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*Design and Operational Parameters  
of Transportable Supercritical Water  
Oxidation Waste Destruction Unit*

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# DESIGN AND OPERATIONAL PARAMETERS OF TRANSPORTABLE SUPERCRITICAL WATER OXIDATION WASTE DESTRUCTION UNIT

by

Robert D. McFarland, G. Ray Brewer, and Cheryl K. Rofer

## ABSTRACT

Supercritical water oxidation (SCWO) is the destruction of hazardous waste by oxidation in the presence of water at temperatures and pressures above its critical point. A 1 gal/h SCWO waste destruction unit (WDU) has been designed, built, and operated at Los Alamos National Laboratory. This unit is transportable and is intended to demonstrate the SCWO technology on wastes at Department of Energy sites. This report describes the design of the WDU and the preliminary testing phase leading to demonstration.

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## I. INTRODUCTION

Supercritical water oxidation of organic, biological, and selected inorganic materials appears to be rapid, nonselective, and complete in a single stage of a supercritical water oxidation waste destruction unit. It is a promising technology for the destruction of many of the wastes found in the Department of Energy (DOE) nuclear weapons production complex, as well as for wastes produced by the Department of Defense (DOD) and industry. It seems to be particularly well suited for radioactive mixed wastes, explosives, and other "high-risk" wastes.

Oxidation in supercritical water is a self-sustaining, low-temperature chemical reaction. Although oxidation in supercritical water has superficial similarities to combustion, it apparently is sustained by a free-radical chain reaction in the absence of a flame and at a much lower temperature than incineration.<sup>1</sup> An oxidant, such as air, oxygen, hydrogen peroxide, or another suitable compound, must be present to achieve the complete destruction of organic compounds and oxidizable inorganic compounds that produce water, carbon dioxide, and other innocuous compounds.

Above the critical point of water (22.12 MPa, 374°C; Fig. 1), many organics are miscible with water, and no phase partition inefficiencies are encountered. The solvent properties of supercritical water are different from those of liquid water; nonpolar compounds are more soluble and salts are less soluble in supercritical water than in liquid water. Transport properties (diffusivity and viscosity) are gas-like. The overall reaction rates are rapid, even though the temperatures are low relative to incineration (residence times are measured in seconds at 600 to 700°C). At the relatively low process temperatures

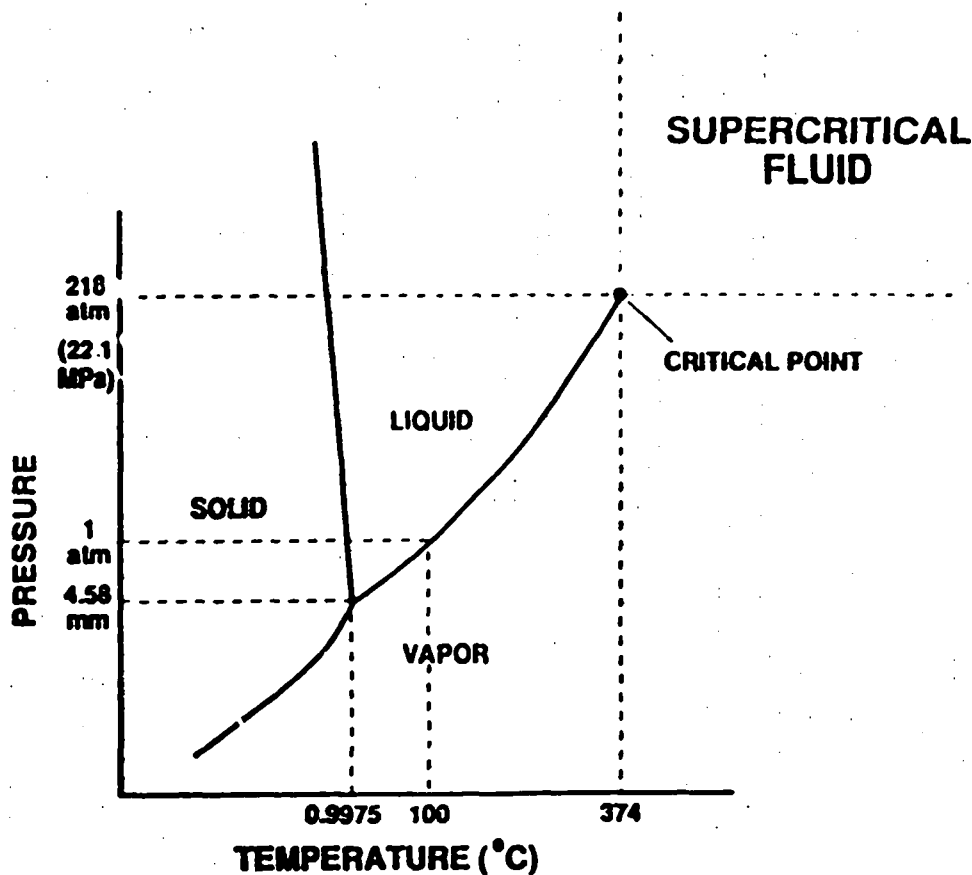


Fig. 1. Phase diagram for water. Not drawn to scale.

(less than 700°C), essentially no oxides of nitrogen are expected. The process pressures (24 to 35 MPa) lead to relatively high fluid densities with small process reactor volumes. These pressures, while relatively high, are within conventional industrial practice. The process is fully contained, with full control of all effluent streams. The process appears to be inherently controllable, with the water acting as a heat transfer medium as well as a solvent (or carrier fluid for slurries).

Many organic wastes, including common industrial materials (such as solvents, greases, lubricants, paints, polychlorinated biphenyls (PCBs), and machining oils); organic components of mixed radioactive wastes; and organic components in process wastewater, including solvents, explosives, plastics, and paper, are candidates for destruction by supercritical water oxidation. Certain high-risk wastes, including explosives, high-level radioactive wastes, and extremely toxic chemicals, are also candidates. Selected inorganics, including cyanides, nitrates and perchlorates, have also been shown to be candidates. Other candidate wastes include contaminated groundwater, soils, and sediments.

A wide range of scale appears to be possible for different applications. Small-capacity units might be designed for intermittent destruction of wastes generated in a single laboratory. Such units might fit on a benchtop. Mid-sized mobile units might be mounted on a truck or trailer for on-site use. Units with larger capacities might be permanently attached to fixed facilities for process wastes, and it is conceivable that very large facilities might be built for decontamination of aquifers, ponds, or lakes. Different designs, both of the reactor vessels and of the overall systems, will be mandated by different applications. Systems for handling solids, such as soils or process parts, will require designs different from those used for handling liquids or slurries. A very large facility might be designed for in-ground placement using oil-field technology.

Because water is the reaction medium, the process is potentially advantageous for a variety of aqueous wastes. Many such wastes have relatively low concentrations of oxidizable compounds. Designs that optimize heat recovery and minimize the need for auxiliary fuels or additional oxidizable wastes will be needed for such wastes. The technology is not restricted to aqueous wastes, however, and its desirable characteristics are likely to lead to its application to nonaqueous wastes in dissolved or slurry form. The design of a supercritical water oxidation waste destruction unit is sensitive to the concentration of the oxidizable waste and to its heat of oxidation because of the need to remove heat generated by the oxidation reaction from the supercritical fluid mixture. For a waste destruction unit intended to process a variety of wastes, such as a mobile unit, the optimum concentration of waste in water is a key variable that will depend both on the nature of the waste and on the design of the unit. One engineering parameter to be considered in the design of a plant is the waste concentration that generates enough heat to maintain the reaction but does not raise the temperature of the walls of the processing vessel beyond design limits. All other factors being the same, both the reactor and the system designs can be quite different, depending on the concentration. Waste concentration can be controlled. Pure or highly concentrated wastes can be diluted with water, and fuel or oxidizable wastes can be added to wastes in low concentrations.

In addition to throughput, type of waste, and concentration, many other factors also influence the engineering design of the reactor and the overall system. Additional factors that influence the engineering design are residence time in the reactor (determined by the kinetics of oxidation of the waste); physical state of the waste and its oxidation products, including the necessity for salt separation; corrosiveness of the waste and oxidation products; availability of reliable components; and specific safety problems associated with some wastes.

There is a body of industrial experience in handling high-purity supercritical steam in electrical power plants. More than 150 electrical power supercritical units are operating in the United States, most of which are rated between 500 and 800 MW. Experience shows that these supercritical power plants provide significant efficiency benefits; comparable outage rates, after an initial learning period; and relatively small added maintenance costs. As a group, their biggest drawback has been that plant start-up takes too long and is too complex to allow U.S. plants to be used for on-off cycling.<sup>2</sup>

The Los Alamos National Laboratory is investigating supercritical water oxidation for the DOE Office of Technology Development and for the Air Force Civil Engineering Support Agency (Tyndall Air Force Base, Florida). The DOE program consists of two separate tasks: a Research and Development (R&D) task and a Demonstration, Test and Evaluation (DT&E) task. The purpose of the DT&E task is to obtain the information necessary for evaluating the technology in preparation for an industrial demonstration and for the process development and scale-up needed to apply the technology to priority wastes, including mixed wastes, in the DOE complex. The purpose of the R&D task is to support the DT&E task by gaining an understanding of certain characteristics of waste mixtures in supercritical water, including the equations of state needed for supercritical reactor design, and to determine the mechanisms of oxidation of wastes important to cleanup of the DOE complex in supercritical water as a basis for developing correlations for scale-up and evaluation of the process.

The major objective of this investigation is to help potential DOE and DOD users evaluate the technology. Several private companies are actively developing and marketing supercritical water oxidation for waste destruction applications in the chemical, petrochemical, and paper industries. The design approaches offered by the different companies vary, and it is important to be able to assist potential users in evaluating specific designs for particular wastes. In addition, the destruction of a number of priority wastes involves high risks or specialized processing requirements (mixed wastes, explosives, and propellants, for example). The application of supercritical water oxidation, particularly to high-risk wastes, requires additional development and demonstration.

A transportable integrated experimental system at a scale of approximately 1 gal/h was designed, built, and used to investigate process variables. This design allows the interchange of reactor sections, thus enabling us to study different designs and materials. The reactor section used for the initial tests is a

tubular reactor. The remotely controlled waste destruction unit can also be reconfigured, with minimum effort, to obtain data on variations in system design. This unit is intended to develop an experience base on operability. Because it is transportable, it can be used to evaluate wastes within the DOE complex. In addition to its ability to evaluate process and design issues, this unit will be used for tests on specific wastes at DOE sites to provide data for site operators to use in their evaluation of the applicability of supercritical water oxidation to their priority wastes.

This report describes the transportable destruction unit and its operating characteristics.

## II. DESIGN OF WASTE-DESTRUCTION UNIT

A major precept for designing the waste destruction unit has been to provide a basic system into which various reactor configurations could be inserted. The basic system uses a supply and mixing subsystem to provide a mixed feed for the reactor and a cooldown and pressure letdown subsystem for postprocessing the reactor effluent. The cooldown/letdown subsystem will eventually include solids-handling components. The unit is designed to meet or exceed ASME mechanical standards to enable all critical operations to be done remotely. The system has been configured to fit on a framework that is roughly 5 ft x 12 ft x 6 ft high, and it can be picked up as a unit and transported on a truck trailer. The total height of the unit varies with the reactor, which is mounted on top of the 6-ft-high framework. The external supplies required are 110-V and 220-V, three-phase electrical power, 160 psi compressed air, and roughly 1 gal/min cooling water. The data acquisition, control, and monitoring subsystem consists of a data acquisition and control unit, a controller, digital readouts, and manual switches. These items are connected to the unit by instrumentation lines.

A schematic of the waste destruction unit is shown in Fig. 2, and photographs of the unit are shown in Figs. 3 and 4.

### A. Supply and Mixing Subsystems

The supply and mixing subsystem includes fluid supply reservoirs, pumps to bring the fluids to operating pressure at the desired flow, and device for mixing the fluids before they enter the reactor. A 50-gal supply tank can be used for water or aqueous waste feed to the system. During the system checkout phase described in this report, the tank was used first for a mixture of acetone and deionized water, then for a pure deionized water feed to the main metering pump. The feed is pumped to the reactor operating pressure of about 4000 psi by a Milton Roy duplex metering pump. The maximum capacity of this pump is 2.2 gal/h (139 ml/minute or 2.3 g/s), but the nominal operating point is 1.1 gal/h. The duplex pump contains two piston pumps, in series, operating 180 deg out of phase to reduce pulsations. There is still, however, a considerable amount of surge in the output. This surge is damped by piston accumulator on the water line near the pump and just before the reactor inlet. The accumulators have a trapped mass of air on the back side of the piston such that the piston is slightly half depressed at operating pressure.

