HEXONE REMEDIATION DEMONSTRATION

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ABSTRACT

The Hexone Remediation Demonstration is funded by the U.S. Department of Energy Hazardous Waste Remedial Action Program to show complete remediation of an industrial-scale quantity of radioactively contaminated hazardous solvent waste. The specific material to be remediated consists of 34,000 gal of hexone (methyl isobutyl ketone), normal paraffin hydrocarbon, and tributyl phosphate complexes as well as 2,000 gal of solvent-saturated water. The solvents, utilized as extractants in nuclear fuel reprocessing plants at the Hanford Site, have been stored in two underground tanks for more than 20 years. The remediation approach is to separate the radioactive constituents, totalling approximately 0.25 Ci, from the waste by two-stage simple distillation and then incinerating the essentially nonradioactive distillate in a hazardous waste incinerator. The distillation operations will be carried out in sacrificial vessels--300-gal-capacity steel tanks with heating coils--that will become the storage containers for the solid radioactive tar residues. The sacrificial distillation vessels will minimize the handling of radioactive tars and the radiation exposure to workers. The distilled condensate, with more than 99.9% of the original radioactivity removed, will be incinerated in a leased or purchased commercial hazardous waste incinerator modified to recover the remaining trace amounts of radionuclides from the offgas. The incinerator will be decontaminated or partially rebuilt for return to nonradioactive service.

Clean closure of the waste tank site will be carried out by excavating the tanks, sandblasting the vessel interiors to remove transuranic rust and sludge, and finally by disposing of the tanks in a low-level radioactive waste burial ground.

INTRODUCTION

The problem of disposing of spent solvents is a pervasive one and is particularly difficult in nuclear facilities where these solvents are contaminated with radioactive material. The problem is complicated further when only batch quantities of radioactive solvents exist, and where the high expense for establishing a full-scale solvent reclamation facility is difficult to justify. This situation exists at the Hanford Site and other nuclear sites.

In 1987, the U.S. Department of Energy Hazardous Waste Remedial Action Program (HAZWRAP) initiated funding for demonstrating the remediation of an industrial-scale batch of radioactively contaminated solvent at the Hanford Site. The material chosen for this demonstration is large enough in volume--36,000 gal--to require an industrial-scale remediation and contains enough radionuclides to make radiological controls essential. At the same time, the radionuclide inventory is sufficiently small to permit treating the waste and maintaining the equipment with only modest shielding and limited remote handling. The facilities for treating the waste solvents are intended to be transportable to allow treatment to occur at other waste sites when transport of the waste is not practical.

THE WASTE REMEDIATION PROBLEM

The specific waste to be treated in this demonstration has been a problem in need of a solution for many years. In the late 1960's, two nuclear fuel reprocessing plants were shut down at the Hanford Site: the small Semiworks Pilot Plant and the large Reduction-Oxidation (REDOX) Facility. Leftover solvents from these facilities were placed in two underground storage tanks at the REDOX Facility site. The tanks, 23,500-gal-capacity carbon steel vessels similar to commercial gasoline storage tanks, were originally constructed in 1950 for storing fresh hexone (methyl isobutyl ketone) received by tank car from vendors. After the facility shutdown, Tank 276-S-141 contained approximately 20,000 gal of essentially pure liquid hexone contaminated with small amounts of radionuclides (2.3 μCi as total alpha and 400μCi as total beta). Tank 276-S-142 contained 14,000 gal of a liquid organic mixture that consisted of 60% hexone, 39% normal paraffin hydrocarbon (NPH), and 1% to 2% of metallic tributyl phosphate (TBP) complexes, as well as 2,000 gal of solvent-saturated water. Tank 276-S-142 contains 99.8% of the radionuclide inventory in the system, with approximately 108,000 and 140,000 μCi total beta and total alpha, respectively. As the tanks age, the need is becoming more pressing to remove the waste from the now 40-year-old vessels. Constructing new storage tanks meeting all current standards would only prolong the waste storage problem. Remediation of the waste and closing of the facilities is the most cost-effective approach.

THE SEARCH FOR A REMEDIATION SOLUTION

The Hexone Remediation Demonstration project was started in late fiscal year (FY) 1987. Numerous remediation options as well as their regulatory strategies were investigated. The options were grouped into two broad categories-

-recycling and destruction. Each option and the three best strategies encompassed are listed below.

A. Recycling Options

A.1 Ship to an offsite nuclear fuel reprocessing facility for reuse as solvent.

