INEL-94/0005
(Formerly EGG-WTD-11316)
Revision 1

Hazard Classification for the Supercritical Water Oxidation Test Bed

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ABSTRACT

A hazard classification of "routinely accepted by the public" has been determined for the operation of the supercritical water oxidation test bed at the Idaho National Engineering Laboratory. This determination is based on the fact that the design and proposed operation meet or exceed appropriate national standards so that the risks are equivalent to those present in similar activities conducted in private industry. Each of the 17 criteria for hazards "routinely accepted by the public," identified in the EG&G Idaho, Inc., *Safety Manual*, were analyzed.

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ACRONYMS

ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers
CFR	Code of Federal Regulations
DOE	U.S. Department of Energy
GOX	gaseous oxygen
IDLH	immediately dangerous to life or health
INEL	Idaho National Engineering Laboratory
LITCO	Lockheed Idaho Technologies Company
LEL	lower explosive limit
LOX	liquid oxygen
NFPA	National Fire Protection Association
RCRA	Resource Conservation and Recovery Act
SAR	Safety Analysis Report
SCFM	standard cubic feet per minute
SD	Supplemental Directive
SCWO	supercritical water oxidation
WRRTF	Water Reactor Research Test Facility

Hazard Classification for the Supercritical Water Oxidation Test Bed

1. INTRODUCTION

U.S. Department of Energy (DOE) Order 5481.1B, *Safety Analysis and Review System*, and DOE Idaho Operations Office Supplemental Directive (SD) 5481.1B, *Safety Analysis and Review System*, require that a hazard classification be conducted for all DOE activities for which DOE has assumed environment, safety, and health responsibility. A hazard classification, also called a hazard class determination, defines the level of hazard posed by an operation. The hazard classification determines whether a Safety Analysis Report (SAR) is required for a non-nuclear operation. Furthermore, it identifies the specific review and approval requirements for the SAR, which defines the active safety systems and operational safety requirements needed to conduct a safe operation.

This report documents a hazard classification conducted for the supercritical water oxidation (SCWO) test bed at the Idaho National Engineering Laboratory (INEL). This reactor will treat simulated mixed waste without the radioactive component. It will be designed to operate with eight test wastes. These test wastes have been chosen to represent a broad cross-section of candidate mixed wastes anticipated for storage or generation by DOE. In particular, the test bed will generate data to evaluate the ability of the technology to treat chlorinated waste and other wastes that have in the past caused severe corrosion and deposition in SCWO reactors.

2. SUMMARY

A hazard classification of "routinely accepted by the public" has been determined for the operation of the SCWO test bed. This determination is based on the fact that the design and proposed operation meet or exceed appropriate national standards so that the risks are equivalent to those present in similar activities conducted in private industry. Each of the 17 criteria for hazards routinely accepted by the public, identified in the EG&G Idaho, Inc., *Safety Manual*, were analyzed. A detailed evaluation of each criterion is presented in Section 4.

3. SUPERCRITICAL WATER OXIDATION TEST BED

3.1 Background

Almost all DOE sites are generating and/or storing mixed wastes, i.e., wastes contaminated with both radioactive and hazardous constituents. These mixed wastes cannot be disposed of by current conventional means such as incineration, landfills, and deep burial. DOE has directed that technologies be developed for the successful treatment of mixed wastes and that facilities be designed and developed for changing the waste into a form that can be legally and inexpensively disposed of. One of the technologies being investigated for treatment of mixed waste is SCWO. This process destroys the organic content of mixed wastes by injecting into a reactor a mixture of water and waste that is pressurized and heated above the critical point of water. Pure oxygen is also injected into the reactor to oxidize the organics. Depending on the waste, small quantities of inorganic radioactive material and salts may remain after processing.

The SCWO process is in an early stage of technical development. The primary challenge is to attain the desired destruction efficiencies while limiting corrosion of plant components. The most important component of the SCWO process is the reactor. Several innovative reactor concepts currently being considered for development include a transpiring wall reactor, tubular reactor, and vessel-type reactor. Each of these designs attempts high-destruction efficiencies and limits corrosion of the reactor walls and internals.

3.2 Process Description

DOE has made a commitment to build a test bed to test and develop various SCWO subsystems and components. The test bed will be located at the INEL's Water Reactor Research Test Facility (WRRTF) (see Figure 1) and will process a maximum of 50 gph of waste. Of the 50 gph, a maximum is 10 percent waste, and the remainder is water. The test bed will be capable of running continuously for up to 100 hr, and will be designed to operate for a total of 17,000 hr over a 5-yr period. The primary purpose of the test bed and the testing effort is to evaluate the operating characteristics of various reactor designs, subsystems, and components.

The detailed requirements for the engineering and design of the test bed are documented in *Design Requirements for the Supercritical Water Oxidation Test Bed* (Svoboda and Valentich, 1994). Reactor design will be provided by private industry. Figure 2 is a process flow diagram that shows the major components proposed for the SCWO Test Bed. The test bed shall consist of a deionized water subsystem; water heating and pressurization subsystem; waste mixing, pressurization and heating; oxygen pressurization; interfaces to the reactor; several phases of pressure and temperature letdown; gas containment and emission; and disposal of the reactor effluent.

The deionizing water system will be sized to produce and store adequate quantities of clean water that will be used to mix with waste, as mixing water to the reactor, and as cooling water. Based on the quantity and BTU content of waste to be processed, a maximum of 400 gph of water will be required with a storage capacity of 5,000 gallons. The waste mixing process involves combining clean water with wastes to simulate the types of constituents that would be