A concentrated organic stream can be introduced into the pressurized water line by a separate metering pump. For this operation we use a single-piston Science Systems, Incorporated (SSI) metering pump that can output up to 10 ml/min. For the system checkout phase, acetone was used as a surrogate waste and was either mixed with the water in the supply tank or introduced through the SSI metering pump. At a nominal water flow rate of 1.1 gal/h and 2% concentration, the waste flow is 1.8 ml/min (0.023 g/s, for acetone). At this flow rate the SSI metering pump speed is slow, so a plenum is provided at the point of injection into the water line to hold the amount of water corresponding to one pump-stroke of acetone. Following this plenum is a 1-m straight line, which allows further mixing before oxygen injection. This line could serve as a preheating section, if necessary.

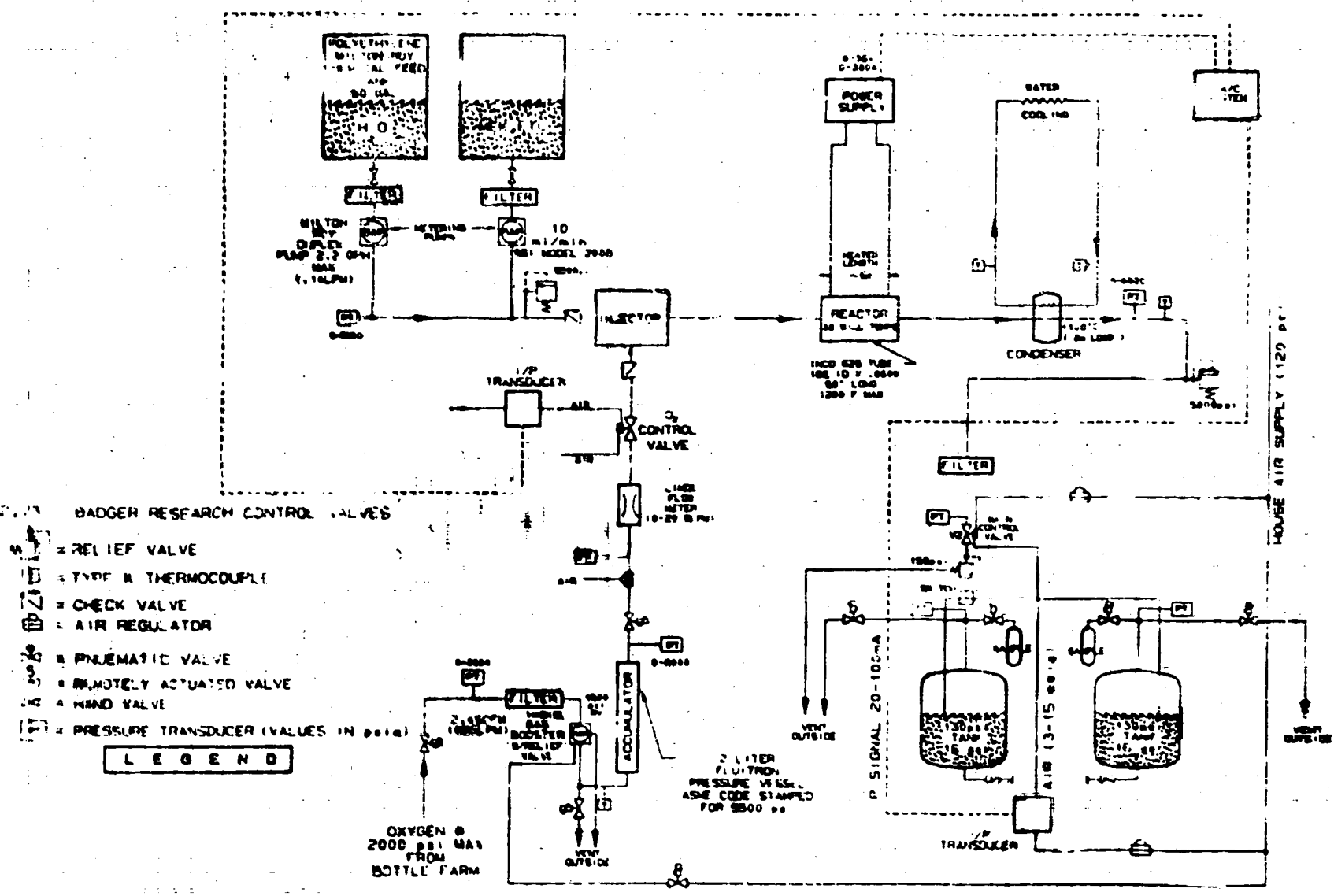


Fig. 2. Schematic flow diagram of the waste destruction unit.

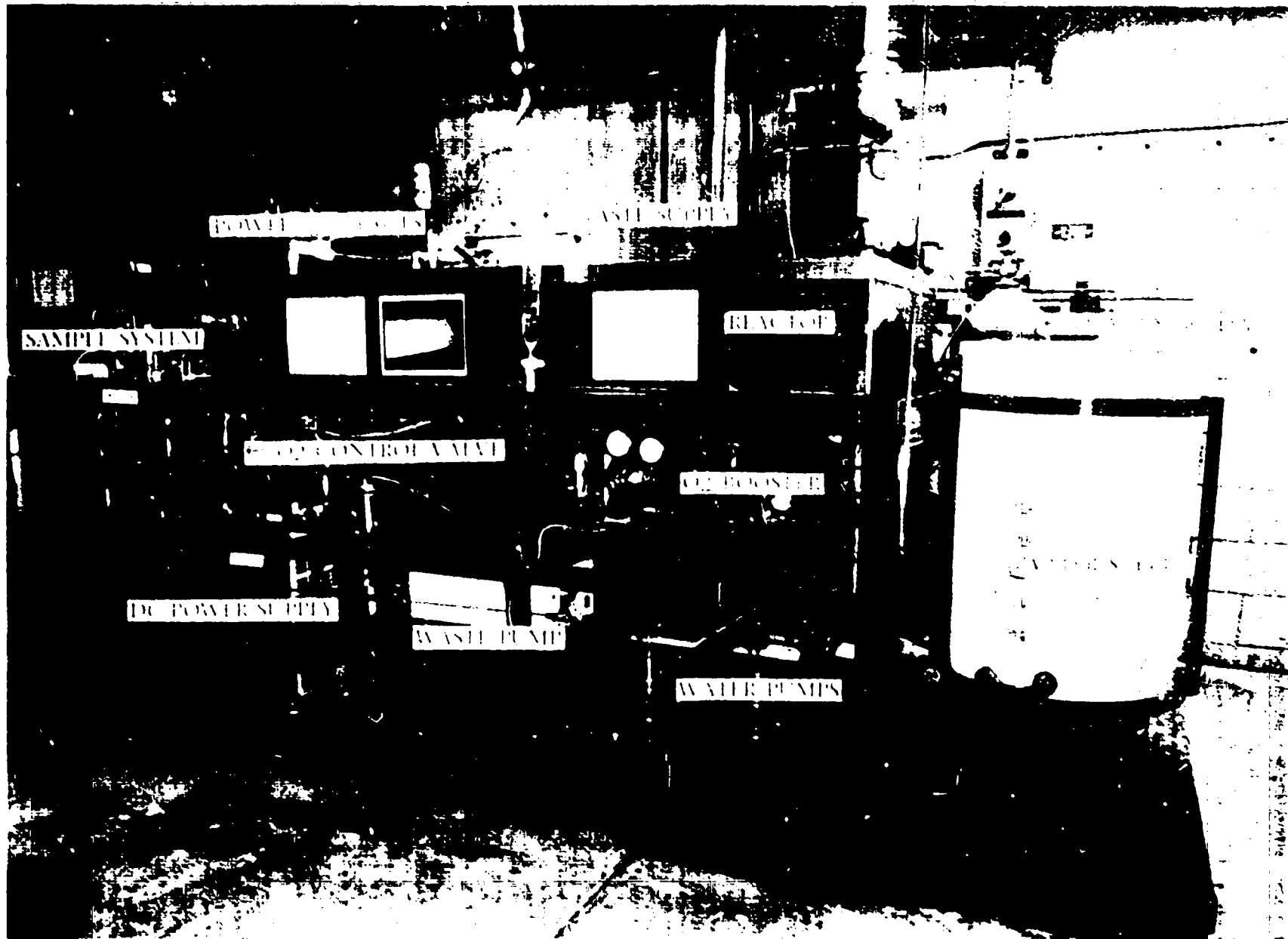
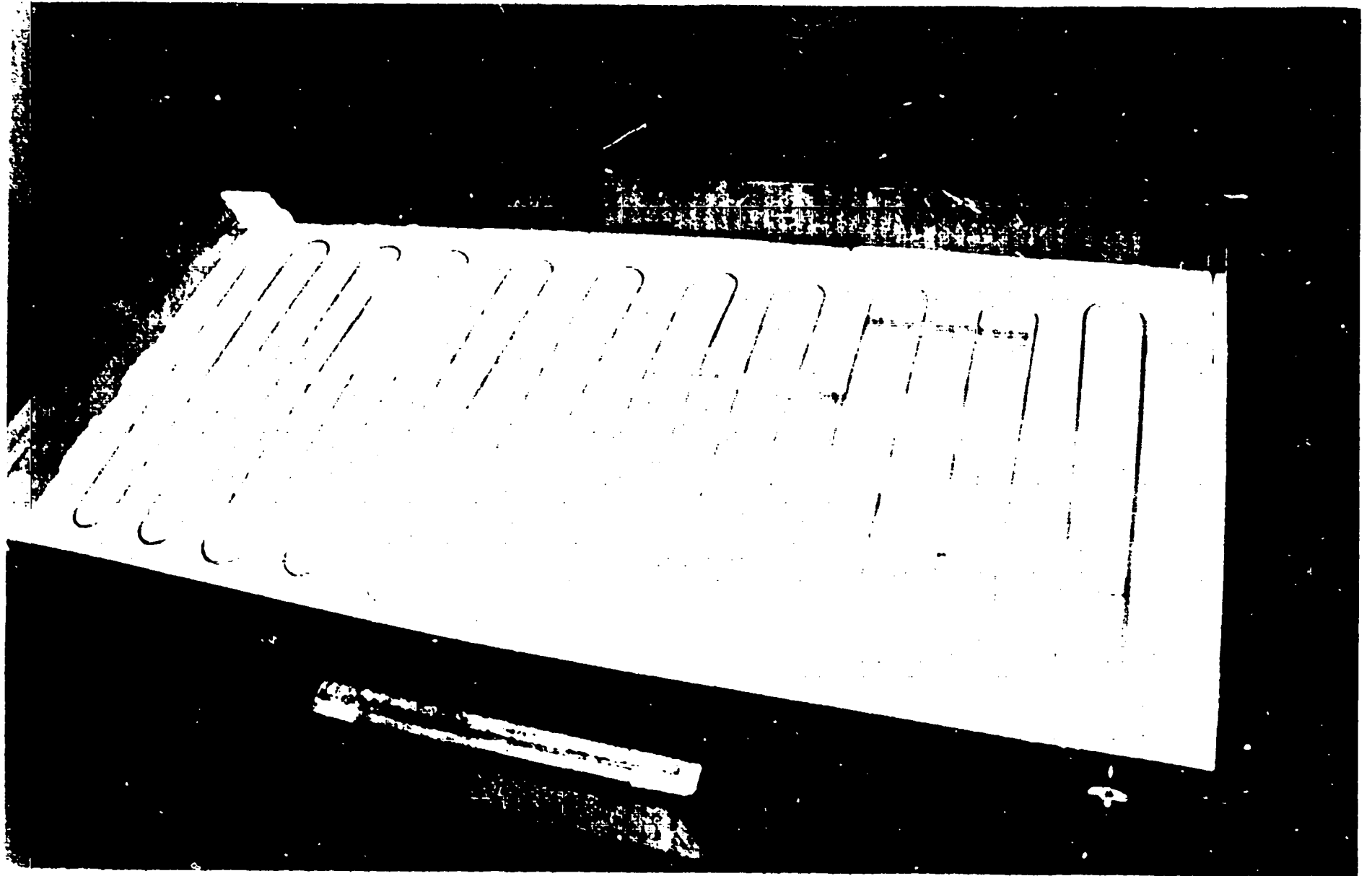


Fig. 3. Waste destruction unit showing some of the principal components. The cooldown and pressure letdown and the sampling components are hidden from view on the back side of the reactor.



