A graphic of a spiral-bound notebook with a grey cover and a white page. The spiral binding is on the left side. The text is centered on the page.

**FUNDAMENTAL PRINCIPALS OF**  
***In Situ* THERMAL TREATMENT**

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How does one fluid phase move in response to the movement of another?

Why is the pressure distribution in the gas phase so important?

What drives mass transfer?

When might heat transfer be important?

## Outline

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General Description of Subsurface Contamination by NAPLs

Description of Thermal Treatment

Thermodynamics of NAPL/Water “Boiling”

Thermodynamics of Steam Stripping via *In Situ* Steam Generation

General Observations and Comments

2

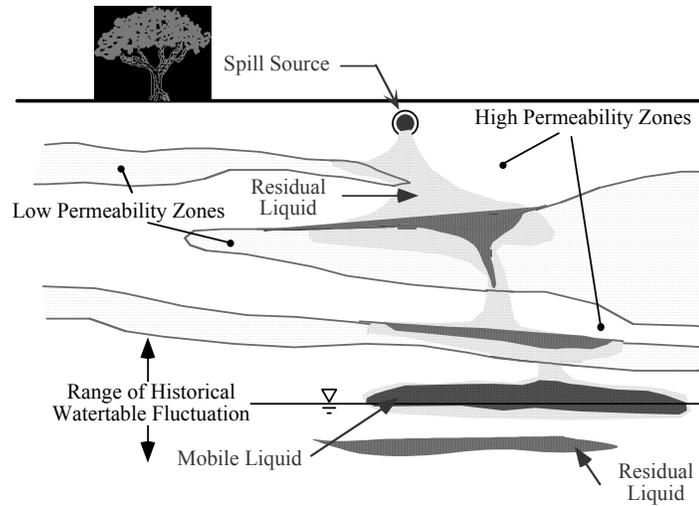
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Why is the pressure distribution in the gas phase so important?

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# General Contamination Schematic

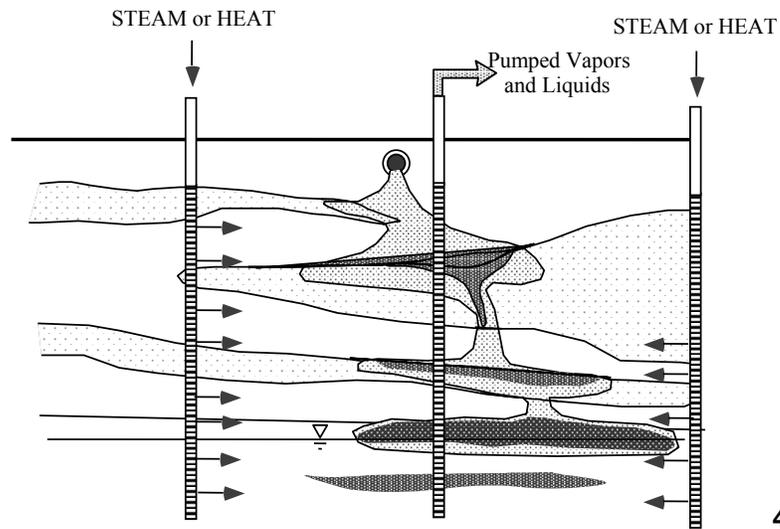


What is a primary flow path? Is it the same for the NAPL as for the vented gases?

How might oxygen transport be important?

What are remediation options for the clean-up of the immobile liquid below the water table?

