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MEETING NEW AIR STANDARDS
WITH A
VOLATILE ORGANIC TREATMENT TRAIN

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) issued the second phase of the organic air emission standards for hazardous waste treatment, storage, and disposal facilities (TSDFs) and hazardous waste generators in December 1994. These standards (referred to as the Subpart CC standards) are designed to further reduce organic air emissions from hazardous waste management activities. To comply with these new air standards, Lawrence Livermore National Laboratory (LLNL) is designing a volatile organic removal and destruction treatment train to modify its existing Waste Water Treatment Tank Farm (hereafter called Tank Farm).

LLNL's Tank Farm consists of six, 7,000-L open-top tanks used to store and treat aqueous low-level radioactive, mixed, and hazardous waste before discharging it to the local publicly owned treatment works. The waste stored and treated in the tanks have elevated volatile organic constituent (VOC) concentrations. According to the Subpart CC standards, tanks handling waste with similar VOC concentrations must be retrofitted with a cover and an emission control device for cover openings that achieves at least a 95% reduction in the total organic content of the vented gas stream. However, LLNL concluded that the removal and destruction of VOCs from waste before they enter the Tank Farm would demonstrate compliance with the Subpart CC standards more effectively and be more cost effective than installation of air emission control devices on the Tank Farm. LLNL has designed this removal and destruction technique to consist of an air stripper, high-efficiency particulate air (HEPA) filter, catalytic oxidizer, scrubber, and mist eliminator.

INTRODUCTION

As part of the Hazardous and Solid Waste Amendments of 1984, Section 3004(n) of Resource Conservation and Recovery Act (RCRA) directs the EPA to promulgate regulations for monitoring and controlling air emissions from TSDFs as may be necessary to protect human health and the environment. EPA completed the first phase of the congressional directive in June 1990 with the promulgation of RCRA air standards that control organic emissions vented from certain hazardous waste treatment processes (i.e., distillation, fractionation, thin-film evaporation, solvent extraction, steam stripping, and air stripping) as well as from leaks in certain ancillary equipment used for hazardous waste management processes. EPA finalized the second phase of the Section 3004(n) directive upon promulgation of the RCRA air emission standards designed to further reduce organic emissions from hazardous waste management activities associated with tanks, surface impoundments, containers, and miscellaneous units operated at TSDFs. EPA is currently developing a strategy for completing a third phase of the Section 3004(n) directive to attain the health-based goals of RCRA.

The second phase of the organic emission standards for TSDFs were published in the *Federal Register* on December 6, 1994 and will be effective in June of 1995. Although the Subpart CC standards are deferred for systems solely managing mixed wastes (waste that contains both hazardous waste and source, special nuclear, or byproduct material subject to the Atomic Energy Act of 1954)[1], the Subpart CC standards apply to LLNL's Tank Farm, which currently manages both hazardous and mixed wastes.

BACKGROUND

LLNL's onsite activities generate a variety of aqueous hazardous and mixed waste. Many of the waste streams contain VOCs such as tetrachloroethylene (PCE), 1,1,1-trichloroethane (MCM), and methylene chloride. The organic concentration of each waste stream ranges between 0 parts per million by weight (ppmw) and 10,000 ppmw. The VOC-containing waste streams are generated at a rate of approximately 586,000 L/y.

The aqueous waste streams are transported from the onsite activities in various size containers for treatment in LLNL's Tank Farm. Wastes are blended in the Tank Farm tanks in a predetermined sequence to moderate reactions and dissipate heat of reactions. Further treatment of the waste is conducted on a batch basis, using one or more of several different treatment techniques to achieve a desired treatment objective. The types of treatments performed include:

- Neutralization/pH adjustment
- Oxidation/reduction
- Cyanide destruction
- Precipitation
- Chelation/flocculation
- Ion exchange
- Adsorption
- Separation.

