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**ASSESSMENT FOR DEVELOPMENT OF AN INDUSTRIAL WET OXIDATION SYSTEM
FOR BURNING WASTE AND LOW-GRADE FUELS**

**Final Report for Period
October 1989 through February 1995**

Cathryn Sundback

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May 1995

Work Performed Under Contract No. FC07-90ID12915

**For
U.S. Department of Energy
Idaho Operations Office
Idaho Falls, ID 83401**

**By
Modell Environmental Corporation
Waltham, MA 02154**

MASTER

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October 18, 1989 through February 28, 1995

May 1995

Cathryn Sundback

Work Performed Under Cooperative Agreement DE-FC07-90ID12915

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Idaho Operations Office
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I. SUMMARY

The ultimate goal of this program was to demonstrate safe, reliable, and effective operation of the supercritical water oxidation process (SCWO) at a pilot plant-level throughput. This program was a three phase program. Phase I of the program preceded MODEC's participation in the program. MODEC did participate in Phases II and III of the program. In Phase II, the target waste and industry were pulp mill sludges from the pulp and paper industry. In Phase III, the target waste was modified to be DOE-generated mixed low level waste; wastes containing RCRA hazardous constituents and radionuclide surrogates were used as model wastes.

A. Phase IIA: Research Unit Planning and Design

Phase II focused on developing the SCWO process at a bench-scale level and verifying the models and correlations that were used in the pilot plant design in Phase III. In Phase IIA, conceptual designs for full-scale and pilot-scale plants were developed and economic evaluations were made of major equipment and operating costs. These designs served as the basis for the design of a bench-scale research unit. Phase IIA began in October, 1989 and was completed in May, 1990.

B. Phase IIB: Bench-Scale Development of SCWO

An existing MODEC unit with several upgrades was accepted as the research unit in Phase IIB. This unit was automated so that continuous, long time operation was feasible. Also, technology was developed and hardware was implemented to prevent solids from plugging the reactor and to automate the removal of solids from the reactor. The bench-scale unit was demonstrated in two five-day tests on waste-activated sludge from a waste treatment plant and a pulp and paper mill sludge. Based on the results of these tests, the proposed concepts and procedures developed to maintain large-scale systems free of solids were judged to be sound and effective.

In preparation for Phase III, data were obtained from the literature or measured on the bench-scale system to upgrade thermodynamic properties, heat transfer coefficients, and kinetic constants used in MODEC's ASPEN process design models and correlations. Using these improved models and correlations, a preliminary process design package was prepared and provided to Applied Engineering; preliminary engineering work including pilot plant and installed cost estimates was conducted by Applied Engineering. Phase IIB was completed in April, 1992.

C. Phase IIIA: Research and Development of Wet Oxidation of Fuels

Phase III focused on demonstrating the technology on the bench level for a DOE-relevant waste stream and designing a pilot plant to process DOE-relevant wastes. As mentioned above, the target waste stream was switched at the beginning of Phase IIIA from pulp and paper mill sludge to DOE mixed waste.

In Phase IIIA, which was completed in December, 1993, a series of tests were conducted with a TRIM[®]SOL surrogate waste in the upgraded bench-scale system. This waste represents a large volume, halogenated mixed waste stream located at the Rocky Flats Plant and is a DOE high

priority mixed waste. The surrogate waste was a mixture of TRIM®SOL, inorganic salts, and water. TRIM®SOL, a cutting fluid, contains about 11 wt% chlorine as organic chloride; the concentration of TRIM®SOL in the mixture varied from 1 to 3.75%. The inorganic salts, which simulated metal and radionuclide components for a spent cutting fluid, were 200 ppm zinc sulfate, 180 ppm lead chloride, and 280 ppm cerium chloride.

The objectives of this phase were to conduct tests to: 1) evaluate the ability of MODEC's SCWO technology to treat a simulated mixed waste; 2) measure the destruction efficiency of the organic materials; 3) identify the fate of the surrogate heavy metals; 3) measure solids deposition of the inorganic salts; and 4) identify the rate, location, and cause of any corrosion that is found. Corrosion measurements were made on Inconel 625 witness wires which were longitudinally placed down all sections of the reactor assembly.

Destruction efficiencies ranged from 99.0 to > 99.98% for organic carbon and 99.2 to 99.98% for organic chloride. The higher values were obtained in long duration tests under constant conditions.

Corrosion occurred in the reactor assembly with the most serious corrosion occurring in the preheat and cooldown sections. Corrosion was mild or non-existent in the reactor at temperatures greater than 400°C. The highest level of corrosion was observed in the preheater and was coincident with deposited solids. The witness wires may have also contributed to corrosion by providing stagnant regions where solids could deposit, harden, and corrode away the protective oxide of the alloy surface. Deposition of inorganic solids occurred in the preheater between the temperatures of 250 to 400°C. Subsequent experience of MODEC in the operation of its own pilot plant has shown that these deposited solids can be readily removed after cooling to room temperature. MODEC has developed proprietary technology for higher throughput systems which prevents the deposition of solids in the reactor assembly; this technology was incorporated into the pilot plant design in Phase IIIB.

Corrosion also occurred in the cooldown section of the reactor assembly. The chloride levels in the aqueous effluent were in excess of 4000 ppm and the pH ranged from 1 to 2. These acids are considered to be corrosive to Inconel 625 and contributed to the corrosion in the cooldown section. MODEC has developed proprietary technology to minimize corrosion caused by low pH liquid effluents; this technology was incorporated into the pilot plant design in Phase IIIB.

