Operating Results from Supercritical Water Oxidation Plants

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Two supercritical water oxidation (SCWO) plants that utilize transpiring wall reactor designs for processing organic wastes are undergoing testing and operation. One plant is designed to destroy Navy excess hazardous materials (EHM). The EHMs represent organic materials found aboard Navy ships. The plant has a nominal waste feed rate of 45 kg/h and utilizes compressed air as the oxidant. Corrosive wastes, including chlorinated solvents (diluted with kerosene) and lube oils, and a salt-producing photographic solution simulant have been processed at feed rates between 45 and 95 kg/h. Tests have been conducted at an operating pressure of 24.1 MPa and reactor temperatures between 594 and 816 °C. Destruction removal efficiencies of better than 99.99% have been obtained. Priority air pollutants NO_X and CO are below 25 and 100 ppm, respectively. Liquid effluent total organic carbon (TOC) levels are consistently below 3.5 ppm. Post-test inspections have not revealed any obvious reactor liner corrosion or salt deposition. A second SCWO plant designed for the destruction of obsolete, colored smokes/dyes and pyrotechnic munitions has been fully commissioned and is currently undergoing validation testing. The plant is designed to process 145 kg/h of a 25 wt % basis slurry of smokes and dyes. The plant uses oxygen as the process oxidant. The reactor operating pressure is 26.3 MPa, and operating temperatures are between 575 and 750 °C. Off-site plant skid fabrication was completed in 1997, site preparation and construction were completed in 1998, and commissioning was completed in 1999. Validation testing will be completed in the fourth quarter of 2000. Production demilitarization processing of smokes and dyes will follow.

Introduction

Because of the U.S. Navy's need to comply with future national and international shipboard waste discharge standards, better shipboard waste treatment methods are required. Supercritical water oxidation (SCWO) was identified as one possible method because of its compatibility with shipboard requirements. The Defense Advanced Research Projects Agency and the Office of Naval Research (ONR) jointly sponsored a program to develop and demonstrate shipboard SCWO.[1] Foster Wheeler was contracted under this program to design, fabricate, and test a shipboard SCWO system.

Similarly the U.S. Army is actively developing alternative destruction methods for obsolete munitions. New technologies are required to replace conventional methods such as incineration that are not suitable because of process emissions of soot, ash, and toxic compounds as well as equipment corrosion. The U.S. Army Armament Research, Development, and Engineering Center, with management oversight of the U.S. Army Defense Ammunition Center, sponsored the development of SCWO for disposal of obsolete smokes, dyes, and pyrotechnics. Sandia National Laboratories was contracted to assess feasibility and develop an operating prototype SCWO plant. Foster Wheeler was subcontracted by Sandia/California to perform detailed design engineering, fabrication, and installation of the prototype plant.

SCWO can effectively treat wastewater with high organic compound concentrations and is being demonstrated in commercially designed systems. SCWO destroys aqueous organic wastes by oxidizing them to CO_2 and water. Operating above the critical point of water (374 °C and 22.1 MPa), SCWO takes advantage of the miscibility of organics, water, and oxygen to rapidly oxidize the organics in the single-phase mixture. Organic feed destruction rates are usually better than 99.99%. Because of the lower than incineration operating temperatures and high concentration of supercritical water, pollutants such as NO_X and SO_X are not generated in noticeable concentrations.

While numerous pilot-plant studies have been conducted on widely varying feedstocks,[2] SCWO is only beginning to be demonstrated in commercial designs. This is largely due to the technical and economic challenges of implementing designs with acceptable reliability and operating characteristics. Two technical problems of SCWO systems are corrosion and salt plugging of the reactor and other system components. A transpiring wall reactor design has been implemented to address these technical challenges. This design utilizes a pressure vessel with an internal transpiring wall liner. As seen in Figure 1, the platelet liner uniformly meters the flow of water to protect the liner from salt deposition and corrosion while providing a thermal and corrosion barrier for the pressure vessel. This allows for higher reaction zone operating temperatures and shorter residence times. The reactor pressure boundary is exposed to controlled-temperature deionized water, resulting in a safer design. Platelet technology