**Fig. 4. Reactor box before thermocouples, top insulation, and cover were installed. Power leads are shown in place, but are not yet welded onto the tubes; they are welded on in a vertical position.**



Oxygen is supplied from standard 2000-psi bottles located on the rig. The oxygen is regulated to 1500 psi and is fed into a Haskel double-acting two-stage gas booster, where it is compressed to the operating pressure of about 4500 psi. The operation of the gas booster is controlled by a pilot switch that turns the booster on when the outlet pressure drops to approximately 4350 psi and turns it off when the pressure reaches 4500 psi. The booster is air driven and, along with several pneumatically actuated valves and electrical current-to-pneumatic pressure (I/P) transducers, is supplied by a compressed air trailer. For operation off-site, an air compressor can supply the required air. The booster output depends on the air pressure, the oxygen supply pressure, and the oxygen output pressure, but it can probably supply oxygen at a flow of at least 30 standard liters per minute (SLPM) at a pressure of 4500 psi in our system. A water flow rate of 1.1 gal/h with a 2% acetone concentration requires an oxygen flow of 4.6 SLPM (0.10 g/s) to supply two times stoichiometric oxygen.

Oxygen from the booster is collected in a 2-liter reservoir or accumulator. At an oxygen flow of 4.6 SLPM and a booster pilot switch dead band from 4350 psi to 4500 psi, the booster turns on about every 4 to 5 min. A high-pressure oxygen regulator was installed to control the oxygen pressure at 4300 psi, with a variation of only 20 to 50 psi. This regulator is dome-loaded with a self-venting hand regulator and a nitrogen bottle in the control room. Between the accumulator and the regulator is a pneumatic ball valve for positive oxygen shutoff. Another pneumatic ball valve, located at the booster outlet, can vent oxygen to the outside. A Linde mass flowmeter is used to measure the oxygen flow rate. The output signal from this meter goes to a digital panel readout and to the data acquisition system for monitoring and control. To control oxygen flow we use a pneumatically actuated control valve and an I/P transducer. A 4- to 20-mA dc signal is sent to the I/P transducer, where it is converted to a 3- to 15-psi proportional pneumatic signal to the valve actuator.

After going through a check valve the oxygen is injected into the water/waste stream. The injector consists of a 1-mm-diam, 40-mm-long hole for the water/waste stream, and a 1-mm-diam, 20-mm-long, hole for the oxygen, intersecting the first hole at right angles. Before oxygen injection, the velocity in the water/waste stream is about 1.5 m/s, the oxygen velocity is about 0.3 m/s, and the combined flow after injection is about 1.8 m/s. Better mixing could be attained with higher velocities, but this would require smaller injector holes. We did not use smaller holes because we were concerned about plugging the holes. The combined flow out of the injector passes through a fine-mesh screen for further mixing.

We are careful to keep the entire oxygen system clean and to use only stainless steel and oxygen-compatible seals (such as Teflon or Viton). A relief valve is set to open at 5000 psi on the water line, and the oxygen booster is provided with a relief valve set at 5000 psi, the maximum recommended pressure for pure oxygen.

## B. Cooldown, Pressure Letdown, and Sampling Subsystem

The mixed fluids are fed to the reactor through a flange connector. At the outlet of the reactor is another flange, just upstream of the entrance to the primary side of a cooldown heat exchanger or condenser. These flange connectors allow relatively simple removal and replacement of the reactor section. A single-pass, counterflow, coaxial-tube heat exchanger cools the reactor effluent with on-site chill water. For operation off-site, we could incorporate a recirculating water system, using a water-to-air heat exchanger to reject the heat to ambient. Because of the small scale of the present waste destruction unit, it is probably not useful to try to reclaim the waste heat. The cooled process fluid passes through a single letdown valve, where its pressure is reduced to essentially atmospheric pressure. The letdown valve controls reactor operating pressure. This control valve and I/P transducer combination is similar to that of the oxygen control valve, except that the letdown valve is a normally open valve, whereas the oxygen control valve is a normally closed valve. After the process stream passes through the letdown valve, it enters an array of seven sample bottles, allowing the entire flow to be diverted to a given bottle for a period

of time. The sample valves are controlled remotely. When the effluent is not being sampled, it passes into a product tank that can be pressurized to 120 psi for complete containment of gaseous and liquid effluent.

### C. Reactor Subsystem

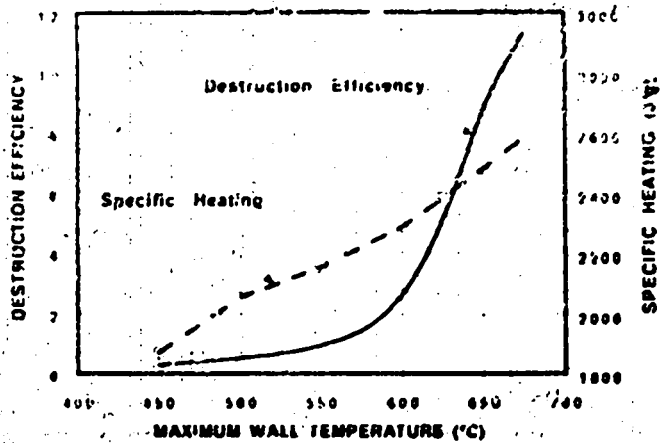
The present reactor is a welded 50-ft length of Inconel 625 tubing, 0.188-in. i.d. by 0.308-in. o.d. This tube is accordion-folded (see Fig. 4) to fit in a 3-ft by 6-ft planar area. The tubing is supported by hardboard insulation, with about 5 in. of alumina-fiber insulation above and below the tubing. The reactor is enclosed in a sheet aluminum box approximately 3 ft x 6 ft x 1 ft high, which is placed on top of the system framework. The desired operating temperature of the mixed fluids is achieved by direct electrical resistance heating of the first 20 ft of reactor tubing. This is done in two parallel electrical circuits. The first 6 ft, 8 in. of tubing comprises one circuit, and the next 13 ft, 4 in. of tubing comprises the other circuit. In this way, the first third of the 20-ft heated section produces two thirds of the total heating. This configuration allows a higher peak fluid temperature for a given maximum allowable tube wall temperature at the end of the heated section because the wall-to-fluid temperature drop is not as high in this lower heating-rate area. At a temperature of 650°C, the Inconel 625 tubing has a maximum operating pressure of 5000 psi (the maximum operating pressure of the system), so 650°C is the maximum operating temperature of the tubing.

Electrical power is provided by a Hewlett-Packard 6469C dc power supply that is rated at a maximum current of 300 A at a maximum of 36 V. At nominal operating conditions (1.1 gal/h of water, 2% or 1.8 ml/min of acetone, and about 5 Sl.PM of oxygen), the total power draw is about 4 kW (263 A, 15.2 V). Power is supplied through 1/2-in. copper cables to three stainless steel leads welded directly to the reactor tubing: the common "hot" lead in the middle and "ground" leads at each end. With this arrangement, electrical potential differences are minimized between the heated portion of the reactor tube and the rest of the system. The leads are about 8 in. long so that they extend above the reactor box. They are sized to reduce heat loss from the reactor tube by offsetting it with heating in the leads and to reduce the temperature at the copper cable connection point to 200°C or lower. The connection temperatures are monitored and have never gone above 160°C.

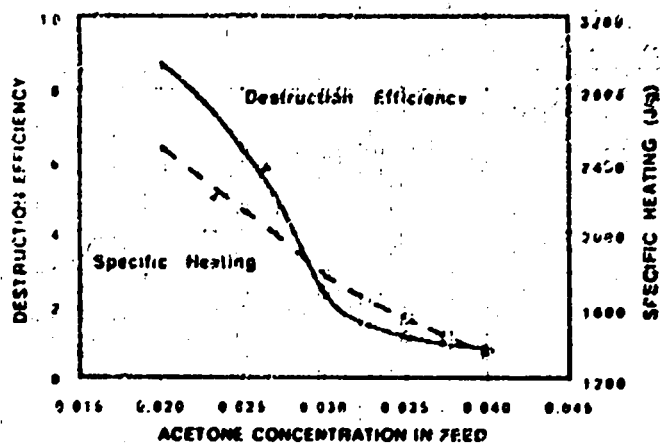
The remaining 30 ft of reactor tubing is wrapped with relatively low-power electrical guard heaters to offset heat loss and to maintain a constant temperature in the last 30 ft of reactor.

The sizing of the reactor tube and the heating profile was the result of many design analysis runs using a one-dimensional flow, heat and mass transfer model. This model is described in Appendix A. The criterion used for the reactor design was 99.9999% (six "nines") destruction of a candidate waste (methyl ethyl ketone (MEK) in this instance) at a concentration of 2% in water. The design flow rate (water plus waste) for these analyses was 1.0 g/s (about 1 gal/h). The oxygen stoichiometric ratio was taken to be 2.0, and the fluid temperature in the portion of the reactor downstream of the heated portion was constant at 650°C. Because no kinetics information was available for the oxidation of MEK under these conditions, the oxidation rate equation for carbon monoxide<sup>3</sup> was used. The use of CO should be conservative in terms of reaction rates. It is possible that CO is an intermediate product in the oxidation of hydrocarbons and oxygenates. Even more conservative would be the use of the rate for methane,<sup>1</sup> which also may be an intermediate product. For the initial reactor, CO kinetics gave a practical length.

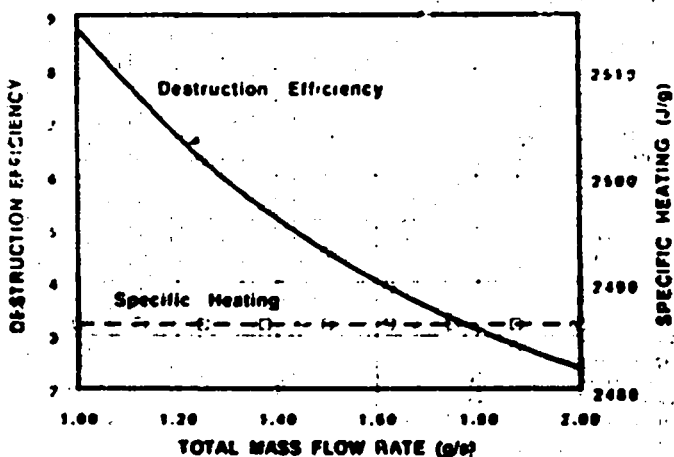
Figure 5 shows the predicted performance of the present reactor using CO oxidation rates. The predicted destruction efficiency decreases rapidly with decreases in the maximum tube wall temperature below 650°C, increases in acetone concentration above 2%, increases in flow rate above 1.0 g/s, or increases in heat loss above zero. Without guard heating, the present reactor (with 6 in. of fibrous alumina insulation above and below the tube) has a heat loss conductance of roughly 0.1 W/m-C. Because we



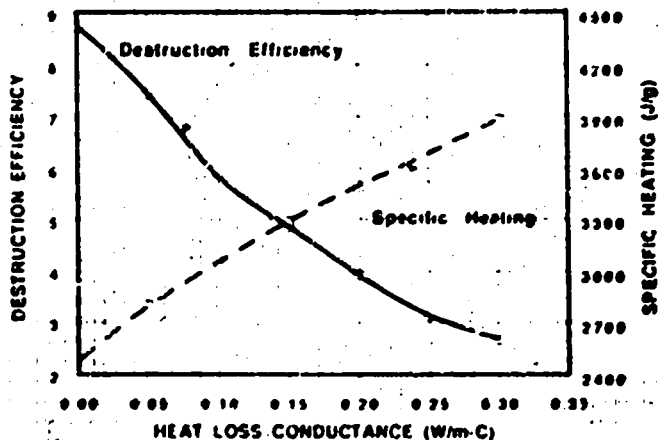
(a)



(b)



(c)



(d)

Fig. 5. Predicted "nines" of destruction using CO oxidation rates and required specific heating (total heating rate divided by total mass flow rate) for the present tube reactor. Shown are the effects of varying (a) maximum tube wall temperature, (b) inlet acetone concentration, (c) total flow rate, and (d) heat loss conductance. Values for these parameters, when they are not the independent variable, are maximum wall temperature = 650°C; inlet acetone concentration = 0.02; total flow rate = 1.0 g/s; heat loss conductance = 0.

believe the use of CO oxidation rates in the predictions to be conservative, we do not expect the destruction efficiency to be as sensitive to these parameters as predicted.

