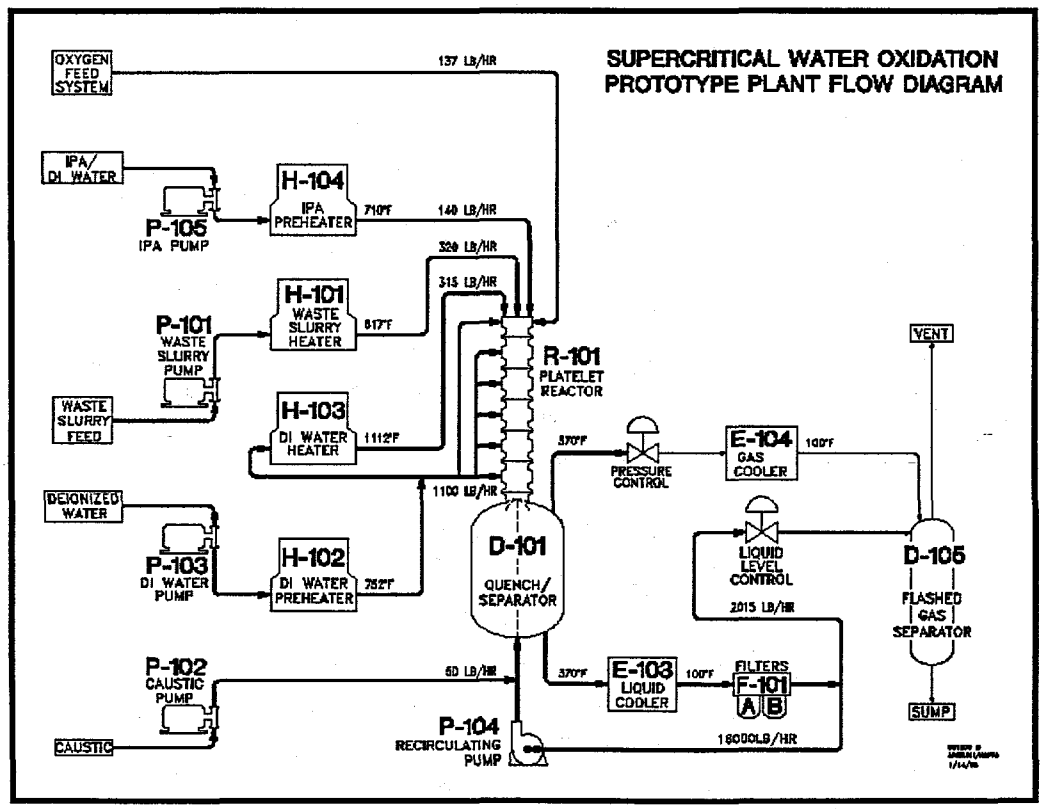

Figure 3. Simplified schematic of the PBA subsystems.

by a control loop linked to the liquid storage. The high-pressure oxygen is delivered to the reactor after a series of check valves at ambient temperature via a Monel line.

Feed preheaters. The four feed preheaters are natural gas-fired burners, individually sized for the waste feed, transpiration water, high temperature initiation water, and isopropanol (IPA) solution. High-pressure diaphragm pumps draw on the reservoirs of deaerated, deionized water, an IPA variable concentration premix station, and the slurry feed system described above. The individual temperature and flow rate setpoints for the heaters and process feeds are controlled by the DCS.

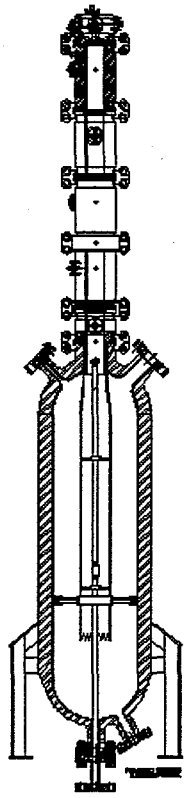

Figure 4. PBA reactor and quench vessel assembly.