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Table 1. Baseline EHM Surrogates for SCWO Testing

no.	selection criteria	EHM surrogate
1	max Btu with max zinc content	lube oil with zinc organophosphate
2	max Btu with max phosphorus contaminant	hydraulic fluid
3	max sulfur content	molybdenum disulfide lube oil (10%) plus diluent[a] (90%)
4	max fluorine content	PCTFE (1%) plus diluent[a] (99%)
5	max chlorine content	TCA] (10%) plus diluent[a] (90%)
6	max solids content	blended paint
7	max salts content	mixed photographic solution (simulant)
8	max antioxidant content	glycol with antioxidant
9	min Btu	gray water at 0.5 wt % concentration
10	min Btu	black water at 0.5 wt % concentration

[a] Diluent is kerosene.

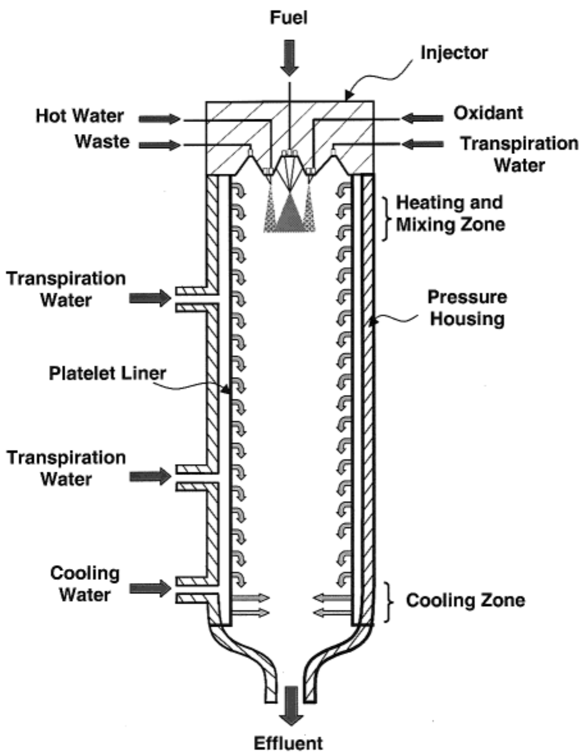

Figure 1. Transpiring wall reactor.

has been implemented by Aerojet GenCorp in military and aerospace applications including cooling of high-pressure rocket engines.[3]

A small-scale engineering evaluation transpiring wall reactor was tested by Sandia National Laboratories[4,5] and was used to establish the design basis for the two prototype systems. This paper describes the design of both systems and validation testing of the shipboard SCWO system.

Shipboard SCWO System Design Requirements

The requirements of the typical naval vessel that will require shipboard excess hazardous material treatment were evaluated by the ONR. That evaluation resulted in a hazardous material composition that is largely petroleum-derived materials. Additionally there are paints, photographic fluids, synthetic lubricants, and sanitary wastes. The 10 excess hazardous material (EHM) surrogates listed in Table 1 were identified as the design basis feedstocks.

Operational and system design features were similarly evaluated and resulted in the following guidelines: (a) 10 h/day continuous processing capability of 45.4 kg/h, (b) minimization of weight and size, (c) destruction removal efficiency (DRE) of 99.99%, (d) automatic operation, (e) safe and reliable operation, (f) high maintainability, and (g) compatibility with shipboard operations.

Shipboard SCWO Design Utilizing a Transpiring Wall Reactor

A process flow diagram is shown in Figure 2. EHM is fed at 45.4 kg/h from a drum and pumped to 24.1 MPa. Kerosene and diluent water are also pumped and blended into the EHM to maintain a uniform waste stream heating value. The mixed EHM feed is heated prior to entering the reactor by heat exchange with hot effluent from the reactor. High-purity water is utilized for the transpiring wall liner and startup heater flows. The liners distribute a metered water flow along the complete length of the reactor. The startup heater is used to initiate SCWO. The hot water along with a metered kerosene stream and air react to release sufficient heat to initiate EHM oxidation. Additional air is provided to fully oxidize all organic EHM compounds. Depending on the EHM composition, acid-forming compounds may be present in the feed. A sodium carbonate solution is added to the EHM feed to neutralize acids. Immediately downstream of the reactor is added quench water to dissolve salts and reduce the effluent temperature. After heat exchange with the in-flowing EHM, the effluent flows through the system pressure control valve. The pressure is reduced, and the effluent is cooled and then discharged.