#### D. Data Acquisition and Control Subsystem

Data acquisition, control, and monitoring are accomplished with a Hewlett-Packard 3852A data acquisition and control unit and a Mac-IIcx Macintosh desktop computer. Software for data acquisition, control, and monitoring was developed within the framework of LabVIEW-2 graphical programming shell. Various functional boards can be inserted into the Hewlett-Packard 3852A. We are using a digital voltmeter and three 20-channel multiplexers (scanners) for data acquisition, a 4-channel digital-to-analog converter (DAC), and a 10-channel relay actuator for control. Three of the DAC channels are being used for continuous control of the two control valves (oxygen flow and pressure letdown) and the dc power supply. The scanners are used to sample voltages from 6 pressure transducers, 38 thermocouples, the oxygen flow meter, 2 power supply circuit voltages, and 2 power supply current-shunt voltages. Of the 38 temperature measurements, 31 are on the reactor tube (see Fig. 6), 1 is on the condenser outlet, 1 each is on the cooling water inlet and outlet, 3 are on the power leads, and 1 is on the oxygen booster outlet.

A LabVIEW-2 program was developed to automate the various steps in data acquisition and recording and certain control functions. The data steps are as follows:

1. Acquire the raw data from the scanners.
2. Convert the raw data to engineering units with known calibrations. Thermocouple data are converted by the scanners.
3. Determine whether any of the channels designated as being "critical" are out of the prescribed bounds. If any are, then the three DAC channels are zeroed and the program must be restarted before they can be given a nonzero value. Zeroing the three DAC channels means that the power supply goes to zero power output, the oxygen control valve goes to full-closed, and the letdown valve goes to full-open. This is considered to be the "shutdown" condition. Critical limits include any reactor-tube temperature over 700°C, any pressure over 5000 psi, any condenser outlet or cooling water outlet temperature over 110°C.
4. Record engineering data for all 60 scanned channels and for the DAC and relay actuator board settings on a permanent file, with a date/time stamp.
5. Display selected data in real time in digital and graphical form on the Mac-IIcx display monitor. Include all system pressures; an x-y plot of the reactor tube temperature vs. distance from reactor inlet, refreshed at each scan; and continuous graphical strip charts (value vs. time) of selected pressures, selected reactor temperatures, power-supply voltage, and oxygen flow rate.

These steps (collectively referred to as a scan) are repeated at a prescribed time period. At present, our scan rate is one scan every 5 s for 60 channels.

Another LabVIEW-2 program replays the recorded data from a test, at any desired rate up to about two scans per second, displaying the same information as is displayed during the test. In addition, the recorded data files are converted to text files that are transmitted to a mainframe computer for back-up and high-quality color plotting.

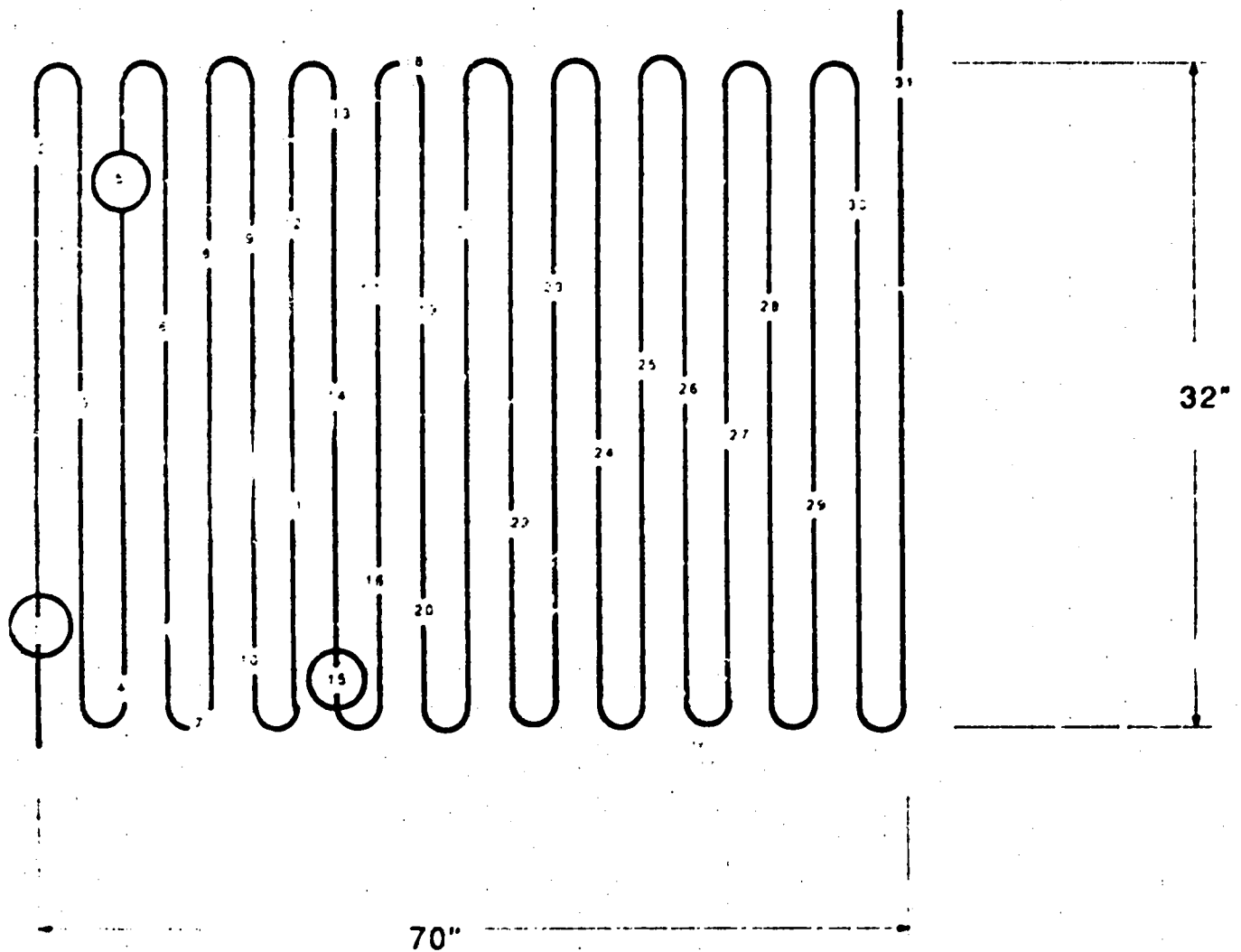


Fig. 6. Sketch of reactor tube showing location of power leads and thermocouples.

### III. OPERATIONAL PARAMETERS

#### A. System Operation

The first test was conducted on the waste destruction unit at the end of August 1990. Through April of 1991, a total of 32 runs had been made on the unit, resulting in a total of 34 t. at temperature and pressure. These runs were used to wring out bugs, evaluate and change equipment components, develop a procedure for rapid and stable start-up, and develop a standard operating procedure. A summary of the test through April 1991 is shown in Table I.

Modifications were made to the system to reduce the variations in system pressures caused by pumping and compression pulsations. These modifications included adding a high-pressure oxygen regulator and two piston-accumulator surge suppressors--one on the water line near the water pump and one just upstream of the letdown valve. In early tests, we tried to control the oxygen flow with a Linde mass flow controller, that is, a mass flow meter with feedback coupling to an integral solenoid valve. However, the solenoid valve was not strong enough to override pressure drops of more than about 100 psi. Since the oxygen pressure varied more than 100 psi, the valve would often shut down completely, trapping low pressure between the valve and the check valve. The valve would not open again until the upstream

TABLE I. Summary of tests through April 1991.

Test	Acetone (%)	Oxygen (psia)	Pressure (C)	Temp* (W)	Power (h)	Duration	Comments
1	0	0	3500-4000	360	3700	0.0	Large pressure oscillations in O <sub>2</sub> shutdown.
2	2.0	20	3500-4000	600	3700	0.4	Pinhole developed in reactor tube from heater short.
3	2.0	0	3000-3500	500	5200	0.4	Oscillations as in Test 1.
4	2.0	0	3000	700	5200	0.4	Water pump leaks.
5	2.0	>20	3500-4000	650	4900	1.1	..
6	0	>20	4000	700	3700 .700	1.3	Water pump leaks; power decreased, but got automatic shutdown when T>700°C.
7	0	>20	3700-4300	700	4800	1.6	Automatic T shutdown, large P oscillations.
8	2.0	>20	3900	670	4300 3200	1.0	..
9	2.0	8-10	3000-4000	660	4200	1.2	Large, rapid P oscillations.
10	1.6	8-10	3900	550	3500	1.2	Automatic power-ramp control - not satisfactory.
11	1.6	8-10	4000	570	3400 3750	1.1	Repetition of Test 10.
12	1.6	4-6	4000	610	3500	4.0	Improved O <sub>2</sub> flow, P control. Ran 4 h. Restart from automatic shutdown due to electrical spike.
13	.	.	.	.	.	.	..
14	0	0	4000	670	5300	0.6	Automatic shutdown due to spurious thermocouple rdg.
15	0	6-8	4300	670	4300 2700	1.3	Stead operation.
16	3.0	7	3000-4000	670	2700	2.5	First use of HPLC pump for acetone injection. Large oscillations in P, O <sub>2</sub> flow.
17	3.0	0	3000-5000	670	4300 2600	1.4	P oscillations.
18	3.0	0	4500-3500	700	2300	1.1	Leaking water pumps caused T shutdown.
19	2.0	4-10	4000	600	2200	0.2	Traveling T spikes, leaking reactor exit flange.
20	3.0	6-8	4000	650	3700	1.4	Large, 5-min P/O <sub>2</sub> oscillations. turned acetone off and on; observed 150°C T change.
21	3.0	5-8	3800	580	3600	0.4	Large, rapid oscillations. Large P spike caused shutdown.
22	2.0	7-8	3900	650	3800	1.1	Small, rapid oscillations. T dropped ~80°C when acetone feed turned off.
23	2.0	0	3500-4200	700	3300	0.7	P very sensitive to control.
24	2.0	5-8	4000	670	4800	1.1	5-min oscillations, but suppressed, possibly due to second surge suppressor.
25	2.0	4-6	4000	680	4000	1.2	Generally smooth test.
26	2.0	4-6	3700	640	4300	0.3	Trial of on/off feed-back loop control--not good.
27	2.0	5	3700	630	4700	1.2	Proportional feed-back control works well for O <sub>2</sub> flow.
28	2.0	5	3800	660	4000	1.7	Sample bottle valved off; caused pressure spike. Proportional (only) control of pressure not adequate because of time lag.
29	(0)	7	3500-4000	550	4900	0.2	Could not establish acetone flow.
30	3.0	7	3700	670	4000	0.9	Relatively smooth on manual P&T control. Acetone on 300°C.
31	3.0	7	3500-4000	660	4500	2.0	Traveling T spikes. Acetone on at 360°C.
32	3.0	7	3700	620	4800	0.9	Smooth. Acetone on at start.

oxygen pressure was reduced by venting. With the addition of a regulator, a better oxygen supply pressure, but it was still difficult to maintain a low pressure drop across the valve. For accurate oxygen flow control, the pressure drop across the control valve should be as high as possible. As a result, we replaced the solenoid valve in the flow controller with a pneumatically actuated control valve. This valve has the potential of becoming a flow controller, using the data acquisition and control (DA&C) system in the loop, although the response rate will be limited to the scan rate of the DA&C system.

Most of the tests were run with 1.1 gal/h water flow, either 2% or 3% acetone, and at least two times stoichiometric oxygen. Some tests were run with no oxygen or acetone, some with acetone only, and some of the early tests with as much as eight times stoichiometric oxygen because of oxygen flow control problems. At one point the water pump seals were leaking so badly that about 25% of the water flow was going on the floor, resulting in an input acetone concentration of about 4% instead of 3%. The pump seals were replaced and no serious leakage problems have occurred since.

In testing without oxygen, it was difficult to control the system pressure in the absence of the pressure-pulse dampening of a compressible fluid. This was particularly true in tests with acetone and no oxygen. In these tests it appeared that there was a reaction at operating temperature. Although this reaction was not highly exothermic, it seemed to be very sensitive to pressure. This sensitivity may have been the thermolysis of acetone to methane and carbon monoxide.

