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PLAN FOR SUPERCRITICAL WATER OXIDATION FOR VX/NAOH HYDROLYSATE

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EXECUTIVE SUMMARY

This report describes the selection and implementation of supercritical water oxidation (SCWO) as the post treatment for the Newport Chemical Demilitarization Facility (NECDF). Activities to date are described followed by recommended future actions to support design and acquisition of the NECDF SCWO unit by a systems contractor. The acquisition of SCWO requires special attention since the overall performance of the NECDF process will be strongly influenced by the reliability of the SCWO systems.

SCWO is the post treatment technology that will mineralize the organic constituents of the hydrolysate produced by the neutralization of the VX agent. When the testing of biotreatment and stabilization of the VX hydrolysate were unsuccessful, SCWO was selected for the NECDF post treatment. This choice was based on the results of comparative treatment tests completed by vendors of various candidate technologies. These vendors included Ecologic; M4 Environmental Management, Inc.; AEA Technology, plc; Solarchem Environmental Systems; and General Atomics (GA).

A second longer treatment test utilizing the same General Atomics $1/25^{th}$ scale SCWO reactor system was conducted to provide additional confidence in the performance of the downflow, cylindrical, solid surface, vertical reactor configuration. This testing again demonstrated the ability of this SCWO system to effectively destroy the hydrolysate organic constituents and to transport the resultant salts through the reactor while producing an effluent stream suitable for disposal. These results confirmed the selection of SCWO as the most effective technology for the treatment of hydrolysate. Additional tests to confirm the kinetics of the SCWO destruction process and the ability of an evaporator to remove the salts from the SCWO effluent were conducted. The results verified the required SCWO reaction conditions and performance of the overall process with positive results.

A comprehensive review of industry experience with SCWO as related to our post treatment requirements was conducted which resulted in four general conclusions. First, the cylindrical, solid surface, vertical reactor was the best chance of successfully treating the VX caustic hydrolysate for NECDF. Successful experience in treatment of waste streams with high salt loading has been limited to this reactor configuration. This includes the results of the NECDF hydrolysate tests. Second, a larger scale longer duration test would substantially reduce the risk in the NECDF unit. Third, materials of construction test should be conducted to provide corrosion data for the selected materials. Fourth, the potential advantages of reduced corrosion and improved salt transport attributed to the transpiring wall reactor have not been demonstrated at the NECDF destruction conditions. This is based on the scale, salt loading, throughput, organic destruction, and corrosion information above.

The materials of construction test is currently in the initial stages to select the best materials for the VX hydrolysate SCWO environment. This testing will be carried out at Idaho National Engineering and Environmental Laboratory (INEEL) in a'vertical SCWO reactor under NECDF reaction conditions. The candidate reactor lining materials to be tested are platinum and platinum based alloys. A zirconia ceramic coating will also be tested.

An engineering scale test at about $1/10^{th}$ full scale will be performed to address the larger scale longer duration test discussed above. This test will utilize the results of the materials of construction testing to design and fabricate the reactor. The EST will provide scale up, system reliability, process monitoring, system control, and other operational information for use in the design of the NECDF system.

The $1/10^{th}$ scale EST will be performed utilizing the downflow, cylindrical, solid surface, vertical reactor. This is the SCWO configuration determined to provide the highest degree of assurance of repeating the successful results achieved at $1/25^{th}$ scale. This configuration has the greatest share of experience for waste streams similar to NECDF hydrolysate. The PMATA hydrolysate tests demonstrated salt transport over a longer period, at significantly higher loading, and much greater flow rate than data for transpiring wall and tubular reactors. The PMATA hydrolysate tests demonstrated organic destruction to the required level simultaneously with satisfactory salt transport. While the materials of construction remains an open item for both configurations, the solution is more direct for the solid wall reactor since only a suitable liner material is required. In the case of the transpiring wall, a suitable liner material is required which can also can be fabricated into a transpiring wall.

This Engineering Scale Test (EST) will provide design data so that the design performance risks for NECDF will be reduced. For this test to be timely, it must be conducted such that the results are available to provide input to the design and acquisition of the NECDF SCWO systems. The program could be delayed if the EST is deferred and included under the systems contractor Scope of Work rather than started before systems contract award. Therefore, the EST should be initiated as soon as possible. This will assure that the results will be available for the systems contractor to complete the NECDF design and procure the SCWO system within the NECDF program schedule.

1. INTRODUCTION

1.1 Purpose

The purpose of this document is to:

- Describe the selection of SCWO as the post treatment technology for VX neutralization/hydrolysate at NECDF.
- Identify SCWO technical development issues or design concerns for hydrolysate treatment by SCWO.
- Describe the NECDF program's acquisition strategy for SCWO.
- Describe the evaluation of candidate SCWO system configurations and recommend a specific configuration to use in future testing.
- Evaluate options and make recommendations for SCWO development testing.
- Assess options and make recommendations on SCWO testing strategy to reduce risk during development.

1.2 Report Organization

This report comprises four sections, a list of references and sources, and several Appendices. The purpose and content of each is as follows:

SECTION 1 INTRODUCTION

This section presents the purpose, content, and organization of the report. It also discusses the general acquisition strategy for the Newport Chemical Demilitarization Facility (NECDF) and the technical objectives for the NECDF project design.

SECTION 2 BACKGROUND

This section contains a summary of the S WCO experience database. The database is evaluated and items are identified for resolution for the design and acquisition of the SCWO unit for NECDF.

SECTION 3 SCWO FUTURE TESTING

This section describes future testing to resolve the open items identified in Section 2. It provides the technical objectives and approach for this testing. A description of the materials of construction testing already initiated is provided.

SECTION 4 - RECOMMENDATIONS FOR SCWO ENGINEERING SCALE TESTING AND ACQUISITION STRATEGY

This section recommends actions and provides rationale for future SCWO tests to meet program schedule, cost, and technical objectives. The recommendation is to coordinate the development of SCWO design data simultaneously with the acquisition of the system contractor.

APPENDICES

Appendices contain the current program schedule, history of the selection of SCWO as a post treatment of hydrolysate for NECDF, and technical data relative to SCWO testing.

1.3 Acquisition Strategy

The acquisition of the SCWO unit for NECDF follows the program's general guidelines. The NECDF acquisition design has been completed by Stone & Webster to enable a systems contractor to: take responsibility for the existing design; complete the detailed design; construct the facility; operate the facility; and close it. The current schedule to complete these activities is shown in Appendix A.

A general procurement approach has been adopted which places responsibility for all equipment acquisition with the systems contractor in order to reduce the total risk. As a result, the use of government furnished equipment (GFE) has been eliminated or at least minimized to the greatest possible extent.

1.4 Technical Objectives

The technical objective of the NECDF design is to demilitarize the Newport stockpile in a safe and effective manner. The design incorporates stringent reliability requirements for the total facility to meet these objectives. This is important because the NECDF's mission-related high fixed operating costs, the safety effects resulting from maintenance activities, and the extension of the operating period caused by equipment failures can all cause severe adverse impacts if reliability standards are not set high for the design. These adverse impacts can increase overall life cycle costs to more than the initial cost of the SCWO equipment. The operating cost for SCWO is only 3.3% of the cost per month to operate the entire facility. Therefore, testing to improve the overall reliability of the SWCO design will be highly cost effective.

The NECDF acquisition design has redundancy of key components, dual trains where appropriate, and large allowances for unanticipated system, operating, and equipment problems to ensure a high overall availability. This approach will accommodate operating problems that can be expected in the early operation of any first time facility.

Additional operating information from timely SCWO technology testing will optimize the design. This optimization could pay dividends by significantly improving the operating performance of the NECDF and minimizing the time required to demilitarize the Newport stockpile in a safe and effective manner.

TABLE OF CONTENTS

2. BACKGROUND

2.1 SCWO Selection

SCWO is the appropriate technology for the treatment of VX/NaOH hydrolysate. This conclusion is based on the selection of SCWO after comparative testing of several candidate technologies. The history of this selection process is presented in Appendix B.

