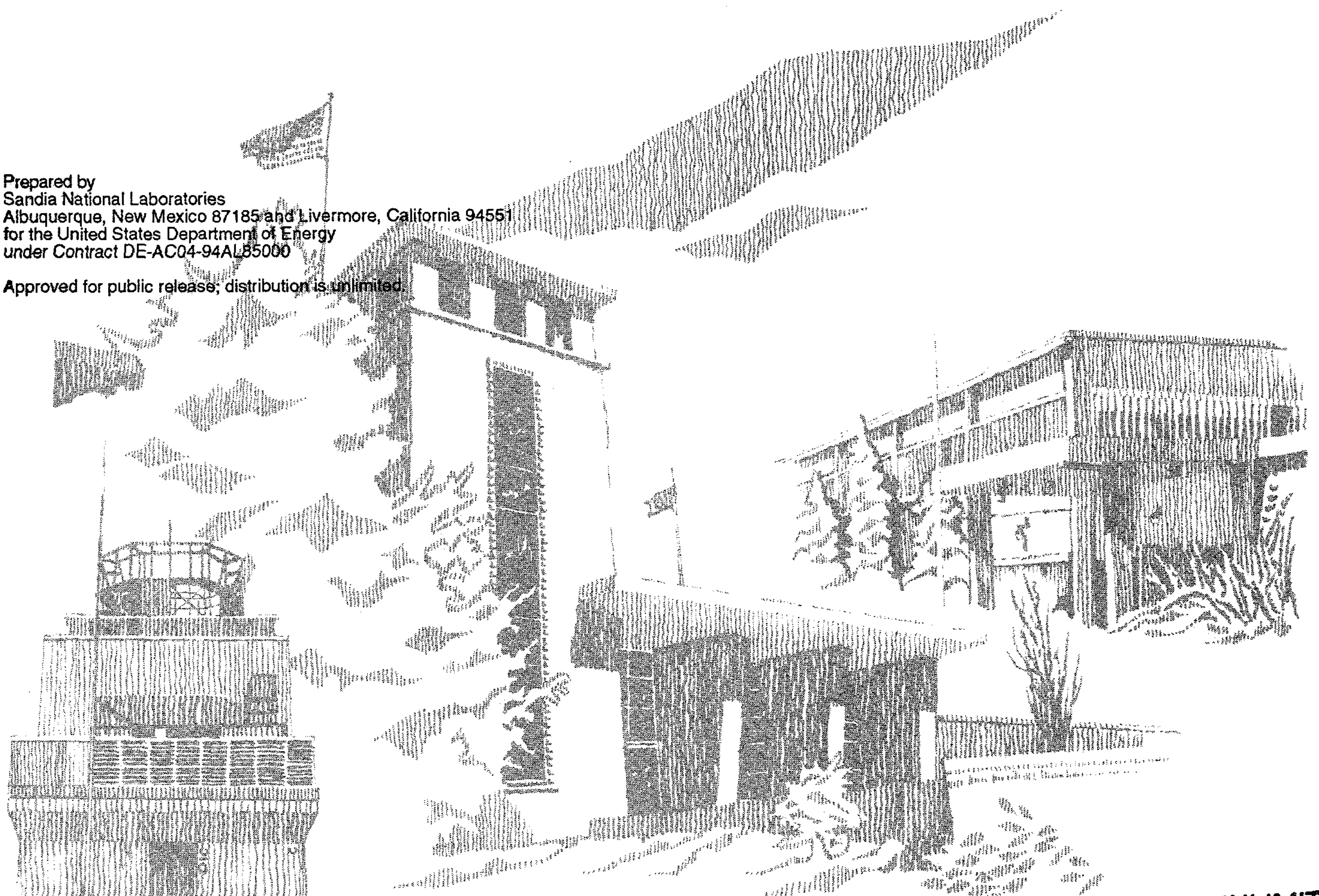
SANDIA REPORT

SAND95-8005 • UC-402
Unlimited Release
Printed June 1995

Pollution Prevention Opportunity Assessment for the Supercritical Water Oxidation Flow Reactor

N. M. Phillips



Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94551
for the United States Department of Energy
under Contract DE-AC04-94AL85000

Approved for public release; distribution is unlimited.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This report has been reproduced from the best available copy.

