WASTE PROCESSING OF CHEMICAL CLEANING SOLUTIONS

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ABSTRACT

Chemical cleaning solutions containing high concentrations of organic chelating wastes are difficult to reduce in volume using existing technology. Current methods for evaporating low-level radioactive waste solutions often use high maintenance evaporators that can be costly and inefficient. The heat transfer surfaces of these evaporators are easily fouled, and their maintenance requires a significant labor investment.

To address the volume reduction of spent, low-level radioactive, chelating-based chemical cleaning solutions, B&W Nuclear Service Company (BWNS) developed the ECOSAFE^R Liquid Volume Reduction System (LVRS). The LVRS is based on submerged combustion evaporator technology that was modified for treatment of low-level radioactive liquid wastes. This system was developed in 1988 and was used to process 180,000 gallons of waste at Oconee Nuclear Station. An improved and modularized system was used at Arkansas Nuclear One to process approximately 170,000 gallons of chemical cleaning waste in early 1991.

The LVRS provides nuclear utilities with an economically acceptable alternative for volume reducing non-standard, difficult to process, low-level Class "A" radioactive solutions. After volume reduction, the concentrated waste solution is processed for burial. BWNS uses a waste solidification process that can solidify 40 to 48 gallons of waste in a standard 55-gallon drum, significantly reducing processing and disposal costs. The distillate from the evaporator undergoes a secondary processing step, if necessary, and is released after it meets all site discharge limits.

The unique BWNS approach provides a straight forward and efficient evaporator/solidification system for processing low-level radioactive waste solutions.

INTRODUCTION

Nuclear utilities are deciding to chemically clean the secondary side of their steam generators in order to remove corrosion products which, after years of operation, are now causing degraded thermal hydraulic performance. The method of choice for U.S. utilities has been the process developed and generically qualified by the Electric Power Research Institute (EPRI) under the funding by the Steam Generator Owner's Group (SGOG). This technology is based on using one solvent to remove the iron deposits and another solvent to remove the copper deposits, if present in significant quantity. A separate heat-up/rinse/passivation solution is also a required solvent in the process. The generic EPRI-SGOG solvent description is presented in Table I.

The volumes of waste solvent generated are dependent on the steam generator size, the area of the generator that is cleaned, the amount of deposits that are removed, the composition of the deposits, and the process efficiency for the minimization of the waste solvent generated. Upon removal of the solvents from the steam generator, after the various steps, they are segregated into distinct storage tanks to allow for more effective processing and disposal.

The chemical cleaning solvent waste is difficult to process by conventional means due to the high concentrations of organic chelants, iron, copper and the low-levels of radioactive isotopes which are present. Due to the large volume of liquid waste produced during a cleaning and due to the high cost of burial, it is more economical to concentrate the liquid by evaporation prior to solidification.

LIQUID VOLUME REDUCTION SYSTEM HISTORY

In late 1987 and early 1988, the Duke Power Company chemically cleaned the four Once-Through-Steam-Generators (OTSG) at Oconee Nuclear Station Unit 1 and Unit 2. Approximately 200,000 gallons of rinse solution was generated and processed by Duke Power using powdered resin in a batch treatment method. A total of 700 cubic feet of powdered resin was used. Approximately 180,000 gallons of spent iron solvent was generated that had the average composition shown in Table II.

The EDTA in the spent solvent reduces the number of viable processing alternatives because of its high concentration, its chelating selectivity and its pH sensitive solubility. To address the volume reduction of this low-level radioactive solvent, BWNS developed the first generation ECOSAFE^R Liquid Volume Reduction System (LVRS) in 1988. This first-of-a-kind system was effectively used to achieve a volume reduction of greater than 85%. The concentrated waste was solidified and sent to burial. The overall volume reduction after solidification was 80%. (1)

TABLE I

Generic Chemical Cleaning Solvent Description

IRON SOLVENT	
Ethylenediaminetetraacetic acid (EDTA):	10 - 15%
Hydrazine (N_2H_4):	1%
CCI-801 corrosion inhibitor:	1%
pH (adjusted with ammonia): applied at 200°F	7.0
COPPER SOLVENT	
EDTA:	5 - 10%
Hydrogen Peroxide (H_2O_2):	2 - 3%
pH (adjusted with ammonia to):	7.0
pH (adjusted with ethylenediamine): applied at 95°F	9.5
RINSE SOLUTION	
Hydrazine:	250 ppm - 300 ppm
pH:	9.8 - 10.5

The general operational sequence includes:

1. Check-out rinse
2. Copper step (optional)
3. Cold rinse/Heatup
4. Iron step
5. Hot rinse/Cooldown
6. Copper step (optional)
7. Cold rinse/Heatup
8. Passivation (applied at 200°F)
9. Cooldown

TABLE II

Spent Chemical Cleaning Solvent From Oconee

EDTA (grams/liter)	127
Iron (ppm)	8,000
Hydrazine (ppm)	6,670
pH	7.9
Radioactivity (microcuries/cc)	
Cs-134	2.4 E-4
Cs-137	1.9 E-4
Co-60	5.3 E-4

A second generation system was developed and built in 1990 to incorporate lessons learned from the 1988 system, modularize the system for easy set-up, add the capability to handle copper solvent, and add a secondary processing system for the distillate. This improved system was used at Arkansas Nuclear One Unit 1 early in 1991 to process approximately 170,000 gallons of iron solvent, copper solvent, and rinse water.