2.2 SCWO Experience Database

Stone & Webster and PMATA conducted literature searches for documented earlier SCWO industry operating and research experience. Table 2- 1 summarizes the SC WO experience database resulting from those literature searches and other direct sources. More detailed information can be found in the sources listed in Section 5. The NECDF design characteristics are listed in the first column on the left in Table 2-l. The system which has tested with hydrolysate is listed in the next column to the right on the first page, followed by other systems with flow schemes and geometries similar to the hydrolysate-tested system. Finally, systems with other geometries, flow schemes, and operating conditions are presented.

The order of the summary descriptions below follows the columns in Table 2-l from left to right:

A. PMATA Hvdrolvsate and Surrogate [Ref 21: These tests processed hydrolysate and surrogate in a 4" x 6' downflow, cylindrical solid wall vertical vessel at 0.15 gallon per minute feed rate. The hydrolysate test was a continuous 8-hour test at $1/26^{th}$ of the NECDF mass flow rate. Salt transport was good over the 8-hour period. Destruction results were satisfactory. The results of this test and others by the University of Texas indicated better destruction at a longer residence time and a slightly higher temperature. The unit's titanium (Ti) liner corroded rapidly in this test and projected unacceptably short life times for the NECDF design. Air rather than oxygen was utilized as the oxidant.

B. Air Force Pronellant Test [Ref 151: A 3.4" x 6' downflow, cylindrical solid wall vertical vessel was used to test destruction of Class 1.1 propellant as a slurry at feed rates from 0.3 to 0.38 gallon per minute. The waste concentration was lower than was the case in the PMATA tests. The solids produced in the reactor differed significantly in composition from the hydrolysate case. The solids transport rate was satisfactory at a slightly lower solids throughput rate than for the hydrolysate case over a 25-hour test. The destruction was satisfactory for the feed which differed significantly from hydrolysate. The oxidant utilized was oxygen. There are no applicable corrosion data.

C. U.S. Department of Energy (DOE) and Idaho National Engineering & Environmental Laboratorv (INEEL) Proiects for Synthesized Wastes [Ref 6 and 81: Two tests were carried out in a 10" x 40" reversing flow, cylindrical solid wall vertical vessel processing synthetic waste streams at flow rates from 0.044 to 0.22 gallon per minute. The salt produced in the reactor differed from the hydrolysate case in both composition and loading rate. The salt transport rate was much lower than in the NECDF case and substantial salt was retained in the reactor during the two tests of about 100 hours each. The destruction was satisfactory for a feed differing significantly from hydrolysate. The oxidant was air. These tests provided experience with chloride and sulfate salts at several weight percent in both titanium and ceramic coated titanium liners.

D. Huntsman and Universitv of Texas Tubular Reactors: EcoWaste Technology (EWT) designed and built the first commercial plant at Huntsman Chemical in Austin, Texas utilizing a tubular SCWO reactor. This 5-gpm unit, in operation 3 years, normally processes non-salt bearing waste. Waste streams with sodium sulfate, phosphate, and carbonate feeds at up to 2 wt.% have been processed. EWT also operates a smaller scale pilot plant for the University of Texas.

E. Subcritical Oxidation Unit: Battelle Pacific Northwest National Laboratory (PNNL) has operated subcritical water oxidation units for the treatment of high pH salt bearing nitrate wastes. These wastes contained their own oxidant (the nitrate). Processing has been at subcritical temperatures and pressures, nominally 660°F and 2500 psig. Based on tests performed at the University of Texas, destruction of hydrolysate will not be sufficient at these subcritical conditions [Ref 16]. However, good stainless steel materials performance up to 660°F in the PNNL high pH environment should support heat exchanger design for SCWO units.

F. Transpiring Wall Reactor [Ref 31: Foster-Wheeler, collaborating with Aerojet and Sandia National Laboratory (SNL), has designed and tested a 1.1” x 36” downflow cylindrical vertical reactor with a transpiring wall to keep corrosive agents and salt off the reactor’s wall. A 3-hour test with 3wt% sodium sulfate salt showed less deposition than with no transpiring fluid, but not a clean wall. This test apparatus was limited in residence time such that organic destruction above 90% Destruction/Removal Efficiency (DRE) based on Total Organic Carbon (TOC) could not be achieved for these tests. No materials of construction testing was performed as part of this program.

G. Proiects Not Yet in Operation:

1. Two SCWO systems are being assembled to process U.S. Navy shipboard waste streams. One is a 4.8” x 7.5’ cylindrical transpiring wall, vertical vessel designed by Foster-Wheeler and one is a 7.25” x 5’ cylindrical solid wall, vertical vessel [Ref 7].

2. The transpiring wall SCWO reactor concept as described in Subsection F above, is being implemented at Pine Bluff for the demilitarization of smokes and dyes. A 0.6-gpm plant is under construction.

3. A SCWO system to process pulp mill wastes is being built at the University of British Columbia.

Table 2-1 SCWO Experience Database Summary

Project name	NECDF Projected Characteristics	Hydrolysate Test Vertical Reactor	Surrogate Test Vertical Reactor	Air Force Propellant Test	Industrial Wet Oxidation (SCWO) for Waste and Low Grade Fuels
Sponsor	PMATA	PMATA	PMATA	Air Force	U.S. DOE
Waste characterization	Hydrolysate, pH 14, 2500 Btu/lb, Na salts of ethylmethyl phosphonic acid. methyl phosphonic acid, thiols	Drained agent hydrolysate, pH 14, 4300 Btu/lb, Na salts of ethylmethyl phosphonic acid, methyl phosphonic acid, thiols	Ethanol, kerosene, DMMP, MPA, 11.6 - 15.1 wt% Na_2SO_3, 8.8 - 11.5 wt% $NaHPO_4CH_2O$	Hydrolyzed Class I. I rocket propellant, 0. I to 6 wt% slurry	Synthesized waste of chlorinated hydrocarbon, NaCl, Na_2SO_4, isopropyl alcohol, NaOH added IO neutralize acid
Flow of waste	4 gpm. 2092 lb/hr	0. 15 gpm of 2500 Btu/lb; 44 lb/h of 4300 Btu/lb drained agent hydrolysate	0.08 - 0. 17 gpm	0.3 - 0.38 gpm	0.22 gpm
Oxidant	Oxygen	Air	Air	Oxygen	Air
Oxidation heat release	5 million Btu/hr	0.19 million Btu/hr	0. 19 million Btu/hr	0.1 million Btu/hr	160,000 Btulhr
Turndown capability (waste flow)	Require 0.8 gpm, to 20% of full capacity	GA states To 20 % of full capacity	GA states to 20% of full capacity	Not available	To 25 % of full capacity
Salt characteristic in reactor	Na_2SO_4 NaH_2PO_4	Na_2SO_4 NaH_2PO_4	Na_2SO_4 NaH_2PO_4	Predominantly Al OOH & NH_4Cl, approx. I wt%	NaCl, Na_2SO_4 2 wt%
Salt throughput	360 lb/hr	14.6 lb/hr	12 - 17.5 lb/hr	9.9 lb/hr	2.2 lb/hr
Principal corrosion issue	High pH due to free NaOH	High pH due to free NaOH	(No NaOH in these tests)	High pH due to NH,, 2000 to 7000 ppm Cl^-	Chlorides, low pH
Approach to corrosion	Corrosion resistant liner Pt or ceramic	Corrosion resistant liner Ti for test; Pt or ceramic liner for use in NECDF	Corrosion resistant Ti liner for test; PI or ceramic liner for use in NECDF	Corrosion resistant Ti liner	Alloy 625 reactor, some nozzle failures
Reactor type	cylindrical, vertical vessel	Down flow cylindrical, vertical vessel	Down flow cylindrical, vertical vessel	Down flow cylindrical, vertical vessel	Reversing flow, cylindrical, vertical vessel
Reactor nominal dimensions, diam x length	TBD	4 inch x 6 ti	4 inch x 6 ft	3.4 inch x 6 ft	10 inch x 40 inches long
Operating conditions, T,P	1200°F, 3500 psig	1112° - 1184°F. 3400 psig	1112° - 1256°F, 3400 - 3800 psig	842" - 1076°F, 4000 psig	1085°F, 3400 psig
Scale up rules	Residence time at T,P	Residence time at T,P	Residence time at T,P	Residence time at T,P	Residence time at T,P
Pressure letdown approach to erosion	Vendor to specify, redundancy is required	Erosion resistant, redundant valve and capillaries	Erosion resistant, redundant valve and capillaries	Erosion resistant, capillaries	Redundant valves
Project status	Conceptual design	Complete	Complete	Complete	Complete
Hours continuously run without plugging	Not yet operated	Hydrolysate treatability test: 8 hr	4 tests, 7' hr	25 hr	102 hr but reactor retained 15.8 % of the input salt
Destruction or effluent quality achieved DRE to mg TOC/L	Require < 15 mg TOC/L	99.98% DRE based on TOC 99.97% DRE based on MPA	98.8 - 99.9% DRE for TOC >99.3 - 99.7 % DRE for MPA	>99.9% DRE based on TOC	99.999% DRE I mg TOC/L
References, reports	S&W design documents	Ref. 2	Ref. 2	Ref. 15	Ref. 6