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[1] The EPA decided to temporarily defer application of the Subpart CC standards to tanks, containers, and surface impoundments that are being used solely to manage radioactive mixed wastes because the air emission control equipment required by the Subpart CC standards may conflict with certain radioactive waste management requirements under the Nuclear Regulatory Commission.

Treated waste may be shipped offsite for disposal or discharged to the City of Livermore Water Reclamation Plant via the sanitary sewer in accordance with established internal discharge limits.

The Tank Farm consists of six, 7,000-L tanks with ancillary equipment such as piping and pumps. The six tanks are equipped with piping systems that allow for pipeline transfer of wastes to and from each tank, to and from a filtration system, and to and from portable tanks and containers. Each tank is a vertical, open-top, cylindrical tank. A roof, constructed of metal sheeting on steel supports, partially protects the tanks from precipitation and weathering. The tanks are equipped with high-level alarms, high-level interlocks, pH probe, treatment reagent lines, and mixers. A diagram of a 7,000-L tank is presented in Figure 1.

Wastes treated in the Tank Farm have average volatile organic concentrations equal to or greater than 100 ppmw. Blending VOC-ladened wastes with other aqueous wastes may be performed to maintain the VOC concentration below 100 ppmw, but the Subpart CC standards do not allow dilution of a waste as a means for complying with the requirements. To comply with the new air emission standards, the open-top design of the tanks in the Tank Farm must be modified, or LLNL must change its hazardous waste management operations.

Tank Modification

Modifying the Tank Farm design requires the installation and operation of one of the following air emission control systems:

- A cover that is connected through a closed-vent system to a control device
- A fixed-roof type cover with an internal floating roof
- An external floating roof
- A pressure system that allows the tanks to operate as a closed system.

In specific cases, the Subpart CC standards allow the use of a fixed-roof-type cover without any additional controls; however, the exothermic reactions created by the treatment methods employed in LLNL's Tank Farm prevent LLNL from qualifying for the special case variance. The tank design modification for LLNL that is most easily implemented and least costly is the installation of a fixed-roof cover connected through a closed-vent system to an air emission control device.

The type of air emission control device incorporated into a tank design modification is not specified by the performance-based standards of the Subpart CC regulations. TSDFs have the flexibility of choosing an air emission control device best suited for the characteristics of the organic emissions. Unfortunately, it is difficult to identify an air emission control device for LLNL's Tank Farm that achieves the performance-based standards. The Subpart CC standards require that the installed air emission control device achieve at least a 95% reduction in the total organic content of the vapor stream vented to the device or, in the case of an enclosed combustion device, a reduction of the total organic content of the vapor stream to a level less than or equal to 20 ppmw on a dry basis corrected to 3% oxygen.