All system components have been designed by utilizing commercial chemical plant practices and the applicable design codes. A more detailed description of the process and mechanical design can be found in ref 7. A photograph of the shipboard SCWO plant as currently configured for testing is shown in Figure 3.

U.S. Army SCWO Design Utilizing a Transpiring Wall Reactor

A SCWO plant featuring a transpiring wall reactor was designed to dispose of obsolete smokes and dyes generated by demilitarization processing at Pine Bluff Arsenal (PBA), Pine Bluff, AR. Figure 4 is a simplified process flow diagram of the plant.[6]

On the basis of tests performed by Sandia National Laboratories,[8] the materials listed in Table 2 were selected as the design basis feeds.

Similar to the Navy SCWO system, the Army plant is based on the Aerojet transpiring wall reactor. The reactor consists of an injector, pressure vessel, and transpiring platelet liners. The injector is designed to direct the incoming flows to efficiently oxidize supplemental fuel and waste (smoke/dye) slurry feeds. In

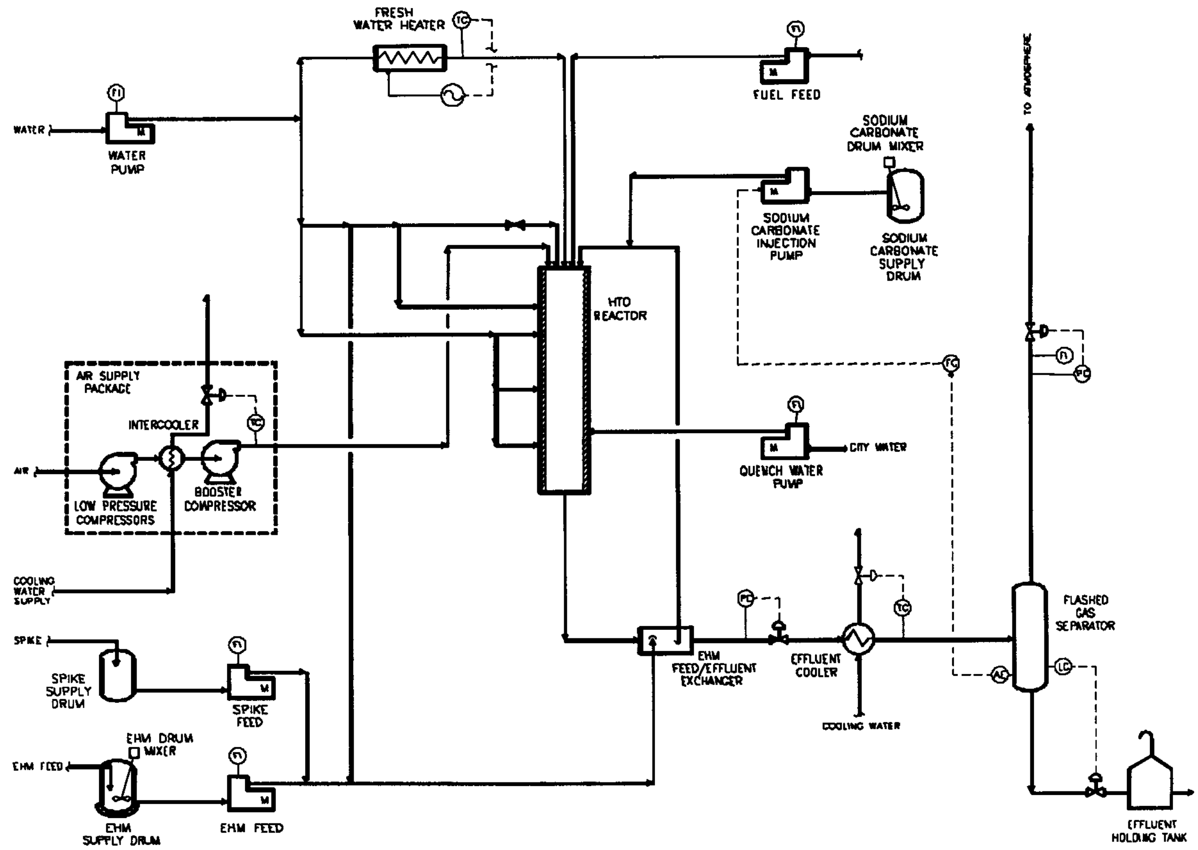

Figure 2. Process flow diagram for a shipboard SCWO plant.

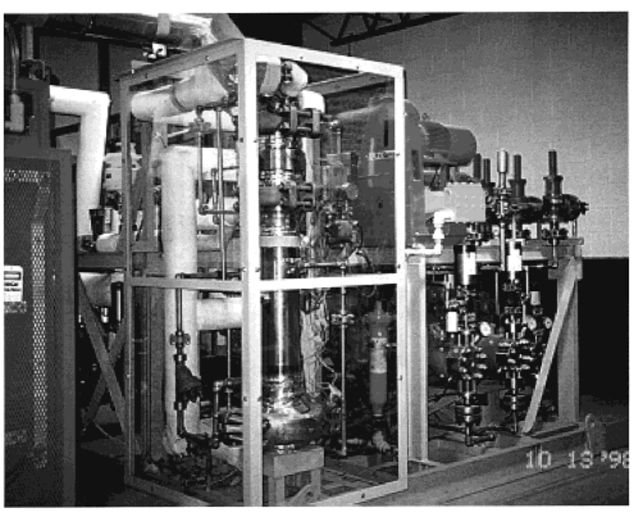

Figure 3. Shipboard SCWO plant.

addition to the waste and fuel feeds, supercritical water and oxygen are flowed through the injector. Oxidation of the organic compounds releases heat and generates CO_2 and H_2O along with acids and salts. The transpiring platelet liner flows supercritical water that forms a film barrier from sticky salts, corrosive acids, and heat. The salts formed during the oxidation are carried out of the reactor. A quench section cools the reactor effluent at the bottom of the reactor. Acids