

# Petroleum Contaminated Low Permeability Soil:

## Hydrocarbon Distribution Processes, Exposure Pathways and In Situ Remediation Technologies

Health and Environmental Sciences Department  
Publication Number 4631  
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API PUBLICATION NUMBER 4631

EDITED BY:

TERRY WALDEN  
BP OIL COMPANY  
4440 WARRENSVILLE CENTER ROAD  
CLEVELAND, OH 44128-2837

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### API STAFF CONTACT

Harley Hopkins, Health and Environmental Sciences Department

### MEMBERS OF THE THE SOIL AND GROUNDWATER TECHNICAL TASK FORCE

&

### MEMBERS OF THE GW-30 PROJECT TEAM

R. Edward Payne, Mobil Oil Corporation (Project Team Leader)

Vaughn Berkheiser, Amoco Corporation

Tim Buscheck, Chevron Research and Technology Company

Steve deAlbuquerque, Phillips Petroleum Company

Lesley Hay Wilson, BP Oil Company

Bob Hockman, Amoco Corporation

Victor J. Kremesec, Amoco Corporation

Al Liguori, Exxon Research and Engineering Company

Jeff Meyers, Conoco, Inc.

John Pantano, ARCO Exploration and Production Technology

Adolfo Silva, Petro-Canada, Inc.

David Soza, Pennzoil Company

Terry Walden, BP Oil Company

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## ABSTRACT

Remediation of hydrocarbon contaminated sites having silty or clayey soils poses special technical challenges to site managers because such low permeability soils typically resist remediation with conventional technologies. Recognizing the limited information available to field practitioners charged with evaluating remediation options for low permeability soil, API initiated a multi-year program to consolidate information on the topic and conduct research on technologies that show promise for removing, or enhancing the removal, of contaminants in this media. The goal is to increase our understanding of the need and ability to remediate such soils in-situ. This report presents a set of ten papers focusing on light non-aqueous phase liquids (LNAPLs) in low permeability soils. Collectively, the papers address four key topics: (1) processes affecting the migration and removal of LNAPLs; (2) exposure potential posed by clay soil hydrocarbons via a soil, groundwater or air pathway; (3) available models for predicting LNAPL removal and (4) techniques presently available to remediate or enhance remediation. Each of the techniques discussed are capable of facilitating removal of hydrocarbons from low permeability soil. However, it is important to evaluate the degree to which human exposure can be further reduced given the effort and cost associated with applying these remediation approaches.

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# SUMMARY OF PROCESSES, HUMAN EXPOSURES AND TECHNOLOGIES APPLICABLE TO LOW PERMEABILITY SOILS

Terry Walden, BP Oil Company  
Cleveland, OH

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## ABSTRACT

This paper summarizes a series of ten focus papers on the topic of light non-aqueous phase liquids (LNAPLs) in low permeability soils. Collectively, the papers address four key issues: (1) physical and chemical processes affecting the migration and removal of LNAPLs; (2) available models for predicting this behavior; (3) exposure potential posed by clay soil hydrocarbons via a soil, groundwater or air pathway; and (4) techniques presently available to remediate or enhance remediation. The goal is to provide guidance and understanding on the need and ability to remediate such soils in-situ. The focus is primarily on the vadose zone of petroleum-contaminated sites.

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## Section 1 INTRODUCTION

Recognizing the limited options available to field practitioners charged with remediating sites with silty or clayey soils, the API initiated a three-year program beginning in 1992 to consolidate information on the topic and conduct research on technologies that show promise for removing, or enhancing the removal, of contaminants in this media. A multi-discipline group was assembled under the umbrella of the API to address the four phases of the problem referenced above. These individuals agreed to work as a team and write *focus papers* on their areas of

expertise, which included topics in the process, modeling, exposure and technology areas. The team included the following:

| <u>Topic</u>            | <u>Author</u>     | <u>Affiliation</u>        |
|-------------------------|-------------------|---------------------------|
| • Process Issues        | David McWhorter   | Colorado State Univ.      |
| • Modeling Issues       | Marian Kemblowski | Utah State Univ.          |
| • Exposure Issues       | Terry Walden      | BP Oil                    |
| • Soil Vapor Extraction | Fred Payne        | ETG, Inc.                 |
| • Bioventing            | Robert Hinchee    | Battelle Memorial Inst.   |
| • Thermal Processes     | Kent Udell        | Univ. of Cal. at Berkeley |
| • In-Situ Soil Mixing   | Robert Siegrist   | Oak Ridge National Lab    |
| • Hydraulic Fracturing  | Larry Murdoch     | Univ. of Cincinnati       |
| • Pneumatic Fracturing  | John Schuring     | NJIT                      |
| • Surfactant Flushing   | Philip Gschwend   | MIT                       |

## Section 2

### PROCESS ISSUES

Low permeability soil refers to silts or clays whose saturated hydraulic conductivity is generally below  $10^{-5}$  cm/s. These soils can be encountered in three distinct types of geologic settings. The first is a massive clay formation where the permeability is very limited and in fact dominated by secondary fractures normally the result of a desiccation or weathering process. The second is a layered or stratified formation where silt or clay layers are interspersed within sandy or higher permeability layers. The third can be considered a subset of the second and consists of silt or clay 'lenses' that tend to be discontinuous and of a limited lateral and vertical extent within a sandy matrix. Fluid (including contaminant) migration is distinct in each setting and the remediation strategies differ accordingly for each media.

In massive clay formations containing natural fractures in non-arid regions, the fractures a short distance above the water table are generally air-filled while the adjoining 'solid' matrix blocks between fractures are water-saturated due to capillary pressure forces. What this means is that should a hydrocarbon spill occur, the LNAPLs will fill the fractures in the soil and bypass the matrix blocks, traveling downward until they encounter the capillary fringe (the area just above the water table), at which point they will spread laterally in cross-cutting fractures. The large

entry pressures required to 'push' the LNAPL into the matrix will tend to keep these separate phase hydrocarbons in the fractures.

Although separate phase product (i.e. LNAPL) invasion into the water-saturated matrix will not occur to any great extent, its constituents will eventually appear in the matrix as a result of the process of diffusion, i.e. movement resulting from the existence of concentration gradients. This is an aqueous phase - not a separate phase - process. The soluble constituents in the LNAPL will dissolve and a concentration gradient will be established between the dissolved hydrocarbon components in the fracture and the uncontaminated pore water in the matrix. The more soluble components will partition out of the LNAPL phase first, and over a period of weeks to months, part or all of the LNAPL mass in the fractures will diffuse into the matrix, with equilibrium established when the matrix storage capacity (including both dissolved and adsorbed phases) is reached.

The process of diffusion has a rather significant impact on remediation strategy. Diffusion is a slow process, and a phrase that is commonly heard is that 'if it takes x amount of years to diffuse into the soil, it will take x amount of years to get out'. In fact, this is extremely optimistic. Simple diffusion calculations indicate that the time to achieve 85% mass recovery is nearly 10 times as long as the time the contaminant is in the ground before remediation begins. So if a spill were to occur 2 years before remediation (defined as an air or liquid flushing system which sweeps the fractures free of contamination), it may take 20 years to get 85% of the mass out, and 200 years to achieve 95% removal, under the conceptual assumptions that were made (see McWhorter, this volume). These long remediation periods are the result of disparate concentration gradients. High gradients drive the contaminants quickly out of the fractures, whereas only low gradients exist when the fractures are cleared, establishing a slow process of reverse diffusion out of the matrix. It is apparent that technologies that rely strictly on diffusion-controlled fluid movement will take a long time to achieve success (if ever) and could therefore have high life cycle costs.

An important example of this concept is in the application of soil vapor extraction. The remediation literature has numerous examples where high vacuum systems (some approaching 25 inches of mercury or 0.8 atm) have been used for clay soils, presumably to improve the zone of influence of the induced air flow around the extraction wells. Air will likely, however, flow through the fractures in a massive

clay formation, or the sandy layers in a stratified formation, and use of the term 'radius' - in implying uniform flow through the subsurface - is misleading in this regard. If the mass transfer of contaminants is diffusion-limited, the air flow rate through the fractures or high permeability layers is immaterial, and the vacuum system should be sized to the smallest unit that will simply keep the fractures swept clear, thereby minimizing operating costs.

### Section 3

## MODELING ISSUES

To define the exposure potential as well as the need for remediating hydrocarbons in low permeability media, a good understanding of the chemical composition of the LNAPL (e.g. crude oil or refined petroleum products), the geology and the subsurface processes affecting LNAPL behavior is needed. Regarding the first element, each key compound's vapor pressure, solubility and mole fraction in the LNAPL mixture are the critical parameters. The geologic factors that control exposure are subsurface permeability, the degree of stratification or fracturing, soil moisture content and distance of the source from the water table (for a groundwater pathway) or the receptor (for a vapor inhalation route of exposure). In order to assess exposure and the need or ability to remediate the site, the following geologic parameters should be measured in each of the three discussed settings:

- |                 |                                                                                                                                                                                                                 |
|-----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Massive Clay    | <ul style="list-style-type: none"> <li>• Permeability and air-filled porosity of the fractures</li> <li>• Average fracture spacing and connectivity</li> </ul>                                                  |
| Stratified Soil | <ul style="list-style-type: none"> <li>• Permeability over discrete intervals</li> <li>• Air-filled porosity in low permeability layers</li> <li>• Average fracture spacing and connectivity, if any</li> </ul> |
| Clay 'Lenses'   | <ul style="list-style-type: none"> <li>• Diffusion coefficient of contaminants in clay</li> <li>• Thickness and length scale of lenses</li> </ul>                                                               |

Tracer data may be used to estimate some of these parameters, such as air-filled porosity or average fracture spacing (which could be calculated from the tracer flow data after assuming or measuring an average aperture dimension). To determine the need for - or efficacy of - remediation, this data could be modeled to determine fate and transport of the contaminants, both with and without remediation. This is

where the third element of the evaluation comes into focus - the subsurface process data. Partitioning, biodegradation and retardation effects need to be considered. Biodegradation in low permeability soils is particularly relevant because of the generally long residence times of dissolved or vapor phase product in the subsurface as it moves between a source and a receptor.