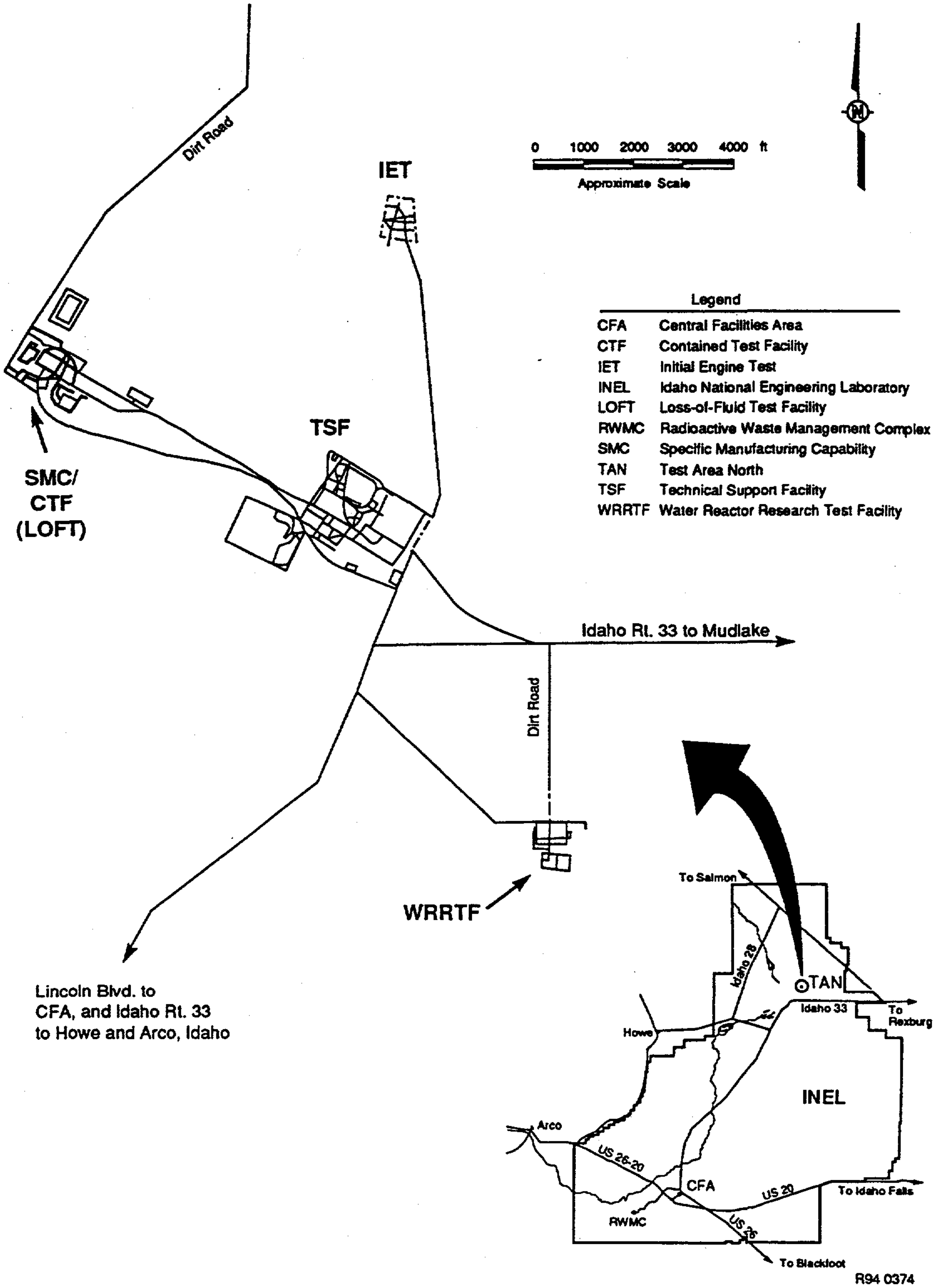

Figure 1. Location map of WRRTF, site of the SCWO test.

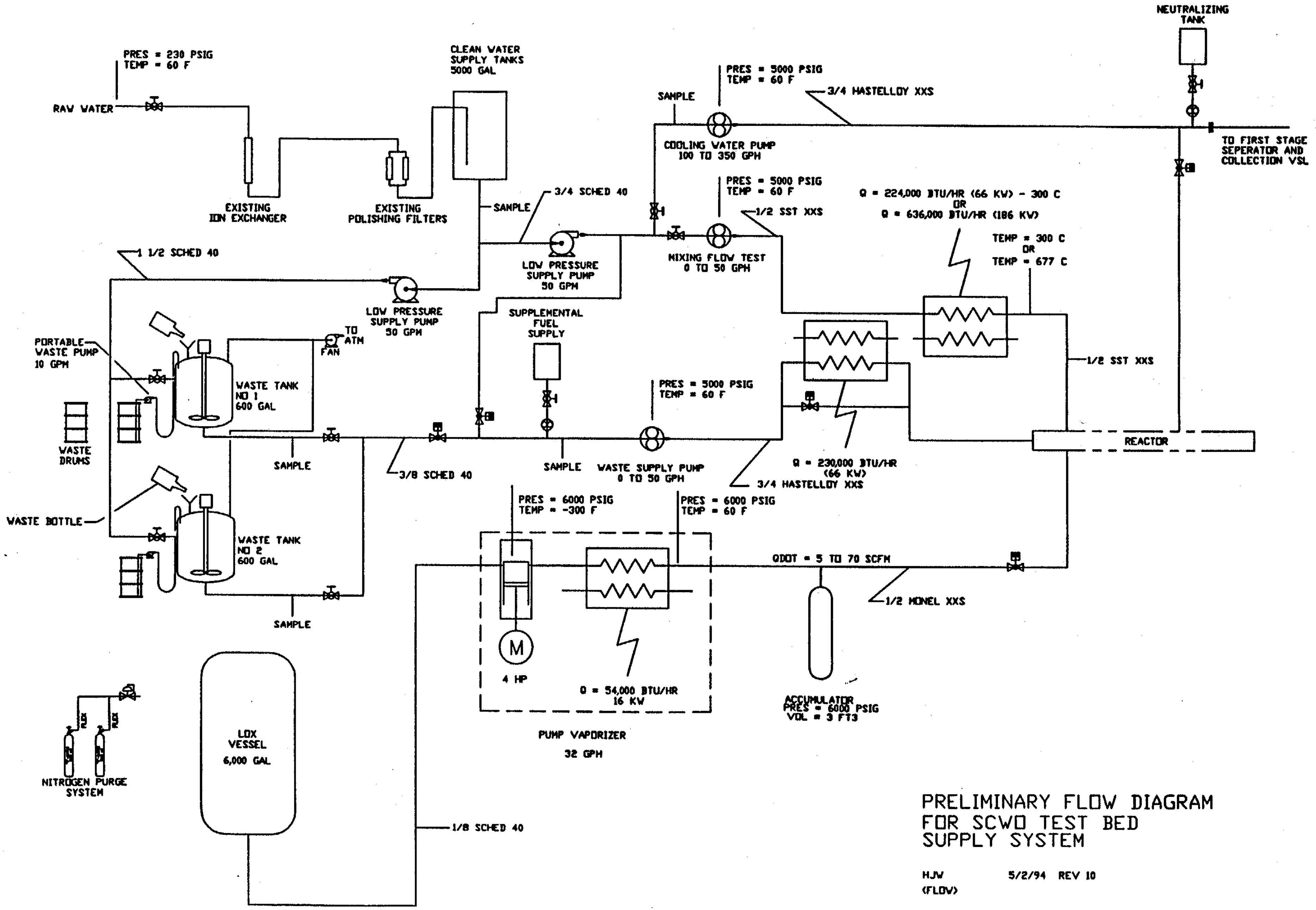

Figure 2. Process flow diagram of major components of SCWO test bed.