Available to DOE and DOE contractors from:

Office of Scientific and Technical Information
P. O. Box 62
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.
Springfield, VA 22161

UC-402

SAND95-8005
Unlimited Release
Printed June 1995

POLLUTION PREVENTION OPPORTUNITY ASSESSMENT FOR THE SUPERCRITICAL WATER OXIDATION FLOW REACTOR

Norman M. Phillips
Sandia National Laboratories/California

ABSTRACT

This pollution prevention opportunity assessment was conducted to evaluate the operation of the supercritical water oxidation flow reactor, which is located in Building 906, Room 107. This assessment documents the processes, identifies the hazardous chemical waste streams generated by these processes, recommends possible ways to minimize waste, and serves as a reference for future assessments of the supercritical water oxidation reactor process.

CONTENTS

ILLUSTRATIONS AND TABLES

POLLUTION PREVENTION OPPORTUNITY ASSESSMENT FOR THE SUPERCRITICAL WATER OXIDATION FLOW REACTOR

Introduction

Department of Energy (DOE) orders 5400.1 and 5400.3 mandate the development of a waste minimization program.[1,2] The program's goals are to:

- reduce volumes of hazardous wastes and toxicity,
- implement a system of tracking and reporting improvements, and
- devise a method for performing tasks.

To satisfy the requirements of this program, Sandia conducts pollution prevention opportunity assessments (PPOAs) to identify waste-generating processes. The information collected from a PPOA then is used to identify waste minimization opportunities.

This PPOA was conducted on the supercritical water oxidation flow reactor, according to the *Pollution Prevention Opportunity Assessment Plan* for SNL/California.[3] The primary purpose of this PPOA is to document the supercritical water oxidation process, identify the waste streams, and serve as a reference for future assessments. It will be reevaluated in approximately 18 to 24 months, after the lab personnel have had enough time to implement recommendations, and the results will be compared to the baseline established in this assessment.

Summary

The supercritical water oxidation flow reactor is used to conduct fundamental research and development on the characteristics of the oxidation process in supercritical water. Studies are conducted to determine the kinetics of the oxidation of various aqueous organic mixtures. The ultimate goal is to develop processes to treat aqueous hazardous waste containing small amounts of organics and to reduce them to nonhazardous waste.

The research is dynamic and conducted on various mixtures of organic materials and water. Therefore, waste streams and volumes of waste generated are not consistent for any length of time. In 1993 and 1994, the supercritical water oxidation process generated approximately 1,000 kg waste per year, but the number, volume, and types of chemicals varied widely. This inconsistency makes identifying waste minimization opportunities difficult.

However, one way to minimize waste from this process would be to determine if each waste generated is indeed a hazardous waste. In some cases, the amount of organic material left in the aqueous solution is less than 100 ppm. The Environmental Operations Department may be able to use the analytical data generated during experiments (the concentration and the type of solution components) to determine whether the effluent from the experiments may be disposed of in the sanitary sewer as nonhazardous waste or if it must be disposed of as hazardous waste. If the organic material concentration is within discharge regulations, the aqueous solution may be discharged to the sanitary sewer.

Facility

The supercritical water oxidation flow reactor is located in Bldg. 906, Rm. 107 (see Fig. 1).

Products

Fundamental research and development of the detailed chemical kinetics of oxidation processes in supercritical water.

Background

Supercritical water oxidation is an emerging technology under development by government laboratories, universities, and private industry for the treatment of aqueous wastes. The process runs at temperatures and pressures above the critical point of water (typically 450–650°C and 240 bar), and applies to waste streams containing 0–20% organics in water.

