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Demonstrating Industrial-Scale Technology for Decontaminating and Destroying Radioactive Mixed-Waste Solvents

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DEMONSTRATING INDUSTRIAL-SCALE TECHNOLOGY FOR DECONTAMINATING AND DESTROYING RADIOACTIVE MIXED-WASTE SOLVENTS

O. R. Rasmussen and W. F. Heine

ABSTRACT

The Westinghouse Hanford Company (Westinghouse Hanford) recently decontaminated 34,000 gal of radioactive hazardous waste solvents and is in the final phase of destroying the solvents by incineration. The solvent, a mixture of hexone (methyl isobutyl ketone), kerosene, and tributyl phosphate was the extractant in a nuclear fuel reprocessing plant in the 1960's and was stored in carbon-steel underground tanks since the plant shut down in 1967. Westinghouse Hanford decontaminated the solvent in a distillation system specially designed to accumulate the radioactive distillation tars in sacrificial vessels for disposal. The distillate, essentially free of radionuclides except for tritium, was shipped in 5,000-gal tank trailer loads to a licensed and permitted commercial incinerator that uses the solvents' fuel value to produce electric power in a co-generation plant. This successful recovery operation makes beneficial use of a material that once posed a significant environmental risk at the Hanford Site. The project was made possible through technology demonstration funding provided by the U.S. Department of Energy's (DOE) Office of Technology Development and its predecessor, the Hazardous Waste Remedial Action Program (HAZWRAP).

INTRODUCTION

Radioactively contaminated solvents from nuclear fuel reprocessing have long posed a severe remediation challenge. In 1987 when the DOE HAZWRAP requested proposals for waste remediation demonstrations, Rockwell Hanford Operations, Westinghouse Hanford's predecessor at the Hanford Site, wanted to remediate 34,000 gal of radioactive hexone waste solvents as an industrial-scale demonstration of waste cleanup technology for use at DOE and commercial sites. The proposal was one of three Hanford Site initiatives originally selected by HAZWRAP and was funded for initial scoping work in late Fiscal Year (FY) 1987. HAZWRAP and the DOE's Office of Technology Development continued to sponsor the demonstration through its successful completion in FY 1992. The Environmental Restoration Program, nominal "owner" of the waste solvents, shared 70 percent of the final commercial incineration contract costs.

THE SOLVENT WASTE SITUATION - 1987

The remediated radioactive solvents have been a problem for many years. The solvents were used in the Hanford Site's Reduction Oxidation (REDOX) nuclear fuel reprocessing plant for extracting plutonium and uranium from dissolved uranium fuel elements. When the REDOX plant was shut down in 1967, the plant's solvent inventory was pumped into two 23,500-gal carbon steel underground storage tanks built in 1950 for storing freshly manufactured solvents.

Tank 276-S-141 received 20,000 gal of hexone distilled in the REDOX steam-stripping column before storage. Tank 276-S-142 received 8,000 gal of hexone and 5,000 gal of a 2:1 mixture of kerosene and tributyl phosphate. The hexone, a highly flammable solvent with a room-temperature flash point, was the normal REDOX solvent and contained very low levels of radioactivity.

The kerosene and tributyl phosphate were used in a once-only extraction operation that recovered americium for space applications from Shippingport Reactor blanket-fuel. The mixture initially contained high levels of short-lived isotopes. By the 1980's, most of this activity had decayed away, leaving 0.14 Ci of hard beta activity and 0.108 Ci of alpha activity. The bulk of this radioactivity, 99.8 percent, resided in Tank 276-S-142. Spread through both tanks as well were 0.76 Ci of tritium, a very weak beta emitter that had exchanged with hydrogen in the hexone molecular structure. Tank 276-S-142 also contained 2,000 gal of solvent-saturated water.

Internal inspections showed that both tanks, although sound, were not aging well and were internally corroded. It was clear that constructing new storage tanks meeting all current standards only would prolong the waste storage problem and that the most cost effective and responsible action would be to remediate the waste and to close the storage site.

THE REMEDIATION TECHNOLOGY ANSWER

Early scoping work quickly identified incineration as the most practical means of destroying waste solvents and was used in industry for solvents that could not be cleaned for reuse. No commercial or DOE facilities existed to incinerate flammable solvents as contaminated with plutonium, americium, and fission products as the REDOX waste. Reuse of the material was ruled out from both practical and societal considerations. The funding required to construct and license a radioactive waste incinerator was well beyond that projected for the demonstration.

