T2VOC Simulation and Optimization of SVE System Pulse Pumping of Vadose Zone Carbon Tetrachloride Contamination at the Idaho National Engineering and Environmental Laboratory

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INTRODUCTION

Vadose zone vapor and aqueous phase carbon tetrachloride contamination beneath an Idaho National Engineering and Environmental Laboratory (INEEL) subsurface disposal area, due to evaporation, diffusion and density-driven flow of vapor, and aqueous phase advection from breached barrels of nonaqueous phase waste, is being remediated with a SVE system. The unsaturated zone in the area of interest consists of fractured basalt intercalated with thin, relatively impermeable sedimentary interbeds. This study focused on a contaminated zone, approximately 88 acres in area, at and above the first sedimentary interbed, 110 feet below ground surface.

While it was recognized that 100% SVE system operation maximizes mass recovery, it was assumed that the diffusion-limited nature of mass transport results in diminishing rates of mass recovery with continued pumping. Pulse pumping may be a more cost-effective means of remediation in such circumstances. T2VOC was used to assess the relative performance of various continuous and pulse pumping schemes starting from common initial conditions and operating for the same length of time. In particular, single-well T2VOC simulations were used to answer two questions: 1) What is the optimum duration, in terms of relative mass recovery, of a single pulse pumping on/off cycle? 2) Given existing SVE pump/treatment system operation, what percentages of the maximum possible treated mass can be achieved with continuous or pulse pumped wells feeding a reduced number of offgas treatment units?

With information on system operation cost per unit time, an answer to the first of these questions makes it possible to estimate reduction in cost per unit mass recovered and treated due to pulse pumping. Resolution of the second question allows a similar evaluation of operating cost reduction, and also an assessment of the capital savings (by foregoing additional or replacement treatment units) while still achieving a given percentage of the maximum possible treated mass.

MODELING ASSUMPTIONS AND APPROACH

Inevitable uncertainties in subsurface structure and properties, initial and boundary conditions, source distribution and loading rates, etc., led to the use of simplifying assumptions. Among these were:

- The modeled subsurface consists of constant thickness, laterally homogeneous basalt and sedimentary layers.
- Contaminant transport results from evaporation at the source and consists of downward redistribution due to combined diffusion and density-driven flow.
- Due to the arid climate, the vadose zone is very dry except in the immediate vicinity of the sedimentary interbed at 110 feet BGS.
- The basalt has little organic content and sorption may be neglected; significant sorption will occur in the interbed.
- Local chemical equilibrium holds.
- A single simulated well may be constructed that represents the average behavior of the three operational wells in the SVE system.

To reduce the impact of these assumptions, results were obtained in relative terms, so that any inaccuracies "canceled out". This consisted of determining maximum achievable mass removals at 100% SVE operation and calculating removal effectiveness of any particular pumping scheme as a percentage of the maximum.

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Modeling consisted of single-well simulations in radial coordinates for a vertical sequence extending 40 feet above and 5 feet below the 5-foot thick interbed. The shallow, breached barrels, buried between 1966 and 1970, remain in place and a great deal of uncertainty exists as to the initial and remaining carbon tetrachloride inventories. Therefore, the contaminant source was accounted for by specifying a constant vapor phase loading rate over a portion of the model top surface. The rate and radial extent of loading was iteratively adjusted to produce a radially symmetric initial plume that roughly matched measured vapor concentrations above and below the interbed. The loading distribution was also adjusted by comparing simulated and measured SVE mass recovery rates starting from similar initial plumes.

All simulations used the same model domain and grid, initial and boundary conditions, and material properties. Cycle duration optimization runs used a constant 235 scfm pumping rate with varied on/off schedules for a total simulation time of 180 days. Runs to assess relative mass treated as a function of the number of treatment units varied both pump rates and schedules, and simulated a 10-week period with 10% down time (effectively a 9-week simulation).

