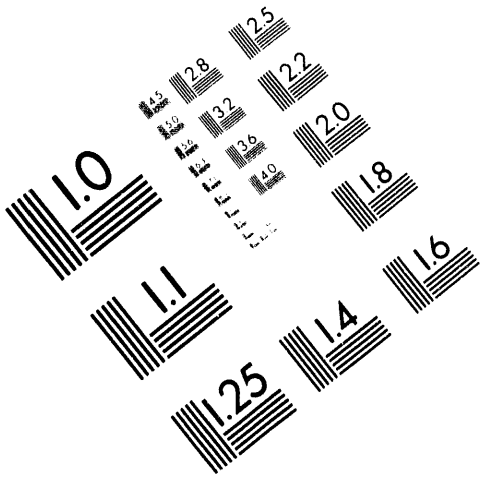

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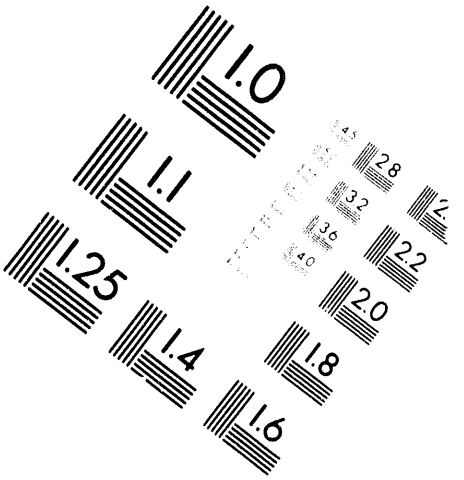