Effort therefore focused on removing the radionuclides from the waste solvents and on incinerating the distillate in a commercial incinerator under contract or lease. Samples of the solvents had been boiled down in early disposal studies in the mid-1970's, and while the tests had shown effective decontamination efficiencies, they also had shown massive tar and residual liquor generation in the hexone-kerosene-tributyl phosphate phase.

DEVELOPMENT TESTS

Laboratory tests were contracted to Pacific Northwest Laboratory (PNL) in Richland, Washington. The PNL technicians withdrew 22 one-quart samples from the underground tanks and launched a new series of waste characterizations and a variety of distillation tests. The distillation results showed that the pure hexone (boiling point 117 °C) and the water phases easily evaporated with very little residue. Contrary to earlier test data, it was shown that the hexone-kerosene-tributyl phosphate mixture could be heated to approximately 400 °F and reduced to a dry solid tar. The tributyl phosphate partially decomposes below its boiling point, leaving hard phosphate complexes coating all hot surfaces. The major liquid breakdown product, butanol, was readily distilled over. The decontamination efficiencies for plutonium, americium, and hard beta emitters exceeded 99.9 percent for all samples.

REGULATORY REVIEW AND PERMITTING

An extensive regulatory review was performed in the projects early stages. *A Resource Conservation and Recovery Act* (RCRA) Part-A permit was submitted to carry out the process under the interim status provisions of RCRA. A Part-B permit was not required because the operating life of the facility was limited. A closure plan currently under preparation and scheduled for submission to Washington State in November 1992 details the closure of the distillation system and hexone tank site. Other documentation prepared for the demonstration included a safety analysis document, an environmental evaluation, as well as RCRA-compliant personnel training, contingency, waste analysis, and inspection plans.

DISTILLATION EQUIPMENT DESIGN

Various distillation equipment options were evaluated, including steam strippers, distillation columns, and different types of evaporators. Special consideration was given to the radionuclide content of the waste and to the tarry nature of the distillation residue. Sacrificial distillation vessels (300-gal steel pressure vessels with heating coils) were chosen as they offer several important advantages:

- Liquid waste is pumped into the vessels and only vapors exit (although in actual practice the weir design did allow some recirculation to the underground tank). When the vessels are filled with the maximum practicable amount of radioactive tars, they are blanked off and become strong primary storage containers for the radionuclides. The vessels were designed to meet 1988 Waste Isolation Pilot Plant container criteria in the event that the tar was classified as transuranic.

- The handling and packaging of radioactive residues is virtually eliminated.

- The heating system remains remote and is not contaminated.

- The requirement for maintaining radioactively contaminated equipment is reduced to an absolute minimum.

- Radioactive exposure to personnel is kept as low as possible. This advantage would be even more significant for wastes with a higher concentration of radionuclides.

The distillation equipment layout is shown in Figure 1 and a process schematic is shown in Figure 2. The waste is pumped into a feed weir that maintains a constant liquid level in the coil-heated distillation vessel. Excess feed overflows via a 40-in. pressure seal loop to the underground feed tank. Vapors pass through two demister elements, are condensed, and again treated by the identical process in the second stage before transfer to rail tank cars for storage.

Figure 1. Hexone Distillation Arrangement.