Table 2-1 (continued) SCWO Experience Database Summary

Project Name	SCWO Data Acquisition Testing	Huntsman Chemical	University of Texas Pilot Plant	PNNL	Sandia National Laboratory
Sponsor	U.S. DOE	Huntsman Chemical	University of Texas	Batelle PNNL	U.S. DOE & U.S. Army ARDEC
Waste characterization	Synthesized waste of chlorinated, sulphonated cutting oil, metal acetates of Ca. Fe, Pb, Zn, Ce, NaOH added to neutralize acid	Amines, long chain alcohols (MW 2000). methanol, 10 wt% methanol equivalent	Thick sludges, amines, ammonia mixtures, pH 12 - 13, no halogens	High pH, organics with Na salts, Hanford tank wastes	3 wt % Na_2SO_4, 5. IS wt% red dye
Flow of waste	0.044 gpm	5-8 gpm	0.5 - 1 gpm	0. I3 - 0. I7 gpm; smaller unit: 0.0044 gpm	0.033 gpm
Oxidant	Air	Oxygen	Oxygen	None, nitrate in waste	Hydrogen peroxide decomposed to 0 ,
Oxidation heat release	Approx. 90,000 Btu/hr	2 million Btu/hr	0.4 million Btu/hr	Minimal, feed/effluent heat exchanger required	Approx. 3000 Btu/hr
Turndown capability (waste flow)	To 25% of full capacity	Turndown not tested at this facility	To 20 to 30% of full capacity	To 20% (judgment) not tested. Avoid laminar flow	Turndown not tested at this facility
Salt characteristic in reactor	NaCl, Na_2SO_4 metallic chlorides	Some trials with Na_2SO_4 Na_3PO_4 1 wt%	Oxides from industrial sludges, some trials with Na_2SO_4, Na_2CO_3 1 - 2 wt%	NaOH becomes carbonates $NaNO_3$ (also the oxidant)	3 wt % Na_2SO_4 1.6 wt% equiv. salt in dye test
Salt throughput	1.5 lb/hr	Approx. 25 lb/hr, some scaling	Approx. 2.5 lb/hr, some scaling	Approx, 10% 7 lb/hr	0.63 - 1.6 lb/hr for salt only test
Principal corrosion issue	Chlorides, salts, metallic chlorides	Confidential to vendor	Variable since many wastes run through this pilot unit	High pH due to free NaOH; Stainless OK exposed to reaction products, 200 hr in batch autoclave	Salt on wall, effl pH 3.3 - 5, corrosion of Ni, Mo by salt, O_2 observer in stainless steel
Approach to corrosion	Ceramic coated Ti liner; some delamination but performed better than metallic Ti.	Confidential to vendor	Ni alloy tubing	Replaceable inner shell vessel made of stainless steel	Radial fluid flow to keep corrosives off' reactor wall (i.e. transpiring wall)
Reactor type	Reversing flow, cylindrical, vertical vessel	Tubular	Tubular	Dual shell, vertical cylinder	Transpiring wall cylindrical, vertical vessel
Reactor nominal dimensions, diam x length	10 inch x 40 inches long	Diam confidential to vendor, length several hundred feet	1 inch x 120 feet	1 inch ID x 6 feet	1.1 inch x 36 inches
Operating conditions, T,P	1112° - 1148°F, 3400 psig	Up to 930°F, 4000 psig	Up to 1150° - 1200°F, 4000 psig	662°F (cannot do 1200 at 3000 psig), 2500 psig	932°F, 3800 psig, 8-9 sec res time
Scale up rules	Residence time at T,P	Confidential to vendor	Residence time at T,P	Residence time at T, P Velocity Avoid laminar flow	Res time at T, P, waste $\propto D^2$; trans water $\propto$ D, platelet eff factor held constant
Pressure letdown approach to erosion	Redundant valves	Valve, erosion resistant	Valve, and patented method with capillaries	Staged, multiple drops.	Single valve in small system
Project status	Completed	In commercial operation 3 years	In operation, various wastes	Complete	Testing completed
Hours continuously run without plugging	94 hr total; full reactor rinses (with feed off) req'd at 40 & 80 hr ~ 13 lb of NaCl remained in reactor	Week, never plugged	"Hours"	0.15 gpm 24 hr, smaller scale: couple of days	3 hr, salt deposits can be removed in <10 min below 662°F
Destruction or effluent quality DRE or mg TOC/L	99.97% DRE, 2 mg TOC/L	10 mg TOC/L	< 10 mg TOC/L	99% DRE based on TOC 1 - 10 mg TOC/L	>90% DRE based on TOC 100% destroyed for the dye
References, reports	Ref. 8	Ref. 12, 13, plant tour in Austin	Plant tour in Austin, Masters thesis forthcoming on salt	Ref. 4	Ref. 3

Table 2-1 (continued) SCWO Experience Database Summary

Project Name	Hydrothermal Oxidation	Hydrothermal Oxidation	Pine Bluff	University of British Columbia
Sponsor	U.S. Navy	U.S. Navy	U.S. Army ARDEC	Noram Engineers
Waste characterization	Excess hazardous matls., fuels, lubricants, high Btu/lb, mostly non sticky solids, chlorides	Excess hazardous matls., fuels, lubricants, high Btu/lb, mostly non sticky solids, chlorides	80 lb/h of dye, 240 lb/hr of water	Plans for pulp mill waste
Flow of waste	100 lb/hr 0.2gpm	100 lb/hr 0.2gpm	0.64 gpm of slurry	0.044 gpm
Oxidant	Air	Air	Oxygen	Oxygen
Oxidation heat release	2 million Btu/hr	2 million Btu/hr	800,000 Btu/hr	TBD
Turndown capability to (waste flow)	Requirement to process 1 lb/hr (0.002gpm) of some EHMs	Requirement to process 1 lb/hr (0.002gpm) of some EHMs	Unit not yet operated	Estimated to be 10%
Salt characteristic in reactor	Primary non-sticky paint pigments, MoO_2	Primary non-sticky paint pigments, MoO_2	Na_2SO_4	TBD
Salt throughput	25 lb/hr max	25 lb/hr max	50.4 lb/hr	max amount to be a few wt%
Principal corrosion issue	Cl present in some EHMs	Cl present in some EHMs	Salt on wall	TBD
Approach to corrosion	Radial fluid flow to keep corrosives off reactor wall (i.e. transpiring wall), Inconel 600 wall material	Ti corrosion resistant liner	Inconel 600 platelet Radial fluid flow to keep corrosives off reactor wall	Confidential to vendor
Reactor type	Transpiring wall, cylindrical, vertical vessel	Down flow cylindrical, vertical vessel	Transpiring wall, cylindrical, vertical vessel	Tubular
Reactor nominal dimensions, diam x length	4.8" x 7.5'	7.25" x 5 ft	4.8 inch x 7.5 feet	Volume 150 cubic inches; dimensions TBD
Operating conditions, T,P	Top 1350°F; bottom 1050°F, 3800 psig, 10 sec res time	1157°F, 3400 psig	Top 1350°F; Bottom 1050°F 3800 psig 10 sec res time	Slightly above critical conditions
Scale up rules	Res time at T, P Waste $\propto D^2$; Trans water $\propto$ D platelet eff factor held constant	Res time at T, P	Res time at T, P, waste $\propto D^2$; trans water $\propto$ D, platelet eff factor held constant	TBD
Pressure letdown approach to erosion	Valve redundancy	Stages pressure letdown valves	Valve redundancy	Pressure regulator
Project status	Unit under construction by Foster Wheeler	Unit under construction by General Atomics	Under construction, operational April 1998	Scheduled operational date is summer 1998
Hours continuously run without plugging	Not yet operated	Not yet operated	Not yet operated	Not yet operated
Destruction (TOC/Lent quality	Project requirement is 99.99%	Project requirement is 99.99%		
References, reports	Ref. 7	Telecon	Presentation to NRC 10/28/97, telephone inquiry	No reports. Info based on Oct 23 and Nov 21, 1997 telecon call.

