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Final Report
Dual Shell Pressure Balanced Reactor Vessel
Cooperative Research and Development Agreement
with Innotek, Inc.

Prepared by
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April 1995

Prepared for
the U.S. Department of Energy
Office of Energy Research-Laboratory Technology Transfer
Under Contract **DE-AC06-76RLO 1830**

Pacific Northwest Laboratory
Richland, Washington 99352

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UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 7830

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Dual Shell Pressure Balanced Reactor Vessel

Introduction

The Department of Energy's Office of Energy Research (OER) has provided support for the development of several chemical processes, including supercritical water oxidation, liquefaction, and aqueous hazardous waste destruction, where chemical and phase transformations are conducted at high pressure and temperature. These and many other commercial processes require a pressure vessel capable of operating in a corrosive environment where safety and economy are important requirements. PNL engineers have recently developed and patented (U.S. patent 5,167,930 Dec. 1, 1992) a concept for a novel Dual Shell Pressure Balanced Vessel (DSPBV) which could solve a number of these problems. The technology could be immediately useful in continuing commercialization of an **R&D** 100 award-winning technology, Sludge-to-oil Reactor System (STORS), originally developed through funding by OER.

Innotek Corporation is a small business who would be one logical end-user of the DSPBV reactor technology. Innotek is working with several major U.S. engineering firms to evaluate the potential of this technology in the disposal of wastes from sewage treatment plants. PNL entered into a **CRADA** with Innotek to build a bench-scale demonstration reactor and test the system to advance the economic feasibility of a variety of high pressure chemical processes.

Hydrothermal processing of corrosive substances on a large scale can now be made significantly safer and more economical through use of the DSPBV. Hydrothermal chemical reactions such as wet-air oxidation and supercritical water oxidation occur in a highly corrosive environment inside a pressure vessel. Average corrosion rates from 23 to 80 mils per year have been reported by Rice (1994) and Latanision (1993). The actual observed corrosion is often uneven, and pitting is sometimes observed. In addition, 316 stainless steel, **Inconel 625** and Hastelloy C-276 have exhibited stress-corrosion cracking when used as pressure vessels for hydrothermal processes. Differential thermal expansion, uneven corrosion, pitting and stress-corrosion cracking limits the use of lined vessels. Undetected breached linings could lead to prolonged hidden corrosion of the pressure vessel. The DSPBV vessel eliminates costly choices between strength and corrosion resistance, between temperature, pressure, and vessel life, between safety and effective operation and maintenance. This new technology combines ordinary steel, specialty metal alloys, and ceramics in a unique, patented design to meet the challenges of corrosive chemistry in pressurized processes.

The DSPBV and its supporting equipment are described in detail in Appendix A.

Purpose/Objectives

The objectives of the proposed work were to:

- demonstrate the operability of the DSPBV, and
- fabricate and test leak detector designs at a laboratory scale, and
- test best leak detector design in the DSPBV, and
- test ceramic pieces for corrosion resistance.

Summary of Activities

The dual shell pressure-balanced reactor vessel (DSPBV) was sized to process 10 gal/hr of hazardous waste at up to 399°C (750°F) and 5000 psia (34.5MPa) with a residence time of 10 min. A stress analysis of the reactor vessel indicated the design has a good safety margin for the chosen operating conditions. The first prototype reactor was purchased by Innotek Corporation and built by Engineered Pressure Systems Inc. (a division of National Forge) in Andover, Massachusetts. It was built as a certified ASME pressure vessel. The vessel dimensions resulting from this design and fabrication activity are shown in Appendix A. These activities were accomplished in the first phase of this CRADA project and additional details on the activities were provided in a previous report (PNL-10146).

Supporting equipment and instrumentation was, to a large extent, transported here from Battelle Columbus. A special air feed system and liquid pump were purchased to complete the package.

A Safe Operating Procedure for the complete system was reviewed and approved by Laboratory Safety staff at PNL.

A leak detector design was established and tested. Response to low levels of water in oil was considered adequate to ensure safety of the pressure vessel.