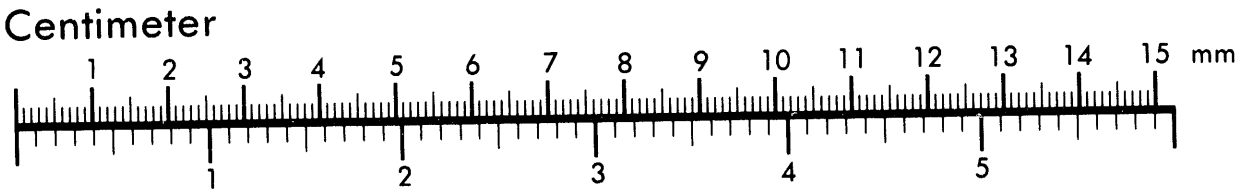

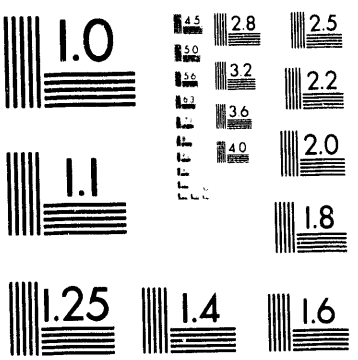

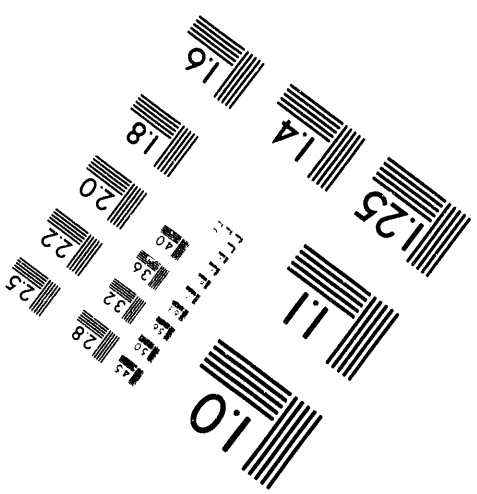

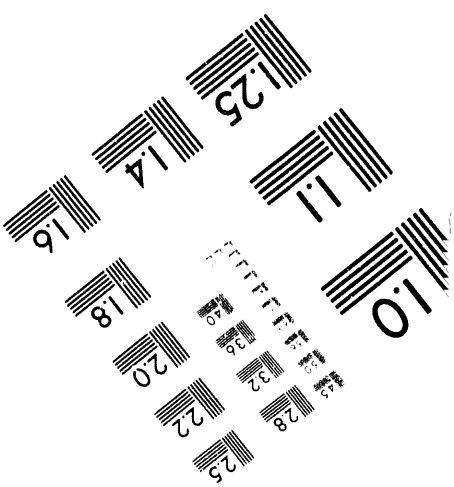

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REMEDIATION OF GROUND WATER CONTAINING VOLATILE ORGANIC COMPOUNDS AND TRITIUM

by
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INTRODUCTION

The Trailer 5475 (T-5475) East Taxi Strip Area at Lawrence Livermore National Laboratory (LLNL), Livermore, California was used as a taxi strip by the U.S. Navy to taxi airplanes to the runway from 1942 to 1947. Solvents were used in some unpaved areas adjacent to the East Taxi Strip for cleaning airplanes. From 1953 through 1976, the area was used to store and treat liquid waste. From 1962 to 1976 ponds were constructed and used for evaporation of liquid waste. As a result, the ground water in this area contains volatile organic compounds (VOCs) and tritium. The principal VOCs in the ground water in this area, in order of decreasing concentration, are trichloroethylene (TCE), perchloroethylene (PCE), chloroform, 1,1-dichloroethylene (1,1-DCE), 1,2-dichloroethane (1,2-DCA), carbon tetrachloride (CCl_4) and 1,1-dichloroethane (1,1-DCA). TCE, the predominant VOC in the ground water beneath this area, is present in concentrations as high as 10,000 parts per billion (ppb), and the maximum tritium concentration is 54,000 picocuries per liter (pCi/L). Maximum Contaminant Levels (MCLs) for TCE and tritium are 5 ppb and 20,000 pCi/L, respectively. The ground water in this area is also known to contain hexavalent chromium that is probably naturally occurring.

The LLNL Site was placed on the U.S. Environmental Protection Agency's (EPA) National Priorities List (NPL) in 1987. The Record of Decision for the Livermore Site, signed in 1992, specifies that the cleanup levels for TCE and tritium are their MCLs, and that extraction systems will be designed to prevent tritium in concentrations above the MCL from entering a treatment system. Ground water remediation in the T-5475 Area is thus complicated by the presence of both VOCs and tritium in concentrations above their MCLs. The local community is concerned about releasing tritium above ground. Different cleanup approaches (e.g. treatment in large diameter vertical wells with horizontal reinjection wells, in-situ air sparging, containment by slurry wall, etc.) were evaluated. However, these options proved to be very costly and/or difficult to operate and maintain. Therefore, LLNL has proposed 'pump-and-treat' technology above grade in a completely closed loop system. The facility will be designed to remove the VOCs and hexavalent chromium, if any, from the ground water, and the treated ground water containing tritium will be reinjected where it will decay naturally in the

subsurface. Ground water containing tritium will be reinjected into areas with equal or higher tritium concentrations to comply with California regulations.

PROPOSED TREATMENT FACILITY

Treatability Tests

Treatability tests were performed to evaluate the feasibility of the closed loop system and to determine facility design parameters. Two separate treatability tests were performed to determine the optimal air to water flow ratio for the air stripper. For each test, about 250 gallons of ground water was air stripped in a stainless steel tank while circulating the water in a closed loop at a flow rate of 20 gallons per minute (gpm). Air was supplied by a blower to air strip the ground water in the air stripping tank. Air flow rate from the blower was maintained at 80 cubic feet per minute (cfm). The air from the blower passed through a heat exchanger, two granulated activated carbon (GAC) canisters (in series), ground water in an air stripping tank, a demister and back to the blower, in a closed loop. As expected VOC concentrations decreased with time (Table 1).

