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TECHNICAL REPORT

Naval Facilities Engineering Service Center, Port Hueneme, CA 93043-4328

DESTRUCTION OF NAVY HAZARDOUS WASTES BY SUPERCRITICAL WATER OXIDATION

TR-2025-ENV

August 1994

By Richard E. Kirts

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The objective of this study was to investigate the feasibility of using supercritical water oxidation (SCWO) to destroy organic hazardous wastes generated by Navy industrial activities. Supercritical water oxidation is the low temperature combustion of organic material in the medium of supercritical steam. The study concludes that SCWO is an economically attractive method of destroying a wide variety of hazardous organic wastes. The estimated Navy need for SCWO technology is a minimum of seven waste processing plants, each having a capacity of 1 gallon per minute of organic material. The estimated capital cost of each plant is $6M. The estimated hazardous waste disposal cost is approximately $8 per gallon of organic material, which is substantially lower than the conventional disposal cost of up to $45 per gallon. It is estimated that SCWO can be implemented on a large scale, and in a safe, reliable, and efficient manner. Waste streams that contain a large amount of mineral-acid forming chemical species or that contain a large amount of dissolved solids present a challenge to current SCWO technology.

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2,000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

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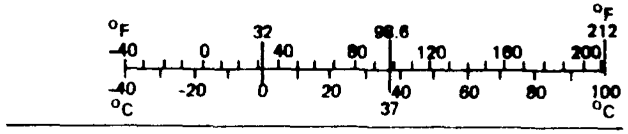
[*] 1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1,000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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The objective of this study was to investigate the feasibility of using supercritical water oxidation (SCWO) to destroy organic hazardous wastes generated by Navy industrial activities. Supercritical water oxidation is the low temperature combustion of organic material in the medium of supercritical steam. The study concludes that SCWO is an economically attractive method of destroying a wide variety of hazardous organic wastes. The estimated Navy need for SCWO technology is a minimum of seven waste processing plants, each having a capacity of 1 gallon per minute of organic material. The estimated capital cost of each plant is $6M. The estimated hazardous waste disposal cost is approximately $8 per gallon of organic material, which is substantially lower than the conventional disposal cost of up to $45 per gallon. It is estimated that SCWO can be implemented on a large scale, and in a safe, reliable, and efficient manner. Waste streams that contain a large amount of mineral-acid forming chemical species or that contain a large amount of dissolved solids present a challenge to current SCWO technology.

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PREFACE

On 1 October 1993, the Naval Civil Engineering Laboratory (NCEL) and the Naval Energy and Environmental Support Activity (NEESA) were consolidated with four other Naval Facilities Engineering Command (NAVFAC) components into the Naval Facilities Engineering Service Center (NFESC).

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OBJECTIVE

The objective of this exploratory development project was to determine the feasibility of using supercritical water oxidation as a method of treating certain waste streams generated by Navy industrial activities. Supercritical water oxidation (SCWO) is the comparatively slow, low temperature combustion of organic material in the medium of supercritical steam. SCWO may be a method of destroying organic hazardous wastes that is both cost effective and environmentally sound. Specifically, the waste streams being considered are organic wastes generated by industrial activities such as the maintenance and repair of aircraft, ships, and motor vehicles. Typical wastes include contaminated oils, solvents and cleaning compounds, paint and paint stripping wastes, pesticides, and herbicides. The project did not assess the feasibility of using SCWO to treat stocks of explosives, propellants, chemical warfare agents, or radioactive mixed wastes (application of SCWO technology to these waste streams is being explored by other agencies and programs).

BACKGROUND

Supercritical water is water at a thermodynamic state above the critical point of water (Figure 1). The critical point of water is approximately 3,208 pounds per square inch pressure (22 MPa) and 705°F (375°C) temperature. Above the critical pressure, water does not boil or condense when heat is added or removed, but it undergoes a continuous change in density.

Near the critical point, the solvating characteristics of water undergo significant changes. The strength of the bonds between the hydrogen atoms and the oxygen atom is greatly diminished near the critical point, resulting in increased hydrogen atom mobility and, thus, reduced molecular polarity. As a result of this change in the molecular behavior of water, many organic compounds that are only sightly soluble in water at normal conditions become very soluble in supercritical water. Figure 2 illustrates this property of supercritical water with n-heptane as the solute. As Figure 2 illustrates, heptane is completely miscible in supercritical water. This characteristic is true for many other hydrocarbons as well.

Conversely, because water loses its polar behavior near the critical point, many ionic salts are much less soluble in supercritical water than liquid water. As a consequence, many salts in aqueous solution precipitate out of solution as the critical temperature of water is approached. Figure 3 illustrates the solubility of some common salts in subcritical and supercritical water. This property can be employed to remove, as a precipitated salt, a large fraction of the metals that may be present in organic hazardous wastes.

The second feature of supercritical water that is important to this waste treatment technology is the fact that gases can be added to supercritical water in all proportions. This means that as much oxygen can be added to a supercritical water-organic waste mixture as is required for the oxidation reactions to go to completion.

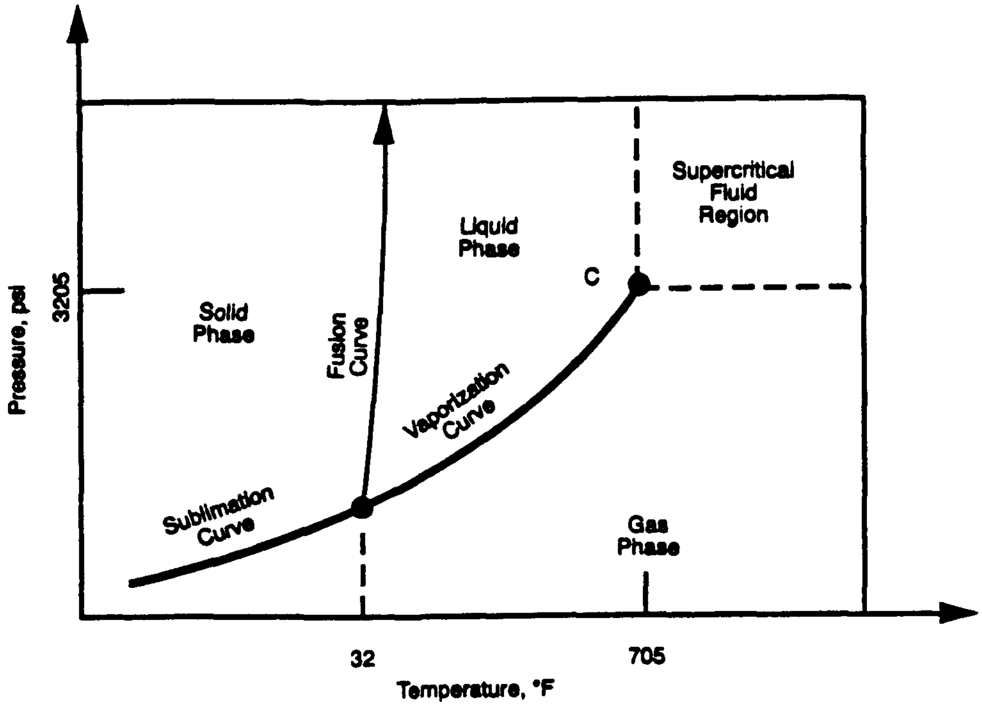


Figure 1
Supercritical fluid region of water.

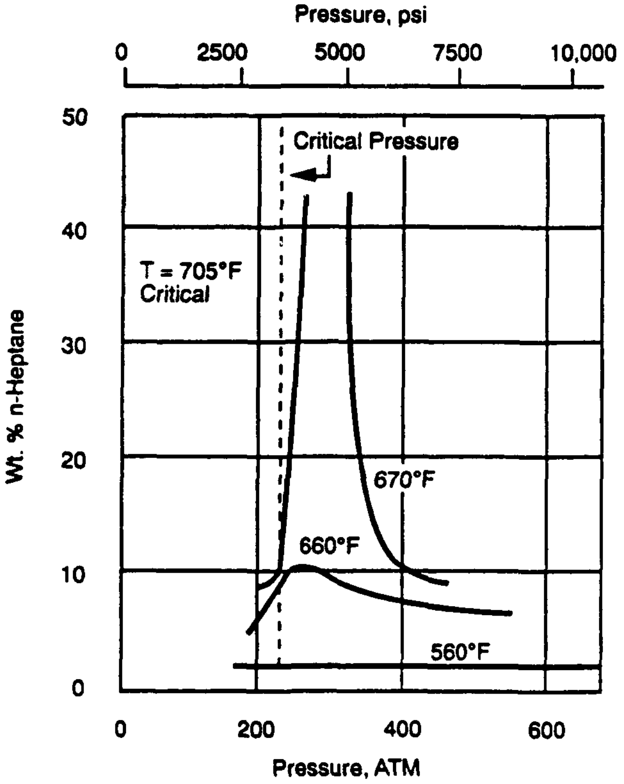


Figure 2
Solubility of n-heptane in water.

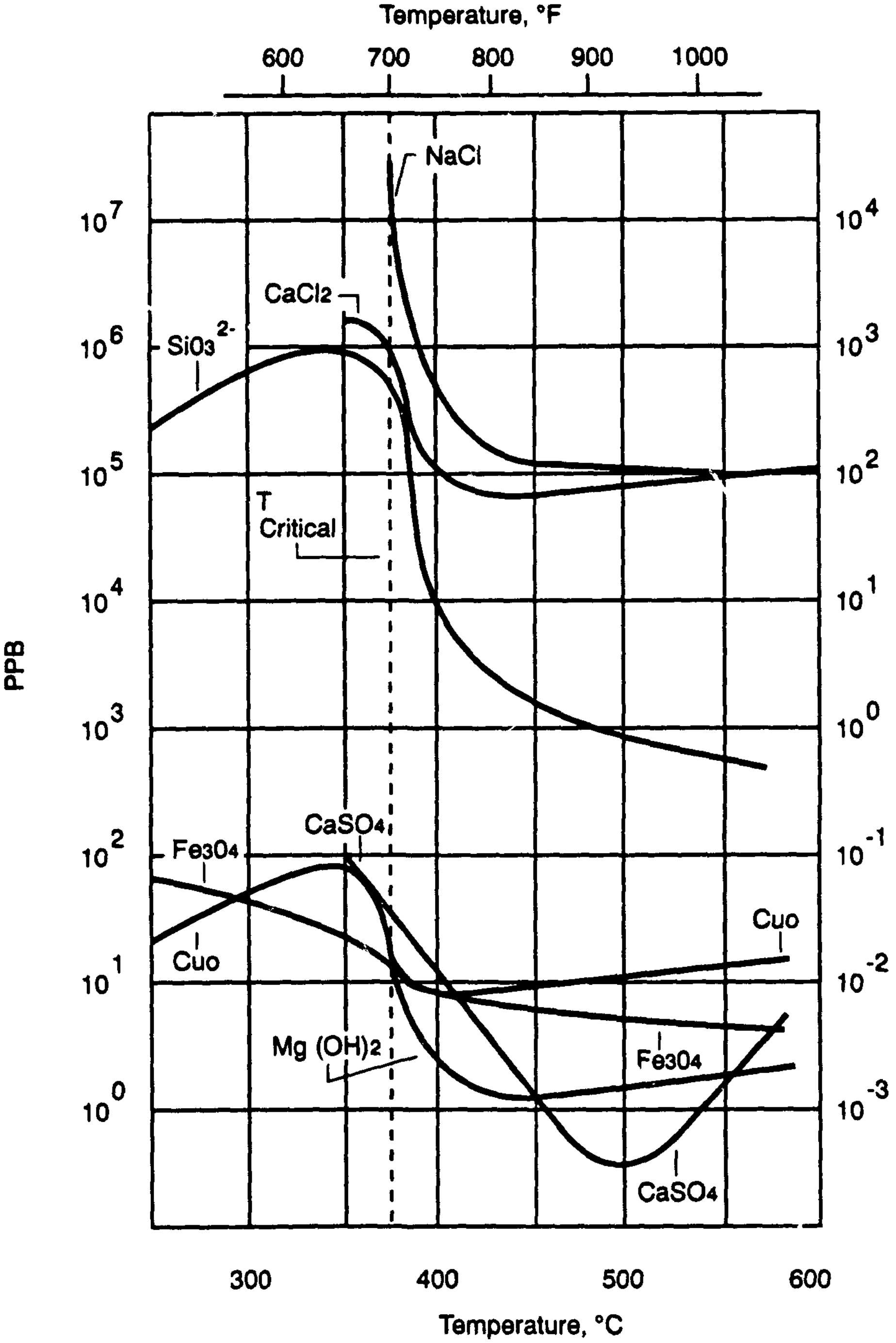


Figure 3
Solubility of selected salts and metal oxides near the critical point of water.

Supercritical water oxidation is the use of water at conditions above its thermodynamic critical point to facilitate oxidizing complex organic substances, organic hazardous wastes for example, into carbon dioxide, water, nitrogen, and other innocuous compounds. SCWO could be defined as follows: SCWO is the oxidation of organic compounds in the medium of supercritical water or, equivalently, SCWO is the low temperature combustion of organic material in supercritical steam.

SCWO is an attractive alternative for management of organic waste materials for several reasons. First, SCWO destroys organic wastes by converting them into water, carbon dioxide, nitrogen, and other environmentally benign chemical compounds. This eliminates or greatly reduces the problem of continuing legal liability for the hazardous waste. Second, unlike hazardous waste incinerators, emissions from the SCWO process are totally controlled: no gases, liquids, or solids can enter the environment without first being tested and, if necessary, treated. Third, public opposition to sitings of hazardous waste dumps and local bans on hazardous waste incinerators are rapidly driving up the cost of hazardous waste disposal. Finally, the SCWO process holds the potential of producing thermal energy, electrical energy, and clean water as process byproducts.

Many hazardous organic wastes are, or can be made into, aqueous solutions, dispersions, or emulsions suitable for treatment by the SCWO process. Examples include oily wastewaters, sewage sludge, organic solvents, pesticides and herbicides, painting operations wastes, PCBs, lubricating oils, fuels, propellants and explosives, hospital wastes, and chemical warfare agents. The SCWO process may also be useful in cleaning solid materials, such as some types of soil or metal parts, that have been contaminated with hazardous substances. The SCWO process may also be used to concentrate certain dilute waste streams in preparation for final disposal by vitrification, encapsulation, or some other process. An example of this application is the oxidation of cutting oil containing particles of radioactive material. The oil is oxidized, leaving a much reduced volume of radioactive material to be removed and dealt with.

The SCWO process does not generate significant air pollution because the oxidation reactions occur at relatively low temperatures and in the presence of excess oxygen. Most of the gaseous discharge from the SCWO process is carbon dioxide, excess oxygen, and elemental nitrogen. Oxides of nitrogen and sulfur are not produced in quantity because the reaction temperature is low.

Also, the SCWO process does not generate significant water pollution. Most of the metallic compounds precipitate out of solution under supercritical conditions or form metal oxides that either coat the interior walls of the process machinery or are carried though the process to the liquid discharge point. These particulates can be filtered out of the waste stream. Chlorine, sulfur, and certain other nonmetals will form an acidic process discharge, but this discharge is easily neutralized before final disposal.

The fundamental SCWO process is illustrated in Figure 4. Water containing the organic waste to be destroyed is pumped by pump A to a pressure exceeding the critical pressure: usually a pressure of 3,600 to 4,000 psi. The water-waste mix is next heated to a temperature exceeding the critical temperature, typically 710 to 750°F, in heater B. Heated oxygen is then added to the supercritical water-waste mix (in mixer C) and the water-waste-oxygen mixture is heated to a temperature of 1,000 to 1,200°F in heater D. The heat added at D may come either from an external source, such as an electrical heating element, or from the heat evolved from the oxidation reactions themselves. An external heater is required for very low heating value wastes such as sewage. High heating value waste, such as waste oils, can provide the required energy input from oxidation reactions. The water-waste-oxygen mixture is kept at an elevated

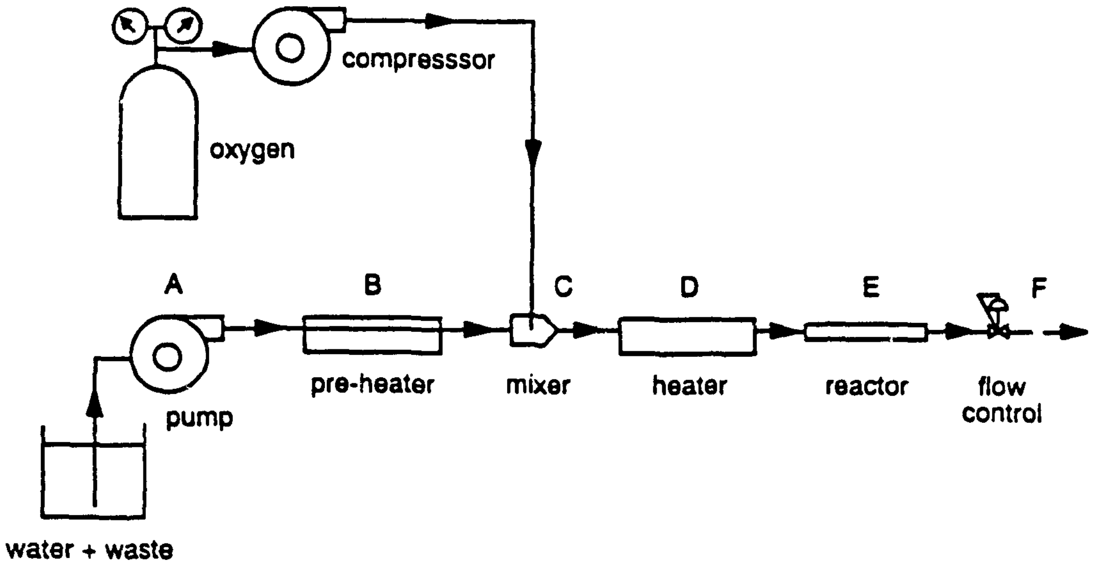


Figure 4
Fundamental SCWO process.

temperature (in reactor E) for the period of time (called the residence time) required for the oxidation reactions to go to completion. Because it is desired to keep the temperature of the reactions relatively low, the residence time is comparatively long, usually 10 seconds or longer. A flow control device at the end of the SCWO unit (valve F) maintains pressure in the system.

APPROACH

The approach used to meet the stated objective is outlined below:

1. Determine the Navy need for SCWO technology -

    A. Determine the composition, quantity, and disposal costs of hazardous waste streams potentially treatable by the SCWO process.

    B. Determine which waste streams offer the greatest potential savings. Estimate potential for treating mixes of several types of waste streams.

    C. Estimate benefits of reduced Navy long term liability.

2. Estimate the economic benefits of SCWO technology -

    A. Determine the optimal process design, i.e., the simplest, lowest cost, configuration that will make SCWO work on Navy industrial wastes.

B. Estimate the expected unit disposal cost with an SCWO system. Estimate the economic sensitivity of the process.

C. Investigate the permitting issues related to the SCWO process. Determine which regulations and codes apply to SCWO equipment and operation.

3. Identify and explore the technology gaps retarding SCWO implementation -

   A. Experimentally determine the destruction efficiencies, oxidation products, solid precipitates, and other characteristics of selected wastes treated by the SCWO process.

   B. Determine the optimal SCWO operating parameters (temperature, pressure, residence time, catalyst).

   C. Identify the critical hardware problems. Problems might include: reliable high pressure pumps, pumping a slurry (such as painting wastes), metallurgy (erosion and corrosion), mixing oxygen with reactants, heat transfer, scale and other deposits, separation and removal of solids, pressure-temperature let down system design, acidity and salinity of discharge water, composition of discharge gases.

   D. Investigate how instrumentation and controls can be applied to the SCWO process to: (a) permit automatic adaption to variations in feedstock composition, (b) ensure zero discharge of gaseous and liquid pollutants, and (c) make an SCWO reactor safe and easy to operate.

WASTE CHARACTERIZATION

Supercritical water oxidation may be a cost effective waste treatment option for waste streams with the following characteristics: (1) the waste stream is a liquid or finely divided slurry or emulsion, (2) the waste stream is at least 3 percent organic matter, (3) the waste stream is costly to dispose, (4) the waste stream is of sufficient quantity to warrant the expense of an SCWO treatment plant, and (5) the waste stream cannot be cost effectively treated by some other process. Specifically excluded in this study are the following hazardous waste streams: propellants, explosives, chemical and biological warfare agents, biological waste, and radioactive wastes. These hazardous waste streams were excluded for one or more of the following reasons: (1) other military services or Federal agencies are taking the lead in studying SCWO applications to the specific waste stream (e.g., radioactive wastes), (2) handling and treatment of the waste stream is outside the charter of the Navy (chemical weapons), (3) the waste stream adds significantly more complication to the SCWO process, such as increased preprocessing requirements, increased operating safety requirements, or increased corrosion (ordnance demilitarization), and (4) the waste stream is too small to warrant the added complexity of incorporating it into an SCWO unit (e.g., biological waste).

Data on the hazardous waste generated and disposed by the Navy are collected and reported by the Naval Facilities Engineering Service Center (NFESC), Port Hueneme, California. The data are reported by activity and generating process. An example of a summary report is presented in Appendix A. Based on the criteria presented above, the following were included as processes that generate wastes treatable by SCWO: chemical paint stripping, expired shelf life items, fluid changeout, industrial maintenance, industrial operations, painting operations, solvent degreasing, ship's offloaded wastes, torpedo cleaning, spill cleanup, and certain medical wastes. Excluded are battery shops (acids), bilge and tank cleaning and derusting (nitrite and citric acid solutions), electroplating (acids and metal bearing solutions), electronics and refrigeration, firefighting operations, ordnance, and ships boiler cleaning. A certain proportion of "one time only" wastes may also be treatable by SCWO. For example, polychlorinated byphenyls (PCBs) are "one time only" wastes generated by electrical transformer changeout. PCBs are readily destroyed by the SCWO process.

A bar graph showing the total amount of hazardous waste disposed by the Navy and the cost of disposal for a recent 3-year period is presented in Figure 5. The estimated total amount of organic hazardous waste generated in 1991 that could be disposed of by SCWO is 9,200 tons. The comparable numbers for calendar years 1990 and 1989 are 10,100 tons and 11,000 tons.

Figure 6 is a breakdown by waste source for the nominal 9,200 tons of SCWO treatable hazardous waste disposed of by the Navy in CY91.

In 1991, the average cost for disposal of liquid organic hazardous wastes at the San Diego, California Naval Complex was $22 per gallon. The comparable cost for Norfolk, Virginia was $17 per gallon. During the same period, the average cost for disposal of liquid hazardous wastes at Pearl Harbor, Hawaii was about $35 per gallon. It is anticipated that these costs will rise. Some specific contract disposal costs for Naval Base Norfolk are presented in Table 1 (Ref 1).

Table 1
Organic Hazardous Waste Disposal Costs for Norfolk Naval Base (CY91)

Waste	$/lb	lb/gal	$/gal
Paint	4.15	10	41.50
Paint Stripping	2.58	8	20.64
Solvent Degreasing	1.81	8	14.48
Pesticides	4.25	8	34.00
POL (clean)	1.89	8	15.12
POL (contaminated)	2.13	8	17.02

The data collected by NFESC can also be tabulated by the generating Navy activity or by the cognizant Engineering Field Division (EFD) (Figure 7).

An estimate of the approximate SCWO plant capacity that is appropriate for Navy shoreside implementation can be obtained from the data presented in Figure 7. It is assumed that in future years the Navy will reduce the amount of organic hazardous waste generated from about 9,200 tons to about 4,500 tons per year. This will be accomplished through the general reduction in industrial activity resulting from force restructuring and downsizing now underway,

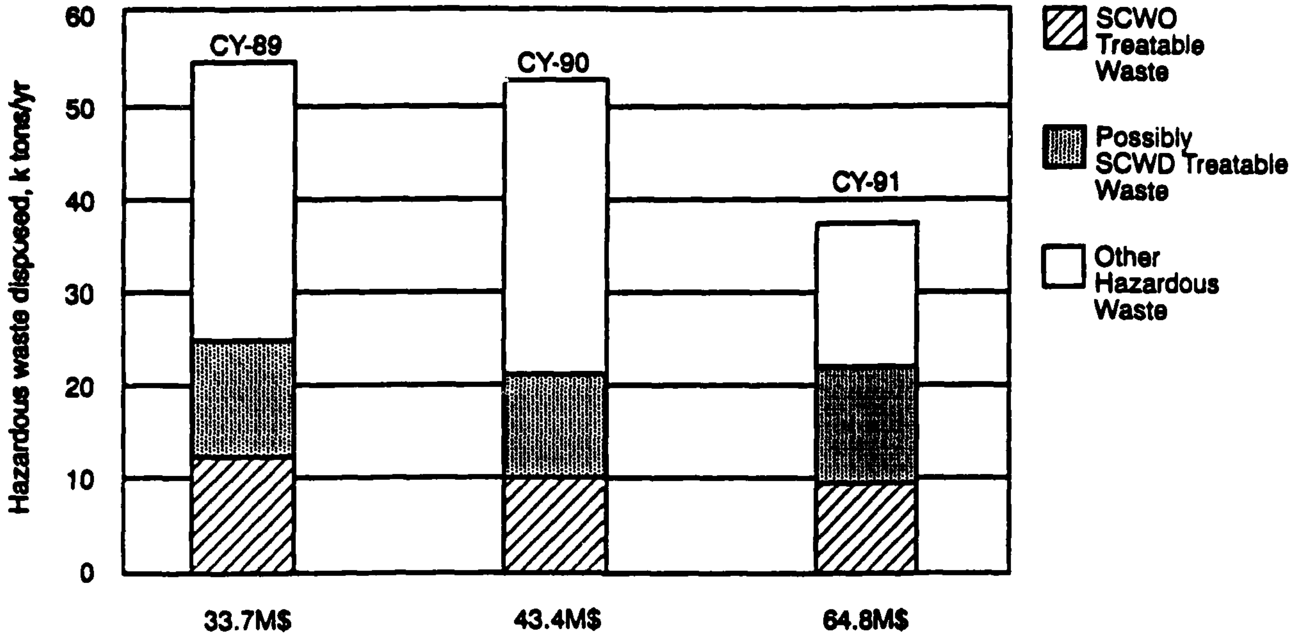


Figure 5
Total hazardous waste disposal cost.