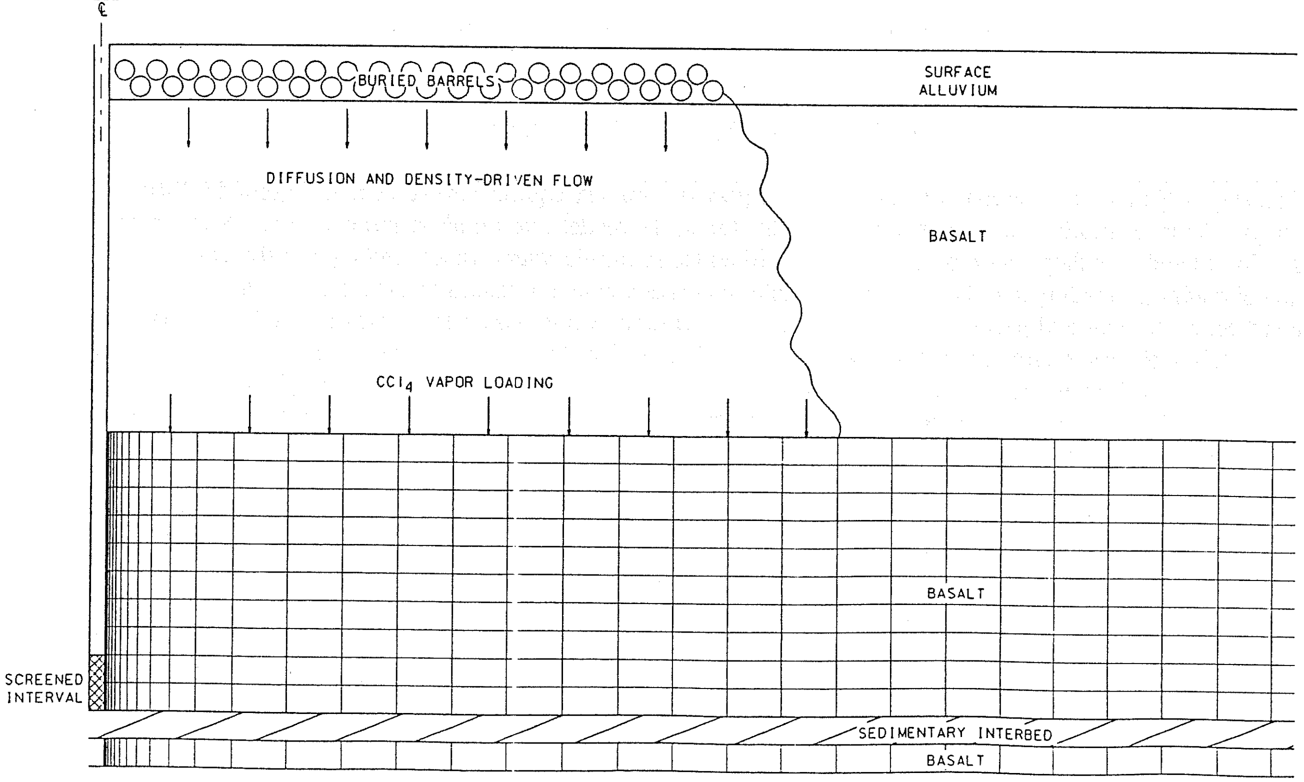
MODEL DOMAIN AND GRID

Figure 1 is a schematic cross-section of the conceptual model domain and numerical grid. The waste drums are buried in surface alluvium and contain a carbon tetrachloride oil absorbed in a calcium silicate binder. The NAPL source is assumed to remain bound within the barrels, which have degraded structurally allowing carbon tetrachloride vapor to migrate downward by diffusion and density-driven flow. The sedimentary interbed at 110 feet BGS, by virtue of matrix sorption and partitioning to its relatively abundant aqueous phase, acts as a barrier, slowing the passage of the contaminant. The extraction well is screened over the 10-foot interval immediately above the interbed.

The model grid begins at 70 feet BGS and extends downward to 120 feet BGS, 5 feet below the bottom of the sedimentary interbed. Vertically, the grid is composed of 12 layers. The bulk of the model domain is composed of the middle 10 layers, each 5 feet thick. The top and bottom layers are very thin for accurate placement of boundary conditions.

Radially, the grid begins at the extraction well centerline and extends outward 1000 feet. There are 37 grid blocks in the radial dimension. The first 13 radial increments have spacings that increase by a constant factor from 6.3 inches at the wellbore to 25.85 feet. The next 23 grid blocks have a constant 39.37 ft radial spacing, and the outer grid block is very thin.