An early patent for the process included data showing 99.99% destruction of many normal and halogenated hydrocarbons, including tetrachloroethylene, DDT, and PCBs. Since then, the number of organic and inorganic chemicals, as well as complex mixtures, treated by supercritical water oxidation has grown considerably.

The application of supercritical water oxidation to most Department of Defense and DOE hazardous wastes requires that the technology be advanced beyond its current level of development. Improvements will not be possible without better predictive models for the time, temperature, density, and concentration dependence of the oxidation process.[4]

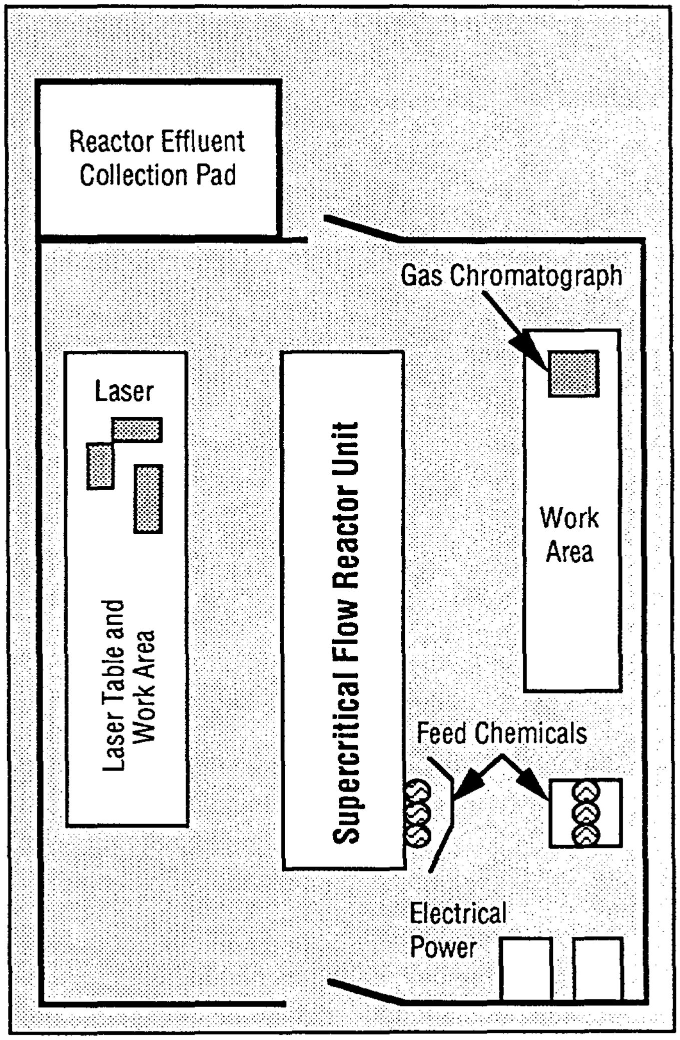


Figure 1. Layout of the Supercritical Water Oxidation Flow Reactor Area, Bldg. 906/Rm. 107.

Process Description

The supercritical water oxidation system comprises five main subsystems or modules: pumping and pressurization, heating, reactor, cool-down and separation, and pressure regulation.[5] Generally, the process follows these steps (see Fig. 2):

1. Aqueous surrogate hazardous waste is pressurized and heated above its liquid/vapor critical point.
2. An oxidizing agent (oxygen, air, or hydrogen peroxide) is injected into the fluid.
3. The mixture is allowed to react for a short duration.
4. The reaction products are cooled and separated. These reaction products include water, carbon dioxide, molecular nitrogen, and other gases, depending on the composition of the waste.