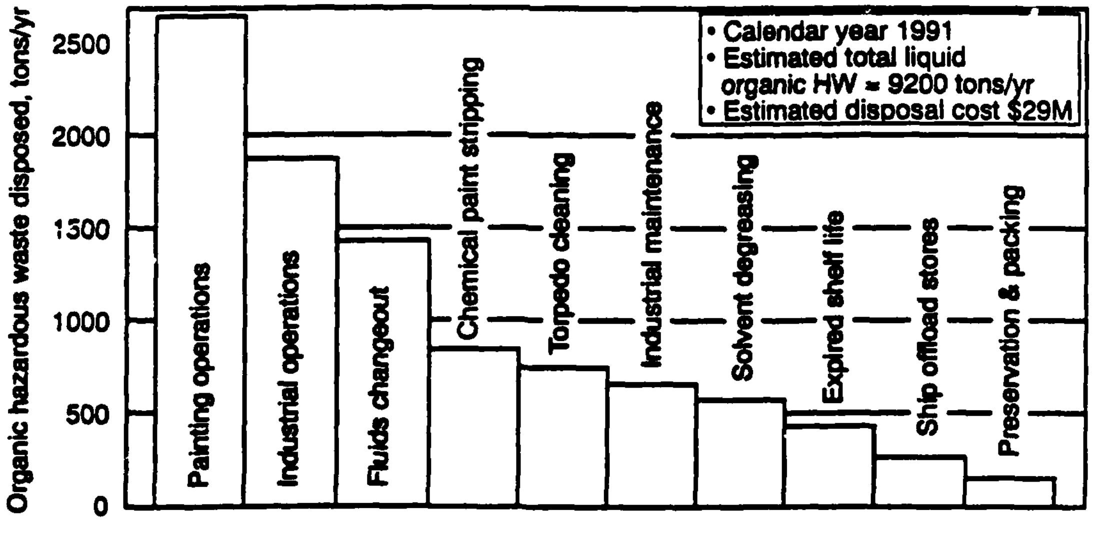


Figure 6
Composition of organic waste stream.

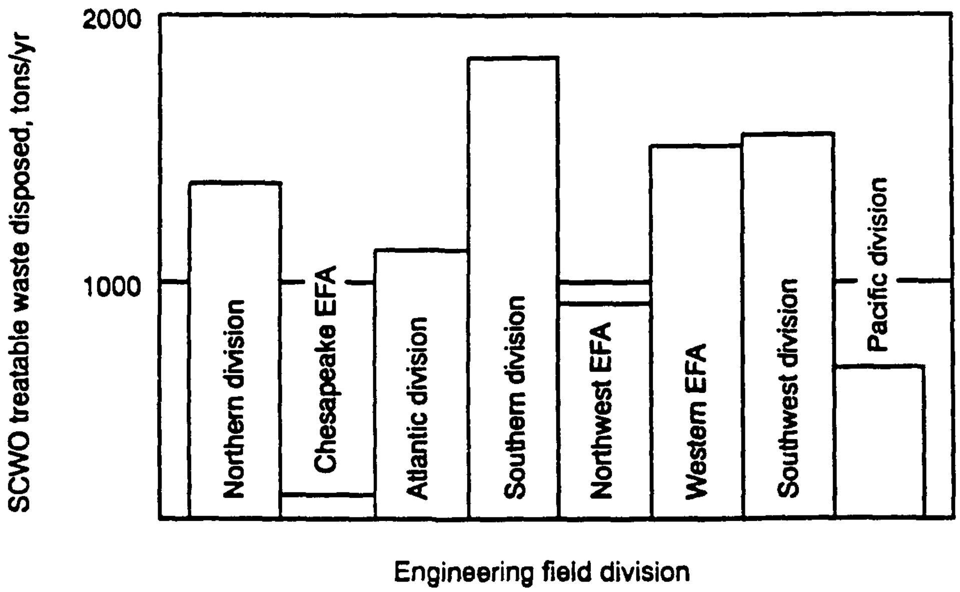


Figure 7
Waste generation by geographic region.

increased substitution of nonhazardous materials for hazardous organic materials, improved recycling and reuse of hazardous materials, and development of better markets for some hazardous wastes. Also, it was assumed that an SCWO plant would operate about 4,300 hours a year, or about 50 percent of the time. If the wastes generated within each EFD are reduced to about half their 1991 levels, and that annual generation rate is divided by 4,300 operating hours per year, an approximate value for the hourly mass flow through an SCWO process is obtained. If an average specific gravity of 0.90 is assumed for the wastes, the flow of organic material in gallons per minute is obtained. These results are tabulated in Table 2. Table 2 shows that an SCWO waste processing plant having the capacity to treat about 1 gallon of hazardous material per minute (or 250,000 gallons per year) is an approximate upper limit on the size of an SCWO plant suitable for Navy use. A total of about seven plants would be required. One plant would be located in the geographic region of each of the generating Engineering Field Divisions or Engineering Field Activities. About eleven SCWO plants of 0.5-gallon per minute capacity could also meet the project waste disposal requirement and provide added operational flexibility.

If the goal of a 50 percent reduction in the amount of organic hazardous waste disposed has not been met by the time SCWO technology is mature, more SCWO plants would be needed, the capacity of each SCWO plant would have to be increased, or the SCWO plants would have to be run more hours (or a combination of these factors) to meet the demand for waste treatment. Note that the plant capacity numbers quoted above are for gallons per minute of hazardous material flowing into the SCWO unit. The total amount of waste and supercritical water flowing through an SCWO unit is significantly larger, anywhere from 10 to 20 times the hazardous waste flow.

Table 2
Estimate of Required SCWO Capacity

Location	Waste (tons/yr)		Waste Flow (gal/min)	Number of Plants at -	
	1991	2000		1.0 Gal/Min Capacity	0.5 Gal/Min Capacity
Chesapeake EFA	109	50	0.05	0	0
Northwest EFA	844	400	0.43	1	1
Atlantic Div	1130	600	0.65	1	1
Northern Div	1437	700	0.75	1	2
Pacific Div	601	300	0.32	1	1
Southern Div	1842	850	0.92	1	2
Southwest Div	1682	850	0.92	1	2
Western EFA	1597	750	0.81	1	2
Total	9200	4500		7	11

ECONOMIC ANALYSIS

To estimate the economic performance of SCWO, two basic pieces of information are required: the cost of building and operating an SCWO plant, and the current cost for disposal of organic hazardous wastes.

Estimated Cost of an SCWO Waste Treatment Plant

A waste stream capacity and composition must be chosen to develop an SCWO plant design.

The amount of waste to be treated by each SCWO plant was chosen to be 250,000 gallons per year waste flow (approximately 1 gallon per minute waste flow).

For preliminary system design purposes, the hazardous organic waste was assumed to be composed of a mixture of waste fuel oil and a chlorinated solvent. The fuel was assumed to be a heavy normal alkane, $C_{13}H_{28}$, and the solvent was assumed to be 1,1,1-trichloroethane, CH_3CCl_3, (or 1,1,1-TCA). The assumed waste stream was 90 percent oil, and 10 percent TCA by weight. These two waste components encompass the two essential features of Navy industrial organic wastes that influence SCWO process design: high heat content and corrosivity. The Navy generates a large quantity of high heating value fluids such as lubricating and hydraulic oils and fuels. The Navy also uses significant amounts of chlorinated compounds such as those found in industrial cleaners, solvents, and paint stripping compounds (although the use of chlorinated compounds is expected to be greatly reduced in the coming years). The calculated lower heating value of this mixture is about 14,700 Btu per pound. The high hydrocarbon content of this waste stream defines both the upper limit on the oxygen requirement for the SCWO system and the maximum waste throughput rate.

"The autoignition temperature of an air-fuel mixture is the lowest temperature at which chemical reaction proceeds at a rate sufficient to result eventually in inflammation. This temperature depends principally on air-fuel mixture, mixture pressure, and the test apparatus" (Ref 1). Data on the autoignition temperature of kerosene are presented in Table 3 (data from Ref 2).

Table 3
Ignition Temperatures of Kerosene

Air Pressure (psi)	Temperature (°F)
75	670
150	490
225	430
300	400
375	385

These data indicate that at the conditions at the inlet to the SCWO reactor vessel (about 3,600 psi and 710°F), diesel fuel should spontaneously ignite. This assumes that the transport medium (dense water vapor) in SCWO has the same influence on reaction kinetics as does the transport medium (nitrogen gas) in a fuel-air mixture.

When organic material is oxidized, chemical energy is converted to heat energy. The heat that is released by oxidation of hydrocarbons raises the temperature of the reactants, products of reaction, and the transport medium. The greater the concentration of organic material, the higher the final temperature that is produced. The amount of organic material that the waste stream can contain has approximate upper limits determined by the maximum allowable temperature the SCWO unit design permits. The maximum allowable temperature is about 1,200°F, based on consideration of the strength of materials from which the reactor is constructed. Even without the materials limitations, it is desirable to keep the reaction temperature low to minimize the formation of oxides of nitrogen and sulfur. The maximum amount of hydrocarbon in the SCWO influent varies from about 15 percent for low heat content wastes such as TCA, down to about 4 percent for high heat content wastes such as used motor oil.

The fundamental SCWO process was described earlier and illustrated in Figure 4. There are several inherent problems with this simplistic design. First, the energy consumption is very high. An SCWO plant based on this design would require a minimum of 5 MW of input heat for every gallon per minute of organic material processed (assuming 3 percent organics in water) (Figure 8). Also, any salts that precipitate out of the influent stream when the critical temperature is reached, or metal oxides that form during the oxidation process, will form deposits on the internal surfaces or accumulate in crevices and low points of the apparatus.

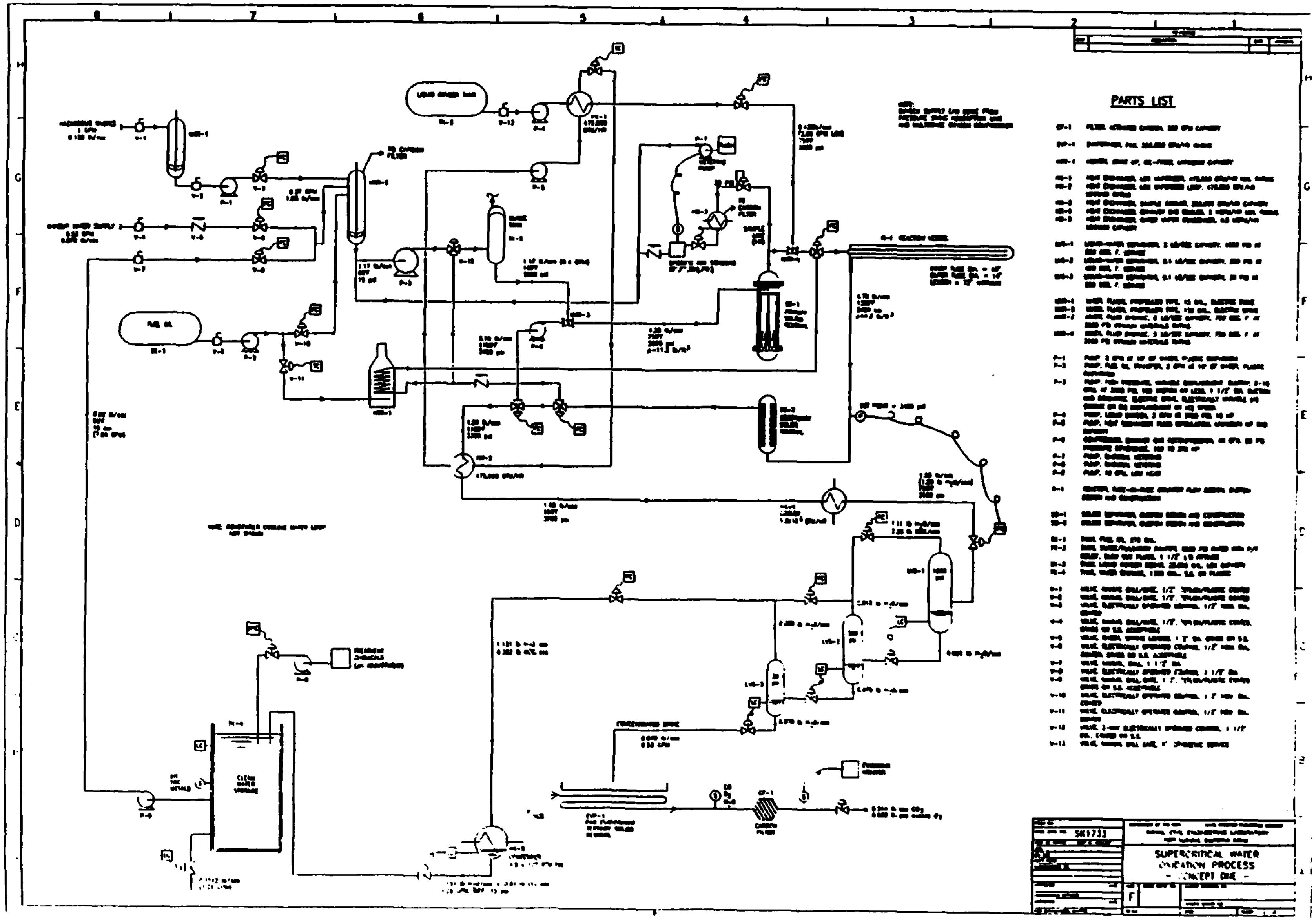


Figure 8
Process diagram for full-scale SCWO plant.

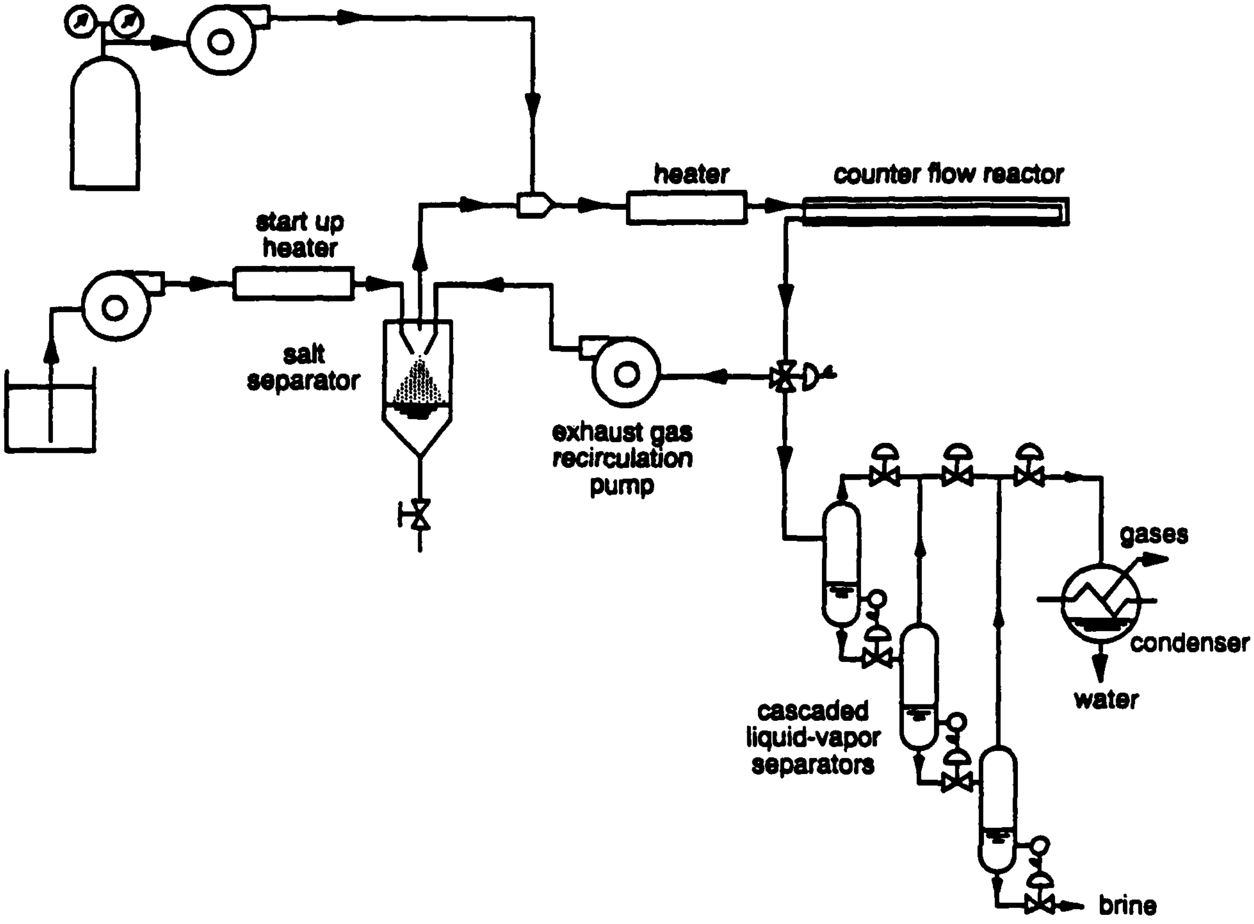


Figure 9
Improved SCWO process.

Control of the system is difficult because of the two-phase flow through the back pressure regulating valve (valve F). The effluent from the system is supercritical steam, noncondensible gases, and particulate matter.

Figure 9 illustrates an improved design. In this design, cold water and organic matter are very rapidly heated to a temperature close to the critical temperature (say 675°F) by directly mixing the cold liquids with a portion of the hot (1,200°F) reactor exhaust gases. This heating takes place in a pressure vessel that functions as a salt separator. When the temperature of the liquid influent approaches the critical temperature, a large fraction of the dissolved salts precipitate out of solution and can be collected in the salt separator. This keeps most of the salts, and perhaps some of the metal oxides, from accumulating in downstream components. A counterflow tube-in-tube reactor recovers additional thermal energy from the hot exhaust gases and transfers it to the influent stream. That portion of the reactor exhaust gas not used for influent preheating is reduced in pressure and temperature (P-T) by means of a sequence of expansion devices and liquid-vapor separators called a cascaded P-T letdown system. This arrangement produces three effluent streams: noncondensible gases, water, and a brine solution. Analyses indicate that the effluent stream for the oil-TCA waste (described above) is 74.5 percent water, 22.4 percent carbon dioxide, 2.5 percent oxygen, and 0.6 percent chlorine. Most of the chlorine combines with the liquid water to form hydrochloric acid. The acid is neutralized by adding an alkali, such as calcium hydroxide, before the water is discharged from the system.

A detailed schematic of a full-scale (1 gallon per minute (gpm) of organic material) SCWO plant was developed by NFESC. The plant schematic is shown in Figure 6 and a description of the sequence of operation of the plant is presented in Appendix B. The process is depicted in pressure-energy coordinates in Figure 10. The equilibrium chemical composition, heat and mass balances, flow rates, heat losses, power requirements, materials consumption rates, pipe and pressure vessel sizing, and other plant parameters for this design were calculated by NFESC. This information was then provided to an engineering firm in a contract statement of work to develop estimates of the capital and operating costs for the full-scale SCWO plant design. The results are reported in Reference 3. Summaries of the estimated capital and operating costs are presented in Tables 4 and 5.

In summary, the estimated cost of a 1-gpm SCWO plant is $5.9M. The estimated annual operating cost is $1.17M. The capital and operating costs for a 0.5-gpm capacity SCWO plant would be somewhat lower.

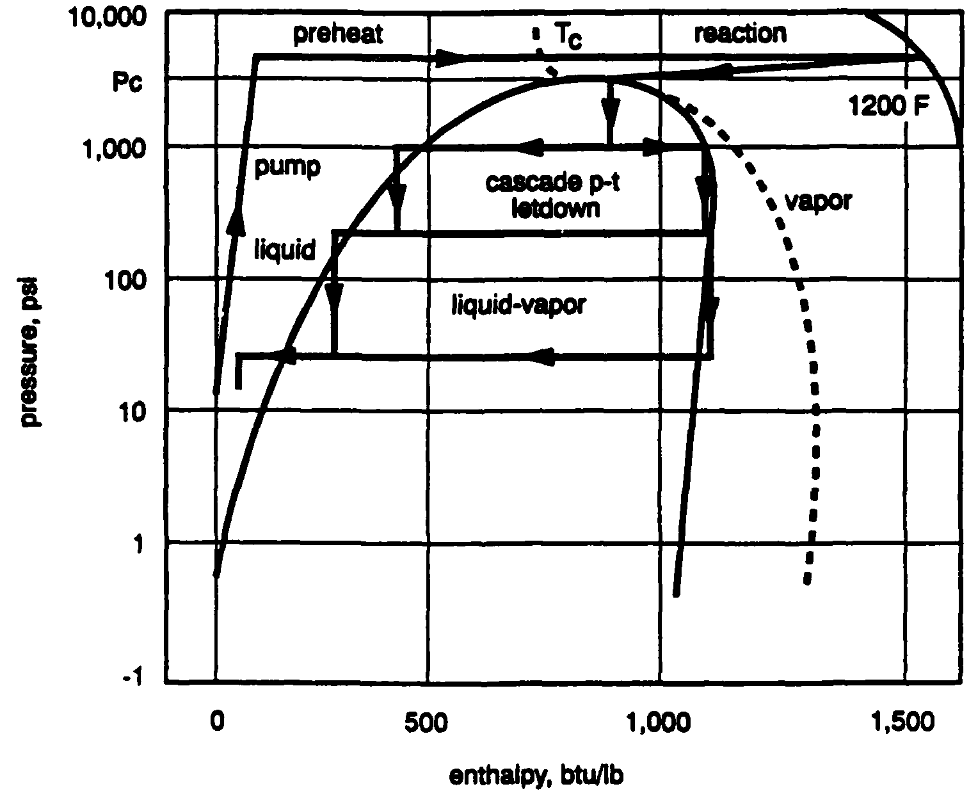


Figure 10
SCWO process in pressure-enthalpy coordinates.

Table 4
Supercritical Water Oxidation System Capital Investment Summary

Basis: 830 tons/yr of liquid organic wastes processed

Subsystem	1992 Capital Investment ($)
Hazardous Waste Preparation and Pressurization	540,000
Startup Heater and Heat Recovery	614,000
Fuel Oil Feed	9,000
Liquid Oxygen Feed	645,500
Solids Separation	652,000
Reactor	387,000
Effluent Sampling and pH Adjustment	108,000
Liquid-Vapor Separation	478,000
Offgas Monitoring and Treatment	432,500
Water Collection and Recycle	8,500
Instrumentation and Controls	70,000
Cooling Tower	121,000
Total Installed Equipment	4,065,000
Plant Building	687,000
Offices and Laboratories	25,000
Office and Laboratory Equipment	20,000
Plant Subtotal	4,797,000
Additional Engineering Fee (3 percent)	144,000
Additional Contingency Fee (20 percent)	960,000
Total Capital Investment	5,900,000

Table 5
Supercritical Water Oxidation System Operating Cost Summary

Basis: 4,000 hrs/yr operation

Description	1992 Annual Cost ($) (CO/CO)[a]	1992 Annual Cost ($) (GO/CO)[b]
Variable Costs		
Utilities (Fuel, Electricity, Water)	79,300	79,300
Chemicals and Other Materials (O_2, NaOH)	346,000	346,000
Total Labor	231,920	231,920
Off-site Disposal	92,800	92,800
Subtotal	750,020	750,020
Fixed Costs		
Plant Overhead (105 percent of Labor)	243,520	243,520
Maintenance (3 percent of Capital Investment)	177,000	177,000
Depreciation (10 percent of Capital Investment)	590,000	0
Taxes and Insurance (2% of Capital Investment)	118,000	0
Subtotal	1,128,520	420,520
Total Operating Costs	1,879,000	1,171,000

[a] CO/CO = Contractor Owned/Contractor Operated
[b] GO/CO = Government Owned/Contractor Operated

Estimated Disposal Cost

Figure 11 shows the resulting estimated disposal cost in dollars per gallon of organic material. The ordinate is the annualized capital cost plus the annual operating cost divided by the amount of organic material destroyed annually (250,000 gallons). The abscissa is the plant life. Figure 11 shows that the per gallon disposal cost is generally lower than disposal costs the Navy currently pays. Note that the unit disposal cost approaches the annual operating cost divided by the amount of material treated. Thus, there are significant economic advantages to minimizing the operating cost (e.g., by minimizing utilities and labor costs) and maximizing the amount of hazardous material treated (e.g., by designing the SCWO plant for maximum unit reliability and maintainability).

Another way of looking at economic performance is presented in Figure 12. Figure 12 shows the payback period for an SCWO plant as a function of current hazardous waste disposal cost. For example, if a Navy activity currently pays $20/gallon to dispose of hazardous waste, an investment of $5.9M in an SCWO plant will pay for itself in less than 2 years. Figure 13 shows that even if the estimate of capital cost turns out to be in error by 100 percent and the actual capital cost is about $12M, the unit disposal cost is $16/gallon (which is still less than the waste disposal cost currently paid).

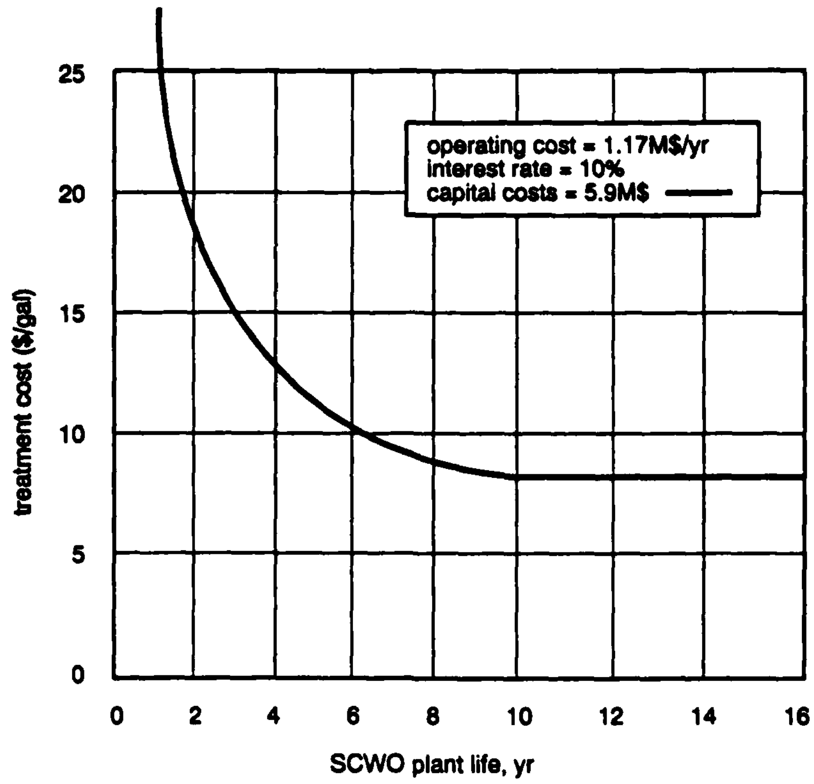


Figure 11
Unit treatment cost.

