

# NTS

## Octane and Cetane Enhancement Processes for Reduced-Emissions Motor Fuels

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Symposium and Poster Session

## Exploration, Characterization and Utilization of California Heavy Fossil Fuel Resources

(Co-Sponsored with Divisions of Geochemistry and Environmental Chemistry)

*Co-Chairmen: Arthur W. Aldag and John G. Reynolds*

## Developing the Understanding of Heterogeneous Catalyst Systems

In Honor of Wolfgang Sachtler  
Recipient of ACS Award in Petroleum Chemistry

*Chairman: George Antos*

Instructions to Authors



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**Symposium on Exploration, Characterization and Utilization  
of California Heavy Fossil Fuel Resources  
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**Removing Petroleum Hydrocarbons from Soil and  
Groundwater by Steam Injection: Numerical Modeling**

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**Introduction**

Many groundwater contamination incidents begin with the release of a petroleum liquid (e.g. gasoline or diesel fuel) into the subsurface. Once there, such a nonaqueous phase liquid (NAPL) poses a long-term threat to large quantities of groundwater because of a combination of interphase mass transfer and transport processes, namely, volatilization, dissolution, gas-water partitioning, advection in the gas and aqueous phases, as well as diffusion. These processes can lead to contamination of soil and groundwater far beyond the extent of the original NAPL spill. Therefore, a complete removal of the NAPL is required to successfully clean up the contamination.

NAPL recovery techniques commonly used today include free product recovery from an extraction well, dissolution into extracted groundwater, and vapor extraction from the unsaturated zone. Free product recovery has been successful at many sites and should be the first step where free product has accumulated above the water table. However, substantial volumes of NAPL can remain after this effort due to capillary

forces that cause trapping of NAPL blobs (residual NAPL) in the soil matrix. Dissolution of these trapped blobs into extracted groundwater is rather time consuming and very expensive because large volumes of water have to be extracted and treated before even modest quantities of residual NAPL can be removed. This is due to the low aqueous solubility of most petroleum hydrocarbons. Vapor extraction involves forcing air through the unsaturated zone, thereby enhancing volatilization of the residual NAPL as clean air comes into contact with it. The vapor is then collected from extraction wells and treated. Vapor extraction has been successfully applied at some sites (3,8,10). However, it is widely recognized that it is suitable only for the removal of the more volatile compounds from highly permeable and well-drained soils.

In the last three years, several enhanced oil recovery (EOR) methods have been suggested for residual NAPL removal. The two EOR methods that have received the most attention are steam injection (1,5,6,7,12) and surfactant flooding (11). Adding thermal energy to the system during steam injection raises the temperature, increases the vapor pressures of the NAPL compounds, and en-

hances vaporization. In surfactant flooding, one hopes to reduce the interfacial tension and thus mobilize the NAPL blobs. Although laboratory experiments have been promising, surfactant flooding is largely untested in the field.

The objective of our work is to use numerical modeling to evaluate the effectiveness of steam injection for gasoline removal at an actual contamination site, and to aid in the process design. The study site is being used as a full scale