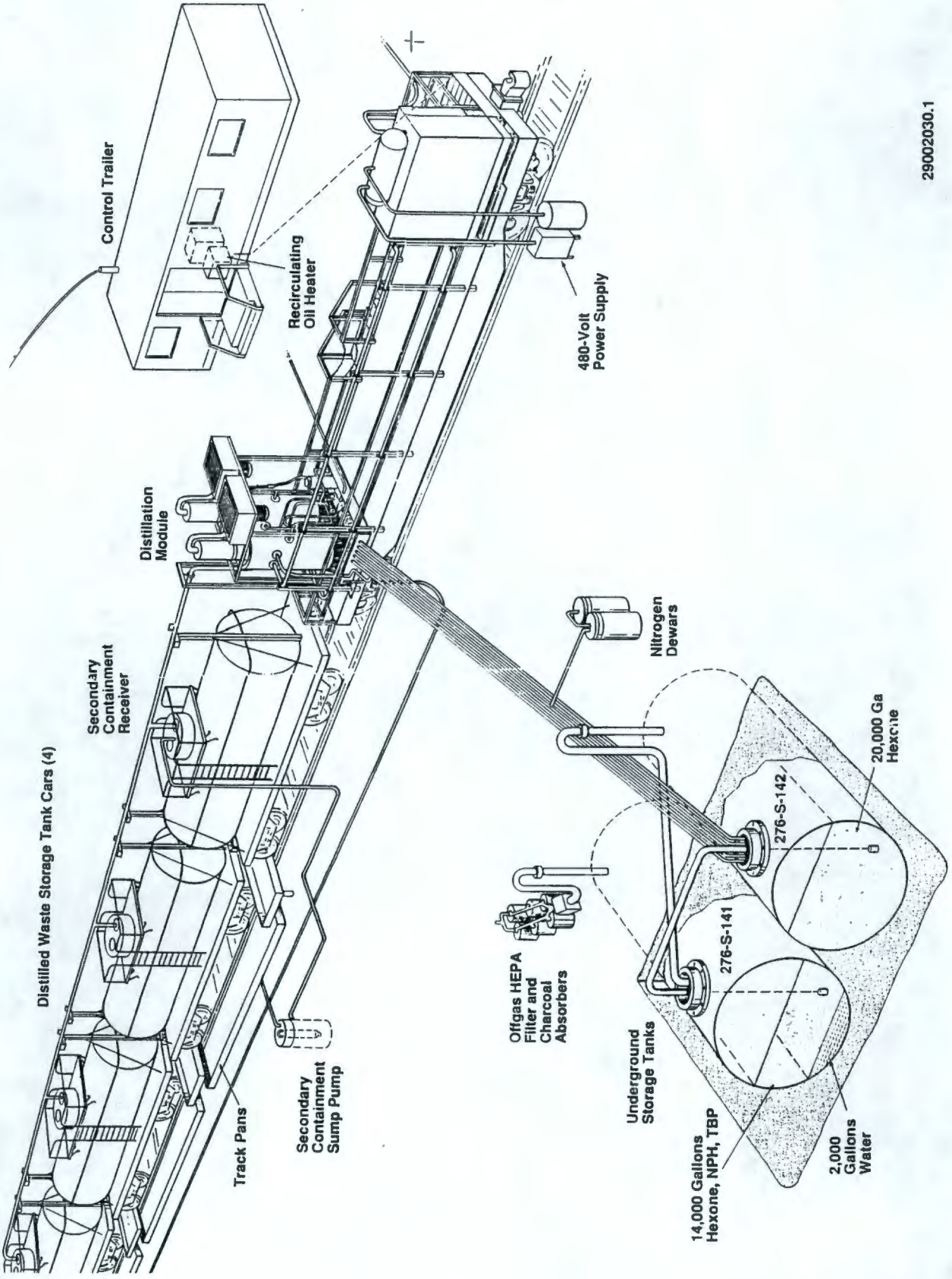
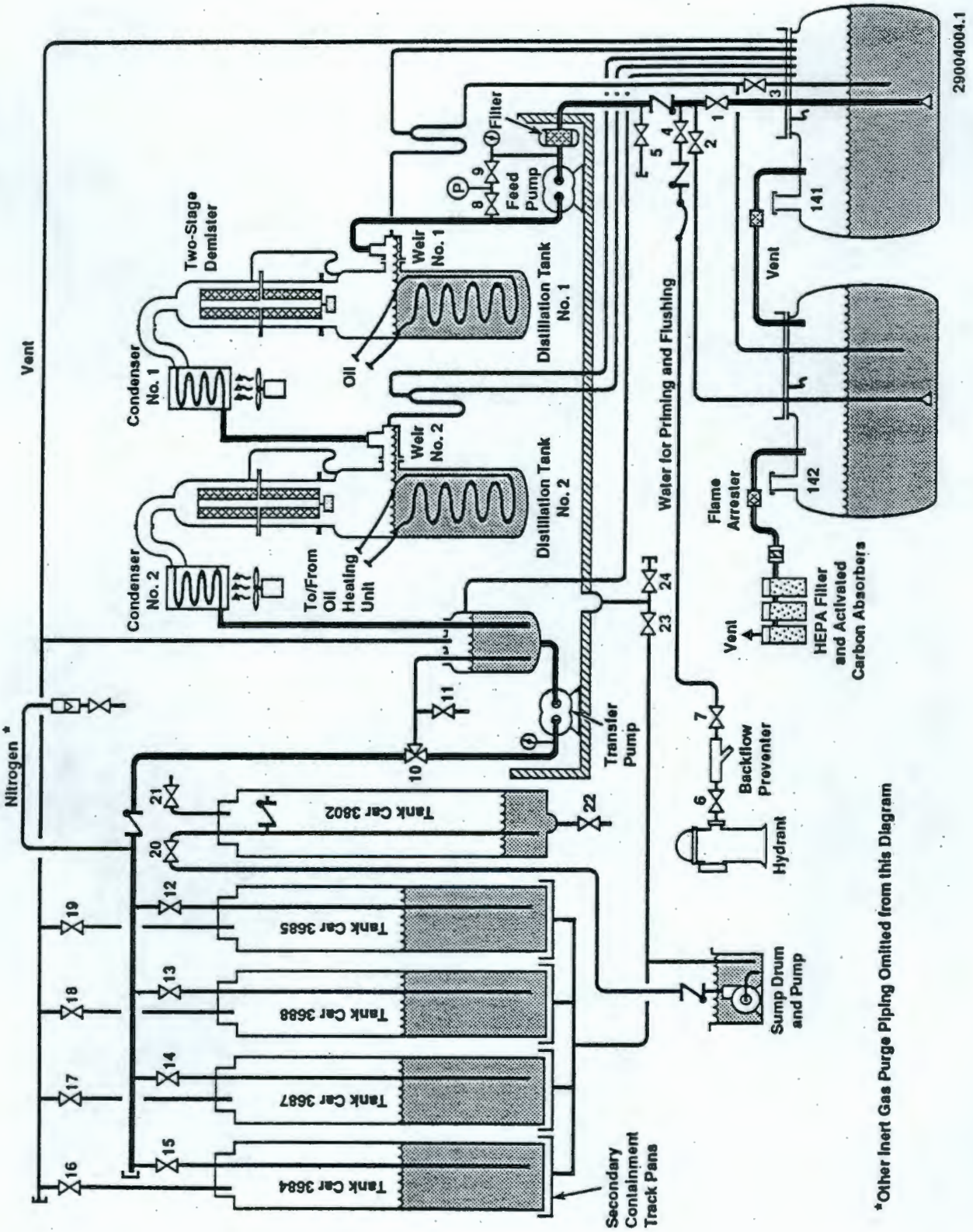