D. Phase IIIB: Design of a Supercritical Water Pilot Plant

When the program was originally planned, a pilot plant was to be designed, built, and demonstrated using DOE non-radioactive surrogate mixed waste. However, this phase of the project was terminated after the completion of the preliminary design because other avenues were available to DOE for pilot plant-scale demonstration of SCWO processing of non-radioactive waste. Phase IIIB was completed in February, 1995.

The pilot plant was designed and testplans were developed to evaluate the following technical issues which affect the viability of the SCWO process with respect to DOE mixed wastes: 1) destruction efficiency, 2) safe operating limits, 3) process corrosion effects, 4) process deposition effects, 5) HWPP design scalability, and 6) model validation. The pilot plant design requirement was for a 500 gallon/day plant. The pilot plant actually designed was for a throughput of 750 gallons/day because this permitted retention of the standard 0.25" reactor tube at the higher linear velocities needed to minimize solids deposition. The MODEC process, however, can be used for lower throughputs by the combined use of more frequent brushing and smaller tube diameters. The potential waste streams were eight simulated concentrated organic hazardous wastes, defined by DOE. These wastes contain RCRA hazardous constituents and radionuclide surrogates.

Prior to the pilot plant design, alternative flowsheets were considered. All equipment components with significant uncertainty in the scaling law which would be required in a full scale plant were incorporated into the pilot plant design. MODEC's proprietary technologies to avoid solids deposition and corrosion in the SCWO Module were incorporated into the design. The pilot plant was designed based on regenerative heat exchange in which energy is recovered from the oxidized process fluid in the cooling exchanger and recycled back to preheat the process fluid to its ignition temperature -- the temperature at which the oxidation proceeds rapidly without any further addition of energy. The process fluid in the bench-scale system was electrically heated to its ignition temperature.

A modular concept was used to design the pilot plant. The pilot plant design consisted of the following major modules: 1) Waste Feed Preparation Module, 2) Waste Feed Module, 3) Organic Feed Module, 4) Oxygen Feed Module, 5) SCWO Module, and 6) Separation Module. The details of the modules and a process flow schematic are included in Section VI of this report.

The preliminary design was conducted in three major steps: 1) design and flowsheeting, 2) preliminary mechanical design, and 3) preliminary instrumentation and controls design. In the first step, mass and energy balances were conducted at flowrates equivalent to 750 gallons/day using the MODEC ASPEN model. From these results, operating conditions were generated which defined the size ranges required for the major equipment. ASPEN simulations were conducted to size the reactor and all exchangers.

In the second step, all remaining equipment were sized which were not sized by ASPEN. The sizing criteria were based on relevant MODEC and Walk, Haydel & Associates experience. The wall thicknesses of all vessels and SCWO Module components were chosen based on the appropriate technical codes and standards. Equipment specifications were prepared for all major equipment components, and at least one quote of cost and delivery time was obtained for each major equipment component. A general arrangement drawing was developed for the pilot plant based on the space limitations of the WRTTF north pit, the area defined by DOE as the site for the pilot plant.

In the third step, all instrumentation and all major control loops were included on the process flow diagrams. The temperature control loops for the SCWO Module were analyzed to evaluate the feasibility of the control strategy. An instrument list and an one-line electrical diagram were

developed. With DOE approval, a HAZOP analysis was not conducted; the appropriate time to conduct the HAZOP analysis was at a later design stage.

A preliminary Sampling and Analysis Plan was developed which addressed issues related to data acquisition, sample collection analysis, and document management. In addition, preliminary test procedures were developed for start-up testing, plant testing, waste testing, materials testing, and operation and maintenance testing.

II. INTRODUCTION

The goals of this program were to: 1) demonstrate MODEC's supercritical water oxidation (SCWO) process at the bench-scale level, 2) design and build a pilot plant, and 3) demonstrate safe, reliable, and effective operation of the pilot plant-level on DOE relevant waste. This program consisted of three major phases; MODEC participated only in Phases II and III. In Phase II, the target waste and industry were pulp mill sludges from the pulp and paper industry. In Phase III, the target waste was modified to be DOE-generated mixed low level waste; wastes containing RCRA hazardous constituents and radionuclide surrogates were used as model wastes.

The objective of Phase IIIB was to design, build, and demonstrate a pilot plant using DOE non-radioactive surrogate mixed waste. This sub-phase was terminated after the completion of the preliminary design because other avenues were available to DOE for pilot plant-scale demonstration of SCWO processing of non-radioactive waste.

The four sub-phases of this program in which MODEC was a participant are documented below. As evident from the Table of Contents, each sub-phase is independently described in Sections III through VI. The objectives as well as the results and conclusions of each sub-phase are included in the appropriate section.

III. PHASE IIA: RESEARCH UNIT PLANNING AND DESIGN

A. Phase Objectives

The objectives of this program sub-phase were to:

- develop a conceptual design for a full-scale plant;
- develop a conceptual design for a pilot-scale plant;
- develop a preliminary design for a research-scale SCWO unit;
- produce development and test plans for a research-scale SCWO unit.

This pilot plant was to be built during Phase IIIB of this contract.

Based on MODEC's agreement with DOE, no written report was provided to the DOE for this phase because of the proprietary nature of this work. The results of this phase were presented to the DOE at a project review meeting on May 15, 1990 (Modell, 1990).