Figure 1. Conceptual Model Domain and Numerical Grid



MATERIAL PROPERTIES

Table 1 summarizes the material properties used for all of the T2VOC simulations. Porous medium parameters were taken from previous INEEL vadose zone studies of the same basalt and interbed bodies[1,2,3]. Relative permeabilities were calculated, for basalt, using a modified version of Stone's three phase method, and for the sedimentary interbed, using Parker's three phase functions[4]. Sedimentary interbed capillary pressures were calculated using Parker's three phase functions. For basalt, it was necessary to code a new capillary pressure routine to match that used in the previous INEEL studies. All parameters used to calculate the thermophysical properties of carbon tetrachloride were taken from the T2VOC VOC data set in the file "voc.dat".

The basalt properties are such that the significance of density-driven flow relative to diffusion is difficult to estimate. Previous studies have shown that density-driven flow may dominate vapor phase transport of carbon tetrachloride if sorption and moisture content are low, and if gas phase permeability is high[5]. It appears that the criteria for significant density-driven flow are met for the present study, except that basalt permeabilities are anisotropic, with a horizontal component above the approximate limit found in Falta, et al[5] (1×10^{11} m^2) and a vertical component well below.

Parameter	Value
Basalt Porosity	.05
Sedimentary Interbed Porosity	.48
Basalt/Sediment Grain Density	2650 kg/m^3
Basalt Horizontal Absolute Permeability	8.88×10^{-11} m^2
Basalt Vertical Absolute Permeability	2.96×10^{-13} m^2
Sedimentary Interbed Absolute Permeability	3.95×10^{-15} m^2
Basalt Organic Carbon Fraction	0.000
Sediment Organic Carbon Fraction	0.002
Temperature	13.8 C
CCl_4 Molecular Weight	153.8 g/mole
CCl_4 Saturated Vapor Pressure	9068 Pa
CCl_4 K_{OC}	.439 m^3/kg
CCl_4 Water Solubility	9.21×10^{-5} mole/mole
CCl_4 - Air Binary Diffusivity	7×10^{-6} m^2/s

Table 1. Material Properties Used for All T2VOC Simulations.

INITIAL AND BOUNDARY CONDITIONS

The first step in T2VOC simulations was to establish a gravity-capillary equilibrium at a net background infiltration rate of 1 cm/yr[6]. This infiltration rate was maintained at the top of the model grid for all subsequent runs. Next, to provide realistic initial and boundary conditions, a period of carbon tetrachloride source vapor loading was simulated, followed by a period of combined loading and SVE operation. Rates and radial extent of loading were iteratively adjusted until field-measured concentrations and past mass recovery rates were reasonably approximated. It was found that a constant loading of 4.54 kg/d over a circular area with a radius of 525 ft produced the best fit to measured concentrations and mass recovery rates. This loading was maintained at the top of the model grid for all subsequent runs. Figure 2 depicts an r-z cross-section of the initial plume obtained from this procedure. All T2VOC optimization simulations commenced from these common starting conditions.

At the bottom of the model grid, thermodynamic variables were held constant at their initial values. These Dirichlet conditions were implemented by specifying the bottom row of grid blocks as inactive. The outer radial boundary was placed far enough away from the well (1000 feet) to make the model domain effectively infinite. Both inner and outer radial boundaries were left in their default zero-normal flux conditions.

To avoid the necessity of allocating an arbitrary division of flux to the well among the two screened grid blocks, the wellbore was assigned atmospheric material properties. This allowed assignment of pumping rates to a single block at the

Figure 2. SVE Simulation Initial CCl_4 Vapor Plume (ppmv)