## General SEE Schematic

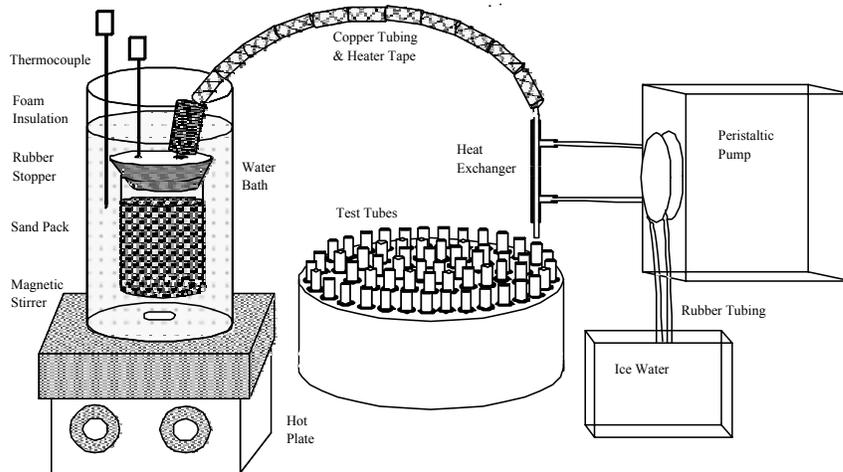


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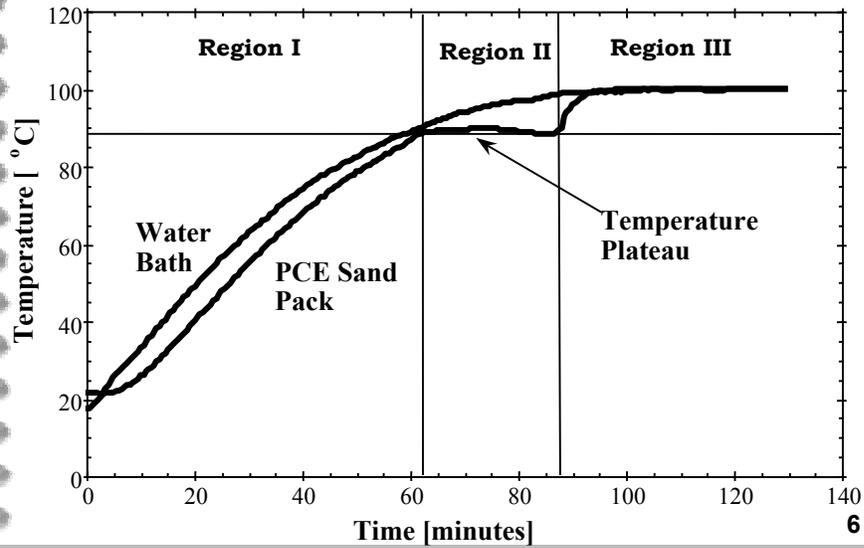
How might oxygen transport be important?

What are remediation options for the clean-up of the immobile liquid below the water table?