VOC concentrations are plotted versus air to water flow ratio (cfm/gpm) in Figure 1. These data indicate that TCE will be reduced from 7,300 ppb to less than 0.5 ppb with an air to water flow ratio of about 17 cfm/gpm. Thus if a water flow rate of 20 gpm is assumed for the design, 340 cfm of air will be needed to effectively treat the ground water.

The treatability tests were conducted outdoors on three different cold days for 1.5 to 2 hours each. The low temperatures resulted in a relatively high condensation of water vapor containing tritium in the GAC canisters. When GAC samples were analyzed they were found to contain 3.7 and 3.4 picocurie per gram (pCi/g) of tritium, and 15.8 and 15.6% water in the first and second GAC canisters respectively. Although tritium concentrations in the GAC were below mixed waste standard, we tried to reduce them further to address community concerns that the GAC could become a mixed waste if tritium is accumulated with time. Therefore, the vapor and carbon were preheated until the vapor temperature at the inlet of the first GAC canister reached 140° F (60° C). The vapor was preheated by the blower, which heats with time during operation. During preheating, the vapor bypassed the water in the air stripping tank. The vapor heated the GAC canisters for about two hours. After the vapor and GAC canisters were preheated, the vapor was passed through the ground water for about 4 hours while the ground water circulated in a closed loop at a flow rate of 20 gallons per minute. GAC samples collected after this test contained 1.16 and 1.15 pCi/g of tritium in the first and second canisters, respectively. This test indicated that preheating of vapor and GAC could reduce the water and tritium content of the GAC, and keep it well below the Department of Energy mixed waste standard of 5 pCi/g. In other words, the test result indicated that with proper temperature control, tritium (i.e. water content) reaches an equilibrium concentration in the GAC that is less than one tenth the concentration for mixed waste classification.

A second set of tests was conducted with two new carbon canisters to confirm that absorption of moisture and tritium by GAC can be reduced by preheating vapor and GAC. For these tests, the vapor was preheated to 60° C, and the ground water was subsequently treated by air stripping for another two hours. This test was run three times on three continuous days. The following week two more tests were run, with two hours of preheating and six hours of air

stripping each day, on two successive days. Figure 2 shows tritium content in the two new carbon canisters versus time for this second set of tests.

Description of the Treatment Process

Based on the treatability test results we believe that the proposed technology is effective and feasible. The proposed facility will treat ground water at a flow rate of about 20 gpm initially, with a capability to increase its capacity to 40 gpm. A schematic flow diagram of the water treatment facility is shown in Figure 3. Ground water will be pumped from the extraction wells through a 5 micron filter to remove solid particulates. The proposed facility will use ultraviolet/hydrogen peroxide (UV/H_2O_2) to oxidize VOCs prior to air stripping. The UV/H_2O_2 system will reduce the TCE, PCE and 1,1-DCE to water, carbon dioxide and chloride ions, and, consequently, less GAC will be needed to treat the vapor phase VOCs. A 50% solution of H_2O_2 will be injected into the influent water to achieve a concentration of 60 to 150 ppm. The UV light disassociates H_2O_2 to form hydroxyl ($OH^{\bullet}$) radicals. The hydroxyl radicals oxidize the VOCs to water, chloride ions, and carbon dioxide. The double carbon-to-carbon bonds of TCE, PCE and 1,1-DCE are readily oxidized under the influence of the hydroxyl radical.

Ground water in the T-5475 Area also contains chloroform, 1,1-DCA, 1,1,1-TCA and 1,2-DCA which are difficult to oxidize because of their single carbon-to-carbon bonds. Therefore, an air stripper will be used following the UV/H_2O_2 treatment unit to reduce the concentration of these compounds to levels below the 0.5 ppb analytical detection limit. The air stripping system will consist of two stainless steel tanks in series. Each tank is divided into 6 aeration chambers of equal size and a quiescent chamber, and each aeration chamber will have an air diffuser. The water will be subjected to intense aeration using two centrifugal blowers in parallel that inject air at the rate of 220 actual cubic feet per minute (acfm) each, for a total of 440 acfm.