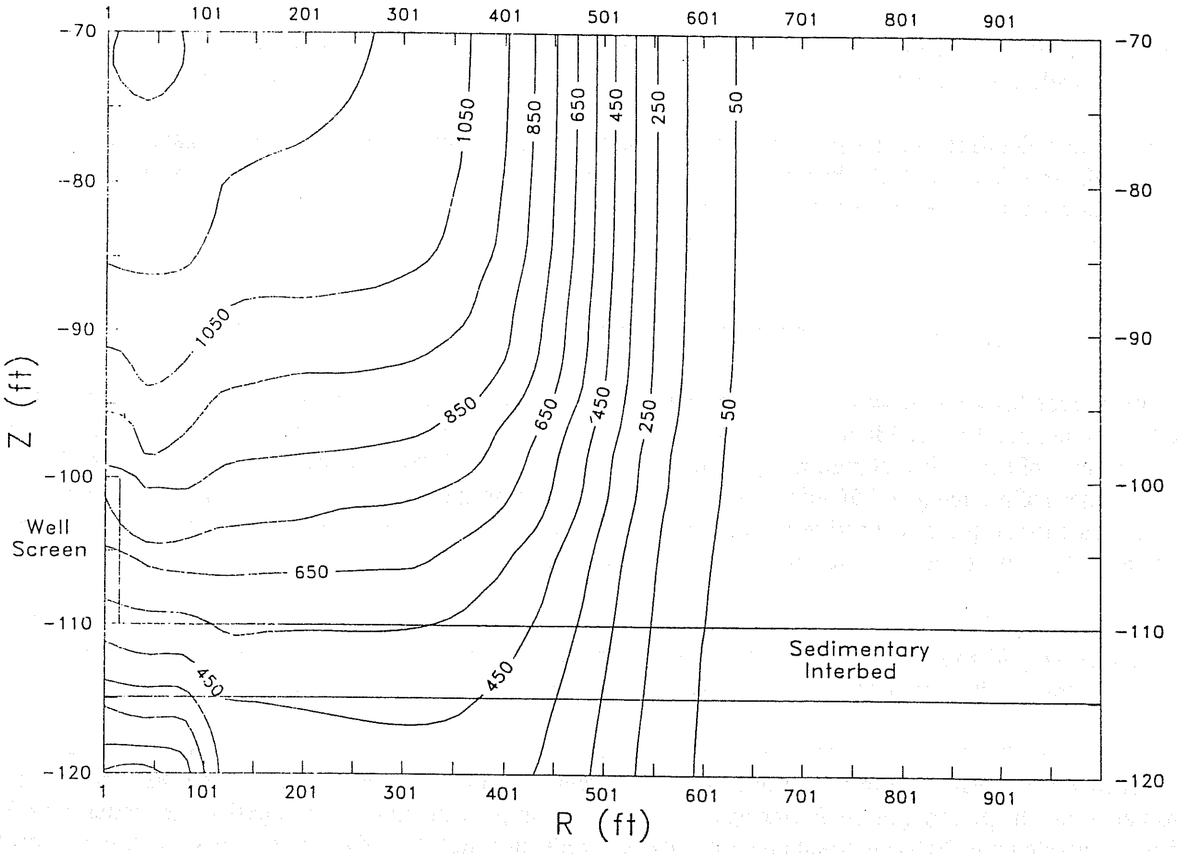
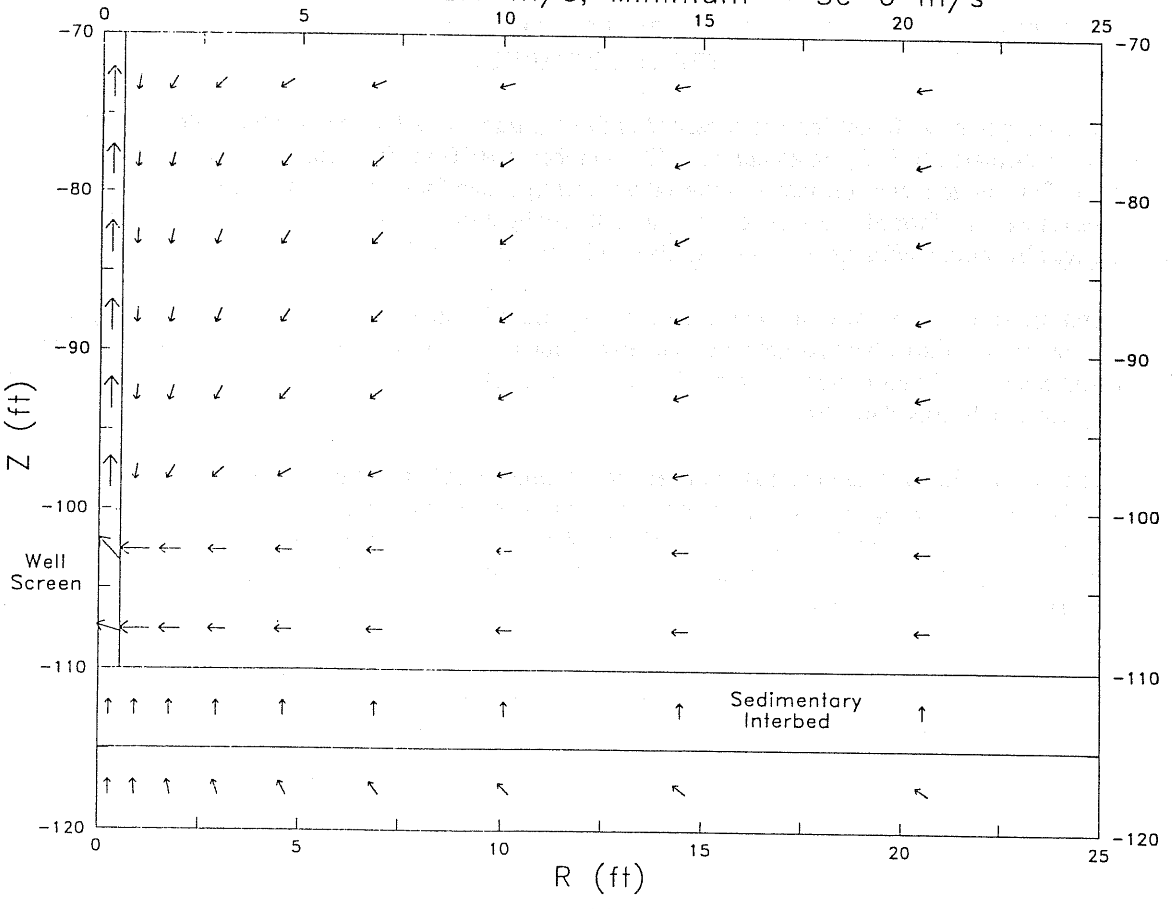