Transpiration-wall reactor. The reactor is 12.1 cm (4.8 in). in diameter (inside) and 300 cm (10 ft) in length from the injector to the quench vessel. It is assembled in five separate sections that are individually supplied with the transpiration water and joined by custom Grayloc fittings. The injector is based on the design used in the small-scale system at Sandia with a 10% solution of isopropanol as the reaction initiation fuel. The waste feed is a slurry of smoke or dye formulation ranging from 10-25 wt% depending on fuel content. The reactor and quench vessel assembly are shown in Figure 4.

Quench and heat exchange. The output of the reactor flows into a quench vessel where it is quenched by a spray of 38 °C water. This vessel provides for the separation of the gaseous and liquid effluents. The quench water continuously recirculates, first passing through a heat exchanger prior to the quench spray head. The liquid effluent is

drawn from this loop using the liquid level in the quench vessel as the control variable. The pH of the recirculation loop is continuously monitored and adjusted with an NaOH solution.

Pressure letdown and effluent release. The system pressure is regulated by controlling the gas flow rate into the low-pressure effluent tank. Gas monitors on the outlet of the low-pressure tank measure CO_2, CO, and O_2 concentrations and the liquid effluent is continuously monitored for TOC.

Testing.

The start-up and demonstration/validation testing is being conducted in four stages that are designed both to serve as a training tool for the PBA operations personnel and to arrive at the best start-up, shutdown and steady operation procedures to be incorporated into the final Standard Operating Procedures (SOP) for the Arsenal.

The first stage of testing was completed in July of 1999. These tests examined the individual performance and control of the various feed subsystems operating at system pressure of 24.8 MPa (3600 psig) and design input feed temperatures without waste, fuel, or oxygen. A number of challenges were overcome during this shakeout period related to flow measurement and preheater performance and control. The numerous control loops for pumps, heaters, effluent valves were tuned for the design flow conditions. Another important aspect of this testing stage was gaining familiarity with the tendency for a number of key piping unions to relax after thermal cycling, identifying that the routine maintenance schedule would need to include checking the torque settings on a number of flanges at important locations.

The second stage involved the operation of the system on just 10 % isopropanol feed and oxygen with only water in the waste supply line. These tests were an extension of the first stage and presented relatively few problems. The only significant difficulty resulted from the low overall heat content of the feed. For these tests, the reactor operated at only about 440 °C, significantly below the design internal temperature of 725 °C. Although reasonable TOC conversion was achieved, a large amount of carbon monoxide was measured in the gaseous effluent.

The third stage of testing was completed in October, 1999. These tests were conducted using a surrogate waste feed consisting of a solution of sugar or a mixture of sugar and sodium sulfate. The feeds are designed to raise the system temperature to the design value. In general these tests have proven to be very successful. For purposes of illustration, several hours of a typical test on 9/22/99 are described below. During this test, 770 kg (1,700 lbs) of 15-wt% sugar solution (waste surrogate) were processed during six hours of continuous operation at a maximum feed rate of 190 kg/hr (420 lbs/hr).

During this test, the internal reactor temperatures were estimated at 500 °C (quench tank entry) and 750 °C (20 cm below the injector) based on energy-balance calculations, since the reactor has no internal thermocouples. The operating pressure was maintained at 24.6-25.6 MPa (3,550-3,700 psig) and the heat release rate from the oxidation of organic feed was 250 kW (860,000 Btu/hr). Figure 5 shows the TOC levels in the liquid effluent, the primary indicator of SCWO destruction effectiveness. The TOC temporarily increased to 45 ppm after the feed introduction of IPA because of the relatively "cold" reactor ($T_{surface}$ = 310° C) as shown in Figure 6. With thermocouples excluded from the reactor internal, the external surface thermocouples provide the best, albeit indirect, temperature indication.