A.2 Remove radionuclides; recycle in commercial sector as nonradioactive solvent or fuel.

A.3 Remove radionuclides; recycle onsite as boiler fuel.

B. Destruction Options

B.1 Ship waste as-is to offsite radioactive hazardous waste incinerator.

B.2 Construct new radioactive hazardous waste incinerator and destroy the waste at the Hanford Site.

B.3 Remove radionuclides; destroy waste at the Hanford Site in leased or purchased commercial nonradioactive hazardous waste incinerator modified to handle very low levels of radionuclides.

Options A.1 and B.1, recycling or destroying the waste in its present condition in an offsite facility, were found to be unavailable in the foreseeable future. Options A.2 and A.3, removing the radionuclides and then recycling the waste as nonradioactive solvent or fuel, were found impractical as there is no deminimis level for unconditional release.

Option B.2, construction of a new radioactive hazardous waste incinerator, was found to be well beyond the budget allocation expected to be available for this project. This left Option B.3, removal of essentially all of the radionuclides followed by destruction in a less costly commercial hazardous waste incinerator modified to handle the remaining trace radionuclides.

It appears that Option B.3 can be carried out a at reasonable cost in a near-term time frame. Therefore, radioactive decontamination followed by incineration was adopted for this demonstration.

WASTE ANALYSIS AND DECONTAMINATION TESTS

The organic and aqueous wastes in the two tanks had been sampled in FY 1976 as part of an earlier effort to find a means of remediating the material. Preliminary distillation tests suggested that the material could be distilled to dryness with a high degree of radionuclide separation. Chemical separation tests were less promising. Another sampling effort was carried out in early FY 1988 with a small pump and a sampling wand. A total of 23 liquid samples were taken in 1-L aliquots from various levels of the tanks, and two scoop samples of tank-bottom rust and sludge were obtained.

The FY 1988 decontamination tests found direct distillation to be highly effective, with greater than 99.9% of the radionuclides remaining in the still-bottom tar fraction. The decontamination results are summarized in Table I. Even better results are expected in a full-scale distillation, as high-efficiency demisting capability will be installed, and some of the iodine can be expected to be held by the iron in the distillation system. It may be noted that nearly three-fourths of the radionuclides carried over are 129I. The process produced 98% to 99% of clean distillate and 1% to 2% of residual tar that could be taken to dryness by heating to 200 °C. The laboratory tests confirmed the feasibility of decontaminating the hexone waste to a condition suitable for contract incineration in a commercial portable incinerator.

REGULATORY REVIEW

By the end of FY 1988, sampling, waste characterizations, and distillation tests had been completed and radioactive decontamination followed by incineration had been identified as the reference remediation technology to be demonstrated. Also, in FY 1988 an extensive regulatory review was conducted, and a Resource Conservation and Recovery Act (RCRA) Part A permit for the proposed distillation and incinerator operation was submitted to the Washington State Department of Ecology. The regulatory strategy calls for carrying out this process under the interim status provision of the RCRA law. Closure of the tank site will be carried out under an approved closure plan.

DISTILLATION EQUIPMENT DESIGN

In FY 1988, the distillation equipment design was initiated. 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. The choice of sacrificial distillation vessels--300-gal-capacity steel pressure vessel with heating coils--offers several important advantages.

- Liquid waste is pumped into the vessels and only vapors exit. 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. New vessels are installed to resume distillation.
- The handling and packaging of radioactive residues is virtually eliminated.
- The requirement for maintaining radioactively contaminated equipment is reduced to an absolute minimum. Radioactive exposure to personnel is kept as

TABLE I

Hexone Radioactivity Levels

Tank	Material	Volume (L)	Composite Sample (pCi/L)			After Double Distillation[a]					
			Total Alpha	Total Beta	^{129}I	Total Alpha (pCi/L)	Total Beta (pCi/L)	^{129}I (pCi/L)	Total Alpha (μCi)	Total Beta (μCi)	^{129}I (μCi)
141-S	Organic	75,700	<31	4,910	5,460	<29	205	55	2.2	15.5	4.2
142-S	Organic	52,000	2,070,000	871,000	34,500	<70	2,450	3,070	3.6	127.4	159.6
	Water	7,600	31,000	12,500,000	Not Analyzed	<38	8,240	1,910	0.3	62.6	14.5
TOTAL									6.1	205.5	178.3
Design Concentration Guide for Drinking Water (for comparison)						300[c]	1,000[d]	500			
Total Activity (Total Alpha + Total Beta[b] in 36,000 gal: Tank Waste = 248,583 μCi; Distillate = 244 μCi Distillation Radionuclide Removal Efficiency: 99.9%											