PROCESS DESCRIPTION

The BWNS waste processing system consists of three major components. These are the Submerged Combustion Evaporator (SCE), the Solidification skid, and the Organic Destruction process. Figure 1 presents a block diagram of the system flow paths. The waste solvent is first pumped to the SCE. Air from a blower and propane enter the burner section of the SCE as shown in Fig. 2 and combustion takes place under the liquid level. The 3,000,000 BTU/hr generated leaves the burner as sensible heat in the combustion gases. The hot gases are released in a tremendous number of small bubbles which create the maximum surface area for heat transfer. Since these gases are directly in contact with the solution, the heat is sensed immediately in the liquid. The noncondensable combustion gases are cooled and leave the solution at the temperature of the liquid, intimately mixed with water vapor. Since the SCE does not have

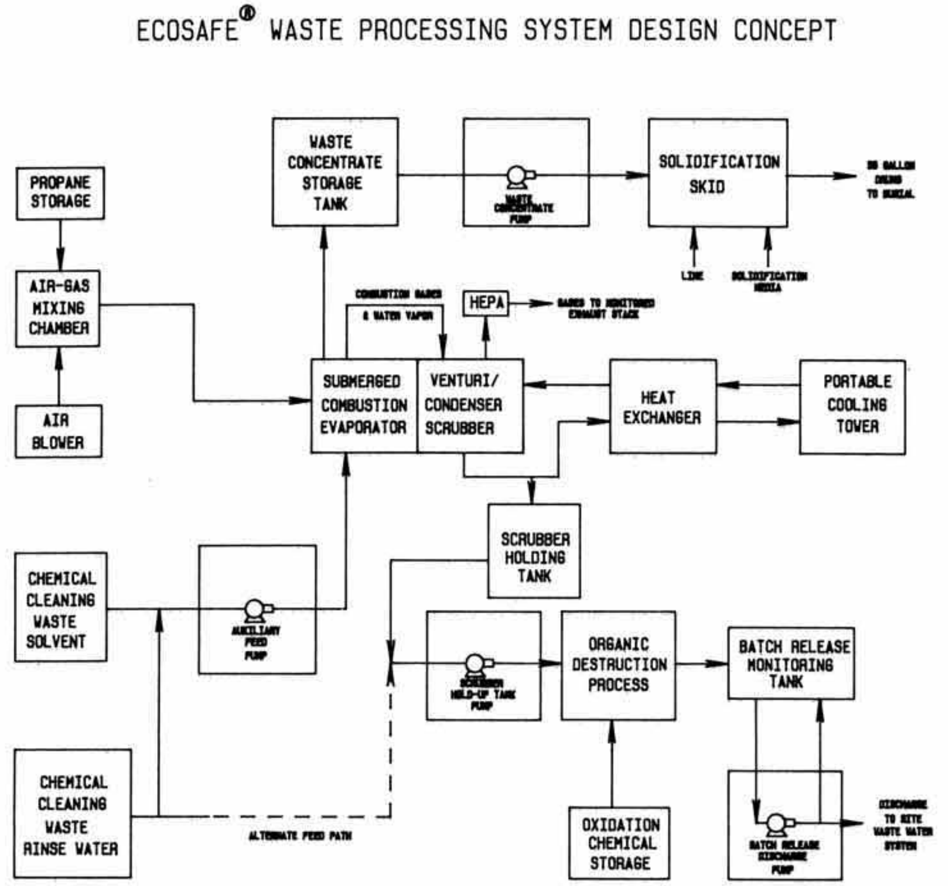

Fig. 1 LVRS Block Diagram.