Tests with water were completed to prove the system could operate at 350°C at pressures up to 3300 psia. These were the conditions needed to later process a Navy waste stream.

A Navy waste stream containing cyanides and organics was processed at 350°C and 3300 psig. Very good destructions were seen.

ct Design

The DSPBV selected operating **pressure**[3500 psia (24.1 MPa)] and **temperature** [700°F (371°C)] were based on literature references (Shaw **et.al.**, 1991 and Dell'Orco et. al. 1992) for lab scale results of SCWO. The 10 minute residence time was a compromise based on these reports. Some wastes can be destroyed in a few seconds and others may require 30 min. The 10 gal / hr (36 L/hr) was considered **sufficient** to provide good data for at least a future pilot scale version of the concept.

The DSPBV uses a thick steel outer shell **as** the pressure boundary and a thin disposable inner liner which can be made from corrosion resistant alloys appropriate for the chemicals being processed. The shell and the inner liner are separated by heat transfer fluid (used here as a pressure transfer fluid). The pressure between the heat transfer fluid and the reading fluid is maintained by an external piston that remains at ambient temperature. A pressure compensator is needed because the heat transfer liquid (Syltherm 800®) expands about 65% in volume between ambient and 750°F (399°C).

A second disposable inner liner is used as a flow diverter so reactants enter and products leave the same end of the vessel. The disposable inner liners allow the study of corrosion characteristics of many materials such as **Inconel**, Hastelloy, zirconium, titanium, titanium-tantalum, or titanium-niobium alloys for a fraction of the cost of building a complete reactor out of these materials. The design is inherently safer than metal clad vessels, because sensors in the heat transfer fluid will detect when the corrosion-resistant alloy has been breached. Metal clad vessels have no simple warning system and penetration of the cladding generally results in rapid deterioration of the parent metal.

Appendix A shows a sketch of the fundamental pieces involved in the pressure balanced piston idea. **Other** options were studied but rejected for either time or money considerations. These concepts included 1) a bellows, 2) a sliding o-ring seal, and 3) the balancing piston with a stationary o-ring seal (instead of welds used in the final design).

The supporting equipment needed to operate the DSPBV can be grouped into 5 categories according to function. The equipment pieces are shown in schematics in Appendix A and include:

- the main reactor and pressure balancing piston,
- waste feed supply tanks and pump,
- Syltherm supply tanks and pump,
- high pressure oxygen supply system,
- pressure let-down equipment

The equipment pictured in Appendix A represents what was used to demonstrate the working operation of the DSPBV.

Significant Accomplishments

- The DSPBV and support equipment have been **built and operated**.
- A leak detector design was built with good sensitivity to water in syltherm. This result was critical to demonstrating the viability of the DSPBV concept.
- A waste stream from the Navy was processed. Organics and cyanides were destroyed.
- Funding has been obtained from the Army to build a pilot scale unit. Innotek and Glitsch Engineering will be building the unit. PNL will provide design support.

Significant Problems

Funding levels have been insufficient to do meaningful corrosion studies. The limited runs that were made did not measurably corrode the metals. Ceramic materials were not tested as planned.

Industry-Benefits Realized

This collaborative research program succeeded in building the first prototype Dual Shell Pressure Balanced Vessel. We believe the concept can be commercially successful on a larger scale and can be fabricated much less expensively than current practice. Simultaneously the concept can enhance safety and operability of many emerging high pressure chemical processes.

The adoption and commercialization of a broad range of new high pressure chemical technologies will be enhanced by the development of the DSPBV. The potential market for this vessel is far reaching particularly in environmental management. Specific technologies include supercritical fluid extraction or oxidation, wet air oxidation, hydrothermal materials processing and sewage sludge to oil conversion.

Successful operation of the DSPBV has launched a product wherein Glitsch Technology Corporation of Parsippany, New Jersey will be designing and constructing a pilot-scale version of both the DSPBV and the **NitRem** process for destroying hazardous wastes.