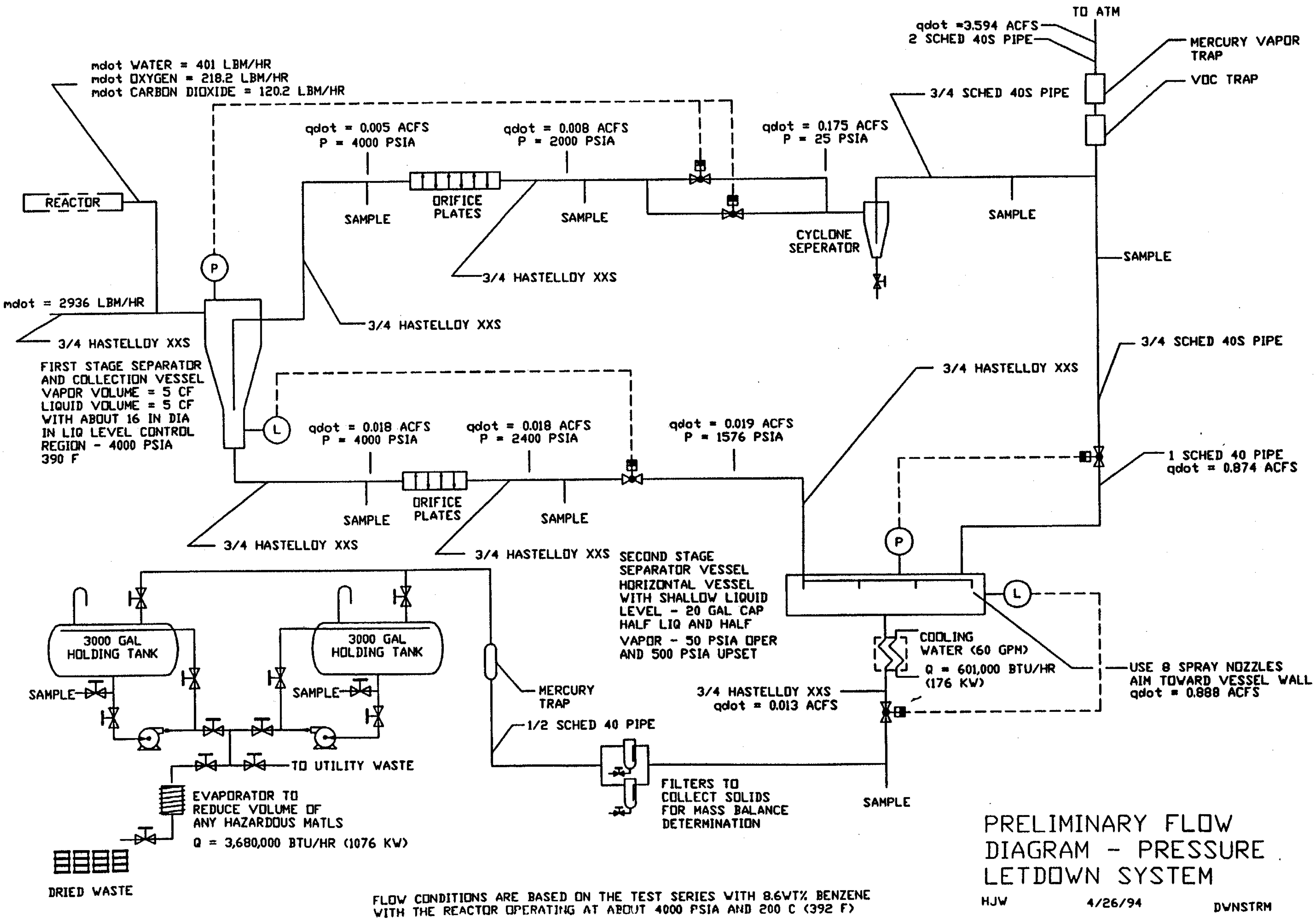

Figure 2. (continued).

present in DOE mixed waste. The series of tests to be conducted will not use any radioactive material in the simulated waste. Only the hazardous chemical constituent will be processed. The waste treatment process is as follows.

The waste and water are mixed with a paddle mixer in two tanks. After mixing, the waste is pressurized by a pump to between 3,500 and 4,500 psig and then brought to temperature (ambient to 572°F) by a direct current electric heater. After heating, the waste is injected into the reactor. Clean water from the storage tank is also injected into the reactor. The clean water is also pressurized to between 3,500 and 4,500 psig and is heated to between ambient and 1,250°F. Gaseous oxygen (GOX) is added to the reactor at a maximum rate of 70 standard cubic feet per minute (SCFM), which is based on a maximum requirement of three times the stoichiometric oxygen required for the waste. GOX is supplied from a liquid oxygen (LOX) storage tank and vaporizer, which are sized to supply about 150 hr of GOX at the maximum usage rate of 70 SCFM. The pump vaporizer system pressurizes the LOX to 5000 psia and the vaporizer heats the oxygen to convert LOX to GOX; the final GOX temperature will be about 60°F. An accumulator is provided to ensure that an adequate volume of oxygen is available to allow a smooth shutdown of the test if electrical power is lost or the pump vaporizer fails. The accumulator is sized to supply about 1 minute of GOX at 70 SCFM. pressurized to a maximum of 6,000 psig. The accumulator will maintain a pressure in excess of about 1,000 psig of the reactor's normal operating pressure to ensure that waste from the reactor does not enter the GOX system. After oxidation in the reactor, cooling water supplied from the deionized water system is added to help reduce the temperature of the fluid and cool the reactor structural components. Effluent is transferred from the reactor to the first-stage liquid and gas separation vessel, which normally operates from 3,500 to 4,000 psig. Gas is separated from the liquid in the vessel and then travels through a series of orifice plates that reduce the pressure to about 2,000 psia, through a pressure control valve that drops the pressure again to 25 psia, and then into a filter that removes particulates and liquid from the gas. The gas is routed through a series of carbon filters that collect any remaining harmful constituents. The gas is then vented to the atmosphere. The liquid from the first-stage separator may also be cooled by adding water into the separator vessel. The liquid leaves the separator vessel and continues through a series of orifice plates that reduce the pressure to about 2,400 psia. A level control valve further reduces the pressure to about 500 psia. The liquid is sprayed into a second-stage separation vessel, which is designed to remove the remaining gas from the liquid. The second-stage separator vessel is controlled at 60 psig by a pressure control valve in the gas vent line. Some of the water will flash to steam as it enters the vessel, which will help separate the gas from the liquid stream and cool the water to about 300°F. The second stage separator is sized to allow about 3 minutes of operation with the outlet valves closed or the lines plugged. This provides sufficient time to make an orderly shutdown. During this type of failure the separator pressure could increase to near 500 psig as the gas in the space is compressed. Thus, the design pressure of the separator for upset conditions is 500 psig. Effluent is sprayed on the walls of the second-stage separator to liberate gases from the fluid. Gas from the second-stage separator is routed to the gas filtering system, and liquid effluent passes through a solids separation filter and then to a storage tank.

After processing a sample is obtained from the storage tank to determine if the liquid is hazardous or nonhazardous. If the sample is determined to be hazardous, the liquid from the storage tank is routed to an evaporator that boils off the free liquid, and the remaining sludge will be collected and disposed in accordance with Resource Conservation and Recovery Act (RCRA) guidelines. Other hazardous solids collected from the test bed separators and filters will also be disposed in accordance with RCRA. If the liquid in the storage tank is nonhazardous, it will be disposed of through a drain to an existing evaporation pond.

The test bed will be designed using standard industry codes and regulations that govern engineering, fabrication, and construction of components such as piping, pressure vessels, tanks, instruments, structural steel, and electrical components. For safety and environmental purposes, the high-pressure systems of the SCWO test bed will be located in the north pit in Test Area North-646 at WRRTF, which is a concrete pit about 30 feet deep. All operations will be performed remotely so that personnel will not be in contact with any of the high pressure/temperature equipment. However, personnel may work around areas of low pressure above the pit area. Provisions for on-line, continuous sampling shall be allowed for in the design of the hardware, so that samples may be obtained in a safe manner while the test bed is operating. A means shall be provided for storage of solids effluent before sampling and disposal. Chemicals shall be stored in accordance to facility environmental permits.