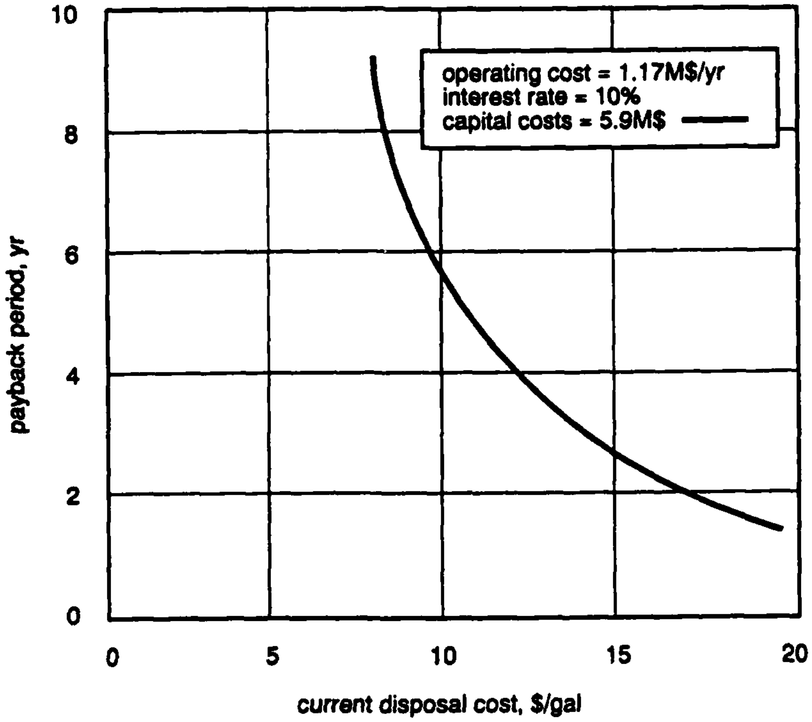


Figure 12
Payback period.

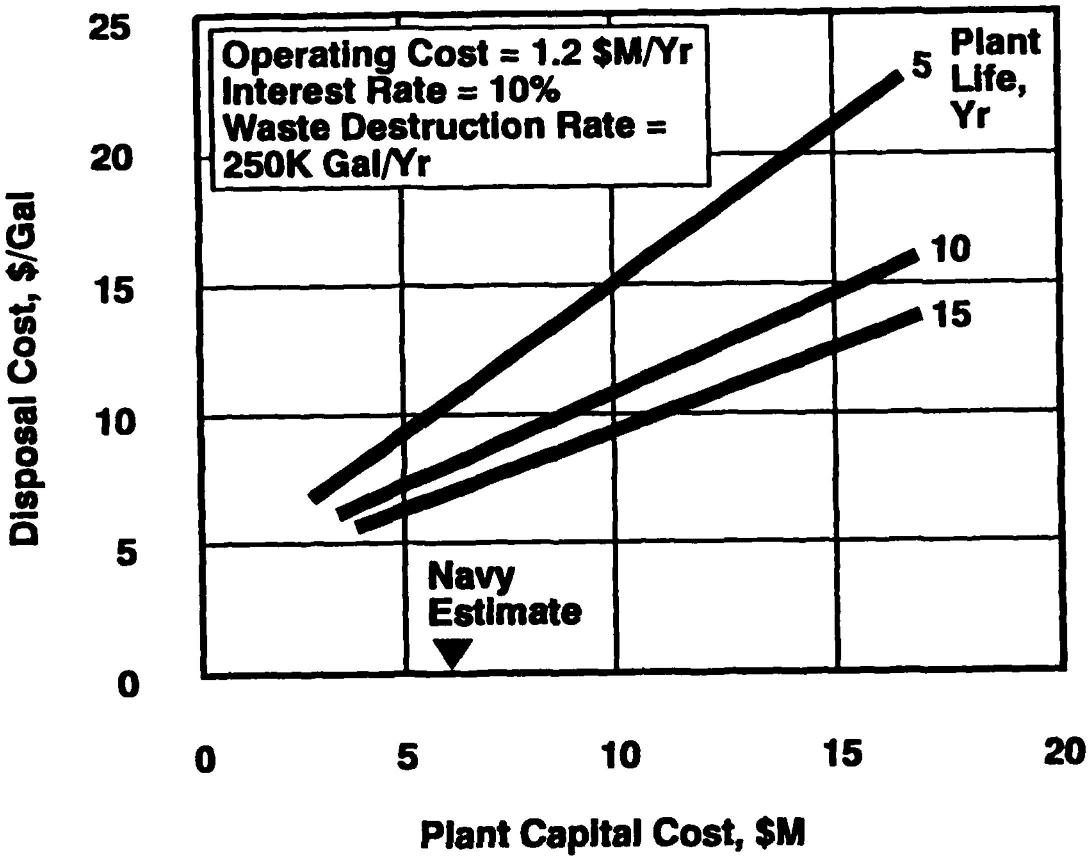


Figure 13
Summary of economic study.

EXPERIMENTAL PROGRAM

Destruction Efficiency Tests

The NFESC contracted with the Combustion Research Facility of Sandia National Laboratory (CRF/SNL) to perform tests on the destruction of organic chemicals found in Navy industrial wastes. The goals of the work were to: (1) confirm that the organic compounds found in typical industrial hazardous waste are readily destroyed by supercritical water oxidation, and (2) provide data on the required reactor temperature and residence time for use in engineering design of a bench scale reactor. The compounds tested by CRF/SNL included paint, chlorinated solvents, petroleum products, alcohols, glycols, organic acids, and pesticides. The tests were conducted using a 0.5-gal/hr capacity SCWO reactor. The CRF/SNL SCWO apparatus is designed to produce isothermal conditions in the reactor vessel. Isothermal operation allows the activation energy, frequency factor, and other properties of the oxidation reaction to be estimated. A summary of the experimental results is presented in Figure 14; experimental results for most of the compounds are presented in Appendix C. The complete results of the CRF/SNL work are presented in Reference 4.

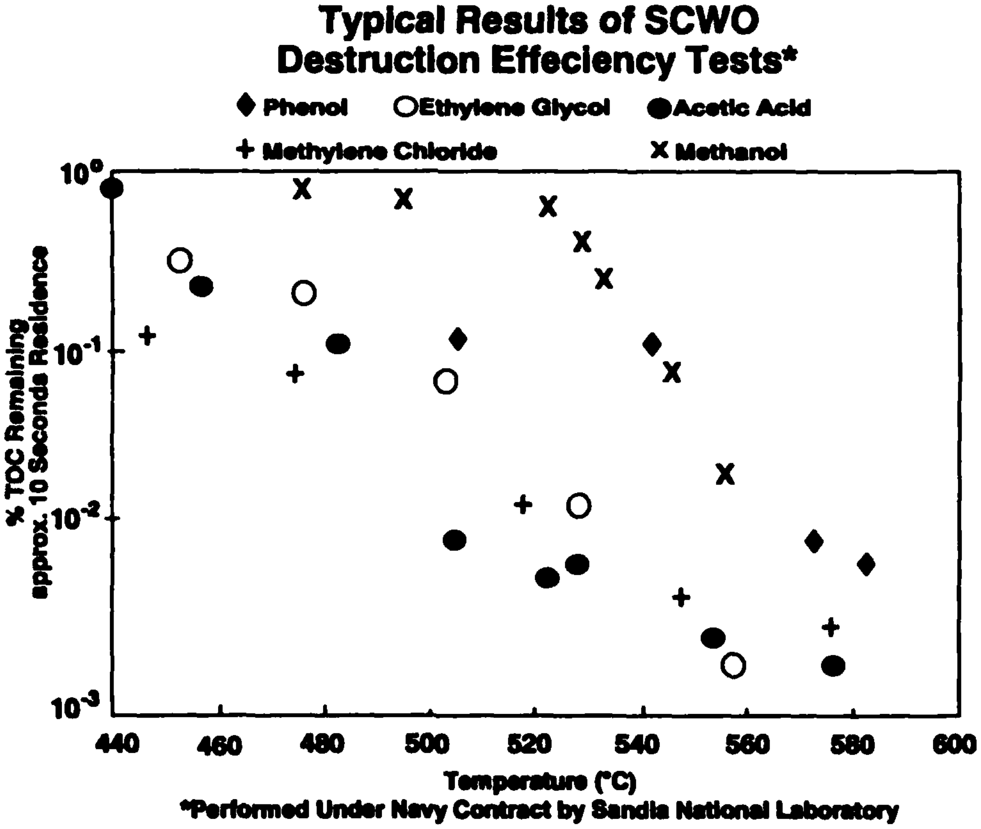


Figure 14
Summary of waste destruction test results.

Quoting reference 4: "The destruction efficiency results show that high destruction of nearly all organic materials can be obtained with residence times well under 30 seconds if temperatures are maintained in excess of 550°C [1,022°F]. In the range of 500-550°C [932-1,022°F] many materials can be destroyed very effectively. However, some of the more robust simple molecules will require residence times of over 30 seconds to obtain destruction efficiencies of 99.99 percent. Operation much below 500°C [932°F] would require residence times of several minutes for many organic solvents." Square brackets, [ ], denote author's comments.

"An important exception to these general observations is the effectiveness with which the chlorinated organics TCA [1,1,1-trichloroethane] and methylene chloride can be removed. Although the TOC [total organic carbon analysis] results are not valid [for these two compounds], the gas chromatography results show that these materials are very rapidly removed. They may not be oxidized completely, but the original primary pollutant is destroyed. This may be due to the rapid hydrolysis reactions that can occur at much lower temperatures. In this class of reactions TCA is most likely converted to acetic acid, and methylene chloride is converted primarily to formaldehyde. These reactions can occur in SCW [supercritical water] in the absence of any oxidizer such that the effective reaction time during which these materials are being destroyed includes not only the well defined oxidation stage, but the poorer defined 'heat-up' time period."

"An important aspect of the overall development and implementation of SCWO as a waste treatment method centers on the reliability and surety of the process. Reliability in effectively destroying wastes is important, but equally important is the reliability and longevity of the processing equipment itself. The greatest concern is associated with corrosion of the high temperature sections of reactor itself. As a simple extension of these destruction efficiency studies, the corrosive nature of these different feeds has been examined. For each of the chemical feeds one of the highest temperature samples was analyzed for nickel and chromium, the two main components of Inconel 625." The results are presented in Table 6.

Table 6
Corrosion Results

Material	Nickel (ppm)	Chromium (ppm)
Methanol-a	n.d.*	0.03
Methanol-b	n.d.	0.07
Phenol	n.d.	n.d.
Ethylene glycol	n.d.	n.d.
Methyl ethyl ketone	n.d.	1.01
Acetic acid	n.d.	3.01
Methylene chloride	30.7	0.02
1,1,1 trichloroethane	49.0	0.55
Latex paint	n.d.	0.09
Herbicide (Roundup)	n.d.	0.12
Motor oil	n.d.	n.d.

*n.d. = nondetectible

"The preliminary observation that can be made from the simple list in Table 6 is that most organic molecules that do not contain chlorine exhibit little or no corrosion. The chlorinated species, however, show very significant attack on the reactor.

Note that all the corrosion observed is metal selective. Neither the mild corrosion in the feeds that remove chromium nor the severe corrosion induced by the chlorinated feeds produces an effluent with a chromium to nickel ratio of 0.33: the ratio of the two metals in Inconel 625 alloy. This shows that there are at least two different types of corrosion mechanism that can be present in these systems. Probably other mechanisms exist if other heteroatoms such as sulfur are present."

Chlorine Removal Studies

Molecules of chlorinated compounds such as 1,1,1-trichloroethane and methylene chloride are raised to a high internal energy state when they are brought up to the critical point of water.

The question arises: at this elevated energy state, are the bonds of the chlorine atoms weakened to an extent that the chlorine atoms can be preferentially removed from the rest of the molecule and be sequestered as a salt? Preferably, could this be accomplished before the chlorinated molecule enters the SCWO reactor and produces hydrochloric acid as a product of oxidation? The Chemical Science and Technology Laboratory of the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland was funded to investigate this question. The Process Measurements Division of NIST operates a small, specially instrumented SCWO apparatus well suited to investigate this question. The NIST SCWO apparatus has a reactor vessel equipped with sapphire windows through which the flow can be studied using optical methods. One of the flow diagnostic methods used by NIST is Raman spectroscopy. The method of Raman spectroscopy passes a powerful laser light through the fluid at a right angle to the direction of flow. The intensity and wavelength of the laser light scattered by the molecules of fluid is then analyzed to determine properties of the fluid, such as chemical composition. Raman spectra at ambient and elevated temperatures for TCA and methylene chloride are presented in Figures 15 and 16. The two figures show Raman spectra obtained at: (a) room temperature, and (b) at 200°C for TCA and 300°C for methylene chloride. In both cases, the compound clearly disappears at temperatures approaching the critical temperature of water. TCA forms one mole of hydrochloric acid (HCl) and one mole of 1,1-dichloroethylene. Dichloroethylene has a double carbon bond, but may decompose further at higher temperatures. The decomposition of methylene chloride varied from 90 percent in early experiments to 60 percent in later experiments. The amount of methylene chloride destroyed varied because of interactions with the surface of the reactor vessel. Initial tests indicated a 90 percent conversion to HCl, which attacked the walls of the reactor producing an effluent containing nickel and chromium salts. Subsequent experiments showed a lower formation (60 percent) of HCl, indicating the reactor walls had been passivated to some extent. These results indicate that it may be feasible to hydrolyse many common chlorinated compounds under near critical conditions and then remove the chlorine from solution as a salt by adding a base, such as sodium hydroxide, to the hydrolyzed waste. Removal of chlorine from the input waste stream would greatly reduce corrosion in SCWO components.

Additional studies were performed at the Department of Chemistry, University of California at Santa Barbara, California, on the Raman spectroscopic signatures of eight typical components of organic wastes. The purpose of the studies was to determine if the analytical technique of Raman spectroscopy could be used for real time analysis of the chemical composition of the effluent of an SCWO system. The results showed that while some pure compounds, such as TCA, produced strong spectra that were in agreement with published data, most of the samples of waste produced moderate to strong background fluorescence so that the Raman signal was partially or totally obscured. It is believed that this problem can be avoided by changing the frequency and power level of the excitation laser or using gated detection techniques.

Computer-Aided Design Results

Several computer codes were written at NFESC to aid in the design of the SCWO unit. One program was written to help in selecting the type and size of the startup heater. Another program was written to aid in selecting among alternatives for insulating the reactor tubes.

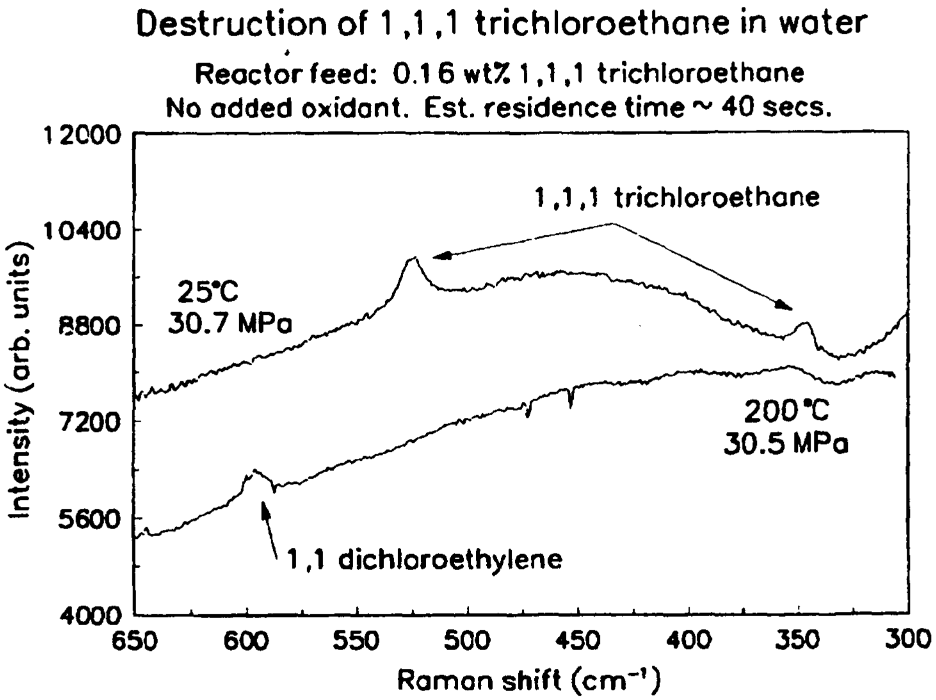


Figure 15
Destruction of 1,1,1 trichloroethane in water.

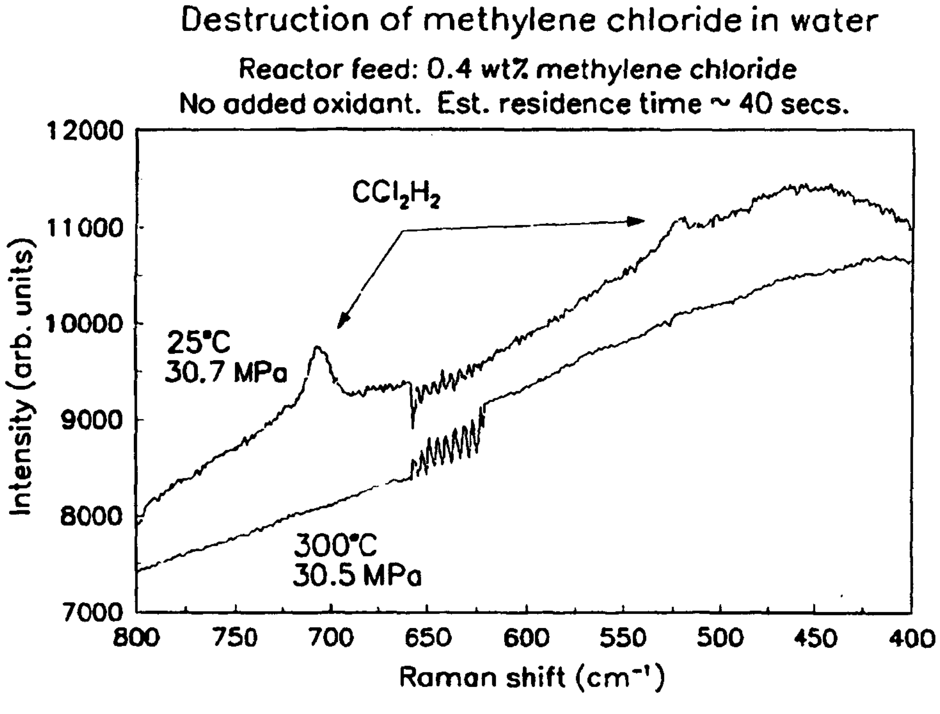


Figure 16
Destruction of methylene chloride in water.

A third program modeled the chemical kinetics of oxidation reactions in supercritical water. This program was used to estimate the length of reactor tube required for the fuel fraction of the waste stream to oxidize and heat the water and waste to operating temperature. Results of the simulated oxidation of diesel fuel in supercritical water are presented in Figures 17 and 18. These results are for an adiabatic process, that is to say, none of the heat released by the chemical reactions is lost to the walls of the reactor vessel. Figure 18 presents only the temperature and concentration on linear scales to emphasize the changes in magnitudes. Note that the oxidation of diesel fuel requires only a short time to get started and is completed over a distance of a few inches of reactor length.

Figures 19, 20, and 21 present data for a more refractory compound: methanol. As Figure 19 illustrates, oxidation of methanol is negligible when methanol is added to supercritical water and oxygen at 750°F. The temperature is too low for the methanol oxidation reactions to occur at a significant rate. Figures 20 and 21 illustrate the oxidation of methanol when the initial temperature is 1,000°F. At 1,000°F initial temperature, the methanol is slowly and completely oxidized. The high value of activation energy and low value of heat content for methanol (compared to diesel fuel) results in a gradual heat release that slowly raises the temperature over a distance of approximately 16 feet.

To destroy methanol in a practical SCWO system, diesel fuel (or similar high heat content, readily oxidized hydrocarbon) would be mixed with the methanol. The diesel fuel would quickly oxidize, raising the temperature of the water, other products of oxidation, and the methanol to a temperature in excess of 1,000°F. At this temperature, the methanol will quickly and completely oxidize.

These simulation results for methanol are comparable to experimental observations made by Sandia National Laboratory of the oxidation of methanol in supercritical water.

Bench Scale SCWO Apparatus Design

A bench scale SCWO unit was designed by the NFESC and was fabricated by contract. Construction details are available in References 5 and 6. A schematic of the design is presented in Figure 22. Photographs of the unit are presented in Figures 23 through 25. The unit is designed to operate on the heat released by the oxidation of the waste stream rather than external application of heat. The design incorporates several other features that make it unique among SCWO designs. First, a device called a salt separator was incorporated into the unit to remove precipitated salts from the fluid stream before the fluid enters the SCWO reactor and other system components. Second, the reactor vessel consists of a manifolded bundle of many separate, small, reactor vessels. This design permits the reactor to be made from low cost, readily available tubing rather than custom parts. Third, the design employs an exhaust gas recirculation pump to recover part of the heat in the exhaust products and use it to preheat the influent waste stream. Heat recovery is accomplished by directly mixing hot exhaust gases with the cold water and waste streams in the salt separator. The ratio of hot exhaust gas to influent is controlled so as to produce a mixture in the salt separator that is at a temperature of about 700°F.

The bench scale apparatus is conveniently described in terms of its different subsystems.

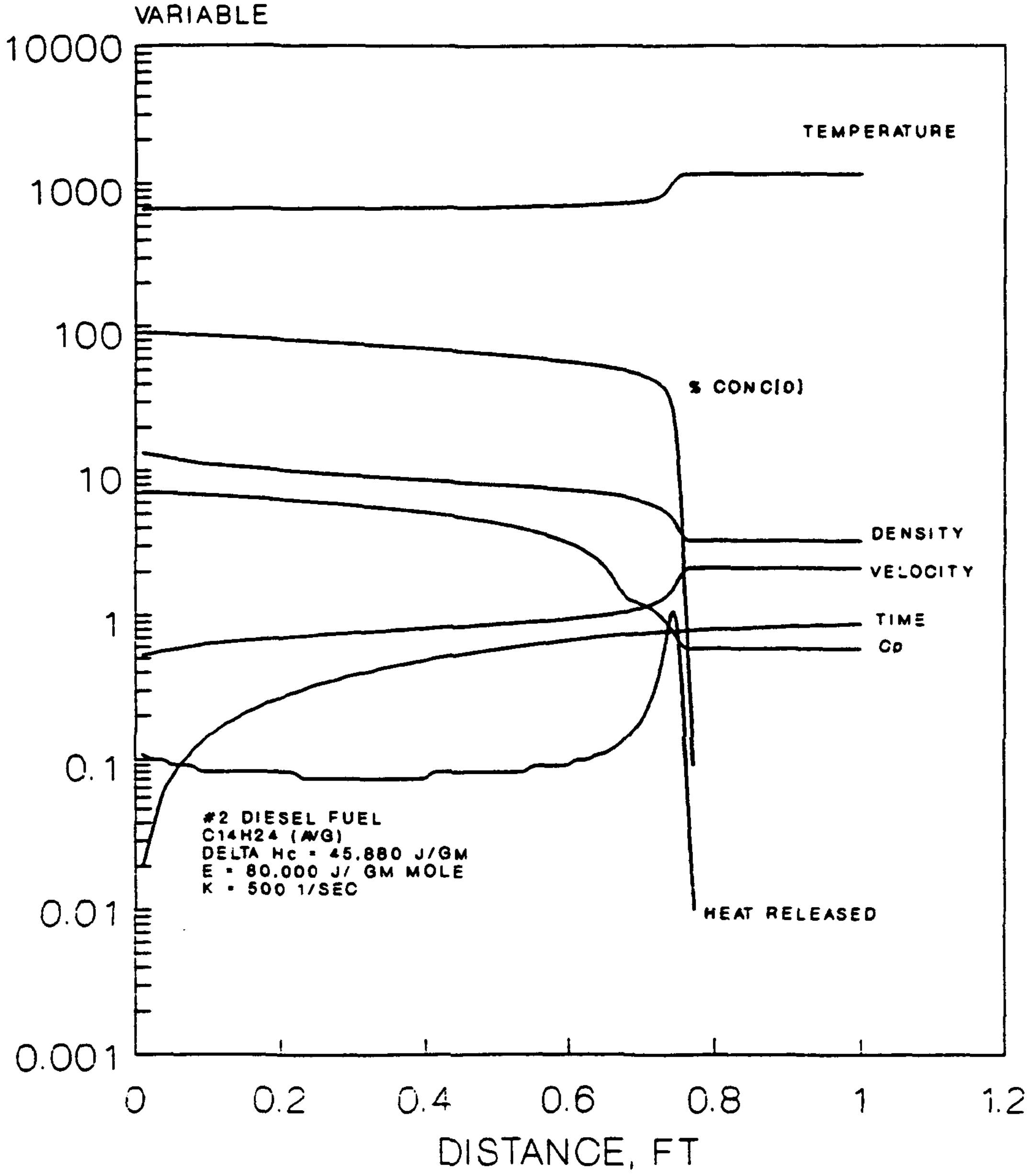


Figure 17
Simulation of oxidation of diesel fuel in supercritical water.

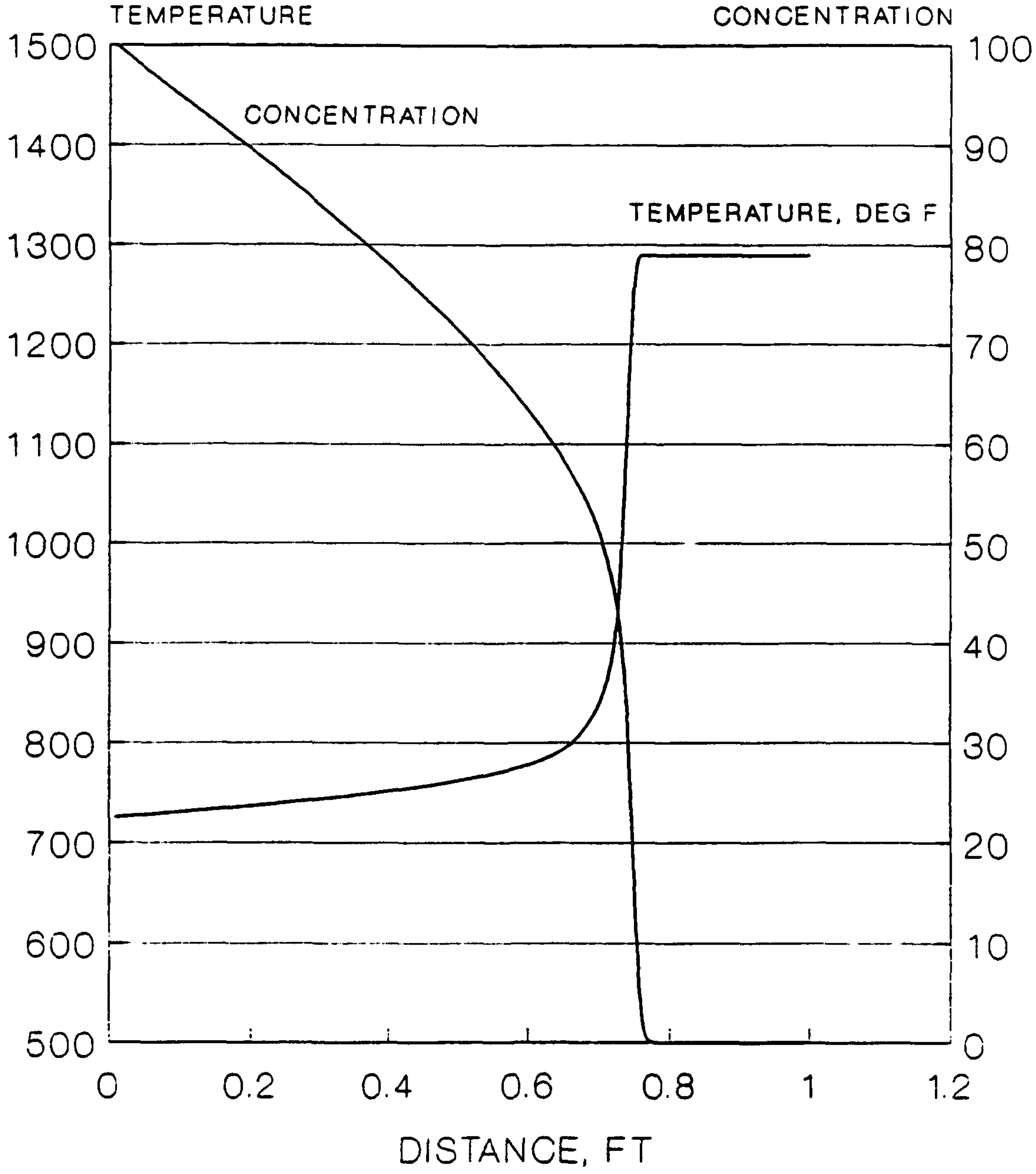


Figure 18
Simulation of oxidation of diesel fuel in supercritical water - detail.