Figure 2. Hexone Distillation System Piping Schematic.



The distillation system was constructed as a modular unit by installing all major components on a 60-ton-capacity railroad flatcar (Figure 3). Use of the railcar reduced fabrication costs as the system could be assembled in the shops and then moved as a complete unit to the site with a minimum of costly field work.

The distillation occurred in two 3-ft-dia. by 6.5-ft-tall cylindrical distillation vessels (Figure 4) in series. Each vessel was surmounted by an 8-ft-tall, two-stage demisting unit and a fan-cooled condenser. A 30-gal transfer tank received the double-distilled hexone product. Four Department of Transportation (DOT) 103-W 10,000-gal railroad tank cars were connected with transfer and vent piping to the transfer tank pumping system. The distillation system had a nominal process capacity of 1.3 gal of hexone per minute, although in actual practice this rate declined as the first-stage distillation vessel gradually filled with tar. When processing water, the rate averaged 0.5 gal/min. Three spare distillation vessels were fabricated to replace units filled with radioactive tar residues, although only one spare actually was used.

The distillation vessels are heated with a heat-transfer oil circulating through pipe coils. A standard commercial oil heating unit is located at the opposite end of the flatcar and is connected to the distillation module with insulated 3-in. piping. All electrical equipment on the distillation module is constructed with explosion-proof components. The electrically fired oil heating system, which is not designed to explosion-proof standards, is located

Figure 3. Distillation System Mounted on Flat Car.