[a]Lower contamination levels are expected in the full-scale distillation product because of the use of high efficiency mist eliminators which are still only laboratory scale.
[b]Where ^{129}I exceeds total beta value, ^{129}I is used as total beta because total beta includes ^{129}I.
[c]Based on ^{239}Pu
[d]Based on ^{90}Sr

PST90.1

low as possible. This advantage would be even more significant for wastes with a higher concentration of radionuclides.

The distillation process is shown schematically in Fig. 1 along with the proposed approach for incineration. The waste is pumped into a feed weir that overflows to the first distillation tank. The vapors are passed through deentrainers, condensed, and again treated by the identical process in the second stage before transfer to rail tank cars for storage.

The distillation system was constructed as a modular unit by installing all major components on a 60-ton-capacity railroad flat car (Fig. 2). Use of the rail car 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 will be carried out in two 3-ft-diameter by 6.5-ft-tall cylindrical distillation vessels (Fig. 3) in series. Each distillation vessel is surmounted by an 8-ft-tall, two-stage demisting unit and a fan-cooled condenser. A 30-gal-capacity transfer tank receives the double-distilled hexone product. Four 10,000-gal-capacity railroad tank cars are connected with transfer and vent piping to the transfer tank pumping system. The distillation system has a nominal process capacity of 2 gal of hexone per minute, although in actual practice this rate will decline as the distillation vessels gradually fill with tar. Three spare distillation vessels were fabricated to replace units filled with the radioactive tar residues.

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 flat car 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 more than the required 25 ft from the distillation module to maintain separation. All flat car-mounted equipment has been installed, and most electrical equipment has been operability tested with shop power. Final operability tests will be carried out in the spring of 1990 when the flat car-mounted assembly is moved to the distillation site.

INERTING AND OFFGAS CONTROL

Two 4,000-ft3-capacity nitrogen gas dewars provide gas for inerting the four distillate receiver tank cars, the distillation module vessels, and the underground hexone tanks. The nitrogen gas also serves as the medium for operating the weight factor dip tube bubblers that are used for liquid level measurements. A demand regulator on the nitrogen supply system will add nitrogen gas as required to maintain the hexone system pressure above ambient pressure to prevent air infiltration.

Purge nitrogen gas from the distillation system as well as noncondensible gases will vent first to Tank 276-S-141 and will then flow via a flame arrester to Tank 276-S-142 before entering the offgas filtration system. This arrangement allows the two underground tanks to be used as vapor condensing pots in the event a power failure, or other event, shuts down one or both condenser fans. While a pressure sensor will shut down the oil heater, vapors will continue to be produced until residual heat in the system dissipates.

Gases vented from Tank 276-S-142 will pass through a flame arrester, a high-efficiency particulate air (HEPA) filter, and then two parallel systems of three activated charcoal absorption units. Excess purge gas supplied by the