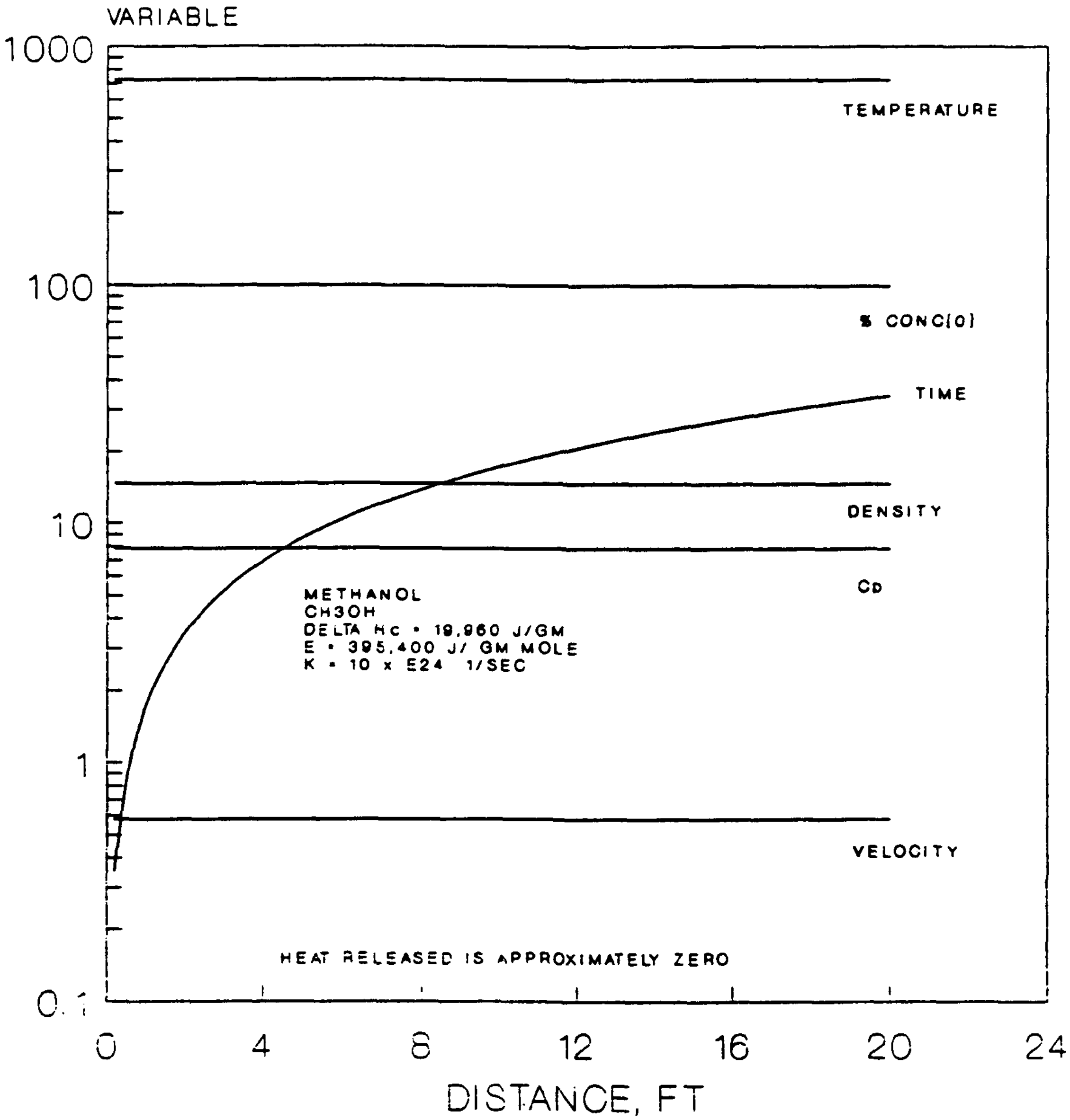


Figure 19
Simulation of oxidation of methanol in supercritical water at 750°F.

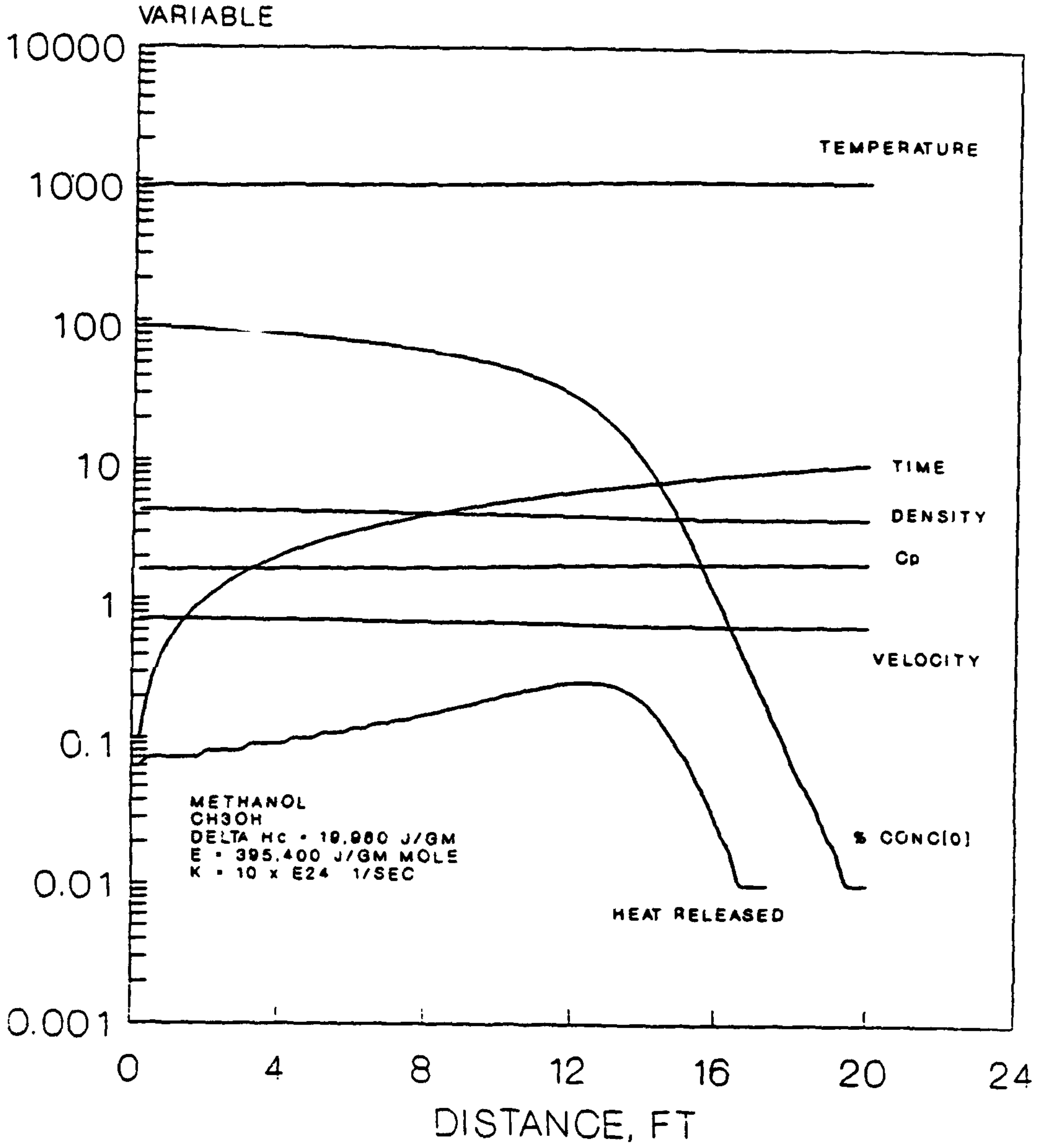


Figure 20
Simulation of oxidation of methanol in supercritical water at 1,000°F.

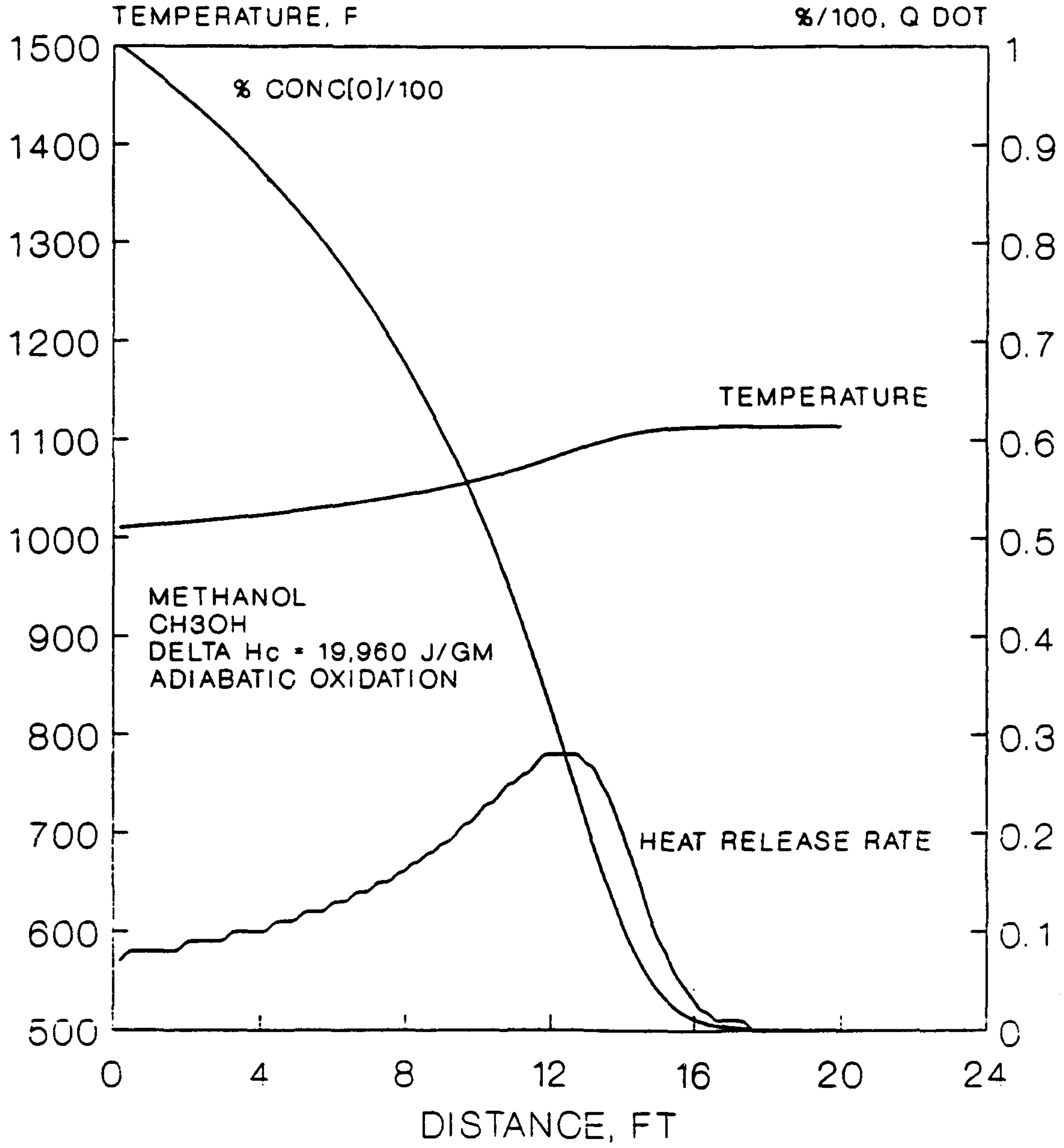


Figure 21
Simulation of oxidation of methanol in supercritical water at 1,000°F - detail.

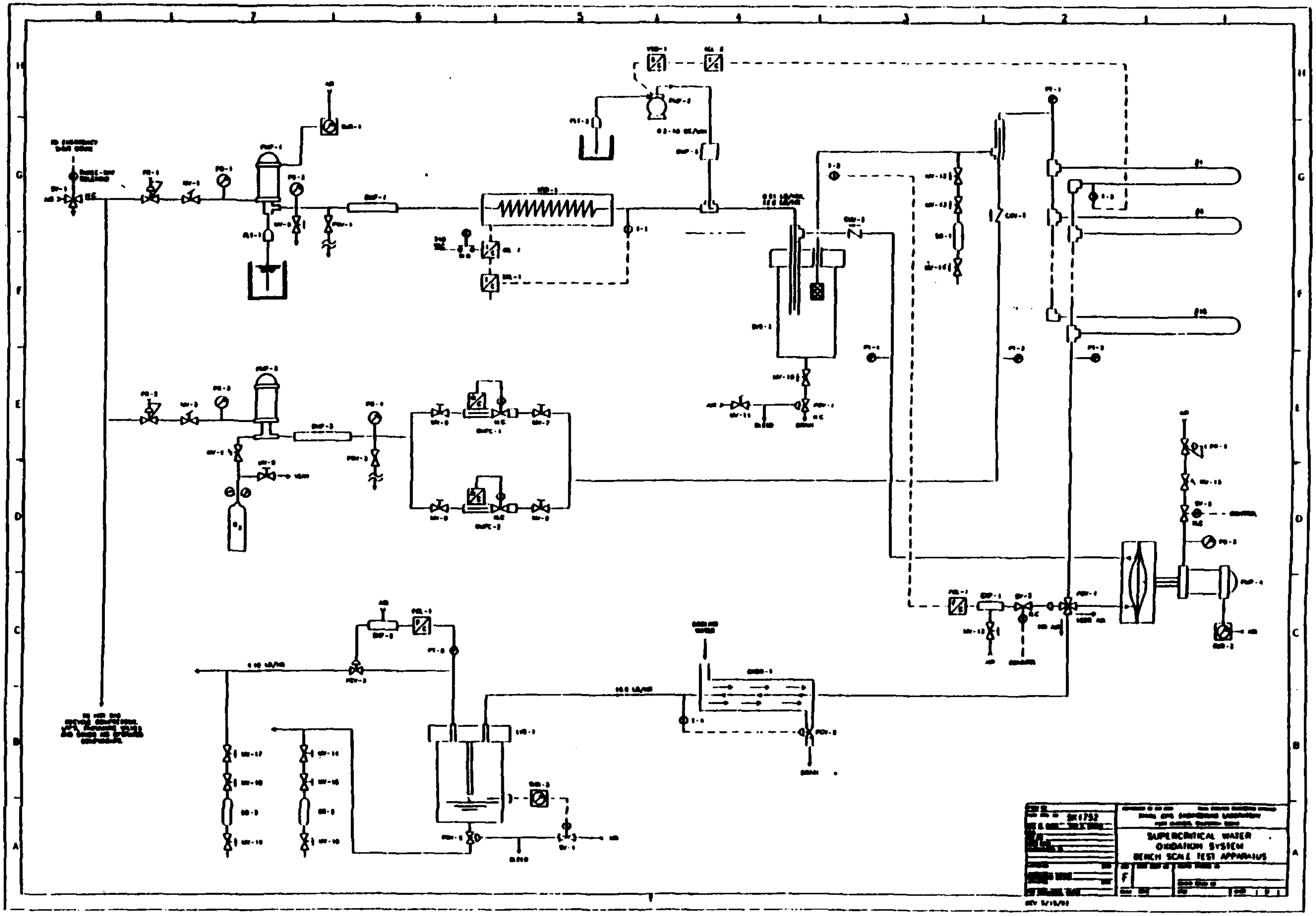


Figure 22
Schematic of NFESC SCWO apparatus.

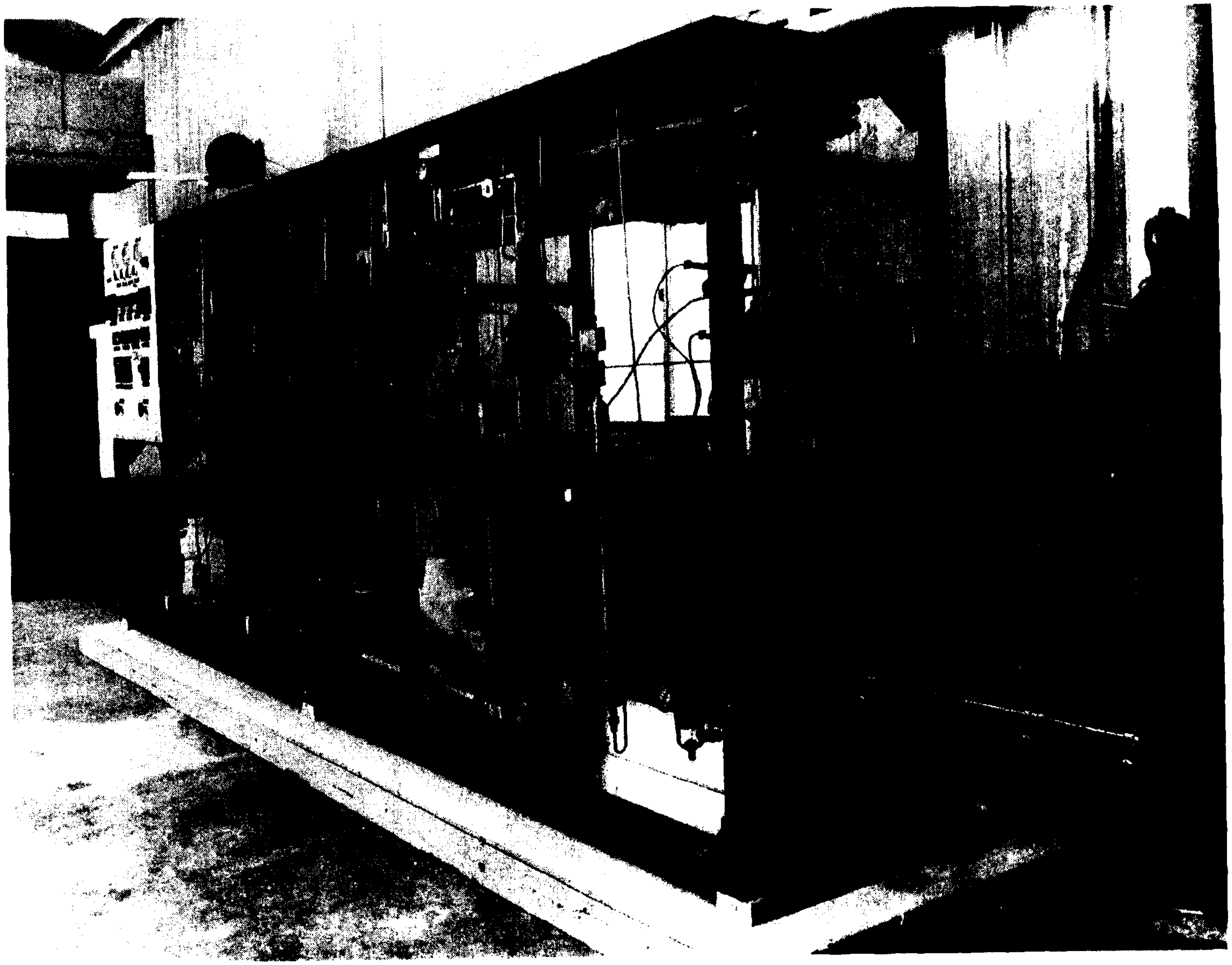


Figure 23
Photo of NFESC SCWO apparatus (view 1).

Figure 24
Photo of NFESC SCWO apparatus (view 2).

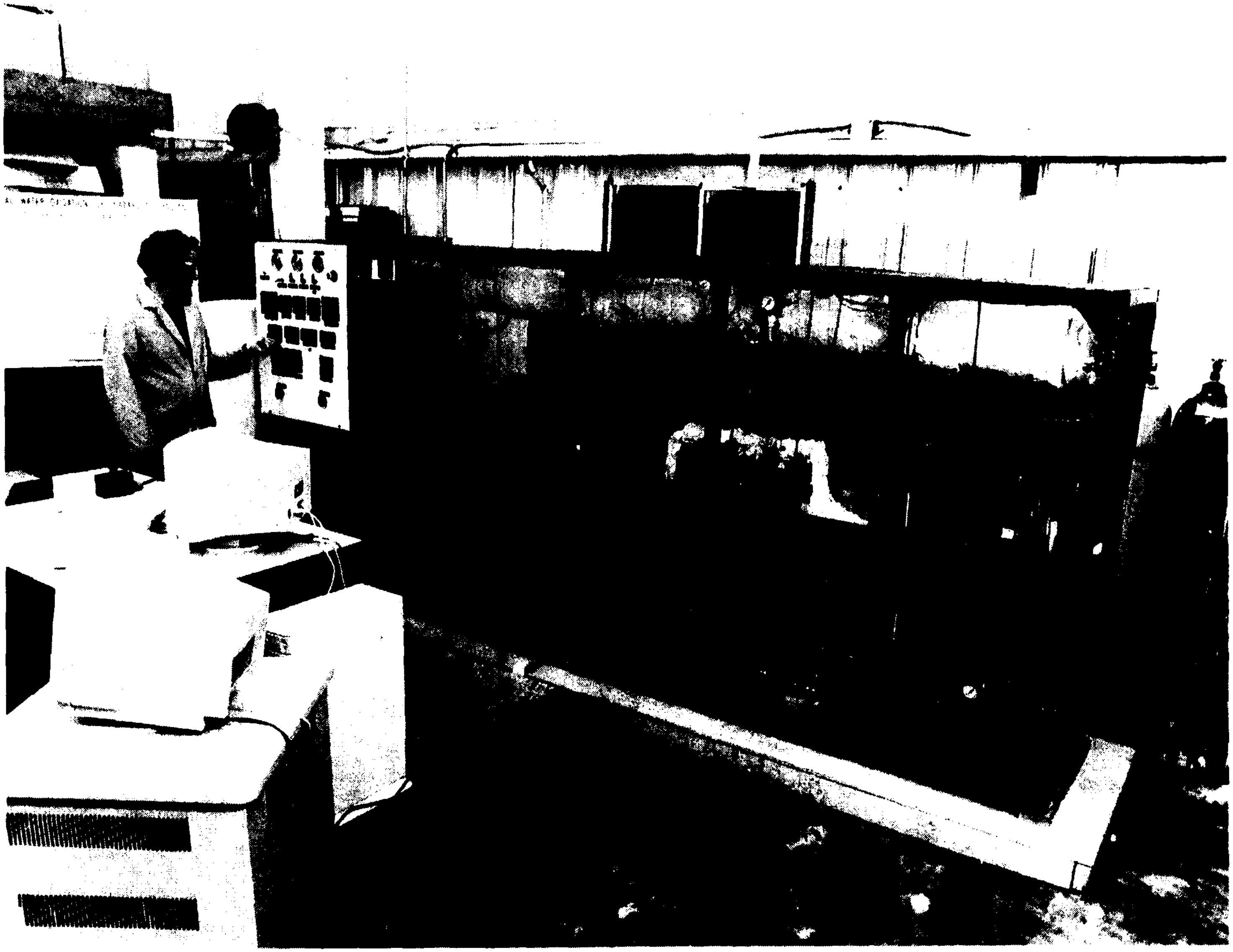


Figure 25
Photo of NFESC SCWO apparatus (view 3).

Water Pressurization Subsystem. Water is pumped to a pressure of approximately 3,600 psi by an air-driven high pressure pump. Pump discharge pressure is directly proportional to the pressure of the drive air supply. For this pump model, 100-psi drive air pressure produces a discharge pressure of 3,600 psi. Discharge pressure is set by adjusting the drive air pressure regulator. The pump has a manually adjustable stroke, so that the displacement can be varied from 0 to 2 cc/stroke. The pump goes through only one cycle with each application of an air pressure signal to a control port. Pump speed is controlled by an adjustable pneumatic timer that supplies control air pulses to the pump control port at preset intervals (typically every 0.5 to 1.5 seconds). Nominal pump capacity is set for 100 cubic centimeters of water per second. Pressure pulses in the pump discharge are dampened to less than 10 percent of their input amplitude by an in-line pressure damper. Other components of the water pressurization system include a water supply tank, in-line filter, pressure gages, flow switch, shutoff valve, drain valve, and pressure relief valve.

Startup Heater Subsystem. The startup heater is used to initially heat the water stream to a temperature greater than the critical temperature. Once the apparatus is producing a sufficient quantity of hot exhaust gas to heat the influent stream by direct mixing, the startup heater is shut off. The startup heater is a 1.5-inch-diameter by 18-inch-long cartridge type electrical heating element with 20 feet of 1/8-inch-diameter stainless steel tubing wrapped in a tight spiral around and along its surface. This spiral of tubing, through which the water flows, is covered by another 12 band-clamp type electrical heating elements. A total of 4.5 kW in electrical heaters comprise the startup heater. A temperature sensor in the discharge flow measures water temperature. The temperature signal is compared to a temperature set point by a digital electronic process controller. The output of the process controller, in turn, operates a current controller that increases or decreases the electrical current supplied to the heaters as required to maintain the temperature set point.

Liquid Waste Pressurization Subsystem. The liquid waste pressurization subsystem pressurizes the waste material to system pressure. The main component of the waste pressurization system is a variable speed pump design for high pressure liquid chromatography systems. The speed adjustment is electronic. The output of the pump can be varied between 0.2 and 10 cc/minute. The pump has a 10-micron particulate filter on the inlet and a pulsation damper on the outlet. Variation in waste flow rate is achieved by varying the pump speed. Waste flow rate is controlled by the temperature of the exhaust gases from the reactor. If the temperature of the exhaust gases drops below the temperature set point (e.g., 1,200°F), the pump speed is increased to supply more fuel (i.e., waste). If the temperature rises above the set point, the waste flow rate is reduced.