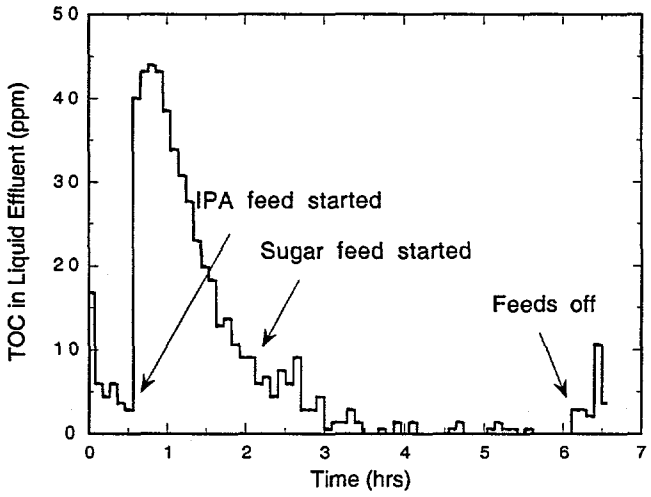

Figure 5. TOC of the liquid effluent during 9/22/99 test. Annotation marks operation as is described in text.

One hour after isopropanol reaction was initiated, as confirmed from increased external surface temperature and CO_2 production, an ambient-temperature 15-wt% sugar solution was introduced. Its effects on the reactor temperature and TOC were relatively minor (see Figure 5 and Figure 6) because its adiabatic flame temperature was similar to the reactor temperature. After 90 minutes of reaction, the reactor was sufficiently heated (T_{skin} > 450° C) to achieve complete conversion, as indicated by the TOC concentrations

decreasing from 45 to <5 ppm. The liquid discharge TOC levels are significantly below PBA requirements of 50 ppm and near the detection level for the on-line TOC analyzer. The corresponding destruction and removal efficiency (DRE) was >99.9%, with an estimated TOC of about 1 ppm. Additional analysis is in progress to provide accurate TOC measurements at these levels.

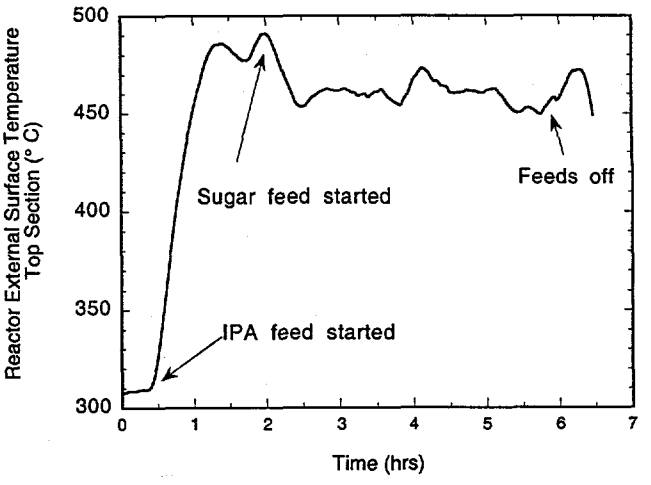

Figure 6. Reactor external surface temperature of top section for the 9/22/99 tests.

The CO level in the gas effluent is a secondary indicator of destruction effectiveness and reached an acceptable value of 40-50 ppm. The concentration of primary gas effluents, CO_2 and O_2, are shown in Figure 7. The balance of the gas effluent is essentially N_2, which was used to pressurize the reactor initially to 24 MPa and was slowly purged from the reactor by the product gases. The final concentrations of CO_2 and O_2 were approximately 85-90% and 5-10%, respectively, indicating an excess oxygen concentration of 5-15%.

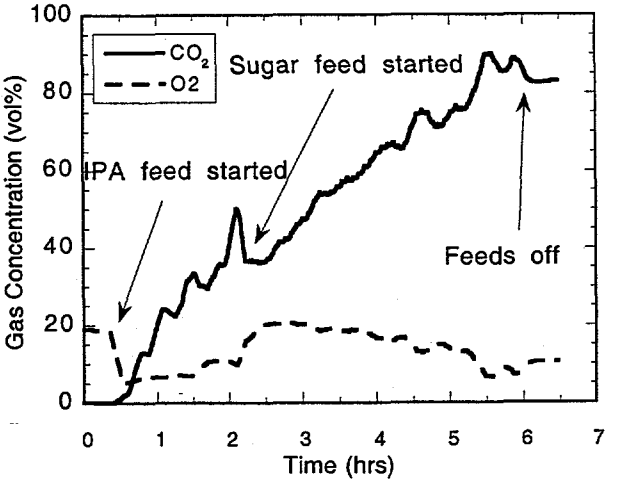

Figure 7. Composition of gas effluent from reactor for during 09/22/99 test. Balance of the composition is mostly N_2.