Given the varied subsurface conditions and contaminant compositions one might encounter and the data requirements for modeling heterogeneity, the use of analytical models for screening purposes rather than numerical models for detailed prediction is considered the most practical approach at the present time. This approach would provide answers to questions such as whether a particular remedial action can be effective and what gross exposure threats are posed by leaving the soil untreated.

## Section 4 EXPOSURE ISSUES

Human exposure to contaminated media can be the result of either direct or indirect contact with soil, groundwater or their vapor emissions. What distinguishes the potential for exposure in clay soils from other more permeable media is the unique soil structure. The small pores comprising the matrix blocks increase the capacity of the soil (relative to a more permeable media), to store and 'sequester' contaminants over time and to retain water in the matrix. The secondary or 'dual porosity-dual permeability' nature of the material, due to the presence of natural fractures, results in non-uniform distribution and transport of LNAPL, water and vapor phases throughout the subsurface. The low permeability of the bulk media affects the migration of contaminants in the vadose and groundwater zones.

### 4.1 SOIL CONTACT

The direct soil contact pathway is strongly influenced in clays by bioavailability of the compounds. Bioavailability is a concept which refers to the fact that contaminants which may be present in the matrix (in the sense they are extractable with a solvent) may no longer pose a toxicity risk because of the way they are retained or sequestered in the soil matrix. In simplest terms, the contaminants diffuse into the interior pores of the soil or into the humic fraction, and are increasingly slow in reappearing at the surface of the soil (where their toxicity can

manifest itself) due to desorption rate limiting mechanisms. While this phenomenon applies to all soils, it is particularly relevant for clay because of its small pore structure. From an exposure standpoint, reduced bioavailability lessens the absorbed dose (and hence risk) of direct soil contact, either by ingestion or dermal contact. Identifying the suite of tests to demonstrate and quantify bioavailability is the subject of recent research led by the Gas Research Institute and the oil industry.

## 4.2 GROUNDWATER EXPOSURE

Exposure via the groundwater pathway is strongly a function of the type of fine-grained geologic setting. In massive clay soils, with no underlying sandy aquifer, there is little exposure threat because the low permeability limits contact in the source zone (because wells would be unproductive and therefore, not used), and downgradient of the source (because of limited plume migration potential). However, for the case where a contaminated clay stratum containing fractures lies above or below an aquifer, mass transfer under two scenarios must be considered:

- If LNAPL is present in the fractures, rainfall or a fluctuating water table flowing through the fractures will release dissolved phase components at their effective solubility limit (defined by Raoult's Law as the pure phase solubility multiplied by the mole fraction of the constituent in the mixture) into the aquifer. Dissolved phase concentrations of the BTEX compounds in excess of their drinking water standards (their MCLs) could occur in the aquifer directly beneath the source.
- If the LNAPL has been depleted from the fractures (by some combination of the processes of volatilization, dissolution, biological degradation or diffusion into the matrix blocks), reverse diffusion of the dissolved phase contaminants from the matrix back into the fractures will occur. Unless the distance between fractures is on the order of meters, the resulting concentration in the fractures will essentially be equal to that of the water held in the matrix. For high matrix concentrations and limited mixing of the fracture leachate in the aquifer, dissolved phase concentrations of BTEX could also exceed their MCLs in the aquifer.

Both scenarios indicate that an exposure risk in the aquifer beneath the source area is possible. However, if the receptor well is downgradient of the source, exposure will be mitigated by natural attenuation processes affecting the BTEX plume.

### 4.3 AIR EMISSIONS

Air emissions from low permeability soils are generally unlikely to pose an inhalation exposure threat from outdoor or indoor vapors. This is true even when the hydrocarbon source is directly adjacent to a basement, an excavated trench, or the soil surface. Diffusional transport is limited by the normally high moisture content of the clay soils, which limits the number and size of the air-filled passages through which the volatile organic vapors can migrate. The vapor plume is further attenuated by the processes of dissolved phase partitioning into the vadose zone pore water, adsorption onto the organic fraction, and biodecay.

## Section 5 TECHNOLOGY ISSUES

Seven technologies were judged to have some potential for the remediation of low permeability soils in the vadose zone. These technologies can be broadly segregated by the type of process they induce:

|                          |                                                                                                                                     |
|--------------------------|-------------------------------------------------------------------------------------------------------------------------------------|
| Contaminant Removal      | <ul style="list-style-type: none"> <li>• Soil vapor extraction (SVE)</li> <li>• Bioventing</li> </ul>                               |
| Mobility Enhancement     | <ul style="list-style-type: none"> <li>• Thermal processes</li> <li>• Surfactant flushing</li> <li>• In-situ soil mixing</li> </ul> |
| Permeability Enhancement | <ul style="list-style-type: none"> <li>• Hydraulic fracturing</li> <li>• Pneumatic fracturing</li> </ul>                            |

To comparably evaluate each technology, an identical set of questions was posed to each of the seven technology paper authors. Generic questions included the effects on contaminant removal posed by high moisture content, the ability to access under buildings, the maximum depth to which the technology is appropriate, and the capability to remediate petroleum products other than gasoline. The two major geologic settings of a naturally-fractured massive clay formation and a stratified formation were described, and in each case, the author was questioned on the technology's ability to remove free product, dissolved product, adsorbed product, and residual product trapped within pore throats. The papers conclude with a breakdown of the costs to close a hypothetical site, commercial availability, case

histories, and a summary of the strengths, weaknesses and complementary technologies which could enhance remedial effectiveness.

The most salient points for each technology follow, concluding with a table summarizing these above items. A common set of cost data (e.g. well costs) has been used to derive comparable data for each technology as applied to the hypothetical site.

## 5.1 REMOVAL TECHNOLOGIES

In-situ technologies that actually remove, not simply enhance the removal, of contaminants from the ground are limited to two air flushing techniques, which are very closely related.

### 5.1.1 Soil Vapor Extraction/Bioventing

Soil vapor extraction and bioventing refers to either the injection or extraction of air through a non-saturated medium. Both rely on the same principle for achieving success, i.e. the ability to sweep air through regions of contamination within the formation. In soil vapor extraction, the air induces volatilization of the contaminants; in bioventing, the oxygen encourages biodegradation. The distinguishing feature between the two processes is the air flow rate, with bioventing requiring less flow because the biodegradation rate (and thus the oxygen demand) is relatively low.

In fine-grained soils, the air will preferentially flow through the fractures in a massive clay and the higher permeability layers in a stratified soil. Remediation of the matrix blocks or the clay layers/lenses will then be diffusion-limited, although for vapor extraction, diffusion refers to the contaminants migrating into the swept fractures, while in bioventing, it refers to oxygen diffusing into the lower permeability regions. The success of both technologies depends on the diffusion path length, i.e. the distance between fractures or thickness of the clay layer.

The overall evaluation of these technologies is that they are reasonably effective, both from a technical and cost perspective. Stratified formations are somewhat problematic for soil vapor extraction because it is difficult to move the air anywhere other than the high permeability layers. In bioventing demonstrations, this was partially overcome by injecting air over narrow-screened intervals at close spacing

in the clay layers. Both technologies may potentially be enhanced by dewatering and induced (pneumatic or hydraulic) fracturing, as long as the geometry and spacing of the fractures is well controlled. Soil warming could also enhance performance, although temperatures that would significantly improve vapor extraction (through pore water evaporation) would be at the expense of biological activity. Optimum temperatures for bioventing would be in the range of 20 to 30°C.

## 5.2 MOBILITY ENHANCEMENT TECHNOLOGIES

Mobility enhancement is broadly defined as a process which accelerates the movement of contaminant vapors or liquids to a subsurface collection system. Surfactant flushing is the typical example of this type of technology, but this definition also includes thermal techniques and soil mixing.

### 5.2.1 Thermal Processes

Soil can be heated through one of two ways: hot fluid injection (hot water, air or steam) or direct heating (electrical resistance (ER) or radio frequency (RF) heating). In the former, the fluids are introduced through wells or trenches. In the latter, the heat is introduced through electrodes or antenna placed in the ground. In both cases, the key design goal is to spread the heat away from the source and maintain roughly uniform temperatures throughout the remedial area. These higher soil temperature must be maintained near the extraction wells to avoid re-condensation or immobilization of the contaminants.

Thermal applications of water, air and steam are different. Hot water would be used to improve mobile LNAPL recovery in water extraction wells by lowering the interfacial tension and contaminant viscosity. Hot air would primarily function to dewater the formation by vaporizing the pore water near the flow channels, thereby improving the performance of vapor extraction. The target for steam is removal of both residual and free phase hydrocarbons which are volatilized and recovered in the gaseous phase or as condensate. Like vapor extraction, hot fluid injection is compromised by the tendency of the fluid to flow through higher permeability layers in a stratified formation or the fractures in a massive clay formation. These preferential pathways make it difficult to uniformly heat the formation, limiting the remedial effectiveness of hot fluid injection as a stand-alone technology.

ER and RF heating systems attempt to raise the vapor pressure of the contaminants to improve hydrocarbon recovery through vapor extraction wells. ER can heat the soil to close to the boiling point of water while RF can heat significantly above the boiling point, providing the added benefit of drying the soil (but at higher cost). These technologies actually perform better in low permeability media since they depend on the water content of the soil to conduct energy (and capillary forces retain higher moisture levels in silts and clays as compared to sands and gravels). Still, sufficient permeability must exist to remove the vapors.

Undoubtedly, thermal technologies improve hydrocarbon recovery (especially of middle distillates) but the costs are high and field experience limited. In low permeability soils, a complementary technology such as fracturing may be needed to ensure more uniform heat distribution and a hydrocarbon removal pathway.

### 5.2.2 Surfactant Flushing

Injection of surfactants through wells can aid in hydrocarbon recovery in one of four ways. The surfactant can promote dissolution of an LNAPL by increasing its solubility in the flushing solution, or it can increase its mobility in the subsurface by lowering the water-LNAPL interfacial tension. Surfactants can also reduce sorption onto soil particles and, finally, may accelerate the release of soil colloids which may be carrying sorbed contaminants.

There are two principal drawbacks to the general use of surfactants. The first is their cost and the other is their tendency to form emulsions which are difficult to break. Unfortunately, in an attempt to overcome the first problem through recycling, the second problem of emulsions manifests itself. There are relatively few examples of surfactant usage in the literature, and the ones that do exist apply mostly to DNAPLs (dense non-aqueous phase liquids which are typically solvents) rather than petroleum hydrocarbons.