The effluent from the process can be evaluated for compliance with applicable discharge regulations before release to the environment.[6]

The supercritical water oxidation flow reactor has a maximum operating temperature of 650°C and a maximum operating pressure of 7500 psi. Flow rates can be varied from about 1.5 mL/sec (nominal ambient-condition feed water, 25°C) to 0.1 mL/sec. A series of Marshal tube furnaces, with a combined power of 4500 W per line, heat the two parallel

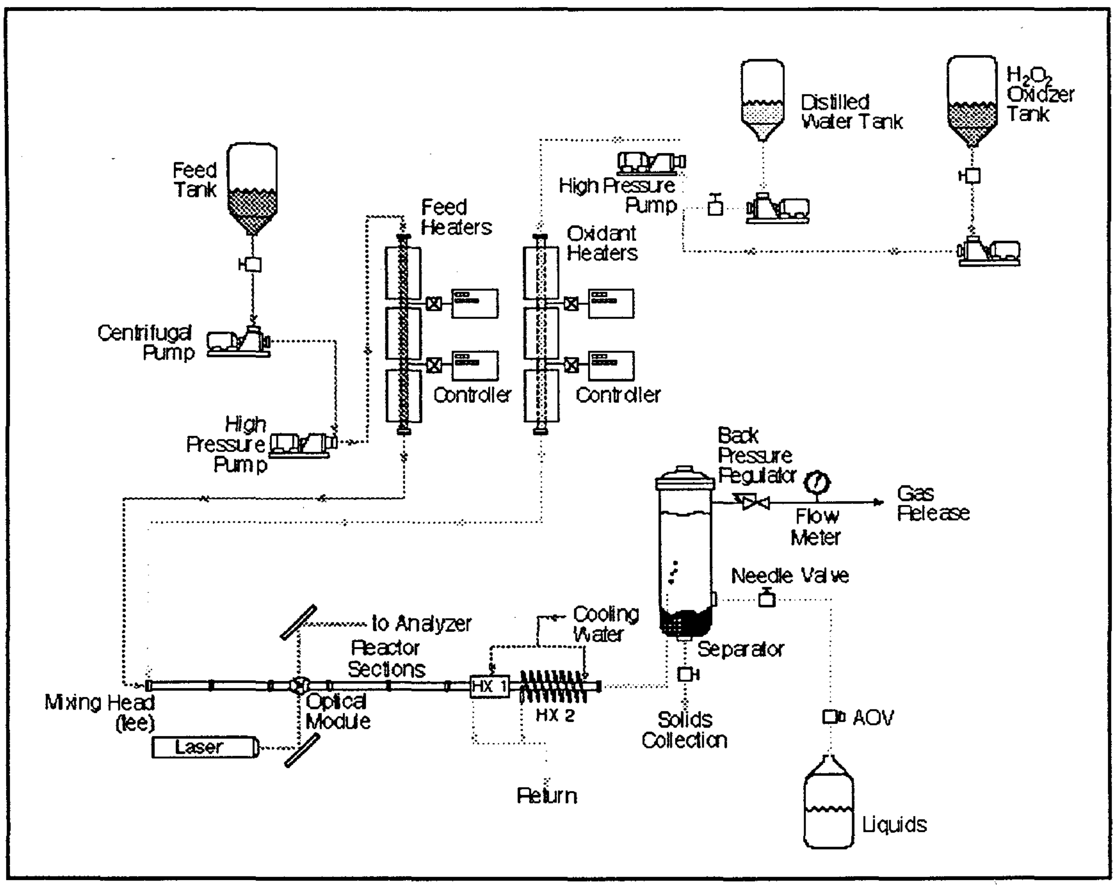


Figure 2. Schematic of the Supercritical Water Oxidation Reactor Process.

preheat lines. These furnaces are individually controlled with Omega process controllers. Six Watlow 375 W cable heaters heat the 400-cm reactor section to maintain isothermal conditions along the reactor. The high-temperature portions of the system comprise 9/16" O.D. 3/16" I.D. Inconel 625 tubing and high-pressure fittings as unions. Inconel 600, sheathed, Type K thermocouples, located directly in the fluid at T-unions, are used to measure the temperature of the feed, oxidizer, and reacting fluid. The reaction is quenched with a counterflow heat exchanger, which lowers the fluid temperature below 400°C in approximately 0.3 sec.[5]

During processing, laboratory personnel measure the concentration of the reactants directly in the reacting flow using laser-based spontaneous Raman spectroscopy.[6]

Waste Stream Profiles

Approximately 99% of the hazardous waste generated by the supercritical water oxidation lab are effluents from the reactor process. Figure 3 is a general process flow diagram for the reactor.