B. Phase Results and Conclusions

B.1 Conceptual Design for Full Scale Plant

A conceptual design for an SCWO plant was developed to process pulp mill sludge. Minimal dewatering of the sludge was required because the sludge could be fed at 10% solids. The reactor was designed to operate under oxidizing conditions at 550 to 650°C where destruction efficiencies of greater than 99% have been demonstrated for organic halides and dioxins. The reactor system was designed to preheat incoming ambient temperature process fluid using energy recovered from the hot oxidized process fluid; the use of regenerative heat exchange eliminated the need for an auxiliary fuel. More than 45% of the sludge heating value was recovered as steam even with the use of regenerative heat exchange. Carbon dioxide was separated from the gaseous effluent and liquefied, eliminating the possibility of uncontrolled emissions. This carbon dioxide could provide a substantial by-product credit.

An economic evaluation was made for SCWO plants with throughputs of 20 to 100 TPD of pulp mill sludge, on a dry basis. Cost estimates were prepared for major equipment and operating costs. A cost comparison was made between a 100 TPD SCWO plant and similarly-sized plants based on competitive processes. The costs for a 100 TPD SCWO plant were lower than the costs for a 100 TPD dewatering plus incineration plant.

B.2. Conceptual Design for Pilot Plant

The throughput of the pilot plant was chosen to be 5 TPD so that safe and reliable operation could be demonstrated at a near-commercial scale. The conceptual design was based on a pulp mill sludge waste stream from the pulp and paper industry. A modular pilot plant design was specified so that the modules could be easily scaled to higher throughput plants.

An economic evaluation was conducted for 5 to 20 TPD pulp mill sludge SCWO plants. Cost estimates were prepared for major equipment and operating costs. Although pulp mill sludge could not be cost effectively processed in a 5 TPD pilot plant, the modular-designed pilot plant could be easily scaled to throughputs of 10 to 20 TPD. Pulp mill sludge can be economically processed in a 10 to 20 TPD SCWO plant where the costs (1993 basis) would be in the range of \$155 to \$285 per dry ton in comparison to costs ranging from \$305 to \$345 per dry ton for dewatering and incineration of sludge.

B.3. Research Unit Development Plan and Test Plan

An original goal of this task was to develop a conceptual design for a research unit. However, MODEC's existing bench-scale SCWO unit, with some modifications, was an acceptable substitute for the research unit. Consequently, the research unit design activities were canceled.

A research plan for Phase IIB was devised to address general design issues and uncertainties to ensure the success of the larger capacity pilot plant in Phase III. Thermodynamic, transport, and kinetic properties required for the process design calculations were identified. The test plan for

the bench-scale testing was developed, in part, based on the level of uncertainty of each property estimation and the impact of each property on the design calculations. Also the test plan included plans for a rigorous performance test to demonstrate the technology before proceeding to Phase III. A project schedule and budget were developed for both the Phase IIB development program as well as the Phase III pilot plant program.

As part of the research plan, a control strategy was developed to ensure safe and reliable operation. The goals of the control strategy were to: 1) automate startup and shutdown procedures; 2) stabilize steady-state operation; 3) monitor operating conditions, display trends, and archive data; 4) alert operators to alarm conditions and execute emergency shutdown when warranted; and 5) provide a communications interface for downloading operator instructions to local controllers. The monitoring and control system was specified to be a distributed control system with a central supervisory computer linked to local distributed controllers located on each process module.

IV. PHASE IIB: BENCH-SCALE DEVELOPMENT OF SCWO

A. Phase Objectives

One goal of this phase of the program was to conduct a demonstration highlighting the safe and reliable operation of the bench-scale unit. Also, several goals were related to the design of a pilot plant including verification of the design correlations and preparation of a pilot plant engineering package.

Specifically, the objectives as a function of task were:

Demonstration of Non-Plugging Reactor and Automated Solids Removal

- Design, install, and test components for a non-plugging reactor and for automated solids removal on the bench-scale system.
- Plan and conduct long-duration tests.

Automation of Bench System and Demonstration of Continuous Operation

- Automate the bench-scale system so that it can be operated over long periods by a single operator.

Verification of Design Correlations

- Conduct a literature search for pertinent data to test and refine MODEC models and correlations.
- Acquire data to verify thermodynamic properties, heat transfer coefficients, and kinetic constants.
- Use literature and experimental data to verify and modify models.

Pilot Plant Layout and Preliminary Engineering

- Prepare a process design package for the pilot plant to submit to Applied Engineering, an E&C subcontractor. The package is to include a flowsheet, preliminary P&ID, mass and energy balances, and sizes of major equipment items.

- Subcontract to Applied Engineering the preliminary engineering including pilot plant layout and installed cost estimates.

The program objectives and results were described extensively in an internal report (Modell, 1991). Based on our agreement with DOE, this report was not officially released to the DOE because of the proprietary nature of the material. Non-proprietary aspects of the program were described in the final report for Phase IIB (Modell, 1992).

B. Phase Results and Conclusions

B.1 Demonstration of Non-Plugging Reactor and Automated Solids Removal

Process improvements were made based on the understanding that the clogging phenomena is related to: 1) buildup of settled solids and 2) formation of deposited solids during preheating. It was theorized that these factors can be minimized through the use of higher process velocities to minimize solids settling and on-line cleaning to remove settled and deposited solids.