formed during oxidation are neutralized by sodium hydroxide that is pumped into the quench flow circuit. The reactor effluent then flows into a pressure vessel where gas and liquid effluents are separated. The gas effluent passes through the system pressure control valve, is cooled, and then flows to the atmosphere. Liquid effluent is circulated in a closed loop, where it is cooled, filtered, and then pumped back to quench the reactor flow. Separator level control drains excess liquid from the system. Liquid effluent is monitored for the total organic carbon (TOC) concentration and then flows into the PBA wastewater system.

Validation testing of the plant is currently underway; results will be presented at a later date. A photograph of the SCWO plant is shown in Figure 5.

Shipboard SCWO Validation Testing

The plant is operated by starting water flows to the pumps and pressurizing with air from a high-pressure air compressor. The startup water heater is then energized, and the outlet temperature is increased. Startup flow rates and conditions are maintained until the heater is ramped to the startup temperature. Fuel flow is then initiated. The fuel stream mixes with the hot water stream and air at the focal point of the injector. Oxidation proceeds, releasing heat. Spike flow (kerosene) is initiated, and the system operating temperature is increased. The air flow rate is raised. EHM flow is pumped and adjusted to test flow rates. When the SCWO system reaches steady-state conditions, the startup heater and fuel flow are shut off. The plant is then operated at test conditions to accumulate up to 30 h for each EHM. Data are recorded both manually and by a data acquisition program in the computer control system.