Low permeability media further complicates the effective use of surfactants. As with other fluid flushing approaches (air or liquid), the surfactant will bypass the lower permeability regions, relying on a diffusional process to reach the contaminants in the clay layers or matrix blocks. Induced fracturing of the soil could alleviate this problem to some extent, but when combined with the cost and emulsion issue, the feasibility of cost-effectively treating a silt or clay media with

surfactants is doubtful and the technology appears to have limited potential at the present time.

### 5.2.3 In-Situ Soil Mixing

In-situ soil mixing refers to the process of physically disturbing the soil with the use of large diameter (up to 14 ft) augers mounted on a drill rig. Overlapping columns of soil are augured down to depths as great as 25 ft. The technology requires that the site be relatively level and free of overhead obstructions; the subsurface must likewise be free of boulders or other large buried objects.

In the process of mixing the soil, treatment of the contaminants can take one of three forms. Grout can be injected down the hollow auger stem to solidify the soil; air can be injected to volatilize the contaminants (which are then collected under a shroud placed on the surface); or a chemical oxidant (e.g. peroxide) can be introduced for promoting contaminant removal through chemical transformation. All three treatments have been demonstrated in the field, although the long term stability (leachability) of the grout has yet to be determined.

Soil mixing is an aggressive technology which causes significant site disturbance (the mixed soil has a volume at least 15% greater than the original volume). It is also very costly (relative to other technologies described in this summary), averaging as much as \$150/cu yd. It has the advantage that it is not very sensitive to the geologic conditions and treatment is extremely fast, taking only on the order of hours for each soil column. The size of the equipment however makes it impractical for service station-type settings. In summary, it is a 'niche' technology that may be uniquely suited to some applications but is not expected to see widespread usage.

## 5.3 PERMEABILITY ENHANCEMENT TECHNOLOGIES

Enhancing the permeability of low permeability media is possible with two techniques that involve artificially fracturing the soil: hydraulic and pneumatic fracturing.

The permeability of silts and clays can be significantly increased by induced fracturing of the soil. It is important however that the fracturing process be controlled, since random fracturing can create unwanted short circuits for a

remedial fluid flushing solution, making it difficult to treat the bypassed area. The goal is to create a pattern of fractures that decrease treatment time by minimizing the distance over which the diffusional process is required to remediate the contaminated zone.

Controlled fractures can be created either hydraulically or pneumatically. Hydraulically, a fracture is nucleated through injection of a fluid, followed by a slurry of granular material and gel to 'prop open' the fracture, thus maintaining a permanent channel in the matrix. In pneumatic fracturing, high pressure air creates the channel, which is 'self-propped' and will tend to close over time. In stiff clays, the time to closure may be on the order of a year or more; it could however be much less in soft saturated clays.

The key to successful fracturing is the ability to propagate the fractures in a horizontal plane. This will occur where the soil is 'overconsolidated', meaning that the horizontal compressive stresses exceed the vertical stresses. Under these conditions, both techniques are capable of initiating fractures to a radius of around 20-25 ft before they begin to rise toward the surface. Fractures can be created with a vertical spacing of 1 to 2 ft, thus providing a reasonably short diffusion path length for remediation. Creating fractures near building foundations must be carefully considered since surface displacements of up to 2 inches have been recorded.

Induced fracturing offers significant potential for remediating low permeability media by incorporating the technology with air flushing technologies or with thermal treatment. With air flushing, it may allow the amount of vacuum (and thus size of the equipment) to be reduced for moving comparable amounts of air through the subsurface. Both hydraulic and pneumatic fracturing have similar costs and installation requirements, but hydraulic fracturing has one distinct advantage. Sand-propped fractures are permanent and will not close over time - a characteristic making it less sensitive to moisture levels and the degree of stiffness in the clay.

## Section 6

### CONCLUSIONS

Distribution and migration of chemical compounds in low permeability soils is controlled primarily by fracture pathways and diffusional processes. If the clay contains natural desiccation fractures, transport of compounds will initially take place through the fractures, but diffusion into the matrix will quickly occur, until the storage capacity of the matrix is reached.

Human exposure can occur by contact with contaminated soil, groundwater or vapor emissions. The low air-filled porosity in typical clay soils severely limits the threat of vapor exposure. Direct soil contact exposure posed by dissolved or adsorbed contaminants that reside solely in the matrix blocks may be mitigated by reduced bioavailability of the compound(s). For groundwater however, where a clay stratum is in contact with a sandy aquifer, mass transfer into the aquifer may readily occur, even if no separate phase product resides in the fractures. Treatment of the clay layer above or below this aquifer may therefore be needed, if a receptor well or compliance point is located in this source area.

Remedial technologies that perform mostly by clearing the fractures of contaminants will be slow in reducing concentrations because reverse diffusion from the matrix into the fractures is much slower than diffusion in the other direction, due to a marked difference in concentration gradients. Because most remedial technologies rely on moving a fluid (air, steam, water or a surfactant) through the media, flow through the fractures, or a sandy layer adjacent to a clay stratum, is inevitable. Acknowledging this constraint, the best approach to remediating silty or clayey soils may be to ensure that the diffusional path length between adjacent fluid channels is minimized. Combining fluid flushing technologies with artificial fracturing (either hydraulically or pneumatically) at minimal vertical intervals may potentially offer the best approach for reducing contaminant concentrations at a reasonable rate. However, the degree to which this mass removal (which will likely be limited) reduces the potential for human exposure should be considered before applying these technologies.

## TECHNOLOGY COMPARISON MATRIX

|                                     | Soil Vapor<br>Extraction     | Bioventing                  | Thermal<br>Techniques                   | Surfactant<br>Flushing                                | Soil Mixing                                       | Hydraulic<br>Fracturing                            | Pneumatic<br>Fracturing                                  |
|-------------------------------------|------------------------------|-----------------------------|-----------------------------------------|-------------------------------------------------------|---------------------------------------------------|----------------------------------------------------|----------------------------------------------------------|
| <b>Applicability</b>                | Volatile fractions           | Middle distillates          | Gasoline, diesel and crude oil          | Diesel and crude oil                                  | Volatiles & semi-volat.                           | Massive clay formations                            | Massive clay formations                                  |
| <b>Strengths</b>                    | Proven technology            | Low cost(f)                 | - Improved HC recovery                  | Residuals reduction                                   | - Fast(f)<br>- Enhanced mass trans.               | Reduce diffusion path length                       | Reduce diffusion path length                             |
| <b>Limitations</b>                  | Low K layers in strat. soils | - Slow(f)<br>- Low K layers | - Non-uniform heating<br>- High cost(f) | - Emulsions<br>- High cost(f)<br>- Limited experience | - Large equipment<br>- Boulders<br>- High cost(f) | - Overconsolidated geology only<br>- Surface heave | - Geology<br>- Surface heave<br>- Fractures close w/time |
| <b>Costs (\$/yd<sup>3</sup>)(a)</b> | \$24 (b)                     | \$23 (b)                    | \$62 (c)                                | \$65 (d)                                              | \$125                                             | \$6 (e)                                            | \$7 (e)                                                  |
| <b>Time to Closure(a)</b>           | 9 months                     | 2 yrs                       | 50 days                                 | 64 days                                               | 50 days                                           | 3 weeks (fracturing only)                          | 3 weeks (fracturing only)                                |
| <b>Availability</b>                 | Widespread                   | Widespread                  | Sparse                                  | Very limited                                          | Sparse                                            | Very limited                                       | Very limited                                             |
| <b>Complementary Technologies</b>   | - Fracturing<br>- Dewater    | - Fracturing<br>- Warming   | - Fracturing<br>- SVE                   | Fracturing                                            | Heating                                           | All fluid flush technologies                       | All fluid flush technologies                             |

### Notes:

- (a): Costs were calculated from information provided in the papers included in this report; closure refers to gasoline cleanup from 1000 to 200 ppm in stratified site, with 100 ft x 100 ft x 15 ft source dimension.
- (b): Includes \$15k for design, \$20k for a pilot study and \$20k for pre and post-soil sampling.
- (c): Assumes steam stripping.
- (d): Assumes 80% recycling of the surfactant.
- (e): Costs are for fracturing only, not subsequent remediation.
- (f): Relative to other technologies described in this report.



# RELEVANT PROCESSES CONCERNING HYDROCARBON CONTAMINATION IN LOW PERMEABILITY SOILS

*David B. McWhorter, Colorado State University  
Fort Collins, Colorado*

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## ABSTRACT

This paper describes the processes associated with predicting the distribution and removal of LNAPL's in low permeability media after a release occurs. It assumes the clay soil contains natural dessication fractures and describes LNAPL behavior in these fractures as well as the matrix blocks between fractures. This behavior is strongly influenced by the presence of water in the fractures and matrix, and equations for predicting the capillary rise of water in both the fractures and matrix are also developed. The paper also shows the dramatic effect that the time between release and remediation plays in affecting the efficient removal of LNAPL's from the subsurface.

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## Section 1

### INTRODUCTION

Contamination of groundwater by organic liquids such as petroleum hydrocarbons and chlorinated solvents creates especially challenging problems for those charged with site investigation and remediation. This paper describes several of the important processes that occur when petroleum hydrocarbons are released into low permeability soils. Particular emphasis is placed on clay and clay-rich till soils characterized by vertical fractures superimposed on a fine-grained matrix. Comments are also directed toward stratified, low permeability soils. The soils considered in this paper are widespread in North America and are particularly difficult to remediate.

Petroleum hydrocarbons are immiscible with respect to both water and air. Also, hydrocarbons are nonwetting with respect to water and wetting with respect to air. For these reasons, the pre-release distribution of water and air in the geologic medium is an important factor in the determination of the hydrocarbon distribution, both during and subsequent to the release. The pre-release distribution of water and air is the first technical issue undertaken for each of the two soil types that are discussed. Emphasis is placed on the way fractures and variable strata influence the water and air distribution. This sets the stage for a description of hydrocarbon infiltration.

Processes that occur during infiltration of LNAPL are considered next. Important questions concerning the potential for LNAPL invasion of the fine-grained matrix and low permeability strata are addressed. This is followed by a description of the way water, air and LNAPL are likely to distribute themselves once the release is terminated and significant fluid motion ceases (i.e., mechanical equilibrium prevails). These distributions are especially relevant to site investigation and the potential for LNAPL removal during remediation efforts.