The theory and correlations for solids settling in pipelines were investigated to determine the process velocity required to minimize solids settling. Correlations were developed to estimate the suspension velocity of particles as a function of particle size and density. The design velocity was chosen to be 20% higher than the critical suspension velocity to account for inaccuracies in the critical velocity correlations and in the estimates of process fluid properties.

Based on these calculations, most reactors used in previous SCWO flow systems had not been designed with sufficient process fluid velocity to prevent solids from settling. A minimum feed rate of 1 L/min is required to avoid settling in an approximately 0.25" I.D. reactor for feeds containing 100 μm particles with densities of 2.7 g/cm³. This theoretical finding was confirmed in off-line suspended solids flow tests in MODEC's bench-scale unit.

Deposited solids buildup was experimentally studied with pulp mill sludges. Deposited solids were generally located in the preheater section of the reactor, usually before the bulk of the fluid reached 350°C. The rate of solids buildup was a function of the pulp mill sludge.

A brush design was conceived to remove settled and deposited solids. The design was a metal brush with an attached "motor" which created a force to allow the brush to overcome friction. A model was developed to estimate the brush resistance as a function of several brush parameters; the model results were confirmed by experimental measurements. In addition, experiments were conducted to determine the minimum flowrate and consequently the minimum motor force required to overcome the brush frictional resistance. Sufficient motor force will be developed at process flowrates of greater than 1 L/min, the design flowrate of the pilot plant. However insufficient motor force was developed at 50 to 100 cc/min, the normal operating flowrate range of the bench-scale unit.

The deposited solids in the reactor required a finite time to harden as similarly observed in heat exchangers. Less force is required to remove the deposited solids if the material is removed before it hardens. Consequently, an "on-line" cleaning procedure was developed to brush the inside of the straight-through reactor while the system was operating. This on-line cleaning procedure will be used in the pilot plant with process flowrates of greater than 1 L/min.

Two five-day tests were conducted with waste-activated sludge from Lawrence Massachusetts waste treatment plant and with a pulp and paper mill sludge. At predetermined times, a rapid turn-around off-line cleaning procedure was used; as discussed above, an on-line cleaning procedure could not be used in the bench-scale system because insufficient motor force was generated at the normal operating flowrates of 50 to 100 cc/min. However, the strategy of this off-line cleaning procedure was closely aligned with the on-line cleaning procedure to be used in larger scale systems. In these tests, most of the solids removed from the reactor were deposited solids which were easily removed using the off-line cleaning procedure. An evaluation of these solids determined that they consisted primarily of calcium sulfate with probable inclusion of metal oxides. Based on the results of these tests, the proposed concepts and procedures for maintaining large-scale systems free of solids appear to be sound and effective.

B.2 Automation of Bench System and Demonstration of Continuous Operation

A set of functional specifications for the control system were developed with the goal to define compatible distributed controllers and supervisory control software that would meet current needs and be expandable to meet future pilot plant needs. Descriptions and specifications were provided for: 1) process points including tagging scheme and database requirements; 2) operator interfaces including process graphics, face plate pages, real time and historical trending, alarm handling, transition logging, and communications with distributed controllers; 3) engineering interface including restricted access, data bases and displays, controller configuration and tuning, and communications with distributed controllers; and 4) distributed controllers including continuous and sequential control functions and estimated I/O requirements.

Manufacturers of distributed controllers and PC-based supervisory control software were contacted. Allen-Bradley was selected for the distributed controller and In-touch was selected for the supervisory control software. Process-specific software was written for the distributed controller to automate normal and emergency operations.

B.3 Verification of Design Correlation

Engineering correlations for thermodynamic properties, transport properties, and reactions kinetics were used in the preliminary design and economic analyses in Phase IIA. In Phase IIB, the uncertainty in the parameters with moderate to high effect on the design calculations was reduced to minimize the level of overdesign required in larger scale systems. The models and correlations were verified and improved in a two-step process: 1) incorporate available literature property data into the engineering models and 2) obtain data not available in the literature through bench-scale experimentation.

Available literature data were incorporated into the engineering correlations for vapor pressures, densities, and enthalpies. Relevant literature experimental data were found for most chemical components. The required missing data were experimentally determined on the bench-scale system and were incorporated into the ASPEN simulation model. After the models and correlations were upgraded, a liquid-vapor phase equilibrium experiment was conducted on the bench-scale system. The measured liquid-vapor phase equilibrium were found to be adequately predicted by the model. The conclusion was drawn that the accuracy of the thermodynamic correlations was adequate for design purposes.

The design of the exchangers is dependent upon the validity of the heat transfer coefficient correlations. Several areas of the models were refined including: 1) uncertainties in the transport coefficients of mixtures in the supercritical regimen and 2) the heat flux dependence of the heat transfer coefficient in the single fluid phase regime. Literature searches were performed for heat flux correlations and transport property correlations for mixtures at relevant densities. Theoretical correlations were used to estimate properties of gaseous mixtures to supplement missing literature data. These correlations for heat transfer coefficients and transport properties were incorporated into MODEC's ASPEN simulation model. A moderately good comparison was achieved between the predicted and measured process fluid and tube wall temperature profiles in the bench-scale system.

A literature search was conducted for kinetic data and correlations at SCWO conditions. Relevant oxidation rate data were found for pure compounds and actual wastes, including activated sludge from sewage treatment plants and pulp mills. These kinetic expressions will be incorporated into the ASPEN models in the future.