Waste Generation

Table 1 and Fig. 4 show the annual waste generation for 1993 and 1994. Note: Figure 4 does not include the following: acetic acid, empty containers, ethylene glycol, phenol, water/ sodium carbonate, and rags/wipes.

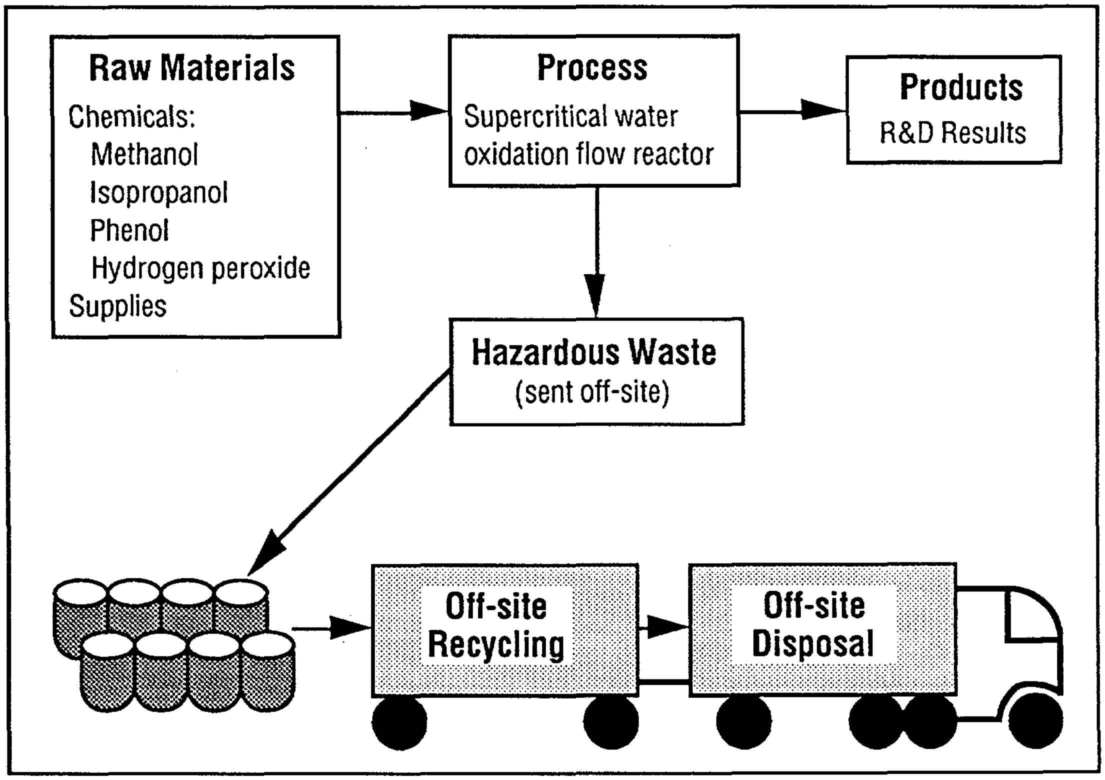


Figure 3. Process Flow Diagram for the Supercritical Water Oxidation Reactor.