Qualitative gas analyses were made of the effluent on at least one of the tests run with acetone but no oxygen. The analyses showed significant amounts of methane and carbon monoxide, as well as some hydrogen and some unidentified higher molecular-weight species. Acetone vapor was significantly reduced, but still present. The formation of three moles of gas from one mole of acetone could have provided pressure surges. Because the pressure would also be sensitive to the reaction as a result of density changes, a highly unstable condition would occur.

Several tests were run with nominally 3% acetone and roughly two times stoichiometric oxygen. In these tests, the power was ramped up relatively quickly. When operating temperature was reached, a long (about 5-min) oscillation in pressure and oxygen flow (and to a lesser degree, temperature) was observed, with no changes in power, oxygen valve setting, or letdown valve setting. The amplitude of the oscillations was about 500 psi on pressure and almost 50% of maximum oxygen flow. Once started, the oscillations seemed to be self-feeding. When the system pressure drops, the oxygen flow increases because of an increased pressure drop across the oxygen control valve. When the oxygen flow increases, the system pressure increases with a delay. The delay occurs because of the compressibility of oxygen and the system volume between the oxygen valve and the letdown valve. When the system pressure increases, the oxygen flow decreases. Then there is a delayed drop in the system pressure, after which the cycle starts all over. When the acetone feed was shut off, the peak reactor temperature dropped about 200°C and the pressure/oxygen flow oscillations stopped. When the acetone feed was turned on, the reactor temperature returned to its former value and the oscillations started again, but with a much smaller amplitude. Figure 7 shows pressures, reactor temperatures, and oxygen flow as a function of time for Test 16. The oscillations are clearly shown, as are the cessation of oscillations that occurred when the acetone was turned off at about 10.45 h and the restart that occurred when the acetone was turned back on, just before 10.80 h.

The oscillations appear to be triggered by the reaction, but whether this is caused by variations in the acetone concentration or by some other phenomenon, we do not yet know. The temperature oscillations (which also disappear when the acetone feed is turned off) seem to result from the pressure oscillations because they appear only in the heated region of the reactor where the fluid is going through the pseudo-boiling regime of water at near-critical temperatures. The pseudo-boiling regime is the pressure-temperature region just above critical pressure where the specific heat (partial derivative of enthalpy with respect to temperature at constant pressure) goes through a pronounced maximum with increasing temperature. In this regime water has a strongly positive Joule-Thompson coefficient (partial derivative of

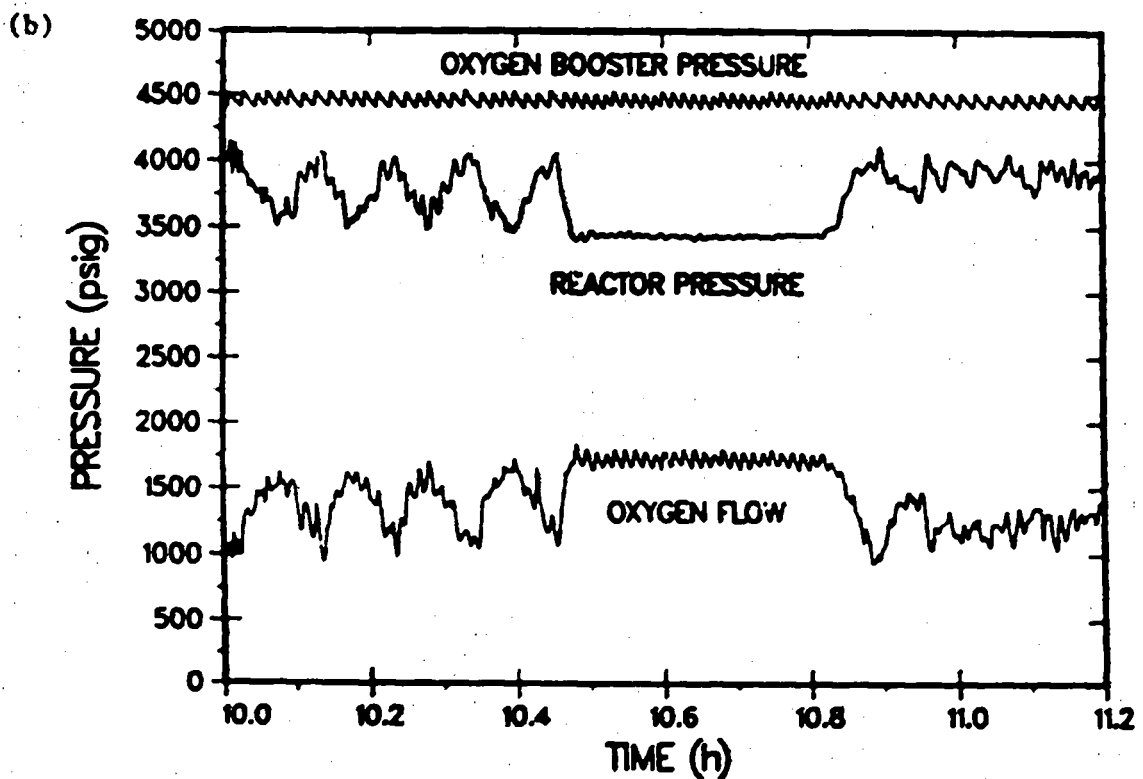
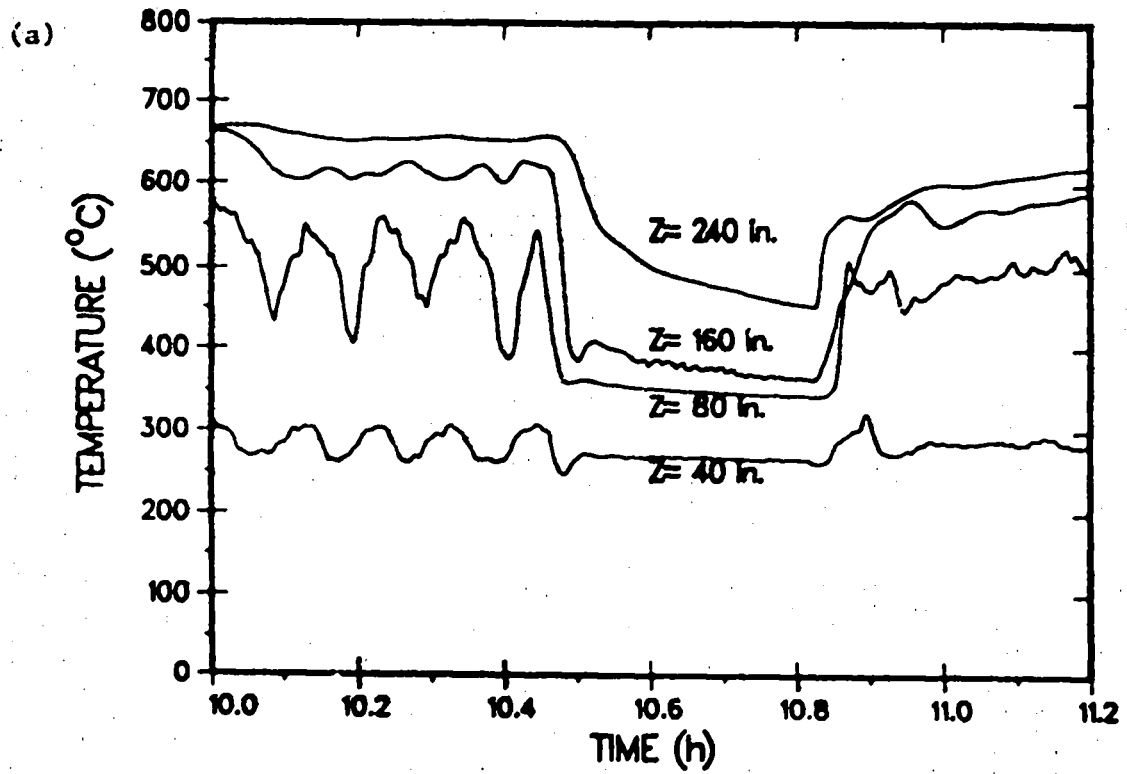


Fig. 7. Reactor parameters as functions of time occurring during the middle part of Test 16: (a) reactor tube surface temperatures at various distances from the inlet; (b) oxygen booster outlet pressure, reactor fluid pressure, and oxygen flow rate (multiplied by 200).



temperature with respect to pressure at constant enthalpy), so increases in pressure result in increases in temperature. The temperature oscillations are, essentially, in phase with the pressure oscillations. When the acetone concentration was reduced to 2%, the oscillations were significantly reduced in amplitude, as were the reactor temperature changes when the acetone was turned off, then back on.

During Test 19 (when the pump seals were leaking badly), two temperature waves were observed to pass through the reactor. The power was ramped up with oxygen and water flow only until a temperature of about 300°C was reached throughout most of the reactor, then the acetone feed was turned on. When the power was increased rapidly, a spike of about 300°C in the reactor wall temperature formed near the end of the heated section and slowly traveled downstream until it collapsed. A second spike then formed and traveled the entire length of the "unheated" portion of the reactor. This temperature wave took about 5 min to travel the length of the reactor, several times the residence time of the process stream in the last 30 ft of reactor. These temperature waves may result from inadequate mixing of acetone, water, and oxygen. After Test 21 we installed a screen in the reactor inlet line to further mix the fluids. This appears to have reduced the temperature-wave problem, although the operating and start-up conditions of Test 19 have not been repeated exactly.

In Test 25, with 2% acetone, the power was ramped up very slowly, that is, it took about 30 min to reach full power after the flows had been established. When full power was reached, we observed two pressure/temperature/oxygen-flow excursions of a different nature than the oscillations observed before (compare Figs. 7 and 8). After these excursions, conditions smoothed out for the rest of the test. The acetone feed was not turned off during this test. Figure 8 shows some measured parameters during Test 25, and Fig. 9 shows the reactor axial temperature profile near the end of the test.