Figure 3. Steady Gas Phase Velocities, 235 scfm Pumping Rate

Maximum = 2.1 m/s, Minimum = 3e-6 m/s



top of the wellbore and resulted in a natural division of flux through the screened grid blocks. Horizontal permeabilities were set to zero within the wellbore to eliminate advective and diffusive fluxes across the well casing.

Figure 3 is a vector plot depicting gas phase velocities within a 25-foot radius of the well for a constant pumping rate of 235 scfm. As the transient flow field develops very quickly compared to pump operating periods, this is the steady flow pattern that controls vapor movement to the well during active SVE pumping. For different pumping rates, the velocity field is essentially a scaled version of the pattern in Figure 3.

SIMULATIONS FOR OPTIMUM PULSE PUMPING CYCLE DURATION

The basic distinction between the various simulated pumping schedules was cycle duration. On/off cycles were repeated until the total simulation time of 180 days was reached. For each cycle duration, different schedules were obtained by varying the percent of the cycle that pumping was active. For example, at 10% pump-on, a 60-day cycle would be composed of 6 days of pumping and 54 idle days; at 20% pump-on, it would be 12 days of pumping followed by 48 idle days; etc. The rate for all periods of active pumping was held constant at 235 scfm. For each schedule, relative results were assessed as the percent of maximum possible mass removal (at 100% operation) for the 180-day simulation time.

It was necessary to modify the T2VOC source code to output, at every time step, the transient carbon tetrachloride vapor mass flux rate at the grid sink block. T2VOC's variable time-stepping facility produced dense time series, which were numerically integrated with a trapezoidal rule to obtain total mass removed by the SVE well.

Cycle durations of 60, 30, 15, 7, and 3 days were simulated at 10% pump-on to 90% pump-on in 10% steps, for a total of 45 runs. Figure 4 summarizes the results of these runs. As would be expected, differences between the various cycle durations narrow as the percent pump-on time approaches 100%. In general, shorter cycle periods are better, with 3-day cycles more favorable up to 30 % pump-on and 7-day cycles producing slightly higher recoveries at pump-on percentages above 40%. Because the greatest interest was in obtaining relative recoveries in the 90% range, 7-day cycles were considered optimal. It should be noted, however, that only small differences exist between 3-, 7-, and 15-day cycles in the desired range.