# Apparatus to Observe “Boiling”

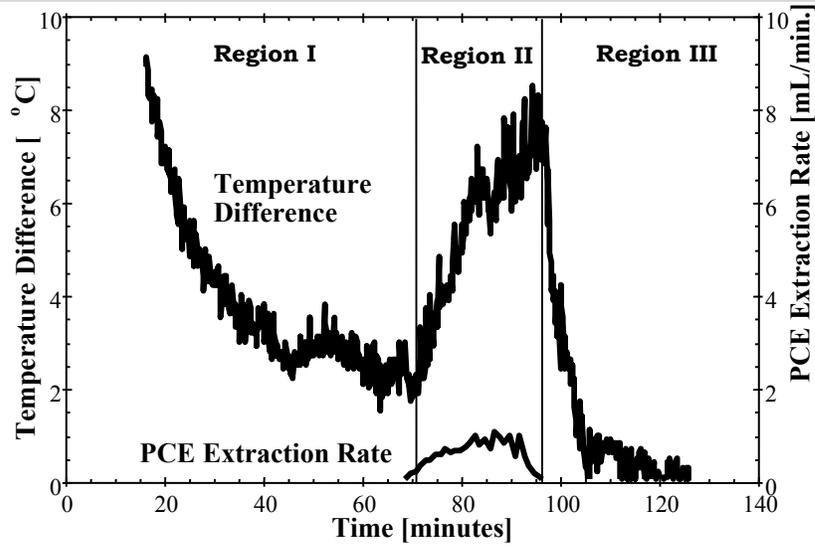


## Boiling Occurs in Region II



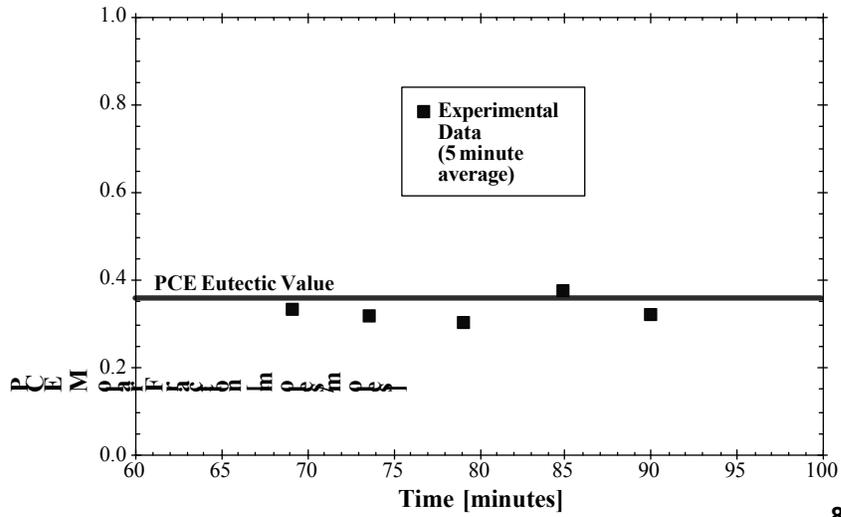
6

# $\Delta T$ Correlates with PCE Extraction Rate During Boiling. Heat Transfer Limited!



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# Effluent Vapor Composition



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## General Conclusions Regarding Heating to the Water Boiling Point

Thermodynamic forces drive the evaporation of all NAPL if the soil/water/NAPL system is heated to boiling point of water.

“Boiling” rate is controlled by heat transfer, not mass transfer.

Heat transfer occurs about 10,000 times faster than aqueous diffusion in porous media and rocks. Thus, NAPL vaporization and removal from hydraulically inaccessible zones is rapid during thermal remediation compared to fluid delivery technologies.

## However

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Compounds vaporized in heated zones may condense on heated zone boundaries. Vapors must be collected promptly and effectively to avoid the spread of contamination. Air co-injection helps to keep VOC in vapor phase, thus facilitating capture. Remaining NAPL concentrations in water are near saturation limit - still orders of magnitude above drinking water standards.

## VOC Removal By H<sub>2</sub>O Vaporization (*In Situ* Steam Stripping)

The fraction of species  $i$  remaining ( $C_{i,w}/C_{i,w0}$ ) is equal to the fraction of water remaining ( $m_w/m_{w0}$ ) to the power of the mass fraction ratio ( $\Gamma = C_{i,v}/C_{i,w} = H\rho_l/\rho_v$ ) minus 1. Where  $H$  is the dimensionless Henry's Law Constant.

$$\frac{C_{i,w}}{C_{i,w0}} = \left( \frac{m_w}{m_{w0}} \right)^{\Gamma - 1}$$

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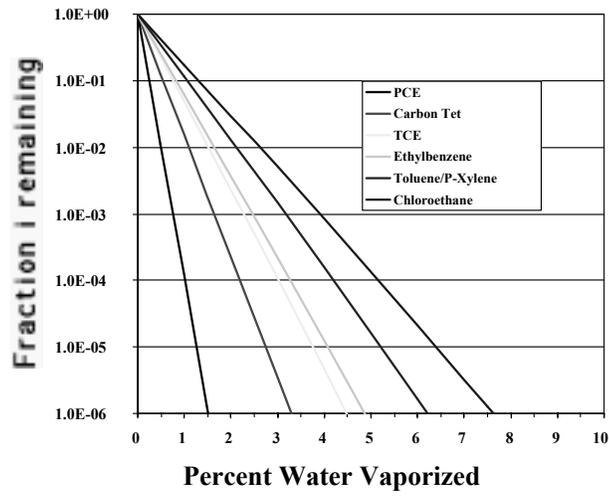
## Values for the mass fraction ratio $\Gamma$ for various chemicals at 20°C.