Industrial hygiene personnel shall evaluate the operations prior to startup testing. They will identify and quantify potential health hazards as required by DOE Order 5480.10. The carcinogen control program requirements are in DOE Order 5480.10. The EG&G Idaho Company Procedure for Industrial Hygiene Workplace Surveys implement the Order. Work control documents or procedures will specify PPE requirements.

3.3 Simulated Waste Composition

The following series of DOE-simulated wastes have been identified for SCWO testing; these wastes cover a wide spectrum of constituents that could be introduced into a mixed waste treatment plant:

- Series 1—aromatics with mercury
- Series 2—nonchlorinated solvents with metals
- Series 3—paper, cloth, and plastic
- Series 4—TRIM®SOL
- Series 5—mixed oils
- Series 6—activated carbon
- Series 7—scintillation fluid
- Series 8—tributyl phosphate.

Each selected series represent mixtures and concentrations of hydrocarbons, heavy metals, salts, and radioactive surrogates. The composition of each series is presented in the document, *Supercritical Water Oxidation Test Bed Functional and Operational Requirements* (Barnes et al., 1994). A detailed discussion about the selection process and each of the wastes is presented in *Mixed Waste Survey for Supercritical Water Oxidation Program* (Barnes, 1993). The test bed will be designed for processing all the test wastes, but the highest priority will be placed on the first four.

For design purposes, the following boundary conditions are observed relative to waste composition:

- The maximum concentration of waste constituents per 50 gallons of waste and reactor mixing water is 10 percent. For the eight series of waste, TRIM®SOL is the most corrosive, although at ambient conditions it has not caused excessive corrosion when in contact with stainless steel (based on observations from existing SCWO test beds). In bench-scale tests conducted, the highest corrosion rates were seen in the preheater, before entering the reactor.

- For the effluent, the most corrosive condition expected is hydrochloric acid, which will be formed from chloride contained in Series 4, TRIM®SOL. The plan is to neutralize the acid; the minimum pH expected after neutralization is 2. For design purposes, it is assumed that the addition of a neutralizing agent will neutralize 80 percent of the acid for any series of wastes containing acid. The remainder of the acid will be concentrated in the effluent at a maximum level of 1,500 ppm. This concentration is in pure effluent and assumes that no cooling water will be added, so the estimate is conservative. An in-service inspection system shall be designed for critical components such as vessels, piping, valves, and pumps.

- Series 2, nonchlorinated solvents with metals, shall be used as the design basis for maximum particulate concentration in the waste feed and effluent. Maximum particulate size allowed in the feed is 100 microns. A total of 2,200 ppm of undissolved solids (assuming no dilution from the cooling waterstream) would be the maximum amount contained in the waste feed. For the effluent, maximum undissolved solids will be assumed to be the amount present in the waste feed (i.e., 2,200 ppm) plus any solids generated by corrosion. A conservative estimate for the maximum quantity of undissolved solids in the effluent is 4,400 ppm.

3.4 Test Bed Studies and Design Documentation

At the time this Hazard Classification was being written, the design of the project was in its final approval stage. Appendix A contains a list of the documents that were generated during the design of the SCWO Test Bed. These documents consist of Engineering Specifications, A&E Specifications, Engineering Design Files, and all the required drawings for the system. The documents were developed in for the following areas: (1) Process, (2) Piping, (3) Vessels, (4) Valves, (5) Equipment, (6) Tubing, (7) In-Line Components, (8) Instruments and Controls, (9) Electrical, (10) Civil/A-E, and (11) Hyro/Cleaning. The documentation is not finalized at this time, however it is not expected to change significantly enough to impact this classification.

The hazard classification assessment in the next section (Section 4. Hazard Classification Assessment) takes all the engineering and design work into consideration when determining the classification. The system was designed to operate under the specified conditions (i.e. at high temperature and pressure, and with hazardous and corrosive materials).

4. HAZARD CLASSIFICATION ASSESSMENT

Section 2 of the EG&G Idaho *Safety Manual* contains requirements for performing a hazard classification in accordance with DOE-ID SD 5481.1B for EG&G Idaho facilities, activities, and operations. An activity may be considered "routinely accepted by the public" without further analysis if it meets each of the criteria of Section 2 Appendix II, Table II-1, "EG&G Idaho Standard for Acceptable Risk Without Further Analysis." An activity that does not meet all of the criteria may still be considered "routinely accepted by the public" if the hazard classification demonstrates that the criteria that are exceeded are controlled to appropriate national standards such that the risks are equivalent to those present in similar activities conducted in the public arena.[a] Any deviations from national codes and standards will be documented to technically justify the design and material used in the system.

Table 1 contains the 17 "routinely accepted by the public" criteria and the analysis for SCWO test bed operation. Two of the criteria were not met: pressure and high temperature. The following two sections discuss flammable material and the hazards that did not meet the criteria. These hazards are common in the chemical and petroleum industry and are mitigated by design and physical and administrative controls.

4.1 Flammable Material

Some of the simulated mixed waste to be processed in the SCWO test bed will be flammable material (F.P. <100°F). 29 Code of Federal Regulations (CFR) 1910.119, *Process Safety Management of Highly Hazardous Chemicals*, requires a process hazard analysis for any process that involves a flammable liquid or gas on-site in one location in a quantity of 10,000 lb or more. The SCWO pilot scale plant will not have on-site in one location more than 10,000 lb of flammable material. The current plans are to run one 100-hr test at the end of the project using a 10 percent waste mixture. Also, the plans are to have less than two 55-gallon drums of benzene in the mixing area at one time. Typically the tests will be 20 to 30 hr long using a 10 percent waste mixture. Storage of simulated waste to be processed will be kept to a minimum.

Based on 29 CFR 1910.119, no process hazard analysis is required for flammable material. This hazard is considered normal in the chemical and petroleum industry and is acceptable while operating within the specified design and legal limits.

The process and facility will be designed and constructed to the applicable National Fire Protection Association (NFPA) National Fire Code Standards as specified in the Functional/Operational Requirements (Barnes et al., 1994) and Design Requirements (Svoboda and Valentich, 1994). All flammable material will be properly labeled, no smoking will be allowed in the building, and the area will be kept clean and free of combustible material and ignition

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[a] Interoffice Correspondence, J. W. Rice to R. F. Bonney, "Interpretation of Routinely Accepted by the Public Hazard Classification for EG&G Idaho Safety Analysis Documentation and Requirements-JWR-05-94," January 19, 1994.

Table 1. Summary of acceptable risk criteria without further safety analysis for the supercritical water oxidation test bed.

Item	Hazard	Criteria	Analysis
1	Rad waste	≤2 nCi/g	There will be no radiological materials involved in this pilot scale plant.
2	Ionization radiation	≤100 mRem/yr on-site ≤10 mRem/yr off-site (Not including natural background radiation)	There will be no radiation resulting from the proposed activities.
3	Fissionable materials	≤15 g	There will be no fissionable material involved in this pilot scale plant.
4	Standard industrial hazards	Any item listed and qualified in the guidance for item 4 (EG&G Idaho *Safety Manual*)	Standard industrial hazards associated with the operation shall be in compliance with Occupational Safety and Health Administration regulations.
5	x-ray equipment	Meets American National Standards Institute (ANSI) x-ray standards	No x-ray equipment will be used.
6	Toxic materials	Potential air concentrations less than 1/2 immediately dangerous to life or death (IDLH)	All concentrations of hazardous chemicals are much less than 1/2 IDLH. See Appendix B for details.
7	Flammable materials	Inventory not more than 110 gal or as covered by identified applicable NFPA code	Some flammable materials will be present during operation (see Section 4.1). The 110 gal limit is not expected to be exceeded.
8	Explosive materials	No high explosives and ≤10 oz low explosives	No explosive materials will be used.
9	Reactive materials	Hazard Level 0 and 1 only	Level 1—material normally stable, but unstable at elevated temperature and pressure; may react with water. All chemical reactions will be controlled and take place in the reactor.
10	Chemical incompatibility	≤1 kg	All chemical reactions will be controlled and take place in the reactor.
11	Lasers	ANSI Z136.1 Class I or II or Class III with enclosed beam	No lasers will be used.