2.3 SCWO Experience Database Evaluation

2.3.1 SCWO Reactor Type

Table 2-2 compares SCWO reactor characteristics and development status with respect to demonstration of hydrolysate treatment requirements from the SCWO experience database. A vertical, downflow, solid surface reactor; a vertical, reversing flow solid surface reactor; a transpiring wall (TW) reactor; and a tubular reactor are compared in Table 2-2.

Table 2-2 Comparative SCWO reactor characteristics and status relative to hydrolysate treatment requirements

Reactor attribute	Cylindrical vertical vessels			Tubular reactor
	Downflow, solid wall	Reversing flow, solid wall	Downflow, transpiring wall	
Suitable for high salt loading?	Yes	Yes	Yes	No
Salt handling capability demonstrated?	Ref. 2 Treatability test demonstrated 12 wt% hydrolysate salts for 8 hr totaling 110 lb.	Ref. 6 Treatability test low salt loading with different salts.	Ref. 3 Test with 3 wt% Na_2SO_4 for 3 hr totaling 1 lb.	Reactor type is not applicable to high salt loading; would plug.
Scale tested Liquid feed (gpm)	Pilot 0.38	Pilot 0.22	Laboratory 0.033	Commercial 8
Processing hydrolysate	Yes (0.15 gpm)	Not tested	Not tested	Not tested
Destruction efficiency data	TOC 99.98% MPA 99.97% EMPA >99.97% VX thiols >99.998%	TOC >99% Simulated Mixed Waste Streams	TOC ≥90% 100% demonstrated on red dye	NA Not characterized further here because not applicable to hydrolysate.

Downflow - uni-directional from inlet at top to outlet at bottom
Reversing flow - inlet at top, supercritical fluid reaction products reverse direction and exit at top
Transpiring wall - inlet at top to outlet at bottom. Purge flow exits radially from chamber wall, turns and exits with process flow at bottom.
Tubular - also referred to as a pipe reactor, plug-flow, high L/D ratio, often helical.

The reactor issues summarized in Table 2-2 were evaluated as follows:

1. Demonstrated Salt Loading Rate

   Plugging of the SCWO reactor with residual salts is a significant design concern. The cylindrical vertical vessel systems have demonstrated capability to accept the

NECDF's high salt loading and the tubular reactor system has not. Therefore, only the cylindrical vertical vessel systems remain in consideration.

The downflow, solid wall reactor experienced 14.6 lb/hr of salt loading; the reversing flow, solid wall reactor experienced 2.2 lb/hr of salt loading; and the transpiring wall reactor experienced 0.33 lb/hr of salt loading. Therefore, the solid wall reactors have demonstrated salt loading 44 times closer to design rates than the transpiring wall reactor.

2. Tested Scale of Operation

Operation and testing at feed rates close to the full design rate lowers the risk in scaling-up to a full scale design from smaller scale test data. SCWO solid wall downflow and reversing flow reactor systems have operating experience at feed rates which are, respectively, 0.095 and 0.055 of the NECDF design rate. The transpiring wall reactor system's operating experience is significantly less at 0.00825 of the NECDF design rate. Therefore, the solid wall systems have a significant advantage in scale-up risk that could only be overcome by progressively larger scale testing of the transpiring wall system.

3. Tested Feed Stream

Success in destroying hydrolysate has been a cardinal criterion for selecting a SCWO system for the NECDF design. To date, only the downflow solid wall reactor system has treated hydrolysate. The destruction efficiency from its hydrolysate treatment tests met the high standards of the program. To date, the reversing flow solid wall and downflow transpiring wall systems have not treated hydrolysate. The transpiring wall system has not demonstrated destruction to the required level.

4. Corrosion at Reaction Conditions

The conditions in the NECDF SCWO are extreme and highly corrosive to many materials. The identification of resistant materials of construction for fabrication of the SCWO reactor should help meet the NECDF design's demand for highly reliable equipment. The transpiring wall reactor experienced deposition of salt on its "transpiring wall" surface during testing [Ref .3]. Deposition of salt is considered a precursor to corrosion; therefore, corrosion cannot be eliminated from consideration at this time merely by assuming that the "transpiring wall" will prevent deposition of salt.

The "transpiring wall" in the transpiring wall reactor is a unique and necessary equipment design feature for its processing concept. It has only been constructed of 3 16 SS and Inconel 600. No method has been identified to manufacture the innermost platelet of this "transpiring wall" in suitably corrosion-resistant material for the SCWO conditions required for NECDF. Therefore, future SCWO tests in the NECDF program will utilize downflow, solid wall reactor systems.

2.3.2 Materials of Construction

The SCWO experience database does not have sufficient materials of construction data to support the confident specification of materials for the NECDF SCWO unit. The experience which does apply is summarized and evaluated below.

The evaluation report on General Atomic (GA) treatability tests for destruction of hydrolysate included an evaluation of recommendations for the reactor liner material [Ref 2]. Those data and other available materials testing information are summarized below:

- The GA test's primary objective was to evaluate SCWO's ability to destroy VX/NaOH hydrolysate. It provided some qualitative corrosion information about the materials used for that test, but the information was insufficient to provide engineering design parameters for the SCWO liner. Relevant materials of construction information from the test included:

  - Significant corrosion of the titanium reactor liner appears to have occurred over the 8-hour test suggesting that titanium is not an appropriate selection.

  - A platinum thermocouple inside the oxidizing zone of the reactor during the test showed no apparent degradation. Previously used titanium thermocouples degraded completely.

- Other materials testing which GA performed as part of a Defense Advanced Research Projects Agency (DARPA) program indicated that a platinum alloy will corrode acceptably slowly in a basic environment at 550°C [Ref 2]. The data are limited and at a lower temperature than the NECDF conditions.

It was determined that materials of construction (MOC) testing was needed to select a material and to size the reactor liner thickness.

2.4 Specific Technical Data Requirements

Evaluation of the data base and SCWO test results identified the following outstanding technical data requirements:

1. Demonstration that on-line monitoring of the SCWO effluent TOC allows sufficiently accurate measurement to provide warning of any reduction in the level of hydrolysate destruction. Demonstrate as near as possible to "real time" monitoring.

2. Demonstration that the process is sufficiently robust to address expected feed stream and process parameter variations such as adjustment of process production rates.

3. Test data sufficient to support the selection of reactor materials of construction and size of the reactor liner for equipment design.

4. Demonstration of extended continuous SCWO operation without plugging due to solids buildup in the reactor, downstream piping, or rapid erosion of the pressure letdown systems.

5. Demonstration that in-line monitoring of the SCWO effluent conductivity provides early warning of solids buildup before reactor plugging is experienced.

6. Demonstration of extended continuous operation of the SCWO unit's feed, pressure letdown, and control systems sufficient to support design for stable, steady state operation, and emergency shutdown.

7. Demonstrates destruction at about $1/10^{th}$ scale of NECDF.

8. Confirmation that correlations are adequate to allow scale-up to the NECDF design size.

Plans for testing to address these issues are presented in Section 3.

3. FUTURE SCWO TESTING

The SCWO testing to date indicates that additional information could be useful during the design of a full-scale production facility for NECDF. There are several areas where further information would improve the projected operational success of SCWO. The overall objective of the future SCWO test program is to demonstrate continuous, stable operation of SCWO for the treatment of hydrolysate in support of the NECDF design.

3.1 Approach

Meeting the overall objective can be advanced by performing a materials of construction (MOC) test and an engineering scale test (EST). Taken together, the MOC and EST address all of the objectives identified in Section 2, as shown in Table 3-1. Tests for monitoring for solids plugging and TOC destruction will be initiated during the MOC tests and repeated during EST. Monitoring is planned to be part of the NECDF system. In addition, data from the MOC test will be used to select the liner material for the EST reactor. Other objectives associated with destruction, plugging, and process robustness will be met primarily by results from the EST but supported by data from the MOC Test.