## B. System Start-Up and Control

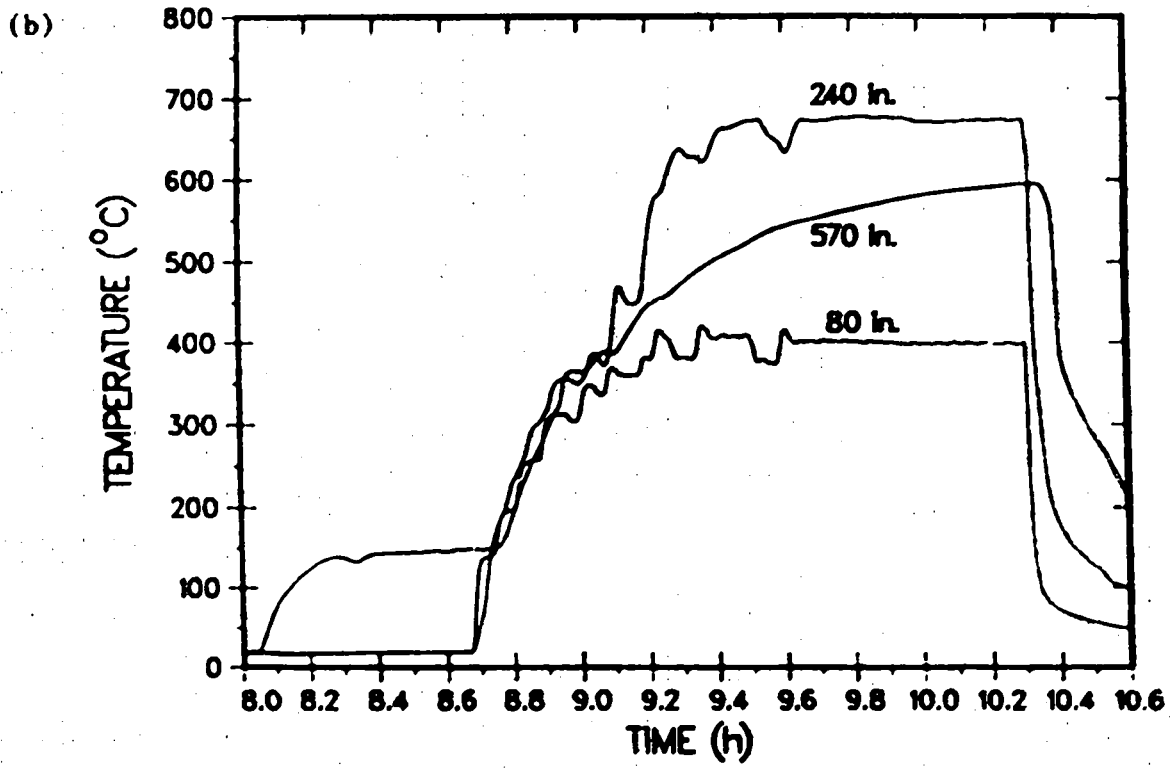
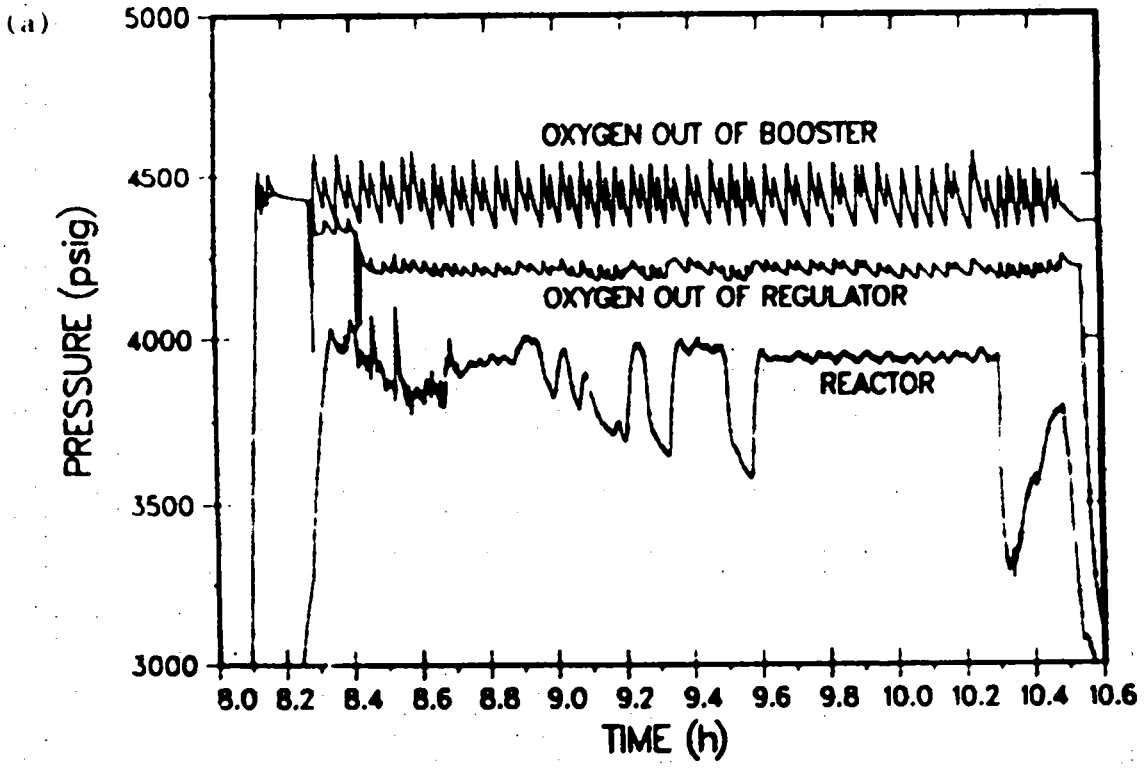
At this time, the power supply output is controlled interactively, that is, by manually adjusting a graphical "knob" on the LabVIEW-2 panel. The position of the oxygen flow valve is automatically controlled, using the measured oxygen flow rate and a control algorithm in the DA&C program as parts of a feedback control loop. Proportional-only control of the oxygen flow seems to be adequate because no significant lag occurs in the process or in the controller. Of course, if the reactor pressure is allowed to go above the oxygen pressure, the oxygen flow will be shut off regardless of the control strategy. We have developed an automatic feedback control algorithm for reactor pressure. Preliminary results indicate that proportional-only control is inadequate because considerable process lag occurs in the responses of pressure and temperature to the control action, causing severe overruns. The use of proportional-plus-differential control appears to be able to correct this.

The current start-up procedure is to start the water and waste pumps at the rated flow, while pumping the oxygen accumulator up to 4500 psi with no oxygen flow. Then we begin the oxygen flow on automatic control at the predetermined rate, and bring the system pressure up to the desired level on automatic control. When steady pressure and flows are established, a baseline sample is taken and the power is ramped up very slowly until operating temperature is reached.

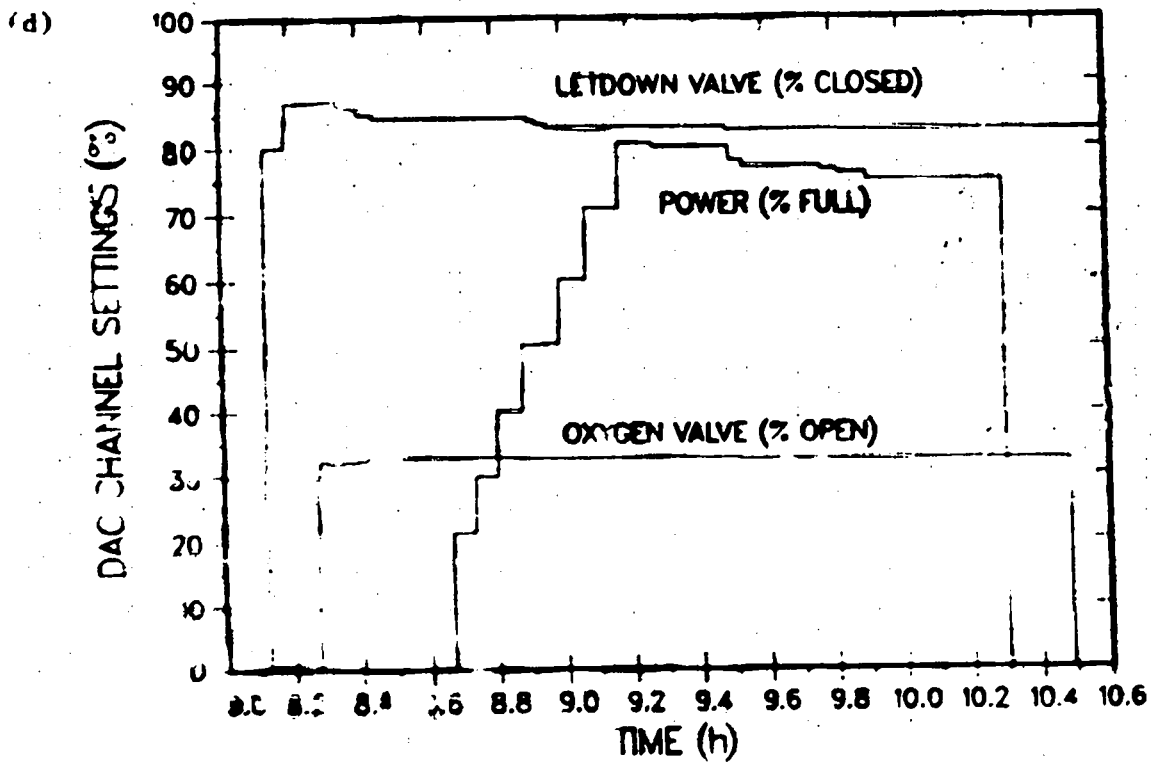
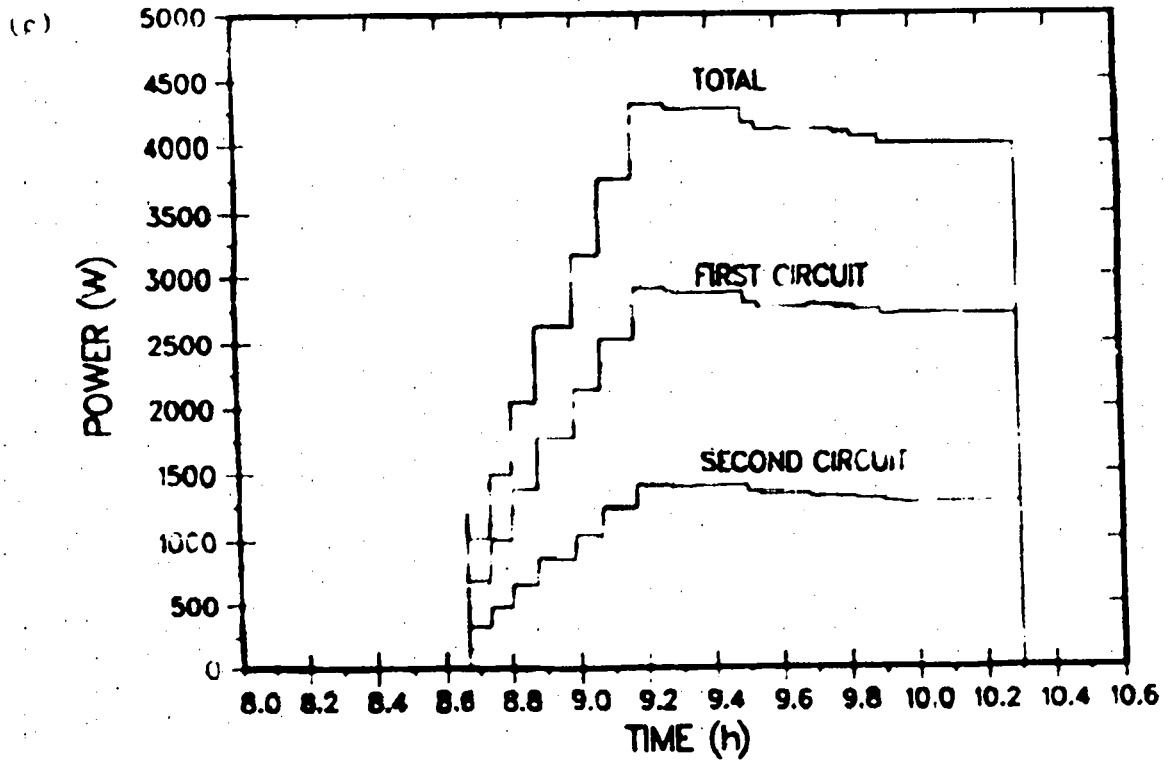
While the details of the start-up procedure are specific to this reactor and system configuration, and after eliminating the initial problems, we have shown that reliable, stable start-up can be achieved consistently. We expect to continue to develop the control system to assure that consistently reliable start-ups can be achieved with different wastes and with changes in the system.

## C. Other Operational Observations

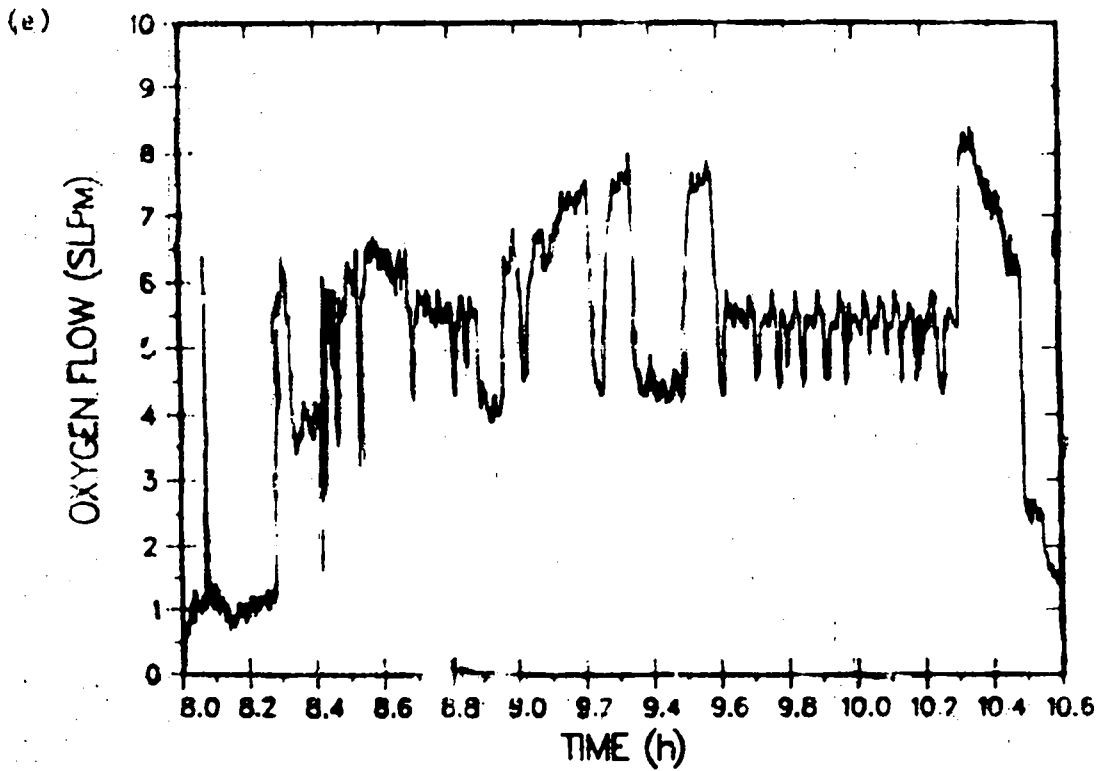
During an early test (Test 2) one of the guard heaters shorted out near the end of the reactor tube and burned a hole in the tube. Although the reactor was at pressure when this happened, the only indication was a sudden drop in system pressure, and steam was seen coming from the reactor. The tube did not fail



**Figs. 8a. and 8b. Reactor parameters occurring during Test 25: (a) oxygen and reactor pressures; (b) reactor tube temperatures at the second power lead, the third power lead, and near the reactor exit.**



Figs. 8c, and 8d Reactor parameters on during Test 757 (c) reactor power in the first circuit (between the first two leads) and the second circuit (between the second and third leads) and the total of both circuits; (d) control settings for the power supply output, letdown valve closure, and oxygen valve opening.



