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Supercritical Water Oxidation Data Acquisition Testing

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FINAL REPORT

VOLUME II

PHASE II NAVY WASTE TESTING

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and Development Program

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1.0 SUMMARY

Supercritical Water Oxidation (SCWO) technology holds great promise for treating mixed wastes, in an environmentally safe and efficient manner. In the spring of 1994 the U.S. Department of Energy (DOE), Idaho Operations Office awarded Stone & Webster Engineering Corporation, of Boston Massachusetts and its sub-contractor MODAR, Inc. of Natick Massachusetts a Supercritical Water Oxidation Data Acquisition Testing (SCWODAT) program. The SCWODAT program was contracted through a Cooperative Agreement that was co-funded by the U.S. Department of Energy and the Strategic Environmental Research and Development Program.

The SCWODAT testing scope outlined by the DOE in the original Cooperative Agreement and amendments thereto was initiated in June 1994 and successfully completed in December 1995. The SCWODAT program provided further information and operational data on the effectiveness of treating both simulated mixed waste and typical Navy hazardous waste using the MODAR SCWO technology.

The SCWODAT program was undertaken in two Phases. Phase I included the DOE simulated mixed waste testing and Phase II the Navy hazardous waste testing. The program concentrated on the acquisition of data through pilot plant testing. The Phase I DOE testing used a simulated waste stream that contained a complex machine cutting oil and metals, that acted as surrogates for radio nuclides. The Phase II Navy testing included pilot testing using hazardous waste materials to demonstrate the effectiveness of the MODAR SCWO technology. The SCWODAT program also included extensive engineering and fabrication activities to prepare the MODAR pilot plant for both the Phase I and Phase II programs.

During Phase I of the SCWODAT program a simulated waste stream consisting of TRIM®SOL, a chlorinated machine cutting oil, was processed over seven test runs. The objective of the program was to destroy the organic constituents present in the simulated waste stream. A second objective of the Phase I testing program was to determine the distribution of the surrogate radioactive constituents in the treated effluents. The TRIM®SOL waste testing conducted at MODAR's facility utilized only simulated mixed wastes, no actual radioactive wastes were processed.

Following the Phase I DOE simulated mixed waste SCWO testing program, the Phase II Navy Waste Testing Program was conducted. The objective of Phase II was to collect treatability data for the application of the MODAR SCWO technology to actual Navy wastes generated at a typical shore side Navy waste depot. The Navy intends to utilize the SCWODAT program test data to determine the advantages of a MODAR SCWO oxidizer for future Navy SCWO projects. In addition, since the wastes tested are similar to many DOE generated hazardous wastes, the Phase

II Navy testing program also supports DOE's treatment options for mixed wastes.

Idaho National Engineering Laboratory (INEL) designed a SCWO test bed system to be used to test privately developed SCW oxidizers to determine the optimum configuration for treating DOE mixed radioactive waste and to support their commercialization through demonstration. In November 1994 the scope of this cooperative agreement was modified to include a technical review of the INEL designed SCWO test bed system by the SCWODAT team.

1.1 CONCLUSIONS

- The MODAR system operated safely while handling flammable feed materials.

- The MODAR system can readily handle the solids generated by Navy feeds, with the possible exception of the adhesive waste.

- The MODAR system had excellent corrosion resistance to the Navy feeds.

- The MODAR system was highly flexible in handling varying feedstock heating values and corrosive compositions. The system was robust and the process operating conditions were steady (as shown in Figures 2 & 3).

- The wastes provided by the Navy were all found to be readily treatable using the MODAR SCWO process. The majority of the Navy wastes required no pre-treatment prior to being pumped to the SCW oxidizer while several required dilution with kerosene to form a pumpable slurry.

- The MODAR pilot plant system configuration, with the exception of the slurry pumping module, was not modified for the Navy portion of testing. The system was able to treat poorly or incorrectly characterized wastes. This was best demonstrated during the treatment of NFESC-500 which was classified as non-chlorinated solvents but in reality was highly chlorinated. The MODAR process configuration and operator capability were able to mitigate the low pH problem caused by the unanticipated acid formation. This capability is essential for commercial treatment of real world wastes.

1.2 RECOMMENDATIONS

- The majority of the Navy wastes were easily treated. We recommend construction of an operating plant to treat Navy wastes, and which can evolve into a system capable of treating most or all of the materials tested in this program.

- Further operation of the effluent water reuse system to determine its performance over a prolonged period. This water reuse will optimize the plant water balance, particularly for high heating value fuels.

- Testing is needed to determine the effectiveness of the originally planned, but not implemented, sludge removal system from the oxidizer to better treat wastes like NFESC-100, paint sludge, that produce solids in the oxidizer.

- Further investigation and testing is needed to treat the problem encountered with NFESC-300, adhesive sludge, in which an insoluble inorganic solid partially obstructed the brine exit line. A higher velocity through this line, achieved by a pumped, recirculated flow, should rectify this problem.

- Tests should be conducted on the Navy wastes using a coated titanium liner to determine its corrosion resistance performance.

2.0 BACKGROUND

Introduction to Supercritical Water Oxidation

Supercritical Water Oxidation (SCWO) is a high pressure oxidation process that blends air, water, and organic waste material in an oxidizer where the temperature and pressure in the oxidizer are maintained above the critical point of water. Supercritical water mixed with hydrocarbons, which would be insoluble at subcritical conditions, forms a homogenous phase which possesses properties associated with both a gas and a liquid. Hydrocarbons in contact with oxygen and SCW are readily oxidized. These properties of SCW make it an attractive means for the destruction of waste streams containing organic materials.

While very simple configurations of the process can easily treat non-halogenated organic compounds, the processing of salt-forming wastes using SCWO has proved to be more complex. Inorganic salts which are soluble at sub-critical conditions, become insoluble and precipitate from SCW solution. As an organic enters the SCWO environment, carbon and hydrogen are oxidized and any inorganic anions present, such as chloride, sulfate, or phosphate form their respective acids. Neutralization of the acids with added cations, such as sodium, calcium, or magnesium, forms "sticky salts." The MODAR process was designed to operate in these harsh conditions.

The SCWO process has inherent advantages over alternative thermal oxidation technologies, such as incineration, in that it is applicable to a wide range of organic materials, the oxidation process occurs within a comparatively small volume environment, and organics are oxidized to very high destruction efficiencies. The benign byproducts of the process are primarily CO_2, N_2, neutral salts, and water. The production of acid gases, particulates, and volatile emissions are negligible. For example, the concentration of the priority pollutants NO_x and CO in the air emissions from the MODAR SCWO process were less than that emitted from a typical gas-fired home water heater. Thus, SCWO is applicable for the destruction of a wide range of hazardous materials which can be oxidized in a controlled manner yielding residuals that are environmentally safe for disposal.

For handling mixed radioactive wastes, the favorable air emissions profile of SCWO is particularly advantageous. Computer simulation indicates that SCWO is expected to produce lower radioactive air emissions than incineration with advanced off gas treatment (Dehmel and Hong, 1994). In comparison with other technologies which are being considered for mixed waste treatment, SCWO has a high level of safety and stability, and can handle high carbon levels without risk of explosion. Supercritical steam power plants are very common, and have been in commercial use since the 1950s. Furthermore, the MODAR SCWO system is designed to provide leak-before-break operation.

Purpose of the SCWODAT Program

The primary purpose of the SCWODAT program was to provide further information on the effectiveness of MODAR's SCWO treatment of a simulated mixed waste (Phase I) of interest to the U.S. Department of Energy and in the treatment of shore side hazardous wastes (Phase II) of interest to the U.S. Navy.

SCWODAT program personnel conducted all testing using MODAR's existing pilot plant located in Natick, Massachusetts. The project concentrated on the acquisition of data through testing with surrogate mixed waste and actual Navy waste materials. Similar to previous SCWO programs conducted by Stone & Webster and MODAR, Stone & Webster was the project manager and MODAR was the sub-contractor. In December, 1995 General Atomics, of San Diego California purchased MODAR, Inc. MODAR and its associated SCWO treatment facilities were relocated in March 1996 to General Atomics' facilities in San Diego. Within this report reference will continue to be made to "MODAR, Inc." and "MODAR technologies" in recognition of the experience and reputation associated with the MODAR name and MODAR SCWO technologies. The use of the MODAR name should also be taken to be a reference to General Atomics.

Objectives of Phase I DOE Testing

DOE was interested in destruction of mixed wastes, including TRIM®SOL, a water soluble cutting oil containing primarily carbon, chlorine, hydrogen, oxygen, sulfur, and phosphorous. TRIM®SOL is difficult to oxidize because it is formulated with surfactants, anti-oxidants, viscosity modifiers, anti-friction agents, and stabilizers. TRIM®SOL, used in solution for machining fuel rods, becomes contaminated with radio nuclides. DOE would like to reduce the volume of this waste by destroying the organic constituents.

The purpose of this program was to determine the organic destruction efficiency of contaminated TRIM®SOL that can be attained using MODAR'S SCWO process, and to determine how surrogate radio nuclides would be distributed. The TRIM®SOL waste testing conducted at MODAR's facility only utilized materials that simulated mixed wastes, no actual radioactive wastes were processed during this testing program.

The specific Phase I SCWODAT objectives were:

1) To demonstrate complete destruction of the organic constituents.

2) To demonstrate effective neutralization of acid forming anions.

3) To control solids generated during in-situ neutralization.