Table 3-l Objectives of the MOC and EST

Objective	MOC	EST
Selection and sizing of reactor liner	√	√
Demonstration of operation without plugging		√
Demonstration of adequate operational control		√
Confirmation of scale-up correlations		√
Demonstration of destruction		√
Demonstration of in-line monitoring for plugging	√	√
Demonstration of on-line monitoring for TOC	√	√
Demonstration of process robustness		√

MOC = materials of construction
EST = engineering scale test
TOC = Total Organic Carbon

3.2 Materials of Construction Test

A Materials of Construction (MOC) Test has been solicited in response to the gap in the SCWO experience database identified in the evaluation described in Section 2. Evaluation of bidders was completed on September 8, 1997. Lockheed Martin Idaho Technologies Company

(LMITCO) at the Idaho National Engineering and Environmental Laboratory (INEEL) was selected to perform the MOC test which is currently in progress.

The scope of the MOC test is:

- Obtain engineering data to select and size liner material(s) suitable for service for NECDF.

- Perform testing at conditions prototypical of the SCWO reactor including pressure, temperature, velocity, destruction efficiency, etc.

- Test the acceptability of the liner material(s) across the full range of the reactor conditions present. Different liner materials may be required along the length of the reactor.

- Select liner material(s) based on the ability to fabricate the SCWO reactor.

- Determine the steady state general corrosion rates.

- Identify the failure modes encountered and determine the level of maintenance, repair, or replacement required at the NECD.

The MOC test is to be performed for 500 hours. Hydrolysate will be used for 200 hours and the remaining 300 hours of testing will be performed with surrogate. The evaluation and selection of the appropriate surrogate is ongoing.

A test plan to meet the MOC test objectives has been prepared by LMITCO. The final selection of the materials to be tested drew on the GA treatability test results, the DARPA test program results, and the responses to a request for candidate materials in the MOC test's RFP. The materials selected for testing are:

- platinum
- yttria stabilized zirconia (YSZ) on zirconium base metal
- YSZ on Hastelloy C-22
- Hastelloy C-22 as a baseline material.

Platinum and YSZ are both expected to have the best chance for a successful test. Although data are limited, the choice of platinum is based on its success in a caustic SCWO environment.

YSZ may provide a cost effective alternative to platinum based on its extensive experience on nickel alloy gas turbine blades in aggressive high temperature environments. YSZ has also been successfully used by Pennsylvania State University as a coating on instrumentation in SCWO environments. Since there is significant experience with YSZ coatings on Hastelloy, it was selected as the base material to detect penetration of the coating. Hastelloy is known to corrode in caustic environments so it will serve as an indicator of the YSZ coating's integrity.

YSZ on zirconium offers the potential benefit of coating a material which is much more resistant to caustic attack. Zirconium does not have experience as a base metal for YSZ. This test will determine if the adherence of the coating on the zirconium base metal is as tenacious as on the Hastelloy C-22 base metal.

Testing Hastelloy C-22 as a base provides a control for the test. It will also support engineering design for its use in subcritical regions of SCWO units.

The test coupons for each material are being fabricated in the form of 2-inch long tubular sections. A set of coupons consisting of one each of platinum, YSZ on zirconia, YSZ on Hastelloy C-22 and Hastelloy C-22, will be epoxied together to create S-inch long arrays. Twelve 8-inch arrays will be inserted into the IO-foot long reactor. Therefore, each material will occur at 8-inch repeating intervals along the reactor length. Adding materials to the array would increase the sequential spacing between each material's coupons and changes in the reaction environment over short distances may not be experienced equally by all materials.

MOC testing is included in the current NECDF program schedule in Appendix A.

3.3 Engineering Scale Test

3.3.1 Test Activities Description

An EST is planned at a scale of $1/10^{th}$ the capacity of the NECDF system. The EST contractor will construct a complete, integrated, computer controlled, fully automated system with all unit operations, processes, and components capable of processing hydrolysate and any appropriate surrogate. Construction of the reactor used for the EST will incorporate materials information developed in the MOC test. The EST program should be designed to meet the objectives defined above and listed in Table 3-l.

Testing at the nominal conditions of 1200°F and 3500 psig will allow confirmation of destruction and salt transport results obtained in the GA test, but for a longer duration. As with the MOC test, surrogate will be used for some of the testing.

The EST program planned to meet these objectives includes:

A Continuous 24-Hour Test

A nominal 24-hour test will be performed to demonstrate ability to meet the same operational and destruction objectives of the earlier PMATA 8-hour test at the EST scale of operation.

A Continuous 120-Hour Test

A nominal continuous 120-hour test will primarily demonstrate operation of the SCWO system without plugging due to solids, while maintaining an effective level of destruction. The ability of the computer control system to maintain temperature and pressure and of the pressure letdown system to perform during continuous SCWO operation are to be demonstrated specifically.

The test performance will evaluate the scale-up correlations used to design the EST SCWO unit and provide a basis for revising the correlations for scale-up to the NECDF SCWO unit, if required. Monitoring systems to measure TOC and salt in the SCWO effluent stream will be used and their measurements will be compared to those done as part of the MOC test. Comparing the results from both tests will provide addition data for scale-up correlations.

<u>A Process Robustness Test</u>

The 120-hour surrogate test is to demonstrate continuous, steady state operation. Hence, several sets of parameter settings are planned to establish an operating regime for adequate system performance. Parameters which will be varied to establish this operating regime include flow rate, temperature, residence time, and oxidant concentration.

These parameters will be varied to evaluate system performance as follows:

1. Reduce feed flow rate to demonstrate a turn down ratio to $1/5^{th}$ of full EST SCWO unit capacity

2. Reduce temperature to 1112°F as suggested by the EWTAJT test results

3. Increase feed flow rate to reduce residence time to 20 seconds as suggested by the GA test results

4. Establish minimum excess oxidant required.

The sets of varied parameter settings are expected to be of 2- to 6-hour duration each and are to be performed with a surrogate that is representative of organic destruction performance.

3.3.2 SCWO EST System Requirements

The SCWO EST system should be a complete, integrated, computer controlled, fully operable unit capable of processing hydrolysate and any hydrolysate surrogate to meet the test objectives. The SCWO unit and ancillary equipment should contain all the unit operations, unit processes, and components necessary for destruction of hydrolysate. Specifically, the necessary feed tanks, oxidant supply, water demineralizers, pumps, heat exchangers, heaters, reactors, coolers, pressure letdown equipment, gas/liquid separators, effluent tanks, structural steel, valves, pipe, fittings, insulation, instrumentation, controls, electrical equipment, monitors, and feed and effluent analyzers should be included.

The SCWO EST system should be specified as follows:

- The SCWO EST unit should operate at about 1/10th the full-scale NECDF rate, i.e., 209 lb/hr of hydrolysate. The NECDF SCWO unit will have a capacity of 2092 lb/hr of hydrolysate.
- The SCWO EST unit should maintain operating temperature at 1200°F with operating pressure at >3206 psia.
- The SCWO EST unit should process hydrolysate within permit requirements.
- The SCWO EST unit should process both hydrolysate and any hydrolysate surrogate.
- The SCWO EST unit should use oxygen as the oxidant.
- The SCWO EST unit should have a turndown capability to 1/5th of full EST capacity.
- The SCWO EST unit should be able to process decon when no hydrolysate is available.
- The SCWO EST unit should be computer controlled with all major control loops fully automated.
- The SCWO EST unit should incorporate the material of construction data from the MOC testing.
- The SCWO EST unit and all feasible support systems should be skid mounted for over-the-road transport.
- The SCWO EST contractor should provide quantitative reactor scale-up calculations, simulation models, correlations, and data reduction methodologies used for this project.

3.4 Evaluation of Other Test Options

The following design options have been suggested as a means to eliminate the need for engineering scale testing. They have been reviewed and summaries of their evaluations appear below:

3.4.1 Option A: Utilize Smaller Capacity, More Multiple SCWO Treatment Trains in Parallel No Engineering Scale Testing

This option uses multiple SCWO trains for the NECDF which are each no greater than 10 times the capacity of the SWCO test unit which treated hydrolysate. This would result in three parallel SCWO units to process 6 ton containers per day; i.e., each at 2 ton containers per day.