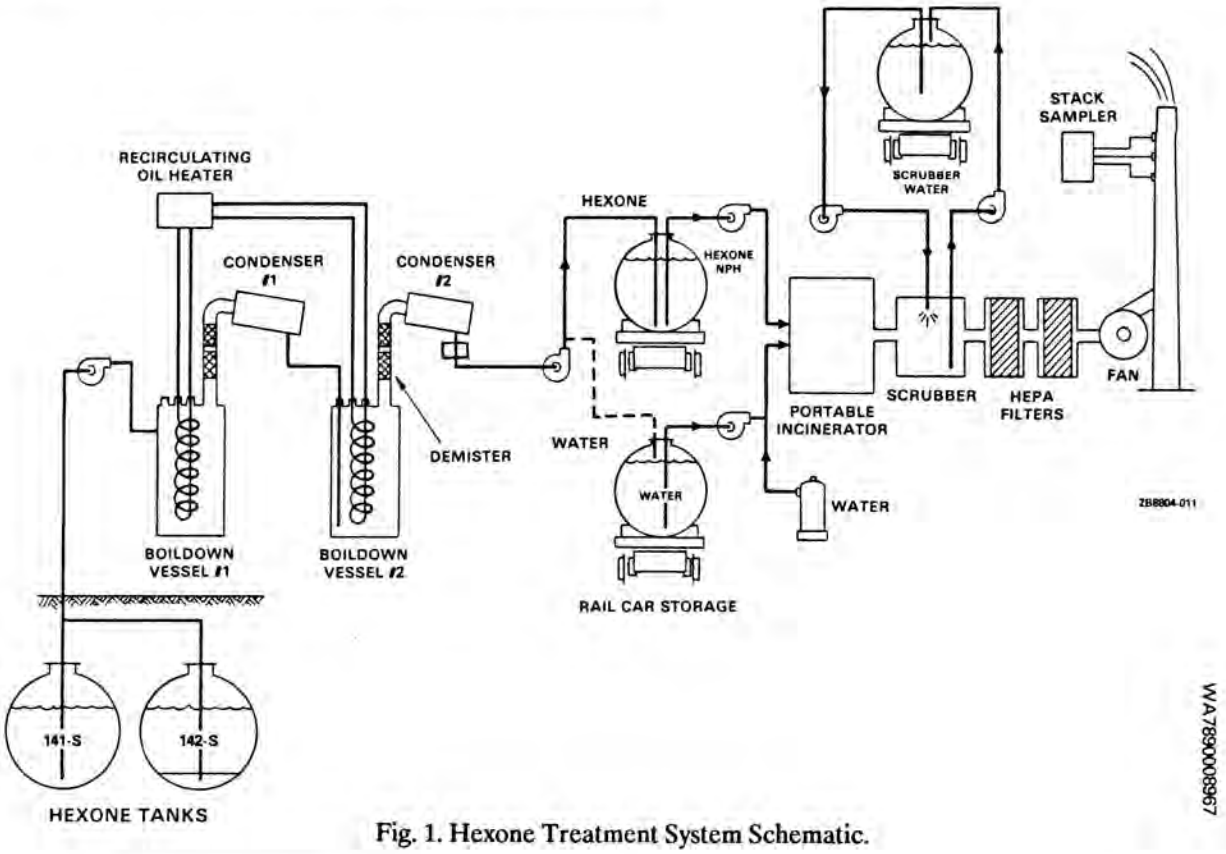

Fig. 1. Hexone Treatment System Schematic.

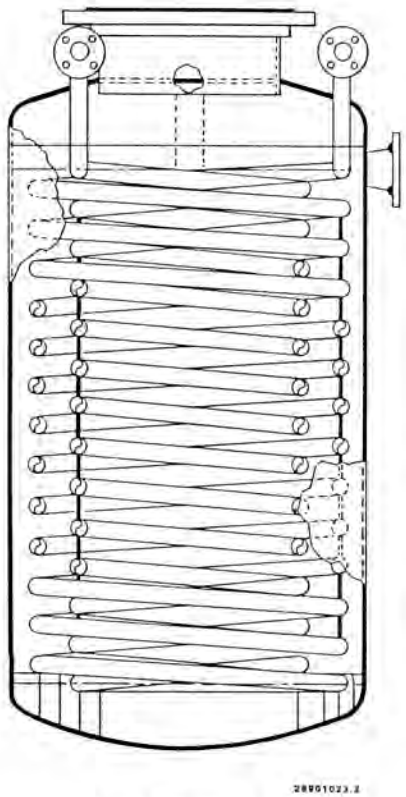

Fig. 2. Distillation Vessel.

demand regulator will keep the ventilation system pressurized with respect to atmospheric pressure and prevent air in-leakage. Monitoring of the vented gases is difficult because of low gas flows (~20 ft3/hour). Grab samples will be taken from the exhaust vent for organic vapors and iodine, and ambient air monitoring in the immediate area of the vent will also be performed.

DISTILLED HEXONE STORAGE TANKAGE

Seven U.S. Department of Transportation (DOT) Tank 103-W cars suitable for transporting flammable solvents, including hexone, were obtained at no cost from the U.S. Department of Defense (DOD) for storing the distilled solvent waste. The cars were found to be in generally excellent condition. Upon arrival at the Hanford Site, all of the cars were triple rinsed by a commercial waste handler to remove residual aircraft deicing solutions and to make them suitable for hexone storage. Four cars were selected for certification to RCRA and DOT standards. The cars were successfully hydrostatically tested and equipped with fill-and-vent piping as well as new relief valves. The recertified tank cars represent a significant cost savings over other means of providing temporary storage capacity between the distillation and incineration phases of the demonstration. While it was originally believed that full compliance with DOT standards for handling hazardous materials would satisfy regulatory requirements, a new review of the Wash-