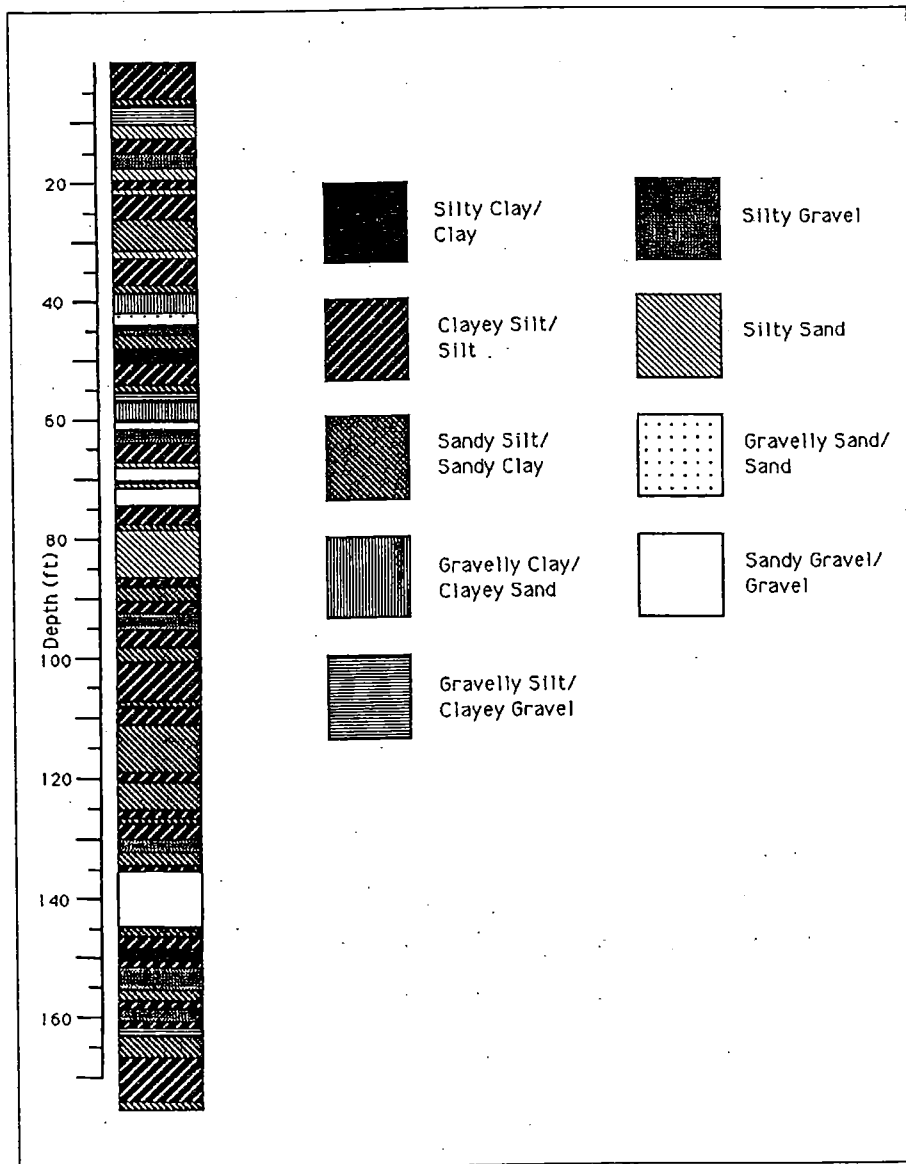


Figure 1. Typical lithologic log.

pilot, and cleanup operations are scheduled to start in early 1992.

To this end, we have developed a numerical simulator capable of handling three-dimensional, three-phase (gas, oil, and water) flow due to capillary and viscous forces as well as gravity. The simulator is fully compositional, allowing interphase mass transfer based on the assumption of local thermodynamic equilibrium. Thermal energy transport by conduction and convection is also included.

### Site Description

The subject site is located in Livermore, California. The contamination resulted from leaking underground storage tanks and it is estimated that some 17,000 gallons of leaded gasoline leaked between 1952 and 1979. The tanks were removed in 1980.

Unconsolidated sediments beneath the site consist of interlayered gravels, sands, silts, and clays that form a highly heterogeneous medium. A typical lithologic log is shown in Figure 1. The more permeable sands and gravels are generally thin, rarely exceeding 3 meters (10 feet). The thickness of the silty and clayey deposits varies over a wider range, up to 9 meters (30 feet) in some places and less than a meter feet in others. The depth of the water table at the site ranges from 27 to 30 meters (90 to 100 feet).

Earlier studies of the site (2,4,9) found that most of the residual oil in the vadose zone was within 12 meters (40 feet) of the location of the storage tanks. Near the water table, NAPL was found to have spread laterally up to 60 meters (200 feet) from the tanks' location due to the slope of the water table. Fluctuation of the water table over the years has also