The fourth and final start-up test stage will be commencing in February 2000. This permits time for a number of improvements to be made on the system diagnostics including changes in several flow meters, the addition of more thermocouples on the reactor external surface, and a modification of the isopropanol solution preparation subsystem. Several other repairs are required to

improve and ensure safe long-term operation in light of the lessons learned over the course of the first three testing stages. In addition, a number of winterization provisions need to be incorporated before the unit can be operated at or near freezing conditions.

Modeling of the Fluid Dynamics of the Reactor

From the point of view of reactor operation, a large payoff can be obtained if the temperature of the flow through the reactor can be accurately estimated from the external reactor thermocouples. An important advantage of the transpiration-wall design is that the pressure vessel can be maintained at a significantly lower temperature than the reacting flow. However, this also impairs an important direct diagnostic (temperature) of the overall reactor operation. As a result, we have begun to develop a computational fluid dynamics (CFD) model coupled with a heat transport model though the platelet liner, transpiration water plenum, and pressure vessel wall to directly relate the external measurements to the internal conditions.

The model under development includes the effects of multispecies flow, heat transfer and chemistry. The work is progressing from development of a general two-dimensional transient computer code for treating supercritical water/waste flows to reactor-specific models representing the Sandia bench-scale supercritical water experiments and the full-scale Pine Bluff supercritical water reactor.

The thermodynamics of supercritical water and reactor operating conditions present the modeler with a unique set of challenges. Flow in the Sandia bench scale reactors can be characterized by the following dimensionless parameters:

$$\mathrm{Re} = \frac{\rho V D}{\mu} \geq 6200 \qquad \text{(Reynolds Number)} \qquad (1)$$

$$\mathrm{Gr} = gA(T)D^3 \geq 2.2 \times 10^9 \qquad \text{(Grashof Number)} \qquad (2)$$

$$\frac{\mathrm{Gr}}{\mathrm{Re}^2} \geq 60 \qquad (3)$$

where

$$A(T) = \frac{\beta \Delta T \rho^2}{\mu^2} \qquad (4)$$

and $\rho, \mu, \beta, \Delta T, g, V, D$ are the density, viscosity, volume expansion coefficient, thermal deviation from reference, gravitational acceleration, mean flow velocity, and reactor diameter respectively. The parameters in equations (1-3) were calculated for a reactor temperature and pressure of 400 °C and 24.12 MPa, assuming the flow stream to be predominantly supercritical water. The characteristic dimension used in the parameters was the reactor diameter. For the Sandia bench-scale experiments, the reactor diameter is only 2.79 cm. A more realistic diameter for the full-size reactor increases the Reynolds and Grashof numbers by more than an order of magnitude.

Equation (1) indicates that reactor flows are turbulent, even when the flow velocity is based on the average flow rate over the entire reactor cross-section. Equations (2-3) indicate that buoyancy plays a key role in reactor fluid dynamics. This high level of buoyancy causes a strong coupling between the energy and momentum equations.

It is well-known that the density and specific heat vary by nearly an order of magnitude over a narrow temperature range near the critical value at a reduced pressure (P/P_{crit}) of 1.1. There are similar variations in the transport properties (viscosity and thermal conductivity). The severe spike in the specific heat near the critical point at the reactor operating pressure is most problematic. This spike can cause numerical difficulties when the enthalpy (energy) equation is integrated in space and time. These numerical instabilities are made worse by order-of-magnitude variations in density and to a lesser extent changes in transport properties. Figure 8 illustrates how the temperature-dependent part of the Grashof number varies over the