The humid vapor emanating from each air stripping tank will be recirculated in a closed loop in order to keep water vapor containing tritium from being released. From the air stripping tank the vapor will pass through a demister immediately above the air stripping tank (Figure 3). The demister will retain all water droplets larger than 10 microns. To minimize condensation of water vapor containing tritium in the GAC canister, the air vapor will be preheated as described above. Vapor temperature above 150° F (65° C) may cause damage to the GAC canister, and vapor temperature below 90° F (32° C) will have high relative humidity, which could adversely affect the adsorption efficiency of the GAC. Therefore, the vapor temperature will be kept between 90° and 140° F (32° and 60° C) for acceptable efficiency, by controlling the flow of water through the heat exchanger through which the vapor passes after it leaves the blower. Next, the vapor will pass through two GAC canisters, in series, to remove VOCs (Figure 3). The air pipe from the air stripping tank to the GAC canisters and the canisters themselves will be insulated to minimize heat loss. No VOCs or tritium will be released to the atmosphere.

The effluent water from the second air stripping tank will pass through two ion-exchange units in series. Resin in the ion-exchange units exchanges chloride ions for the chromate ions of the hexavalent chromium. Hexavalent chromium will be reduced to concentrations at or below the discharge limit of 11 ppb prior to reinjection. The treated water will be reinjected at one or more injection wells located in the

area of high tritium concentrations to comply with California regulations.

SUMMARY

Ground water in the T-5475 Area contains VOCs and tritium above MLCs. Treatability tests indicate that air stripping in a closed loop system can effectively remove VOCs from the ground water without releasing VOCs or tritium to the atmosphere. To minimize waste generation and GAC use, a UV/H_2O_2 system will be used to destroy VOCs with double carbon bonds. Temperature control of the GAC is necessary to prevent condensation of water containing tritium. Treatability tests indicate that with proper temperature control, tritium reaches an equilibrium concentration in the GAC that is less than one tenth the concentration for mixed waste classification.

ACKNOWLEDGMENT

The present work is performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Table 1. VOC removal from ground water by air stripping, Trailer 5475 treatability tests

Time (Min)	Air/water flow ratio (cfm/gpm)	TCE (ppb)	PCE (ppb)	Chloroform (ppb)
0	0.0	7,300	680	960
30	9.6	47	11	21
45	14.4	12	1.9	1.9