Additional units would be installed as standbys. At any given time, three units would be operating and 1 or 2 units would be in standby mode.

This option would cut the scale-up risk, but would not confirm the basic SCWO design parameters at issue for SCWO's application to hydrolysate. Without additional tests, the SCWO unit design will remain individually at the present level of risk and hydrolysate destruction conditions will not have been confirmed for the NECDF installation.

3.4.2 Option B: Smaller Capacity, More Multiple SCWO Treatment Trains in Parallel Engineering Scale Testing Performed

This case would require 3 trains operating in parallel to process 6 ton containers per day for the NECDF. EST would be performed at $1/10^{th}$ scale, but the EST results would not be used to design SCWO units to individually process 6 ton containers per day.

This option should not be the primary concept for the facility installation. The design with one 100% backup unit is the most cost effective and simple. The complexity and additional cost of four or more independent SCWO trains operating simultaneously should not be the first choice. The decision to use smaller capacity, multiple SCWO treatment trains in parallel should be deferred until the EST tests are complete. The multiple unit approach can be adopted if required by the results of the $1/10^{th}$ scale EST.

3.5 Summary

The following items summarize important features of the planned SWCO testing program:

1. The MOC testing should be done utilizing hydrolysate and surrogates.
2. An EST should be performed at about $1/10^{th}$ scale with the same configuration as for the NECDF acquisition design.
3. The EST and MOC tests will both provide design information to meet the NECDF program's technical objectives for post treatment systems.
4. There is no existing SCWO test unit capable of performing the EST. A unit must be assembled for the SCWO EST.

4. RECOMMENDATIONS FOR SCWO ACQUISITION

4.1 Acquisition Strategy and Testing Required

The previous sections of this report have concluded that:

- The general NECDF procurement approach places all equipment acquisition responsibility with the systems contractor. Government-furnished equipment (GFE) has been eliminated or at least been minimized.

- The downflow, solid wall, cylindrical vertical vessel is the reactor with the highest probability for success at the NECDF within the program schedule.

- Testing with a SCWO unit is required to establish an engineering basis for selection of materials of construction.

- An EST is needed to demonstrate automated control, destruction, and extended operation without plugging at $1/10^{th}$ the NECDF scale. The EST will provide the longer duration testing that is generally needed to confirm design and long term performance data.

4.2 Performance of the Engineering Scale Test

The EST will provide design data to support the cost effective selection of a full-scale unit. The results should be available at or soon after system contract award to maintain the NECDF program schedule. The alternatives are:

- complete the design for the NECDF based only on tests already completed and the MOC testing in progress

- have the EST performed by the System Contractor.

In the first alternative, insufficient design information is available to prepare a design within the NECDF technical objectives. In the second alternative, the program could be greatly delayed due to the lead times to acquire the required test system. The EST results would not be available for selecting a SCWO vendor and completing the NECDF design within schedule. Therefore, the EST should be started before systems contract award for the systems contractor to maintain the schedule in Appendix A.

Table 4-l shows the Trade Off Matrix of factors in this question.

Table 4-l Trade Off Matrix

	Perform Engineering Scale Test (EST)		
	Before systems contract award	After systems contract award	No Further Testing
PRO	Reduce technical risk by accumulating operating and engineering information applicable to NECDF.		Can maintain current acquisition strategy.
	Can initiate EST now and resolve any unknown problems in timely manner. The Systems Contractor (SC) can incorporate results of the test into the NECDF design.	Can maintain current acquisition strategy.	
CON	SCWO test not part of systems contract	Delays start of SCWO test, prevents timely availability of design input information, no test data for minimizing SCWO technical risk.	More technical risk.

The results of the EST will be available for use by the System Contractor for the NECDF design by incorporating two requirements in the contract for the SCWO EST. First, the government should own and have the right to use any new equipment and systems purchased for the EST. Second, the SCWO EST contractor should be required to provide engineering, design, fabrication, assembly, and test information to the systems contractor.

The performance of a SCWO EST by the government before award of the System Contract will provide substantial design information to all potential SCWO vendors. Vendors whose expertise has been limited to configurations other than the vertical solid wall reactor would have sufficient information to be competitive for the Newport SCWO system.

The SCWO EST will be conducted with a specific reactor type. Qualified SCWO vendors will be able to use the SCWO EST data to prepare their designs. They will be free to present their qualifications to do so irrespective of direct hydrolysate experience and can be evaluated without hydrolysate experience being required.

The performance of the SCWO EST at the earliest possible opportunity represents the least total risk to program objectives and therefore, the best option. This option would require the solicitation of a SCWO EST contractor prior to the systems contract award.

4.3 Recommended Specific Actions for Future SCWO Tests

The following actions are recommended for future SCWO testing:

1. Complete the SCWO MOC tests.

2. Competitively select one SCWO EST contractor.

- Require the EST contractor to give the government unrestricted rights to the EST SCWO technology for the NECDF and to provide the NECDF system contractor with data used to design, fabricate, deliver, and start up the EST SCWO systems.

- Develop a SCWO EST statement of work (SOW) applicable to a downflow vertical solid wall cylindrical reactor.

- Send the SOW to qualified candidate SCWO EST contractors for comment.

- Review and incorporate the comments to the SOW as required.

3. Perform the EST in a downflow vertical solid wall cylindrical reactor to achieve the technical objectives specified in this document.

4.4 Additional Recommendations

Additional recommendations are as follows:

1. Continue to investigate options to produce additional hydrolysate. Additional hydrolysate would allow:

- substantial expansion of MOC tests with hydrolysate rather than a surrogate.

- performance of longer duration EST tests with hydrolysate.

2. Do not reduce the design throughput of an individual SCWO reactor as a means to eliminate the need for testing.

5. REFERENCES CITED AND OTHER RELATED SOURCES

1. "Treatability Study for Treatment of VX Hydrolysate Effluent From Neutralizationof VX Chemical Nerve Agent," prepared for PMATA by Stone & Webster, Sept. 20, 1996.

2. "Evaluation of Confirmatory Testing of Supercritical Water Oxidation for Treating VX/NaOH Hydrolysate," prepared for PMATA by Stone & Webster, May 30, 1997.

3. "Transpiring Wall Supercritical Water Oxidation Reactor Salt Deposition Studies," Sandia Report. SAND96-8255•UC-702, September 1996.

4. Preliminary Proposal, Capabilities in Hydrothermal Processing, Battelle, Pacific Northwest National Laboratory,November 25, 1996, marked PNNL Sensitive.

5. "Reactions at Supercritical Conditions: Applications and Fundamentals," AIChE Journal, Vol. 41, No.7, July 1995.

6. "Assessment and Development of an Industrial Wet Oxidation System for Burning Waste and Low Grade Fuels," Final Report Phase IIB, Contract No. DE-FC07-88ID12711, January 1994.

7. "Hydrothermal Oxidation of Navy Shipboard Excess Hazardous Materials," Sandia Report, SAND97-82 12•UC-702, March 1997.

8. "Supercritical Water Oxidation Data Acquisition Testing," Contract No. DE-FC07-94ID 13303, Final Report, Volume I, Phase I DOE Testing, Idaho Operations Office, November 1996.

9. "Design Requirements for the Supercritical Water Oxidation Test Bed," EGG-WTD- 11 199, Rev.0, May 1994.

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13. "Turn Off the Heat," pp. 43-47, Industrial Wastewater, July/August 1996.

14. "Review and Evaluation of Alternative Chemical Disposal Technologies," Panel on Review and Evaluation of Alternative Chemical Disposal Technologies, Board on Army Science And Technology, Commission on Engineering and Technical Systems, National Research Council, 1996.