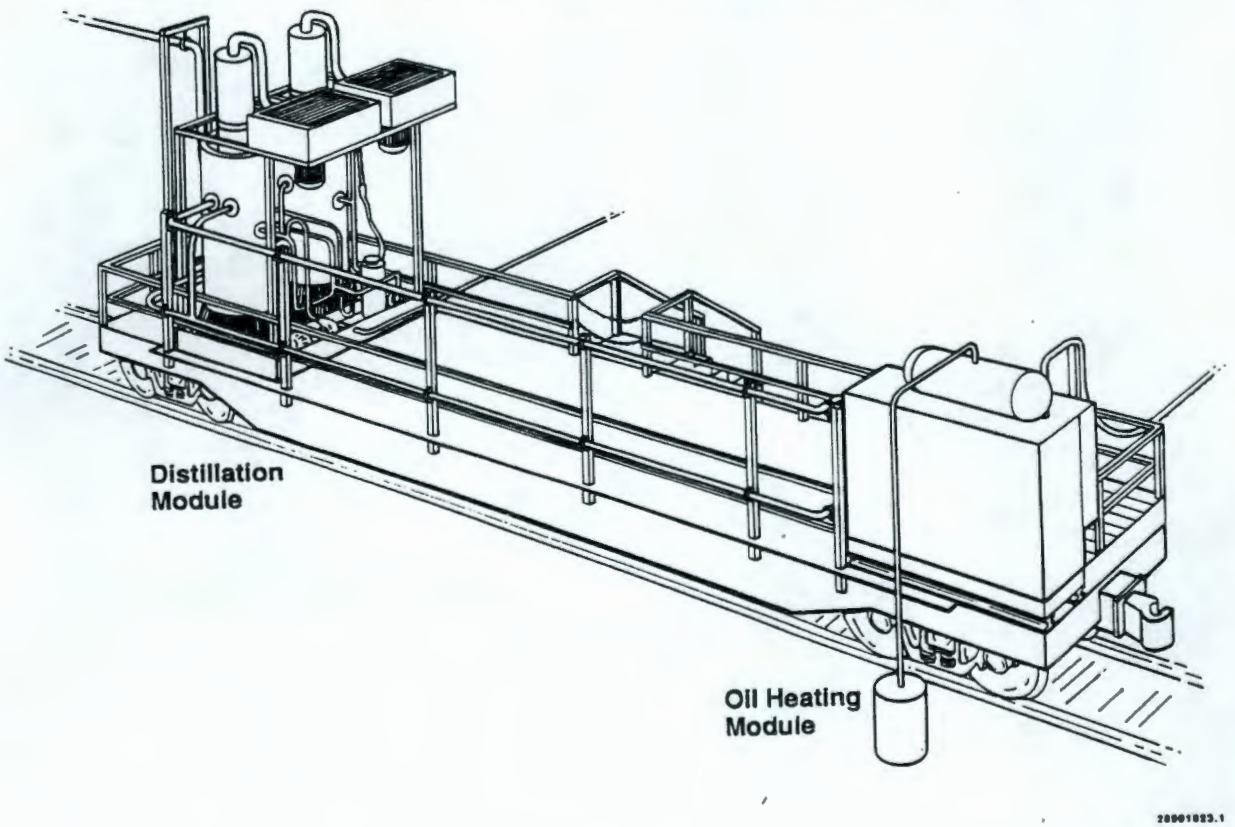
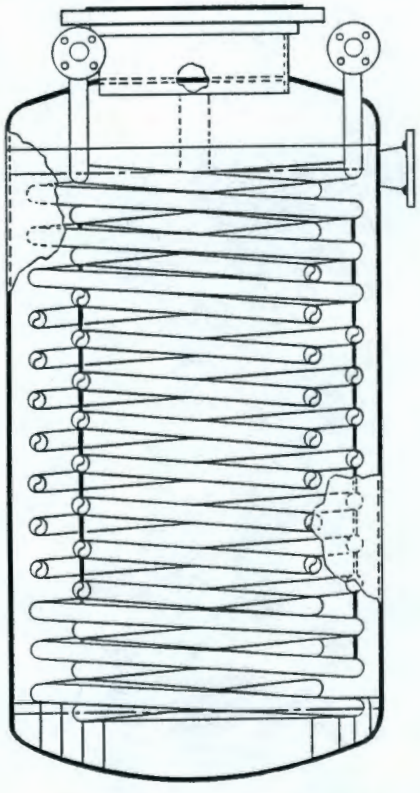


Figure 4. Distillation Vessel.



more than the required 25 ft from the distillation module to maintain safe separation. All components of the distillation system, including piping, tank cars, and secondary containment facilities, are fully grounded. A 30-ft light pole with four vapor lights is bolted to the frame of the flatcar for near-daylight visibility at night.