B.4. Pilot Plant Layout and Preliminary Engineering

Applied Engineering of Orangeburg, SC, an engineering and construction company with a construction approach that involves the building of modules in a factory environment followed by field assembly of the modules, was selected to potentially construct the pilot plant and future SCWO commercial systems. In this phase, the preliminary engineering was subcontracted to Applied Engineering, including pilot plant layout and installed cost estimates. MODEC supplied the process design package to Applied Engineering which included a process flowsheet, mass and energy balance results, major equipment sizes, and preliminary P&ID's. The upgraded ASPEN model was used to size all major equipment components and to calculate the material and energy balances for the system.

A suitable high pressure sludge feed pump was identified prior to supplying this process design package to Applied Engineering. A reliable sludge feed pump is a critical equipment item and could account for 15 to 25% of the total major equipment cost. Pumps similar in design to the chosen pump have been used in Europe to pressurize sewage sludge to 70 atm and ceramic slurries to 250 atm. The pump manufacturer and MODEC were confident that this pump could meet all SCWO sludge pumping requirements.

In 1991, Applied Engineering estimated (with accuracy of $\pm 25\%$) that a modular 5 TPD MODEC plant would cost \$3.2 million and require 40 weeks to construct on a prepared site. This preliminary engineering package was included in the above referenced internal report (Modell, 1991).

V. PHASE IIIA: RESEARCH AND DEVELOPMENT OF WET OXIDATION OF FUELS

A. Phase Objectives

The SCWO demonstration project has become part of a program to develop SCWO technology for treatment of DOE mixed wastes containing RCRA hazardous constituents and radionuclides. This project was the first step to design, build, and demonstrate a pilot plant using MODEC's SCWO process for treating mixed low level wastes. Beginning with this phase, the design of the pilot plant to be built in Phase IIIB will no longer be based on pulp mill sludge waste but rather on DOE waste containing RCRA hazardous constituents and radionuclide surrogates.

The objectives of this phase were to conduct tests to: demonstrate destruction efficiency for a surrogate waste, define operational limits of MODEC's SCWO technology and MODEC's bench-scale unit, and define the specifications required for a pilot plant. The specific objectives of the tests were to:

- Evaluate the ability of MODEC's SCWO technology to treat a simulated mixed waste.
- Measure the destruction efficiency of the organic materials.
- Identify the fate of the surrogate heavy metals.
- Measure solids deposition of the inorganic salts.
- Identify the rate, location, and cause of any corrosion that is found.

The scope and results of this project were documented in a proprietary document written by Modell Development Corporation (Modell, 1993) and in a non-proprietary document written by Idaho National Engineering Laboratory (Beller, 1993(1)).

B. Phase Results and Conclusions

The waste stream, TRIM[®]SOL as a simulant with radionuclide surrogates, was used to represent a large volume, halogenated mixed waste stream located at the Rocky Flats Plant. This waste is a DOE high priority mixed waste; viable treatment options for this waste need to be identified to comply with regulatory requirements. The major component of the waste was TRIM[®]SOL, a cutting fluid manufactured by Master Chemical Company. TRIM[®]SOL contains about 11 wt% chlorine as organic chloride. The surrogate waste was a mixture of TRIM[®]SOL, inorganic salts, and water. The concentration of TRIM[®]SOL in the mixture varied from 1 to 3.75%. The inorganic salts, which simulated metal and radionuclide components of a spent cutting fluid, were 200 ppm zinc sulfate, 180 ppm lead chloride, and 280 ppm cerium chloride.

The tests were conducted in MODEC's bench-scale SCWO system with a throughput of 30 gallon/day of waste and water. The MODEC SCWO bench-scale process can be divided into the following sections:

- Waste Feed and Pressurization
- Oxygen Feed and Pressurization
- Reactor, including pre-heat, reactor, and cool-down sections
- Solids/Liquid/Gas Separator System
- External Heat Input

The experiments consisted of tests to provide the following information related to the overall Phase IIIA objectives: 1) to determine the maximum tolerable concentration of TRIM®SOL with measurable, but safe levels of corrosion; 2) to determine the deposition rate of solids in the reactor and the ease or difficulty of removing the solids; and 3) to determine the rate and type of corrosion occurring.

Four test series were completed and were defined as follows:

Test Series 1	Conduct baseline and system calibration.
Test Series 2	Optimize operating conditions using TRIM®SOL and water only.
Test Series 3	Process TRIM®SOL Surrogate for liquid/solids samples.
Test Series 4	Process TRIM®SOL Surrogate with witness wires for corrosion data.

The goal of Test Series 2 was to identify the optimum operating conditions for processing TRIM®SOL including the highest concentration which could be processed without measurable corrosion. Nickel and chrome levels were monitored in the liquid effluent during processing to assess corrosion.

Test Series 3 was conducted with 3.75 wt% TRIM®SOL Surrogate. The goal of these tests was to collect enough solids to perform a TCLP test. The optimum conditions determined in Test Series 2 were used in Test Series 3. The surrogate additives were used to determine the fate of the metals and radionuclide surrogate after SCWO processing.

Test Series 4 was also conducted with 3.75 wt% TRIM®SOL Surrogate. These tests were conducted over a longer time period to generate corrosion data. The operating conditions were the same as used in Test Series 3. Corrosion measurements were made on Inconel 625 witness wires. Witness wires were longitudinally placed down all sections of the SCWO reactor and were exposed to 20 and 38 hours of SCWO conditions with the surrogate feed.