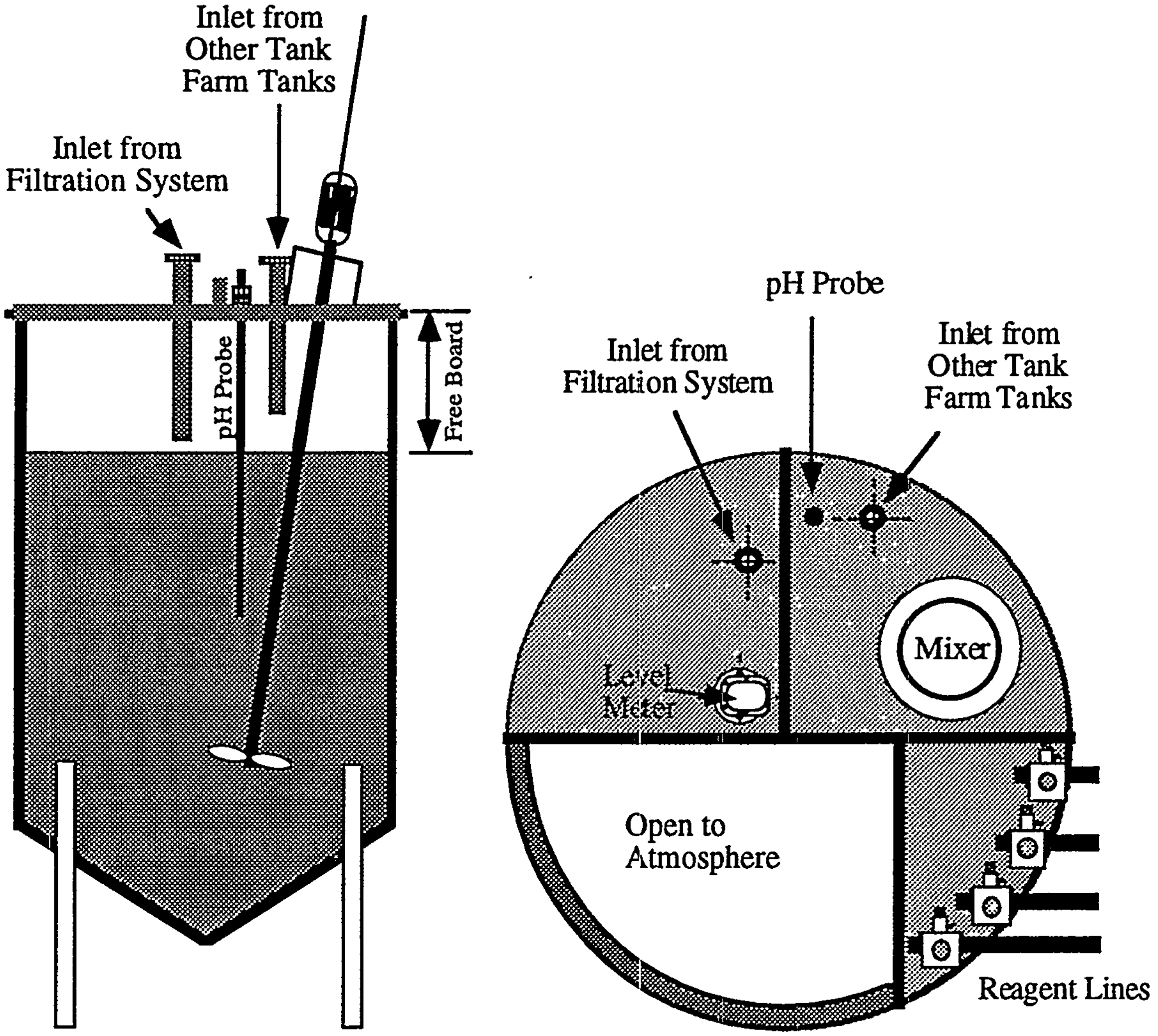

Figure 1. 7,000-L Tank of LLNL Waste Water Treatment Tank Farm.

The organic emissions from the Tank Farm are a result of evaporation at the liquid surface of the waste, and the evaporated organics are dispersed into the atmosphere by displacement during tank filling, diffusion, or wind. The rate of organic emissions depends on the physical and chemical characteristics of the waste, temperature of the waste, tank design, tank condition, and operational characteristics. Although mixing and exothermic reactions within the tanks increase mass transfer rates, the blending of the waste reduces both the VOC concentrations and the overall organic emission rate while the waste remains in the tank. Low organic emission rates make it difficult to achieve the 95% removal standard. The Subpart CC standards suggest two air emission control systems to achieve the performance standards: adsorption systems and thermal destruction.

Adsorption systems work best on air emissions that are below the economic threshold for thermal oxidation. Adsorption systems include adsorbents that may be either polar or nonpolar. Polar sorbents have a high affinity for water vapor and are ineffective in air streams that have any appreciable humidity, but most air streams associated with waste treatment are humid. Nonpolar adsorption, like activated carbon, is effective at removing all but the most volatile compounds associated with waste treatment systems. Adsorption capacity of an adsorbent is directly proportional to the concentration of the adsorbate. Thus, all else being equal, more adsorbent is required to remove a lower concentration contaminant with equal efficiency than to remove the same contaminant at higher concentrations. EPA suggests that the minimum air stream VOC concentration for carbon adsorption to economically achieve a 95% removal efficiency of VOCs is 1,000 ppm by volume.