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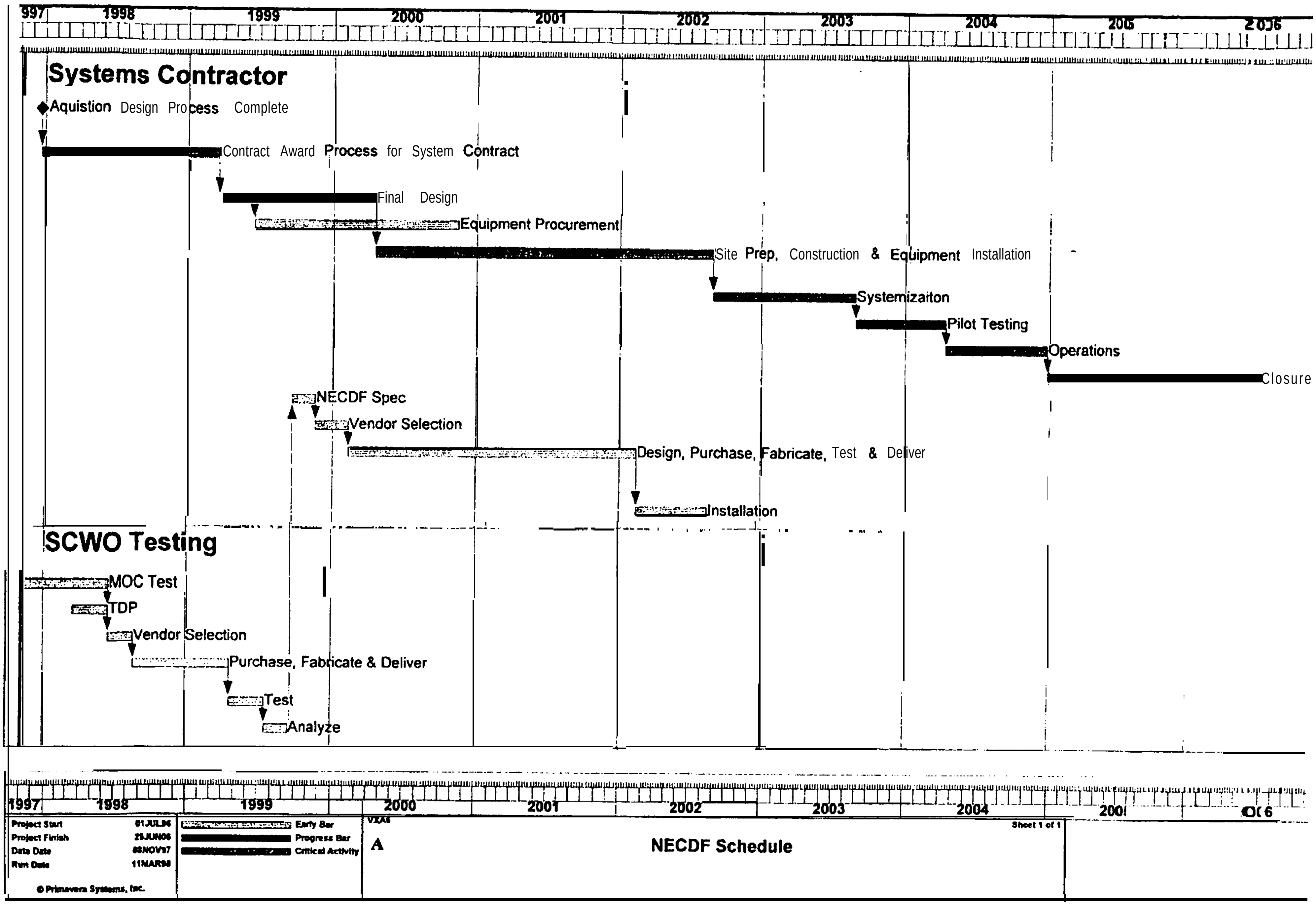
16. " Supercritical Water Oxidation of Methylphosphonic Acid - Destruction Efficiency and Kinetics," University of Texas at Austin, November 25, 1997.

17. "Testing Assisted Hydrothermal Oxidation to Destroy VX/NaOH Hydrolysate," SRI Final Report, October 10, 1997.

18. Decision Paper for Onsite Post Treatment of Hydrolysate at NECDF.

19. Life Cycle Cost Estimate for NECDF.


1997
1998
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Final Design
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Site Prep, Construction & Equipment Installation
Systemizaiton
Pilot Testing
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NECDF Spec
Vendor Selection
Design, Purchase, Fabricate, Test & Deliver
Installation
SCWO Testing
MOC Test
TDP
Vendor Selection
Purchase, Fabricate & Deliver
Test
Analyze
Project Start 01JUL96
Project Finish 29JUN06
Data Date 03NOV97
Run Date 11MAR98
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Early Bar
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Sheet 1 of 1

B. SELECTION OF SCWO

B.l History

Water and caustic chemistry VX neutralization process options were pursued from the laboratory testing in late 1994 through the Mettler and chamber testing in 1995. In late November 1995, offsetting advantages and disadvantages were identified for both VX water and VX caustic neutralization reactions. Onsite biodegradation was not being considered due to consistently poor test results. Stabilization of a solidified hydrolysate stream was an onsite post treatment option. Shipping hydrolysate to an unspecified Treatment, Storage and Disposal Facility (TSDF) was an offsite post treatment option During this period, the VX/water hydrolysate could not be shipped to other locations for treatability testing which severely restricted investigation of post treatment options for the VX/water reaction products.

B.2 Additional Technologies

In August 1995, the U.S. Army advertised in the Commerce Business Daily for technologies that were sufficiently developed to be alternatives to incineration for destruction of HD stockpiles at Aberdeen, Maryland and VX stockpiles at Newport, Indiana. The U.S. Army evaluated and selected several technologies for further consideration from those submitted in response to their advertisement [Ref 1].

The technologies selected as potentially effective for both agent and hydrolysate treatment were:

- Catalytic Extraction Process (CEP) / M4 Environmental Management, Inc. (M4 Environmental)
- Gas-Phase Hydrogen Reduction / Eco Logic International, Inc.
- Silver (II) Electrochemical Oxidation / AEA Technology plc (AEA)

The technologies selected as potentially effective for hydrolysate treatment were:

- Supercritical Water Oxidation (SCWO) / General Atomics (GA)
- UV Oxidation/ Solarchem Environmental Systems (Solarchem)
- Electron Beam Treatment

B.3 UV Oxidation and Stabilization

The treatability tests by Solarchem in January 1996 utilizing UV Oxidation for the hydrolysate required extensive dilution and a large number of units to achieve destruction. The stabilization testing of hydrolysate conducted through March 1996 at Southwest Research Institute (SwRI) was not successful because 40 to 50% of the organophosphate constituents leached out of the solidified hydrolysate.

B.4 Off Site Wastewater Treatment

In April 1996, it was decided to investigate and adopt, if appropriate, off site treatment of the hydrolysate. This procedure added calcium hypochlorite (bleach) followed by shipment to the DuPont Chambers Works industrial wastewater treatment facility. A series of experiments investigated the effects of this bleach addition and the ability of the DuPont facility to treat hydrolysate quantities representative of full-scale plan operations. The results of these experiments were discouraging, and treatability studies using other technologies were renewed.

B.5 Renewed Hydrolysate Treatability Testing

Four technologies were selected for renewed tests based on ratings by the blue ribbon technology selection committee in late 1996 [Ref 1]. Electron beam technology was eliminated based on immaturity and UV/Oxidation was eliminated based on results of earlier tests (see paragraph B.3 above).

The four treatment technologies selected for testing were:

- Catalytic Extraction Process (CEP) / M4 Environmental Management, Inc.
- Gas-Phase Hydrogen Reduction / Eco Logic International, Inc.
- Silver (II) Electrochemical Oxidation / AEA Technology plc
- Supercritical Water Oxidation / General Atomics

The treatability studies included tests to demonstrate destruction of sample quantities of VX/NaOH hydrolysate provided by PMATA, sampling and analysis to quantitatively determine the effectiveness of the process, and preparing a mass balance for the test results. These data were used to prepare a mass balance, simplified process flow diagram (PFD) and an order of magnitude cost estimate for a full-scale facility to treat 30,560 pounds of VX/NaOH hydrolysate per day which results from processing 10,000 pounds of VX per day.

General Atomics (GA) was selected as the SCWO vendor because its concept design had been favorably reviewed by the blue ribbon technology selection committee in late 1996. Additionally, GA offered an existing facility capable of processing the quantity of hydrolysate necessary to demonstrate handling of the salt formed in the SCWO reactor when the organics are destroyed to the required level.