The waste feed and the liquid, gaseous, and solids effluent streams were sampled throughout these tests. Liquid waste feed samples and liquid and solids effluent samples were analyzed at off-site laboratories. The gaseous effluent samples were analyzed with on-line gas chromatography equipment.

Destruction efficiencies ranged from 99.0 to > 99.98% for organic carbon and 99.2 to 99.98% for organic chloride. The higher values were obtained in Test Series 4, which was conducted over a prolonged period under constant conditions.

As expected, deposition of inorganic solids occurred in the reactor assembly, between temperatures of 250 to 400°C. Most of the inorganics in the feed remained in the reactor during steady state operation. However, ongoing experience of MODEC has shown that deposited solids are readily removed by high velocity flushing and brushing after cooling to room temperature. As previously discussed, MODEC has proprietary technology for higher throughput systems which prevents the deposition of solids in the reactor assembly; this technology was incorporated in the DOE IIIB pilot plant design.

The most serious corrosion occurred in the preheat and cooldown sections. Corrosion was mild or non-existent in the reactor section where the temperature was relatively constant and significantly above the critical temperature of water. The chloride levels in the aqueous effluent were in excess of 4000 ppm and the pH ranged from 1 to 2. Although such acids are considered to be corrosive to Inconel 625 and contribute to corrosion in the cooldown section, the corrosion in the preheater section was always associated with deposited solids. In the proposed pilot plant, which will function at higher flow rates, MODEC anticipates that it will be able to remove these solids on-line and that this will reduce or eliminate preheater corrosion, which MODEC believes is due to the interaction of the solids with the chrome oxide passivation layer.

VI. PHASE IIIB: DESIGN OF A SUPERCRITICAL WATER PILOT PLANT

A. Phase Objectives

As mentioned, this SCWO demonstration project was to be the initial step to demonstrate SCWO pilot plant operation with non-radioactive waste. If the demonstration project was successful, a SCWO pilot plant for mixed waste processing was to be built. However, the SCWO demonstration project was terminated following the completion of the preliminary design because other avenues were available to DOE for pilot plant-scale demonstration of SCWO processing of non-radioactive waste.

The pilot plant throughput was designed to be 750 gallon/day, rather than the design specification of 500 gallons/day, to permit use of a standard 0.25" reactor tube at the higher linear velocities needed to minimize solids deposition. The potential waste streams were eight simulated concentrated organic hazardous wastes, defined by DOE (Barnes, 1993). These wastes contain RCRA hazardous constituents and radionuclide surrogates. The performance requirements for the pilot plant were: 1) to evaluate SCWO for its ability to treat mixed waste and 2) to prove that MODEC's SCWO technology can be successfully scaled from a laboratory scale unit to a pilot plant with a tenfold increase in throughput. The pilot plant was designed and testplans were developed to evaluate the following technical issues which affect the viability of the SCWO process with respect to DOE mixed wastes:

1. Destruction efficiency.
2. Safe operating limits.
3. Process corrosion effects.
4. Process deposition effects.
5. HWPP design scalability.
6. Model validation.

B. Phase Results and Conclusions

The design activities were performed by Modell Environmental Corporation (MODEC) and their subcontractors, Walk, Haydel & Associates, Inc. (WH&A), New Orleans, LA and Energy & Environmental Engineering, Inc. (E³I), Somerville, MA. The design was completed in conformance with the performance specification (Beller, 1993(2)), the Configuration Management Plan and the Quality Assurance Plan for the project. As previously noted, the sole exception was the design throughput of 750 gallons/day rather than the design specification of 500 gallons/day.

The success criteria for the pilot plant project were defined at the program kick-off meeting on May 4, 1994 (Rodgers, 1994) and are consistent with the objectives defined above. Prior to the pilot plant design, the characteristic parameters were estimated for each waste and are given in Table 1 for the as-received wastes. The parameters are: heating value; acid anion concentrations; heavy metal, radionuclide surrogate, and alkali metal cation concentrations; and organic solids concentration. The estimation methods were described in the Documentation for the Scope Definition Meeting (Sundback, 1994).

As described in the Documentation for the Preliminary Design Review (Sundback, 1995), each of these concentrated organic wastes must be diluted to a pre-determined heating value, based on the ignition temperature of the waste. The waste concentration is typically in the range of 2 - 7 wt% waste. The acid anions are liberated during waste oxidation and create an acidic liquid effluent which can cause corrosion; MODEC's proprietary technology was incorporated into the pilot plant design to minimize corrosion by low pH liquid effluents. In standard SCWO processes, the heavy metal, radionuclide surrogate, and alkali metal cations can settle or deposit in the system, causing plugging and corrosion; the pilot plant design incorporated MODEC's proprietary technology to minimize solids deposition.

Prior to the pilot plant design, alternative flowsheets and alternative reactor designs were considered. All equipment components with significant uncertainty in the scaling laws which would be required in a full scale plant were incorporated into the pilot plant design. The reactor design was chosen so that: 1) all solids waste components could be maintained in suspension flow at a flowrate equivalent to 750 gallon/day and 2) the SCWO Module could be incorporated into the location defined by DOE, the WRTTF north pit area.