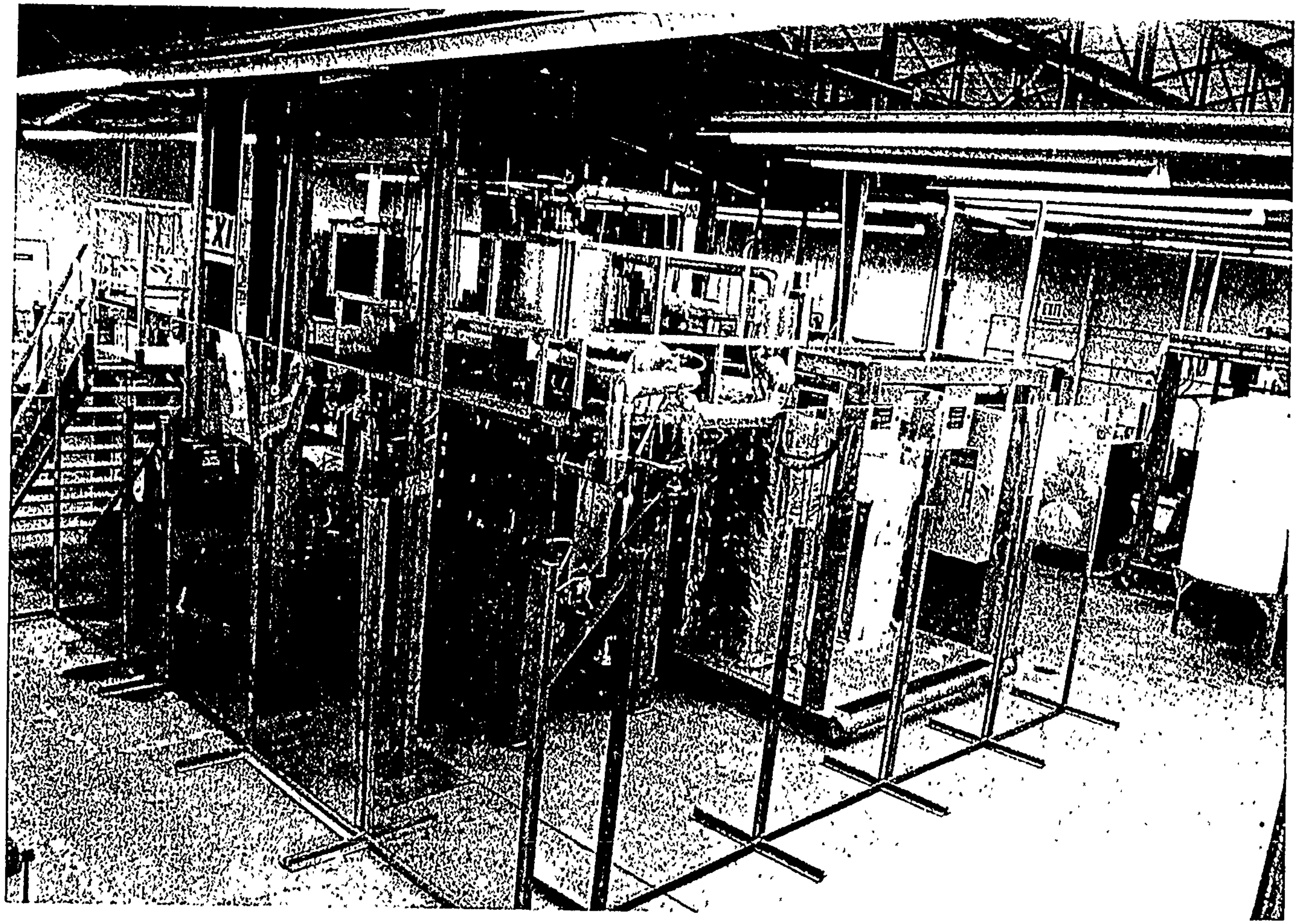
4) To determine the effect on destruction efficiency and distribution of surrogate metals contained in the simulated mixed waste.

5) To evaluate materials of construction in all environments of the process.

As part of the Phase I activities, SCWODAT program personnel also participated in an engineering review of an INEL designed SCWO Test Bed System. DOE plans to use this Test Bed System in the future to test privately developed SCWO oxidizers. This will permit the determination of the optimum oxidizer design for treating a variety of DOE mixed radioactive waste (Barnes, C.M., "Mixed Waste Survey for the SCWO Program," Idaho National Engineering Laboratory Publication EGG-WTD-10984, November, 1993) and support of the commercialization of privately developed oxidizers through technology demonstrations. The SCWO Test Bed System will be developed to eventually allow DOE testing of actual mixed wastes (radioactive) within the controlled environment of a DOE facility.

Objectives of Phase II Navy Waste Testing

Following the Phase I DOE simulated mixed waste tests, the Phase II testing program was conducted on actual Navy hazardous wastes. The objective was to demonstrate the ability of the MODAR SCWO technology to treat Navy wastes generated at a typical shore side Naval facility. The Navy can utilize the MODAR test data to determine the advantages of a vessel oxidizer in future Navy SCWO projects. In addition, since the wastes tested were similar to many DOE generated hazardous wastes, these data will support DOE's treatment options for mixed wastes.



3.0 ENGINEERING AND DESIGN

Process Concept

At the beginning of the SCWODAT program, a process concept was developed to test configurations that were expected to optimize the MODAR SCWO process for treatment of TRIM®SOL solution containing metal surrogates. The MODAR pilot scale plant was modified to meet the objectives of the Phase I testing as set by DOE. After this testing, the pilot plant was reconfigured to perform treatability studies of several Navy waste materials. The Navy waste materials differed from the TRIM®SOL in the following ways:

a. The TRIM®SOL was a well characterized material; an elemental analysis was available, whereas the Navy wastes were only broadly classified as flammable liquid, non-chlorinated solvent, grease, adhesive, aqueous fire fighting foam or paint waste.

b. The TRIM®SOL was a liquid with metal surrogates added as water soluble acetates, whereas the nine Navy wastes ranged from clear liquid to paint sludge with solid debris.

Design Basis

Since the prime objective of the Navy program was to demonstrate treatability, the following design basis was established:

a. Treatability of each waste by SCWO, as measured by organic carbon destruction efficiency.

b. Modifications to the pilot plant for Navy testing would be made to facilitate handling feeds and effluent containing solids.

c. The duration of the treatability tests would be based on the volume of Navy waste material shipped to Natick for testing. Several wastes would be treated in sequence, without opening the oxidizer to determine the condition of the oxidizer after each waste.

d. Air flow to the process would not be optimized relative to the stoichiometric requirements.

e. All water flow would be once-through the process until treatability had been demonstrated for all nine Navy wastes. Then, water reuse would be implemented.

f. The Navy Facility which generated the tested wastes produces larger volumes of organic materials than aqueous. To maintain the process heat balance, water would be added to the aqueous portion.

Process Description

The MODAR process configuration for this series of tests is shown in Figure 1. Organic wastes and aqueous wastes were pumped separately to approximately 3300 psig with metering pumps. Compressed air and water were heated using electrically powered heaters. The above streams were introduced into the oxidizer via a coaxial nozzle. Salts formed during oxidation at 600°C, as well as a portion of the metal oxides from the grease, adhesive, and paint wastes, either dropped into the brine zone at the bottom of the oxidizer or remained in the oxidizer. Water soluble salts and metal oxides exited the bottom of the oxidizer through a brine cooling and letdown train.

Most of the hot supercritical water and gases exited near the top of the oxidizer. This hot stream was quenched with cool water to under 300°C in order to:

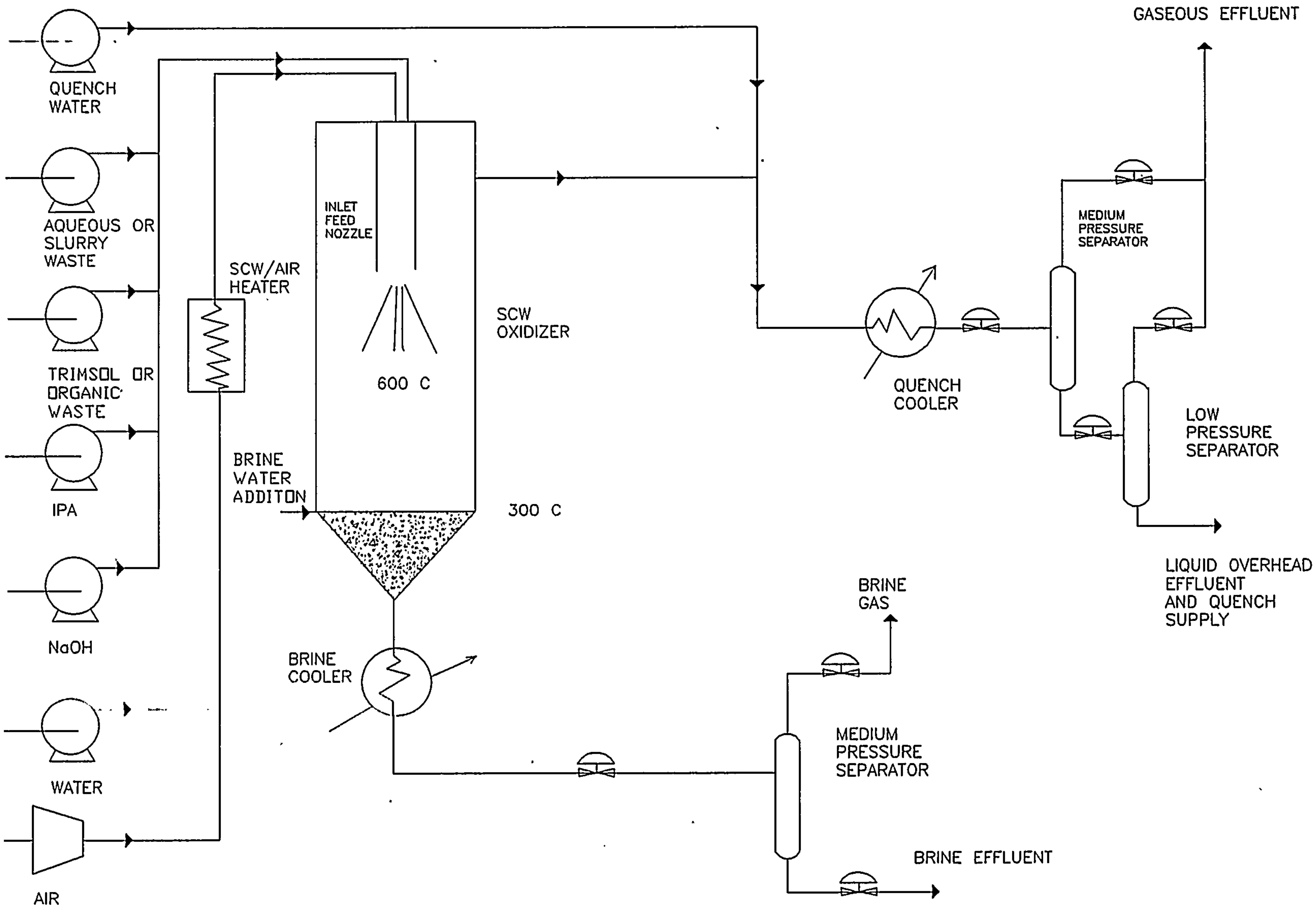
1) Solubilize the small quantity of entrained sticky salt exiting the oxidizer to avoid plugging of the downstream components.