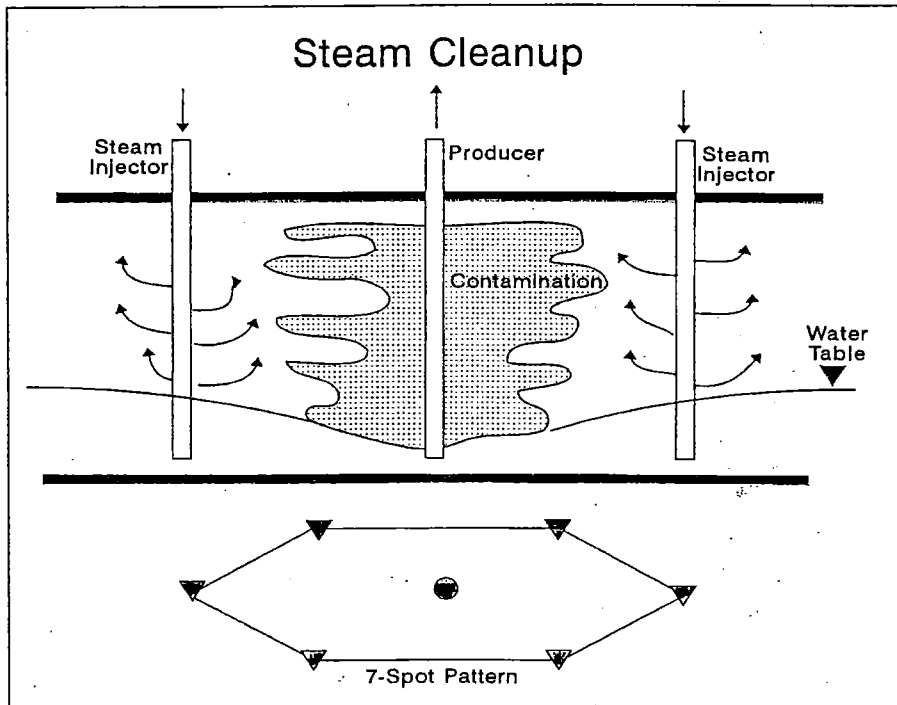


Figure 2. Steam clean up — proposed arrangement of injection and producing wells.

caused some gasoline to be trapped below the current average water level. Analysis of soil samples indicated that residual gasoline is present to a depth of 10 meters (30 feet) below the water table (i.e. approximately 40 meters (130 feet) below the ground surface). At the present time, gasoline saturations range from 0.1 in the fine-grained silty materials to 0.05 in the coarser materials.

### Model Construction

The pilot has been designed as a seven-spot pattern with a distance of 18 meters (60 feet) between the production well and the six surrounding steam injection wells (Figure 2). The injection and production wells for the project will be completed within a depth of 50 meters (160 feet) from the ground surface, covering the known vertical extent of the contamination. Because of symmetry,

simulation of only one-twelfth of the seven-spot pattern is required. The areal configuration of this minimum symmetry unit and the finite difference grid are shown Figure 3. In the vertical plane, the model contains seven layers, covering a total of 50 meters (160 feet) from the ground surface (Figure 4). It is clear from Figure 1 that a seven-layer model is only an approximation of the layering found at the site. However, such an averaging is necessary to keep the problem manageable. A similar averaging scheme was used in a model for a nearby site (referred to as the "clean" site) where a pilot 30-day steam injection was performed in July and August of 1991. Our model of the clean site yielded a satisfactory history match, lending some credence to the layering scheme adopted here.

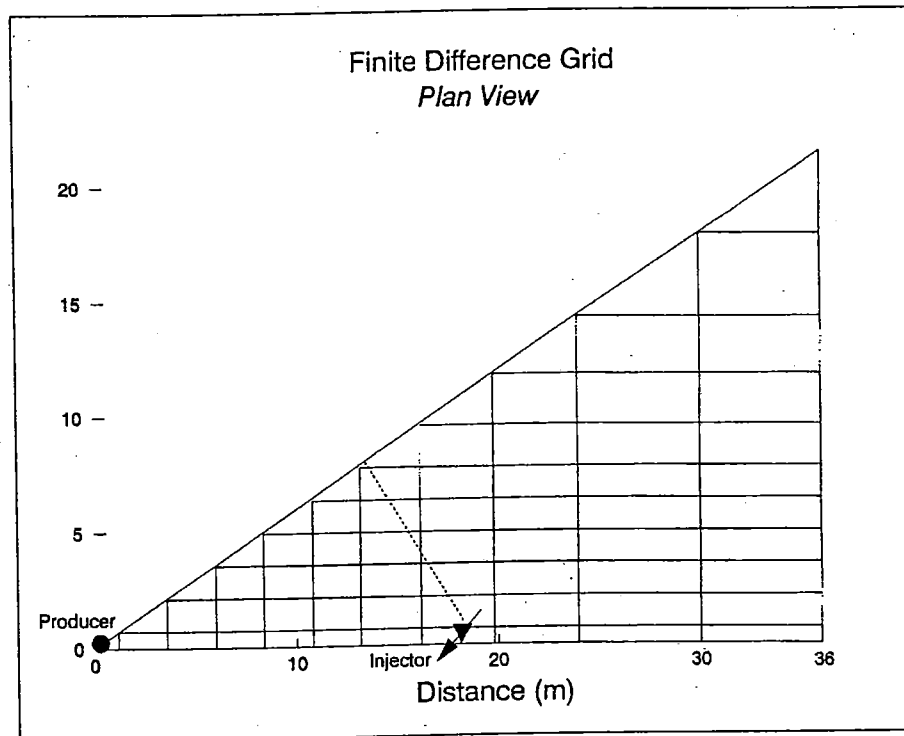


Figure 3. Finite difference grid - plan view.