Four DOT 103-W rail tank cars suitable for transporting flammable solvents were obtained at no cost from the Department of Defense for storing the distilled solvent waste. All of the cars were rinsed, hydrostatically tested, internally inspected, and equipped with new fill and vent piping as well as new relief valves.

A secondary containment system was designed to meet RCRA requirements and consisted of steel pans under the distillation module and under the four hexone receiver cars. The 21 pans drained via a header system to a sump vessel equipped with an automatic transfer pump. An 11,360-gal-capacity tank car, large enough to receive 110 percent of the volume of the largest vessel in the system, acted as the drainage receiver vessel. Rainwater pumped to the receiver car was sampled routinely before disposal.

Pressure, temperature, and liquid-level sensors from the distillation system and associated tankage were connected via explosion-proof electronic transmitters to a datalogger for recording process and operating data. An office trailer was installed at the site to house the datalogger and to maintain logbooks and operating documentation.

INERTING AND OFFGAS CONTROL

Two 4,000 ft^3 gas capacity liquid nitrogen dewars provided gas for inerting the four distillate receiver tank cars, the distillation module vessels, and the underground hexone tanks. The nitrogen gas also served as the medium for operating the weight factor dip tube bubblers used for liquid-level measurements. A demand regulator on the nitrogen supply system added nitrogen gas as required to maintain the hexone system pressure about 0.2-in. water above ambient pressure to prevent air infiltration.

Purge nitrogen gas from the distillation system as well as noncondensible gases vented first to Tank 276-S-141 and flowed via a flame arrester to Tank 276-S-142 before entering the offgas filtration system. This arrangement allowed the two underground tanks to be used as backup vapor condensing pots. Gases vented from Tank 276-S-142 passed through a flame arrester, a high-efficiency particulate air filter, and then two parallel systems of three activated-charcoal absorption units in series.

DISTILLATION OPERATIONS

As expected, distillation operations proceeded very smoothly for the 20,000-gal tank batch of nearly pure hexone. Process rates of 1.3 gal/min were easily maintained without approaching the 40-in. hydrostatic pressure limit imposed by the weir overflow loops.

The next material processed was 2,000 gal of water, where process rates dropped to 0.5 gal/min due to the high heat of evaporation of water. The system was operated conservatively and no attempt was made to raise processing rates by increasing the oil temperature, as volatile organics could enter the system at any time.

The challenging phase of the operation began with processing of the 14,000 gal mixture of hexone, kerosene, and tributyl phosphate. The overflow weir recirculation system allowed much of the hexone phase to be boiled out of the organic liquids early on. As temperatures were increased to distill the higher-boiling fractions, tributyl phosphate breakdown tars became a problem. Thick tars started accumulating in the first-stage distillation vessel. While all of the tar had been expected to remain in the distillation vessel, soft tar also started building up in the feed weir and in the overflow seal loop, partially plugging the loop and causing cycling in the vessel liquid level.

The first stage vessel was replaced with a spare vessel after 8,000 gal of the mixed organics had been processed, and process rates fell. At the same time the feed weir was cleaned out because it was two-thirds filled with tar as well as rust flakes from the underground tanks. The long fiber-mesh first-stage demister was replaced with a short wire-mesh pad to reduce demister pressure drop.

The last 7,000 gal of mixed organics proved the most troublesome. Several process outages were required to remove tar from the feed weir and to flush the overflow drain line. As the end of processing approached, oil temperatures were raised to 500 °F and held for several shifts to wring out the maximum amount of distillate.