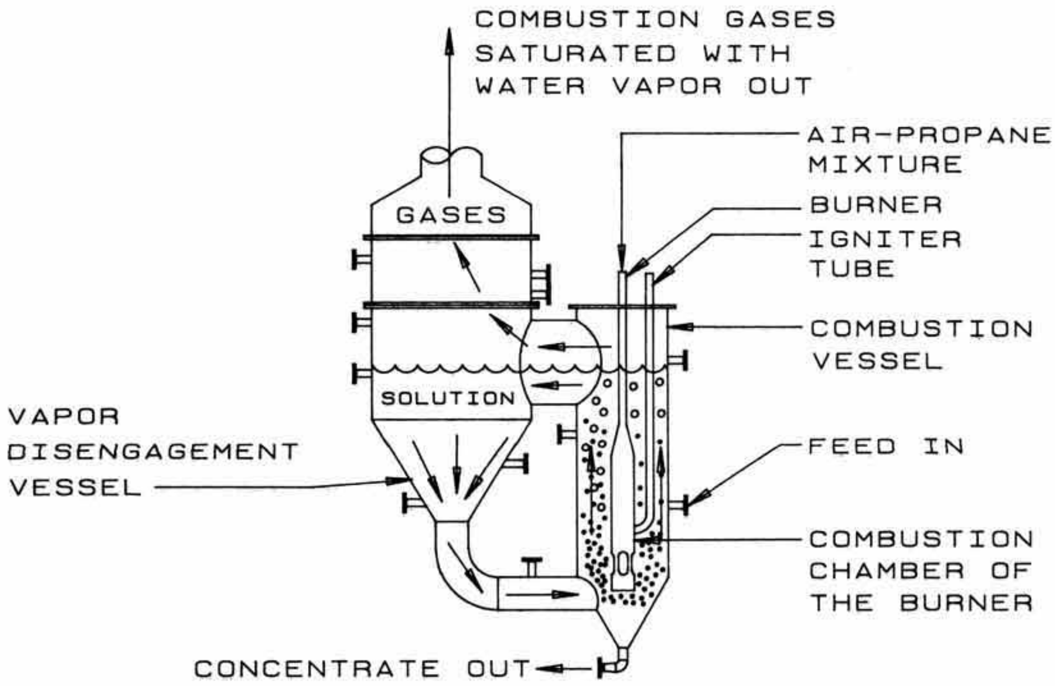

Fig. 2. Submerged Combustion Evaporator.

heat transfer surfaces which could become fouled during operation, it requires only minimal maintenance.

Bubbling combustion gases through the liquid results in a boiling point depression. Therefore, under submerged combustion conditions, the solvent boils at a temperature appreciably below its atmospheric boiling point. For example, burning propane with 5% excess air, the boiling point of water has been found to be approximately 192°F. As the amount of excess air is increased, the boiling point decreases accordingly. (2) The BWNS evaporator also operates under a small vacuum since the combustion gases and water vapor are drawn from the vapor disengagement chamber by a venturi/scrubber system.

The waste liquid feed to the SCE passes through a magnetic flow meter with a flow totalizer that is used to meter and control the feed to the evaporator. The evaporator feed control valve is set by the operator at an equilibrium flow rate of 3 to 6 gallons per minute. When the evaporator concentrate reaches the desired concentration (determined by specific gravity measurement), a process valve is opened to allow pumping of the bottoms to the waste concentrate storage tank. The operator controls the evaporator level by adjusting the feed to and/or discharge from the evaporator. When the system reaches equilibrium, the rate of evaporator concentrate removal plus the rate of distillate production is equal to the rate of feed.

The waste concentrate storage tank serves as a feed tank for the solidification skid. The waste tank volume is heated and continuously recirculated using a pump to prevent stratification or solids precipitation. A measured quantity of concentrated waste is charged to each 55 gallon drum for solidification. Hydrated lime is used for neutralization and Aquaset II (Fluid Tech Inc.) is used for solidification of the Class "A" waste.

The evaporator off-gas, consisting of water vapor, excess air, and combustion gases, flow through a multi-stage demister prior to entering the condenser/scrubber unit. In this venturi-type scrubber, the gases are contacted with clean cooling water. The water vapor is condensed and the noncondensable gases are scrubbed. The scrubbed exhaust gases pass through an air cooler to lower the dewpoint of the gas and remove additional water vapor from the exhaust stream. The gas then passes through a HEPA filter/blower to a monitored exhaust stack.

The process water in the condenser/scrubber unit is recirculated, cooled, and monitored. A process water heat exchanger and cooling tower is used to maintain a scrubber system equilibrium temperature of approximately 90°F. The water volume in the scrubber increases continuously during operation as the water vapor from the SCE is condensed. The excess water (condensed distillate) is removed continuously from the scrubber system and collected in the scrubber holding tank.

The distillate water is then pumped from the scrubber holding tank to the organic destruction process for secondary treatment. The organic destruction process destroys the small amount of EDTA, ethylenediamine (EDA), and hydrazine in the distillate by means of chemical oxidation using hydrogen peroxide and ultraviolet (UV) light. The organic molecules absorb energy from the UV light making them more receptive to the hydroxyl radicals provided by the hydrogen peroxide. This combination promotes a breakdown of the organic molecules. When the reaction is carried to completion, the organics are converted to carbon dioxide and water. (3)

After the organics are broken down, the water enters a precipitation tank where the pH is adjusted and metal flocculants are added. The water then passes through a series of micron sized filters to lower the iron and/or copper levels to dischargeable limits. The water is then stored in a batch release monitoring tank where it is continuously recirculated and if necessary, a final pH adjustment is made. The nuclear site chemist samples and analyzes this tank to confirm that all site discharge limits are met prior to directing its final release.