Table 1. (continued).

Item	Hazard	Criteria	Analysis
12	Electrical	No more than 600V; if more than 600V, then no more than 25mA and no more than 50J stored energy	No high voltage is required for the operation.
13	Kinetic energy	No unusual or unique high kinetic energy systems	Only normal industrial hazards are expected.
14	Pressure	Stored energy no more than 0.1 lb TNT (equivalent) if pressure is more than 3,000 psig	High-pressure sources will be present (see Section 4.2).
15	High temperature	Incapable of environmental interaction to cause overpressure or to initiate release of hazardous materials	High-temperature sources will be present (see Section 4.2).
16	Biohazards	Review by an industrial hygienist indicates that special controls are required	No biohazards are expected.
17	Asphyxiants	Oxygen between 19.53 and 23.57%	Gas monitoring equipment will be used.

sources. The storage of flammable and combustible liquids for use in the process will be located in a Uniform Building Code, Uniform Fire Code, and NFPA approved "hazardous storage building." The building will be located 50 feet from the existing facility. The facility and operation will have the appropriate heating, ventilating and air-conditioning system suited for the SCWO test bed requirements to prevent buildup of ignitable vapors. A qualified fire protection engineer has conducted a review of the facility and has determined that a potential for a fire is minimal.

An oxygen monitoring system shall be installed in the north pit. A series of oxygen monitors shall be located in the pit and capable of detecting either an abnormally high or low concentration of oxygen in the air. A high concentration indicates a leak in the oxygen supply system, while a low concentration indicates a potential leak in the process equipment piping. The monitors shall be designed to alarm both locally and at the control console when an abnormal condition is detected. Based on the FMEA study for the oxygen system (Johnson and Welland, 1994), several safeguards will be in place to prevent, or mitigate, possible failures. Failure modes that may lead to a potential fire hazard include, overpressurization of the GOX and overheating of the LOX. The safeguards that will be in place are pressure safety valves, rupture disks, pressure controller and indicator, temperature transmitter and indicator, remote controlled valves, and high pressure alarms. Valves and piping coming in contact with the gas stream, in the high-pressure gaseous oxygen portion of the system, shall have components fabricated from materials that will not ignite when exposed to the temperatures and pressures specified (EG&G Idaho, 1994.)

Appendix D contains calculations of benzene vapor concentration in the north pit resulting from a rupture in the piping system during operation of the SCWO Test Bed. The calculations indicate that under extreme accident conditions, the lel of benzene (1.4 percent) would not be reached. The flammable material expected in the simulated waste does not pose any unusual risks that are not standard industrial hazards. Therefore, based on 29 CFR 1910.119 and design, construction, and standard work control documentation, this hazard is of acceptable risk to the public without further safety analysis.

4.2 High Pressure/Temperature Systems

The following SCWO test bed systems/or processes operate at high temperature and pressure: (a) high-pressure waste delivery (up to 4,500 psig and 572°F), (b) high-pressure mixing water supply to reactor (up to 4,500 psig and 1,250°F), (c) high-pressure reactor and first-stage separator cooling water (up to 4,500 psig and 100°F), (d) GOX accumulator (up to 6,000 psig and approximately 100°F), and (e) second-stage high-pressure separation (reduced from 4,500 psig to 50–500 psig and cooling from 482°F). Figure 2 depicts the process flow and shows where the system is pressurized/heated and depressurized/cooled.

All vessels and associated piping will be designed and constructed to meet applicable codes and standards such as American Society of Mechanical Engineers (ASME)—Boiler and Pressure Vessel Code, Section VIII, Divisions 1 and 2, and Section IX, Welding Qualifications. The detailed codes and standards are specified in *Design Requirements for the Supercritical Water Oxidation Test Bed* (Svoboda and Valentich, 1994).

Highly corrosive compounds will be present in the SCWO test bed effluent. A technically justified corrosion allowance shall be specified to determine the minimum required wall thicknesses of each system component to allow for general corrosion. The corrosion allowance shall be determined by evaluating known data relative to the corrosion rates of materials subjected to process conditions similar to those expected for the SCWO test bed. Stress corrosion cracking is also a key design concern. Materials and component geometry shall be selected to prevent or mitigate the effects of stress corrosion cracking. A corrosion measurement system shall be provided so that plant performance can be measured. This will be documented in procedures and plans prior to startup.

The SCWO test bed design requirements for engineered safety-related systems are contained in various codes and standards that are used for design of pressure and energy systems in private industry. Additional safety standards are contained in the EG&G Idaho *Safety Manual*. The design shall comply with all applicable Federal, state, and local health, safety, and environmental codes. The following are key safety issues associated with the design of the SCWO test bed; these are described in more detail in *Design Requirements for the Supercritical Water Oxidation Test Bed* (Svoboda and Valentich, 1994):

- High-pressure and high-temperature systems shall be remotely operated because the SCWO test bed is comprised of several high-pressure and high-temperature systems containing hazardous materials.

- All pressurized systems shall be provided with at least one device specifically designed for overpressure relief. All ASME code vessels shall be provided with individual safety relief devices. All piping systems shall be evaluated to determine where pressure relief shall be provided based on accidental valve, component, or equipment failures that would cause buildup of excess pressure. Relief pressures shall be no higher than allowed by the governing design code. Relief pressures may be lower than code requirements depending on process and safety requirements for a specific system.

- In addition to remote operation, the high-pressure and high-temperature systems shall be shielded from personnel. The plan is to locate the test bed in the north pit at WRRTF. This configuration shall allow the high-pressure portions of the plant to be located in a concrete-lined pit, approximately 30 feet deep.

- The north pit shall also serve as a means for containment of fluids in case of a spill or other emergency condition.

- The process and control systems shall incorporate human factors design into the logic and operation of the test bed. Consideration shall be given to control of the system during normal operation with emphasis on emergency response and safe shutdown during upset and alarm conditions. Each process shall be evaluated for (a) the need for level, pressure, temperature, or other types of alarms to alert an operator of an upset condition; (b) pressure relief in the event of operator error and equipment failure, and in the event of an emergency condition, all systems shall incorporate a means for pressure relief to prevent explosions or rupturing of system components; (c) automatic control of process elements such as temperature, flow, and pressure shall be evaluated to ensure that modulation of these elements are performed by the control system with minimum operator intervention; and (d) interlocks: an evaluation shall be performed to determined what emergency and alarm conditions require automatic shutdown of other portions of the process system.