Diffusion of dissolved chemicals into the fine-grained matrix and low permeability strata is the final process described. This process occurs because of chemical disequilibrium that exists, even after the bulk fluids are no longer in motion. An analysis for a simple, idealized case is presented to illustrate how difficult it is to remove dissolved chemical from fine-grained matrix and low permeability strata once they have become contaminated.

## Section 2

### MASSIVE CLAY/TILL SOILS

#### 2.1 DESCRIPTION

These soils consist of a network of interconnected fractures of variable aperture and spacing superimposed on a porous matrix. Typically, the characteristic fracture aperture is orders of magnitude greater than the size of interstitial openings in the porous matrix. The fraction of total porosity contributed by the open fractures usually is very small. Fracture porosities are often less than 1 percent while matrix porosities may be 40 percent or greater (Freeze and Cherry, 1979). On the other hand, it is the fractures that are primarily responsible for the overall fluid transmissive capacity of the bulk medium. While having only a modest effect on total porosity, the frequency and aperture of fractures are the controlling factors in respect to the bulk medium permeability.

Fracture apertures typically are within the range of 1 to 200 microns. Within an individual fracture, the aperture is thought by the author to be log-normally distributed. The void volume represented by the fractures is directly dependent upon both the fracture aperture and fracture spacing in three dimensions. Fracture spacing is not uniform, of course, and neither do the matrix blocks bounded by fractures form regular rectangular or cubic boxes. Nevertheless, it is this view of fractured porous media usually invoked to estimate the void volume contributed by fractures. Freeze and Cherry (1976) and Parker (1992) mention fracture porosities as low as  $10^{-5}$ .

Fracture aperture and volume are not often constants in clays. Rather these features are dependent upon the water content of the clay. The fractures in a swelling/shrinking clay are more open when the clay tends toward dryness and vice-versa. Within the context of this paper, the more important effect of desiccation is to permit the spontaneous imbibition (entry) of pure phase hydrocarbons into the matrix blocks. This process will be significant in desiccated clays, even though the matrix permeability is very small. As will be shown in subsequent discussion, pure phase hydrocarbons are generally excluded from water-saturated matrix blocks under the typical conditions taken as the basis for discussion in this work.

Classical analyses of the behavior of subsurface fluids rests on the concept of a representative element of volume, or REV (Bear, 1972). The REV is a volume element that is small relative to the overall scale of the flow process, but is large relative to pore scale. Variables of interest (e.g. pressure, concentration) that are included in the analysis are thought of as average values within the REV. Measurement devices used to sense the variables of interest automatically yield the average values for porous media because the measurements are made at scales much larger than the pore scale. Thus, there is a direct correspondence between the predicted and measured variables.

The same concepts can be applied to a fractured porous medium but often the direct correspondence between the variables in the analysis and those that are measured is lost. This is because the scale of the measurement is smaller than the characteristic dimension of the REV and, thus, the measurement does not yield the mean value that is required by the analysis. Several measurements within a block of the medium may be required to obtain an average value in conceptual correspondence to that predicted by the 'equivalent porous medium' approach.

This and other shortcomings of the equivalent porous medium approach have spawned other conceptualizations that give explicit attention to interactions between the fractures and the matrix. One such approach views the fractured porous medium

as being comprised of two completely overlapping continua that interact via mass transfer between them. That is, one calculates the fluid behavior in the fractures as if they occupied all the space. The same is done for the matrix. Interactions between fractures and matrix are accounted for by calculating mass transfer between the two solution spaces. Other approaches view the porous matrix as a continuum but treat individual, discrete fractures imbedded in the matrix.

There appears to be no single conceptualization of fluid behavior in fractured porous media that works best for all purposes. The brief foregoing discussion is presented only to provide context for subsequent descriptions of LNAPL behavior in massive clay and clay-rich till soils. In particular, there exists no generally accepted conceptual or mathematical model that can be applied to the task at hand. Instead the process description that emerges in the following paragraphs does so through a discussion of a collection of individual phenomena without the benefit of a cohesive model capable of quantitatively tying them all together. Quantitative descriptions of processes in homogeneous porous media are much more advanced than for fractured and highly stratified porous media.

The following discussion makes use of a 'typical' fractured clay or till. The first step is to analyze the pre-spill distribution of water and air in the fractures and the matrix. This is necessary because the way LNAPL moves through the medium following a release is highly dependent upon this distribution. The infiltration of LNAPL, with an emphasis on the potential for entry into the matrix, is discussed next. Once the source is terminated, the fluids redistribute themselves and eventually approach static equilibrium. This equilibrium distribution has important implications for site investigation and the potential for removal of the non-aqueous phase. Finally, the processes of matrix contamination and decontamination by diffusion are described.

## 2.2 PRE-SPILL MOISTURE DISTRIBUTION

The medium into which LNAPL infiltrates is conceptualized as a fractured porous medium extending only a very few meters above the water table (Figure A-1). When the system is at hydrostatic equilibrium, the air-water capillary pressure at a distance  $z$  above the water table is (Corey, 1976)

$$P_c \equiv P_a - P_w = \rho_w g z \quad (1)$$

where:  $P_c$  = capillary pressure (F/L<sup>2</sup>)  
 $P_a$  = air pressure (F/L<sup>2</sup>)  
 $P_w$  = water pressure (F/L<sup>2</sup>)  
 $\rho_w$  = water density (M/L<sup>3</sup>)  
 $g$  = gravitational constant (F/M)  
 $z$  = vertical coordinate (L)

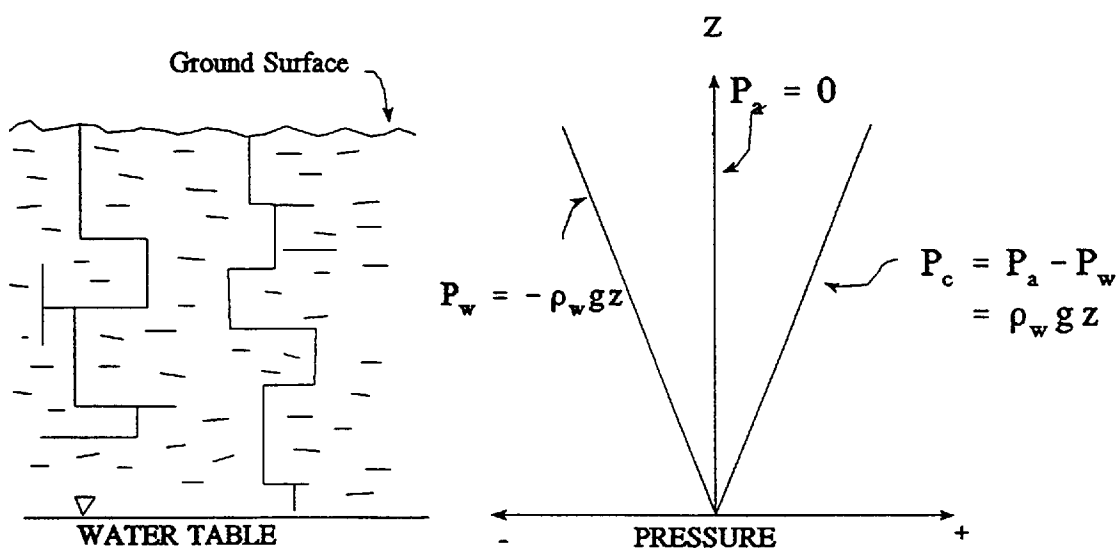


**Figure A-1. Distributions of Air, Water and Capillary Pressures at Static Equilibrium.** Note above the water table, the fluid pressure is under tension, so the hydrostatic pressure line is negative. Since the atmospheric gauge pressure is zero, the capillary pressure is positive and is equal to the hydrostatic pressure measured relative to the water table, positive towards the surface.

The capillary pressure at any  $z$  is the same in the fracture or in the matrix. However, because the characteristic size of a fracture opening is larger than the matrix or interstitial opening, the water content in the fractures can be expected to be much less than in the matrix at the same capillary pressure.

The capillary pressure at which the opening between two parallel smooth solid planes will desaturate is given by (Corey, 1986)

$$P_e = \frac{2 \sigma \cos \alpha}{b} \quad (2)$$

where:  $P_e$  = entry pressure ( $F/L^2$ )  
 $\sigma$  = air-water interfacial tension ( $F/L$ )  
 $\alpha$  = contact angle  
 $b$  = fracture aperture ( $L$ )

The opening remains filled with water until the air pressure exceeds the water pressure by an amount equal to  $P_e$ . By equating the capillary pressure from Eqn. 1 with the entry pressure of Eqn. 2, one obtains an estimate of the height above the water table at which fractures will remain saturated (i.e., contain no continuous air):

$$Z_e = \frac{2 \sigma \cos \alpha}{\rho_w g b} \quad (3)$$

Table A-1 contains estimated values of  $Z_e$  as a function of aperture. Note that  $Z_e$  can be thought of as the height of the capillary fringe in fractures. At heights greater than  $Z_e$  the fracture will contain some continuous air. Of course Eqn. 2 is based on a highly idealized fracture and the values of  $Z_e$  in Table A-1 can be regarded as no more than rough estimates.

| $Z_e$ , meters                                                                   | $b$ , microns |
|----------------------------------------------------------------------------------|---------------|
| 1.22                                                                             | 10            |
| 0.82                                                                             | 15            |
| 0.61                                                                             | 20            |
| 0.49                                                                             | 25            |
| 0.41                                                                             | 30            |
| 0.35                                                                             | 35            |
| 0.31                                                                             | 40            |
| 0.24                                                                             | 50            |
| 0.20                                                                             | 60            |
| 0.12                                                                             | 100           |
| $\sigma \cos \alpha = 60 \text{ dynes/cm}$ , $\rho_w g = 980 \text{ dynes/cm}^3$ |               |

**TABLE A-1. Estimated Heights Above a Water Table At Which Fractures Remain Saturated**

Based on Table A-1, a fractured porous medium with fracture apertures in the range of 10 to 40 microns can be expected to consist largely of air-filled fractures at heights of about 1 meter or greater above the water table. The matrix, however, is much less likely to contain any significant air-filled pores because interstitial openings are very much smaller.