If LLNL were to use carbon adsorption technology on its Tank Farm design modification to achieve the performance standard, the fixed-roof cover would require an actively vented system connection to the carbon adsorption air emission control device. A passive vented system on the Tank Farm would maintain low organic emissions in the air stream, and the amount of carbon necessary to meet the performance-based standard would be impractical. However, it is still difficult to achieve the 95% removal efficiency using an actively vented system with a carbon adsorption system. Adsorbers that operate periodically or where the concentration of the contaminate varies greatly, such as in batch operations with varying waste streams, can be quickly impaired. In addition, an actively vented system on a tank containing aqueous waste increases the humidity of the vented gas stream. Excessive humidity in the gas stream can reduce the effectiveness of adsorption systems. Gas streams close to saturation can cause capillary condensation, which occupies potential adsorption sites and blocks access to the carbon pores.

Thermal destruction of vented organics can achieve the Subpart CC performance standards using flares or other thermal oxidation units. However, it is extremely difficult to obtain a permit in the State of California for direct-fire or flame techniques because these techniques are not viewed positively by the public. Use of other thermal oxidation units as air emission control devices are economically impractical for the low organic emission rates associated with LLNL's Tank Farm operations.

Changes in Waste Management Operations

The difficulties in using available technologies to meet the Subpart CC performance standards forced LLNL to evaluate altering its waste management operations. In particular, LLNL investigated the removal of the VOCs from the aqueous wastes before the wastes are introduced into the Tank Farm. The Subpart CC regulations allow TSDFs to remove or destroy the organics in the waste by a treatment process that significantly reduces the volatile organic concentration so that storage and treatment units operated downstream of the treatment process in the waste management sequence do not have to use air emission controls. This alternative does not require the owner or operator to perform any volatile organic concentration waste determinations for the hazardous wastes prior to blending, yet still accommodates the blending of wastes that have different volatile organic concentrations.

Based on the varying characteristics of LLNL's aqueous waste streams and because it is extremely difficult to obtain a permit in the State of California for direct-fired and flame units, removal or destruction of the volatile organics is an acceptable alternative to modifying the Tank Farm design. LLNL's preferred option to remove VOCs from the waste is air stripping, but the volatile organic removal or destruction method following the air stripping poses similar problems for an air emission control device installed with a fixed-roof cover.

Using effective air stripping of LLNL's aqueous wastes, the worst case VOC concentrations (typically MCM, PCE, and methylene chloride) in the gas stream exiting the air stripper will be 1–10% organics. Condensation following air stripping has potential rewards, and LLNL will evaluate them further; however, the condensed organics will require treatment prior to disposal. Because many of the wastes have radionuclides, solvent recovery was not considered. Carbon adsorption systems are prohibitively expensive for removal of VOCs in the gas stream from the air stripper because of high organic concentrations.

The methods LLNL investigated to destroy the VOCs in the gas stream exiting the air stripper include ozonation and catalytic oxidation. Ozonation uses ozone to oxidize organic contaminants in two ways:

1. By direct oxidation with ozone gas
2. By the generation of free radical intermediates, such as hydroxyl radicals.

Contaminants most amenable to direct oxidation by ozone include aromatics such as polycyclic aromatic hydrocarbons and chlorinated ethenes. The major concern using ozone is that it is not good with low-molecular-weight chlorinated organics, and the concentrations of the gas stream are extremely high for cost-effective systems.