By the time all possible distillate had been recovered, the first stage distillation vessel (replacement unit) also held 125 gal of tar as well as 70 gal of high-boiling kerosene residuals. The second-stage vessel contained about 15 gal of tar and 1 gal of residual kerosene. The four 10,000-gal rail tank cars held 33,000 gal of distillate. The distillate radionuclide content totalled less than 223 μCi of penetrating alpha and beta activity for a decontamination factor of greater than 1,100 across the distillation system. (In this calculation, detection limits were used as the actual number where radionuclides were nondetectable.) Decontamination results are summarized in Table 1. No decontamination was measured for tritium as this very low-energy isotope is exchanged into the hexone molecular structure and cannot be extracted.

Table 1. Decontamination/Removal Efficiencies.

	Alpha	Beta, μ/Ci*	Total, μ/Ci
Initial radionuclide inventory, μ/Ci	108,000	140,000	248,000
Final radionuclide inventory, μ/Ci	<30.5	192.6	223.1
Removal efficiency, %	99.972	99.86	99.91

*Does not include tritium exchanged into hexone matrix.

INCINERATION

The distillation operation decontaminated the waste solvents to a level low enough to be acceptable for destruction in a fully licensed commercial incinerator. Transportation and incineration services were bid competitively and awarded to a consortium of Chem Nuclear Environmental Services, Diversified Scientific Services (DSSI), and Kindrick Trucking.

The distilled solvents were hauled in nominal 4,900-gal shipments by tanker truck from the Hanford Site to DSSI's incinerator in Kingston, Tennessee. The same 5,100-gal trailer was used for all shipments. The trailer tank was purged with nitrogen gas before loading and rinsed with ethanol after each shipment. At DSSI the solvents were unloaded, sampled, and blended with other waste materials for incineration.

The DSSI incinerator is a co-generation steam electric plant that produces electricity for the DSSI facilities and feeds surplus power into the local power grid. The incinerator is fully licensed by the Nuclear Regulatory Commission, the U.S. Environmental Protection Agency (EPA), and the State of Tennessee to burn and destroy radioactive hazardous waste solvents. The

plant's incineration rate achieves a nominal 2 gal/min. The offgas stream is cleaned rigorously with scrubbers and filters to meet all regulatory requirements. The tritium (0.76 Ci) is released as a gas to the atmosphere in accordance with DSSI's permit that allows discharge of 22 Ci of tritium per year.

TAR DISPOSAL AND HEXONE SITE CLOSURE

Three 300-gal sacrificial distillation vessels have been removed from the distillation system and currently are undergoing sampling and analysis. The vessels will be boxed and stored at a permitted mixed waste storage facility at the Hanford Site for ultimate treatment and disposal. All interconnecting piping between the distillation unit and the empty underground storage tanks has been cut up and packaged into lined 55-gal galvanized steel drums for shipment to the mixed-waste storage facility. The distillation system itself has been refurbished with spare distillation vessels and is being offered for future use. A half-dozen waste solvent batch candidates are under review. The system may be used in its present location or moved by a locomotive to a new processing site.

The underground tanks will be cleaned by dry blasting (grit or dry ice), removed from the ground, and hauled to a permitted Hanford disposal site. It is expected that the hexone site can be clean closed. A closure plan is scheduled for submittal to the EPA in November 1992.

COST

The cost of the hexone remediation demonstration is expected to total $4.0 million, which is a relatively modest cost for resolution of a radioactive and hazardous waste problem of this nature.

Decontamination expenses, including characterization, technology development, and solid waste disposal, consumed 71 percent of this cost, with shipping and incineration of the distillate accounting for the remainder. Commercial shipping and incineration charges totalled $19.20 per gal.

CONCLUSION

Onsite distillation/decontamination followed by commercial incineration has proved to be a practical and cost-effective means of remediating industrial-size volumes of hazardous, flammable, and radioactive waste solvents. The use of sacrificial distillation vessels virtually eliminated the need to handle the intractable distillation tars and provided a convenient and secure storage/disposal container for the radioactive still bottoms. Use of concrete shields around the vessels reduced personnel radiation exposure to essentially nil. The operations were carried out safely without personnel injuries, chemical exposures, fires, spills, or radioactive-contamination events.

Small-scale distillation systems using sacrificial distillation vessels are expected to have future applications when radioactive organic and aqueous liquids require safe disposal.

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