Follow-on Work

The design and fabrication of the first DSPBV have led to funding from the US Army to build a pilot-scale unit. Innotek and Glitsch engineering will be involved in the construction of the unit. PNL will provide technical support.

Existing hydrothermal equipment at PNL (including the DSPBV) will be used to generate design data as it is needed by Glitsch.

Operation of the pilot-scale unit by the Army will complete the bridge between science in the laboratory and private industry utilization.

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Appendix A

**Description
of the**

Dual-Shell Pressure-Balanced Vessel (DSPBV)

also known as the

Dual Shell Reactor

A.0 INTRODUCTION

The Dual Shell Pressure-Balanced Vessel (DSPBV) was developed to test and demonstrate a novel reactor design for moderate temperature, high pressure corrosive conditions. The DSPBV utilizes electrical heat and an oxidant to convert an aqueous organic feedstock into clean water and an exhaust gas composed of mainly nitrogen and carbon dioxide. Conversion occurs at moderate temperature (350 °C -400°C) and high pressure (3500 - 4000 psi). The DSPBV is designed to process 10 gal/hr of dilute organic waste in water.

The initial objective of the test system was to prove that the DSPBV concept will work safely in corrosive environments. Secondary objectives are to determine potential waste destruction efficiencies for various aqueous organic feedstocks that might be encountered in **Hanford** waste streams. Municipal sewage sludge **effluent** treatment is another targeted feedstock. Testing with aqueous organic waste feedstocks takes place in the Materials Reliability center (MRC). The results generated from the testing will be used for design of larger scale treatment facilities.

Feedstocks that may be tested vary **from** dilute organic chemical **bearing** water wastes **containing from** 100 to 100,000 ppm organic contaminants to sewage sludge effluents having about 5% dry solids. Each feedstock is evaluated on an individual basis for environmental and health hazards.

A.1 TEST FACILITY DESCRIPTION

The MRC contains a 100 ft by 50 ft high bay with adjoining office space. The building is conditioned with evaporative coolers and forced-air electric heaters mounted on the roof. The high bay contains a crane with a 20-ton capacity with an 30 ft hook height that has access to the entire high bay floor area. The available utilities are:

- **Richland** city water for process and cooling water
- 480 V, 208 V, and 120 V electrical power
- 100 psig compressed air
- Sewer connections to the **Richland** publicly owned treatment works (POTW)

The MRC facility contains a sprinkler-water **fire** control system connected to the city **water main**.

A.2 TEST SYSTEM DESCRIPTION

Figure A.1 is a construction print for the DSPBV. The DSPBV uses a separate inner shell that fits close to the wall of the outer shell of the pressure vessel made of 1U4 Cr - 1/2 Mo carbon steel (SA182 F11). The **inner** shell is constructed of Incoloy 825 (SB423, 424,425). A pressure-transfer fluid, Syltherm 800, is placed in the **annulus** between the pressure vessel and the Incoloy 825 inner shell. The pressure-transfer fluid is kept physically separate and in hydrostatic equilibrium with the fluid entering the reactor. The pressure balancing is achieved by an external piston. Because the fluid pressure is

Figure A.1 DSR construction print

balanced on both sides of the inner shell, the inner shell is not under **significant** stress, so stress-corrosion cracking is minimized. The inner shell's thickness is determined by corrosion potential rather **than** strength; thus, it must only be **thick** enough to support its own weight and act as an envelope to separate the corrosive reactants from the carbon steel pressure vessel. The DSPBV design provides adequate space between the inner shell and the pressure vessel to allow for **any** degree of differential thermal **expansion**. The strength and corrosion resistance **specifications** of the pressure vessel are **decoupled from** the specifications of the inner shell.

While the pressure-transfer fluid balances the pressure, its electrical properties are continuously monitored to assure the integrity of the inner shell. A significant change in conductivity of the **pressure-transfer** fluid alerts operators to a breach of the inner reactor so it **can** be replaced before the carbon steel pressure vessel corrodes. The ability to continuously **monitor** the integrity of the **working** reactor is a fundamental safety advance in reactor design.