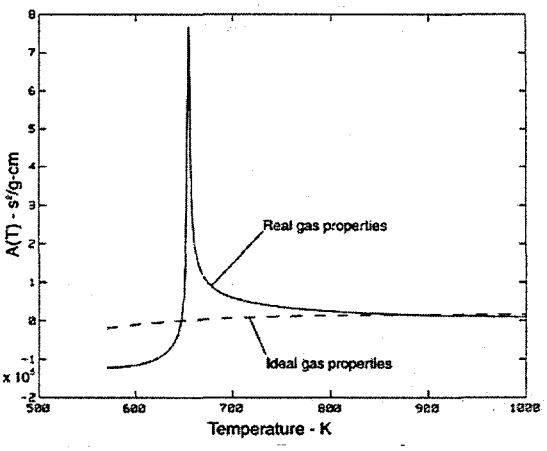

Figure 8. Temperature dependent Grashof parameter, A(T), variation with temperature for water at 24.1 MPa.

reactor temperature range. The same variation for an ideal gas (based on the molecular weight of water) is shown for comparison purposes.

The Sandia developed chemically reacting flow code CURRENT has been modified to include the thermodynamic and transport properties of supercritical water based on the NBS steam tables and transport data. An ideal-mixture model has been implemented in which mixture properties (density, specific heat, viscosity, and thermal conductivity) are determined from the individual component properties and component mole fractions. Ideal-gas equations of state for the all components other than water are assumed. The present formulation does not preclude the addition of real gas equations of state for mixture components. These will be added as needed.

In order to account for the expected turbulent flow characteristics in supercritical water reactors, a number of turbulence models have been implemented. These include a simple enhanced viscosity model, the $k-\varepsilon$ model, and Durbin's V2F model.

Calculations have been performed using the implemented mixture model, with full buoyancy and turbulent flow. In order to eliminate the numerical difficulties discussed in the previous section, these initial calculations were performed with an ideal-gas equation of state for water. The calculations were intended to simulate flow through the Sandia laboratory scale transpiring wall reactor. An example of computed results is shown in Figure 9. A mixture of high temperature water and CH_3OH enters the top of the reactor through a small opening at the reactor

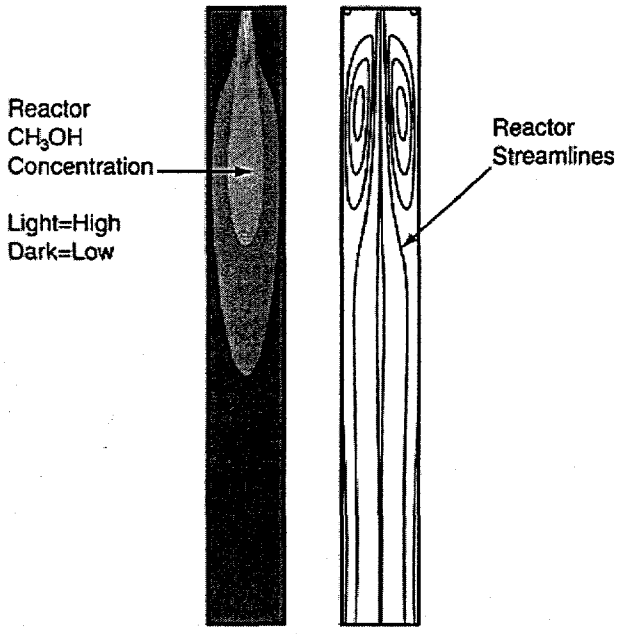

Figure 9. Reactor cross-sections showing methanol concentrations and flow streamlines.

centerline. Low speed/low temperature transpiring water enters the reactor through the side walls over the entire reactor length. The distribution of CH_3OH is shown on the left with high concentrations represented by light gray and low concentrations represented by dark gray. Flow streamlines are shown on the left. A strong recirculation zone is evident near the top of the reactor.

Work is currently underway to determine the most efficient means for achieving numerical convergence using the NBS equation of state for supercritical water. The implementation of chemistry will follow shortly.

Summary

Testing of the Pine Bluff Arsenal prototype SCWO reactor system is proceeding to the final stage of processing obsolete smoke and dye munition formulations. The reactor has operated predictability and appears to function well at the design flow rates. The surrogate testing has established that the waste feed can be added with no preheating. The TOC and carbon monoxide content of the liquid and gas effluent are within PBA operations constraints. Improvements in the operation of the reactor or in future designs will benefit from the CFD modeling establishing a method that will relate external measurements to the internals of the reactor.

Acknowledgement.

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