Figs. 8c. Reactor parameters occurring during Test 25. (e) flow rate.

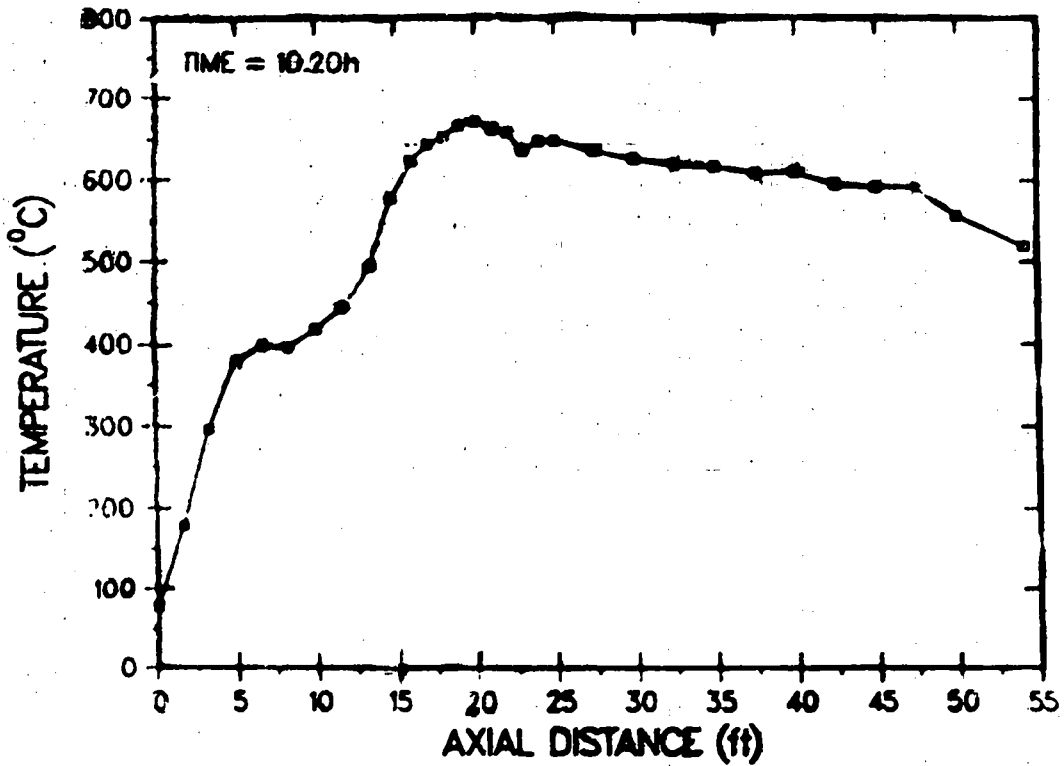


Fig. 9. Reactor tube temperatures as a function of distance from the reactor inlet at a time slice near the end of Test 25, when operation was steady

catastrophically. In this respect, the supercritical water (plus oxygen and, possibly, small amounts of CO<sub>2</sub>) appeared to behave more like an incompressible fluid than a gas. In addition, the relatively small volume of the reactor (just over 0.25 liter) led us to believe that possible failures in a reactor of this design will constitute no major hazard as long as proper precautions are taken to protect personnel from steam leaks. Subsequent repair of the reactor section consisted of welding the hole shut, and there has been no recurrence of a problem of this type.

In Test 19 a leak occurred in the flange at the reactor exit. We were unable to maintain the system pressure, and steam was observed coming from the flange. Posttest inspection showed that the silver plating on the silver-plated Inconel O-ring had eroded. The O-ring was replaced with another of the same type, and no other leak occurred through Test 32.

An attempt was made to duplicate the start-up procedure reported by Sandia National Laboratories, Livermore, on the Modell Development Corporation reactor.<sup>4</sup> The system was initially pressurized with oxygen. The letdown valve rapidly iced up and completely shut off the flow. The isentropic expansion of oxygen from 4000 psi to atmospheric pressure in a single stage could drop the oxygen temperature to its liquefaction point, and any moisture in the valve would freeze.

Before changing the water pump seals, we had continual problems with leakage and had to tighten the packings repeatedly. Eventually, the pump motor burned out, possibly because of over-tightening the packings. Since replacing the packings, we have had no serious leakage problems and have only rarely needed to tighten the new packings.

The Hewlett-Packard dc power supply provides full-rated output current (300 A) at about half the rated voltage. This is consistent with our present load. It is not clear, however, whether we will be able to get full-rated current at full-rated voltage (36 V). Above 300-A output, the power supply is shut down by an overcurrent trip. This trip, however, is on the input (ac) current, which should increase proportionately to the power because the input voltage is a constant 220 V. The power supply has a floating electrical ground, and this ground can be different from that of the framework. Occasionally the instrumentation channel voltages spike and cause an automatic shutdown. These spikes could be caused by differences in ground potentials.

During Test 10, an excessive pressure drop was observed in the letdown valve when the valve was fully open. An inspection revealed that the valve was partially plugged with a fine black material. There was not enough of the material for analysis. The annular flow passage in these control valves is very tiny because of the small flows and large pressure drops. These valves certainly would not work in a system with suspended solids in the effluent. We have had no repeat of this type of valve plugging.

#### D. Chemical Analysis

As operational procedures were being developed and the unit was being modified for better operation, chemical sampling and analysis techniques were also being developed. Most of our analyses have been done with a Hewlett-Packard gas chromatograph. Additional analysis, using high-performance liquid chromatography (HPLC), will be necessary to determine destruction efficiencies and material balances.

Sampling and analyzing liquid and gaseous effluents are essential for obtaining material balances and destruction efficiencies. The present sampling system has seven 300-ml sample bottles, into which the complete effluent flow is directed for predetermined periods of time. Each sample bottle has its own three-way valve. The valves are set up in series so that the flow can either be diverted to a given sample bottle or can be passed on to the next valve. When no sample is being taken, the effluent passes through all seven valves to a 16-gal product tank that can be pressurized to contain both gaseous and liquid effluents.

The first sample is taken before the power is ramped up, but all feeds are present and steady. This sample is used to determine the feed concentration. We then take samples at various times during the test.

usually when conditions are as steady as possible, recording the time, pressure, and average reactor temperature.

Quantitative liquid chromatographic analyses were done on samples taken during Test 25. These samples were taken with 2% acetone in the feed and with about two times stoichiometric oxygen. The results of these analyses give an acetone destruction efficiency of 99.9985%, or nearly five nines.

#### IV. CONCLUSIONS AND RECOMMENDATIONS

The transportable supercritical water oxidation waste destruction unit has now been operated at flow rates of about 1 gal/h at operating temperature and pressure for about 30 h. It is built to ASME standards, with remote control, data acquisition, and monitoring. We have developed start-up, control, and operating procedures.

We will continue to improve the operation of this system. In the immediate future we will develop automatic control procedures for both start-up and steady operation. The system will then be used to investigate process variables and to develop data on the operability and effectiveness of the process. These data will also help us understand the issues involved in scaling up the process. In addition to the acquisition of process data, this unit will be used for performing tests on wastes at various DOE sites.

The reactor section will be removed when experiments with hydrocarbons and oxygenates are concluded and will be examined metallographically for corrosion, erosion, and deposition. Information from this examination will be used to recommend new materials as appropriate. In addition, materials tests will be carried out for more severe environments, such as those that would be present in the destruction of halogenated hydrocarbons and other wastes.

Some of the variations in the system design that will be tested are injection of oxygen at various points in the system, self-cooled reactor concepts, scaled-down versions of proposed commercial reactors, and solids handling capabilities. The destruction of halogenated hydrocarbons may produce solids, and solids are usually found in real wastes.

The primary, early, objective of work with this transportable waste destruction unit will be to obtain operating data as a basis for permitting and transporting of the unit to DOE sites for on-site testing of priority wastes. Discussions toward this objective are being held with representatives of Hanford, Savannah River, Pantex, and Rocky Flats. In addition, coordination is taking place with OTD Integrated Demonstrations.

#### ACKNOWLEDGMENTS

We are indebted to P. E. Trujillo, Jr., and D. A. Counce for the chemical analyses and to F. T. Finch for helpful discussions.

## APPENDIX A

### FLOW REACTOR SIMULATION MODEL

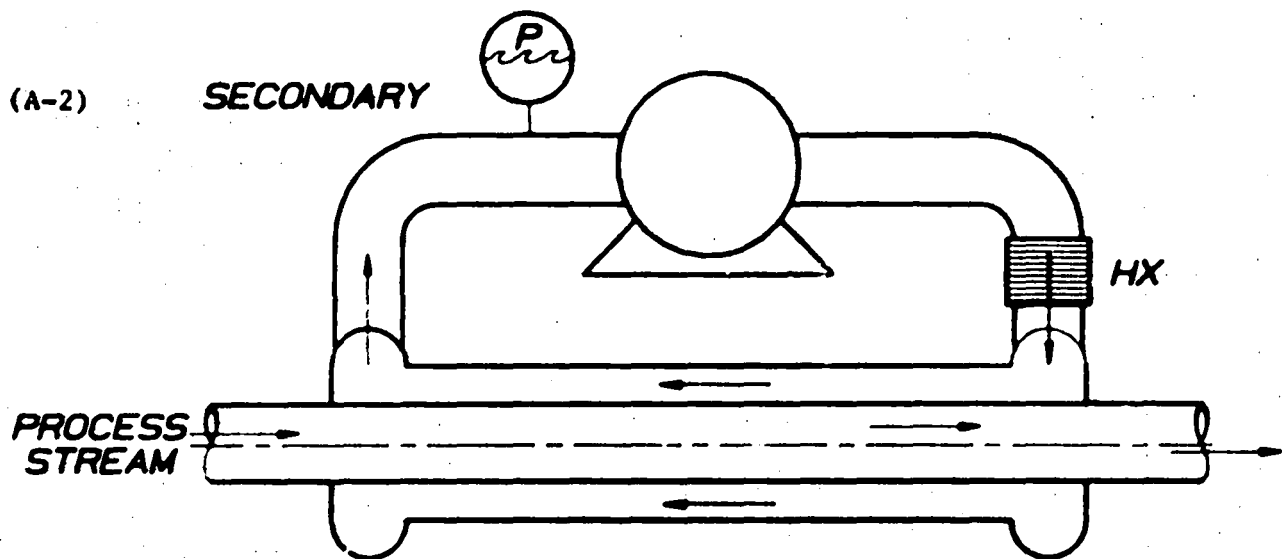
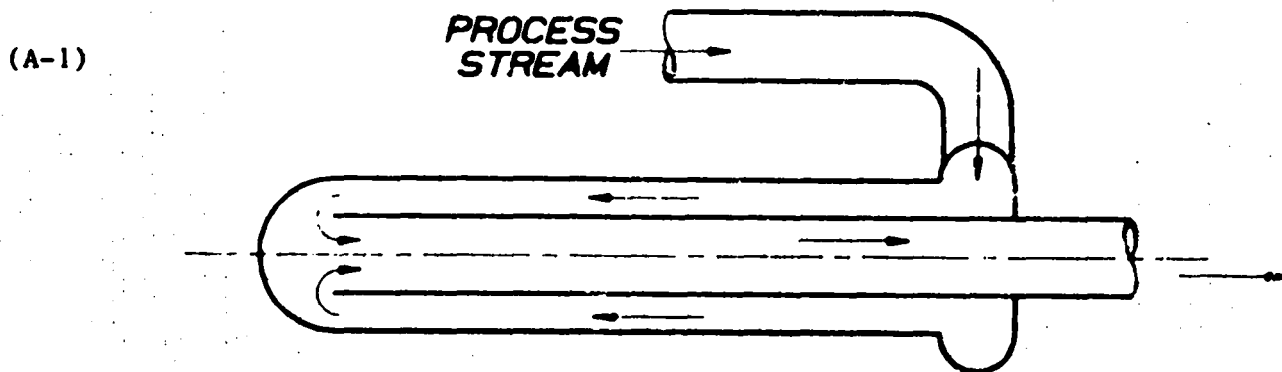
The flow reactor simulation model is a finite-difference solution of the one-dimensional, steady equations of energy, momentum, and species concentration with reaction. Numerical integrations of the finite-difference equations are made along the flow path to obtain pressure, temperature, and species concentrations at each point. A temperature and concentration-dependent chemical reaction is incorporated, with the attendant change in species concentrations and heat source (or sink). Heat transfer from the flow passage(s) to ambient is calculated, as is heat transfer between flow passages in reactor geometries with counterflow configurations. Besides the heat sources from the chemical reaction, heat sources caused by resistance heating, either outside the flow passage walls or in the walls themselves, may be specified.