The DSPBV working reactor unit is designed to monitor, protect and preserve the integrity of the carbon steel pressure vessel. The working inner shell is designed for easy replacement as needed. The removable inner shell allows us to test alternate liner materials easily and cheaply.

The DSPBV reactor is a test system designed for obtaining proof-of-principle **information as** well engineering data for the conversion of aqueous organic feedstocks into harmless gases and recyclable water.

Capacity of the test system is 10 **gal/hr** liquid feed with a design flow rate of 10 **gal/hr**. Design working conditions are reactor temperatures of 700 - 750 °F at 3500 psi. The DSPBV was built by Engineered Pressure Systems **Inc.** of **Andover**, MA. to ASME pressure vessel code for operation up to **750°F** (399 °C) and 5000 psia

Figure A.2. shows a sketch of the **fundamental** pieces involved in the pressure balanced piston idea. Other options were studied but rejected for either time or money considerations. These **concepts included** 1) a bellows, 2) a sliding **o-ring** seal, and 3) the inner shells with a stationary o-ring seal (instead of welds used in the final design).

The equipment **can** be **grouped into 6 categories** for purposes of discussion **The** modules are :

- the main reactor and pressure balancing piston,
- process feed tanks, pump, and heat exchanger,
- **Syltherm** supply tank,
- high pressure air supply system,
- pressure let-down equipment, and
- instrumentation.

Figure A.3 shows schematically a picture of the main supporting equipment for the DSPBV. This includes the air supply system and the **pressure** letdown vessel.

Figure A.2 Schematic of reactor and pressure-balancing piston

Figure A.3 DSR and major supporting equipment

Process Feed Tanks and Pump

The process feed tank is 304 stainless steel 50 gal capacity with a metal lid to minimize evaporation into the room. The process feed tank is on an electronic **scale** which is tied to the data acquisition system. Weight readings are used to provide values for process feed flow-rate to the reactor.

A second tank made of polyethylene contains deionized (DI) water for flushing out the reactor between runs. The flushing is done after each **run** to cool the reactor. A third **tank** is used to recirculate water through the shell of the product coolers and feed preheaters.

The process feed pump is an **air** operated, high pressure, positive displacement pump. It will normally operate off **building** air and requires 28 SCFM at full capacity. The pump can be safely operated for at least 10 minutes using air from the storage cylinders of the high pressure **air** system. This **will** allow safe shutdown of the system in the event of failure of the **building** air compressor. The tanks **and** pump are shown in Figure A.4

Syltherm Supply Tank

The syltherm supply **tank** is a carbon steel vessel protected with a safety relief valve that releases at 5 psig. The vessel is designed to have a nitrogen purge. When the reactor annulus is to be filled with Syltherm, a small pump whose suction line is in the **Syltherm** supply tank forces Syltherm into the bottom and out the top of the reactor. When the reactor annulus and pressure balancing piston are full, the **fill** valves at the top and bottom of the reactor are closed.

High Pressure Air Supply System.

The **air** supply system is an industrial unit typically used to **fill** self-contained breathing tanks for fire **departments**. The system can deliver up to 4 ACFM air **at** 6000 psig. The compressor is designed for intermittent use **only**. Consequently two ASME vessels have been included to hold ~300 SCF (150 SCF ea.) air at 6000 psig. {Our operating storage tank pressure will be closer to 4000 psig). Typical air consumption rates will be ~ 2 SCFM, so the demands on the compressor will not be too frequent once the tanks are full.

The complete air supply system is shown schematically in Figure A.5. The air compressor module including the two process air supply tanks has its own internal gauges and sensors **to** protect it from over-pressure, or over-temperature. It also cycles periodically (every 15 **min**) to remove liquid water that may have collected in the compressor. Outlet gas from the compressor to the air supply tanks is filtered to remove any entrained oil from the compressor.