Table 1. Hazardous Waste Generation Summary (1993–94)[7]

Waste Stream I.D.	Waste generated (kg) in 1993	Waste generated (kg) in 1994
Acetic acid	3	0
Acetone	109	0
Amido napthol	61	0
Calcium sulfate	81	0
Empty containers	13	5
Ethylene glycol	1	1
HCL/iodine	2	2
HCL/methylene chloride	78	2
Phenol, crystallized	0	0.7
1,1,1-trichloroethane	16	4
Water with 3% methanol	220	1072
Water with sodium carbonate	22	9
Water with nickel, chromium	261	0
Water with sodium hydroxide	36	1
Rags/wipes	5	0.2
Total	**908**	**1097**

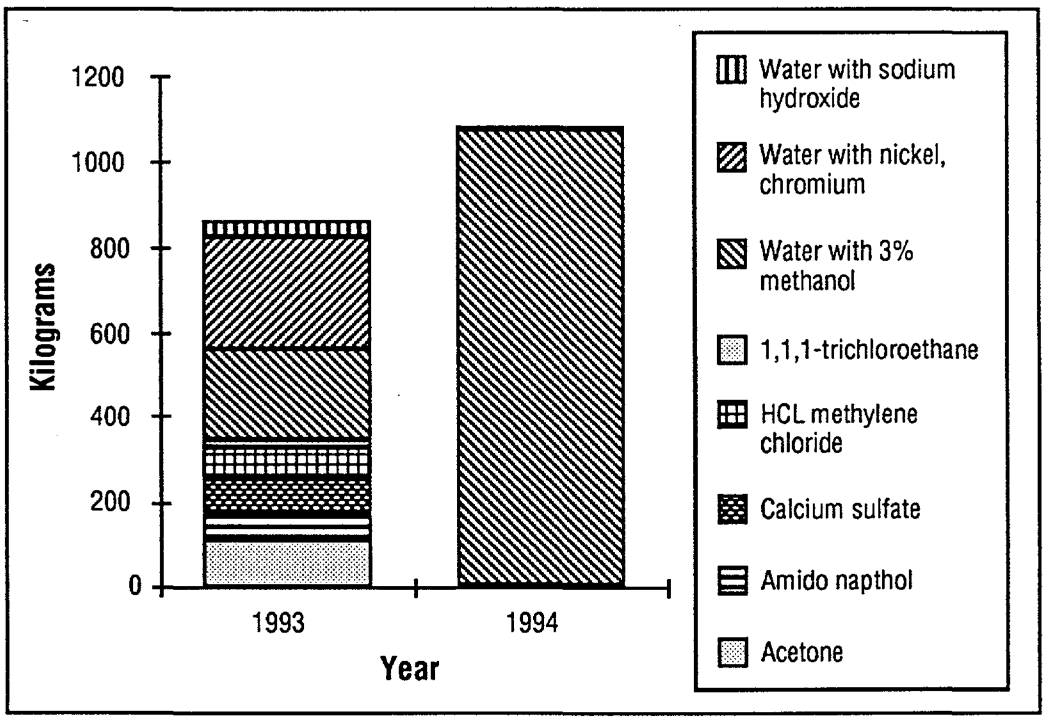


Figure 4. Waste Generation Summary (1993–94).

Because the supercritical water oxidation laboratory is doing fundamental research and development, the waste streams and volumes are not consistent from one period to the next. The reactor is not run continuously and typically generates only 10–20 gal. waste per week.[8] The variability can be seen in Table 1 and Fig. 4. In 1993, a variety of wastes was generated in quantities up to 261 kg. In 1994, the major waste was 1072 kg water/methanol (with ≤3% methanol). The other wastes generated in 1994 totaled only 25 kg.

The cost of disposal and transportation of the waste generated in 1994 was approximately $700, which does not include handling and administrative costs.[9]

Similarly, the waste streams will change throughout 1995. Research is planned on mixtures of water and methanol, isopropanol, phenol, and methylene chloride/hydrochloric acid.