Except for convective heat transfer between the flow passage wall and the fluid, there is no lateral diffusion of heat, mass, or momentum. Convective heat transfer between wall and fluid is represented by the heat transfer coefficient multiplied by the temperature difference between wall and fluid. Diffusion of heat or mass in the flow direction is assumed to be negligible except for that caused by advection (that is, heat and mass carried along with the fluid). This assumption has been verified with simple calculations for heat diffusion (conduction), and is assumed to hold for mass diffusion by analogy, making the assumption that the Lewis number (ratio of mass diffusivity to thermal diffusivity) is of the order of unity. Two basic assumptions in the analysis are that the various species are mixed at every point, and that they all have the same flow velocity, that is, there is no flow-direction separation or streaming. For the most part, these reactors operate at supercritical-water pressures and temperatures, and the common chemical species have densities of about the same order of magnitude.

Either of two analysis cases can be chosen. In the "design" case, the desired outlet waste concentration is specified and the required reactor length (in the flow direction) is calculated. In the "rating" case, the reactor length is specified and the outlet concentration of waste is calculated. In either case, the inlet species concentrations, inlet temperatures, inlet pressures (and, in some cases, outlet pressures), flow passage geometry, total flow rates, heat loss coefficients, and electrical heating profile are specified, along with several control parameters and flags.

Three reactor types are currently available in the simulation code. The "one-stream regenerative" (OSR)-type (Fig. A-1) consists of two concentric tubes. The process stream enters the central tube or the annulus at  $Z=0$  and flows to the common end at  $Z=L$ , then turns and flows back through the other flow passage to the outlet at  $Z=0$ . The "two-stream counterflow" (TSC)-type (Fig. A-2) also incorporates two concentric tubes, but the streams in the two tubes are independent. The process (primary) stream enters the inner tube at  $Z=0$  and flows to its outlet at  $Z=L$ . The secondary (cooling or heating) stream enters the outer tube at  $Z=L$  and flows to its outlet at  $Z=0$ . In the present version of the code, the secondary stream is assumed to have no chemical reactions and, therefore, no change in chemical make-up. The third reactor type, which was used in the studies for the present waste-destruction unit reactor, is the "one-stream, single-pass" (OSS)-type (Fig. A-3), in which the process stream enters the single circular tube at  $Z=0$  and flows to the exit at  $Z=L$ . For all types, numerical integrations are carried out in the positive  $Z$  direction. If two counterflowing streams are present, the integrations are simultaneously carried out in both streams (in the positive flow direction in the primary stream and the negative flow direction in the secondary stream). The single tube, or the pair of concentric tubes, in this analysis is considered to be a module, and many of these identical modules could be stacked in parallel to make a larger reactor.

Other major options built into the code are the reaction rate constants, the properties to be used for the waste species and the type of heat transfer coefficient. Other options are available for various iteration procedures. For example, we can change electrical heating rates until the maximum wall temperature equals a specified value within a specified tolerance.

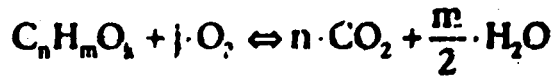


Figs. A-1, A-2, A-3: Three possible reactor configurations: (A-1) one-stream regenerative, (A-2) two-stream counterflow, and (A-3) one-stream single-pass.



## Theoretical Basis

In this discussion, the term waste is used to denote the oxidizable component of the feed, whether that is a waste, a simulant, an added fuel, or a combination of these. The stoichiometric and mass conservation equations are, at present, written assuming the waste to be a single hydrocarbon or oxygenated hydrocarbon species and assuming that the only products of the oxidation reaction are carbon dioxide and more water. If the waste can be represented by  $n$  atoms of carbon,  $m$  atoms of hydrogen, and  $k$  atoms of oxygen, the overall stoichiometric equation becomes



where

$$j = n + \frac{m}{4} - \frac{k}{2}$$

Excess oxygen, water in the feed, and any nitrogen (such as that which would be present if air were used as the oxidant) are simply carried along and become a part of the overall energy balance. Similar equations can be written for other oxidants such as hydrogen peroxide.

Intermediate steps in the oxidation process could readily be accommodated using multiple, simultaneous, reaction rate expressions and introducing intermediate products such as methane, carbon monoxide, and hydrogen. For simulations to date, however, we have used only the overall oxidation reaction.

In the following discussion,  $Z$  is the flow-direction distance from the primary inlet, the subscript  $i$  denotes conditions at the present  $Z$ -station, and  $i-1$  denotes conditions at the previous station. Numerical integrations are always carried out in the positive  $Z$ -direction. The numerical integration equations represent explicit solutions of the conservation equations in  $Z$ , that is, energy, pressure, and concentration changes over the  $Z$ -segment from station  $i-1$  to station  $i$  are based only on conditions at station  $i$ . For this reason, and because the oxidation reaction can become very fast at high temperatures, very small increments must be employed to ensure numerical stability. In this code the  $Z$ -increment size is the minimum of a specified maximum allowable value and the flow distance corresponding to the conversion of a given fraction of the remaining waste, as

$$\Delta Z = \phi \cdot \frac{V_{i-1}}{k_{i-1}}$$

where  $\Delta Z = Z_i - Z_{i-1}$  (m) (always positive)

$V$  is the mixed mean fluid velocity (m/s);

$k$  is the reaction rate constant ( $s^{-1}$ );

$\phi$  is a specified fraction, usually 0.01 to 0.02.

This typically results in several thousand axial stations for reacting streams, but it ensures stability. For two reacting streams, we use the minimum value for each.

The following energy equation is cast in terms of total fluid enthalpy for a constant-pressure process:

In finite-difference form, it is

$$H_i = H_{i-1} + \frac{\delta \cdot \Delta Z}{\dot{m}} \cdot \dot{Q}'_{w,i-1}$$

where  $H$  is the total fluid enthalpy (J/kg);

$\dot{m}$  is the total mass flow rate in the fluid passage (kg/s);

$\dot{Q}'_w$  is heat transfer rate per unit length from wall to fluid (W/m);

$\delta$  is + 1.0 for the primary stream, -1.0 for the secondary stream.

For a single flow passage (as in OSS-type reactors), the heat transfer rate is given by

$$\dot{Q}'_{w,i-1} = \frac{U'_w}{U'_w + U'_o} \cdot [U'_o \cdot (T_o - T_{i-1}) + \dot{Q}'_G]$$

where  $U'_w$  is conductance per unit length from wall to fluid (W/m-°C);

$U'_o$  is conductance per unit length from ambient to wall (W/m-°C);

$T$  is local fluid mixed-mean temperature (°C);

$T_o$  is ambient temperature (°C);

$\dot{Q}'_G$  is wall heat generation per unit length (W/m).

For OSR- and TSC-type reactors with two flow passages, the heat transfer between the two passages is also included in the heat transfer rate in each passage, again, based on temperatures at the previous Z-station.

There is no source term in the energy equation for the heat of reaction because the enthalpies of the various species are given on a common basis, and they include any heats of formation. For an adiabatic reaction, then, the enthalpy of the products is the same as that of the feed, but this enthalpy corresponds to a different mixed-mean fluid temperature for the products. The difference in enthalpy at a given temperature and pressure is the difference in the heats of formation, which is the heat of reaction. When the enthalpy is found, the mixed-mean fluid temperature is found, by an iterative procedure, from the property tables for the local composition and total pressure.

Total enthalpy, specific heat at constant pressure (used to determine heat transfer coefficients), and specific volume are determined, for the mixed fluid stream on the basis of mass fractions. Transport properties for the mixture (thermal conductivity and viscosity - used to determine heat transfer coefficients and friction factors) are determined according to the gas-mixing rules given in Reid and Sherwood.<sup>5</sup>

Other local parameters determined by numerical integration are the remaining waste concentration and the fluid static pressure.

The mass fraction of waste remaining for a first-order reaction is

$$\ln(F_i) = \ln(F_{i-1}) - \frac{k_{i-1}}{V_{i-1}} \cdot \Delta Z \cdot \delta$$

where  $F$  is the mass fraction of waste (kg, waste/kg, total).

Higher-order reaction equations would require slightly different numerical-integration equations. Once the mass fraction of waste is known, the concentrations of the other species is calculated from the stoichiometric coefficients and the species concentrations in the feed.

The total static fluid pressure is

$$P_i = P_{i-1} - \left( \frac{f \cdot G^2}{2 \cdot \rho \cdot D_H} \right)_{i-1} \cdot \Delta Z \cdot \delta + (\rho \cdot V^2)_{i-1} - (\rho \cdot V^2)_i$$

where P is total fluid pressure (Pa);

f is the friction factor;

$\rho$  is fluid mixed-mean density (kg/m<sup>3</sup>);

$D_H$  is coolant passage hydraulic diameter (m);

G is fluid mass velocity =  $m/A_f = \rho \cdot V$  for one-dimensional flow.

For reactor fluid passages of constant cross section, G is a constant for each flow passage. Correlations for heat transfer coefficients and friction factors can be found in Burmeister.<sup>6</sup>

Reaction rate constants (k) are determined from the simple form of the Arrhenius equation:

$$k = A \cdot \exp\left(\frac{-E}{R \cdot T}\right)$$

where A is the frequency factor (s<sup>-1</sup>)

E is the activation energy (J/mole)

R is the gas constant (J/mole-K)

T is the absolute temperature (K).

Other expressions for reaction-rate constant could be incorporated.

### Iterations to Satisfy Boundary (End) Conditions.

For the OSS-type reactor with a single fluid stream, no iterations are required to satisfy the end conditions. Inlet conditions are given, and numerical integration continues until the specified length (rating case) or the specified waste fraction (design case) is obtained.

For the OSR reactor design case, inlet and outlet waste fractions are specified and numerical integration continues until the waste fractions of the two streams are the same. Since the outlet temperature is not specified, however, iterations must be made, varying the estimate of outlet temperature until a match of temperatures at  $Z=L$  is obtained. The same is true of pressure, but pressure drops in these reactors are very small, and the procedure used here is to specify both inlet and outlet pressures and to ignore any mismatch of pressure at  $Z=L$ . For the rating case, iterations must be made, varying both outlet temperature and outlet waste fraction to obtain a match in temperature and waste fraction at  $Z=L$ , since L is specified. It is very difficult to obtain a solution for this case when there is good thermal coupling between the two streams, possibly because the physical situation may be somewhat unstable. In design-case situations where it is permissible to consider the reactor to be adiabatic (no heat loss to ambient), the outlet temperature can be calculated at the start since the overall change in constituents is known.

The TSC reactor requires iterations only to satisfy the specified secondary inlet temperature at  $Z=L$ . In some situations this can be circumvented by specifying the secondary outlet temperature instead. Otherwise the TSC reactor is similar to the OSS reactor in this respect. If chemical reactions were allowed in the secondary stream, however, the situation would become more complicated.

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