Catalytic oxidation is well suited to the destruction of VOCs in vent gas streams, especially when the hydrocarbon concentrations are 25% or less of their lower explosive limit with flow rates ranging from 14 standard m^3/min to over 2,800 m^3/min. Catalytic oxidation systems are normally designed for destruction efficiencies that range from 90–98%. The destruction efficiency for chlorinated hydrocarbons is typically quite low; however, recent catalyst developments have produced products that can effectively destroy chlorinated hydrocarbons. For example, in a joint venture of King, Buck & Associates Inc. (KBA) in San Diego, California and Catalytic Combustion Corp. in Bloomer, Wisconsin, a catalytic oxidizer system demonstrated the capability of treating 5.7 m^3/min of chlorinated VOCs at a concentration of more than 2,000 ppm.

SYSTEM DESCRIPTION

Based on the potential of catalytic oxidation, LLNL selected an air stripper followed by nonflame catalytic oxidation using a halocarbon destruction catalyst as the removal and destruction system to comply with the Subpart CC standards. The design of the system consists of an air stripper followed by a heat exchanger, preheater, catalytic oxidizer, and scrubber. A diagram of the unit is provided in Figure 2.

The catalytic oxidizer system will be operated on a batch basis as needed. Typical waste management activities will require the system to operate six hours per week. As waste streams are transported from the onsite activities in various containers, the containers will be incorporated into a blending sequence. The blending sequence will be developed to optimize the volatile content of a blended waste stream for air stripping. In addition, the blending sequence will be designed to limit reactions and dissipate reaction heat.