Oxygen Supply Subsystem. The oxygen required for combustion of the organic compounds is supplied from 244 standard cubic foot capacity gas cylinders. The oxygen pressure is boosted to SCWO system pressure by means of an air-driven gas compressor. Operation of the air-driven compressor is similar to that of the air driven pump: oxygen discharge pressure is determined by the pressure of the air supplied to the pneumatic drive mechanism. Pressure pulsations in the discharge from the oxygen compressor are attenuated by an in-line damper. The flow of oxygen is then metered into the SCWO apparatus through a heated bypass tube type mass flow meter and introduced into the reactor vessel through a long, porous tube made of sintered metal. This is done to minimize the chance of a detonation in the organic-oxygen mixture. The flow of oxygen can be either preset to a specific value or controlled by a process control signal such as the amount of oxygen or carbon monoxide in the exhaust gases. Other components of the oxygen supply subsystem include air and oxygen pressure gages, air pressure regulator, air shutoff valve, oxygen shutoff valve, oxygen vent valve, pressure relief valve, and flow check valve.

Salt Separator Subsystem. The purpose of the salt separator is twofold: (1) to preheat the influent stream to critical temperature using waste heat, and (2) to precipitate and remove salts from the influent stream. The salt separator is a long, vertical, pipe-like pressure vessel. At the top of the vessel, a stream of water and organic waste material is mixed with a portion of the hot exhaust gases from the reactor. The proportion of hot exhaust gases to influent water-waste is such that the temperature of the resulting mixture is close to the critical temperature (e.g., 700°F). Heating of the influent stream is through direct contact with the exhaust gases and is very rapid. The mixed water-waste-exhaust gases are directed downward, toward the bottom of the vessel. The salts and oxides that form when the critical temperature is exceeded collect on the sides and bottom of the salt separator. The salts are removed at service intervals by redissolving them in subcritical water and blowing them out the bottom drain of the pressure vessel with low pressure air. A ceramic filter removes any carry-over particles in the gases leaving through the top of the salt separator. A sample port is located near that exit of the salt separator to permit collection and subsequent analysis of the gases leaving the salt separator.

Oxidation Reactor Subsystem. The oxidation reactor subsystem provides the time, at temperature, required for complete oxidation of the organic materials in the process stream. The oil fraction of the waste will autoignite at a temperature between 500 and 600°F when oxygen is present. The oxidation of the oil fraction of the waste provides most of the chemical heat release required to bring the temperature of the water, products of oxidation, and remaining waste to the desired operating temperature (e.g., 1,200°F). The reactor vessel provides sufficient volume for the refractory components of the waste to be oxidized. The volume required for this reactor is about 53 cubic inches. This volume can be configured in several ways: a 1/4-inch-diameter tube 170 feet long, a 9/16-inch-diameter tube 43 feet long, or a 1-inch-diameter tube 12 feet long. Small diameter tubing is the lowest in cost and most readily available, but the long length of tube required presents problems of packaging and large pressure drop. The solution used in this design was to divide the total mass flow through the system into ten equal mass flows. The length of 1/4-inch reactor tube required for each flow is then 17 feet, which can be shortened to about 8 feet by bending the tube into a "U" shape. Balanced flow inlet and outlet manifolds ensure equal flow through each tube. Each of the ten reactor tubes is very well insulated to maintain high gas temperature. Thermal insulation is achieved by surrounding each reactor tube with a vacuum to minimize conduction and convection losses, and configuring the reactor tube/vacuum jacket system to minimize heat loss by radiation. The reactor tubes are coated with a low emissivity material to minimize the heat radiated by the tube and the interior of the vacuum jacket is polished to minimize the heat absorbed by the jacket. The vacuum jacket is a thin-walled aluminum tube. The vacuum jacket tubing also serves as an added protective barrier should a reactor tube burst. A vacuum is continuously maintained on all 10 tubes by means of a vacuum pump. This reactor subsystem is illustrated in Figure 26.

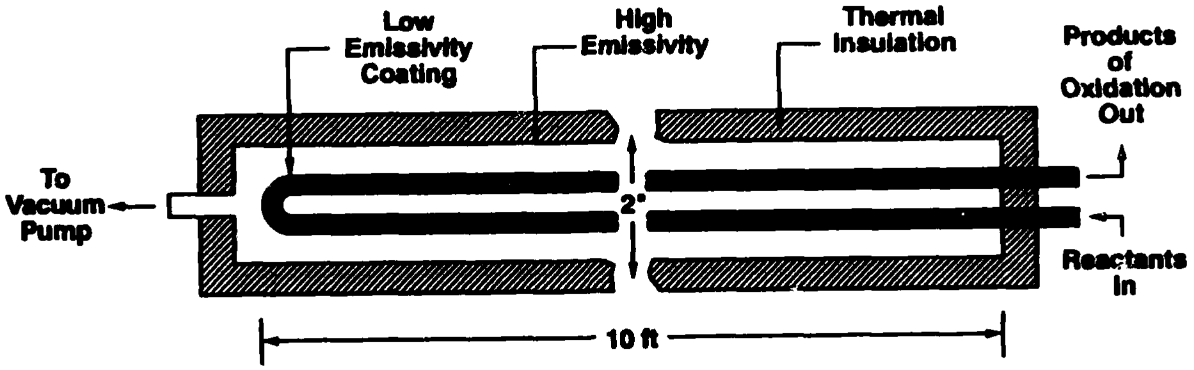


Figure 26
Tubular reactor.

A second reactor system was designed and built in response to a concern that the exhaust gas from the original reactor design would not be at a sufficiently high temperature to permit experimental verification of several design concepts, particularly the concept of recycling hot exhaust gases to reduce external energy consumption. Design studies of the original "U" tube reactor indicated that, even with as good a thermal insulation as is practical, it could be very difficult to maintain desired reactor discharge temperature of 1,200°F (650°C). Computer-aided design studies indicated that gas temperature could drop 200 to 300°F (from an initial temperature of 1,200°F) over the length of the reactor tube. This means the reactor effluent would not be hot enough to effectively preheat incoming water and waste streams. A second reactor subsystem was therefore designed and built that guarantees that the exhaust gases will be at a specified temperature. This second reactor design is illustrated in Figure 27. This reactor is a 200-foot continuous length of alloy tubing coiled into a helix and placed in an electrically heated furnace. The reactor coil was wound using a large machine lathe and a specially designed and built mandrel. A sensor at the discharge of the reactor tube measures the gas temperature. An electronic controller uses this signal to adjust the supply of electrical current to the heating elements of the furnace. In this manner, heat is added to the gases in the reactor (by radiation from the hot furnace wall) in the amount required to produce the desired gas discharge temperature.

Exhaust Gas Recirculation Subsystem. The exhaust gas recirculation subsystem pumps a portion of the hot exhaust gases from the reactor back to the salt separator to heat the incoming water and waste mixture. The amount of exhaust gas that is recirculated is controlled by the temperature at the gas outlet of the salt separator. If the temperature of the gas leaving the salt separator drops below the temperature setpoint (e.g., 700°F), a pneumatically operated valve is opened to divert more hot gas to the salt separator. Conversely, if the temperature of the gas rises above the set point, the valve closes. The hot gas is pumped to the pressure in the salt

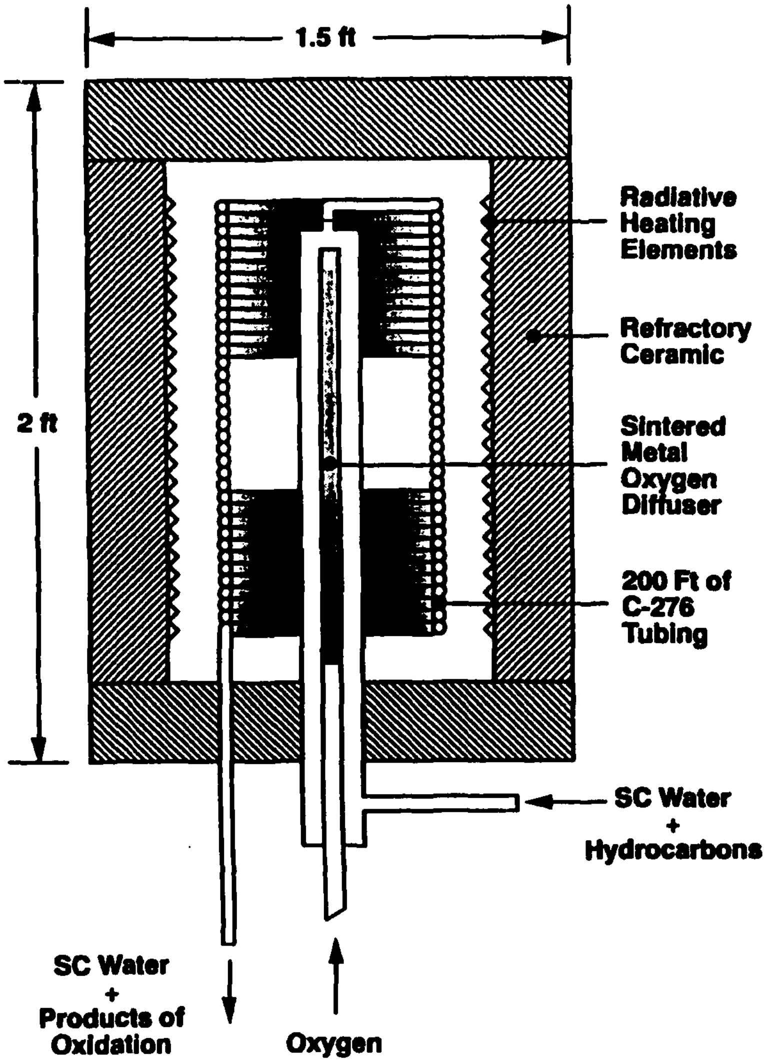


Figure 27
Coiled reactor.

separator by a specially designed and built pump. After analysis by NFESC of several alternative pump designs, the design shown in Figure 28 was selected for detailed design and fabrication. The design uses a metal bellows to move the hot gases. The pressure difference the pump must overcome is estimated to be small: about 2 inches of water. The pressure and temperature of the gases on both the interior and exterior of the bellows are approximately equal. This minimizes the power input required to pump the gases, minimizes stress on the bellows, and minimizes heat loss from the gases. The reciprocating pump drive shaft is driven by an air motor. The controls for the drive unit are identical to those used on the water pressurization pump.

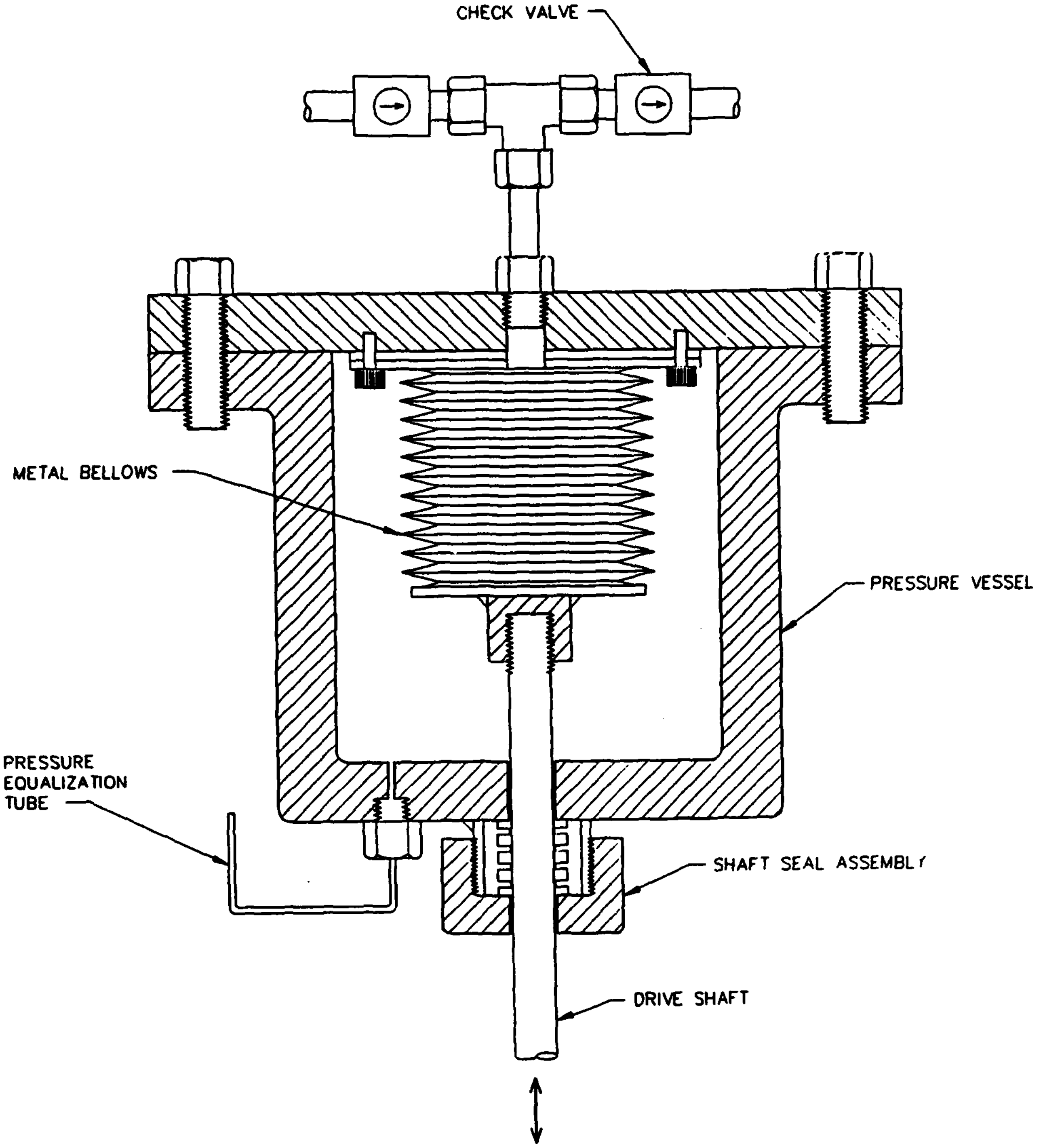


Figure 28
Hot gas recirculation compressor.

Condenser Subsystem. The condenser subsystem uses a flow of cold water to cool and condense the reactor exhaust gases. The condenser is a simple tube-in-tube design. Process gases enter the inner tube; water and noncondensible gases (such as carbon dioxide and oxygen) exit the inner tube. Cold water flows in the annulus between the inner and outer tubes. The flow of cold water is controlled by a thermostatic valve to keep the condensate temperature at a temperature of about 100°F.

Liquid-Vapor Separator Subsystem. The liquid-vapor separator mechanically separates the fluid stream from the condenser into its liquid and gaseous components. The liquid-vapor separator is a pressure vessel with a plate which divides the interior into two chambers. A mixture of liquid and gases enters in one chamber and is directed toward the bottom of the separator. Most of the liquid fraction of the stream collects at the bottom of the vessel, while the gases flow to the second chamber where they exit the separator. A demister in the second chamber traps any small droplets of liquid that are carried over into the second chamber. When liquid in the bottom of the separator accumulates to a certain depth, a liquid level switch is closed. Switch closure activates a timer controlled valve that supplies air to a pneumatically actuated liquid discharge valve. The discharge valve is open for a time sufficient to discharge most of the liquid into an effluent collection tank.

Back Pressure Control Subsystem. The back pressure control subsystem maintains pressure in the SCWO apparatus at a preset level. A pressure sensor on the gaseous effluent discharge line generates an electrical signal that is a measure of SCWO system pressure. The measured pressure is compared to the desired pressure level by a digital electronic process controller. Any error between the two values is converted to an air pressure signal that is used to open or close the pressure regulating valve.

Effluent Sampling Subsystem. Sample bottles with isolation valves are connected to the gaseous and liquid discharge lines. A high pressure sample bottle is also located at the discharge from the salt separator. Because of safety concerns, sampling valves are pneumatically actuated.

Data Acquisition and Display Subsystem. Supervisory control, data acquisition, and data display are achieved through a computer interface to the system. The control computer contains two circuit boards that give the ability to read 32 channels of analog data and eight channels of digital data. These two boards also permit output of four analog control voltages and eight digital switch closures. A third circuit board, called an IEEE-488 interface card, permits data to be written to and read from a large variety of "smart" instruments, such as programmable voltmeters and scanning thermocouple meters. The data are acquired, analyzed, filed, and displayed using software written for the LabWindows® data acquisition software from National Instruments Corporation. The code was written by NFESC in the C computer language and compiled to achieve rapid program execution. The graphical user interface acquires and displays data from the SCWO system in several user selected formats. The interface also permits the experimenter to turn pumps, heaters, and other system components on and off and to change system set points, such as waste or oxygen flow rate, from the computer terminal.

Framework Subsystem. The laboratory scale SCWO unit is contained within a steel frame and is covered with Lexguard® polycarbonate plastic and sheet metal safety shields. A small fan provides positive ventilation for the enclosure. The unit is approximately 12 feet long, 5 feet high, and 3 feet deep. Maximum electrical power consumption is 40 amps at 240 volts. Maximum oxygen consumption is 0.9 SCFM. Nominal driver-air consumption is 15 SCFM at 100 psi.

Test Plan

A detailed plan of experimentation was developed for the bench scale SCWO apparatus. The test plan for the bench scale SCWO apparatus includes experiments to:

1. Establish that a controllable exothermic chemical reaction can be achieved in the medium of supercritical water.
2. Measure the performance of exhaust gas recirculation as a method of preheating the influent waste steam.
3. Measure the effectiveness of the salt separator device.
4. Investigate the formation and neutralization of acid forming compounds.
5. Investigate active flow rate control as a method of assuring acceptable destruction efficiencies.
6. Measure deposition of scale and other solids within system components.
7. Assess the effects of corrosion and oxidation on system components.
8. Measure heat transfer rates.
9. Investigate methods of removing salts and other deposits from interior surfaces of the apparatus.
10. Investigate the use of effluent recirculation as a method of increasing destruction efficiencies.
11. Investigate alternative SCWO component designs, e.g., hydrodynamic salt separators, vacuum insulated reactor vessels, and ceramic walled reactor vessels.
12. Measure the destruction efficiency of actual samples of Navy industrial wastes.

As a consequence of a delay in delivery of the SCWO unit to NFESC and the unexpectedly long time required to make the SCWO apparatus operational, the experimental plan had to be greatly abbreviated to match project budget and schedule constraints.

Hazards and Operability Study

An analysis of the hazards inherent in the design and operation of the bench scale SCWO unit was conducted by contract. The results are presented in Reference 7. The contractor also produced a test certification and safety report (Ref 8).

Other Plans and Procedures

A detailed SCWO apparatus operating procedure, a project environmental impact assessment, and a project safety plan were prepared by the NFESC. The project safety plan was submitted to the NFESC Environmental and Safety Office in March 1992. The safety plan was approved in July 1993.

Installation

The unit was delivered to NFESC in December 1992. Facilities work required to install the unit included installing two new 240-VAC electrical circuits, installing a large capacity air compressor (15 SCFM at 130 psi), and installing a condenser cooling water supply and drain. These facility modifications were completed in January 1993.

The time between January 1993 and July 1993 was occupied fixing construction flaws and implementing design modifications. While many of these flaws were readily fixed with materials on hand, other flaws were costly and time consuming to fix.

Multiple leaks were discovered when an attempt was made to pressurize the unit. Leaks from compression type tube fittings were usually easy to stop, but leaks around threaded fittings, especially the custom machined Hastelloy C-276 fittings, were often difficult to fix. Several fittings had to be welded to achieve a seal.

Heating the unit up to temperature revealed yet another series of problems. The electrical heating elements on the startup heater burned out because of a mislocated temperature sensor. The heater was completely rebuilt, but later plugged from salt deposition on the interior surface of the heater tube. The startup heater was rebuilt a second time. The use of de-ionized water rather than tap water eliminated the mineral deposition problem in the startup heater.

Initial experimental results showed that addition of compressed oxygen to the supercritical water stream lowered the temperature of the resulting mixture by an undesirable amount. This problem was corrected by designing and building an oxygen preheater. The oxygen preheater is an electrical band heater surrounding a coil of 1/8-inch stainless steel tubing. Oxygen discharge temperature is controlled by a digital electronic temperature controller.

The salt separator pressure vessel developed leaks at the cover-vessel interface as the salt separator was heated to high temperatures. Experiments showed that the bolts holding the cover to the body of the vessel were failing to maintain their torque settings after several temperature cycles. Consultation with the manufacturer of the pressure vessel resulted in replacing the original cover bolts with a better grade of bolt and use of belleville washers to better maintain bolt tension.

The high pressure liquid chromatography pump used for pressurizing the waste stream did not perform as specified over its full 0 to 10 cubic centimeters per minute output range. The pump apparently cavitated at speeds greater than the speed corresponding to 5 cc/min. As a consequence, output did not increase substantially above about 5 cc/min, regardless of the setting of the speed control. Also, the pump would not run when pumping against system pressure

(3,600 psi) at the lower end of the flow range (<3 cc/min). Thus, the range of waste flow rates was restricted to between 3 and 5 cc/min. Rather than rely on the setting of the waste pump speed controller for an indication of waste flow rate, the waste container was placed on a small electronic platform scale and the weight recorded at regular intervals. The limited waste flow rate range caused by the marginal performance of the waste pump restricted the range of operability of the SCWO unit. For example, only a limited range of hydrocarbon/oxygen ratios can be achieved.

Initial testing also revealed that the condenser was mislocated relative to the liquid-vapor separator, causing condensate to accumulate in the condenser and related piping. Discharge of this large volume of liquid water caused a very significant drop and operating pressure and temperature during a liquid blow-down cycle. The condenser was relocated to a position above and sloping downward toward the liquid-vapor separator.

By July 1993, the startup problems with the SCWO had been corrected and the system was successfully brought up to operating temperature and pressure using supercritical water generated by the startup heater.

Operating Permits

Application was made to the State of California, Department of Toxic Substances Control, Alternative Technology Division, for a permit to operate the NFESC SCWO apparatus. Permit applications were also made to the Ventura County Air Pollution Control District and City of Oxnard Sanitation District. Conditional operating permits were granted in August 1993. The permits allow testing of hazardous hydrocarbon materials, but not actual Resource Conservation and Recovery Act (RCRA) waste materials. Permission to test actual wastes was withheld pending State review of experimental results on nonwaste materials.

Patents

Four patent disclosures were filed as a result of this work. Navy patent case #74780 discloses a modular reactor vessel design that is believed to have advantages in safety and thermal efficiency over existing designs. Navy case #74781 discloses a reactor vessel lined with multiple layers of ceramic materials. Each ceramic layer in this design has a specific function such as high corrosion resistance, high thermal insulation, or a coefficient of thermal expansion that matches that of the support substrate. Navy case #74782 discloses several SCWO system design features that are believed to offer improvements in system thermal efficiency, improved solids removal, improved resistance to corrosion, and an improved organic throughput rate. A patent disclosure was also prepared for a system improvement that: (1) increases the rate at which organic material that can be processed, and (2) improves thermal efficiency. Increasing the percentage of organic material processed per unit time in an SCWO unit is significant because the higher the allowable organic concentration in the feedstock, the smaller (and less costly) the SCWO unit needs to be for a given capacity. The disclosure also describes a method of recovering and using waste heat that does not require an exhaust gas recirculation pump.

Bench Scale SCWO Results

The nominal operating parameters for the SCWO apparatus were: water flow = 50 cc/min, fuel oil flow = 2.3 cc/min (2.0 gm/min, 0.21 moles/liter concentration, or 4 percent fuel oil by weight), and oxygen flow = 6 standard liters/min. The stoichiometric oxygen requirement is 4.9 standard liters/min, so 20 percent excess oxygen was supplied. If the fuel was completely oxidized in a well insulated reactor vessel, the fluid temperature should rise to about 1,200°F.

A fundamental feature of the NFESC SCWO design is the use of high energy content wastes, such as waste oils, as the heat source to drive the process rather than expensive electricity. As stated previously, this feature requires that the fuel component of the fuel-waste mix spontaneously ignite when oxygen is added and completely oxidize within a short distance of reactor length. Available data on autoignition temperatures indicates that this should happen but in practice autoignition was, at first, very difficult to achieve. Diesel fuel and oxygen were injected into supercritical water to form a mixture at 720°F and 3,400 psi. This state is well above the published conditions for autoignition of kerosene and diesel fuel (in air); yet there was no clear indication of deflagration in supercritical water, such as a marked rise in fluid temperature. The hydrocarbon vapors condensed in the cooler sections of the SCWO apparatus were carried through the unit and discharged through the liquid side of the liquid-vapor separator.

At the conclusion of experiment #5, a large volume of steam suddenly appeared, emanating from the reactor insulation. The system pressure also dropped precipitously. The emergency shutdown procedure was activated and the unit was quickly brought to safe conditions. Examination of the reactor tubes revealed that an explosion had occurred in the #2 tube. The tube was blown open at one location and bulged in two other places (see Figure 29). It is believed that the explosion was caused by the addition of an excessive amount of oxygen to a reactor tube containing hot hydrocarbon vapors. Because of a problem with flow balancing between the reactor tubes, reactor tube #2 carried more flow than other tubes and was, as a consequence, considerably hotter than the other tubes. When experiment #5 was concluded, the pressure set point of the automatic back pressure control system was reset to atmospheric pressure to lower system pressure to a safe level. The rapid lowering of system pressure caused the oxygen remaining in the high pressure oxygen accumulator to rapidly flow into the SCWO reactor tubes. The explosion was the result. The other reactor assemblies were opened and the tubes examined, but no other damage was discovered. The lesson learned was that this problem could have been prevented by shutting off the oxygen supply to the reactor at the end of operation and purging the system with nitrogen.

Since it was necessary to rebuild part of the reactor to repair the damaged tube, it was decided to rebuild the entire reactor into a configuration of five tubes in series to eliminate a flow imbalance problem and improve the quality of temperature instrumentation. Five reactor tubes in series provide one flow path with a total length of 100 feet. This length provides the design a 12-second residence time for the nominal flow rate of 50 cc/min. The 20 thermocouples that had been located on one of the reactor tubes (in the parallel configuration) were redistributed such that the first of the series of five reactor tubes has eight thermocouples along its length, and each of the remaining four reactor tubes each has three thermocouples distributed along its length.