Figure A.4 Water and feed supply tanks plus feed pump

Figure A.5 Air supply system for the DSPBV

Pressure Letdown Equipment

Product exiting the reactor passes through three heat exchangers. These heat exchangers share shell side fluid with another set of heat exchangers designed to preheat the incoming feed. Pressure letdown after cooling occurs in two stages. The first stage **will** drop the pressure **from** 5000 **psia** to 2500 **psia** across the **main** pressure regulating valve. This will release some dissolved gases (primarily CO₂) . From there, the **two**-phase mixture will pass through a final heat exchanger and then expand into a 2-gal autoclave where liquid and gases will separate. Pressure on the autoclave is determined by the pressure set on the gas stream outlet. Liquid flow out the system is determined by the liquid level sensor.

Instrumentation

Type K thermocouples are used to monitor fluid temperatures into and out of the reactor. Pressure transducers monitor pressures. Electronic mass flow meters monitor air flow. Process liquid flow rate is determined by weight loss from the feed tank and by a turbine flow meter. The air supply is monitored continuously using a mass flow meter.

An FMC electropneumatic (NIT 200) controller sets the control parameters (**proportional/integral**) on the air supply to the liquid pump. Another control module monitors differential pressure across the pressure balancing piston. The controller will bleed off **Syltherm** if the Syltherm pressure exceeds the process feed pressure by more than 100 psi. It will also decrease the process feed flow rate if process liquid feed pressure exceeds the **Syltherm** pressure by more than 100 psi. Components of the control system are shown in Figure 6.A.

For **data** reduction purposes there are two computer systems and one stripchart recorder collecting process data. The backup computer (IBM® clone) collects raw data (voltages or **milliamps**). The primary computer (**Macintosh**®) converts most signals to numbers **meaningful** for process control (temperatures/pressures/flows). The primary computer does no real-time process control but does provide operators with immediate feedback on process variables and sounds audible alarms when conditions are beyond specified limits.

Table 1 summarizes the process variables being monitored and their positions at the recording locations. The temperature measurement locations are shown in Figure A.7. Traditional pressure gauges provide backup readings for the reactor fluids and the air supply cylinders.

Figure A.6 Flow and pressure control instrumentation

Table A.1 Process variables measured and recorded

Description	Abbr	T/C dist box	Recorder	IBM clone	Macintosh
Thermocouples					
Reactor liquid in @ 40"	RA40	1	1	1	1
Reactor liquid in @ 20 "	RA20	2	2	2	2
Reactor liquid in @ 0"	RA0	3	3	3	3
Reactor liquid out at 0"	RB0	4	4	4	4
Reactor liquid out @ 20"	RB20	5	5	5	5
Reactor liquid out @ 40"	RB40	6	6	6	6
Syltherm 800 @ 10"	RO10	7	7	7	7
Syltherm 800 @ 30"	RO30	8	8	8	8
Syltherm 800 @ 50"	RO50	9	9	9	17
Reactor skin @ 0"	RS0	10	10	10	18
Reactor skin @ 20"	RS20	11	11	11	19
Reactor skin @ 40 "	RS40	12	12	12	20
Heat exchanger 1 inlet	HX1A	13	13	13	21
Heat exchanger 2 inlet	HX2A	14	14	14	22
Heat exchanger 3 inlet	HX3A	15	15	15	23
Reactor inlet	RCTA	16	16	16	24
Heat exchanger 4 inlet	HX4A	17	17	17	25
Heat exchanger 5 inlet	HX5A	18	18	18	26
Heat exchanger 6 inlet	HX6A	19	19	19	27
Letdown vessel inlet	LDVA	21	20	20	28
Heat exchanger water inlet	HXWA	22	21	21	29
Heat exchanger water outlet	HXWB	20	22	22	30
spare		23			
spare		24			
Others					
Air flow "A"	MFMA		23	23	9
Air Flow "B"	MFMB		24	24	10
Reactor pressure	RCTP		25	25	11
Letdown vessel pressure	LDVP		26	26	12
Process feed line pressure	LIQP		27	27	13
DP Syltherm/process feed	OWDP		28	28	14
Feed Weight in Kg	WTKG		29	29	15
Feed flow in GPH	FGPH		30	30	16
spare			31	31	
spare			32	32

Figure A.7 Temperature measurement locations

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