Material Balance

Because supercritical water oxidation is a dynamic research program and the types of wastes generated are inconsistent, a material balance on the process is not feasible.

Waste Minimization Recommendations

Because this research generates such a wide variety of wastes, identifying many waste minimization opportunities is difficult. However, waste from the reactor is primarily water with a low concentration of organics. In some cases, the concentration of organic matter is ≤100 ppm. This waste stream may not be a hazardous waste. Environmental Operations Department personnel could analyze it and determine if it should be disposed of as a hazardous or nonhazardous waste. If it is nonhazardous, it could be released to the sanitary sewer. Each waste generated would require analysis to determine if it is hazardous or nonhazardous before it could go to the liquid effluent control system and if nonhazardous, on to the sewer system.

Other waste minimization options were identified:

- If possible, reuse the effluent containers after the waste material has been commingled or disposed of;
- Consider reprocessing the surrogate waste through the reactor to reduce the contents in the effluent to below regulatory limits. (This recommendation is reasonable for a much larger operation; however, a comparison of the current waste generation rate and cost of disposal to the costs associated with the research and development time spent by the staff to reprocess the effluent, it would not be cost effective at the current level of operation.)

References

1. U.S. Department of Energy (DOE), Order 5400.1, *General Environmental Protection Program* (November 9, 1988).
2. U.S. DOE, Order 5400.3, *Hazardous and Radioactive Mixed Waste Program* (February 22, 1989).
3. U.S. DOE, SNL/California, *Pollution Prevention Opportunity Assessment Plan for SNL/CA*, PD457712 Issue 3 (August 11, 1994).
4. S. F. Rice, *Kinetics of Supercritical Water Oxidation*, SERDP FY 1994 Proposal (1994).
5. S. F. Rice, R. R. Steeper, and C. A. LaJeunesse, *Destruction of Representative Navy Wastes Using Supercritical Water Oxidation*, Sandia National Laboratories/California, SAND94-8203 (1993).
6. C. A. LaJeunesse, et al., *A Supercritical Water Oxidation Reactor: The Material Evaluations Reactor (MER)*, Sandia National Laboratories/California, SAND91-8623 (1992).
7. SNL/California, *Waste Storage Log* (1993 and 1994).
8. Rice, Steve, 1994, Sandia Supercritical Water Oxidation Flow Reactor, personal communication with N. M. Phillips.
9. SNL/California, *ES&H Table for FY93 Hazardous Waste Disposal Volumes and June 1994 Costs and Vendors* (1994).

UNLIMITED RELEASE

INITIAL DISTRIBUTION

U. S. Department of Energy (2)
Albuquerque Operations Office
Attn.: J. L. Arellano, KAO
J. E. Orban, WMD
P. O. Box 5400
Albuquerque, NM 87115

MS1305 R. Davis, Org. 7576
MS1305 M. Walsh, Org. 7576
MS9001 J. C. Crawford, Org. 8000
Attn.: E. E. Ives, 5200
J. B. Wright, 5300
M. E. John, 8100
R. J. Detry, 8200
W. J. McLean, 8300
L. A. Hiles, 8400
P. N. Smith, 8500
L. A. West, 8600
R. C. Wayne, 8700
M. T. Dyer, 8800
D. L. Crawford, 8900
MS9021 K. W. Gordon, Org. 8535
MS9052 S. F. Rice, Org. 8361
MS9222 G. Faulkner, Org. 8642
MS9222 D. N. Nissen, Org. 8642
MS9222 H. J. McConnell, Org. 8642
MS9222 N. M. Phillips, Org. 8642 (15)
MS9222 S. J. Raubfogel, Org. 8642
MS9222 K. K. Shepodd, Org. 8642

MS9021 Technical Communications Department, 8535 for OSTI (10)
MS9021 Technical Communications Department, 8535/Technical Library, 13414
MS0899 Technical Library, 13414 (4)
MS9018 Central Technical Files, Org. 8523-2 (3)