2) Use corrosion-resistant titanium alloys in pressurized process components at temperatures where the ASME Section VIII Code provides allowable stress values.

Final overhead effluent temperature reduction to 45°C was achieved prior to gas-liquid separation. The gas effluent from the overhead and brine systems was combined and the flow measured. A slipstream was sent for on-line gas analysis. The aqueous overhead and brine streams were maintained separate for flow measurement and sampling.

The organic Navy wastes were pumped at a rate determined to give a reasonable length run for each waste material. Aqueous waste was pumped to the oxidizer at a rate sufficient to control the oxidation temperature. Most of the wastes were not expected to form acids, and therefore no neutralization was anticipated. However, the MODAR process was always configured to add caustic soda or sodium bicarbonate for neutralization should it have been necessary.

FIGURE 1
MODAR PILOT PLANT
SYSTEM CONFIGURATION FOR SCWODAT TRIMSOL/NAVY CAMPAIGN



4.0 TESTING SUMMARY

The following sections describe the objectives and approach for the Phase II Navy waste testing of the SCWODAT program.

4.1 OBJECTIVE

The objective of the Navy waste testing was to conduct short duration tests to determine the performance of the MODAR SCWO system in treating nine typical wastes selected by the Navy. The data gathered will be used by the U.S. Navy in evaluating the reliability of SCWO systems and the type of SCWO process best suited for treating waste streams generated by shore side activities. In addition to the nine individual Navy wastes, a composite sample of wastes selected by the Navy was processed to measure performance of the SCWO system.

The composite waste was prepared from the selected nine wastes in the same proportion that they were generated at the shore side facility. The composite waste test data will allow the Navy to determine whether segregation of wastes at the facility would be required prior to treatment by SCWO. Processing the wastes with high destruction efficiency was a major objective of this portion of testing.

4.2 APPROACH

A Navy waste test plan was created outlining the approach that would be taken for this portion of the project. SCWO test runs processed each of the nine wastes. For economy of operation, several of the wastes were processed sequentially in a single run.

Prior to the first test run, the Navy wastes were categorized as: aqueous, organic, and potentially "hard-to-pump". The sequence for processing these wastes was to treat the aqueous wastes, followed by the organics, and ending with the potentially "hard-to-pump." wastes. After the nine individual Navy wastes had been processed, the composite Navy waste sample was tested.

4.3 WASTE DESCRIPTION

Nine different types of Navy waste samples were selected by the Naval Facilities Engineering Service Center (NFESC) Project Engineer to be evaluated for treatability (see Table 1). These waste samples varied from aqueous to organic and represented the types of wastes generated at Navy shore side facilities and collected at the Public Works Center, San Diego (PWC-SD) for final disposal. PWC-SD supplied approximately 15 gallons of each of the nine wastes. Later, additional quantities were delivered for the composite Navy waste test.

4.4 WASTE PREPARATION

Upon receipt of the wastes at MODAR's facility, small samples were removed from each container and were examined to determine the pretreatment requirements necessary for pilot scale pumping of each Navy waste. The analyses included:

1) Gross physical observations and characterizations
2) Determination of suitable diluents
3) Inter-waste stream compatibility *(if mixed together did any gross physical changes occur, such as polymerization, phase separation, etc.)*

Waste preparation procedures were developed based on the observations with the overall goal of producing the highest attainable concentration of each waste material that could be reliably pumped. All aqueous wastes were diluted with water to:

- Meet the through-put requirements of the pilot plant
- Maintain the heat balance
- Extend the steady state run time to a minimum of 2.5 hours

Kerosene was selected as the diluent for the potentially "hard-to-pump" organic waste materials (NFESC's 100, 300, and 400). The aqueous Navy waste streams and the remainder of the organic based waste streams were deemed pumpable as received with the MODAR waste feed system. No compatibility problems were identified.

Navy waste preparation procedures selected and implemented for each waste stream are given in Appendix A.

4.5 PROCESS TESTING

After completing the fabrication of the waste feed system and the necessary Navy waste preparations, the process testing began. Each waste test run varied in length depending on the type and number of wastes processed.

Run 951

The goal of Run 951 was to process NFESC-1000, NFESC-200, and NFESC-800, the three aqueous Navy waste streams, as well as NFESC-600 an organic waste. Another goal was to test the overhead effluent water reuse system to reduce the amount of effluent that would be produced. The reuse system was designed so the effluent would be sent through mixed bed ion exchange cartridges, then sent to various water tanks of the oxidizer system. Each of the wastes were successfully processed in this run with no difficulties.

Run 952

The organic wastes, NFESC-700 and NFESC-500, as well as NFESC-400, the first potentially "hard-to-pump" waste were processed in this test run. NFESC-700, the chlorinated oil, was treated first and successfully processed.

After processing the chlorinated oil waste, NFESC-500 was pumped to the system. This was classified as a non-chlorinated solvent, however, the actual waste received and treated had a substantial quantity of acid forming organic chlorine. The total chlorine composition was on the order of 25 weight percent. The presence of organic chlorine in the feed material was indicated by a precipitous drop in the pH and a large increase of chloride ion concentration in the overhead effluent. NaOH flow in to the oxidizer was quickly initiated to neutralize the acid. After making this minor system adjustment, the waste was successfully processed at the design flowrate.

There were two shipments to Natick of the so-called non-chlorinated solvents. The 25 weight percent chlorine material, described above, had been shipped for the individual waste run. Later, a second drum containing 85 weight percent chlorine solvent was delivered for the composite waste test described later in this report.

The final waste processed in this run was NFESC-400 the grease waste. To facilitate pumping, kerosene was used for slurrying. The waste slurry was successfully processed over a period of approximately 18 hours.

Run 953

Run 953 was a short duration run in which the paint sludge, NFESC-100, was successfully processed over a period of approximately 13 hours. This waste was slurried in kerosene.

Run 954

The adhesive sludge NFESC-300 was also slurried in kerosene and successfully processed over a period of 18 hours.

Run 955

The objective of Run 955 was to treat a composite Navy waste stream consisting of the wastes in proportion to the rate generated by shore side activities. The composite consisted of the same Navy waste samples as previously treated, with the exception of NFESC-500, the non-chlorinated solvent. This so-called non-chlorinated waste was found to have an organic chlorine concentration of 85 wt%. The Navy, therefore, instructed Stone & Webster to exclude this waste. The organic portion of the waste slurry was mixed with kerosene to facilitate pumping, while the aqueous portion was diluted with de-ionized water for the reasons previously described.

The main goal of this run was to successfully process the composite waste. A secondary goal was to use a simplified water reuse system. Several modifications were made to the reuse system for Run 955. The first was to eliminate the Run 951 ion exchange treatment system. Instead, the reuse supply was confined to the quench water system and the aqueous waste makeup water. City water was used for the brine water addition rather than deionized water to reduce operating costs. The reuse system was successful in dramatically improving the plant water balance.

After processing approximately 75 percent of the waste feed, a compressor mechanical failure forced a system shutdown and delay of the completion of the test run. A rented back-up compressor was installed and the run was restarted several days later. The remainder of the waste was successfully processed.

5.0 ANALYSIS OF INDIVIDUAL WASTES

5.0.1 WASTE DESTRUCTION

All NFESC Navy wastes were readily oxidized with high destruction efficiency at operating conditions of 590°C and 3300 psi. The Navy Public Works Center, Environmental Chemistry Laboratory Code 910 at the San Diego Naval Air Station, North Island facility determined the TOC values of the waste feed materials, except where noted. An O.I. Corporation TOC analyzer Model 700 was used for all effluent TOC measurements. The destruction efficiency was calculated based on Navy waste feed carbon and effluent TOC measurements. The destruction efficiency results are summarized in Table 2.

The key flows used for the mass based destruction efficiency calculations are shown in Table 3. The reportable destruction efficiencies were determined primarily by the mass input rate of organic carbon and the analytical detection limit, which was 0.5 mg carbon/L. For example, in Table 3 during Run 952, the chlorinated waste oil, NFESC-700, had a mass input rate above 65 grams of carbon per minute. The effluents were below the analytical detection limit, so the calculated efficiency was 99.9947 percent. In contrast, in Run 951, the aqueous fire fighting foam, NFESC-800, had a TOC of only 1220 mg carbon per kilogram of waste. The mass input rate of waste carbon was only 0.15 g/min, resulting in a relatively low calculated destruction efficiency of 97.5 percent (Table 2). It should be noted, however, that the destruction efficiency was 99.995 percent when the calculation included the carbon of the auxiliary fuel.