SIMULATIONS FOR RELATIVE RECOVERY AND TREATMENT WITH A REDUCED NUMBER OF OFFGAS TREATMENT UNITS

The most recent SVE system configuration has consisted of three extraction wells, each feeding a dedicated Recuperative Flameless Thermal Oxidation (RFTO) treatment unit. The number of RFTO units required to remove and treat a specified amount of carbon tetrachloride may be reduced by placing a manifold between the wells and the treatment units. T2VOC simulations were performed to assess, given system throughput limits, the percent of maximum possible recovery that can be achieved by routing effluent from three wells to only one or two RFTO units.

For a given operating period, the maximum mass of carbon tetrachloride that can be removed and treated by the SVE system is limited by process throughput parameters. The extraction wells can each deliver a maximum of 350 scfm of vapor effluent and each RFTO unit is capable of treating a maximum of 400 scfm. Operational history of the SVE system has included approximately 10% down time.

Given these limits, the maximum possible mass removal and treatment would be achieved by operating each well at 350 scfm for 90% of the given operating period, with a dedicated treatment unit for each well (3 wells, 3 units). A 10-week base period was chosen, resulting in a 9-week total simulation time. All pulse pumping scenarios used 7-day cycle durations as per the results presented in the previous section. The simulated well is assumed to represent the average behavior of the three wells in the SVE system, and interaction effects between wells are neglected.

The system may operate with fewer RFTO units than wells either by pulse pumping with staggered start times or pumping all wells continuously at a reduced rate. If n represents the number of units to which the combined effluent from m wells is routed, then the maximum allowed pumping rate for m simultaneously operating wells is (400n/m) scfm or 350 scfm, whichever is lower. Pulse pumping schedules must have on-time percentages equal to (100m/3), with start times staggered by one-third of the cycle length, so that treatment capacity is not exceeded.

Figure 4. Percent of Maximum Possible Mass Removed vs. Percent of Cycle Pump is On for Different Cycle Durations.