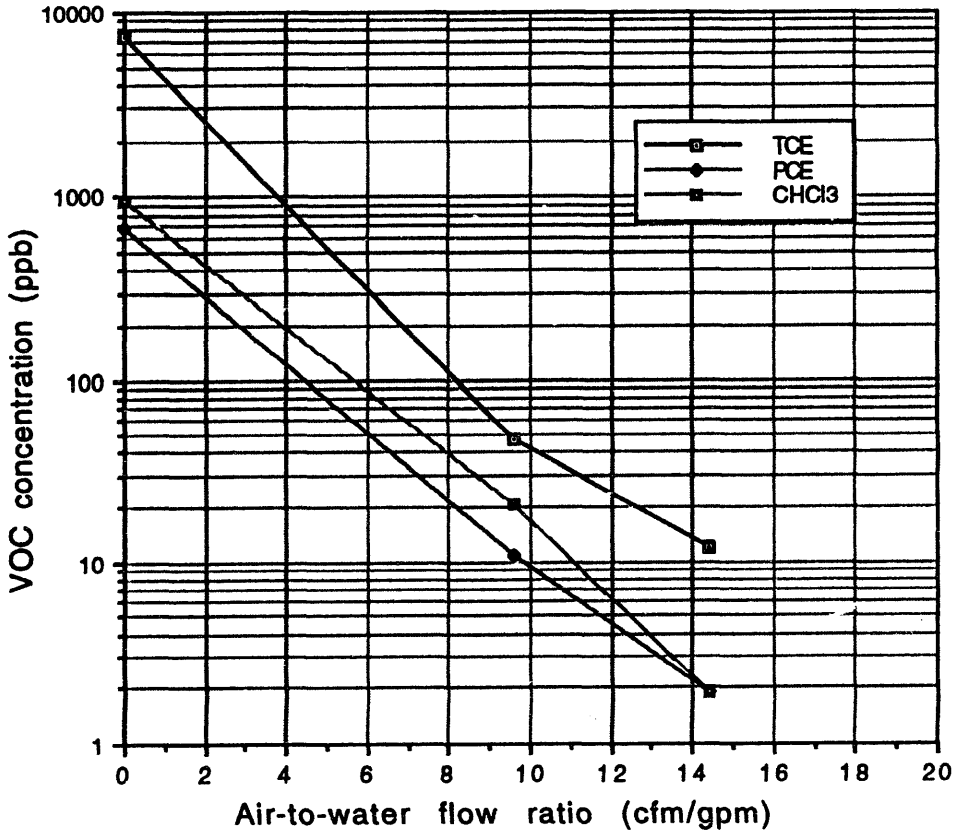

Figure 1. VOC concentration vs air-to-water flow ratio, Trailer 5475 treatability test