EQUIPMENT DESCRIPTION

The entire Liquid Volume Reduction System has been incorporated into functional modules that allow for quick and flexible assembly at a nuclear power plant. The modular design offers a number of distinct advantages:

- compact arrangement reduces the need for a large site laydown area
- premade hoses with high grade quick connect couplings minimize setup time
- flexible arrangement within available laydown area prevents concerns for time consuming piping alignment and assembly
- each functional module contains all pumps, valves, piping, and controllers for independent operability
- modules provide inherent containment and weather protection for important system hardware
- site only has to provide clean water and one 480 volt electrical connection

The three major systems are housed in converted "Sea-Land" containers:

1. Evaporator Trailer (Figs. 3 - 7)
2. Solidification Skid (Figs. 9 and 10)
3. Organic Destruction Trailer (Figs. 11 - 15)

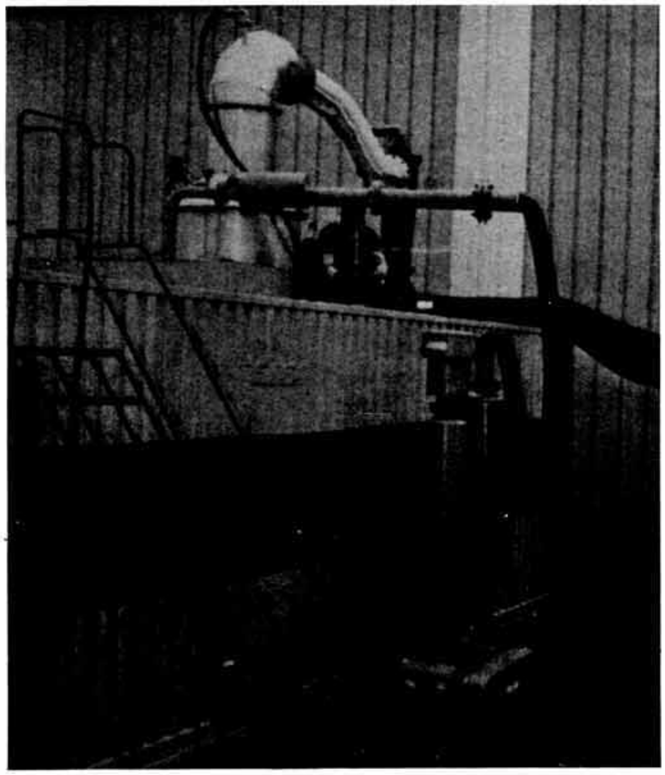

Fig. 3 . Outside of evaporator trailer.

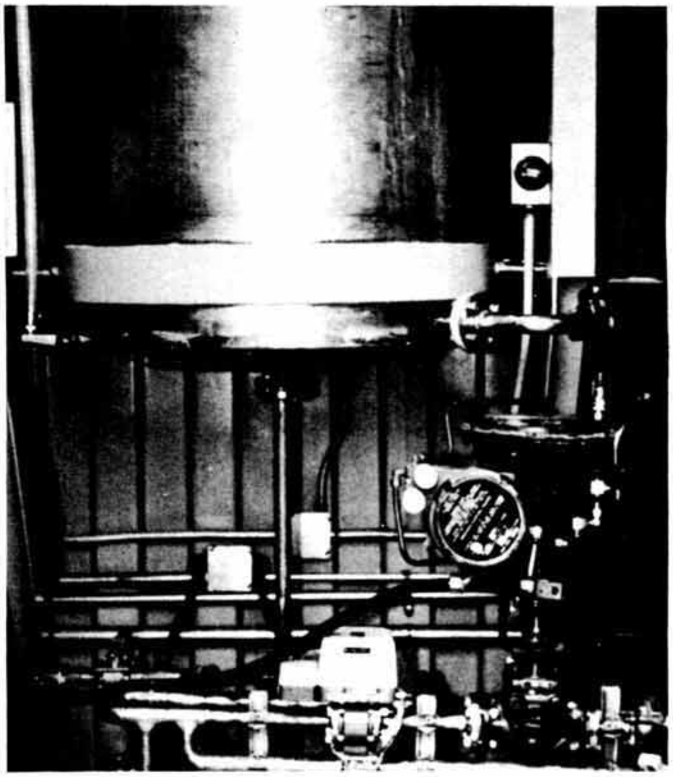

Fig. 4. Feed system for SCE.

All of the trailers are heated and ventilated through a common HEPA filter/blower. Each trailer has a floor that is a steel drip tray designed to contain any accidental liquid spills. All waste stream piping and components are made of stainless steel with the hose runs made from EPDM with stainless steel connections.