In addition to monitoring and recording of system process parameters and operating observations, effluent samples are taken. Samples include gas and liquid effluents. The gas samples are continuously extracted from the stack and analyzed for CO, CO_2, HC, and NO*X*

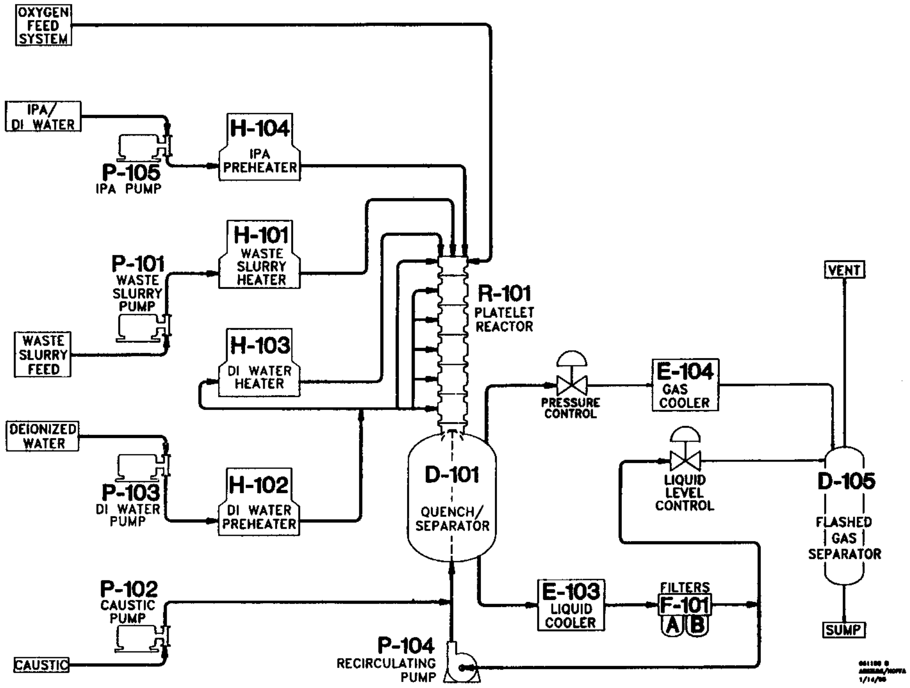

Figure 4. PFB SCWO plant process flow diagram.

Table 2. PBA SCWO Design Basis Feeds

no.	description	composition
1	orange dye	$Na_2(C_{16}H_{10}N_2O_7S_2)$
2	red dye	80 wt % $Na_2(C_{18}H_{13}N_3O_8S_2)$ and 20 wt % $Na_3(C_{16}H_9N_4O_9S_2)$
3	green dye (I)	80 wt % $Na_3(C_{16}H_9N_4O_9S_2)$ and 20 wt % $Na(C_{27}H_{31}N_2O_6S_2)$
4	green dye (II)	80 wt % $Na_3(C_{16}H_9N_4O_9S_2)$, 20 wt % $Na(C_{27}H_{31}N_2O_6S_2) + 10H_2O$
5	blue dye (I)	30 wt % $Na(C_{27}H_{31}N_2O_6S_2)$, 20 wt % $Na(C_{37}H_{36}N_3O_6S_2)$, and 50 wt % $C_{12}H_{22}O_{11}$
6	blue dye (II)	30 wt % $Ca(C_{27}H_{31}N_2O_7S_2)_2 + 10H_2O$, 20 wt % $Na(C_{37}H_{36}N_3O_6S_2)$, and 50 wt % $C_{12}H_{22}O_{11}$
7	CS	$C_{10}H_5ClN_2$
8	pyrotechnic	31.5 wt % $KClO_3$ 18 wt % $C_{12}H_{22}O_{11}$ 3.5 wt % $MgCO_3$ 4.7 wt % $C_{24}H_{12}O$ 9.4 wt % $C_{17}H_{10}O$ 32.9 wt % $C_{28}H_{21}O_2N_2$

using conventional continuous emissions analyzers. The oxygen concentration is monitored by an in situ instrument in the stack. Additionally, independent air emissions monitoring consultants sample stack gases during testing. Similar to the gas effluent, the liquid effluent is continuously monitored. Analyzers for continuous pH measurement and TOC are in operation. Liquid effluent samples are also taken manually in bottles and then sent to an independent laboratory for analysis. Results of the laboratory analyses are used in the DRE calculations.

