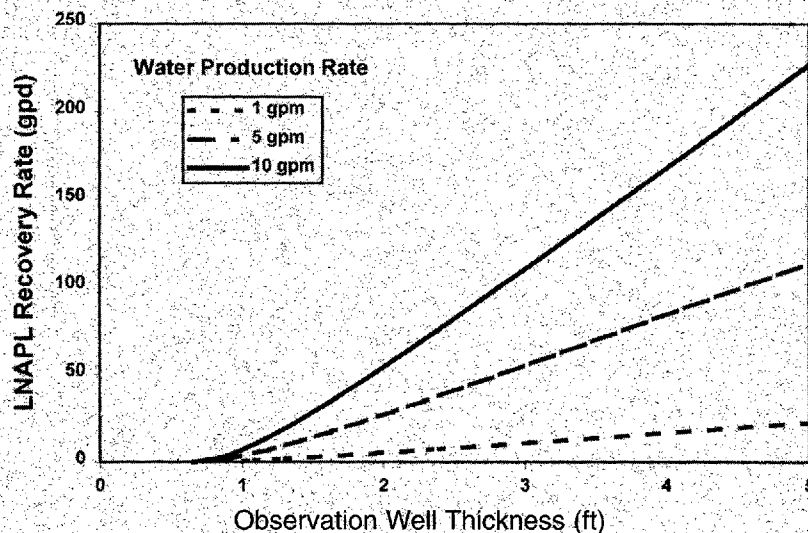
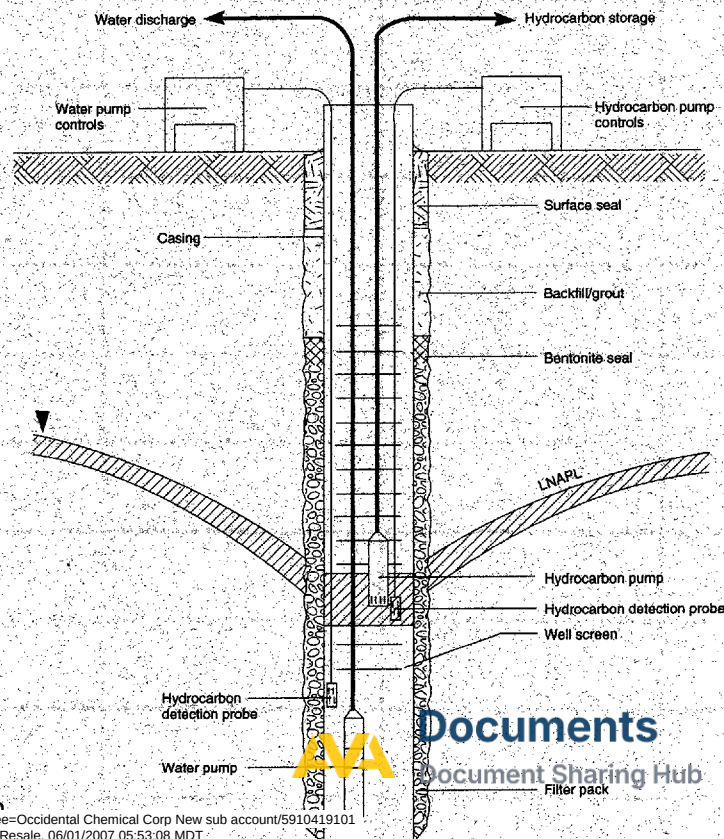


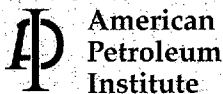
FREE-PRODUCT RECOVERY OF PETROLEUM HYDROCARBON LIQUIDS



HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4682
JUNE 1999



Dual-Pump Recovery System



American Petroleum Institute Environmental, Health, and Safety Mission and Guiding Principles

MISSION

The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. We recognize our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to the following principles using sound science to prioritize risks and to implement cost-effective management practices:

PRINCIPLES

- To recognize and to respond to community concerns about our raw materials, products and operations.
- To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.
- To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.
- To advise promptly, appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.
- To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.
- To economically develop and produce natural resources and to conserve those resources by using energy efficiently.
- To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.
- To commit to reduce overall emission and waste generation.
- To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.
- To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.
- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.



FREE-PRODUCT RECOVERY OF PETROLEUM HYDROCARBON LIQUIDS

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4682

PREPARED UNDER CONTRACT BY:

**RANDALL J. CHARBENEAU
RUSSELL T. JOHNS
LARRY W. LAKE
MICHAEL J. McADAMS, III
UNIVERSITY OF TEXAS
AUSTIN, TEXAS**

JUNE 1999



**American
Petroleum
Institute**



Documents

Document Sharing Hub

FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

All rights reserved. No part of this work may be reproduced, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the publisher, API Publishing Services, 1220 L Street, N.W., Washington, D.C. 20005.