A treatability study for the Silver (II) Electrochemical Oxidation was not performed with hydrolysate but included tests to evaluate effects of salt on the electro-chemicalcells. These results were considered along with the results from other Silver(B) tests involving treatment of VX agent at Porton Down.

The conclusions from the evaluation [Ref 2]of the above treatability studies performed between June and August 1996 were:

1. each technology demonstrated reduction of the thiols and the organic compounds containing the carbon phosphorus bond in the VX/NaOH hydrolysate by at least 99%

2. SCWO appeared to be the most suitable and effective of the technologies for destroying hydrolysate.

Other factors supporting the selection of SCWO were:

- the existence of multiple potential SCWO vendors,
- the research base at national laboratories and academic institutions,
- the completenessof the destruction,
- the suitability of the process to our aqueous stream.

Therefore, SC WO was selected for further testing.

B.6 Follow On Supercritical Water Oxidation Testing

Follow on testing of the SCWO technology was performed in February 1997 by GA to confirm the conclusions reached in the August 1996 tests. The confirmatory testing used apparatus partially modified to address the problems found during the August 1996 tests. Evaluation [Ref 3] of the February 1997 tests concluded that SCWO is effective and suitable for the treatment of VX/NaOH hydrolysate confirming earlier conclusions [Ref 2].

Tests at a commercial evaporator vendor were performed to verify that the non-organic salts in the SCWO effluent could be removed so that the recovered water could be reused in the process. These tests also determined that the evaporator could produce a salt solid suitable for disposal.

The confirmatory testing evaluation in Ref 3 included a review of the available materials data to support selection and sizing of the liner material for a full-scale facility. This review determined that material corrosion data were needed.

B.7 Additional Supercritical Water Oxidation Testing

Additional SCWO testing was planned in parallel with the confirmatory testing at GA to:

1. Determine destruction kinetics in SCWO.

2. Review alternate approaches to SCWO such as catalysts for applicability to VX hydrolysate.

3. Identify potential issues relating to full-scale performance of the NECDF SCWO installation.

4. Perform materials of construction (MOC) testing.

A survey of candidate testing organizations indicated capability from:

- Eco Waste Technology (EWT) / University of Texas (UT),
- Massachusetts Institute of Technology (MIT),
- Sandia National Laboratory (SNL),
- Los Alamos National Laboratory (LANL),
- Idaho National Engineering & Environmental Laboratory (INEEL),
- Stanford Research International (SRI), and
- Battelle Pacific Northwest National Lab (PNNL).

A request for proposal (RFP) was issued to all and responses were received from EWTAJT, SRI, LANL, INEEL, and SNL. LANL and MIT both declined because of other priorities within their respective organizations. PNNL elected not to respond to the RFP due to conflict of interest concerns as stated in its letter dated January 2 1, 1997.

EWT/UT responded with a proposal to address Item 1 in Section B.7, electing to utilize methyl phosphonic acid (MPA) rather than hydrolysate. EWT stated that neither its commercial unit at Huntsman Chemical nor its pilot unit at the University of Texas could test with hydrolysate. EWT was, therefore, awarded a contract to provide surrogate (MPA) destruction data over the temperature range of interest to corroborate the MPA destruction reported in the GA test. The EWT tests have been completed utilizing a bench scale reactor. The data indicate that MPA is the most refractory constituent in hydrolysate, but that it can be destroyed in a defined range of temperature and residence time [Ref 4).

SRI responded with a proposal to test the benefits of a catalyst with a small batch reactor system to address Item 2 in Section B.7 and a contract to do so was placed with SRI. The SRI process offered the potential for hydrolysate of destruction at lower temperatures through the addition of sodium carbonate. Destruction at lower temperatures could reduce design requirements for a full-scale facility and potentially provide an alternative design. The SRI tests have been terminated because the initial results were inconclusive and showed no benefit to be gained from the addition of sodium carbonate [Ref 5].

Sandia National Laboratory responded with a proposal to test utilizing their transpiring wall reactor scheme. A review was made of a test report [Ref 6] of results for the application of the Transpiring Wall reactor to smokes and dye feeds. This report presented the most up-to-date results using this type of reactor. It indicated that, even with transpiration cooling, some salt deposition occurred on the reactor walls with a feed containing only 5% dye. This caused concern that corrosion mechanisms similar to those on a solid wall reactor were present and brought to question the benefit of the transpiring wall reactor if the same materials issues would need to be addressed. Hence, it was decided not to pursue testing of the transpiring wall in our program as discussed in Section 2.3 of the report to which this is Appendix B.

PNNL indicated they had the capability to perform tests to treat hydrolysate at a scale similar to tests performed at GA. PNNL declined responding to the RFP due to concerns that testing could jeopardize future business development opportunities. PNNL has recently notified the U.S. Army that they no longer have contractual concerns and are interested in performing tests. Stone & Webster has reviewed the capability of the PNNL equipment to perform testing under the conditions required for hydrolysate treatment. It has been determined that the PNNL equipment is not capable of the pressure and temperature operating regime required for our application and no testing is planned utilizing that equipment.

B.8 References

1. "Review and Evaluation of Alternative Chemical Disposal Technologies," Panel on Review and Evaluation of Alternative Chemical Disposal Technologies, Board on Army Science And Technology, Commission on Engineering and Technical Systems, National Research Council, 1996.

2. "Treatability Study for Treatment of VX Hydrolysate Effluent From Neutralization of VX Chemical Nerve Agent," prepared for PMATA by Stone & Webster, Sept. 20, 1996.

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6. "Transpiring Wall Supercritical Water Oxidation Reactor Salt Deposition Studies, " Sandia Report, SAND96-8255•UC-702, September 1996.

APPENDIX C

Numerical Comparison of SCWO Reactor Scales

Parameter	Unit	Scale Designation: Mass balance, full scale	PMATA treatability test, 1/25th	MOC Test, 1/100th	1/10th	1/6th	1/3rd
Scale							
Scale based on VX relative to GA		25.3	1	0.3	2.5	4.2	8.4
Scale based on total liquid input relative to GA		31.4	1	0.3	3.1	5.2	10.5
Capacity per train	TC/day	6	0.24	0.07	0.6	1	2
Feed							
Drained agent hydrolysate	lb/h	1128	43.6	12.2	113	188	376
TCC water	lb/h	965	0.0	10.4	96.5	161	322
HP dilution water	lb/h	937	48.8	9.6	93.7	156	312
Auxiliary fuel	lb/h	0.0	2.0	0.0	0.0	0.0	0.0
Total liquid input	lb/h	3029	96.6	32.2	303	505	1010
VX equivalent	lb/h	375	14.8	4.1	37.5	62.5	125
Oxidant							
Type		Oxygen	Air	Oxygen	Oxygen	Oxygen	Oxygen
Flow	lb/h	1313	282	13.8	131	219	438
Length of test	h	6760	8	200	24	24	24
Inventory requirements							
VX	lb	2,535,000	118	813	900	1500	3000
	lb/gal	8.41	8.41	8.41	8.41	8.41	8.41
	gallons	301,504	14	97	107	178	357
Drained agent hydrolysate	lb	7,622,182	348	2440	2706	4510	9020
	lb/gal	9.70	9.70	9.70	9.70	9.70	9.70
	gallons	785,745	36	252	279	465	930
Reactor							
Diameter	in	10	4	1.5	3.75	5	6
Length	ft	15	6	10	10	9	11
Length/diameter ratio (L/D)	ft/ft	18	18	80	32	22	22
Surface/volume ratio	ft^{-1}	4.8	12.0	32.0	12.8	9.6	8.0
Mass input	lb/h	4341	379	46	434	724	1447
Fluid density	lb/ft^3	5	5	5	5	5	5
NRe		76,271	16,633	5388	20,339	25,424	42,373
Velocity		0.44	0.24	0.21	0.31	0.29	0.41
Residence time	s	34	25	48	32	31	27
Salt, anhydrous	lb/h	397	14.6	4.3	39.7	66.2	132
	$lb/h\ ft^2$ XS	729	168	351	518	486	675
	lb/h ft perim	152	14.0	10.95	40.5	50.6	84.4
	$lb/h\ ft^2$ wall	10.1	2.33	1.10	4.05	5.62	7.67
Scale multiplier					0.100	0.167	0.333