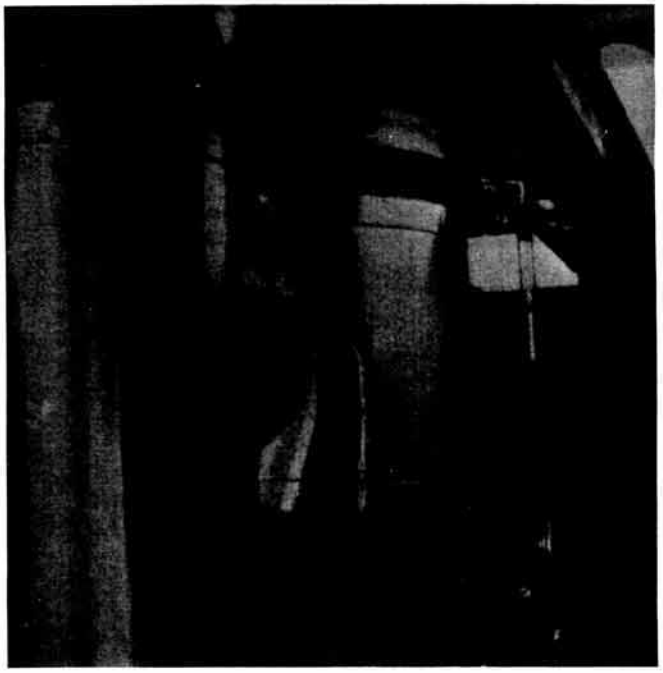

Fig. 5. Submerged combustion evaporator.

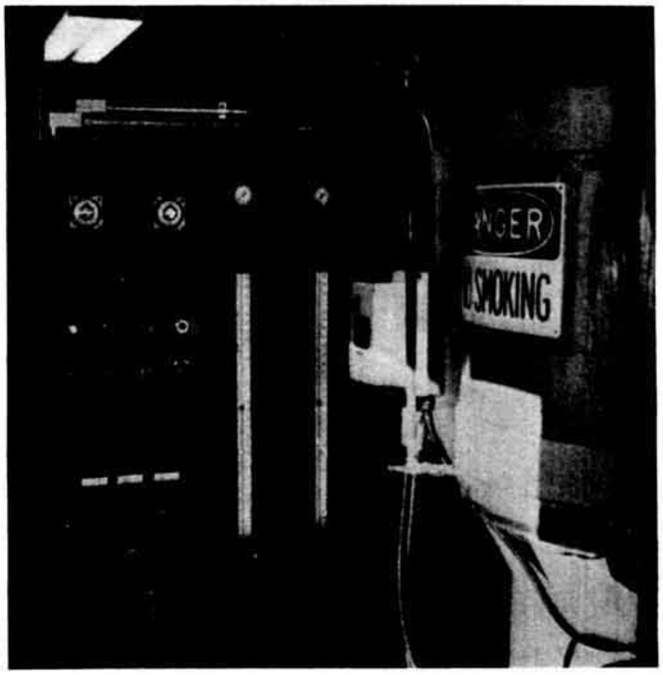

Fig. 6. SCE control panel.

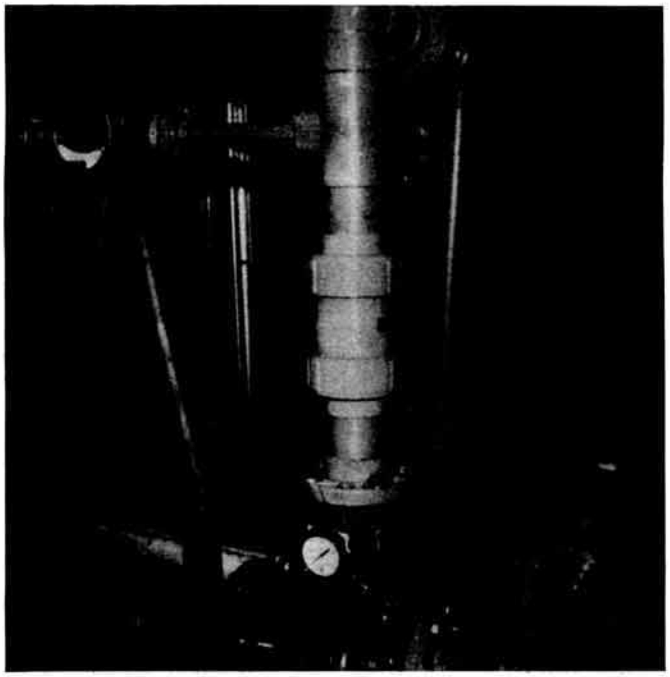

Fig. 7. Condenser and cooling water piping.