Thomas et al. (1968) provide a means of estimating the entry pressure of fine-grained matrix material. The empirical relationship determined by these authors is:

$$P_e = 7.37 k^{-0.43} \quad (4)$$

where:  $P_e$  = the entry pressure in psi  
 $k$  = intrinsic permeability in millidarcys

Unlike all other equations in this paper, Eqn. 4 is not dimensionally consistent; only the units specified can be used. Of course the results calculated from Eqn. 4 can be subsequently converted to any set of desired units. Table A-2 contains estimates of

the height above a water table at which Eqn. 4 predicts the matrix would begin to desaturate. The data in Table A-2 are expressed in units usually employed by hydrogeologists. The hydraulic conductivity,  $K(L/T)$ , is directly proportional to intrinsic permeability and is the quantity most often measured by hydrologists, either in the laboratory or the field. The height  $Z_e$  in Table A-2 is simply the pressure,  $P_e$ , expressed as the height of water required to generate pressure,  $P_e$ .

It is expected that the matrix blocks in a massive clay/till would exhibit a hydraulic conductivity on the order of  $10^{-6}$  cm/s or less. Therefore, the data in Table A-2 indicate that matrix blocks located 5 m or less above the water table will be water-saturated.

| $Z_e$<br>meters | Hydraulic Conductivity<br>cm/s |
|-----------------|--------------------------------|
| 37              | $1 \times 10^{-8}$             |
| 18.6            | $5 \times 10^{-8}$             |
| 13.8            | $1 \times 10^{-7}$             |
| 6.9             | $5 \times 10^{-7}$             |
| 5.1             | $1 \times 10^{-6}$             |
| 2.6             | $5 \times 10^{-6}$             |
| 1.9             | $1 \times 10^{-5}$             |

**Table A-2. Estimated Heights Above a Water Table At Which Matrix Blocks Will Be Partially Desaturated**

The above discussion suggests that for water tables about 3 m deep, fractures in the upper two-thirds of the vadose zone will be largely air-filled. Matrix blocks throughout the 3-meter zone above the water table will be saturated with water. Of course, any deviation from static equilibrium as would result from, for example, infiltration or evaporation will affect the moisture distribution in way not accounted for in the above analysis. Downward water flow due to infiltration will cause the

fractures to be wetter than predicted here and upward flow due to evaporation will cause the vadose zone very near the ground surface (i.e., within a few centimeters) to be dryer. Evaporation creates a thin zone of dry soil near the surface toward which water flows from below by capillary action.

### 2.3 LNAPL INFILTRATION

The infiltration of LNAPL into the geologic medium preferentially occurs along paths already containing a continuous air phase. Because the LNAPL is a wetting phase in respect to air, it spontaneously imbibes into air-filled openings. As indicated above, fractures are likely to be the only air-filled openings in massive clay/till materials, except near the water table where they too will be water saturated.

On the other hand, spontaneous imbibition of LNAPL into the water-saturated matrix does not occur. The LNAPL is a nonwetting fluid with respect to water and spontaneous displacement of water does not occur. In fact, the pressure of the LNAPL must exceed the water pressure by a threshold value, the entry pressure, in order to initiate penetration.

Entry pressures required for an LNAPL to displace water from the matrix are shown for several LNAPLs in Figure A-2 as a function of the hydraulic conductivity of the porous medium. As before, the entry pressures,  $P_e$ , are expressed as the height of a water column required to generate the pressure  $P_e$ . Expressing pressure in this manner is highly convenient and not unusual (e.g., 14.7 psi = 10.4 m of water = 761 mm of mercury). These curves were calculated from Eqn. 4 after adjustment to account for the different interfacial tensions of the various LNAPL-water fluid pairs. The interfacial tensions given in Appendix A-I were employed. Clearly the entry pressure depends strongly on both the type of LNAPL (i.e., the interfacial tension) and type of porous medium as indicated by the hydraulic conductivity. Recall that hydraulic conductivity  $K(L/T)$  is directly proportional to intrinsic permeability,  $k$ .

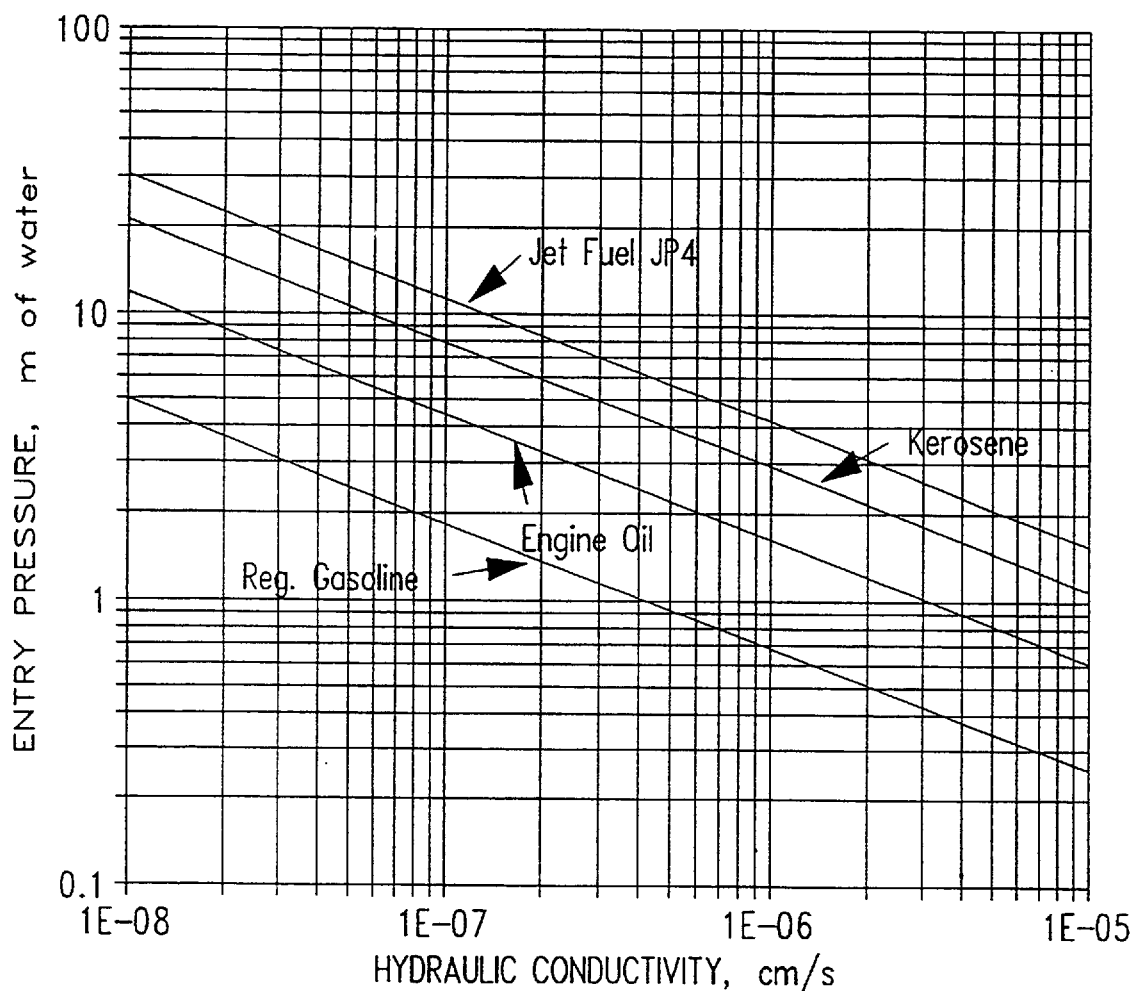
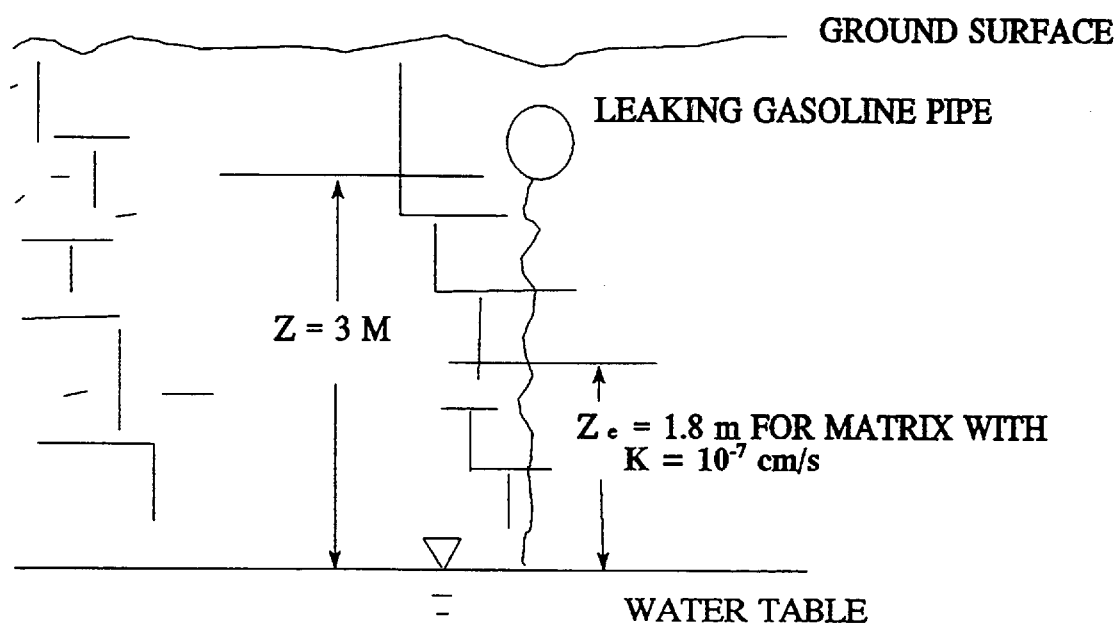


**Figure A-2. Entry Pressures for Various LNAPL's as a Function of Hydraulic Conductivity.** Note that the entry pressure is a direct function of the oil-water interfacial tension. Jet fuel has an interfacial tension almost 2.5 times that of engine oil (hence its higher entry pressure).