The high-pressure/temperature systems described are common in private industry. All pressure vessels and associated piping required for this test bed are commercially available. Barriers and controls will be put in place to prevent or mitigate personnel injury such as exposure to hazardous chemicals due to system failure. Personnel will not be allowed in or around the pit during operation of the SCWO Test Bed. Exposures to hazardous chemicals (i.e., benzene, hydrogen chloride, heavy metals, etc.) during operation are not expected, assuming that appropriate procedures and work control documents are followed. The risks associated with this operation are no greater than at any other private industry pilot plant operation.

4.3 Classification

The hazards associated with the operation of the SCWO test bed have all been determined to be "routinely accepted by the public." Two of the criteria in Table 1 were not met: pressure and high temperature. However, these hazards have been evaluated and have been determined to routinely accepted by the public. Therefore, no further safety analysis is required for this operation.

5. REFERENCES

Barnes, C. M., et al., 1994, Supercritical Water Oxidation Test Bed Functional and Operational Requirements,EGG-WTD-11200, EG&G Idaho, Inc., February.

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Johnson, D. A., and Welland, H. J., 1994, Failure Modes and Effects Analysis for the Supercritical Water Oxidation Test Bed, INEL-94/0015, LITCO Internal Report, October.

Svoboda, J. M., D. J. Valentich, 1994, Design Requirementsfor the Supercritical Water Oxidation Test Bed, EGG-WTD-11199, Revision 0, EG&G Idaho, Inc., May.

Appendix A

Documents Pertaining to the Supercritical Water Oxidation Test Bed

Appendix A

Documents Pertaining to the Supercritical Water Oxidation Test Bed

Engineering Specifications

ES-51542	A turnkey Liquid and Gas Sampling System for a Supercritical Water Oxidation Facility
ES-51534	Specification for Procurement of a Second Stage Separator for the Supercritical Water Oxidation Test Bed
ES-51535	Supercritical Water Oxidation Mixing Flow and Waste Heaters
ES-51536	Supercritical Water Oxidation Oxygen Supply System
ES-51538	Supercritical Water Oxidation Ambient Pressure Evaporator
ES-51540	Specification Procurement of Flow Control Valves (FCV) for the Supercritical Water Oxidation Project (SCWOP)

Architectural Engineering (A-E) Specifications

Division 1 -- General Requirements	
01005	Summary of Work
Division 2 -- Sitework	
02200	Earthwork
Division 3 -- Concrete	
03300	Cast in Place Concrete
Division 5 -- Metals	

05100	Structural Steel and Miscellaneous Metals
Division 9 -- Finishes	
09900	Painting
Division 15 -- Mechanical	
15015	Field Fabrication and Installation of Piping
15016	Equipment and Component Installation
15017	Tubing Material and Installation
15141	Centrifugal Pumps
15150	Storage Tanks, Mixing Tanks, and Associated Equipment
15153	SCWO Positive Displacement High Pressure Pumps
15154	Metering Pumps
15250	Insulation for Mechanical Systems
15412	Pressure Testing of Mechanical Systems
15413	Piping, Tubing, and Component Labeling
15755	Heat Exchanger
15887	Solid Separation Filters
15888	Gas Letdown Particulate Filter
15889	Gas Letdown Volatile Organic Compound Filtering System
15890	Mercury Resin Trap
Division 16 -- Electrical	
16000	Electrical General Provisions
16170	Uninterruptable Power Supply
16500	Lightning
16781	SCWO CCTV Monitoring System
16901	General Instrumentation
16902	Process Control Interface
16920	Motor Control Centers

Engineering Design Files (EDFs)

TDF Numbers	Title	Author	Issue Date
ID121217/2001	Calculation of Feed and Effluent Compositions for Eight Test Waste Cases	C. Barnes	03/24/94
ID121217/2002	Test Bed Worst Case Air Emissions	C. Barnes	03/24/94
ID121217/2003	Orifice Plates to Help Reduce Pressure	B. Reed	07/25/94
ID121217/2004	Design of Rx and 1st stage separation, 2nd stage separation, and Oxygen Accumulators	D. Valentich	06/10/94
ID121217/2005	Pressure Loss Calculations for Low Pressure Water and Simulated Waste	H. Welland	07/25/94
ID121217/2006	Pressure Loss Calculations for High Pressure Water and Simulated Waste from High Pressure Pumps to Reaction Vessel	H. Welland	07/25/94
ID12127/2007	Preliminary SCWO Test Bed Operating Processes for Startup, Steady State, Shutdown, and Maintenance	H. Welland	07/27/94
ID121217/2008	Energy Requirements for Evaporator Operation	S. McBride	06/09/94
ID121217/2010	Hazardous Occupancy Study	S. Austad	07/22/94
ID121217/2011	Mixing Tanks and Waste Tanks Containment	S. Austad	06/15/94
ID121217/2012	Pressure Loss Calculations for Liquid Effluent for the 1st Stage Separator to the 2nd	H. Welland	07/25/94
ID121217/2013	Pressure Loss Calculations for Gaseous Effluent from the First Stage Separator to the Atmosphere	H. Welland	07/25/94
ID121217/2014	Pressure Loss Calculations for Liquid Effluent from the Second Stage Separator	H. Welland	07/25/94
ID121217/2015	High Temperature Heater	S. McBride	07/13/94
ID121217/2016	Super Critical Water Oxidation (SCWO) Nitrogen Purge Orifice Sizing	S. McBride	

TDF Numbers	Title	Author	Issue Date
ID121217/2017	Concrete Flow Slab Adequacy	S. Austad	08/15/94
ID121217/2018	Valve List	J. Sekot	08/03/94
ID121217/2019	Selection of Flow Control Valves (FCVs)	J. Sekot	08/03/94
ID121217/2020	Selection of Hand Valves for High Pressure Service	J. Sekot	08/03/94
ID121217/2021	Selection of Hand Valves for Low Pressure Service	J. Sekot	08/03/94
ID121217/2022	Selection of Remote Operated Valves	J. Sekot	08/03/94
ID121217/2023	Selection of Pressure Relief Valves and Check Valves	J. Sekot	08/16/94
ID121217/2024	Pipe Wall Thickness Calibrations	R. Easter	08/02/94
ID121217/2025	Performance Category Determination	C. O'Brien	08/08/94
ID121217/2026	Discussion of the Allowable Stresses	C. O'Brien	08/08/94
ID121217/2027	Preliminary Stress Analysis of the SCWO Test Bed	C. O'Brien	08/08/94
ID121217/2028	Preliminary Phase Calculation for the 1st Stage Separator	C. Oh	08/09/94
ID121217/2029	Process Simulation Results	D. M. Ginosar	
ID121217/2030		C. O'Brien	

Drawings

(See SCWO Test Bed Design Drawing Index Sheets 1 and 2.)

Appendix B

Summary of Simulated Waste Exposure Concentrations

Appendix B

Summary of Simulated Waste Exposure Concentrations

For each waste stream series, the maximum feed waste capacity was assumed. The input rate of 50 gal/hr for a 100-hr test assuming 15 percent is waste and remaining volume being water was used. This would make the incoming expected volume to be 750 gallons of waste. This involves a maximum amount of waste per waste series. The release of hazardous waste was assumed to be on the ground floor (the open area). The assumptions were extremely conservative; this was intended in order to bound any possible release.