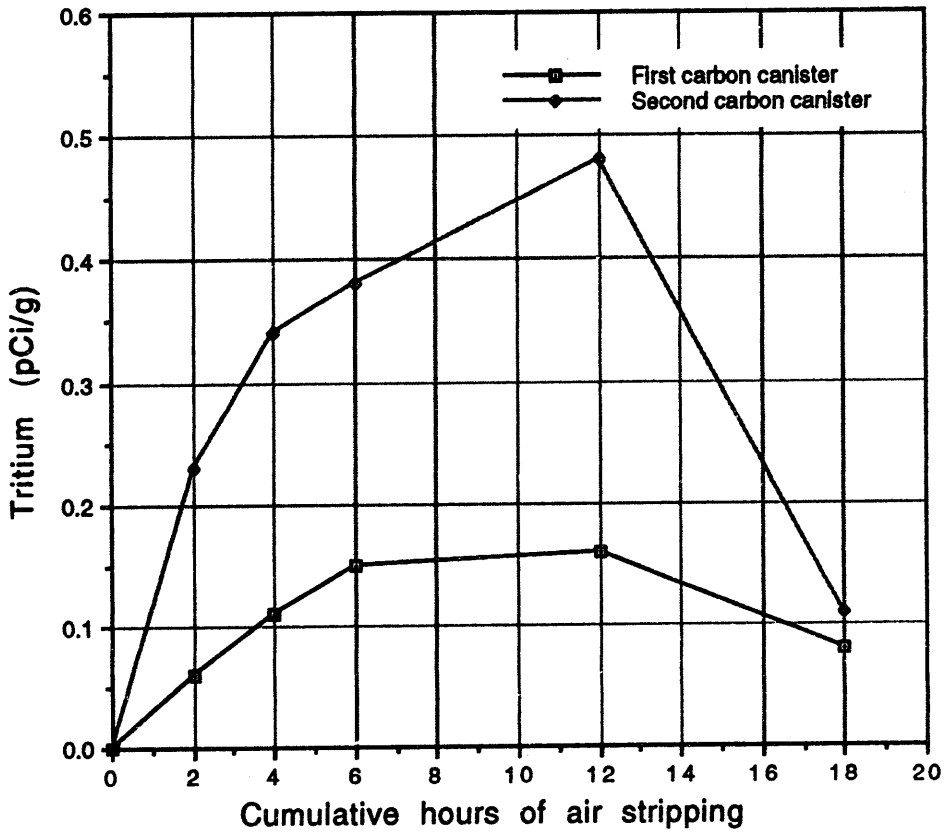

Figure 2. Tritium concentration in new carbon canisters

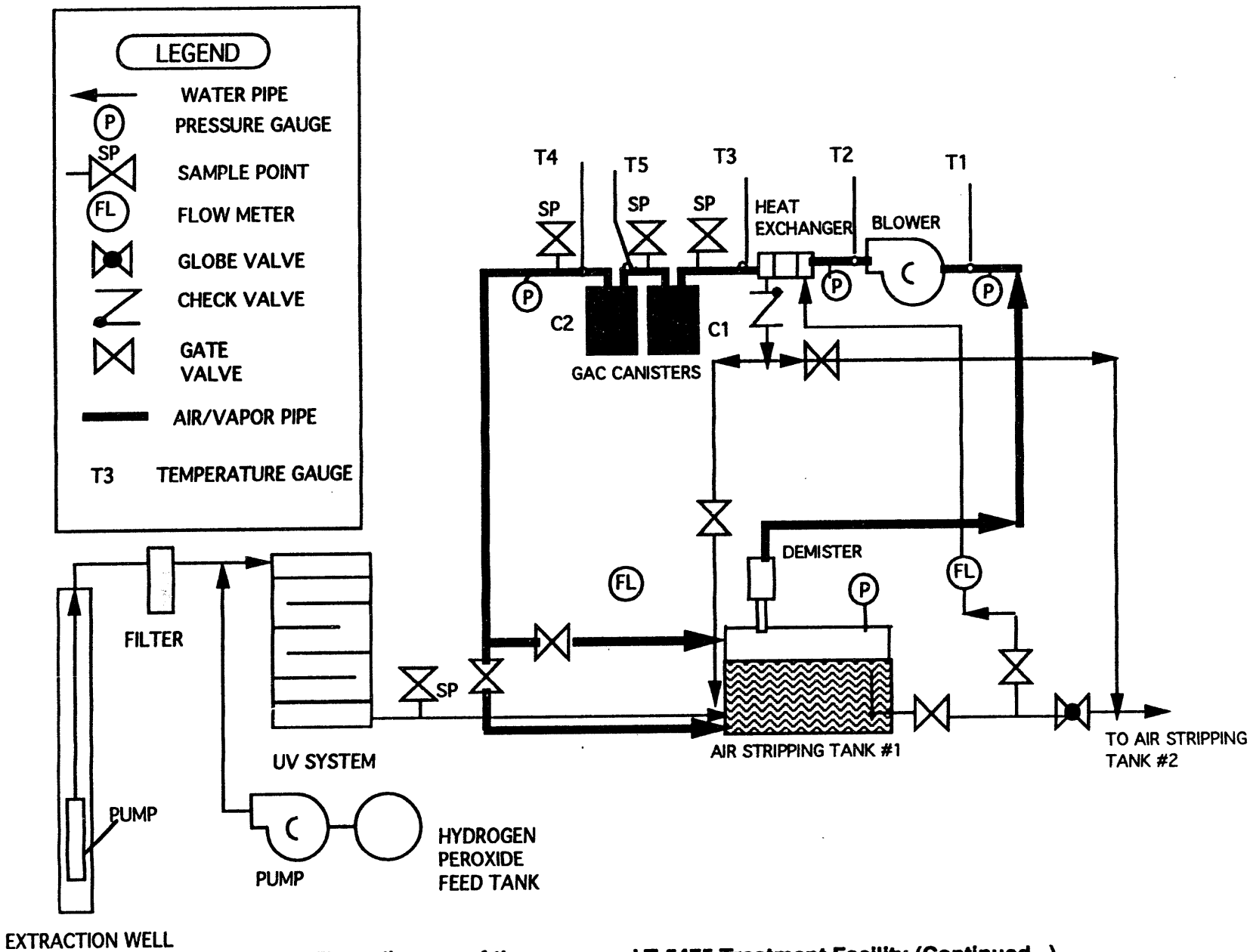

Figure 3. Flow diagram of the proposed T-5475 Treatment Facility (Continued...)