To assess corrosion, a coupon has been placed downstream of the reactor outlet. The coupon is made of the same material as the transpiring wall liner and is exposed for the entire duration of testing for each EHM. In addition to the corrosion coupon, post-test reactor inspections are performed using a fiber-optic camera. The camera is inserted downstream of the reactor and is capable of recording digital and video images of the reactor walls and injector face. Assessment of the condition of the liner and injector face with respect to possible crack formation, corrosion, structural deformation, and deposition is performed and recorded.

Process Data

Process instrument readings are recorded by the distributed control system. Historical and real-time plots are used for process monitoring and data analysis. Figures 6−9 show the reactor pressure, reactor outlet temperature and EHM feed rate for the kerosene, polychlorotrifluoroethylene (PCTFE), trichloroethane (TCA), and photographic simulant test runs.

The data plots in Figures 6−9 indicate the steady nature of the process at design conditions. The plots also show the process to be controllable as configured.

DRE Calculation

A primary design criterion for the SCWO system was destruction of organic compounds in the EHM to at least 99.9%. DRE is calculated by

$$\% \text{ DRE} = \left[1 - \left(\frac{\text{mass of TOC}_e/\text{time}}{\text{mass of TOC}_f/\text{time}}\right)\right] \times 100$$

where DRE = destruction removal efficiency, TOC_e = total organic carbon in effluent/time, and TOC_f = total organic carbon in feed/time.

Results and Discussion

Table 3 summarizes the results of validation testing.

Kerosene was used during commissioning because it was readily available as spike and it would simulate high heating value materials without highly corrosive

Figure 5. PBA SCWO plant.

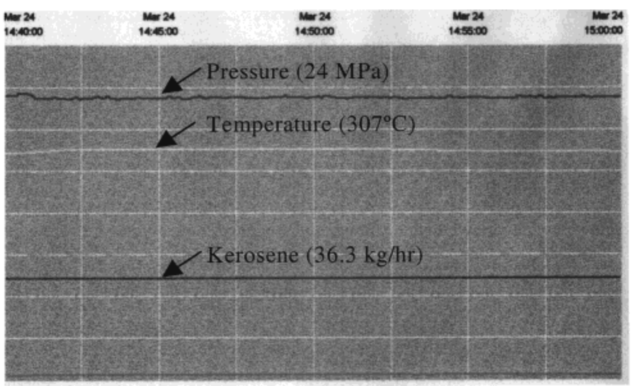

Figure 6. Process data: kerosene commissioning test.

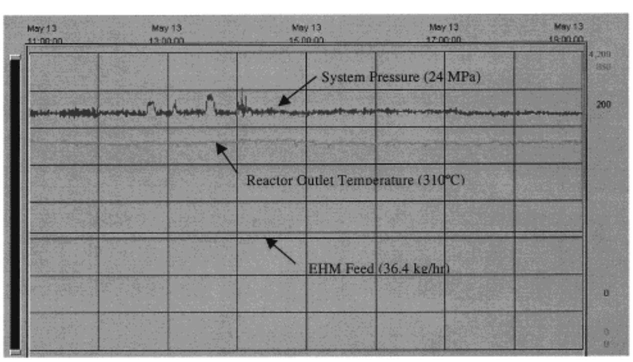

Figure 7. Process data: PCTFE test (5/13/99, 8.5 h).

or salting properties. During the early stages of testing, flow rates of approximately 36 kg/h were achieved. As the operating experience developed, the full design rate, 45 kg/h (~2 MMBtu/h), was attained. A DRE greater than 99.98% was achieved while processing kerosene as the EHM.

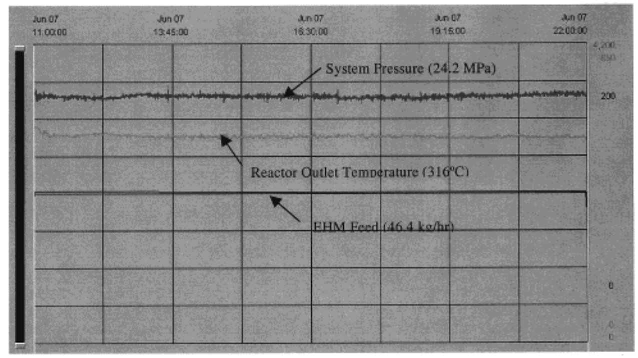

Figure 8. Process data: TCA test (6/7/99, 11 h).