Tables 4 through 12 provide the details of the aqueous and gas effluent qualities for each of the individual waste runs. These data represent steady state treatment conditions. The liquid analyses were of composite samples. The gas analyses were the arithmetic averages of many readings over the steady state period.

All of the gas effluent qualities were excellent. The gas analysis consisted of two parallel trains:

Train 1	Train 2
CO Analyzer	NO_x Analyzer
O_2 Analyzer	
Gas Chromatograph	

The gas chromatograph (GC) was configured for CO, CO_2, O_2, N_2, and N_2O. The infrared CO analyzer had a detection limit of 1 ppmv and the gas chromatograph's CO limit was 50 ppmv. Several of the wastes processed contained nitrogen. At the oxidation temperature utilized, organic nitrogen was converted to a mixture of nitrogen gas and nitrous oxide, N_2O. When nitrous oxide was present it interfered with the infrared analysis of CO giving a false high concentration. When N_2O was present, MODAR relied on the gas chromatograph, with its attendant CO ppm detection limit of 50 ppm, to measure CO in the gas effluent. Six of the nine Navy wastes had CO measurements in the gas effluent that ranged from 1 ppm to 11 ppm by infrared analysis, while of the remaining three wastes, two were reported at <50 ppm by gas chromatograph and one reported at <30 ppm by infrared analysis (see Tables 4-12).

The concentration of the priority pollutants NO_x and CO in the air emissions from the MODAR SCWO process were less than that emitted from a typical gas-fired home water heater. The concentrations of a typical residential water heater are NO_x 80 ppm and CO 35 ppm.

Successful SCW oxidation was achieved processing Navy wastes in these physical forms:

- Aqueous Solution
- Aqueous Suspension
- Aqueous Containing Particulates
- Organic Solution
- Organic Containing Particulates
- Organic Slurry

5.0.2 OPERABILITY AND IN-OXIDIZER SOLIDS HANDLING

Successful SCW oxidation was continuously achieved switching on-line from one Navy waste to another during the following runs:

Run 951
  Aqueous Cleaning Solution to
  Latex Paint to
  Aqueous Fire Fighting Foam to
  Waste Oil.

Run 952
  Chlorinated Waste Oil to
  So-called "Non-chlorinated" Solvents to
  Mixed Grease.

Table 13 summarizes the noteworthy events observed during the oxidation of each Navy waste. The wastes are listed in the order in which they were treated.

The following wastes were easily treated:

NFESC No.	Description
1000	Aqueous Cleaning Solution
200	Latex Paint
800	Aqueous Fire Fighting Foam
600	Waste Oil, Flammable
700	Waste Oil, Chlorinated
400	Mixed Grease

The so-called "non-chlorinated" solvents NFESC-500, required significant neutralization due to its actual high chlorine content.

The paint sludge waste NFESC-100, produced powdery, low bulk density paint pigments which collected in the oxidizer. A third quarter 1995 project scope change incorporating a Navy required composite waste test was traded for the previously planned solids removal system that would have addressed solids build-up in the oxidizer.

The adhesive waste NFESC-300, produced an insoluble inorganic solid that was analyzed by General Atomics' SEM/EDX laboratory. Table 14 shows the results of this analysis. This material was found to contain significant proportions of Ti, Al, Si, Ca, and Zn. Another analysis by the University of New Hampshire's Instrumentation Laboratory established that it contained no un-oxidized carbon as shown in Table 15. The University of New Hampshire laboratory specifically analyzed for only carbon, hydrogen, and nitrogen in this solid sample. Consequently, the results do not total to 100 weight percent. Similar solids behavior was observed following 40 hours of steady state composite waste testing.

5.0.3 NAVY WASTE NEUTRALIZATION

Most of the Navy wastes required little or no neutralization during processing. When needed, dilute $NaHCO_3$ added to the quench flow yielded the pH 5 target.

The "non-chlorinated" solvents (NFESC-500) ironically, were heavily chlorinated. The Navy laboratory had detected 0.01 weight percent chloride by EPA Method 9252 and 0.38 percent total halogens by Method 9020. MODAR suspects a labeling error.

On initiating treatment, the effluent pH plummeted to 1.0. Quick operator response, in turning on a standby neutralizing agent, allowed for the recovery of the overhead effluent and brine pH, maintenance of the waste flow rate, and maintenance of high destruction efficiency. Having the capability to treat poorly or incorrectly characterized waste is a necessity for real-world waste treatment.

All of the effluent streams characterized in Tables 4 through 12 have very low acidity to neutral pH. Despite varying Cl^- content, cations present balance HCl's potential acidity. When necessary, Na^+ was added to the quench water as $NaHCO_3$. Additional cations such as Ca^+, Mg^+, K^+ (none of which were analyzed) also neutralize the HCl.

5.1 ANALYSIS OF COMPOSITE NAVY WASTE

5.1.1 COMPOSITION

The composition of the combined Navy wastes is shown in Table 16. All the organic wastes were combined as a single stream, separate from the aqueous wastes which were combined into a second stream. The grease, adhesives, and paint sludge solid wastes were slurried with the flammable waste oil and chlorinated waste oil organic liquids. Kerosene was added to this mixture to reach a pumpable viscosity resulting in a suspended solids content of approximately 40 percent. Prior to the composite waste test, a drum of NFESC-500, "non-chlorinated" solvents was analyzed using a Dexsil Corporation *Percent-A-Clor* quantitative chlorine test kit. The result was 85 weight percent chlorine. The Navy instructed that this material be excluded from the composite test.

The composite was formulated to maintain the individual wastes in the same ratio as their U.S. Navy Public Works Facility generation rate. The high heating value of the organic materials dominated the low heating value and comparatively small volume of the three aqueous wastes that were diluted with deionized water or reused process effluent to provide sufficient material for an extended treatability run. When treated simultaneously, the aggregate heating value of the streams was 4200 kJ/kg. From Table 16 the organic mass was 344 kg of the total 3194 kg of composite or 11 weight percent of the composite.

5.1.2 EFFLUENT WATER REUSE

As noted, most of the Navy wastes were high heating value materials. Therefore, effluent water reuse is necessary to effect an attractive plant water balance. At hour 20 of the composite test, effluent water was reused for quenching and making up the aqueous waste mixture. For ease of plumbing, the brine water makeup was switched from demineralized water to Natick city water rather than reused effluent water.

5.1.3 KEY OPERATING PARAMETERS

Table 17 shows the operating parameters of the composite waste test Run 955.

MODAR's pilot plant is configured to use air as the oxidizer. This was not changed for the Navy waste tests. As shown in Table 17, the oxidizer flow rate was 25% in excess of the stoichiometric requirement, excluding purge air. No attempt was made to minimize this. Table 18 shows the effluent quality achieved during steady state operation of the composite waste test.

Table 19 presents several of the key flows of the Navy composite waste test run. When reusing process effluent, the waste destruction efficiency was 99.9965%. Including the kerosene used for slurrying (which introduced more carbon), the destruction efficiency was 99.9987%. The destruction efficiency calculation is shown is Appendix B.

Twice during the Navy waste testing, the Massachusetts Water Resources Authority (MWRA) Toxic Reduction and Control Department made unannounced inspections and sampling of effluents to verify sewer permit compliance. MWRA Sample ID No. 39510703 taken on 11/27/95 tested the brine and overhead effluents for Run 954, while MWRA Sample No. 39510699 taken on 12/19/95 tested the brine and overhead effluents for Run 955. Although the MWRA samples were taken after the test runs, they were taken from the brine and overhead effluent storage tanks at the MODAR facility which contained the respective process effluents. MWRA's chemical analyses showed compliance within all permit limits. Table 20 summarizes the compliance quantitatively.

As noted in Table 13, at hour 32 an increase in the pressure drop across the brine outlet piping was noticed. Following the test and partial disassembly of the oxidizer, the same inorganic material seen in the individual adhesive waste test was observed. At hour 35 the level transmitter on the low pressure gas/liquid separator failed, sending approximately 0.1% of the water flow into the gas effluent line. This small volume was easily removed by a protective knockout pot which had been installed for that purpose. A spare level transmitter was not available. At hour 40, the process air compressor seized. Prior to the beginning of Run 955, a manufacturer's authorized technician performed a day long evaluation of the compressor and concluded that it was in good operating condition. However, as a precaution, a rental contract for a backup compressor was initiated at the start of Run 955. After installation of the rented unit, the remainder of the waste was processed.

Table 17 presents other operating parameters of the composite waste test and the MODAR SCWO process in general. Particularly important were the maximum and minimum heating values the oxidizer vessel could handle. In the simplest terms, the MODAR vessel oxidizer could accept pure water (no heating value) to pure fuel (nominally 46,500 kJ/kg). This was achievable by pumping high and low heating value feeds separately and blending by choice of pumping rates to meet heating value requirements. In this configuration, no waste preheating was necessary.

With a lined oxidizer vessel and standby neutralization capability, the MODAR process can treat chlorinated hydrocarbons. In the blended feed, which again was accomplished by proper pumping rates, the mineral acid content should be less than 5 weight percent. The maximum dissolved solids content is 10 weight percent.

5.1.4 SAFETY

SCWODAT program personnel followed the Health and Safety Plan that was prepared for the project.

No safety related incidents occurred at any time during the Navy waste program.

6.0 MATERIAL OF CONSTRUCTION

Liner No. 1 after Repairs

The refurbished Liner No. 1 was used in all the runs of the Navy waste testing Phase II (Runs 951- 955B). The refurbished Liner No. 1 was inspected visually in December 1995 upon completion of testing. All deposits had been removed from the liner prior to the inspection, except for some remaining sticky solid deposits at the bottom of the liner. These solid deposits formed primarily during the Navy composite waste test. In individual waste runs, powdery, much less sticky, relatively light deposits were reported.