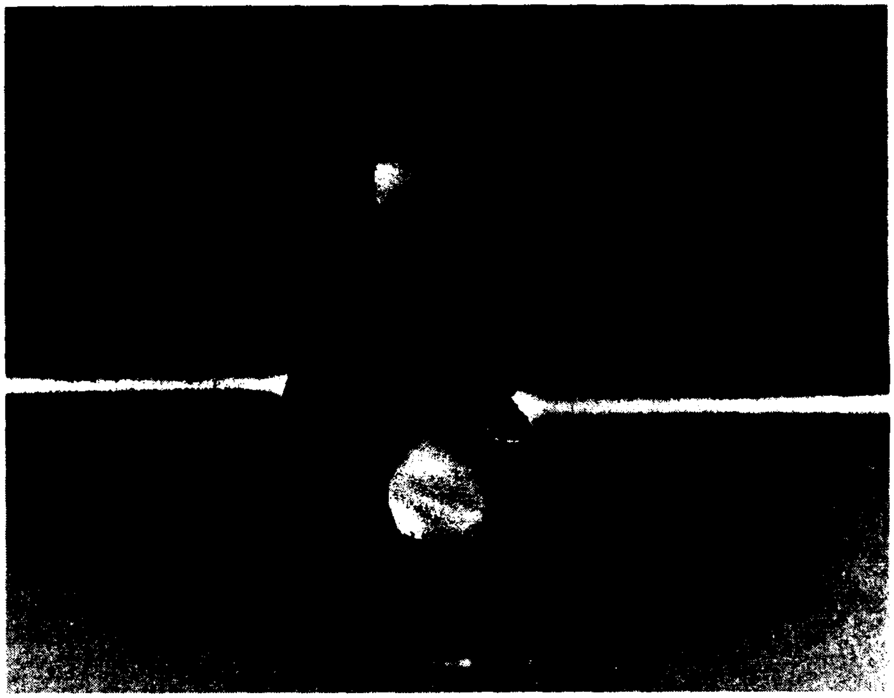


Figure 29
Photo of burst tube.

Additional experiments with fuel oil were conducted with the series reactor configuration, but no indication of autoignition and oxidation of fuel oil was observed.

Acetone was next tried as a fuel. Acetone was tried because it is completely miscible in water, so solvency of the fuel at near- or supercritical conditions is not in doubt. No evidence of significant oxidation was observed, but this may have been because acetone has a high autoignition temperature.

N-hexane, a light, straight-chain paraffin, was also tried as a source of hydrocarbons. Hexane ignited and released sufficient heat to raise the temperature to the fluid stream to about 800°F. Varying the amount of oxygen added to the fuel-supercritical water mixture indicated that the temperature rise was limited by incomplete mixing of fuel and oxidizer. The temperature of the fluid stream increased each time the amount of oxygen added to the stream was increased. The temperature continued to rise until the maximum amount of oxygen input capability (30 standard liters per minute) was reached. This was equivalent to 500 percent excess oxygen. Incomplete combustion was verified by the presence of fuel in the liquid discharge pipe.

It was conjectured that oxidation was occurring only in the fluid boundary layer adjacent to the sintered metal oxygen discharge pipe. Because the flow velocity is so low (and at times zero), the flow is laminar and excess oxygen contacts hydrocarbon molecules only by diffusion across fluid streamlines. Since the densities of the gases are very high (compared to gases at ordinary conditions), diffusion is comparatively slow. Because the heat release rate is slow, heat is lost to the environment through the reactor insulation system at almost the same rate as it is released, resulting in a very slow rate of increase in reactor wall temperature. The temperature of the fluid drops rapidly as it flows along the reactor, eventually reaching a temperature where the chemical reactions essentially stop. The unreacted fuel and oxygen exit the reactor through the liquid discharge pipe and the backpressure regulator valve.

A new oxygen mixing assembly was designed, fabricated, and installed to promote better contact between oxygen and hydrocarbon molecules. Oxygen and supercritical water were mixed as opposing flow streams in a small diameter mixing tee assembly. This arrangement worked appreciably better, as temperatures near the reaction zone exceeded 1,200°F (the design temperature). To achieve this temperature, however, an excessive amount of oxygen was required (about three times the stoichiometric requirement). It was apparent from experiment #15 that thorough mixing of hydrocarbon and oxygen are vital to achieving high temperatures and efficient oxygen utilization. In addition, it is important that a continuous flow through the SCWO apparatus be maintained at all times. This is difficult to achieve in the NFESC SCWO unit. When the liquid discharge valve opens, the pressure (and temperature) in the SCWO apparatus drops because the volume of the system has increased. When the pressure drops below the pressure set point, the backpressure regulating valve closes. After the liquid has been discharged from the liquid-vapor separator and the liquid discharge valve has closed, the SCWO system pressure might be several hundred psi below the pressure set point. Thus all outlets from the apparatus are closed while water vapor, oxygen, and hydrocarbons are pumped into the unit to build the pressure back up to the set point value. While the apparatus is being pumped back up to normal operating pressure, there is no flow though the apparatus, mixing of fuel and oxidizer is greatly reduced, and what oxidation does take place is localized. Once normal operating pressure is reached, the backpressure regulating valve opens and flow is established. When this occurs, the temperature rises dramatically and the reaction zone is spread over several feet of reactor length. These flow control and mixing problems can be solved by modifying the SCWO apparatus.

In experiment #16, a new oxygen mixing apparatus was tested. The apparatus consisted of a 1/4-inch mixing tee followed by a length of sintered metal rod that served as a porous plug. The theory behind this design is that the mixture of water vapor, hydrocarbons, and oxygen will be forced into intimate contact by flow through the myriad of small passages in the porous plug. A potential problem with this design is that char, tars, and other products of pyrolysis can easily plug the passages in the mixer. This design performed very well (until it did plug up). Results are presented in Figure 30. Figure 30 shows that 1,200°F reactor inlet temperature was achieved using approximately the minimum (stoichiometric) oxygen flow of 5.7 standard liters per minute.

Several other designs of mixing apparatus were built and tested, including mixing tees of several sizes, a lance type mixer, a packed bed mixer, and a multiple orifice mixer. The multiple orifice mixer was chosen for the final design because it combines good mixing (as measured by oxygen consumption) with ease of construction and freedom from plugging. The multiple orifice mixer consists of a tube whose interior volume is divided into a series of chambers by several orifice plates. Supercritical steam, hydrocarbons, and oxygen are initially mixed in a mixing tee before entering the first orifice. The mixture is then accelerated to a high velocity through the orifice. The discharge from the first orifice enters the first chamber, where the flow undergoes additional mixing as the flow decelerates and swirls around inside the first chamber. Next, the flow is accelerated through the second orifice into the second chamber, and so forth.

With an efficient and reliable mixer in place, several experimental runs were made at an elevated and sustained reactor inlet temperature. The SCWO unit was run at a peak operating temperature of 1,200°F for periods exceeding 30 minutes. Both hexane, number 2 diesel fuel, and isopropyl alcohol (or IPA, C_3H_7OH) were used as hydrocarbon sources. IPA was tested because it is a good solvent for many aqueous hazardous wastes and because of the difference in heating values between the two chemicals. A 70 percent IPA in water solution was used for these experiments, so that the effective heating value of IPA was about one half that of hexane. Experiments verify that twice the volumetric flow rate of IPA is required to attain an operating temperature of 1,200°F.

Hexane, diesel fuel, and IPA all appeared to be completely oxidized in the SCWO process. Liquid effluent was clear, colorless, and odorless (Figure 28). Hexane and diesel fuel oxidized very quickly, in fact most of the oxidation appeared to take place in the mixer. Examination of oxidation colors on the exterior surface of one of the tee mixer assemblies indicates that the maximum temperature occurs about 6 inches after the introduction of oxygen. This compares favorably with the predictions of the computer simulations presented earlier. IPA oxidizes much more slowly than hexane or diesel fuel. The maximum temperature produced by the oxidation of IPA occurs about 3 feet downstream from the point of addition of oxygen.

Several experiments were performed to investigate alternative methods of controlling system back pressure. In one experiment, the system pressure sensor and back pressure regulating valve were placed upstream of the condenser. In this position, the back pressure regulating valve must control the flow of high temperature gases. Erosion of the valve stem and seat and sticking caused by particulate matter in the fluid stream are also possible disadvantages of locating the back pressure valve in this position. A valve located in this position must have a flow coefficient about 50 times larger than a valve located in the noncondensible gases discharge pipe. Experiments with the NFESC SCWO unit indicate that near steady flow through the SCWO apparatus can be achieved with the back pressure regulating valve located upstream of the condenser. Unfortunately, the valve chosen for these experiments would intermittently stick as the valve body heated, making control of long duration experiments impossible. Following these experiments, the SCWO unit was reconfigured to the original design: with the back pressure control valve on the noncondensible gases discharge pipe.

A major problem with the NFESC SCWO reactor design is the high rate of heat loss from the reactor. To assure adequate destruction of a wide range of organic hazardous waste materials, it is required that the process stream be kept at a temperature of approximately 1,200°F for a period of 10 seconds or more. Typical steady state temperature profiles through the reactor are presented in Figure 31. As Figure 31 shows, the temperature of the process stream drops from a high value of between 1,100 to 1,200°F near the inlet to the reactor to a temperature of less than 700°F at the outlet from the reactor. This high rate of heat loss is due to the high surface area to volume ratio of the reactor design and the poor performance of the thermal insulation system. The vacuum insulation system did not work as anticipated, in fact it did not seem to matter if the vacuum pump was on or not. The problem of high heat loss rate can be reduced by: (1) reducing the surface area of the reactor, (2) reducing the heat transfer coefficient from the process stream to the reactor wall, and (3) reducing the temperature difference between the process stream and the environment. The third design option listed above was chosen as the basis of a new reactor design. This coiled reactor design was described earlier and illustrated in Figure 24. A photo of the alternative reactor design is presented as Figure 32.

Experiment #24 was the initial test of the coil reactor. The initial test was performed with the heating elements turned off so that the thermal insulation properties of the furnace could be assessed. Experiment #24 was a success: the highest reactor discharge temperature to date was achieved. Data from experiment #24 are presented in Figures 33 and 34.

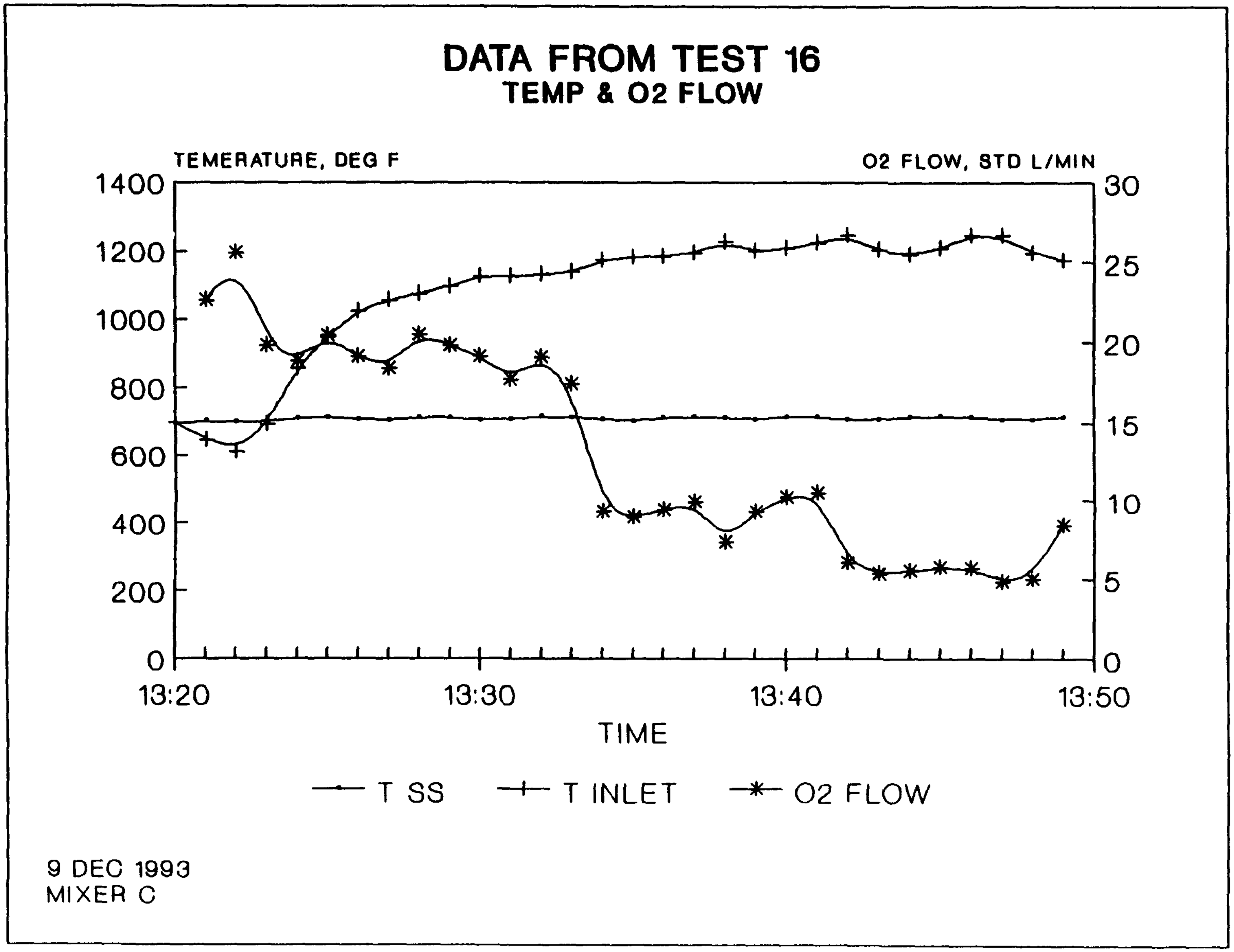


Figure 30
Data from Test 16 - temperature and oxygen flow.

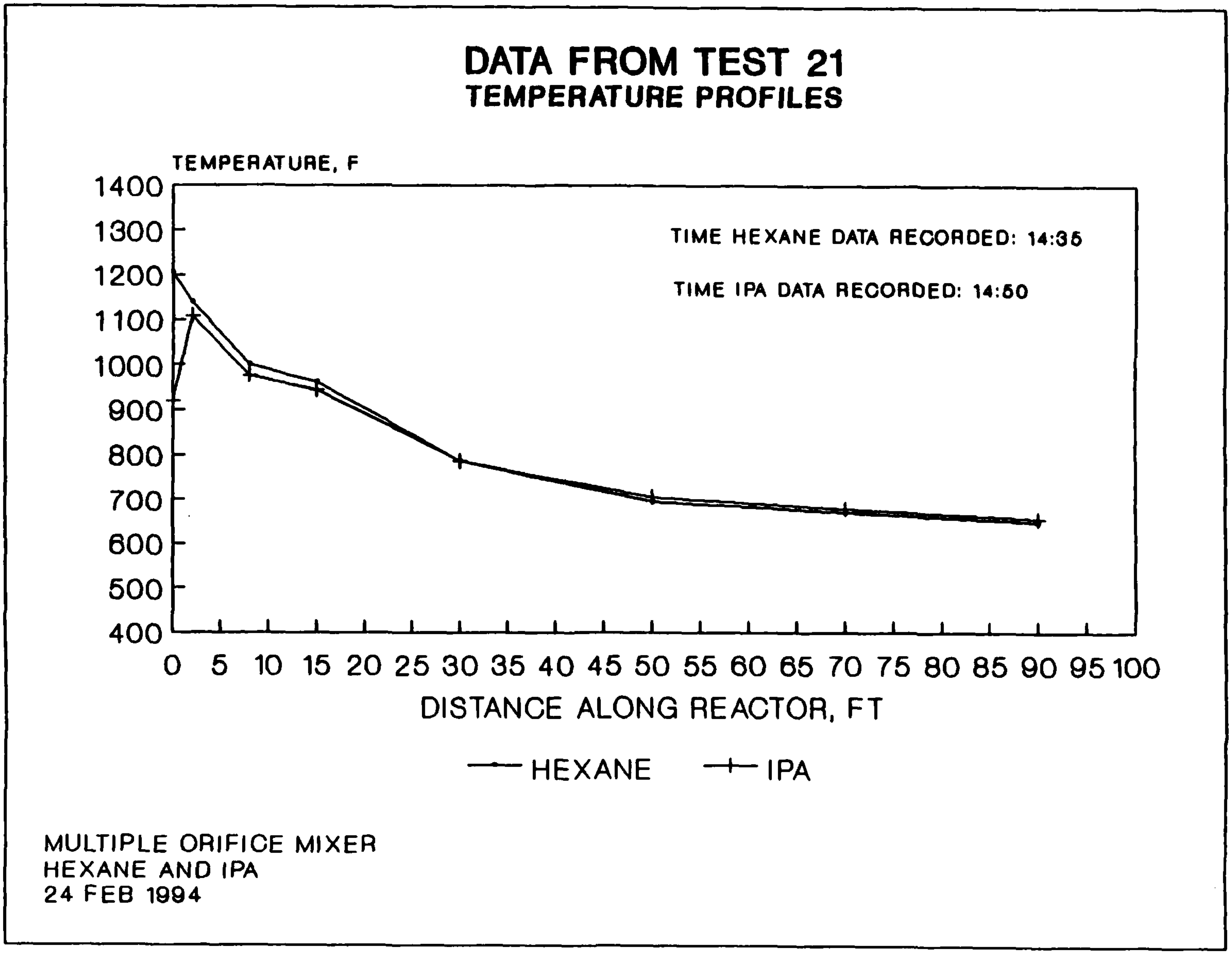


Figure 31
Data from Test 21 - temperature profiles.

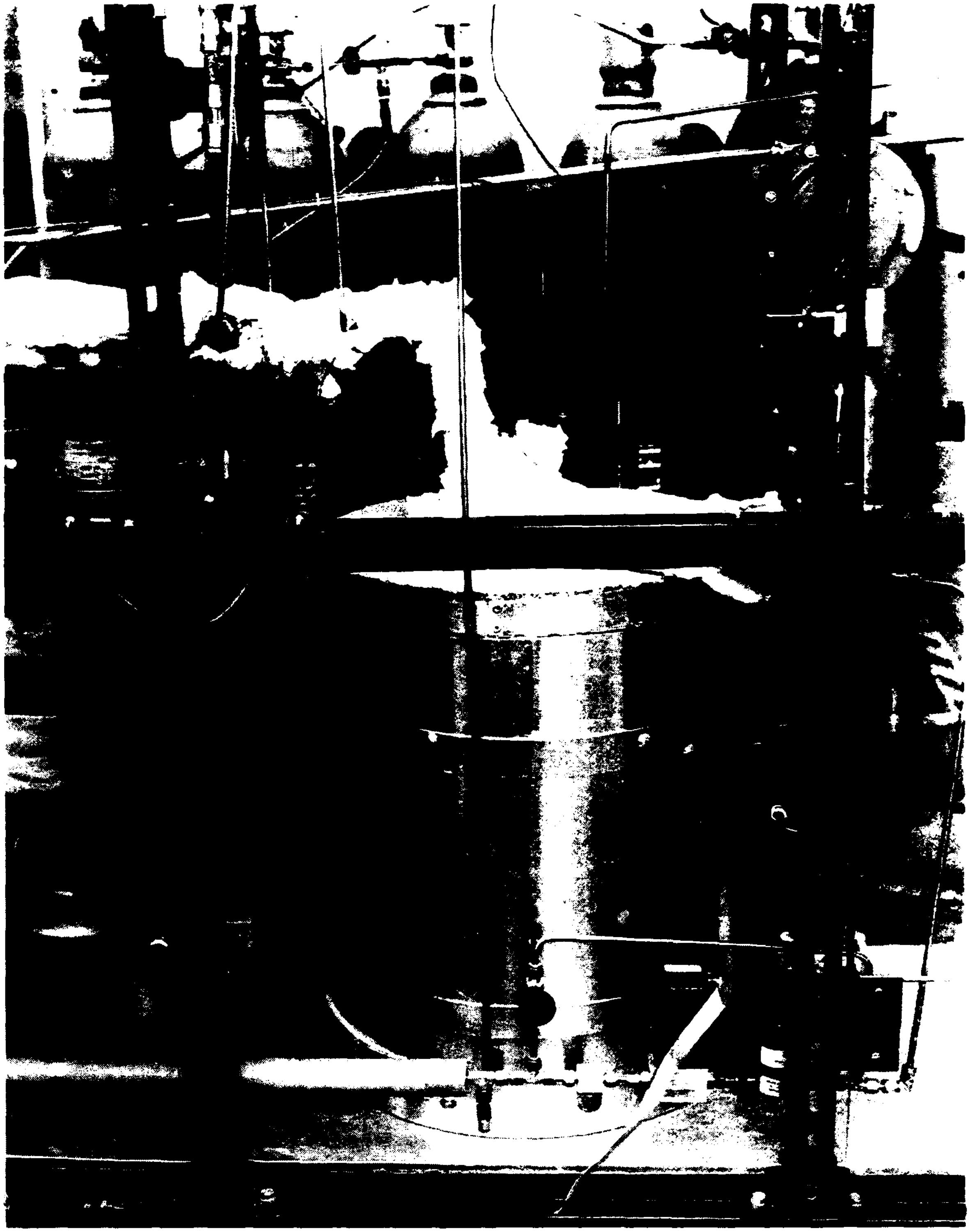
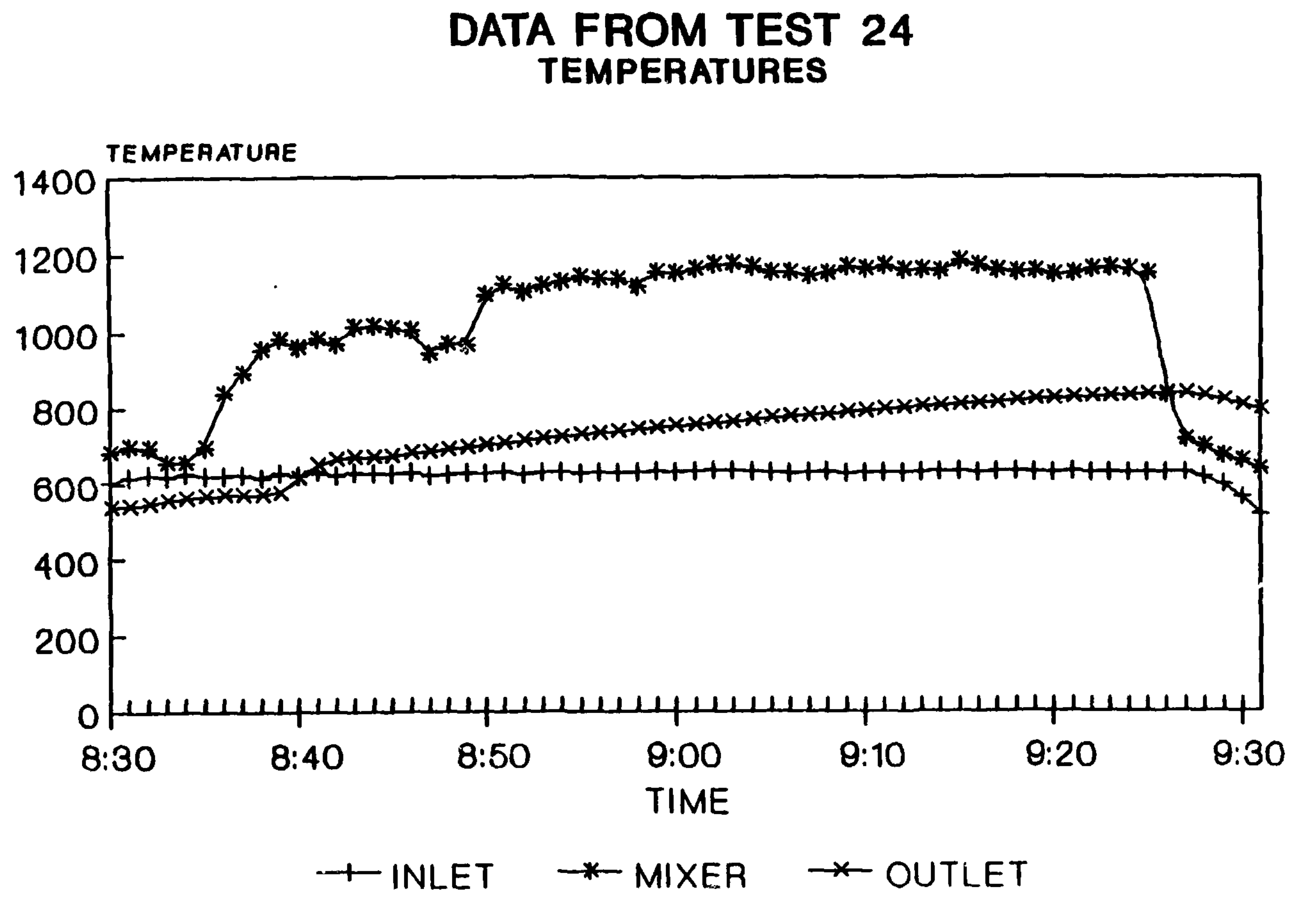


Figure 32
Photo of type II reactor.



COIL REACTOR
HEXANE
4 APRIL 1994

Figure 33
Data from Test 24 - temperatures.

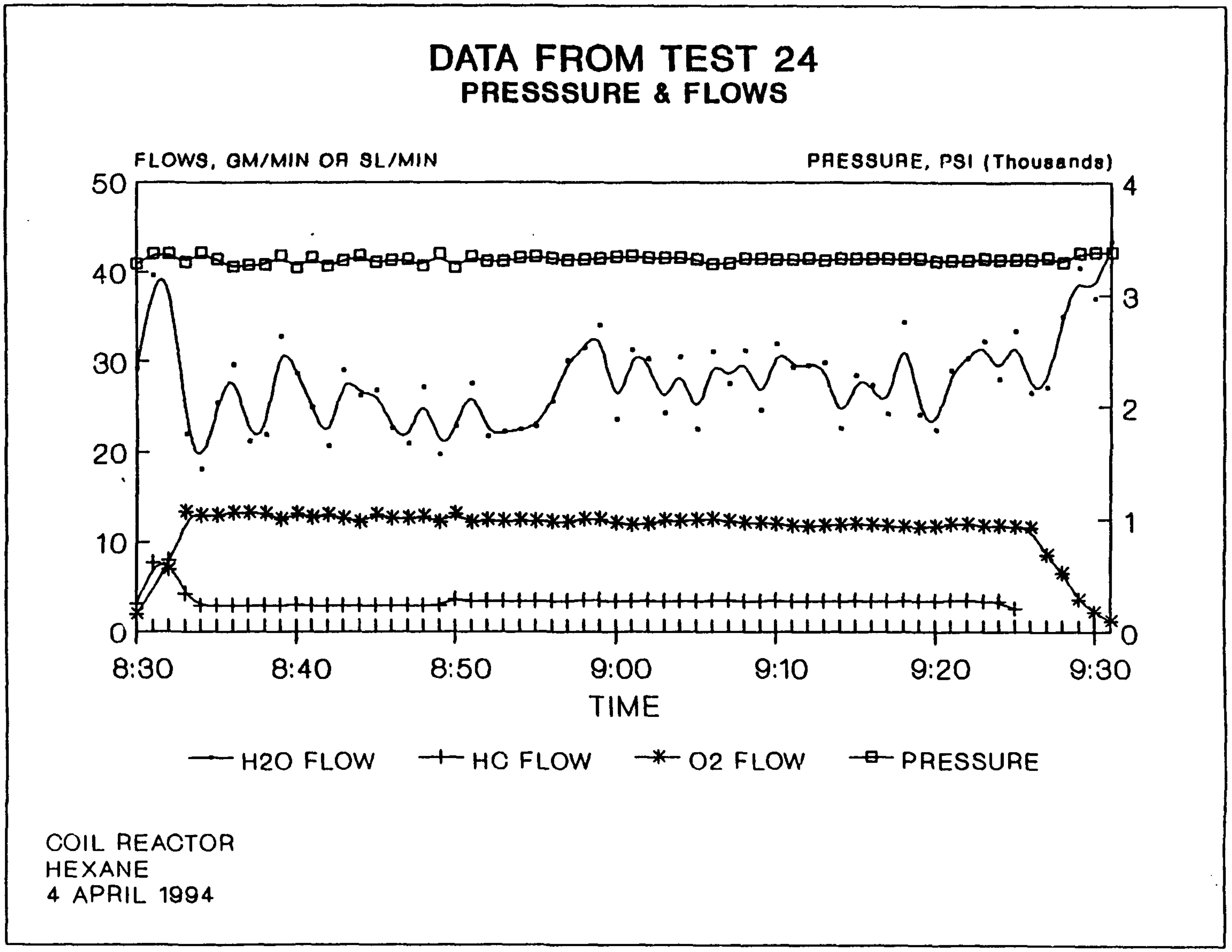


Figure 34
Data from Test 24 - pressure and flows.