	Molecular Weight (g m <sup>-1</sup> )	Vapor Pressure (kPa)	Water Solubility (mg l <sup>-1</sup> )	Mass Percentage		$\Gamma$
				Water Phase	Vapor Phase	
Benzene	78.11	12.7	1780	0.18 %	28 %	156
Toluene	92.13	3.80	510	0.05 %	11 %	216
Ethylbenzene	106.2	1.27	160	0.02 %	4%	278
p-Xylene	106.2	1.17	190	0.02 %	4%	216
TCE	131.40	10.0	1100	0.11 %	33 %	302
PCE	165.83	2.5	140	0.01 %	13 %	896
Carbon Tetrachloride	153.80	15.1	1160	0.12 %	48 %	415
Chloroethane	64.90	100.7	5710	0.57 %	100%	175
Dichloromethane	84.90	58.4	1940	1.94 %	80 %	41

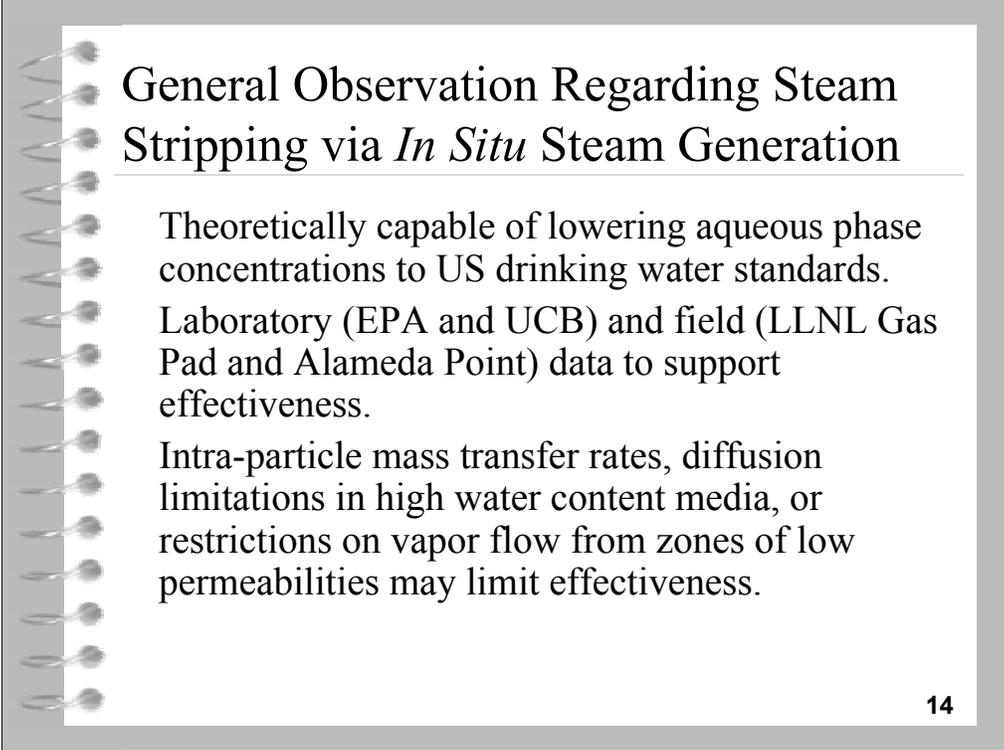
For Reference: 
$$\frac{C_{iw}}{C_{i,w0}} = \left( \frac{m_w}{m_{w0}} \right)^{\Gamma - 1}$$

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# Fraction $i$ remaining vs. % water removed



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## General Observation Regarding Steam Stripping via *In Situ* Steam Generation

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Theoretically capable of lowering aqueous phase concentrations to US drinking water standards.

Laboratory (EPA and UCB) and field (LLNL Gas Pad and Alameda Point) data to support effectiveness.

Intra-particle mass transfer rates, diffusion limitations in high water content media, or restrictions on vapor flow from zones of low permeabilities may limit effectiveness.

## How can we promote *in situ* steam stripping?

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### Depressurization during SEE

- Turning off steam while turning up vacuum decreases pressure, and thus temperature, in the steam zone. Decrease in soil and water temperature releases energy to drive water vaporization.

### Electrical Heating

- Once temperature has reached the water boiling point, additional heat generation goes to boiling water, producing *in situ* steam stripping.

## Concluding Observations

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Steam Enhanced Remediation can easily exploit robust vaporization mechanisms, allowing effective *in situ* application.

Risk of contaminant spreading with all thermal techniques is considerable but manageable with care.

While implementation is direct, relatively inexpensive, and reasonably predictable, effective and safe implementation require substantial expertise.