On the inside surface of the refurbished Liner No. 1, there was a fairly thin scale-like deposit ranging in color from light pink to cream. In the areas where this scale was missing, there was no apparent corrosion below mark 29" (distance from the top of the liner), very little corrosion between mark 19" and mark 29", and pronounced pitting between mark 9" and mark 19". Above mark 9", there was no pitting and most scale was intact. Over the 10 inch high area between mark 9" and mark 19", there were areas of a fairly extensive "general" corrosion. The corrosion could be described as clusters of multiple overlapping pits as well as a number of isolated wide open pits. The depth of attack in most cases was close to or under 1/64 inch, but some were as deep as 1/32 inch. Corrosion affected both the titanium base metal and the seam weld; the severity of attack in the weld metal and in the base metal were comparable.

Corrosion to refurbished Liner No. 1 could have occurred primarily in Run 952 when so-called "non-chlorinated" solvents were treated and the resulting oxidizer pH was very low before corrective actions were taken.

7.0 FABRICATION

Waste Feed Preparation Equipment Design

As part of the Navy waste portion of the program a new waste feed system was designed to deliver a variety of Navy wastes including waste oils, organic liquids with suspended solids, aqueous solutions with suspended solids, viscous organic liquids, adhesive waste material, and heavy organic sludges. The following design objectives were identified:

- Safe operation with flammable materials
- Particle size reduction
- Prevention of solids settling in process lines
- Proper materials of construction

To achieve these goals, the waste feed system was designed with two recirculation loops: a short loop designed to condition the waste feed material until it met the particle size requirements; and a long loop that delivered the conditioned waste to the suction of the high pressure waste feed pump. In addition to these loops the waste feed system had several support sub-systems including a seal flush loop, backwash loop, a nitrogen purge system, and an exhaust blower with an associated flame arrestor and activated carbon filter.

Waste Feed Preparation Equipment Operation

Initial operation with any Navy waste feeds was confined to the short loop to observe the flow characteristics of the material being processed. However, before any processing began, non-pumpable Navy waste material was analyzed and diluted to facilitate pumping. The maximum quantity of Navy waste contained in the waste feed tank at one time was 15 gallons, with lesser quantities for those wastes that required additional dilution.

During short loop operation, the Navy waste material entered the pump/grinder which simultaneously reduced the particle size and supplied the pumping head required to move the fluid through the conditioning loop. The pump/grinder reduced the particle size in two dimensions to meet the upper particle size limit of the high pressure feed pump. The pump/grinder also added heat to the fluid which increased the waste volatility. A cooling water loop through the pump casing and an external tube-in-shell liquid cooled heat exchanger controlled the waste fluid temperature. From the pump/grinder the Navy waste entered a filter where any agglomerations were broken and returned to the waste feed tank. The short loop cycled the contents of the waste feed tank every 3 minutes, while a mixer agitated the contents of the feed tank to prevent settling of particles. Once the waste feed was pretreated sufficiently for the high pressure pump, the fluid was allowed to flow through the long loop to the oxidizer.

The long delivery loop passed the conditioned Navy waste material to one head of the high pressure feed pump which was fitted with custom pump valve assemblies to accurately and repeatably deliver particulate laden wastes to the SCWO oxidizer. The feed pump head drew the required quantity of conditioned waste material from the loop to feed the oxidizer, while the remainder of the waste was recirculated back to the feed tank.

The waste feed tank was open to the atmosphere to facilitate charging and insertion of an agitator. Because of the hazardous nature of all of the Navy wastes handled and the volatility of some of the wastes, the feed system included a dedicated vent hood and fan blower to remove any fumes released during processing. The blower directed the fumes to an activated carbon filter before release to the environment inside the MODAR facility. A nitrogen system was provided to blanket the surface of the waste material in the feed tank if needed. The main purpose of the nitrogen blanket was to avoid waste feed polymerization, which was anticipated with the paint and adhesive wastes.

TABLE 1

WASTE DESCRIPTIONS

SAMPLE CODE	WASTE SAMPLE	DESCRIPTION	CATEGORY
NFESC-100	Paint waste (oil based)	Dense, semi-solid mixture consisting of paint pigment and thickened paint vehicle.	Potentially "Hard-to-pump"
NFESC-200	Latex Paint		Aqueous
NFESC-300	Adhesive sludge	Mixture of remnants of various adhesives	Potentially "Hard-to-pump"
NFESC-400	Mixed grease	Mixture of different grease-type lubricants	Potentially "Hard-to-pump"
NFESC-500	Non-chlorinated solvents	Mixture of non-chlorinated organic solvents	Organic
NFESC-600	Waste oils		Organic
NFESC-700	Waste oils (chlorinated)		Organic
NFESC-800	AFFF (Aqueous Fire Fighting Foam)	AFFF are complex organic salt solutions	Aqueous
NFESC-1000	Citric acid and TEA	Aqueous solutions used as cleaning solvents	Aqueous

TABLE 2

SCWODAT PHASE II
TEST RESULTS

		Organic Carbon Destruction Efficiency %	
		Waste Carbon Only [1]	All Carbon [2]
Navy Wastes	NFESC No.		
Paint Sludge	100	>99.96	>99.995
Latex Paint Waste	200	99.9995	99.9998
Adhesive Sludge	300	99.994	99.994
Mixed Grease	400	99.88	99.98
Non-Chlorinated Solvents	500	>99.996	Same. No Auxiliary Fuel
Non-Chlorinated Waste Oils	600	>99.994	Same. No Auxiliary Fuel
Chlorinated Waste Oils	700	>99.995	Same. No Auxiliary Fuel
Aqueous Fire Fighting Foam	800	>97.5 [3]	>99.995
Aqueous Cleaning Solution	1000	99.87	99.994
Composite of 8 Wastes		99.997	99.9987

[1] *Based on waste's carbon only*

[2] *Based on total carbon input: waste's carbon plus auxiliary fuel's carbon*

[3] *Analytical detection limits the calculation of destruction efficiency.*

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Table 3

Key Flows

MODAR Run No.		951	951	951	951	951	952	952	952	953	954
NFESC Waste No.		1000	200	200	800	600	700	500	400	100	300
Identification		Aq. Cleaning Solution	Latex Paint	Latex Paint	AFFF	Waste Oil Flammable	Waste Oil Chlorinated	Non-Chlor. Solvents**	Mixed Grease	Paint Sludge	Adhesive Waste
Run Date		October 19,1995	October 19,1995	October 19,1995	October 19–20, 1995	October 20,1995	October 24,1995	October 25,1995	October 25–26, 1995	November 8–9, 1995	November 15–16, 1995
Steady State											
Duration	Hours	2.6	2.7	2.8	4.7	6.2	4.7	5.2	18	13.3	15.1
Waste Flow	mL/min	100	152	156	120	100	97	124	22.5	24.98	34.83
Waste Sp. Gravity	g/mL	1.1	1.0	1.0	1.03	0.87	0.91	0.97	0.83	0.83	0.83
Waste Run,Steady State	kg	17.16	24.62	26.21	34.75	32.36	24.89	37.53	20.17	16.54	26.19
Waste TOC	mg/kg	37,000	276,000	276,000	1,220	630,000	743,000	700,000	462,000	438,000	197,000
Waste C Flow	g/min	4.07	41.95	43.06	0.15	54.81	65.58	84.2	8.63	9.08	5.7
Nozzle Core Diluent		Water	Water	Water	Water	Water	Water	Water and NaOH	Kerosene	Kerosene	Kerosene
Reason for Diluent		To Lengthen Steady State	To Lengthen Steady State	To Lengthen Steady State	To Lengthen Steady State	To Maintain Heat Balance	To Maintain Heat Balance	To Maintain Heat Balance and Neutralization	To Slurry the Waste	To Slurry the Waste	To Slurry the Waste
Auxiliary Fuel		IPA	IPA	IPA	IPA	None	None	None	Kerosene	Kerosene	Kerosene
Aux. Fuel Rate	mL/min	170	129	107	171	0	0	0	67.5	86.03	77.17
Aux. Fuel Sp. Gr.	g/mL	0.78	0.78	0.78	0.78	0	0	0	0.83	0.83	0.83
Aux. Fuel C Flow	g/min	79.56	60.37	50.08	80.03	0	0	0	48.46	61.76	55.4
Effluents											
Overhead	L/min	6.85	Completely Recycled	7.17	7.12	6.64	6.57	6.94	6.3	6.56	6.3
Overhead TOC	mg/L	0.5	1.0	1.0	0.5	0.5	0.5	0.5	1.4	0.5	0.5
Overhead C Flow	g/min	0.00343	0	0.00717	0.00356	0.00332	0.00329	0.00347	0.00882	0.00328	0.00315
Brine	L/min	0.38	0.43	0.40	0.36	0.41	0.40	0.41	0.40	0.44	0.47
Brine TOC	mg/L	5	0.5	0.5	0.5	0.5	0.5	0.5	2.9	0.5	0.6
Brine C Flow	g/min	0.0019	0.00022	0.0002	0.00018	0.00021	0.0002	0.000205	0.00116	0.00022	0.00028
Destruction Efficiency											
All Organic C	%	99.9936	99.9998	99.9921	99.9953	99.9936	99.9947	99.9956	99.9825	99.9951	99.9944
Waste Organic C only	%	99.8692	99.9995	99.9829	97.5125	99.9936	99.9947	99.9956	99.8843	99.9614	99.9397
			Waste feed tank foaming interrupted test.					**Waste is Actually Highly Chlorinated. MODAR Estimate of Waste TOC.	Grease is 25 wt% in kerosene. 0.83 is specific gravity of the slurry.	Paint sludge is 22.5 wt% in kerosene. 0.83 is specific gravity of the slurry.	Adhesive waste is 31.1 wt% in kerosene. 0.83 is specific gravity of the slurry.