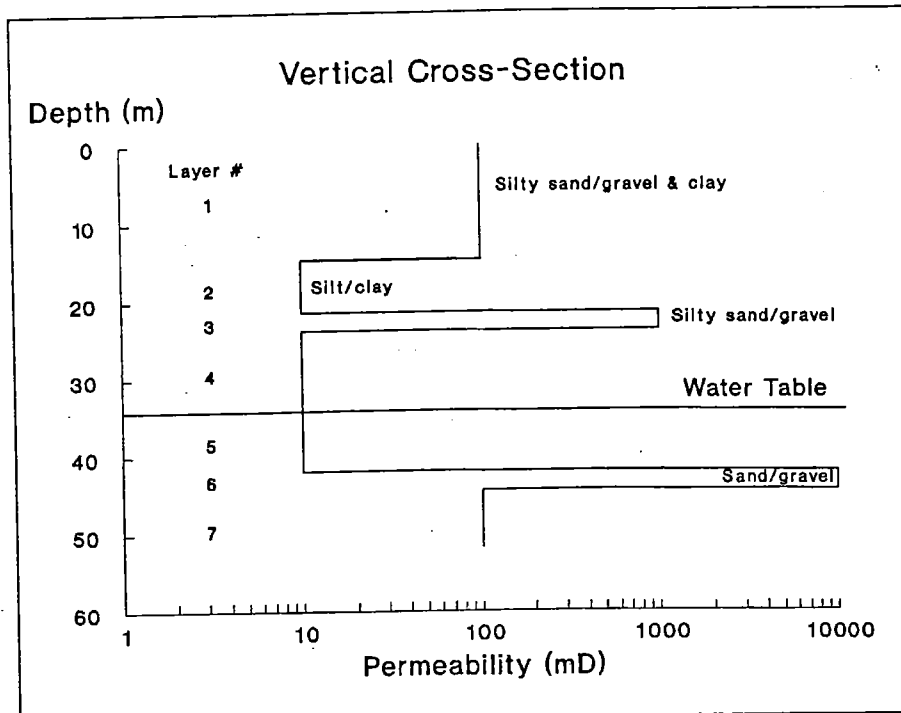


Figure 4. Model vertical cross section—layering and soil permeabilities.

**Table 1.**  
**Soil Property Data**

<b>Sands and gravel</b>	
Permeability (md)	10000
Porosity	0.2
Irreducible water saturation (%)	10
Residual oil saturation (%)	5.5
<b>Silts and clays</b>	
Permeability (md)	10
Porosity	0.25
Irreducible water saturation (%)	15
Residual oil saturation (%)	6.5
Heat Capacity (J/kg-K)	720
Thermal Conductivity (W/m-K)	3.1

The soil property data used for the simulations described here are based on a combination of data from cores and values published in the literature for each soil type. These data are listed in Table 1.

### Simulations

Prior to simulating the proposed steam injection, three simulations were carried out in sequence to obtain conditions representative of the current subsurface conditions at the site. The first of these simulations generated gravity-capillary equilibrium conditions in the absence of a NAPL (only water and gas phases were present). The bottom boundary of the model was held at a pressure that is the sum of atmospheric pressure and a hydrostatic pressure that corresponds to the height of the average water table above that boundary. Atmos-

pheric conditions were maintained at the top boundary. This simulation included water and air as chemical components.