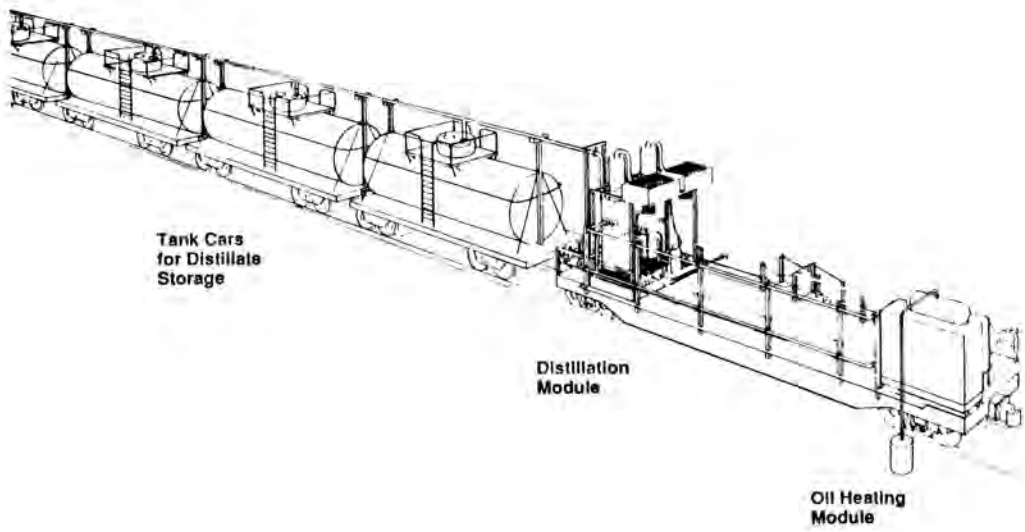

Fig. 3. Hexone Distillation System.

ington State codes and RCRA regulations showed that full RCRA compliance is also applicable to storage in tank cars. The main impact of this interpretation was to require secondary containment for the tank cars as well as to require a system for daily level measurements and inspections. The secondary containment system, as designed, consists of steel track pans under the four hexone receiver cars. The 20 pans drain 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% of the volume of the largest vessel in the system, acts as the drainage receiver vessel. Liquids pumped to the receiver car will be sampled before disposal to the environment or to the hexone storage tank system. The steel drain pans have been fabricated and installed at the hexone tank site.

PROCESS CONTROL AND DATA ACQUISITION

Pressure, temperature, and liquid level sensors from the distillation system and associated tankage will be connected via electronic transmitters to a data logger for recording process and operating data. An office trailer was installed at the site to house the data logger and to maintain logbooks as well as design and operating documentation.

SAFETY AND ENVIRONMENTAL DOCUMENTATION

A significant level of effort was expended in FY 1989 on the preparation of safety and environmental compliance documentation. The main safety evaluation was carried out as a safety analysis review. Preparation of the review required not only considerable research but also resulted in performing additional laboratory testing. Investigative work in the laboratory focused primarily on establishing that no significant concentrations of potentially explosive peroxides existed in the hexone waste, and that the residual distillation tars do not contain significant exothermic materials in the temperature ranges reached during final heating to dryness. All questions were successfully resolved, and the review concludes that the hexone distillation operation can be carried out safely in the demonstration unit.

The environmental compliance documentation effort resulted in a number of documents. An environmental evaluation was conducted and approved by the U.S. Department of Energy. The Washington State Department of Social and Health Services, Office of Radiation Protection, will also be notified of the remediation.

FUTURE PLANS

The immediate thrust for early FY 1990 is to complete the installation work at the hexone tank site, including positioning of the hexone distillation system, laying the secondary containment piping, and installing the process and utility tie-ins. Actual distillation of the hexone waste will be initiated in the spring of 1990; the distillation system design does not include the extensive insulation and heat

tracing that would be required for operation in subfreezing conditions.

Upon completion of distillation in the summer of 1990, the distilled product will be thoroughly characterized in the laboratory to provide the necessary radiological data for finalizing the incineration contract.