C=carbon

TABLE 4

NFESC - 1000
AQUEOUS CLEANING SOLUTION
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	4600	21
Cl	mg/L	3900	29
SO_4	mg/L	340	<1
pH		7.2	5.7
TOC	mg/L	5	0.5

Gas Effluent[1]		
CO	ppmv	<50[2]
CO_2	Vol %	8.1
O_2	Vol %	9.3
N_2	Vol %	83.1
NO_x	ppmv	<1
N_2O	ppmv	<100

[1] *Includes purge air which may not participate in the oxidation reaction.*

[2] *N_2O interferes with infrared CO analysis. Gas chromatograph's CO detection limit was not exceeded at 50 ppmv.*

TABLE 5

NFESC - 200
LATEX PAINT
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	480	No Net Effluent Flow This Water Reused
Cl	mg/L	500	
SO_4	mg/L	310	
pH		6.6	
TOC	mg/L	<0.5	

Gas Effluent[1]		
CO	ppmv	<50[2]
CO_2	Vol %	8.7
O_2	Vol %	9.0
N_2	Vol %	83.0
NO_x	ppmv	<1
N_2O	ppmv	<100

[1] *Includes purge air which may not participate in the oxidation reaction.*

[2] *N_2O interferes with infrared CO analysis. Gas chromatograph's CO detection limit was not exceeded at 50 ppmv.*

TABLE 6

NFESC - 800
AQUEOUS FIRE FIGHTING FOAM
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	580	27
Cl	mg/L	1250	78
SO_4	mg/L	530	5.2
pH		6.1	3.6
TOC	mg/L	<0.5	<0.5

Gas Effluent[1]		
CO	ppmv	5
CO_2	Vol %	8.3
O_2	Vol %	8.5
N_2	Vol %	83.2
NO_x	ppmv	<1

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[1] *Includes purge air which may not participate in the oxidation reaction.*

TABLE 7

NFESC - 600
WASTE OIL-FLAMMABLE
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	130	18
Cl	mg/L	380	35
SO_4	mg/L	90	5.2
pH		5.0	3.7
TOC	mg/L	<0.5	<0.5

Gas Effluent[1]		
CO	ppmv	11
CO_2	Vol %	7.8
O_2	Vol %	10.5
N_2	Vol %	82.8
NO_x	ppmv	<1

[1] *Includes purge air which may not participate in the oxidation reaction.*

TABLE 8

NFESC - 700
WASTE OIL-CHLORINATED
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	34	27
Cl	mg/L	10	14
SO_4	mg/L	2	2
pH		5.2	4.6
TOC	mg/L	<0.5	<0.5

Gas Effluent[1]		
CO	ppmv	8
CO_2	Vol %	7.3
O_2	Vol %	10.5
N_2	Vol %	81.7
NO_x	ppmv	<1

---

[1] *Includes purge air which may not participate in the oxidation reaction.*

TABLE 9

NFESC - 500
NON-CHLORINATED SOLVENTS [1]
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	21,000	660
Cl	mg/L	35,000	680
SO_4	mg/L	930	2
pH		5.2	5.1
TOC	mg/L	<0.5	<0.5

		Gas Effluent [2]
CO	ppmv	<30 [3]
CO_2	Vol %	8.6
O_2	Vol %	9.1
N_2	Vol %	81.7
NO_x	ppmv	<1
N_2O	ppmv	<100

---

[1] *Waste is actually highly chlorinated.MODAR's post-test analysis shows 25 wt% Cl.All reported values are at the 4 hour mark after the waste and caustic were turned on.*

[2] *Includes purge air which may not participate in the oxidation reaction.*

[3] *N_2O interferes with infrared CO analysis. The infrared CO meter read no greater than 30 ppm during this test.*

TABLE 10

NFESC - 400
MIXED GREASE
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	700	100
Cl	mg/L	110	47
SO_4	mg/L	30	19
pH		4.8	5.1
TOC	mg/L	2.9	1.4

Gas Effluent[1]		
CO	ppmv	3
CO_2	Vol %	6.6
O_2	Vol %	11.3
N_2	Vol %	81.8
NO_x	ppmv	<1

[1] *Includes purge air which may not participate in the oxidation reaction.*

TABLE 11

NFESC - 100
PAINT SLUDGE
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	<1	27
Cl	mg/L	110	56
SO_4	mg/L	58	14
pH		5.1	5.8
TOC	mg/L	<0.5	<0.5

Gas Effluent[1]		
CO	ppmv	<1
CO_2	Vol %	7.1
O_2	Vol %	10.3
N_2	Vol %	75
NO_x	ppmv	<1

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[1] *Includes purge air which may not participate in the oxidation reaction.*

TABLE 12

NFESC - 300
ADHESIVE SLUDGE
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent	Gas Effluent[1]		
Na	mg/L	40	58	CO	ppmv	3
Cl	mg/L	60	45	CO_2	Vol %	8.2
SO_4	mg/L	190	50	O_2	Vol %	9.3
pH		2.8	5.1	N_2	Vol %	76.8
TOC	mg/L	0.6	<0.5	NO_x	ppmv	<1

[1] *Includes purge air which may not participate in the oxidation reaction.*

TABLE 13

NOTEWORTHY EVENTS

NFESC #	Identification	Event	Comments
1000	Aqueous Cleaning Solution	Gel observed in treated effluent sample bottles approximately 2 days after collection. Analysis identified Si.	No run time implications or equipment problems.
200	Latex Paint	Foaming in stirred feed tank at low level caused loss of suction flow to high pressure pump. Test interrupted, but restarted with mixer off.	Easily rectified.
800	Aqueous Fire Fighting Foam	None	
600	Waste Oil	None	
700	Waste Oil, Chlorinated	None	
500	Solvents, non-chlorinated	On initiating treatment,the effluent pH plummeted to 1.0. Without interrupting the waste flow, the operators responded by pumping in neutralizing agent. Effluent pH recovered to 5.0. Destruction efficiency remained at >99.996 % throughout. After the test the chlorine content of the waste was measured to be 25 wt%	With on-line pH measurement and standby neutralizing agent pumping capability, the unknown chlorine content was easily handled.
400	Mixed Grease	None	
100	Paint Sludge	None during test. Paint pigments accumulated in the oxidizer. Observed after the test.	A third quarter 1995 project scope change incorporating the Navy required composite waste test was traded for a previously planned paint pigment/sludge removal system that would have addressed the solids build-up in the oxidizer.
300	Adhesive Sludge	Differential pressure indicates partial plugging of brine outlet piping. Post-test inspection showed tenacious, inorganic deposits on brine outlet fitting.	The adhesive waste produced insoluble inorganic agglomerations containing Ti, Si, Al, Ca, and Zn.
All but 500	Composite wastes in proportion to their generation rate.	At hour 32, differential pressure indicated partial obstruction of brine outlet piping. At hour 35, level transmitter of low pressure gas-liquid separator failed sending 10 g/min of water into the gaseous effluent. This was trapped in a downstream knockout pot. At hour 40, process air compressor seized. Rented compressor installed and remaining waste was treated.	The adhesive waste produced insoluble inorganic agglomerations containing Ti, Si, Al, Ca, and Zn. Implement redundancy Implement more reliable compressor.

TABLE 14

COMPOSITION OF TENACIOUS BRINE LINE SOLID

	Weight %	
Element	At Section IS	At Section OS
Na	5.5	10.2
Mg	3.2	3.0
Al	27.4	23.4
Si	12.5	9.1
P	3.7	2.2
S	1.2	2.4
Cl	0.6	2.1
K	1.3	1.0
Ca	11.8	7.7
Ti	17.1	11.8
Cr	0.8	2.1
Fe	4.2	2.8
Zn	10.7	22.1
Normalized Total	100.0	99.9

X-ray analysis by General Atomics' SEM/EDX Lab. Jan. 24, 1996. A random chunk of solid from the brine line was analyzed. OS means outside surface of the solid, IS designates an interior surface.

TABLE 15

COMPOSITION OF TENACIOUS BRINE LINE SOLID

Element	Weight %
C	0
H	0.1
N	0.16

Analysis performed by University of New Hampshire Instrumentation Laboratory, December 21, 1995

TABLE 16

NAVY WASTE
COMPOSITION OF THE COMPOSITE WASTE

Organic Waste	Identification	kg	
NFESC-100	Paint sludge	66.1	
NFESC-100	Paint sludge tramp		11.8 kg oversize, not treated
NFESC-300	Adhesive	12.3	
NFESC-400	Grease	6.1	
	Subtotal	84.5	
NFESC-500	Non-chlorinated solvent[1]	0	
NFESC-600	Waste oil, flammable	66.6	
NFESC-700	Waste oil, chlorinated	16.4	
	Subtotal	83.0	
	Kerosene	176.5	
Total Organic		344.0	
Aqueous Waste	**Identification**	**kg**	
NFESC-200	Latex paint	18.0	
NFESC-800	Aqueous fire fighting foam	20.0	
NFESC-1000	Aqueous cleaning solution	12.3	
	Water	2800	
Total Aqueous		2850.3	

[1] *MODAR analysis showed this material to contain 85 wt% Cl. It was excluded as instructed by the Navy.*