How can one determine if the matrix entry pressure is exceeded during infiltration along the fractures? Typically, in the case of a slow leak, the LNAPL enters the soil at or near atmospheric pressure. Thus, the greatest LNAPL pressure during infiltration is likely to be zero gage and occur in the immediate vicinity of the source. Furthermore, the process of LNAPL infiltration is not expected to influence the water pressure in the matrix in any significant way. That is, the distribution of water pressure in the matrix can be taken as hydrostatic.

Suppose the point of entry of LNAPL is  $Z$  meters above the water table as shown in Figure A-3. Then the water pressure there is  $-\rho_w g Z$ . With zero pressure in the LNAPL at the source, the LNAPL-water capillary pressure is  $\rho_w g Z$ . Again, it is convenient to express this pressure as equivalent height of water, in which case it becomes simply  $Z$ . The conclusion is that the matrix entry pressure will likely be exceeded if the LNAPL source at  $Z$  is located more than  $Z_e$  meters above the water table, (i.e., if  $Z > Z_e$ ) where  $Z_e$  is determined by the ordinate in Figure A-2.

As an example, consider a zero-pressure release of gasoline into a fractured till at a point 3 meters above the water table. Note that the gasoline is assumed to reside in a continuous NAPL column and not be in a residual state (with snapped-off NAPL globules). Suppose that the hydraulic conductivity of the matrix is  $10^{-7}$  cm/s, corresponding to an entry pressure of 1.8 m of water, according to Figure A-2.



LNAPL-water capillary pressure at  $z = 3 \text{ m}$  is 3 m of water. This exceeds the LNAPL-water entry pressure of 1.8 m of water. Therefore, invasion of the matrix by LNAPL is to be expected.

**Figure A-3. Example of a Situation in which LNAPL Invasion of the Matrix is Expected**

Because the LNAPL-water capillary pressure of 3 m of water in the vicinity of the source exceeds the estimated entry pressure, some invasion of the matrix is to be expected for this hypothetical case. Had the LNAPL been engine oil, no invasion of the matrix would be anticipated because the entry pressure for engine oil is much greater than for gasoline.

The question now is how rapidly the LNAPL will make its way downward through a fracture to the saturated zone (i.e., the top of the capillary fringe in that fracture). The time required for the LNAPL in a individual fracture to reach a depth  $L_f$  below the ground surface can be estimated from the generalized Green-Ampt formula (Green and Ampt, 1911, Bouwer, 1978):

$$t = \frac{f}{K} \left[ L_f - h_{cf} \ln \left( \frac{L_f + h_{cf}}{h_{cf}} \right) \right] \quad (5)$$

where:  $t$  = time (T)  
 $L_f$  = depth of infiltration "front" (L)  
 $h_{cf}$  = capillary drive (L)  
 $K$  = conductivity of the fracture to LNAPL (L/T)  
 $f$  = fraction of fracture cross-section that is air filled (dimensionless)

Equation 5 is dimensionally consistent and any set of consistent units may be used. The capillary drive,  $h_{cf}$ , represents the capillary action that results in the spontaneous imbibition of the wetting fluid. Recall that the LNAPL is the wetting fluid with respect to the displacement air. To a close approximation, the capillary drive can be taken to be equal to the air-LNAPL entry pressure, expressed as an equivalent height of LNAPL (i.e., the height of a column of LNAPL that will generate the pressure equal to the air-LNAPL entry pressure).

Insight into how rapidly LNAPL will reach the top of the tension-saturated zone (i.e., the top of the capillary fringe) can be gained by putting  $f = 1$  and  $h_{cf}$  equal to the air-LNAPL entry pressure expressed as an equivalent height of LNAPL. Further, the

hydraulic conductivity of the fracture can be estimated from (Corey, 1986):

$$K = \frac{b^2 \rho_o g}{12 \mu_o} \quad (6)$$

where:  $b$  = fracture aperture (L)  
 $\rho_o g$  = unit weight of LNAPL (F/L<sup>3</sup>)  
 $\mu_o$  = dynamic viscosity of LNAPL (FT/L<sup>2</sup>)

Each of the above parameter estimates is exact for a smooth-walled fracture of constant aperture, but are only rough approximations for a real fracture.

Figure A-4 shows the time estimated from Eqns. 5 and 6 for LNAPL to reach a depth of  $L_f = 2$  m as a function of fracture aperture. Viscosity, density, and interfacial tension data appearing in Appendix I were used.

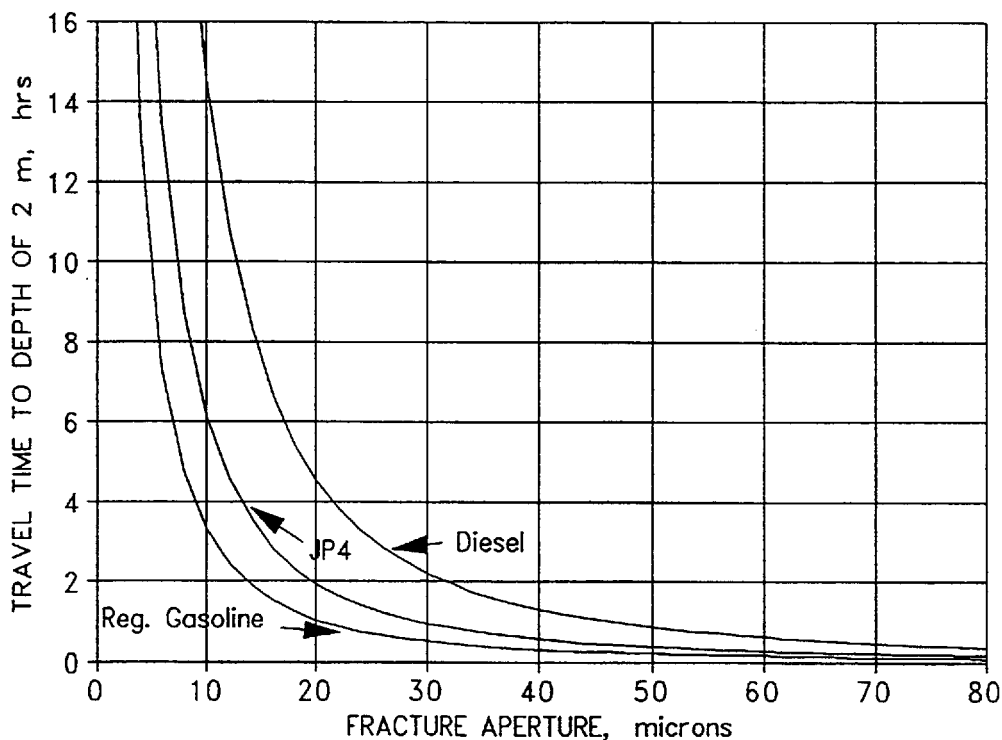


Figure A-4. Time for LNAPL to Infiltrate to a Depth of 2 m

The conclusion supported by Figure A-4 is that LNAPL will travel a distance of 2 m in vertical fractures in a matter of hours or less, even in fractures with apertures as small as 10 microns. Diffusion of LNAPL components into the water-saturated matrix during infiltration will be insignificant due to the small travel time. However, residual LNAPL, formed during redistribution of LNAPL following the cessation of the release, may remain in the fracture for long periods and significant diffusion into the matrix is to be expected after infiltration is complete. Any invasion of the matrix by LNAPL however will increase its travel time to the tension-saturated zone.

Cross-cutting fractures provide the opportunity for LNAPL to spread laterally during the infiltration process. Forces responsible for lateral spreading are, again, capillary drive and gravity. However, the component of gravity acting along cross-cutting fractures is proportional to the sine of the fracture dip angle. Therefore, gravity is most important in steeply-dipping or vertical fractures and has no influence on LNAPL movement in horizontal fractures. Lateral spread of LNAPL during infiltration is expected to be minimal in media with predominantly vertical fractures.

The most significant lateral spread of LNAPL occurs when the infiltrating LNAPL encounters the tension-saturated region just above the water table. At this point the driving force due to gravity is reversed. During air displacement, gravity acts downward on the LNAPL and is proportional to the LNAPL density minus the density of air. Upon encountering the saturated zone, the buoyant force acts upward with a magnitude proportional to the water density minus the LNAPL density. Also, the displacement process shifts from a spontaneous one (LNAPL displacing air) to a nonspontaneous one (LNAPL displacing water). These changes cause the downward movement of LNAPL to cease. Continued infiltration of LNAPL is accommodated by lateral spreading with the pressure gradient as the dominant driving force.

## 2.4 STATIC DISTRIBUTION OF FLUIDS

This analysis again utilizes the idealization of a fracture as the constant-aperture space between two parallel, solid planes. Figure A-5 shows two of the possible



The principles of fluid statics, together with Eqn. 4, lead to the following equations for the location  $h_w$  of the water table and  $h_o$  of the 'oil table' relative to the LNAPL-water interface in the fracture:

$$h_w = \frac{2}{b} (\sigma_{ao} \cos \alpha_{ao} + \sigma_{ow} \cos \alpha_{ow}) - \frac{\rho_o}{\rho_w} T \quad (7)$$

and

$$h_o = T - \frac{2 \sigma_{ao} \cos \alpha_{ao}}{\rho_o g b} \quad (8)$$

where:  $h_w$  = water table location relative to the LNAPL-water interface (L)  
 $h_o$  = oil table location relative to the LNAPL-water interface (L)  
 $\rho_o$  = LNAPL mass density (M/L<sup>3</sup>)  
 $T$  = thickness of LNAPL layer (L)  
 $b$  = fracture aperture (L)  
 $\sigma$  = interfacial tension (F/L)  
 $\alpha$  = contact angle

and subscripts  $ao$  and  $ow$  denote air-LNAPL and LNAPL-water, respectively. The oil table is defined as the surface on which the LNAPL pressure is zero gage.

Putting  $h_o = 0$  in Eqn. 8 yields the combination of parameters for which all of the LNAPL in the fracture exists at negative gage pressure, i.e. held in the fracture by capillarity. LNAPL at negative pressure will not enter a piezometer or monitoring well and will not be detected by these devices. Figure A-6 shows the maximum thickness  $T_m$  that can exist in a fracture at negative pressure. Fluid properties used to prepare Figure A-6 are those in Appendix A-I. The curves for all other fluids tabulated in Appendix A-I fall between the two extremes shown in Figure A-6.