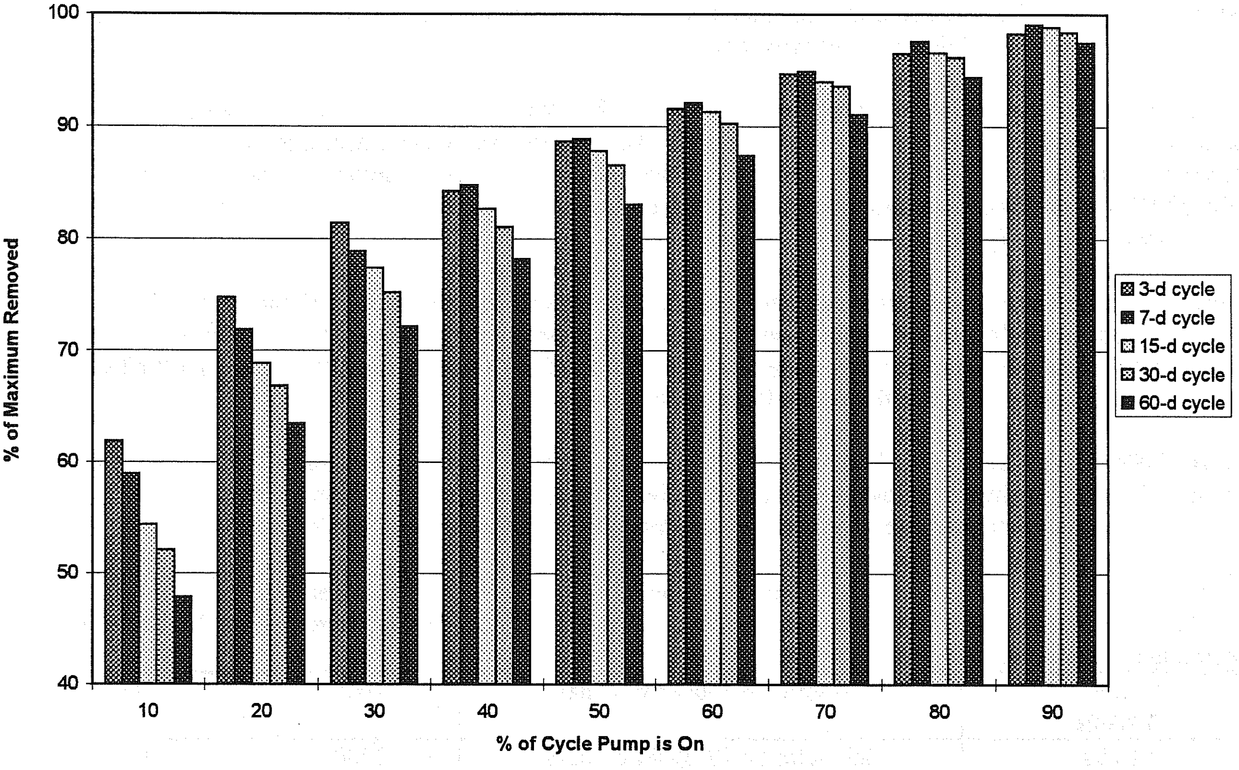
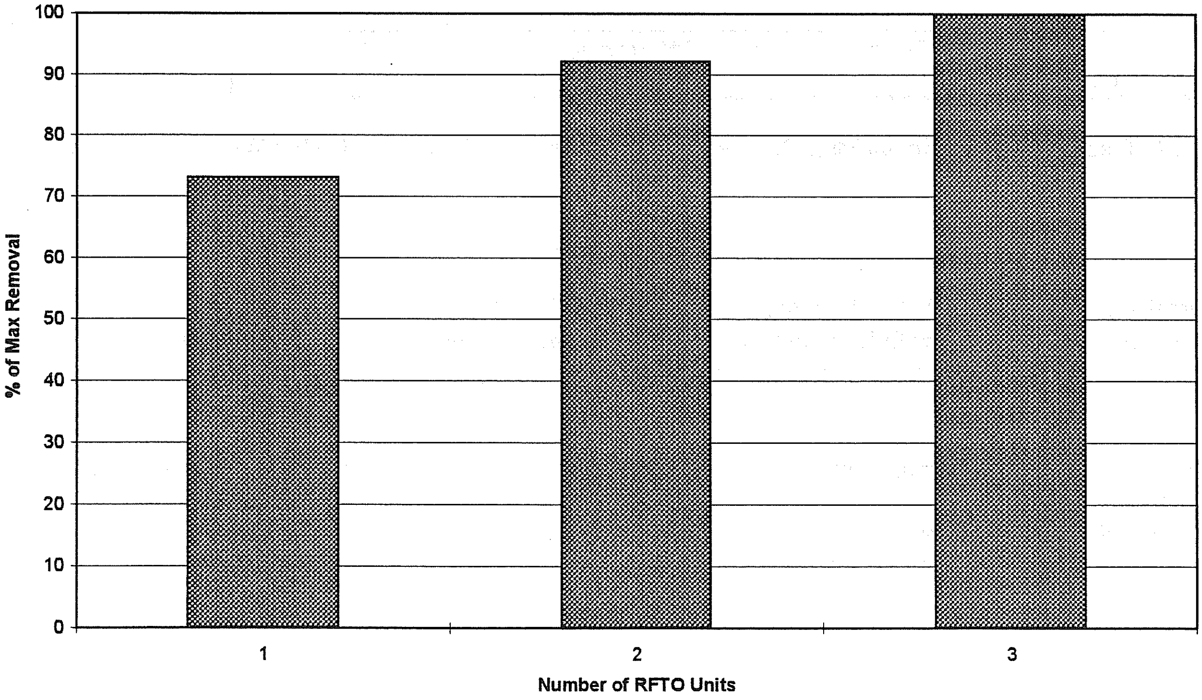


Figure 5. Achievable Percent of Maximum Possible Mass Removal and Treatment for Different Numbers of RFTO Units.



For a number of wells (m) equal to or greater than the number of treatment units (n), the possible unique permutations that adhere to the system throughput limitations are described in Table 2. It is important to remember that staggered start times for pulse pumping schemes allow all three wells to operate for the entire 9-week period while fewer than three are pumped simultaneously. Table 2 also lists simulation results for the various 1- and 2-unit schemes. The total system mass recovered is the combined figure for all three wells.

A total of six runs were required to determine the percentage of the potential maximum removal that can be achieved with a particular configuration over the 63-day operating period. The first run was a continuous pumping run at 350 scfm for 63 days to determine the maximum possible mass removal and treatment. As noted above, this case corresponds to the use of three RFTO units. The remaining runs consisted of continuous and pulse pumping scenarios for each of the two possible treatment unit configurations.