B-1. Series 1—Aromatics with Mercury

Assumptions:

1. 750 gal of waste present.
2. Benzene will volatilize in an area of $72m^2$ (open area 26×30 ft^2).
3. The density of this waste stream is 0.91 g/cm^3.
4. Diphenyl mercury (2,000 ppm) will be assumed to be all mercury. Diphenyl mercury does not have an IDLH listing.
5. Biphenyl does not have an IDLH listing (it is toxic by ingestion).
6. Diphenylamine does not have an IDLH listing (poison by ingestion).
7. Benzene, phenol, and mercury bound any detrimental health effects for this waste series.

Table B-1 presents calculated IDLH percentages for Series 1 waste (see support calculations in Appendix C for details).

Table B-1. Series 1—aromatics with mercury.

Chemical	Amount	IDLH (mg/m^3)	Worker exposure (mg/m^3)	IDLH (%)
Benzene	80 wt%	9.75E+03	2.20E+03	22.53
Phenol	2.5 wt%	9.50E+02	7.50E-01	0.08
Diphenyl mercury (assumed all mercury)	2000 ppm	1.0E+01	6.02E-01	0.60

B-2. Series 2—Nonchlorinated Solvents with Metals

Assumptions:

1. 750 gal of waste present
2. Acetone and methanol will volatilize in an area of 72 m^2 (open area 26 × 30 ft^2)
3. The density of this waste stream is 0.80 g/cm^3
4. Acetone and methanol are a 50/50 wt% mixture
5. Chromium, selenium, silver, neodymium, samarium, and europium do not have an IDLH listing
6. Arsenic, barium, cadmium, and lead bound any detrimental health effects from metals, for this waste series.

Table B-2 presents calculated IDLH percentages for Series 2 waste (see support calculations in Appendix C for details).

B-3. Series 3—Paper, Cloth, and Plastic

No analysis was required for this waste. This is common nonhazardous commercial waste.

B-4. Series 4—Trimsol

No analysis was performed on this waste series. Trimsol is a commercially available machine shop cutting fluid. It is made up of petroleum oils, chlorinated hydrocarbons, phenol, glycol, plus other elemental constituents such as sodium and calcium. The other wastes that were analyzed bound any detrimental health effects caused by trimsol.

Table B-2. Series 2—nonchlorinated solvents and metals.

Chemical	Amount	IDLH (mg/m^3)	Worker exposure (mg/m^3)	IDLH (%)
Acetone	50 wt%	4.84E+04	3.75E+03	7.74
Methanol	50 wt%	3.33E+04	1.27E+03	3.81
Arsenic	3,000 ppm	1.00E+02	7.94E-02	0.08
Barium	3,000 ppm	1.10E+03	7.94E-02	0.01
Cadmium	3,000 ppm	5.00E+01	7.94E-02	0.16
Lead	3,000 ppm	7.00E+02	7.94E-02	0.01

B-5. Series 5—Mixed Oils

Assumptions:

1. 750 gal of waste present.
2. The waste consists of 50 wt% ethylene glycol, 10 wt% monoethanolamine, 10 wt% diethanolamine, 10 wt% triethanolamine, 5 wt% boric acid, 15 wt% motor oil, and 500 ppm PCB. Only PCB has an IDLH listing.
3. The density of this waste stream is 1.05 g/cm^3.
4. Only PCB will be analyzed as the hazardous constituent.

Table B-3 presents calculated IDLH percentages for Series 5 waste (see support calculations in Appendix C for details).

B-6. Series 6—Spent Activated Carbon

No analysis was required for this waste.

B-7. Series 7—Scintillation Fluid

Assumptions:

1. 750 gal of waste present for each product.
2. This waste series will consist of two different products. Two scintillation fluid products appear to the most common in DOE wastes—Instagel and AtomLite.
3. Instagel contains 70% Xylene and proprietary alkylpolyethoxyethanol and arylhydrocarbons. Akylpolyethoxyethanol and arylhydrocarbons do not have an IDLH listing.
4. Xylene will volatilize in an area of 72m^2 (open area 26 × 30 ft^2).
5. Xylene bounds any detrimental health effects caused by Instagel.
6. AtomLite contains 64% 1,2,4 trimethylbenzene and 36% synthetic organic surfactants.
7. The contents of AtomLite do not have an IDLH listed.

Table B-3. Series 5—mixed oils.

Chemical	Amount	IDLH (mg/m^3)	Worker exposure (mg/m^3)	IDLH (%)
PCB	500 ppm	1.0E+01	1.74E-02	0.17

8. Xylene in Instagel and the Aromatics in Series 1 waste bound any detrimental health effects caused by exposures to AtomLite. Therefore, AtomLite will not be analyzed.

Table B-4 presents calculated IDLH percentages for Series 7 waste (see support calculations in Appendix C for details).

B-8. Series 8—Tributyl Phosphate

Assumptions:

1. 750 gal of waste present.
2. The waste consists of 45 wt% tributyl p-Paraffins.
3. n-Paraffins may be different types of hydrocarbons (mainly alkanes such as octane, undecane, tridecane and tetradecane), there are no specific IDLH values listed for Paraffins. The effects of paraffin hydrocarbons vary with the volatility. It will be assumed that the volatile chemicals already analyzed bound any detrimental health effects. Therefore, no specific paraffins will be analyzed.
4. The density of this waste stream is 1.0 g/cm^3.

Table B-5 presents calculated IDLH percentages for Series 8 waste (see support calculations in Appendix C for details).

Table B-4. Series 7—scintillation fluid.

Chemical	Amount	IDLH (mg/m^3)	Worker exposure (mg/m^3)	IDLH (%)
Xylene	70 wt%	4.41E+03	1.97E+02	4.46

Table B-5. Series 8—tributyl phosphate.

Chemical	Amount	IDLH (mg/m^3)	Worker exposure (mg/m^3)	IDLH (%)
Tributyl phosphate	45 wt%	1,384	1.41E+01	1.02
Dibutyl phosphate	5 wt%	1,446	1.57E+00	0.11

Appendix C

Support Calculations

Appendix C

Support Calculations

C-1. Volatile Chemical Release

For a volatile chemical release, it is assumed the liquid (one whose vapor pressure is greater than 1.0 mm Hg at 20°C) is released and the contents are completely emptied out onto the ground and the entire contents are released via evaporation.

In theory, the evaporation rate for volatile chemicals is as follows (Clewel, 1983):
$Q = (22.2)(U)^{0.75}(A)(1+(4.3E\text{-}3)(T_p)^2)(M_B)(P_{vB})/((M_H)(P_{vH}))$

where

Q = liquid evaporation rate (mg/s)

U = air velocity across surface (m/s)

A = area of evaporating surface (m^2)

T_p = temperature of the pool (°C)

M_B = molecular weight of spilled chemical

M_H = molecular weight of hydrazine

P_{vB} = vapor pressure of spilled chemical (mmHg)

P_{vH} = vapor pressure of hydrazine (mmHg).

The above calculations were performed on the 4 chemicals listed in Table B-1 whose vapor pressures are greater than 1.0 mm Hg at 20°C. Table B-1 contains the parameters used for calculations within the WRRTF building.