TABLE 17

COMPOSITE WASTE OPERATING PARAMETERS

Oxidizer Operating Pressure	3,300 psi average
Oxidizer Temperature Main Reaction Zone	580°C average
Waste Residence Time In Oxidizer	Less than 1 minute
Waste Concentrations	
Organic Stream NFESC-100, 300, 400, 600, 700	48.7 wt% in kerosene
Aqueous Stream NFESC-200, 800, 1000	1.8 wt% in reused effluent water
Total Waste/Net Added Water	0.042 - 0.057
(Total Waste + Kerosene)/Net Added Water	0.078 - 0.097
Oxidizer	Air
Oxidizer Mass Flow Rate	1700 g/min
Excess Oxidizer, Estimated	25%
Water Flow Rate, Net	1520 g/min
Waste Destruction Efficiency	
Based on waste's carbon only	99.9965%
Based on all carbon (including the kerosene)	99.9987%
Maximum and Minimum Allowable Waste Heating Value	Using the oxidizer vessel and pumping high and low heating value wastes separately, the MODAR process can accept pure fuel to pure water. Blended heating value is 4200 kJ/kg (1800 BTU/lb)
Maximum Allowable Dissolved Solids Content	10 wt%
Maximum Allowable Particulate Size	Depends on grinding equipment and high pressure pump. For this program: 420 μm
Maximum Allowable Mineral-Acid-Forming Chemical Content	Approximately 5 wt% in blended feed. 85 wt% of an actual compound e.g. tetrachloroethylene

TABLE 18

NFESC - 100, 200, 300, 400, 600, 700, 800, 1000
COMPOSITE WASTE
EFFLUENT QUALITY

		Brine	Overhead Aqueous Effluent
Na	mg/L	780	70
Cl	mg/L	170	190
SO_4	mg/L	16	58
pH		7.0	5.8
TOC	mg/L	0.8	0.5

Gas Effluent[1]		
CO	ppmv	1.4
CO_2	Vol %	11.2
O_2	Vol %	5.4
N_2	Vol %	86.7
NO_x	ppmv	<1

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[1] *Includes purge air which may not participate in the oxidation reaction.*

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Table 19

Key Flows

Composite Waste

MODAR Run No.		955A	955A	955A	955B
NFESC Waste No.		All except 500	All except 500	All except 500	All except 500
Identification		Composite Waste No water reuse	Composite Waste No water reuse Maximum Flow Tested	Composite Waste Aqueous effluent reuse	Composite Waste Aqueous effluent reuse
Run Date		December 5, 1995	December 5, 1995	December 5–6, 1995	December 12, 1995
Steady State					
Duration	Hours	20.83	6	19.17	11.95
Organic Waste Flow	mL/min	63.57	72.86	58.19	47.43
Waste Sp. Gravity	g/mL	0.90	0.90	0.90	0.90
Waste Run, Steady State	kg	71.5	23.61	60.24	30.61
Waste TOC	mg/kg	530,000	530,000	530,000	530,000
Organic Waste C Flow	g/min	30.32	34.75	27.76	22.63
Aqueous Waste Flow	mL/min	13.51	13.7	12.01	12.15
Waste Sp. Gravity	g/mL	1.001	1.001	1.001	1.001
Waste Run, Steady State	kg	16.9	4.94	13.83	8.72
Waste TOC	mg/kg	9,600	9,600	9,600	9,600
Aqueous Waste C Flow	g/min	0.13	0.13	0.12	0.12
Nozzle Core Diluent:Organic		Kerosene	Kerosene	Kerosene	Kerosene
Reason for Diluent		To slurry organic sludges for pumping	To slurry organic sludges for pumping	To slurry organic sludges for pumping	To slurry organic sludges for pumping
Nozzle Core Diluent:Aqueous		DI Water	DI Water	Reused Effluent Water	Reused Effluent Water
Reason for Diluent		To extend run time and maintain heat balance	To extend run time and maintain heat balance	To extend run time and maintain heat balance	To extend run time and maintain heat balance
Organic Slurrying Agent		Kerosene	Kerosene	Kerosene	Kerosene
Flow Rate	g/min	59.79	68.53	54.73	44.61
C Flow	g/min	51.72	59.27	47.34	38.59
Effluents					
Net Overhead	L/min	6.6	6.4	1.08	1.07
Overhead TOC	mg/L	0.5	0.5	0.5	0.5
Overhead C Flow	g/min	0.0033	0.0032	0.00054	0.00054
Brine	L/min	0.56	0.6	0.56	0.43
Brine TOC	mg/L	0.5	0.5	0.8	0.5
Brine C Flow	g/min	0.00028	0.0003	0.00045	0.00022
Destruction Efficiency					
All Organic C	%	99.9956	99.9963	99.9967	99.9988
Waste Organic C only	%	99.9882	99.990	99.9965	99.9967
		Organic waste is 48.7 wt% in kerosene. 0.90 is the specific gravity of the slurry. Aqueous waste is 1.8 wt% in DI water. 1.001 is the specific gravity of the mixture.	Organic waste is 48.7 wt% in kerosene. 0.90 is the specific gravity of the slurry. Aqueous waste is 1.8 wt% in DI water. 1.001 is the specific gravity of the mixture. No feed interruption. This run segment is the final six hours of the segment at left.	Organic waste is 48.7 wt% in kerosene. 0.90 is the specific gravity of the slurry. Aqueous waste is 1.8 wt% in reused effluent water. 1.001 is the specific gravity of the mixture. No feed interruption.	Organic waste is 48.7 wt% in kerosene. 0.90 is the specific gravity of the slurry. Aqueous waste is 1.8 wt% in reused effluent water. 1.001 is the specific gravity of the mixture.

C=carbon

TABLE 20

MASSACHUSETTS WATER RESOURCES AUTHORITY DISCHARGE LIMITATIONS AND ANALYSES

Pollutant	Daily Maximum Limit (mg/L)	MWRA[1] Test No.39510699 (mg/L)	MWRA[2] Test No. 39510703 (mg/L)
Cr $^{+6}$	0.5	<0.015	<0.015
Cr, total	1.0	<0.01	<0.01
Mo	Not Specified	<0.1	1.5
Ni	1.0	<0.04	<0.04
Chlorinated Naphthalenes	0.8	<0.002	<0.002
Hexachlorobutadiene	3.0	<0.002	<0.002
Pentachlorophenol	0.05	<0.002	<0.002
Phenol	5.0	<0.002	<0.002
Phenol Compounds	0.5	<0.002	<0.002
Trichloroethylene	0.07	<0.005	<0.005
Any toxic organic not elsewhere limited	1.0	Not Detectable	Not Detectable
pH	5.5 - 10.5	6.0	NA

[1] *Overhead Effluent*

[2] *Brine Effluent*

Figure 2

Composite Waste Test Steady State Operation

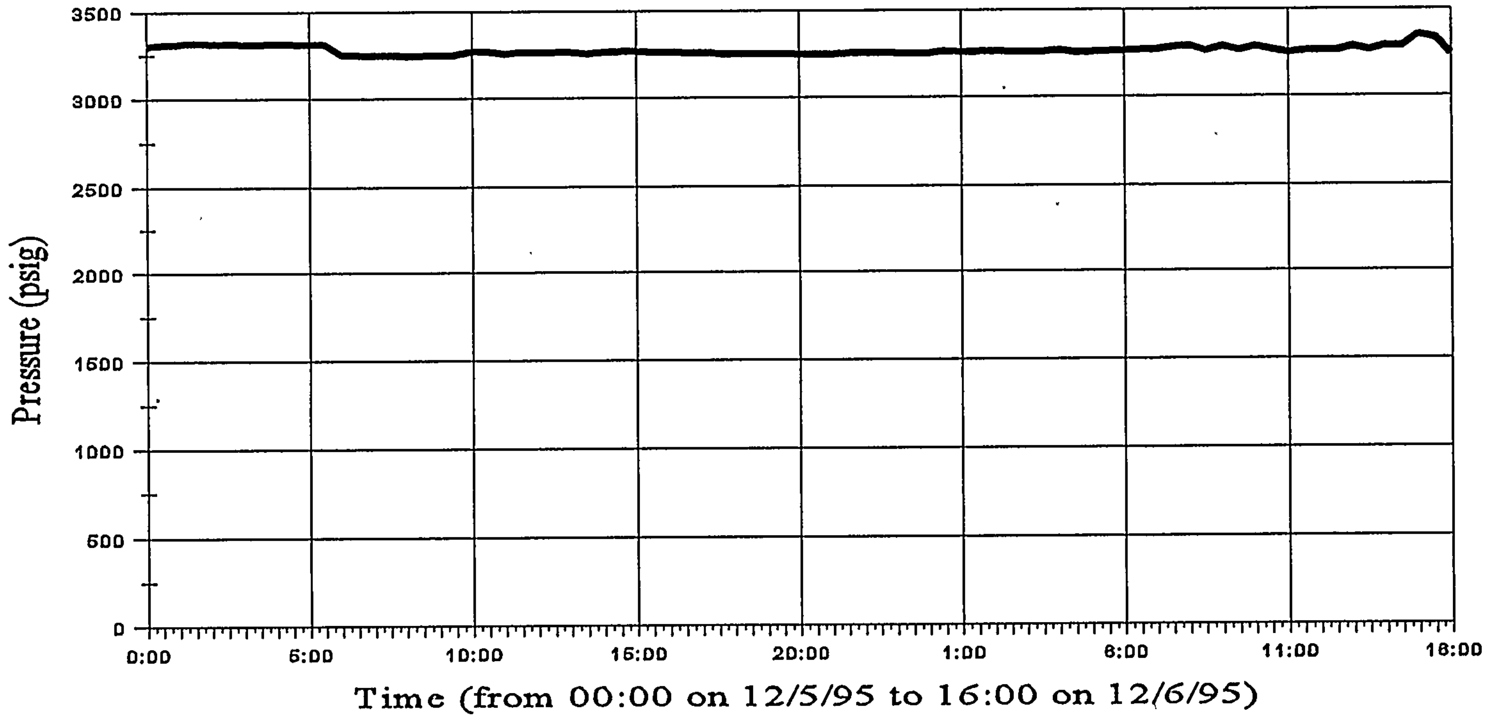
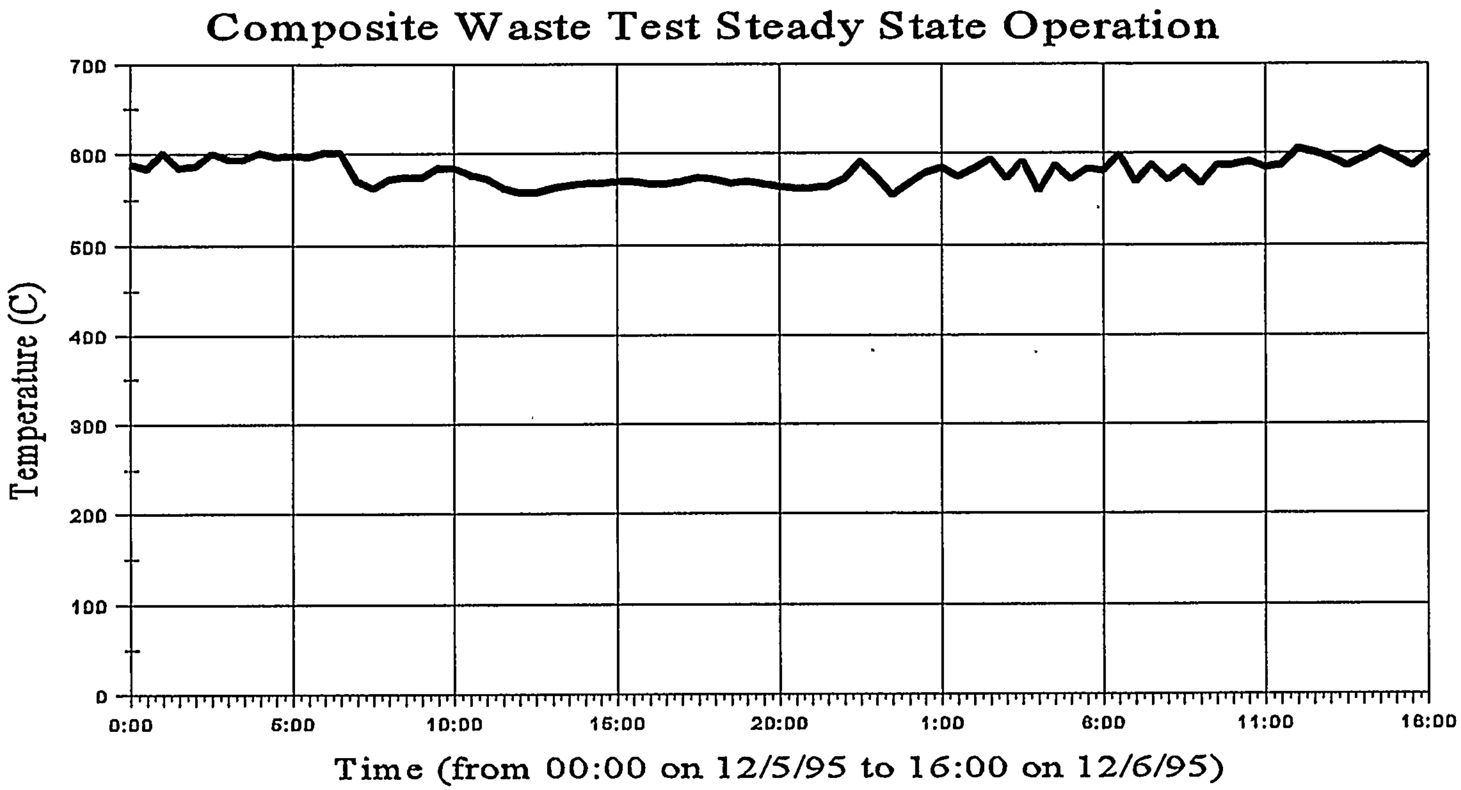