The second simulation represented the gasoline spill. Using the gravity-capillary equilibrium conditions obtained from the first simulation as initial conditions, a NAPL of specified composition was injected at the ground surface for a period of 20 years. A constant injection rate of 2.3 gallons per day was specified, resulting in a total of 17,000 gallons of NAPL injected over the 20-year period. The composition of the injected NAPL is related to that of gasoline in the following way. We divided the components of weathered leaded gasoline into three groups according to the number of carbon atoms: C<sub>5</sub>-C<sub>6</sub>; C<sub>7</sub>-C<sub>8</sub>; and C<sub>9</sub>+. Within each group, the compound with the highest mole fraction was identified and its physical/chemical

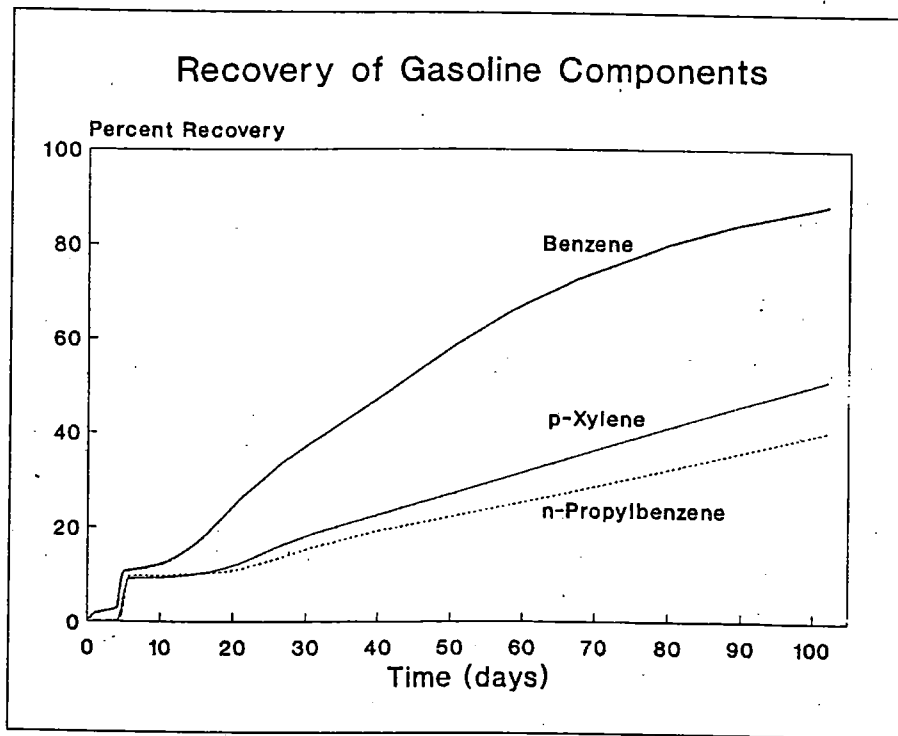


Figure 5. Model results—recovery of gasoline components.

properties were used to represent that group. The three pseudocomponents that resulted from this exercise are benzene (C<sub>6</sub>H<sub>6</sub>); p-xylene (C<sub>8</sub>H<sub>10</sub>); and n-propylbenzene (C<sub>9</sub>H<sub>12</sub>).

The third simulation was then performed to represent a 10-year period following the removal of the tanks and during which there was no NAPL injection. The NAPL already present in the soil continued to be redistributed by gravity and capillary forces however. Also, vaporization and gas phase diffusion continued to transport NAPL components both to the ground surface and to other parts of the aquifer. Results from this simulation were used as initial conditions for simulating the proposed steam injection.

The steam injection simulation was for a period of 100 days. Steam was injected into layers 2 through 6 while the production well was open to layers 2 through 7. The rate of steam injection was controlled by specifying the injection pressure and temperature, and the injectivity of each layer to which the well is open. An injection pressure of 3.5 bars, corresponding to a saturation temperature of 148°C was specified. The quality of the injected steam was 90 percent. Similarly, each layer open to the production well was assigned a productivity index. It was assumed that the pump is located in layer 5 and that its pressure is 0.8 bars.

### Results and Conclusions

The results of the steam injection simulation are summarized in Figure 5 which shows the percentage recovery of each hydrocarbon component as a function of time. Our simulations indicate that vaporization and subsequent advection to the production well is the dominant recovery mechanism. Consequently, benzene, the most volatile of the components was more easily removed than

the other two. At the end of the 100-day simulation period, 90% of the original benzene-in-place had been removed. By comparison, 51% and 40% respectively, of p-xylene and n-propylbenzene had been recovered. The simulation period will be extended in future simulations to determine the time required for complete recovery of the contaminants. In conclusion, the results of this study indicate that steam injection should be successful for remediation at this site.

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