Experiment #25 was designed to test the coil reactor with the heating elements turned on and using diesel fuel as the hydrocarbon. Difficulty was experienced in getting a large fraction of the fuel to burn. Only a low (850°F) temperature could be achieved using the stoichiometric amount of oxygen and the liquid discharge contained significant amounts of unburned diesel fuel. About 300 percent excess oxygen was required to reach the operating temperature of 1,200°F. These were the symptoms of poor mixing of fuel and oxygen experienced in earlier experiments. The liquid level control switch in the liquid-vapor (L-V) separator malfunctioned (probably due to a coating of partially burned fuel oil) and caused the L-V separator to fill to the top with water. The water, in turn, effectively plugged the gas discharge valve causing the system pressure to rise rapidly. To reduce the system pressure and blow the liquid out of the L-V separator, the liquid discharge valve was manually actuated. A brief time later, there was a loud "BANG" in the reactor, accompanied by clouds of steam and smoke. The remote "Emergency Stop" switch was pushed and the system safely brought down to low temperature and pressure. Examination of the reactor showed that the wall of the mixing assembly was burned through in six different places (see Figure 35). Little remained of the orifice plates and orifice spacers (only one small piece of an orifice was found at the bottom of the furnace). The cause of the failure is believed to be the vigorous localized burning of partially oxidized diesel fuel in the mixer chambers. This was initiated when the flow of oxygen (already abnormally high) increased suddenly due to the sudden drop in downstream pressure caused by opening the liquid discharge valve. The metal tube wall yielded at one local hot spot, resulting in rupture of the mixing tube. Now, with no back pressure to control the flow of oxygen, very large amounts of oxygen flowed into the mixer, resulting in burning of the mixer assembly internal parts and tube walls. The walls of the mixing assembly are extremely thin around the edges of the holes formed by burn through, and the interior of the mixer tube showed significant flow of molten metal (the minimum temperature at which melting occurs for alloys of the type used in the mixer is about 2,500°F). This failure could have been prevented by safety systems that limit the flow rate of oxygen.

The coil type reactor system was rebuilt but recurring problems with the oxygen mass control system caused significant delays in the experimental program.

In anticipation of evaluating the concept of exhaust gas recirculation as a method of conserving energy, the recirculation pump (which had not been operated since the SCWO system was delivered to NFESC) was tested. The pump was found to be inoperable. The pump was disassembled and it was found that the metal bellows assemble had been severely damaged and the drive shaft bent (Figure 36). The damage indicates that the pump was dropped on its drive shaft.

Because of the desire to report progress in a timely manner and because of the time and expense required to repair the oxygen control valve and the exhaust gas recirculation pump, it was decided to terminate the experimental work reported in this document with experiment #27.

A summary of the experiments conducted in this study is presented in Table 7. The lessons learned in the course of the experimental program were incorporated into the design of an improved SCWO system.

Figure 35
Photo of burned mixer.

Figure 36
Photo of damaged exhaust gas recirculation pump.

Table 7
Summary of Experiments on Bench Scale SCWO Unit

Experiment No.	Date	Comments
1	8 Aug 1993	SCW and dry N_2 only. Problems with balancing flow. Indications of significantly reduced flow through instrumented reactor tube (outlet manifold temperature greater than temperatures measured in instrumented tube).
2	26 Aug 1993	Fuel oil used as hydrocarbon source. Problem with waste feed pump (pump stops at low flow rate settings). No evidence of spontaneous ignition, i.e., no recorded temperature rise.
3	31 Aug 1993	Difficulty reaching critical conditions at inlet because of poor flow regulation and excessive pressure drop during liquid blowdown. Salt separator vessel developed leak during operation. Salt separator bypassed for subsequent experiments. No definite indication of oxidation.
4	31 Aug 1993	Reactor rebuilt to a five tubes in parallel configuration to promote more rapid heating to supercritical conditions at inlet. No indication of oxidation occurring. Oil accumulation in liquid-vapor separator.
5	2 Sep 1993	Detonation in #2 reactor tube. Tube split open.
6	24 Sep 1993	Reactor reconfigured as five, 20-foot tubes connected in series (100-foot total length). Thermocouples distributed over entire length. No indication of rapid oxidation.
7	26 Oct 1993	Sticking pressure regulating valve. Test aborted. Valve disassembled and repaired.
8	28 Oct 1993	Problem free experiment - but no evidence of oxidation.
9	29 Oct 1993	Tried acetone (CH_3COCH_3) as hydrocarbon source. No evidence of rapid oxidation.
10	1 Nov 1993	Tried n-hexane (C_6H_{14}) as hydrocarbon source. No evidence of oxidation. Discovered in-line filter plugged; possibly little or no fuel input in experiments #9 and #10. Fuel scale (used to record weight of hydrocarbon supply versus time) stopped working.

Table 7. Continued

Experiment No.	Date	Comments
11	2 Nov 1993	Tried n-hexane again. Oxygen mass flow meter would not regulate flow (would not settle on set point). Also, check valve in hydrocarbon supply line found to be defective, allowing backflow into HC supply circuit. Order placed for new check valve.
12	8 Nov 1993	Another experiment with n-hexane. Replaced HC supply line check valve. HC pump would not prime. Problem traced to damaged "O" ring in inlet check valve. Oxygen flow controller would not regulate flow, causing excessive oxygen flow. Could not reach critical temperature at reactor inlet. Problem traced to defective oxygen check valve. Defective check valve allowed oxygen supply line to fill with SC water, which condensed. Liquid water interfered with operation of oxygen flow controller.
13	17 Nov 1993	New high temperature check valves installed. System pressure tested. Experiment with n-hexane. Positive indications on exothermic reaction. Temperature increased as amount of oxygen increased. Apparent mixing problem. Able to control temperature by changing amount of fuel added.
14	18 Nov 1993	Fabricated and installed mixing tee assembly for mixing SCW-HC and O_2. Autoignition and oxidation of n-hexane occurred but no significant increase in fluid temperature was observed. Oxidation reactions apparently still limited by mixing rate.
15	29 Nov 1993	Fabricated and installed mixing tee assembly for mixing SCW-HC and O_2 from 1/8-inch components instead of 1/4-inch used previously. Idea was to increase flow velocity to promote mixing. Significant improvement in oxidation efficiency was achieved. Temperatures exceeding 1,200°F were achieved at reactor inlet and short distance into reactor. Oxidation of hexane nearly complete, but oxygen consumption too high (about 700 percent excess O_2). Significant temperature loss over length of reactor. Outlet temperature did not exceed 550°F.

Table 7. Continued

Experiment No.	Date	Comments
16	9 Dec 1993	Fabricated, installed, and tested a new mixing assembly consisting of a 1/4-inch mixing tee followed by a porous (sintered metal) plug. The idea is that the components will be intimately mixed by being forced through the small channels in the porous plug. A possible problem could be plugging of the small passages in the sintered metal with products of pyrolysis. Excellent results were achieved. The design temperature was achieved with minimum (stoichiometric) oxygen consumption. Unfortunately, the porous element did plug up after about 1 hour of operation.
17	13 Dec 1993	Fabricated, installed, and tested a mixing assembly consisting of a 1/4-inch mixing tee followed by a closed end tube with several small diameter holes drilled around the periphery of the closed end. Basically the same as the porous plug, but having fewer, larger pores. Worked reasonably well, oxygen consumption being about 150 percent stoichiometric.
18	21 Dec 1993	Fabricated, installed, and tested a mixing assembly consisting of a 1/4-inch mixing tee followed by an open ended tube exhausting into a larger diameter tube tightly packed with small chips of stainless steel. The packed bed of metal chips acts as an orifice. Performance about the same as previous design.
19	12 Jan 1994	Fabricated and installed a mixing assembly consisting of a 1/4-inch mixing tee followed by an open ended tube exhausting into a larger diameter tube containing a number of orifices in series. Each orifice consisted of a closely fitting steel plug with a small diameter hole bored through off center. The orifices were separated by metal spacers, so that the assembly was comprised of a series of orifices followed by mixing chambers. Oxygen mass flow metering valve failed and was sent to manufacturer to be repaired. Burst disk failed (reason unknown). Replacement disks ordered.
20	23 Feb 1994	Tested sequential orifice mixer with manual control of oxygen flow. Ran system for over 30 minutes at 1,200°F at close to stoichiometric oxygen requirement. No sign of plugging. Also ran system on isopropyl alcohol (IPA, C_3H_7OH). IPA will be used as the solvent/fuel for water based wastes such as some paints and pesticides.

Table 7. Continued

Experiment No.	Date	Comments
21	24 Feb 1994	Additional testing of multiple orifice mixer using hexane and IPA as the hydrocarbon. Examination of the temperature profile through the reactor confirms the results of computer simulation of oxidation of alcohol, specifically, that the heat release rate of alcohol is significantly slower for alcohol than for fuel oil. For oxidation of alcohol, the peak temperature occurs several feet into the reactor. For oxidation of fuel oil, oxidation occurs quickly (mostly in the mixing assembly) and the maximum temperature is reached at the entrance to the reactor.
22	2 Mar 1994	Placed the pressure regulating valve upstream of the condenser (rather than on the gas discharge side of the liquid-vapor separator). Objective was to eliminate control problems caused by intermittent opening of liquid discharge valve. Experiment indicated that better control of system pressure could be achieved by this method if the control valve does not stick (due to deposits on the stem or differential thermal expansion) or wear excessively. In this system, the valve worked very well until it got hot, then it would fail to open all the way. System was reconfigured to original design.
23	30 Mar 1994	Installed new Type 2 reactor, consisting of a 200-foot length of C-22 tubing coiled into a helix and enclosed in an electric radiant furnace. Inoperative fuel/SCW check valve permitted oxygen to mix with hydrocarbons before entering the mixing assembly. This caused the tubing carrying the fuel/SCW mix to locally overheat and burn through. System was safely shut down using the emergency stop switch. Damaged tubing and check valve were replaced.
24	4 Apr 1994	Successful operation of Type 2 reactor was achieved. This experiment was performed with the furnace heating elements switched off in order to measure the nominal heat loss rate from the reactor coil. Even with the heaters off, the outlet gas temperature reached its highest value to date: 850°F.

Table 7. Continued

Experiment No.	Date	Comments
25	5 Apr 1994	Operation with diesel fuel. Evidence of poor mixing: fuel in liquid discharge, low temperature (850°F) at stoichiometric oxygen. 25 SLPM of O_2 (about 300 percent excess O_2) required to reach operating temperature. Liquid level sensor in L-V separator failed. Mixer tube had catastrophic failure.
26	20 Apr 1994	Reactor repaired. Automatic O_2 control valve received from repair shop and installed. System operated on hexane with furnace turned on. Liquid level sensor failed to operate correctly and L-V separator filled with water again. O_2 control valve worked briefly, then stuck in closed position. System shut down.
27	21 Apr 1994	Oxygen mass flow control valve failed to respond to control input. System shut down without attempting to run experiment.

CONCLUSIONS

Supercritical water oxidation appears to be a technically, environmentally, and economically attractive method of destroying a wide variety of hazardous organic wastes. The estimated Navy need for SCWO technology is a minimum of seven waste processing plants of 1 gallon per minute of organic material capacity. The estimated capital cost of each plant is $6M. The estimated disposal cost is approximately $8 per gallon, which is substantially lower than current disposal costs of $15 to $35 per gallon. It is estimated that SCWO can be implemented at a large scale and in a safe, reliable, and cost effective manner. Waste streams that contain a large amount of mineral-acid forming chemical species or that contain a large amount of dissolved solids present a challenge to current SCWO technology. Solutions to the problems of corrosion and material deposition are under development by several organizations.

A comprehensive waste characterization study was performed. It was determined that the Navy generates about 10,000 tons of organic hazardous waste per year that could be effectively destroyed using the SCWO process. Organic wastes are about 20 to 30 percent of the total Navy waste stream. It is estimated that disposal of these wastes costs the Navy approximately $40M per year.

An independent study performed for the Chief of Naval Operations (Code N45) by Naval Facilities Engineering Command Headquarters estimated that life-cycle savings for a full-scale

SCWO plant range from $15M to $30M depending on the location of the plant. Estimated life-cycle savings for Navy-wide implementation is $100M to $300M.

A conceptual design of a large-scale SCWO system for Navy application was produced. The capacity of the SCWO system was based on the amount of waste produced in geographical regions having concentrations of Navy activities. There is a need for at least seven large regional SCWO plants each with a capacity of 1 gallon per minute of organic material (about 12,000 gallons per day of waste plus water). Eleven SCWO plants of about 6,000 gallons per day total throughput could be used in place of the seven large regional SCWO plants. SCWO plants in the 5,000- to 7,000-gallon per day capacity range are currently under development by private industry.

Experimental studies were conducted to determine if SCWO can effectively destroy components of the Navy organic hazardous waste stream. Results prove that typical organic wastes are destroyed with an efficiency of at least 99.999 percent in an SCWO system operating at 1,200°F reactor temperature, 3,600 pounds per square inch reactor pressure, and 10 seconds reactor residence time.

A small SCWO pilot plant was designed, built, and installed at NFESC to test several engineering design ideas and acquire operating experience. Over 100 hours of operating experience were accumulated in the course of performing many different experiments. Numerous problems were overcome in making the SCWO unit operational. Some problems were caused by flaws in the design of the unit, while other problems were caused by component failure and operational errors. The SCWO process was found to be effective and easily controlled. Safety hazards were judged to be acceptable if design, construction, and operating criteria and procedures were carefully followed.

In summary, supercritical water oxidation appears to be a technically, environmentally, and economically attractive method of destroying a wide variety of hazardous organic wastes. The estimated Navy need for SCWO technology is a minimum of seven waste processing plants of 1 gallon per minute of organic material capacity.

ACKNOWLEDGMENTS

The author wishes to acknowledge the very significant contributions to this project of Mr. Raymond Cappillino of NFESC. Mr. Cappillino, a senior technician at NFESC, was responsible for installation of the NFESC bench scale SCWO unit and performed most of the required system modifications. In addition, Mr. Cappillino assisted in operation of the apparatus, data acquisition, and data reduction. The author also acknowledges the support of the NFESC shops and facility support personnel. The author also wishes to thank Mr. Michael Bryant of Arthur D. Little, Inc. for his many suggestions on the design and construction of the bench scale SCWO apparatus.

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Appendix A

TYPICAL HAZARDOUS WASTE GENERATION DATA REPORTED BY PROCESS CODE

CY90 HAZARDOUS WASTE GENERATION BY PROCESS CODE
NAVYWIDE

GENERATION PROCESS	GENERATED TONS	BACKLOG TONS	STORED TONS	TREATED TONS	DISPOSED TONS	RECYCLED TONS
None Reported	51.97	0.00	37.04	0.08	14.84	0.00
Abrasive Blasting	9,815.39	435.89	719.08	212.17	4,239.41	5,080.62
Battery Shops	775.03	41.28	65.85	29.57	181.91	538.99
Bilge/Tank Derusting	37.35	19.72	6.39	8.90	41.79	0.00
Bilge/Tank Emptying/Cleanin	36,328.51	2,297.85	66.83	11,629.75	14,794.98	12,134.80
Biological Operations	39.04	8.67	19.46	0.03	28.22	0.00
Boiler Lay-up	412.39	3.70	1.40	2.88	56.20	355.60
Chemical Paint Stripping	1,569.94	62.20	94.06	180.51	1,320.61	36.90
Electronics & Refrigeration	72.98	3.01	3.07	15.95	45.09	11.89
Electroplating	2,253.22	123.48	225.58	759.27	1,369.23	22.63
Expired Shelf Life/Non-ship	424.88	54.58	103.94	46.41	287.09	42.02
Firefighting Operations	555.60	16.44	66.96	38.27	269.82	197.00
Fluids Changeout	8,610.62	268.13	420.35	381.73	3,374.33	4,702.19
Forced Obsolescense	2.53	0.22	0.57	0.00	2.18	0.00
Industrial Maintenance	953.22	22.01	68.14	187.43	661.77	53.60
Industrial Operations	2,201.90	92.92	151.34	746.90	1,150.57	243.41
Industrial Waste Treatment	3,495.75	932.60	1,071.68	540.86	2,815.38	0.43
Installation Restorations	1,389.07	5.42	32.41	13.74	1,211.48	136.86
Medical	27.24	3.10	4.83	3.71	20.94	0.87
Miscellaneous	15,497.67	233.07	283.54	3,285.60	3,795.20	8,366.31
NEW Bilge/Tank Emptying/Cle	1,089.36	0.00	160.00	0.00	929.36	0.00
NEW Electroplating	193.61	0.00	0.00	0.00	193.61	0.00
NEW Expired Shelf Life/Non-	3.11	0.00	0.32	2.19	0.60	0.00
NEW Fluids Changeout	0.51	0.00	0.00	0.51	0.00	0.00

CY90 HAZARDOUS WASTE GENERATION BY PROCESS CODE
NAVYWIDE

GENERATION PROCESS	GENERATED TONS	BACKLOG TONS	STORED TONS	TREATED TONS	DISPOSED TONS	RECYCLED TONS
NEW Industrial Operations	0.01	0.00	0.00	0.01	0.00	0.00
NEW Miscellaneous	4,910.35	0.00	0.00	1.35	4,909.00	0.00
NEW Research & Development	3.41	0.00	2.78	0.63	0.00	0.00
NEW Torpedo Cleaning	6.44	0.00	0.00	0.00	0.00	0.00
One-Time Only	3,643.43	73.31	221.91	369.29	3,097.94	27.60
Ordnance, Demil/Disposal	1,016.03	3.26	3.53	971.14	44.62	0.00
Ordnance, Evaluation	46.15	0.70	0.90	41.00	3.62	1.33
Ordnance, Manufacturing	1,697.95	5.93	30.00	1,565.89	102.99	0.00
Painting Operations	4,556.57	358.53	627.37	934.42	3,221.58	129.63
Pipe Flushing	601.79	83.27	26.61	271.83	91.18	295.44
Preservation & Packaging	33.39	1.42	10.87	0.04	23.80	0.09
RCRA Corrective Action	2,185.64	218.02	0.00	0.00	1,793.66	610.00
Research & Development	163.40	2.85	14.71	19.08	75.39	57.08
Ship's Boiler Cleaning	1,154.94	8.49	3.95	851.06	308.42	0.00
Ship's Off-loaded Stores	407.83	8.74	46.83	73.87	126.22	169.65
Ship's Wastes	12,226.76	55.25	35.49	4,661.18	1,053.67	6,531.67
Solvent Degreasing	1,399.75	77.94	160.40	208.93	616.76	491.60
Spill Clean-up	1,107.59	185.34	143.82	51.08	1,088.84	9.20
Torpedo Cleaning	1,295.58	50.95	39.25	90.97	1,178.90	0.25
WASTEWATER	4,461.00	0.00	0.00	4,461.00	0.00	0.00
	126,718.91	5,758.28	4,971.25	32,659.22	54,541.17	40,247.65

Appendix B

SEQUENCE OF OPERATION
OF
SUPERCRITICAL WATER OXIDATION SYSTEM

THEORY OF OPERATION

Hazardous organic compounds such as chlorinated solvents, PCBs, pesticides, paint, and paint stripping chemicals can be oxidized into environmentally benign compounds such as water vapor, carbon dioxide, sodium chloride, and nitrogen gas by: (1) dissolving the organic compound in supercritical water, and then (2) adding oxygen so that the organics are oxidized (combusted) into nontoxic forms. The oxidation reactions take place at a low temperature (compared to incineration), so that undesirable products of high temperature oxidation, such as NO_x and dioxin, are not formed. Supercritical water is water at conditions that exceed 705°F and 3,200 psi.

The sequence of operation for the SCWO is explained in the following paragraphs (refer to Figure B-1).

STARTUP

Cold water from the makeup water supply or the clean water storage tank is pumped to 3,600 psi by pump P-3 and is diverted by valve V-12 so that it flows to an oil- or gas-fired startup heater, HTR-1. The heated water flows from the heater to the reactor vessel R-1. A flow control valve diverts most (90 percent) of the flow leaving R-1 back to the high temperature water heater, HTR-1. The remaining 10 percent of the flow follows the liquid branch of the liquid-vapor separator to the salt evaporator pan EVP-1, from where it is diverted to a drain. The bypass of a small amount of water is required to establish circulation through the system.

The circulating water is slowly heated by HTR-1 and the water, in turn, heats the reactor vessel and connecting piping. After a period of time, the water is heated to supercritical steam conditions of 1,200°F at 3,600 psi. When this condition is reached, a small amount of fuel oil is added to the makeup water stream and the effluent from the reactor (R-1) is monitored to determine if oxidation of the fuel oil occurs. When conditions in the reactor are such that oxidation occurs (detected by a temperature rise across the reactor and the presence of carbon dioxide in the reactor effluent), increasing amounts of fuel oil are added to the makeup water until the oxidation reaction is self-sustaining. After self-sustaining reaction has been achieved, the startup heater is slowly valved out of the circulation loop and the system runs on energy from the fuel oil.

The fuel oil supply valve is gradually closed while the hazardous waste supply valve is simultaneously opened. The hazardous waste valve is opened the maximum amount compatible with the energy input requirement of the system. In this design, the mix of hazardous waste, fuel oil, and water must be about 1,300 Btu per pound.

NORMAL OPERATION

Hazardous liquid organic materials are first finely divided and blended in mixer MR-1. Next, the organic waste materials are mixed with water and sufficient fuel oil (to meet the minimum energy input requirement) in mixer MXR-2. Mixer MXR-2 also serves to keep particulates in suspension. Most of the water for the process is continuously recirculated. Makeup water is required to replace the amount of water formed by oxidation of the organic materials (this amount of water is discharged from the system).

The water/organics emulsion is next pumped up to approximately 3,600 psi by pump P-3. A fluid mixer MXR-3 mixes the cold liquid influent with hot (1,100°F) exhaust gases discharged from the reactor. The amount of hot exhaust gas mixed with the liquid influent is proportioned so that the temperature of the resulting mixture is about 750°F. The mixing takes place immediately before the fluid stream enters the salt removal system. The solvent properties of supercritical water are almost the inverse of water at normal conditions. As a consequence, many ionic salts (e.g., sodium chloride and calcium sulfate) precipitate out of solution under supercritical conditions, while most organic compounds and gases become completely soluble in supercritical water. The mixture of supercritical water vapor and organic vapors (and a lesser amount of salts and other solids) is next transported to the reactor vessel.

At the entrance of the reactor vessel, oxygen gas is added to the vapor mixture. The amount of oxygen that is added is that required for complete combustion of the organic material in the influent stream. The proposed source of oxygen for the SCWO system is purchased liquid oxygen. Liquid oxygen is pumped to 3,600 psi by pump P-4 then vaporized with process waste heat using a heat transfer loop consisting of two heat exchangers (HX-1 and HX-2), a heat transfer fluid circulating pump (P-5), and a temperature control system.

After oxygen has been added to the vapor mixture, the mixture enters the reactor vessel. The reactor vessel is basically an insulated tube of sufficient length to provide the residence time required for the reactions to go to completion. The oxidation reactions occur at relatively low temperature, which implies a slow reaction rate. Thus, a comparatively long reactor tube is required. The reactor vessel may be on the order of 100 feet in length, but folded into a compact shape. The chemical reactions that take place in the reactor vessel convert the hazardous organic materials into water vapor, carbon dioxide, nitrogen gas, and nontoxic compounds of chlorine, sulfur, phosphorous, and other elements. The chemical reactions also release heat, which raises the temperature of the fluid stream. The amount of temperature rise is controlled by regulating the energy content of the influent stream. In this design, the energy content is controlled so as to produce a gas temperature at a reactor discharge of 1,200°F.

The gases discharged from the reactor pass through a filter element that removes soot and other small particulates. A portion of the reactor effluent is compressed by compressor P-6 and used to heat the influent stream. The remaining gases pass through two heat exchangers (HX-2 and HX-4) which cool the gases to approximately the critical temperature (705°F). The gases then pass through a cascade type pressure-temperature (P-T) letdown system. The P-T letdown system separates the fluid stream into three parts: a liquid water part, a noncondensable gases part, and a concentrated brine part. The liquid water part may be acidic due to the presence of chloride, carbonate, sulfate, and other anions. If the liquid water part is acidic, the water is neutralized in the clean water storage tank by mixing in alkaline solution. The noncondensable gases are typically gases such as carbon dioxide and nitrogen. The metallic salts that are not removed in the salt separator (or are a product of the oxidation reactions) tend to concentrate in the liquid phase of the liquid-vapor separators (LVS-1, LVS-2, and LVS-3). The result is a liquid fraction from LVS-3 that may contain a high percentage of salts. The water in this fraction is evaporated using waste heat, leaving only a concentrated brine or a mixture of salts to be disposed.

SHUTDOWN

The SCWO system is shut down by first closing off the supply of hazardous waste, while simultaneously opening the supply of fuel oil. The system is run on fuel oil for a brief period of time. The amount of fuel oil added to the water is then gradually reduced so as to produce a reactor discharge temperature that slowly decreases with time. This is done to minimize thermally-induced stresses in the components. When the concentration of fuel reaches a value such that the reaction is not self-sustaining, the fuel, oxygen, and water supply valves are closed. The circulating pump (P-3) is stopped and the components are allowed to slowly cool to ambient temperature.

NOTES

The following items are not explicitly shown in Figure B-1 but should be considered in cost and design calculations:

1. Operating Hours:

The proposed SCWO system would be operated about 4,000 hours per year. It is planned that the unit would be brought up to operating temperature during one working shift on Monday, then operated to destroy hazardous waste materials for about 100 continuous hours (4 days and 3 working shifts per day). Following the period of operation, the SCWO would be allowed to cool, then residual salts cleaned out of the system and the unit prepared for the following week's operation.