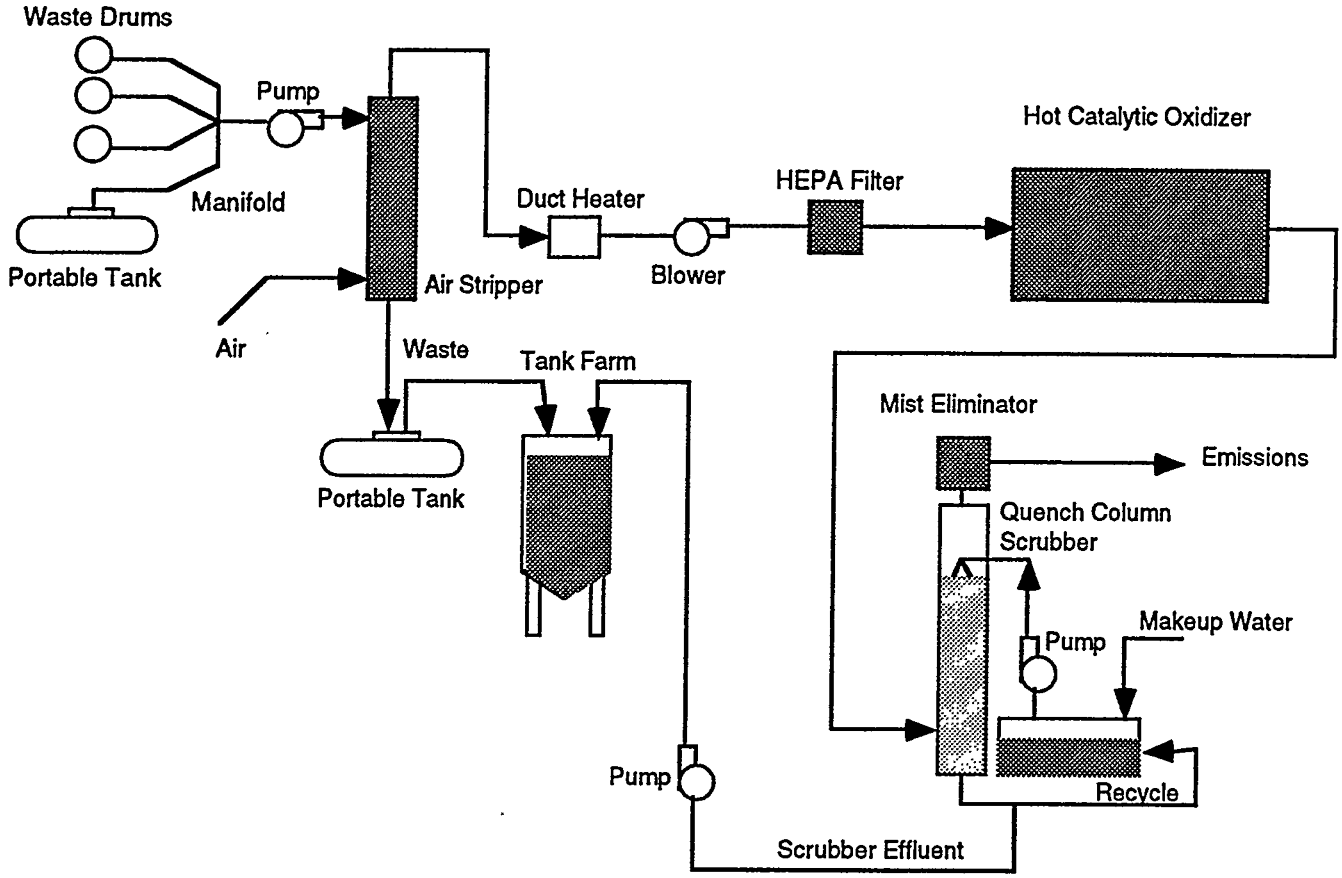

Figure B. Catalytic Oxidation System.

According to the determined blending sequence, up to four containers will be emptied using a vacuum pump. The pumped waste will be blended via a pipe manifold system. The blended waste stream will then be piped to an air stripper at controlled flow rates up to 57 L/min based on the volatile content of the blended waste stream. As containers are emptied, they will be replaced manually with containers containing waste according to the blending sequence schedule.

The air stripper will be designed to remove at least 95% of the VOC content from the blended waste streams. An air stream of approximately 14 m^3/min will strip the VOCs from the blended waste streams. The stripped aqueous waste stream will be pumped to a 4,200-L portable tank with a condenser installed on the vent line or to one of the open-top tanks of the Tank Farm. The actual location to which the aqueous waste stream will be pumped will depend on the precautions necessary to ascertain that the system has adequately stripped the blended aqueous waste stream. The stripped aqueous waste stream will have a concentration less than 50 ppmw in order to comply with the Subpart CC standards.

The VOC concentration of the gas stream exiting the air stripper will range between 300–50,000 ppm. The gas stream will be directed to a duct heater to elevate the temperature of the air stream from ambient temperature to 38°C. The gas stream will then enter a blower followed by a HEPA filter to remove radionuclides associated with the mixed wastes. After filtration, the gas stream will enter a hot catalytic oxidizer to oxidize the organics. The catalytic oxidizer will contain approximately 0.28 m^3 (10 ft^3) of a halogenated hydrocarbon destruction catalyst capable of achieving greater than 99% destruction efficiency. The air stream exiting the oxidizer, typically at a temperature between 370–540°C, will then be quenched and neutralized using a sodium carbonate solution in a quench column. The quench column will scrub the acid gas generated during oxidation. The neutralizing solution can be recycled or treated in LLNL's Tank Farm. The gas exiting the quench column will be demisted and exhausted to the atmosphere.

The capital cost of the system is approximately $250,000. Electrical power requirements are largely required for the pumps, duct heater, and hot catalytic oxidizer. The power costs will be approximately $15 per hour of operation. The catalyst will have to be replaced, but since the system is only operated periodically, catalyst replacement should only be necessary once every six years at an approximate cost of $85,000.

STATUS AND PLANS

The VOC removal and destruction system will require permitting under RCRA and the Clean Air Act. Regulators from both the Bay Area Air Quality Management District and California Department of Toxic Substances Control currently support the catalytic oxidizer system to comply with the Subpart CC standards based on preliminary discussions.

LLNL is currently completing a specification package on the catalytic oxidizer system design. The system will not be on-line before June 5, 1995; therefore, an implementation schedule for installation of the equipment will be developed and placed in the facility operating records in order to comply with the Subpart CC standards. The Subpart CC standards require the system to be in operation by December 1997.

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