TABLE 1

SUMMARY OF WASTE CHARACTERIZATION PARAMETERS FOR AS-RECEIVED WASTES

SERIES	DESCRIPTION	HEATING VALUE (kJ/kg)	<---	ACID	ANION	---	HEAVY METAL CATION (ppm)	RADIONUCLIDE SURROGATE CATION (ppm)	ALKALI METAL CATION (ppm)	ORGANIC SOLIDS (wt%)
			Cl ⁻ (ppm)	SO ₄ ⁻² (ppm)	PO ₄ ⁻³ (ppm)	BO ₃ ⁻³ (ppm)				
1	Aromatics with Hg	41371	0	0	0	0	1435	0	0	0
2	Nonchlorinated Solvents with Metals	26765	0	0	0	0	12014	3895	0	0
3	Paper, Cloth, Plastic	29000	28000	0	0	0	0	0	0	100
4	TRIMSOL	34925	115000	30000	0	0	122	1306	7132	0
5	Mixed Oils	19899	250	0	0	47573	0	0	0	0
6	Spent Activated Carbon	32792	0	0	0	0	1605	0	3043	100
7	Scintillation Fluid	36834	0	0	0	0	0	0	3274	0
8	Tributyl Phosphate	36934	0	0	208808	0	0	0	0	0

B.1. Design Description

As shown in Figure 1, the pilot plant design consists of the following major modules:

- Waste Feed Preparation Module
- Waste Feed Module
- Organic Feed Module
- Oxygen Feed Module
- SCWO Module
- Separation Module

In the Waste Feed Preparation Module, a macerator is used to size-reduce solids to a processable size and to homogenize the waste after dilution to the proper heating value. The waste flow is metered and pressurized to 3800 psi in the Waste Feed Module. Oxygen is metered and pressurized to 3800 psi in the Oxygen Feed Module. During start-up, a water stream is metered and pressurized in the Waste Feed Module and combined with cleaning burning organic which is metered and pressurized to 3800 psi in the Organic Feed Module.

During waste processing, the combined diluted waste and oxygen stream enters the SCWO unit of the SCWO Module. The SCWO unit is a tubular plug-flow reactor which consists of a preheater exchanger, a reactor, and two cooling exchangers. In the SCWO Module, the material of construction is Inconel 625 for all tubes which contact the process fluid. The process fluid enters the SCWO unit at 3800 psi and approximately ambient temperature. De-ionized water is used in the regenerative heat exchange loop to recover energy from the oxidized process fluid in the cooling exchanger and to recycle this energy back to the preheat exchanger where the process fluid is heated to its ignition temperature.

The oxidation of the organics increases the process fluid temperature from the ignition temperature to 600°C. The length of the reactor is sized so that the residence time of the process fluid at 600°C is long enough to achieve the desired organic destruction efficiency.

The process stream is cooled in a series of cooldown exchangers. The first cooling exchanger is the main regenerative cooldown exchanger; energy recovered from the process fluid in this exchanger is recycled back to the preheater. Finally, the process fluid is cooled down to approximately ambient temperature in the final cooldown exchanger. As mentioned, energy is recovered and recycled in the regenerative heat exchange loop with a very pure water stream. The operating pressure of this water stream is high enough during energy recovery and recycle to avoid a supercritical transition. After exiting the preheater, the water stream is cooled in auxiliary cooling exchangers 1 and 2 and then depressurized. The near ambient temperature and pressure water is held in a storage vessel. Water from this storage vessel is pressurized by the regenerative heat exchange loop pump. This pressurized water stream is heated in auxiliary cooling exchanger 2 and in electrically-heated heating exchanger 2. Finally the high pressure water stream is heated by the hot oxidized process fluid in the cooling exchanger and is cooled by the process fluid in the preheater.

FIGURE 1. PROCESS FLOW SCHEMATIC

During start-up, a water and oxygen stream fed to the SCWO unit is heated by the regenerative heat exchange loop water, which is heated by the electrically-heated heating exchanger 1.

Finally, the fluids in the auxiliary cooling exchanger 2 and the final cooldown exchanger are cooled using low pressure cooling water.

In the Separation Module, the gas, liquid, and solids phases are separated from each other and depressurized to approximately atmospheric pressure. In the high pressure separator, the gaseous phase containing CO_2 and excess O_2 is separated from the liquid/solids phases. The gaseous effluent is depressurized to approximately atmospheric pressure.

This liquid/solids stream flows through one of two solids separators until the differential pressure across the solids separator in-use exceeds the design differential pressure. The liquid/solids stream is then switched to the alternative solids separator and the solids in the original solids separator is discharged.

The liquid stream exiting the solids separator is depressurized and gaseous CO_2 is separated from the liquid stream in the medium pressure separator. The gaseous effluent is depressurized to approximately atmospheric pressure. Finally the liquid stream leaving the medium pressure separator is depressurized to approximately atmospheric pressure. The final gas/liquid separation occurs in the low pressure separator.

The depressurized gaseous effluent from each separator is combined and vented to the atmosphere after flowing through one of two parallel volatile organic carbon (VOC) trap/mercury vapor trap systems. Prior to the trap system, a portion of any gaseous effluent stream or a portion of the combined gaseous effluent stream can be circulated through the on-line gas analyzer system.

The solids effluent and the liquid effluent are further processed in the solids and liquid effluent treatment systems, respectively. Salts are separated from metals in the solids effluent treatment system. In the liquid effluent treatment system, soluble salts are removed from the liquid effluent and the liquid effluent pH is neutralized. The solids effluent and liquid effluent treatment systems were not designed in the preliminary design phase of this project.