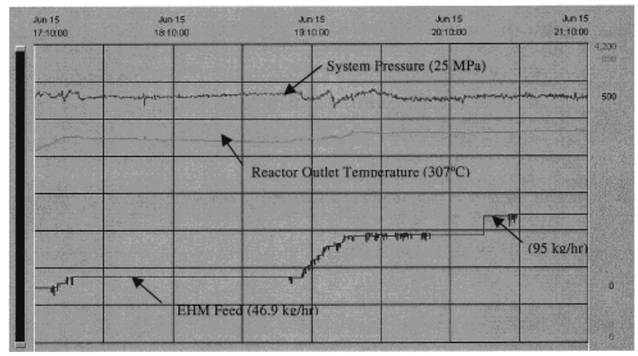

Figure 9. Process data: photographic simultant test (6/15/99, 4 h).

Table 3. Test Results

feed[a]	feed rate (kg/h)	pressure (MPa)	outlet temp (°C)	DRE (%)	CO (ppm)	NO_X (ppm)	TOC (ppm)
kerosene[b]	36.3	24.0	307	>99.98	0−84	0−1	2.8
PCTFE	36.3	24.0	310	>99.99	1−20	1−2	1.4
TCA	46.4	24.2	316	>99.99	0−2	7−13	3.3
photo	46.9	25.0	307	>99.99	50−100	4−25	1.3

[a] Feed compositions are listed in Table 1. [b] Commissioning test run. See ref 9.

Because of the project schedule and budget constraints, the most corrosive and highest salt-producing EHM feeds were tested next. Reordering the feeds to test the more challenging feeds allowed evaluation of the transpiring wall reactor with respect to DRE, corrosion, and salt-plugging performance. These EHM feeds were PCTFE, TCA, and photographic solution simulant. Both PCTFE and TCA contain chlorine, with PCTFE also having fluorine. Both generate corrosive acids during oxidation. The photographic simulant generates the highest amount of salts of the feed materials used in the shipboard design. Organic materials in PCTFE and TCA were destroyed to greater than 99.99%. After each test, the transpiring platelet liner, injector, and reactor outlet piping were visually inspected using a fiber camera. No obvious corrosion was observed. The injector operated in a plug-free manner. Additionally, the tests indicated low levels of both CO and NO_X in the gaseous effluent. Because of project time constraints, an opportunity to optimize the reactor operation and further reduce the emissions levels was not possible. Analytical laboratory results for TOC in the liquid effluent consistently indicated single-digit values. The photographic solution simulant was the next EHM tested. This feed has the highest level of generated salts and a low heating value. Because of the low heating value, spike was fed in addition to the EHM to maintain the reaction temperature. Both PCTFE and TCA EHM feeds did not require spike because their formulations were high in kerosene content. Over 1300 kg of the photographic simulant was processed at feed rates between 45 and 95 kg/h. No reactor plugging was observed. Liquid effluent TOC levels were measured at 1.3 ppm, indicating greater than 99.99% DRE for TOC. Post-test inspections did not reveal any platelet liner corrosion.

Conclusion

Corrosive and salt-producing shipboard hazardous materials have been destroyed in a transpiring wall, SCWO reactor at feed rates between 45 and 95 kg/h. Performance testing indicates that the transpiring wall reactor is an effective reactor design with respect to DRE, corrosion, and salt plugging. DREs for all validation tests while processing PCTFE, TCA, and photographic simulant containing materials were greater than 99.99%. Post-test inspections did not reveal corrosion and salt plugging of the reactor liner.

Detailed design information describing Foster Wheeler's shipboard SCWO system has been forwarded to a naval shipbuilder, who is evaluating integration of SCWO systems into the naval fleet.

Acknowledgment

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