Figure 3



Composite Waste Test Steady State Operation

APPENDIX A

TABLE A.1

WASTE PREPARATION

NFESC Designation	Waste Description	Procedure
100	Paint Sludge	3
200	Latex Paint	1
300	Adhesive Sludge	3
400	Mixed Grease	2
500	Solvents, Non-Chlorinated	1
600	Waste Oil	1
700	Waste Oil, Chlorinated	1
800	Aqueous Fire Fighting Foam	1
1000	Aqueous Cleaning Solution	1
Aqueous Composite	NFESC's 200, 800 & 1000	4
Organic Composite	NFESC's 100, 300, 400, 600 & 700	5

Waste Preparation Procedures

The following procedures describe the preparations applied to selected wastes. In any future SCWO Navy facility, the waste preparation and feed systems would be designed for automatic on-line preparation to minimize operator handling of the individual wastes. The procedures selected here were intended for ease of operation in a pilot scale test facility.

Procedure 1

Waste material required no special processing prior to feeding to the oxidizer. Waste material was transferred to waste feed system in as received condition.

Procedure 2

a) Removed and weighed out predetermined quantity of waste material from container.
b) Weighed out predetermined quantity of kerosene from 55 gallon drum. From this quantity, removed, labeled and set aside approximately 1 gallon to be used in clean up procedures.
c) Added waste material and kerosene to open top 30 gallon metal drum.
d) Inserted and secured propeller mixer to drum and commenced mixing.
e) Probed and stirred occasionally with paddle to assure that a homogeneous slurry was obtained.
f) When slurry was homogeneous, rinsed off tools into drum with approximately 1 gallon fresh kerosene.
g) Transferred slurry with pneumatic drum pump to waste feed system and treated per SCWO waste test requirements.

Procedure 3

a) Removed and weighed out predetermined quantity of waste material from container.
b) Weighed out predetermined quantity of kerosene from 55 gallon drum. From this quantity, removed, labeled and set aside approximately 1 gallon to be used in clean up procedures.
c) Added kerosene to open top 55 gallon metal drum.
d) Inserted and secured pneumatic drum pump to 55 gallon drum.
e) Mounted and secured propeller mixer to drum.
f) Stacked a #7 sieve onto a #14 sieve and secured over drum.
g) Activated drum pump and mixer and recycled fluid through sieve stack back into drum.
h) In batch fashion, applied raw waste material onto sieve stack and rinsed with recirculating fluid. When oversized material blocked sieve, halted rinsing and collected material from sieves. Processed all waste material, weighed and recorded separated oversized material.
I) Processed oversized material through hand operated meat grinder twice.
j) Removed sieve stack and replaced with #40 sieve.
k) In batch fashion, applied ground oversized material to #40 sieve and rinsed through with fluid recirculating back into drum. When tramp material blocked sieve, halted rinsing and collected tramp from sieve.
l) Processed all ground oversized material, weighed and recorded tramp material removed with #40 sieve.

m) Utilized approximately 1 gallon of clean kerosene removed in Step b), rinsed sieves, grinder and other tools through #40 sieve back into 55 gallon drum. Collected remaining tramp, added to that obtained in Step l) and re-weighed and recorded.
n) Circulated slurry in waste feed system, short loop mode, for a minimum of 15 minutes.
o) Performed high pressure pumping test.
p) Evaluated pumpability. Modified dilution ratio if required and repeated pumpability test.
q) When slurry was deemed pumpable, treated per SCWO waste testing procedures.

Procedure 4

a) Removed and weighed out predetermined quantities of aqueous waste materials from containers.
b) Mounted #40 sieve into large mouth funnel with discharge into 15 gallon poly container.
c) Poured waste materials through sieve and combined into 15 gallon poly container. (Note: no appreciable quantity of particulate was separated during this step)
d) Combined waste composite material with predetermined quantity of DI-water or recycled SCWO process effluent in off-skid mixing tank per SCWO waste testing procedure.
e) Treated aqueous waste composite per SCWO waste testing procedure.

Procedure 5

a) Removed and weighed out predetermined quantities of organic waste materials from containers.
b) Processed NFESC's 100 and 300 per waste preparation Procedure 3, Steps b) through m).
c) Added NFESC's 400, 600 & 700 to slurry obtained in Step b).
d) Mixed thoroughly with propeller mixer probing occasionally with paddle to assure homogeneous mixture.
e) Circulated slurry in waste feed system, short loop mode, for a minimum of 15 minutes.
f) Processed slurry per SCWO waste testing procedure.

APPENDIX B

Destruction Efficiency Calculation - Composite Navy Waste
Run 955A December 5-6, 1995
Data from Table 19

Carbon Input **(g Carbon/min)**

Organic Waste:

$$58.19\ \frac{\text{mL}}{\text{min}} \times \frac{0.9\ \text{g}}{\text{mL}} \times \frac{1\ \text{kg}}{1000\text{g}} \times \frac{530{,}000\text{mg Carbon}}{\text{kg}} \times \frac{1\ \text{g}}{1000\text{mg}} = 27.76$$

Aqueous Waste:

$$12.01\ \frac{\text{mL}}{\text{min}} \times \frac{1.001\ \text{g}}{\text{mL}} \times \frac{1\ \text{kg}}{1000\text{g}} \times \frac{9{,}600\text{mg Carbon}}{\text{kg}} \times \frac{1\ \text{g}}{1000\text{mg}} = 0.12$$

Slurrying Kerosene:

$$54.73\ \text{g/min} \times 0.865\ \frac{\text{g Carbon}}{\text{g kerosene}} = 47.34$$

Total Carbon Input = *75.22*

Carbon Output

Overhead Effluent:

$$\frac{1.08\ \text{L}}{\text{min}} \times \frac{0.5\ \text{mg}}{\text{L}} \times \frac{1\ \text{g}}{1000\ \text{mg}} = 0.00054$$

Brine Effluent:

$$\frac{0.56\ \text{L}}{\text{min}} \times \frac{0.8\ \text{mg}}{\text{L}} \times \frac{1\ \text{g}}{1000\ \text{mg}} = 0.00045$$

Total Carbon Output = *0.00099*

Destruction Efficiency

$$[1 - (0.00099/75.22)] \times 100 = \mathbf{99.9987\%}$$