2. Operating Personnel:

It is assumed that three people will be required to operate the unit: (1) an operating engineer (preferably a licensed boiler operator) to actually operate and maintain the system, (2) a hazardous waste handling technician to load waste into the SCWO unit, rinse drums, and so forth, and (3) a supervisor to make operating decisions, conduct and interpret analyses of discharge liquids and gases, and keep records.

3. Heat Rejection System:

A forced draft heat exchanger or cooling tower is required to supply cooling water to the main condenser (HX-5).

4. Instrumentation and Control:

Flow, temperature, pressure, pH, and [illegible]ors are required for both monitoring and control. The system is expected to be highly automated, with programmed startup, run, and shutdown sequences of operation. Overall control logic and data acquisition functions are provided by an industrial grade personal computer or equivalent. Local loop control is provided by individual programmable controllers.

5. Safety:

The SCWO runs at high temperatures and pressures and uses hazardous, flammable, and possibly reactive materials as the feedstock. Therefore, safe operation is of paramount importance, both from a personnel and a regulatory compliance viewpoint. Materials and components must be chosen that will withstand the temperatures, pressures, and corrosive conditions developed within the SCWO system. Piping and pressure vessels must meet applicable code requirements. Valves and fittings must be selected so as to preclude fugitive emissions from the system. Remote operation from a control room is a design option.

6. Analytical Instrumentation:

Instrumentation must be provided that can conclusively prove that the SCWO system is working as designed and that no hazardous influent or toxic products of reaction are being released to the environment. It is anticipated that instrumentation must keep a continuous record of the quality of the liquid and gases discharged from the SCWO system.

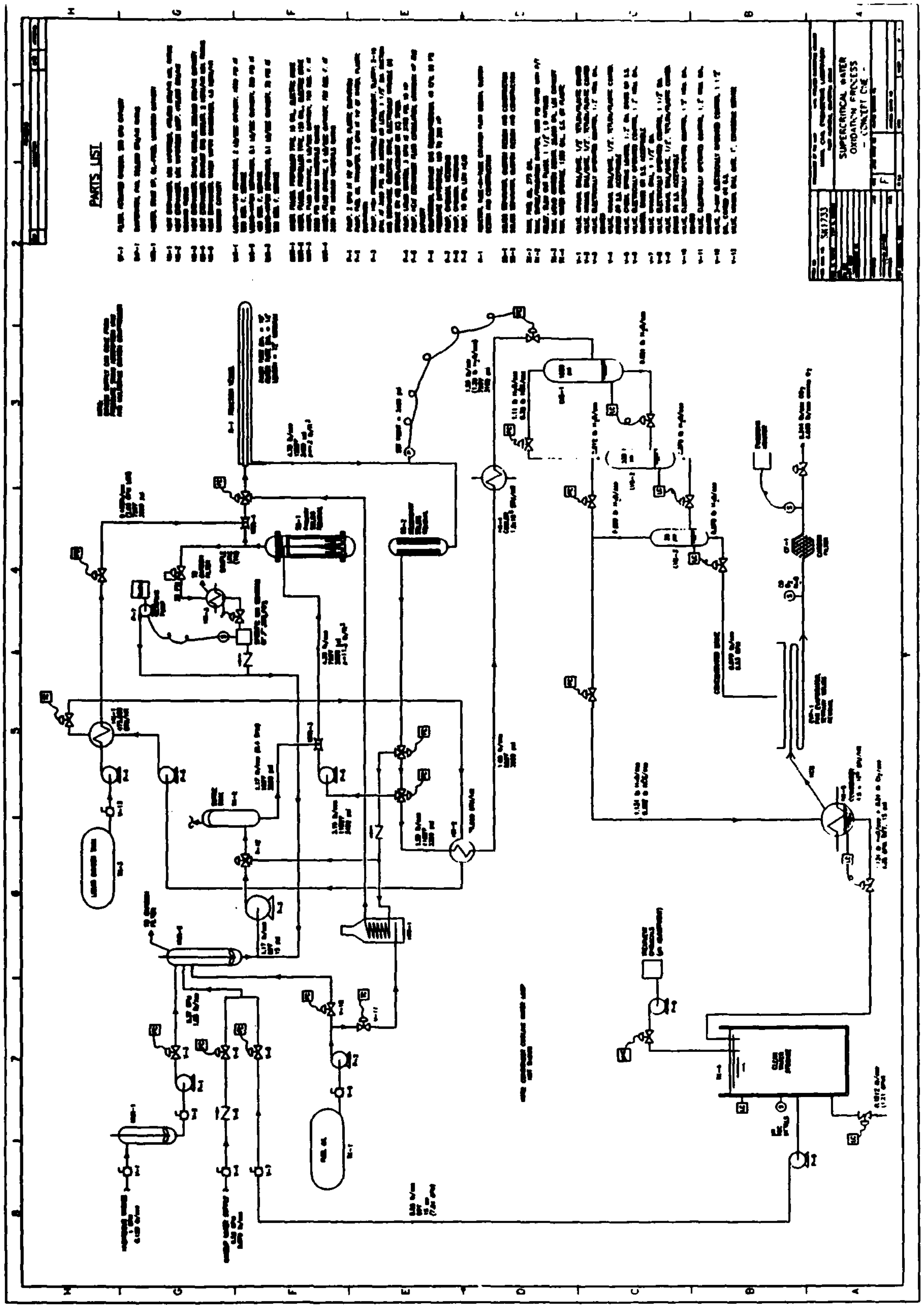

Figure B-1
Process diagram for full-scale SCWO system.

Appendix C

RESULTS OF ORGANIC WASTE DESTRUCTION EFFICIENCY TESTS

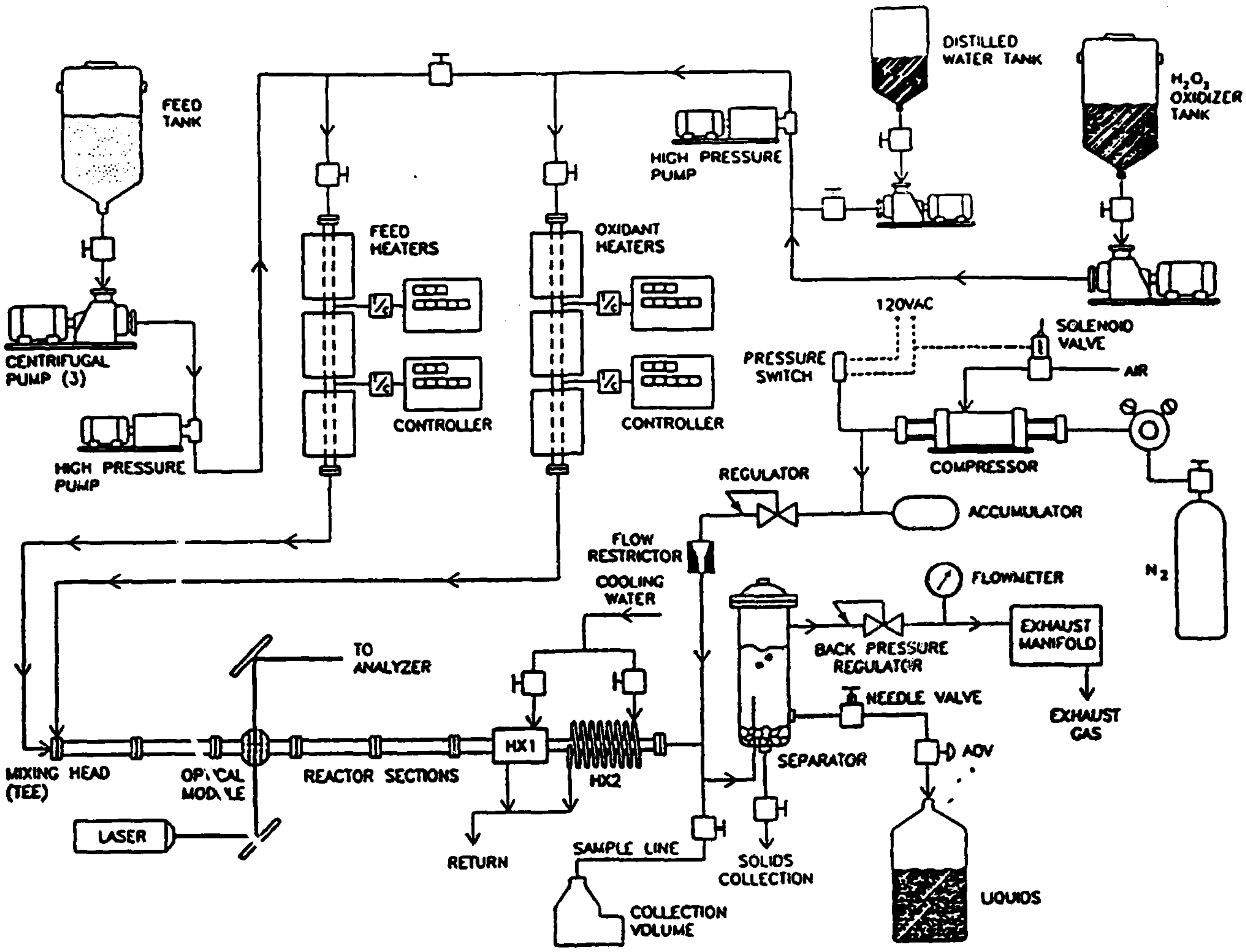

Figure C-1
Schematic diagram of Sandia's SCWO flow reactor. The overall system is composed of five main subsystems or modules: pumping and pressurization, heating, reactor, cool down and separation, and pressure regulation. Each subsystem can be modified easily without affecting the operation of another subsystem. Note that the feed and oxidizer may be preheated separately or together depending on the configuration of the valves supplying the preheat system.

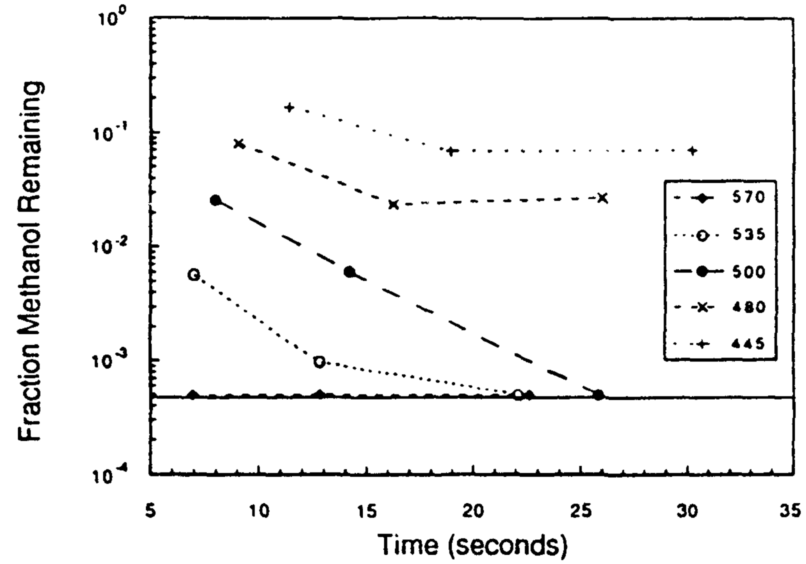

Figure C-2
Results from the oxidation of methanol as a function of residence time and temperature as determined using gas chromatography. The solid line at 5×10^{-4} indicates the experimental detection limit.

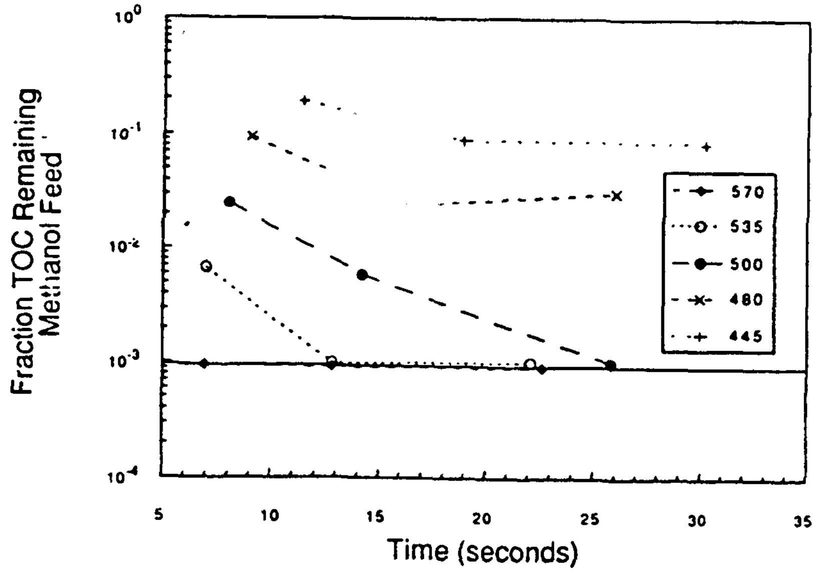

Figure C-3
Results from the oxidation of methanol as a function of residence time and temperature as determined using total organic carbon. The solid line at 9×10^{-4} indicates the experimental detection limit.

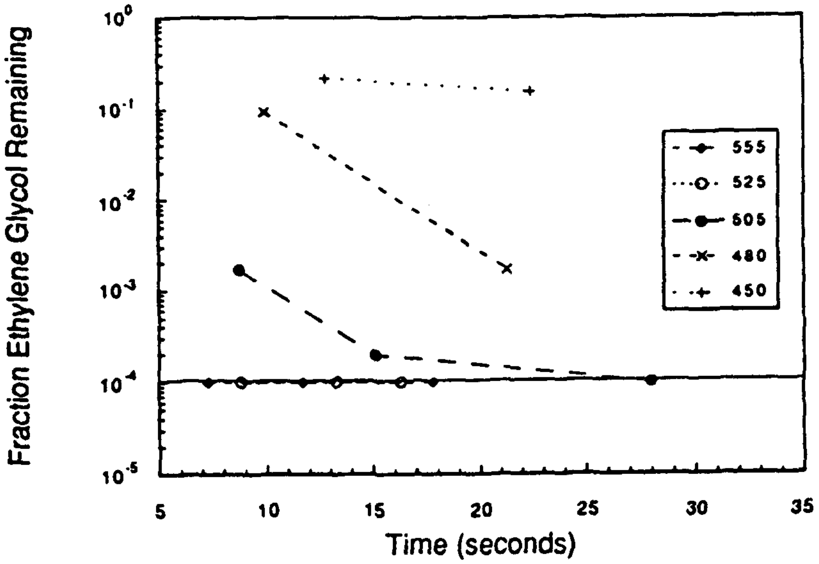

Figure C-4
Results from the oxidation of ethylene glycol as a function of residence time and temperature as determined using gas chromatography. The solid line at 1×10^{-4} indicates the experimental detection limit. The reliability of these g.c. results are suspect because of inherent difficulties with g.c. and ethylene glycol discussed in the text.

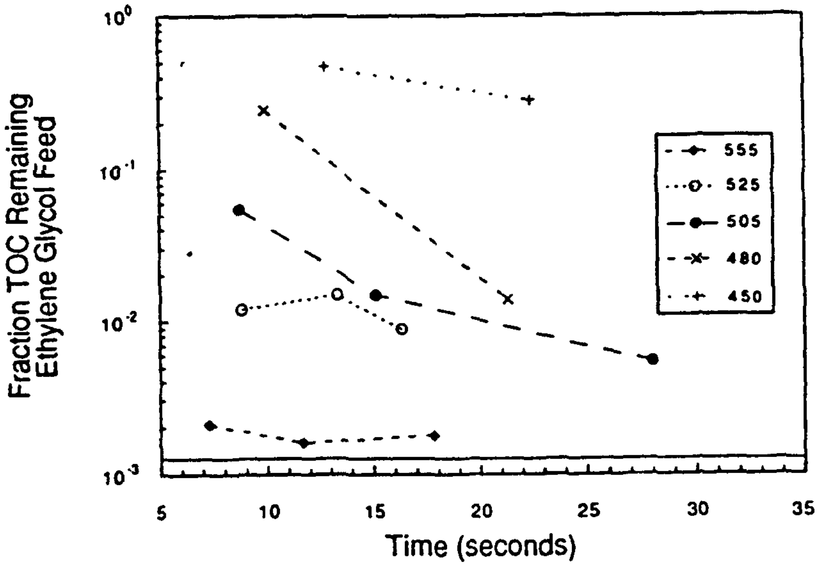

Figure C-5
Results from the oxidation of ethylene glycol as a function of residence time and temperature as determined using gas chromatography. The solid line at 1.2×10^{-3} indicates the experimental detection limit.

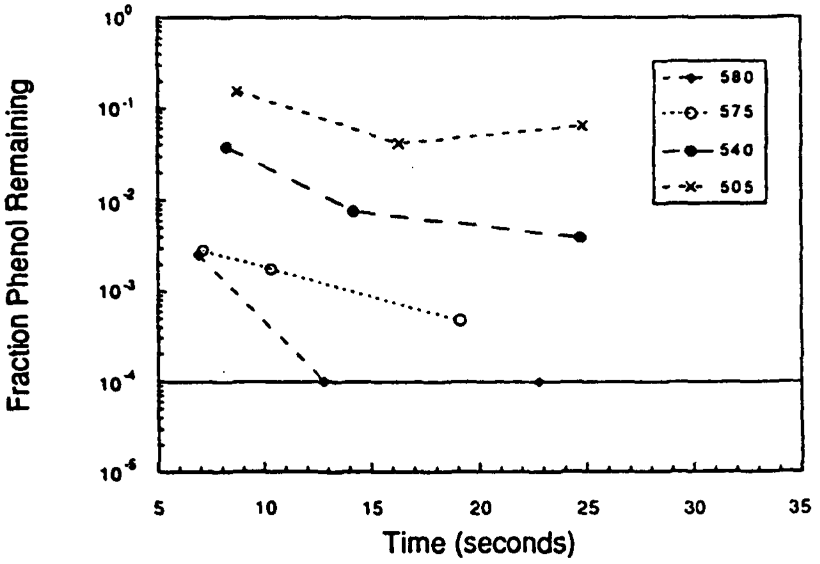

Figure C-6
Results from the oxidation of phenol as a function of residence time and temperature as determined using gas chromatography. The solid line at $1x10^{-4}$ indicates the experimental detection limit.

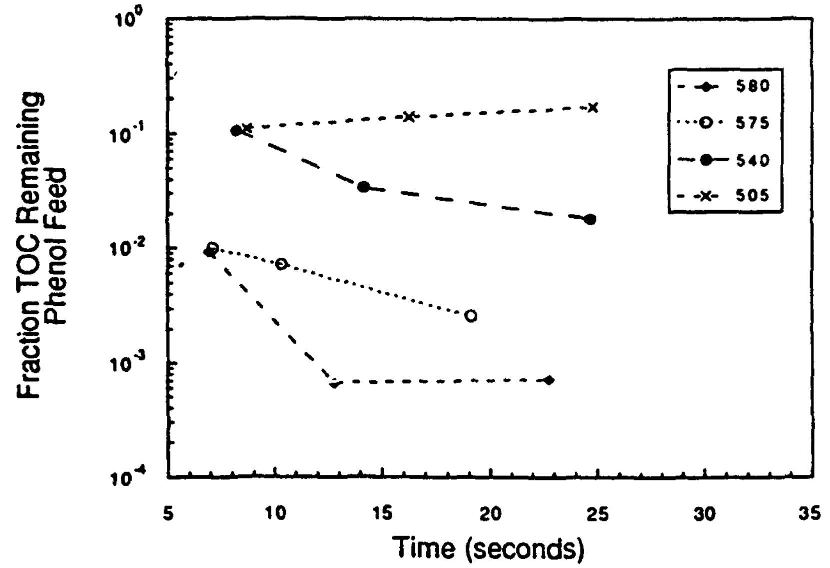

Figure C-7
Results from the oxidation of phenol as a function of residence time and temperature as determined using total orgranic carbon. The solid line at $6x10^{-4}$ indicates the experimental detection limit.

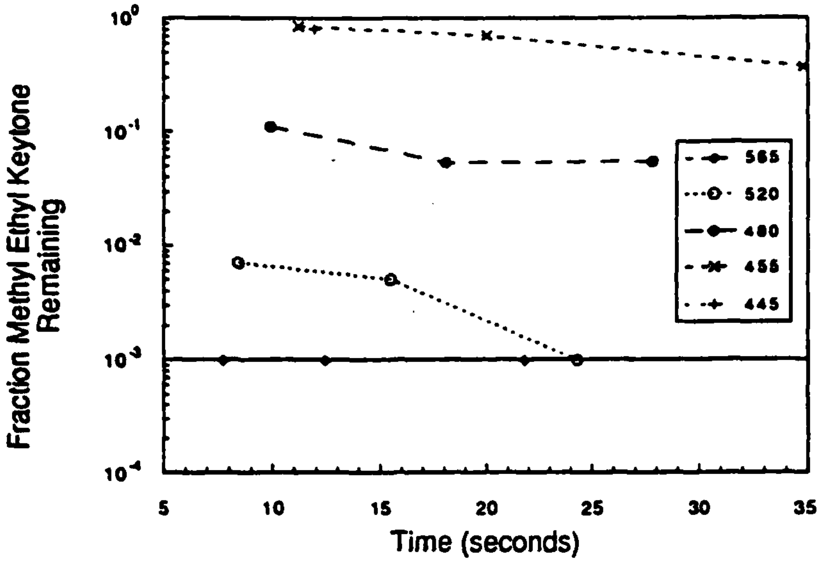

Figure C-8
Results from the oxidation of methyl ethyl ketone as a function of residence time and temperature as determined using gas chromatography. The solid line at $1x10^{-3}$ indicates the experimental detection limit.

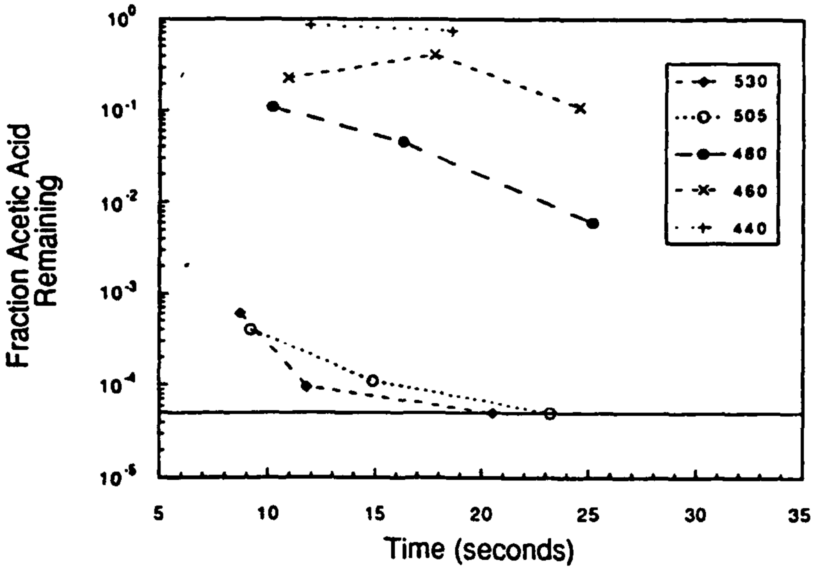

Figure C-9
Results from the oxidation of acetic acid as a function of residence time and temperature as determined using gas chromatography. The solid line at $5x10^{-5}$ indicates the experimental detection limit. Note that the highest temperature point for acetic acid is only 532°C.

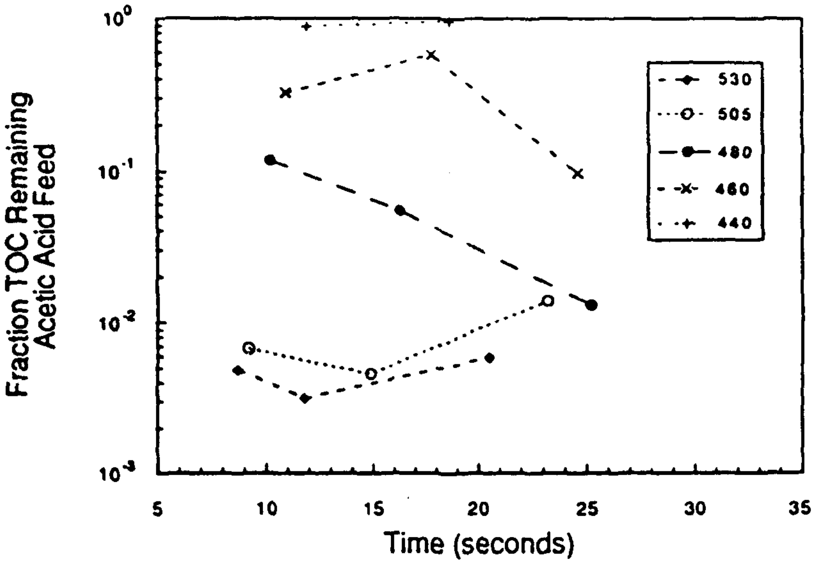

Figure C-10
Results from the oxidation of acetic acid as a function of residence time and temperature as determined using gas chromatography. The experimental detection limit was $1x10^{-3}$.

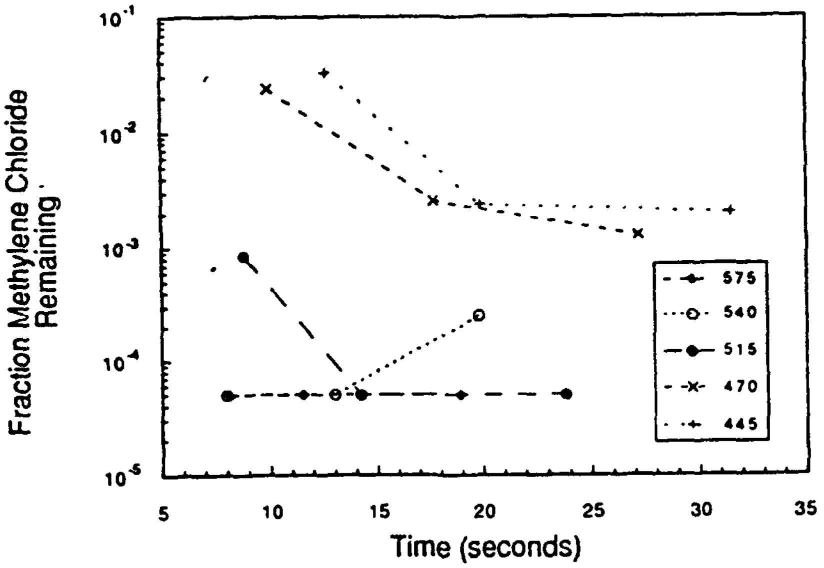

Figure C-11
Results from the oxidation of methylene chloride as a function of residence time and temperature as determined using gas chromatography. The solid line at $5x10^{-5}$ indicates the experimental detection limit.

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