The distilled organic material will contain very low levels of radionuclides. It is planned to bring a commercial portable incinerator to the Hanford Site on a contract basis in FY 1991 to incinerate the distilled waste. A proposed incineration system is shown in Fig. 4. The system is based on a trailer-mounted plasma incinerator, although a different incinerator may be utilized. Any incinerator components that may become slightly contaminated will be decontaminated or replaced. The incinerator offgas will be filtered and, if necessary, passed through a silver zeolite bed for iodine removal. The underground tanks will be excavated, sandblasted for transuranic rust removal, and transported to the low-level radioactive waste disposal facilities. The final stage in the project plan calls for sampling and restoration of the hexone tank site, and for the dissemination of the experience and technology developed to other facilities in FY 1992.

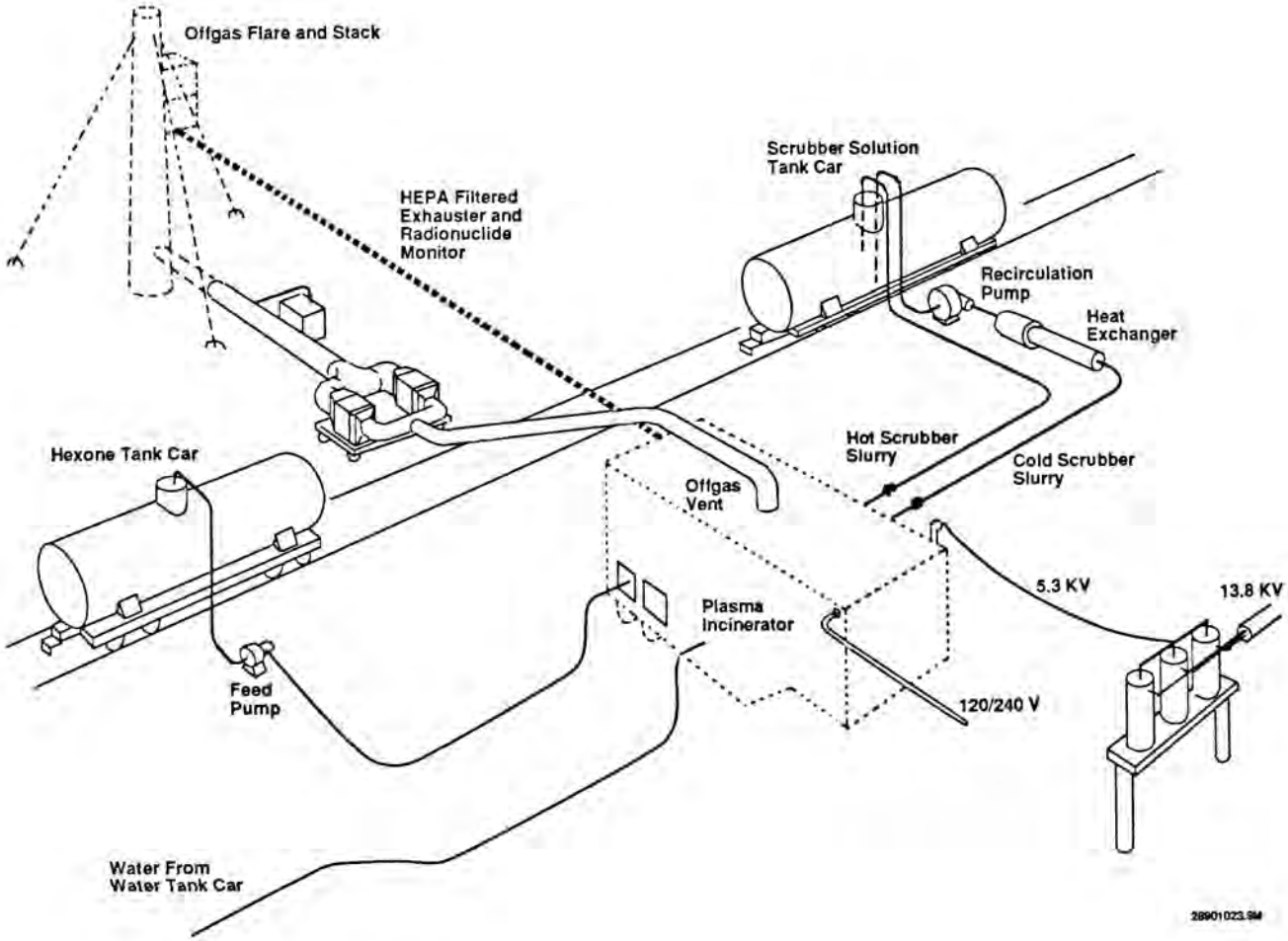

Fig. 4. Proposed Hexone Incineration System.