Detailed process flow diagrams with process stream data were included in Chapter 1 of the Documentation for Preliminary Design Review (Sundback, 1995). These process flow diagrams depicted all instrumentation and major control loops.

B.2. Design Process

Based on the flowsheet shown in Figure 1, the preliminary design was conducted in three major phases:

1. Design simulation and flowsheeting.
2. Preliminary mechanical design.
3. Preliminary instrumentation and controls design.

B.2.1. Design Simulation and Flowsheeting

Mass and energy balances were conducted at flowrates equivalent to 750 gallon/day for a range of waste ignition temperatures. These balances were conducted using ASPEN PLUS, version 8. From these results, ranges of operating conditions were generated which defined the size ranges required for the major equipment.

ASPEN simulations were conducted to size all exchangers used to preheat and cool the process fluid and to preheat and cool the regenerative heat exchange water. These simulations provided estimates of heat exchanger lengths and temperature differences required for a given set of inlet and/or outlet conditions.

In addition, ASPEN simulations were used to estimate the length of the reactor required to heat the process fluid from its ignition temperature to 600°C, based on organic oxidation kinetic constants measured in MODEC experimental systems. The residence time in the maximum temperature zone of the reactor was set equal to the residence time in the same zone of the existing MODEC 500 gallon/day pilot plant; the desired destruction efficiencies have been demonstrated in the MODEC 500 gallon/day pilot plant. The length of the maximum temperature zone of the reactor was estimated from this residence time.

The design parameters, requirements and constraints were given in Chapter XI., Preliminary Design Specifications in the Documentation for Preliminary Design Review (Sundback, 1995).

B.2.2. Preliminary Mechanical Design

All remaining major equipment were sized including all pumps, compressors, auxiliary exchangers, phase separator vessels, gas accumulator vessels, and low pressure storage vessels. The sizing criteria were based on the ASPEN simulation results together with relevant MODEC and WH&A experience. All wall thicknesses of vessels and SCWO Module components were chosen based on the appropriate technical codes and standards. The stress calculations for these equipment components were given in Chapter X., Analysis and Calculations Supporting Preliminary Design of the Documentation for Preliminary Design Review (Sundback, 1995).

Equipment specifications were prepared for all major equipment components and were included in Chapter II., Preliminary System Specifications of the Documentation for Preliminary Design Review (Sundback, 1995). The materials of construction for each equipment component were selected to provide adequate corrosion resistance and physical strength. The materials of construction were given in the equipment specifications as well as in Chapter III., Materials Selection. The appropriate technical code or standard used to specify each equipment component was given in Chapter XII., Code Boundaries and Design Calculations. None of the equipment specified required manufacturers to provide a "first of its kind component"; the major equipment specified was similar to the equipment in the MODEC 500 gallon/day pilot plant.

The geometry restrictions were included in the equipment specifications for the SCWO Module components. These equipment restrictions were based on the space limitations of the WRTTF north pit, the area defined by DOE as the site for the pilot plant. The arrangement of the SCWO Module was depicted in the General Arrangement Drawing, included in Chapter VIII., Preliminary General Arrangement Drawing.

Each equipment specification was sent to two or three appropriate equipment manufacturers obtained from MODEC and WH&A manufacturer databases. At least one quote was obtained for each equipment component. The cost and delivery time estimates were included in Chapter II., Preliminary System Specifications. No potential component manufacturers were visited because all manufacturers had previously sold equipment to MODEC or WH&A.

B.2.3. Preliminary Instrumentation and Controls Design

As mentioned above, all instrumentation and all major control loops were included on the process flow diagrams. The temperature control loops for the SCWO unit were analyzed to evaluate the feasibility of the control strategy.

An instrument list was included in Chapter VII., Preliminary Instrument List. All instrumentation was included which was depicted on the process flow diagrams. The instrumentation to measure the process and control variables and the controller were listed for each control loop. A one-line electrical diagram was included in Chapter IX., Preliminary One-Line Electrical Diagram. The one-line electrical diagram depicts the power requirements for the major equipment components and can be used to estimate the power utility costs for the pilot plant.

The pilot plant was designed to ensure that the system could safely and quickly respond to alarm conditions. Tables of alarm events and pilot plant system responses were developed and are included in Chapter IV., Safety Features. The safety features were incorporated into the process flow diagrams and are included in the Documentation for Preliminary Design Review. However, these safety features were not included in Figure 1 because MODEC considers these features to be proprietary information. As specified in the Statement of Work for Phase IIIB of this contract (Modell, 1993), a hazards analysis (HAZOP) was to be conducted for the preliminary design. Given the tables of alarm events and system responses, MODEC and WH&A both believed that little new information would be uncovered in a HAZOP analysis because of the preliminary stage of the design; WH&A routinely coordinates and conducts HAZOP analyses. A HAZOP analysis would be more appropriate at a later design stage.

In accordance with the performance specification (Beller, 1993(2)), MODEC and E³I prepared a preliminary Sampling and Analysis Plan to address issues related to data acquisition, sample collection analysis, and document management. This plan was included in Chapter V., Preliminary Sampling and Analysis Plan. In addition, preliminary test procedures were developed for start-up testing, plant testing, waste testing, materials testing, and operation and maintenance testing. These test procedures were given in Chapter VI., Testing Requirements.

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