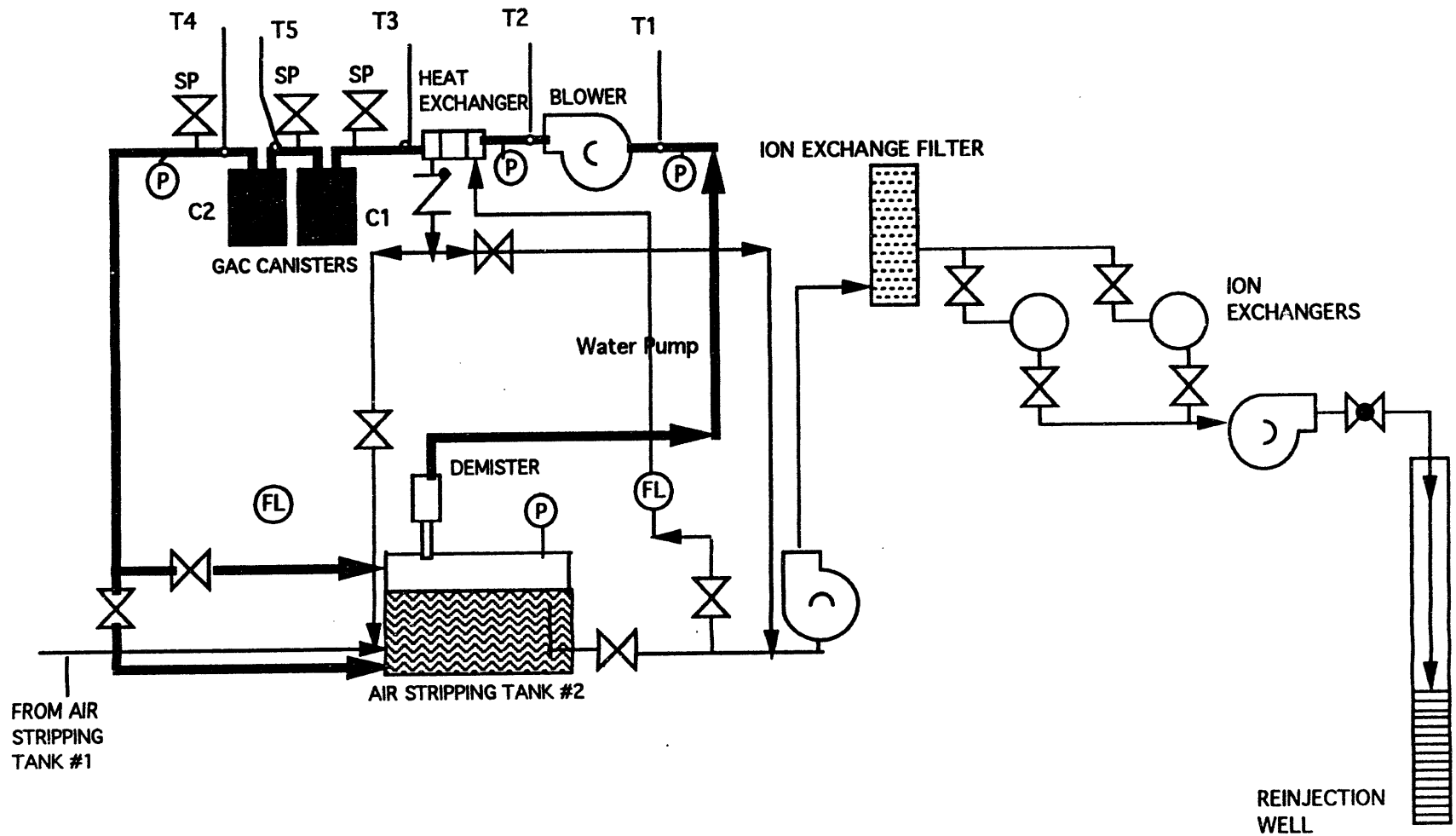

Figure 3. (...Continued) Flow diagram of the Proposed T-5475 Treatment Facility

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