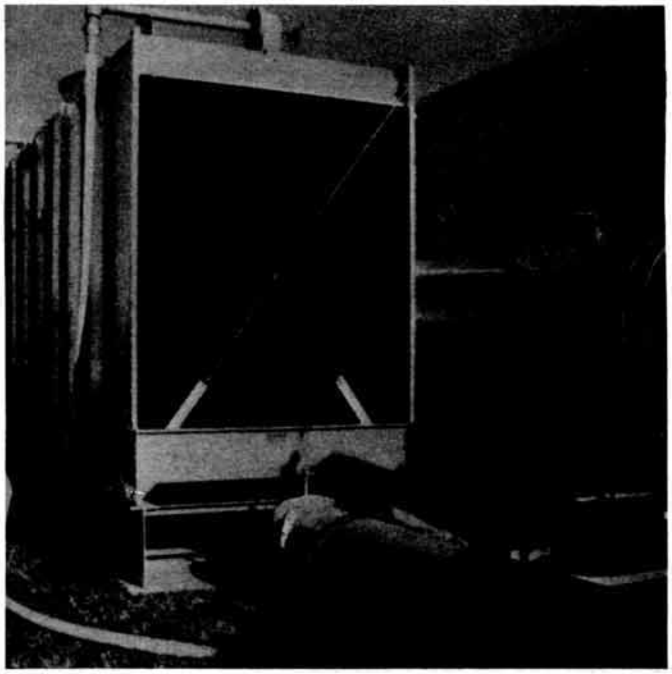

Fig. 8. Cooling tower, heat exchanger and scrubber holding tank.

Fig. 9. Solidification skid outside.

Fig. 10. Solidification unit.

Auxiliary equipment includes:

1. Cooling Tower (Fig. 8)
2. Heat Exchanger (Fig. 8)
3. Scrubber Holding Tank (Fig. 8)
4. Waste Concentrate Tank (Fig. 16)
5. Batch Release Monitoring Tank (Fig. 17)
6. "SandPiper" Pump Skids
7. Air Blower and Propane Vaporizer
8. Portable Chemistry Laboratory
9. Integrated Water Chemistry Monitoring System is used to log chemistry data and track system performance

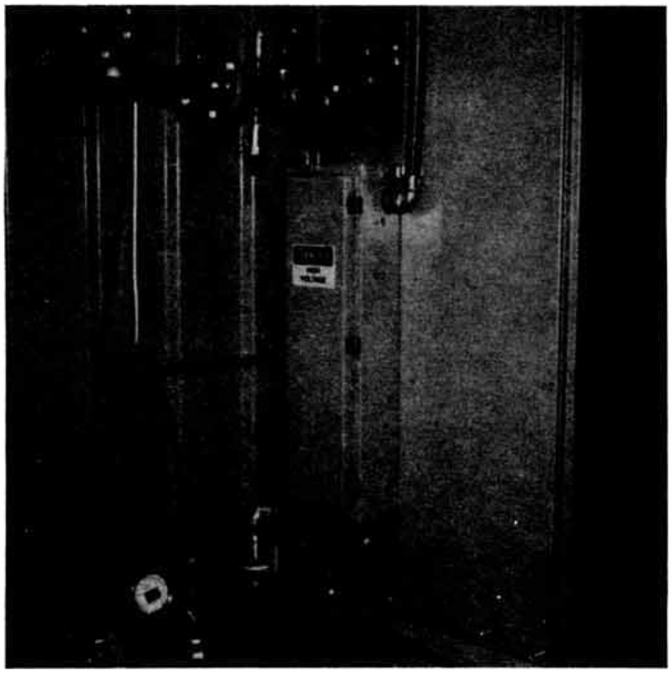

Fig.11. Organic destruction unit inlet and outlet connections.

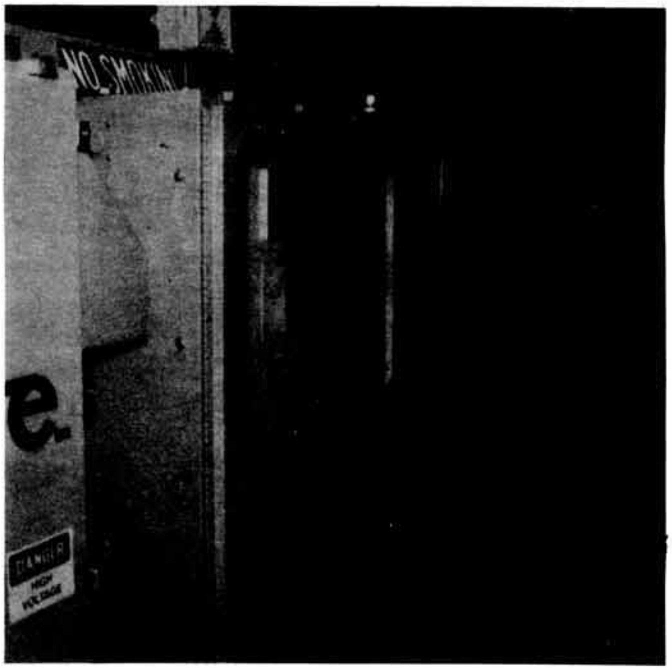

Fig. 12. Organic destruction unit control and alarm panel.

Fig.13. Metal Precipitation Tanks.