While these calculations are based on a highly idealized model of a fracture, it may, nevertheless, be concluded that large thicknesses of LNAPL can reside in fractures at negative pressure and would be incapable of flowing into a monitoring or extraction well. Even if the volume of LNAPL is such that  $T$  exceeds  $T_m$ , a highly significant

fraction of the LNAPL will be at negative pressure and inaccessible by wells or drains. For example, only 50 percent of a 30 cm thickness of regular gasoline in a 20 micron fracture is potentially recoverable by direct pumping.

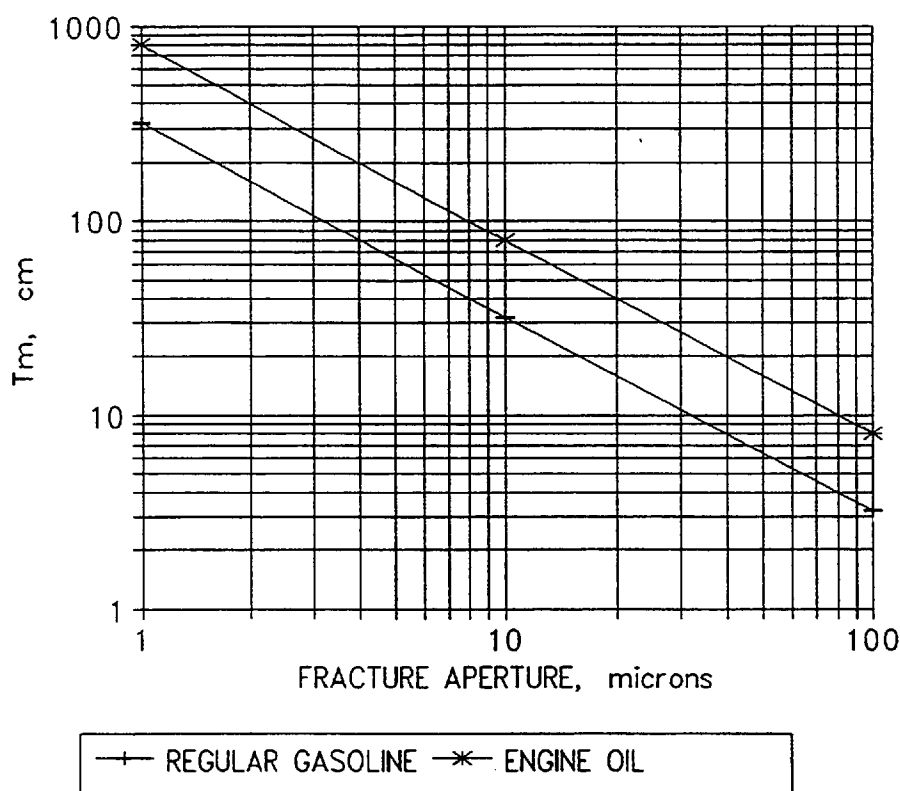


**Figure A-6. Maximum Thickness of LNAPL that can Exist in a Fracture at Negative Pressure**

Equation 7 indicates where the LNAPL is likely to be located in the fracture relative to the water table. Large thicknesses  $T$  in fractures with large apertures will be located so that a part of the LNAPL is below the water table (i.e.,  $h_w$  is negative). Thin layers of LNAPL in fractures with small apertures reside above the water table. Furthermore, Eqns. 7 and 8 show that it is possible for LNAPL at positive pressure to be located entirely above the water table where the water pressure is negative.

Because real soils contain fractures with a variety of apertures, little or no uniformity of LNAPL thicknesses and locations is to be expected. While cross-cutting fractures that interconnect the LNAPL in many vertical fractures cause the LNAPL pressure to be uniform in horizontal planes, the variety of apertures still produces a nonuniform upper surface of the LNAPL body as a whole. And there exists a distribution of apertures in a single fracture that causes an individual fracture to exhibit properties of a porous medium at some scale (Kueper and McWhorter, 1991, 1992).

Finally it should be mentioned that the LNAPL at mechanical equilibrium in the fractures is not likely to coexist in the matrix. That is, LNAPL that readily enters the fracture is not likely to also enter the matrix. Very large thicknesses of LNAPL would be required to develop LNAPL-water capillary pressures sufficient to exceed the entry pressures calculated in Figure A-2. Note that LNAPL-water capillary pressures increase with elevation at a rate proportional to the difference  $\rho_w - \rho_o$ . This rate of increase is typically a factor of 5 less than in an air-water system. Therefore, if the air-water capillary pressure prior to the LNAPL release was insufficient to effect air entry into the matrix, the LNAPL-water capillary pressure will likewise be insufficient to initiate LNAPL invasion of the matrix. The exception occurs when the LNAPL-water interfacial tension is more than a factor of 5 less than air-water interfacial tension. This is rarely the case, and if the matrix was water-saturated prior to the release, it is highly likely that LNAPL will not enter the matrix during or after the release. However, as discussed in the next section, dissolved constituents will enter the matrix via aqueous diffusion.

## 2.5 MATRIX CONTAMINATION BY DISSOLVED COMPONENTS

While the high entry pressure of water-saturated matrix blocks is expected to prevent LNAPL invasion, matrix waters may, nevertheless, become contaminated.

Constituents of the LNAPL in the fractures dissolve into the contiguous aqueous phase and diffuse through the water into the matrix. The rate of diffusion is enhanced by the tendency for dissolved chemicals to partition to the solid by

adsorption.

The maximum mass of a particular chemical species that can be stored in dissolved and adsorbed form in a saturated matrix block per unit volume of soil can be deduced from the work of Feenstra et al. (1991):

$$M_m = \phi_m R C_o \quad (9)$$

where:  $M_m$  = maximum mass of an individual species that can be stored in the dissolved and adsorbed form in the matrix per unit bulk volume ( $M/L^3$ )  
 $\phi_m$  = porosity of the matrix (dimensionless)  
 $R$  = retardation factor (dimensionless)  
 $C_o$  = effective solubility ( $M/L^3$ )

The retardation factor is defined by (Freeze and Cherry, 1979):

$$R = 1 + \frac{K_d \rho_b}{\phi_m} \quad (10)$$

where:  $K_d$  = distribution coefficient ( $L^3/M$ )  
 $\rho_b$  = dry bulk density ( $M/L^3$ )

The distribution coefficient,  $K_d$ , characterizes the tendency for dissolved constituents to partition to the solid. Adsorption of organic species is a strong function of the amount of organic matter in the soil (Karickhoff et al., 1979) and  $K_d$  is usually estimated from:

$$K_d = f_{oc} K_{oc} \quad (11)$$

where  $f_{oc}$  is the fractional organic content of the soil and  $K_{oc}$  is the organic carbon partition coefficient. Mercer and Cohen (1990) list values of  $K_{oc}$  for several

compounds important in many LNAPL's.

The potential for mass storage of chemicals in the dissolved and adsorbed state in the matrix is often significant relative to the mass that can be stored in fractures in the liquid state. Consider benzene as an example and suppose that  $f_{oc} = 0.005$ . Then  $K_d$  is estimated to be about  $0.4 \text{ cm}^3/\text{g}$ , and  $R$  is 1.9 for a matrix material with  $\rho_b = 1.7 \text{ g/cm}^3$  and  $\phi_m = 0.36$ . The pure-phase solubility of benzene is  $1750 \text{ mg/l}$  (Mercer and Cohen, 1990) and Eqn. 9 predicts  $M_m = 1.2 \text{ kg}$  of dissolved and adsorbed benzene per cubic meter of matrix material.

Assume the fracture porosity to be 0.001. Then the volume of liquid benzene in the fractures can be no greater than  $1 \text{ l/m}^3$ , corresponding to a mass of about  $0.87 \text{ kg/m}^3$ . In this example, the capacity for storage as dissolved and adsorbed chemical in the matrix exceeds the capacity for storage in the fractures. Of course, it is not expected that benzene would occur as a pure phase, as assumed in this example. The effective solubility of benzene in water, when the benzene is only one component of a hydrocarbon liquid, is far less than the pure phase solubility. The calculation is presented here only to illustrate that quite significant mass of chemical can be stored in the matrix.

Parker (1992) has calculated diffusion from fractures into matrix blocks for several DNAPL's under a variety of circumstances. A salient conclusion of this work is that the liquid phase contaminant in a fracture is eliminated by the diffusion process in time intervals ranging from weeks to several months, depending on the chemical in question, the fracture aperture, and the organic carbon content of the soil. Parker's calculations have not yet been extended to the complex chemical mixture comprising the typical LNAPL (e.g., gasoline). Nevertheless, Parker's analysis leaves little doubt that significant mass loss from the liquid in the fracture occurs in time periods on the order of weeks to months. Also, the mass loss due to diffusion is generally most rapid for the most soluble species. For this reason, the chemical composition of any remaining liquid in the fracture is significantly modified.

Attempts to remove dissolved and adsorbed chemical from the matrix are severely limited by the rate at which diffusion in the reverse direction can be effected. The concentration of dissolved chemical in the fractures can be reduced by flushing with air or water, thus establishing a reverse gradient in the vicinity of the fracture faces. However, the reverse gradient is not as great, on the average, as is the gradient during the contamination period. Also, diffusion in the interior of the matrix blocks proceeds inward concurrently with outward diffusion on the boundaries. These factors combine to cause the process of contaminant removal from the matrix to be much slower than the process of becoming contaminated in the first place.

A simple analysis for diffusion in a semi-infinite matrix block demonstrates the difficulty. Let  $M_R$  be the dissolved and adsorbed mass remaining after a period  $t_R$  of 'remediation'. Remediation in this case refers to the act of reducing the chemical concentration in the fractures to zero. The mass diffused into the matrix during a time interval  $t_D$  prior to remediation is  $M_D$ . Then the fraction of  $M_D$  that remains in the matrix at remediation time  $t_R$  is (see Appendix A-II for derivation):

$$\frac{M_R}{M_D} = \left( 1 + \frac{t_R}{t_D} \right)^{1/2} - \left( \frac{t_R}{t_D} \right)^{1/2} \quad (12)$$

Only as  $t_R$  approaches infinity will remediation be complete. Perhaps more revealing from a practical point of view is the fact that only 85 percent of the mass is removed (i.e.,  $M_R/M_D = 0.15$ ) when remediation has proceeded for an interval 10 times as long as the contamination interval. If the LNAPL had been present in the fractures for 2 years prior to the initiation of remediation, 85 percent removal would require 20 years. Ninety-five percent removal requires a remediation interval 100 times as long as the contamination interval.