While results were similar for continuous and pulse pumping, continuous pumping recovered slightly more mass. The difference was most noticeable in the 2-unit scenarios, as the only pulse pumping scenario was limited by the maximum well rate, leaving unused treatment capacity. The difference narrows for 1-unit scenarios because the most efficient pulse pumping scheme can make full use of the available treatment capacity.

Figure 5 is a histogram of the achievable percentage of maximum possible removal for the different unit configurations. For one unit, 73.1% of maximum removal can be achieved by pumping all three wells continuously at 133 scfm. For two units, 92.1% of maximum removal can be obtained by continuously pumping all 3 wells at 267 scfm each.

Configuration # Units, # Wells Operating Simultaneously	Run Description	Total System Mass Recovered (kg)	Percentage of Max Possible Removal
3 Units, 3 Wells	350 scfm on 100% for 63 days	2965.2	100
2 Units, 3 Wells	267 scfm on 100% for 63 days	2730.3	92.1
2 Units, 2 Wells	7-d cycle, 67% on @ 350 scfm for 63 days	2574.9	86.8
1 Unit, 3 Wells	133 scfm on 100% for 63 days	2166.9	73.1
1 Unit, 2 Wells	7-d cycle, 67% on @ 200 scfm for 63 days	2153.4	72.6
1 Unit, 1 Well	7-d cycle, 33% on @ 350 scfm for 63 days	2057.4	69.4

Table 2. Percentage of Maximum Mass Recovery and Treatment for All Applicable Unit/Well Configurations.

CONCLUSIONS

T2VOC simulations have shown that both capital equipment and SVE system operation cost savings can be realized by reduced rate continuous pumping with fewer treatment units and/or pulse pumping. For recoveries greater than 80% of maximum, 7-day cycles have been found to be near-optimal for pulse pumping. If lower recoveries are acceptable, use of 3-day cycles would be more efficient.

While reduced rate continuous pumping was shown to be slightly more efficient than pulse pumping in terms of mass recovery for treatment with only one or two RFTO units, pulse pumping may be preferable if it reduces operating costs sufficiently. Reliable cost estimates may be combined with T2VOC simulation results to determine a SVE system configuration that maximizes carbon tetrachloride mass recovered and treated per dollar spent.

REFERENCES

[1] Magnuson, S.O., 1995, *Inverse Modeling for Field-Scale Hydrologic and Transport Parameters of Fractured Basalt*, INEL-95/0637, Lockheed Martin Idaho Technologies, Idaho Falls, ID.

[2] Magnuson, S.O., and D.L. McElroy, 1993, *Estimation of Infiltration from In Situ Moisture Contents and Representative Moisture Characteristic Curves for the 30', 110', and 240' Interbeds*, EG&G Engineering Design File #RWM-93-001.1, EG&G Idaho, Inc., Idaho Falls, ID.

[3] Magnuson, S.O., and A.J. Sondrup, 1996, *WAG 7 Subsurface Pathway Flow Model Development and Calibration*, INEL-96/0297, Lockheed Martin Idaho Technologies, Idaho Falls, ID.

[4] Falta, R.W., K. Pruess, S. Finsterle, A. Battistelli, 1995, *T2VOC User's Guide*, LBL-36400, Lawrence Berkeley Laboratory, UC Berkeley, CA.

[5] Falta, R.W., I. Javandel, K. Pruess, P.A. Witherspoon, October 1989, "Density-Driven Flow of Gas in the Unsaturated Zone Due to the Evaporation of Volatile Organic Compounds", Water Resources Research, Vol. 25, No. 10, pp 2159-2169.

[6] Cecil, L.D., J.R. Pittman, T.M. Beasley, R.L. Michel, P.W. Kubik, P. Sharma, U. Fehn, and H. Gove, 1992, "Water Infiltration Rates in the Unsaturated Zone at the Idaho National Engineering Laboratory Estimated from Chlorine-36 and Tritium Profiles, and Neutron Logging," Proceedings of the 7th International Symposium on Water-Rock Interaction - WRI-7, Y.K. Kharaka and A.S. Meest editors, Park City, UT.