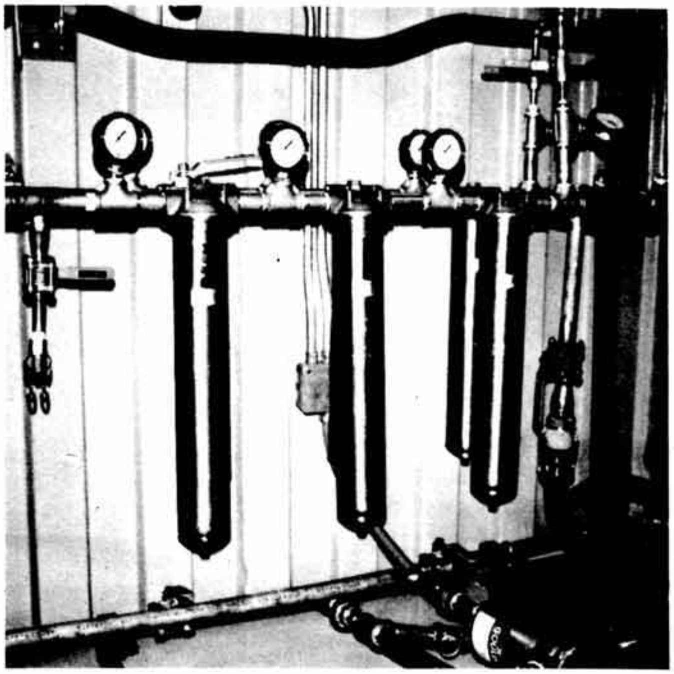

Fig. 14. Filter system.

Figure 3 shows the outside of the SCE trailer during initial set-up and testing in Lynchburg, VA. The blower outside the trailer provides the air that mixes with the propane prior to entering the SCE through the roof of the trailer. The stainless steel exhaust ductwork on the roof directs the water vapor and combustion gases to the venturi scrubber. Figure 4 shows the feed tank, feed control valves, flow meter and feed pumps inside the SCE trailer.

The SCE is shown in Fig. 5 with the burner section in the foreground and the vapor disengagement section in the background. The SCE Control Panel is pictured in Fig. 6. From this panel, the operator can monitor the air and

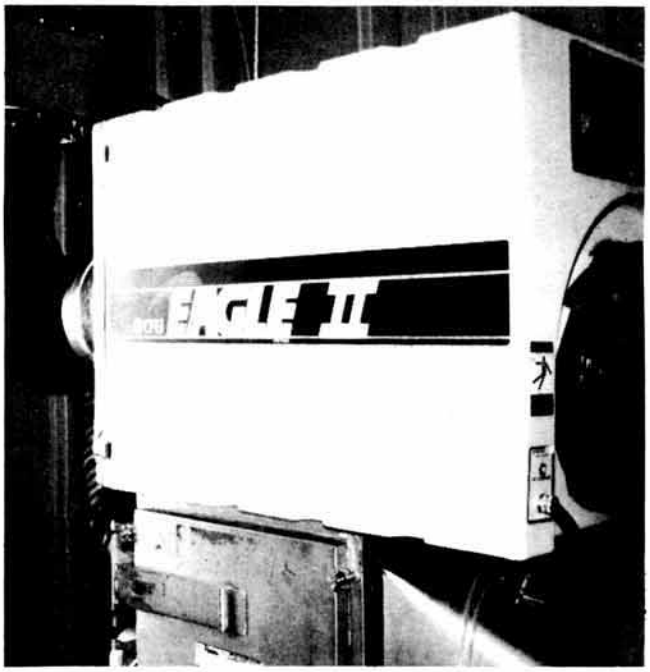

Fig.15. LVRS HEPA Filters.

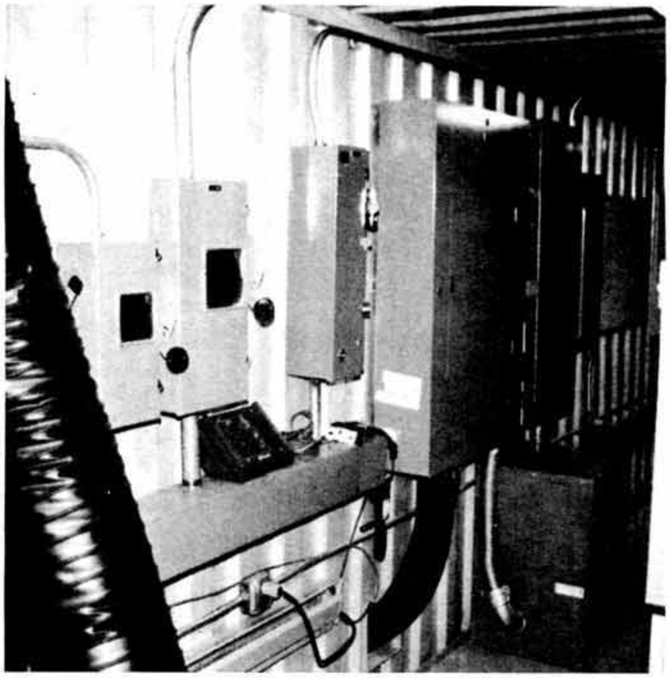

Fig.16. LVRS Electrical Distribution.