### Section 3

## STRATIFIED LOW PERMEABILITY SOILS

Many of the principles employed in the discussion of massive clay/till soils are relevant to stratified, low permeability soils as well. The soils of concern in this section are fine-grained and exhibit an overall low permeability. But the profile is not homogeneous. Rather the soil is regarded as being comprised of randomly distributed layers of variable thickness, each with a different permeability (hydraulic conductivity). The outline of subjects undertaken in the present case is the same as in the previous discussion.

### 3.1 PRE-SPILL MOISTURE DISTRIBUTION

At mechanical equilibrium, the distributions of fluid pressures are independent of the geologic medium in which the fluids reside. Thus, Eqn. 1 calculates the air-water capillary pressure in the stratified porous media of concern in this section. As in the previous case, there exists a capillary fringe (or tension-saturated zone) immediately above the water table in which the porous medium contains no continuous air phase. The capillary pressure at points above the top of the capillary fringe exceeds the air-water entry pressure, at least for some strata, and continuous air co-exists with water in the pores.

However, the entry pressure of a stratified soil is not uniform. The layers with low hydraulic conductivity have higher entry pressures and vice-versa (see Table A-2). Given a random distribution of strata with different textures, the zones high above the water table exhibit higher overall air contents than those near the water table. However, a particular stratum with low hydraulic conductivity may remain water-saturated, regardless of where it is located in the profile.

The relationship between water saturation and capillary pressure is called the capillary pressure-saturation curve or, sometimes, the water retention curve. In general, this relationship must be measured and it is different for each soil type in

the profile. Even for a particular stratum the capillary pressure-saturation curve is not unique; it depends upon the saturation history (i.e., on the history of wetting and drying).

Insight to the variability of water saturation that is to be expected in a stratified soil is gained by examining a popular algebraic expression for the capillary pressure-saturation curve (Brooks and Corey, 1966):

$$S_w = (1 - S_r) \left( \frac{P_c}{P_e} \right)^{-\lambda} + S_r, \quad P_c \geq P_e \quad (13)$$

$$S_w = 1.0, \quad P_c \leq P_e$$

where:  $S_w$  = water saturation; i.e. the fraction of pore space occupied by water (dimensionless)  
 $S_r$  = residual saturation (dimensionless)  
 $P_c$  = capillary pressure ( $F/L^2$ )  
 $P_e$  = air-water entry pressure ( $F/L^2$ )  
 $\lambda$  = pore-size distribution index (dimensionless)

At static equilibrium the value of  $P_e$  (expressed as an equivalent height of water) is numerically equal to the elevation of the point in question relative to the water table elevation. Hence,  $S_w(z)$  can be computed if the parameters  $P_e$ ,  $\lambda$ , and  $S_r$  are known for each stratum. By far, the biggest influence on  $S_w$  is imparted by  $P_e$ . Clearly, a jagged, highly irregular water-saturation distribution is to be expected, owing to abrupt changes of  $P_e$  from stratum to stratum. Because the soil under consideration is of overall low permeability, all entry pressures are rather large, and the overall water content is high.

### 3.2 LNAPL INFILTRATION

As in the previous discussion, LNAPL spontaneously imbibes into pore space occupied by continuous air. Infiltration proceeds, therefore, along paths in which

there existed continuous air prior to the release of LNAPL. However, in contrast with the vertically fractured soil, the infiltrating LNAPL is likely to encounter a water-saturated stratum that it is unable to readily penetrate. Recall that the LNAPL-water entry pressure must be exceeded for the initiation of LNAPL invasion.

Upon encountering a water-saturated layer (and the layer can be quite thin), the LNAPL begins to spread laterally. At the same time, the LNAPL pressure increases as more LNAPL accumulates from above. If the pressure becomes sufficiently great, the LNAPL-water entry pressure of the water-saturated layer is exceeded and LNAPL once again moves downward. Prediction of the degree of lateral spreading and the eventual breakthrough of LNAPL is severely constrained because of the lack of knowledge of the media properties at the very small scale required.

Consider the following situation in which a stratum of known hydraulic conductivity is located at elevation  $Z$  above the water table and  $(D - Z)$  below ground surface. If LNAPL should accumulate on this stratum to the maximum possible depth of  $(D - Z)$ , then the maximum LNAPL-water capillary pressure that can develop is:

$$P_{cm} = (\rho_w - \rho_o) g z + \rho_o g D \quad (14)$$

Penetration of the stratum will not occur if the capillary pressure calculated from Eqn. 14 is less than the entry pressure estimated from Figure A-2. Clearly, a water-saturated stratum is more likely to form a barrier to further downward migration if it is located near the water table (i.e., small  $Z$ ). Also, it is apparent that the likelihood of a water-saturated layer above the water table preventing any further downward migration of LNAPL becomes less as the depth  $D$  to the water table increases.

### 3.3 STATIC DISTRIBUTION OF FLUIDS

Owing to the essentially unknowable distribution of capillary properties in a stratified soil, the calculation of fluid distributions is not practical, although possible in principle. However, there is value in the examination of fluid distributions in

homogeneous soils. In particular, the way that overall soil texture influences the fluid distribution is important.

Air, water and LNAPL distribute themselves at mechanical equilibrium as shown in Figure A-7 (Farr et al., 1990, Lenhard and Parker, 1990). It is observed that there exists a zone in which all three fluids coexist. Below that zone is one in which only LNAPL and water fill the pores. The bottom of the LNAPL zone may be located somewhat below the water table or above it, depending upon the volume of LNAPL and the capillary properties of the fluid-porous medium system.

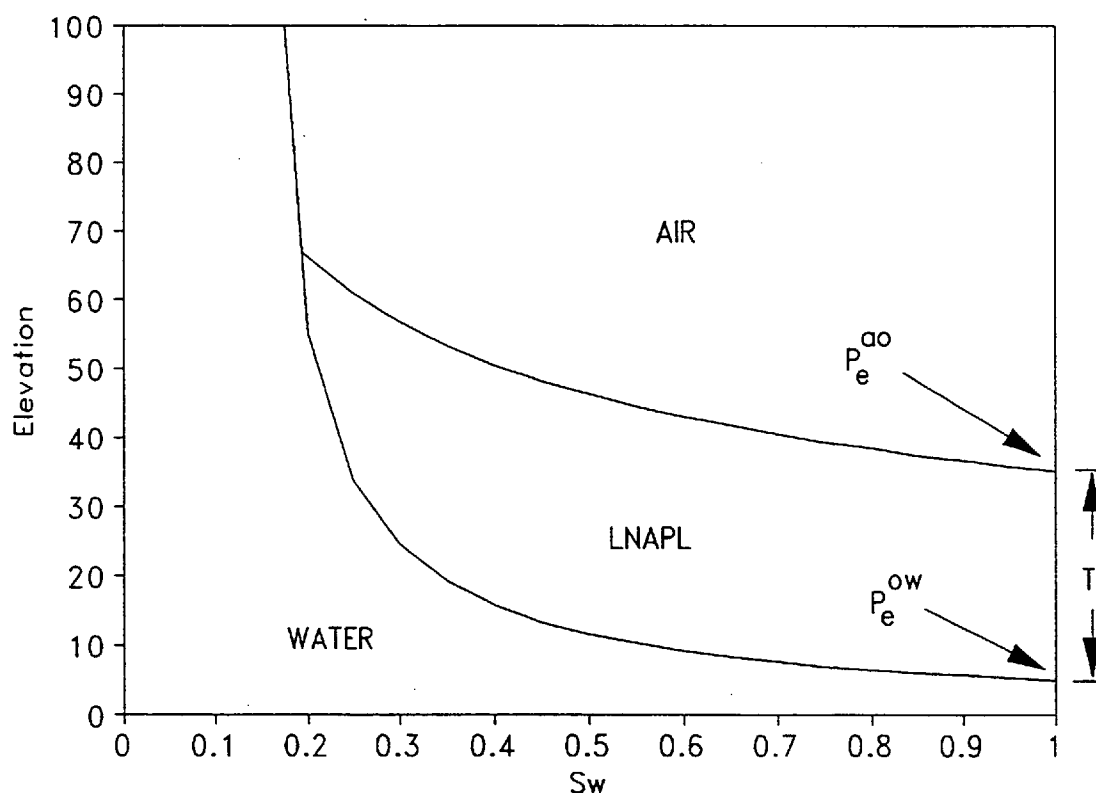


**Figure A-7. Fluid Distributions in a Homogeneous Porous Media at Static Equilibrium**

The capillary pressure at the bottom of the LNAPL body is the LNAPL-water entry pressure. At the bottom of the zone in which air exists, the capillary pressure is the air-LNAPL entry pressure. All of the LNAPL in the soil resides at negative gage pressure if:

$$T \leq P_e^{ao} / \rho_o g \quad (15)$$

Low permeability soils with no cracks, root holes or other macro-features have large entry pressures. For this reason, low permeability soils are capable of storing significant quantities of LNAPL at negative pressure. Such LNAPL has no potential to be detected or removed by wells.

It is possible to relate  $T$  in Eqn. 15 to the volume of LNAPL present for homogeneous soils. However, stratification of the soil and fluctuation of the water table largely invalidate the numerical results of such a computation. A rising water table entraps some LNAPL in the form of occluded bubbles and globules. Such LNAPL is known as residual. A large rise in the water table can deplete the entire mobile LNAPL body into residual. When the water table falls, the residual LNAPL again becomes continuous and potentially mobile. Most of the LNAPL is found to reside in the more permeable strata.

### 3.4 CONTAMINATION BY DISSOLVED COMPONENTS

During infiltration of LNAPL into a stratified soil, it is to be expected that significant lateral spreading will occur in the more permeable layers. At any particular location, low permeability layers may remain water-saturated, yet be bounded above and below by strata containing LNAPL. Components of the LNAPL dissolve in the contiguous water and diffuse into the water-saturated strata. As with the matrix blocks in a fractured porous medium, removal of the dissolved contaminants from such strata is diffusion-controlled.

## Section 4

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