The containers are assumed to be breached in the open area just above and adjacent to the North Test Pit. The spill area is approximately 72 m^2 (26 × 30 ft^2). It was assumed that the air velocity in the building was approximately 0.009 m/s, which is a typical velocity across a floor surface based on previous studies. One such study is the *Safety Analysis Report for the Mixed Waste Storage Facility and Portable Storage Units at the Idaho National Engineering Laboratory (Draft)*, EGG-WM-10846, March 1994. It was assumed that the temperature inside the building would be approximately 20°C (68°F). The vapor pressures for each of the chemicals were found using the appropriate formulas given in *The Properties of Gases and Liquids* (Reid, 1987). The

Table C-1. Parameters for calculation of volatile chemicals.

Chemical	U (m/s)	A (m^2)	T_p (°C)	M_B (g/gmole)	M_H (g/gmole)	P_{vB} (mmHg)	P_{vH} (mmHg)
Benzene	9.0E-03	7.2E+01	2.0E+01	7.8E+01	3.2E+01	7.4E+01	1.1E+01
Acetone	9.0E-03	7.2E+01	2.0E+01	5.8E+01	3.2E+01	1.7E+02	1.1E+01
Methanol	9.0E-03	7.2E+01	2.0E+01	3.2E+01	3.2E+01	1.1E+02	1.1E+01
Xylene	9.0E-03	7.2E+01	2.0E+01	1.1E+02	3.2E+01	5.0E+00	1.1E+01

vapor pressure for Hydrazine was found using the formula given in the *Handbook of Chemical Hazard Analysis Procedures* (FEMA, 1988). The molecular weight of hydrazine is 32 g/gmole.

Using the data shown in Table C-1, the evaporation rates for each of the chemicals were calculated and are listed in Table C-2.

The concentrations of the volatile chemicals the worker is exposed to within building are found using the following relation:

$$C = (Q)(\chi/Q)$$

where

Q = liquid evaporation rate (mg/s, values are shown in Table C-2)

χ/Q = dispersion coefficient (s/m^3) = 1.0.

The dispersion coefficient of unity is conservative for calculating concentrations within a building, therefore $C = Q$.

C-2. Nonvolatile Releases

These calculations were performed on the 9 remaining chemicals shown in Table C-3. The respirable release fraction used for these calculations was 2.1E-05 for the liquid waste (DOE-STD-0013-93, *Recommended Values and Technical Bases for Airborne Release Fractions, Airborne Release Rates, and Respirable Fractions at DOE Non-Reactor Facilities*). The duration of the release for these calculations is assumed to be 1 minute.

Table C-2. Volatile chemical concentrations.

Chemical	Exposure concentration (mg/m^3)
Benzene	2.2E+03
Acetone	3.7E+03
Methanol	1.3E+03
Xylene	2.0E+02

Table C-3. Results of the concentration exposures.

Chemical	Waste series density (g/cm^3)	Weight fraction	Concentration (mg/m3)
Mercury	0.91	2.0E-03	6.0E-02
Phenol	0.91	2.5E-02	7.5E-01
Arsenic	0.80	3.0E-03	7.9E-02
Barium	0.80	3.0E-03	7.9E-02
Cadmium	0.80	3.0E-03	7.9E-02
Lead	0.80	3.0E-03	7.9E-02
PCB	1.05	5.0E-04	1.7E-02
Tributyl phosphate	0.95	4.5E-01	1.4E+01
Dibutyl phosphate	0.95	5.0E-02	1.6E+00

$$C = (LV)(DEN)(WF)(RF)/(RV)$$

where

C = concentration (mg/m^3)

LV = liquid volume (750 gal or 2.9E+06 cm^3)

DEN = density of the waste series

WF = weight fraction

RF = respirable release fraction (0.000021 for the liquid)

RV = room volume (1,850 m^3).

substituting the constants yields the following:

$$C = 33(DEN)(WF)$$

C-3. References

Clewel, H. J., 1983, "A Simple Formula for Estimating Source Strengths From Spills of Toxic Liquids," ESL-TR-83-03, May.

Federal Emergency Management Agency (FEMA), *Handbook of Chemical Hazard Analysis Procedures*, 1988.

Reid, R. C., et al., *Properties of Gases and Liquids*, Fourth Edition, 1987.

Appendix D

Calculations of Benzene Vapor Concentration in the North Pit

Appendix D

Calculations of Benzene Vapor Concentration in the North Pit

The following is a calculation of benzene vapor concentration in the North Pit resulting from a rupture in the piping during operation of the Supercritical Water Oxidation Test Bed.

Assumptions (five-minutes release time):

1. The flow rate into the system is 409 lb/hr, also used as the release rate.
2. The system was shut down after the rupture was detected (5 minutes release time).
3. 8% of the flow stream is benzene, 92% water.
4. The fluid is released to the atmosphere at T=300°C; Perfect Gas Law.
5. Pit volume is 26x40x30 ft^3 (31,200 ft^3).
6. The rupture occurs in the piping before entering the reactor.

Calculation

Total amount of release = (409 lb/hr)(1 hr/60 min)(5 min) = 34 lbs

8% Benzene => 2.7 lbs benzene vapor; 31.3 water vapor

Perfect Gas => $\rho = PM/RT$ Gas Constant (R) = 10.732 psi ft^3/lb-mole °R

For benzene vapor

$$P = 14.7 \text{ psi}, M = 78.11 \text{ lb/lb-mole}, T = 300^\circ C = 1032\ ^\circ R$$

$$\rho_{\text{benzene}} = 0.104 \text{ lb/ft}^3 \quad => \quad 2.7/0.104 = 26 \text{ ft}^3 \text{ benzene}$$

therefore

26/31,200 = 0.0008 or 0.08% benzene vapor in the pit

Assumptions (one-hour release time):

1. The flow rate into the system is 409 lb/hr, also used as the release rate.
2. The system was shut down after one hour of release.
3. 8% of the flow stream is benzene, 92% water.
4. The fluid is released to the atmosphere at T=300°C; Perfect Gas Law.
5. Pit volume is 26x40x30 ft^3 (31,200 ft^3).
6. The rupture occurs in the piping before entering the reactor.

Calculation

Total amount of release = (409 lb/hr)(1 hr) = 409 lbs

8% Benzene => 33 lbs benzene vapor; 376 water vapor

Perfect Gas => $\rho = PM/RT$ Gas Constant (R) = 10.732 psi ft^3/lb-mole °R

For benzene vapor

P = 14.7 psi, M = 78.11 lb/lb-mole, T = 300°C = 1032 °R

$\rho_{benzene}$ = 0.104 lb/ft^3 => 33/0.104 = 317 ft^3 benzene

therefore

317/31,200 = 0.01 or 1.0% benzene vapor in the pit

Conclusions

The lower explosive limit (LEL) for benzene is 1.4 percent. A rupture with a release time of five minutes at 409 lb/hr would not result in a fire or an explosion because 0.08 percent benzene vapor in the pit is much lower than the LEL. A loss of pressure in the system would be detected within five minutes (depending on the location and size of rupture).

A one-hour release is extremely conservative; the system would be shut down almost immediately after pressure loss was detected. The one-hour release calculation was conducted for illustrating that even under extreme accident conditions, the LEL for benzene would not be easily be reached. A fire or explosion is an extremely remote possibility because there is not enough fuel. A fire in the reactor is an even more remote possibility since the fuel has been partially oxidized.