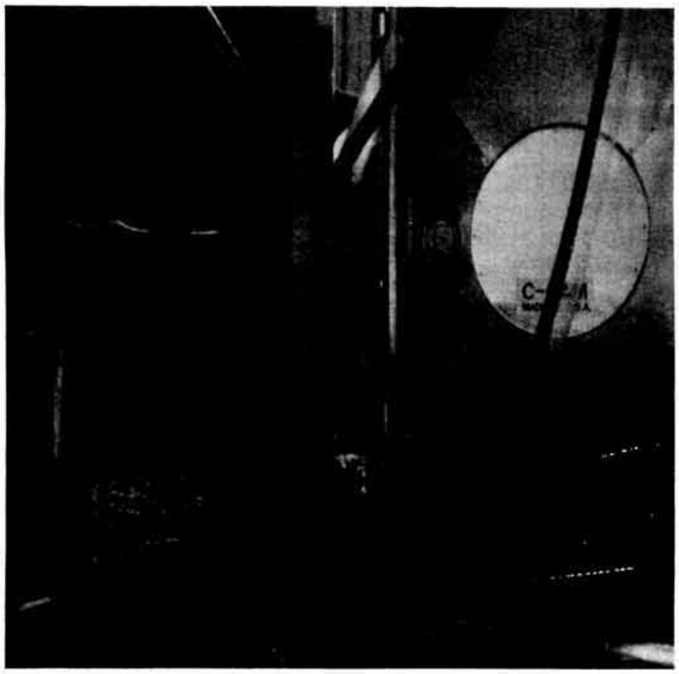

Fig.17. Waste Concentrate Tank and Pump.

Fig.18. Batch Release Tank.

propane flow rates, ignite the burner, start/stop the blower, shut the unit down and monitor alarms.

The Scrubber/Condenser system is also located at one end of the SCE trailer as shown in Fig. 7. Figure 8 shows the cooling tower and horizontal heat exchanger in the foreground that provide the cooling water to condense the water vapor from the SCE. Also shown in the background is the stainless steel scrubber holding tank.

The dry material (lime and Aquaset II) used in the solidification process is stored in stainless steel bins on load cells which are mounted to the roof of the trailer as shown in Fig. 9. By using the load cells and an electrically operated valve, the operator inside the trailer meters the proper amount of dry material into the 55-gallon drums containing the concentrated waste. Figure 10 shows the controls, hydraulic lift and pneumatic mixer that are used inside the trailer to solidify the waste.

Figures 11 and 12 show the modular organic destruction equipment that uses a combination of UV light and hydrogen peroxide to break down the organics in the distillate water.

The discharge of the organic destruction unit enters one of two polyethylene precipitation tanks as shown in Fig. 13. Metal flocculants are added to these tanks and the water is then pumped through a series of micron sized filters to remove suspended solids and flocculated metals. The filter bank shown in Fig. 14 allows for up to 6 filters to be in service at any one time.

The organic destruction trailer also houses two HEPA filter/blowers, shown in Fig. 15, that are used in the Liquid Volume Reduction System. One HEPA filter is used for the exhaust gases coming from the SCE and Scrubber systems while the second is used as a ventilation blower for the three major trailers. Both HEPAs discharge through a common monitored exhaust stack. This trailer also serves as the electrical distribution center for the LVRS. The site only needs to supply 480 volt service to this trailer. From this trailer, both 480 volt and 240/120 volt power is then distributed to the rest of the system.

Figure 17 shows the end of the 6000 gallon waste concentrate tank and the pump skid that is used to recirculate the tank and feed the solidification system. The batch release tank shown in Fig. 18 is a 20,000 gallon tank commonly used in the oil industry and referred to as a frac tank.

CONCLUSION

At present, this system has only been used to process liquid waste generated during chemical cleaning processes. However, due to the independent modular design of the system, portions of the equipment could easily be used to fill specific utility needs. For instance, the solidification trailer could be used to process unique waste streams that only need to be solidified. The organic destruction and filtering system can be independently deployed to process water with organics or metal problems.

In the future, BWNS will be conducting R&D with its nuclear partner, Framatome, to further reduce the volume of waste that needs to be buried due to chemical cleaning of nuclear steam generators.

REFERENCES

1. D. B. Semmler and R. M. Propst, Duke Power Company and J. M. Storton, K. S. Mayo, and R. T. Brandt, Babcock & Wilcox, "Waste Processing of Chemical Cleaning Solutions at the Oconee Nuclear Station", Nuclear Plant Journal, July-August 1989.
2. P. E. Minton, Handbook of Evaporation Technology, Noyes Publications, Park Ridge, NJ, 1986.
3. Peroxidation Systems Inc., "Perox-Pure Organic Destruction Process", Tucson, AZ, 1989.