Copyright © 1999 American Petroleum Institute

ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACT

Harley Hopkins, Health and Environmental Sciences Department

MEMBERS OF THE SOIL AND GROUNDWATER TECHNICAL TASK FORCE

&

MEMBERS OF THE GW- 50 PROJECT TEAM

Phil Bartholomae, BP Amoco, PLC

Brian Bean, Phillips Pipeline Company

Chen Chiang, Equilon Enterprises, LLC

Steve Jester, Conoco, Inc.

Ravi Kolhatkar, BP Amoco, PLC

Victor Kremesec, BP Amoco, PLC

Urmes Kelmser, Chevron Research and Technology Company

R. Edward Payne, Mobil Business Resources Corporation

Patrick Shevlin, Equistar Pipeline

Terry Walden, BP Amoco, PLC

Lesley Hay Wilson, BP Amoco, PLC

PREFACE

Spreadsheets have been developed to perform many of the calculations presented in Sections 3.5 and 3.8 and the nomograph calculations presented in Sections 5.7 and 5.8 for single- and dual-pump recovery systems and for vacuum-enhanced systems. The MS Excel spreadsheet (workbook) for Sections 3.5 and 3.8 titled *LNAPL Distribution.xls* and the spreadsheet (workbook) for Sections 5.7 and 5.8 titled *LNAPL Recovery.xls* are available for download from the web address www.api.org/ehs/fpr/tools.htm. Application and use of these spreadsheets are described in Appendices C and D.



Table of Contents

<u>Section</u>	<u>Page</u>
Executive Summary	ES.1
Section 1 INTRODUCTION	
1.1 Purpose and Scope	1.1
1.2 Background	1.2
1.3 Organization	1.4
1.4 Supplementary References	1.4
Section 2 SUBSURFACE MIGRATION OF LNAPL AND GROUNDWATER	
2.1 Subsurface Environment	2.1
2.2 Description of Subsurface Flow	2.3
2.3 Fluid Saturation and Capillary Pressure	2.4
2.4 Hydraulic Gradient.....	2.6
2.5 Darcy's Law.....	2.7
2.6 Relative Permeability.....	2.8
2.7 Groundwater Recovery by Wells	2.10
2.8 Air Flow to a Well	2.13
Section 3 SIGNIFICANT VARIABLES AND PARAMETERS	
3.1 LNAPL Fluid Properties: Density and Viscosity	3.2
3.1.1 Fluid Density	3.2
3.1.2 Fluid Viscosity	3.3
3.2 Soil Texture	3.6
3.3 Porosity and Fluid Saturation	3.8
3.3.1 Porosity	3.8
3.3.2 Fluid Saturation.....	3.10
3.4 Capillary Pressure Relationships.....	3.11
3.5 Formation Free-Product "Thickness" Under Vertical Equilibrium.....	3.18
3.5.1 Background and Theory.....	3.18
3.5.1.1 Vertical Distribution of Fluid Saturation.....	3.20
3.5.1.2 LNAPL and Water Distribution.....	3.23



3.5.1.3	Free-Product LNAPL Volume	3.25
3.5.2	Results for Different Soil Textures.....	3.27
3.5.3	Discussion.....	3.34
3.6	Hydraulic Conductivity and Intrinsic Permeability	3.34
3.7	Relative Permeability.....	3.35
3.8	Effective LNAPL Layer Saturation and Relative Permeability.....	3.39
3.9	Residual LNAPL Saturation.....	3.42
3.10	Water Table Fluctuations and Vertical Equilibrium	3.43

Section 4 FREE-PRODUCT RECOVERY TECHNOLOGY

4.1	Interceptor Trenches	4.1
4.1.1	Advantages and Limitations	4.2
4.1.2	Common Site Conditions for Use	4.3
4.1.3	Operation and Maintenance	4.4
4.2	Skimmer Well Free-Product Removal Systems.....	4.6
4.2.1	Advantages and Limitations	4.7
4.2.2	Common Site Conditions for Use	4.7
4.2.3	Operation and Maintenance	4.8
4.3	Single- and Dual-Pump Recovery Systems.....	4.9
4.3.1	Advantages and Limitations	4.10
4.3.2	Common Site Conditions for Use	4.12
4.3.3	Operation and Maintenance	4.12
4.3.4	Separation and Treatment of Extracted Water	4.14
4.4	Vacuum-Enhanced Recovery	4.15
4.4.1	Advantages and Limitations	4.15
4.4.2	Common Site Conditions for Use	4.16
4.4.3	Operation and Maintenance	4.17
4.5	Selection of Free-Product Recovery Systems	4.18

Section 5 ANALYSIS AND DESIGN OF FREE-PRODUCT RECOVERY SYSTEMS

5.1	Modeling Free-Product Recovery Systems	5.1
5.2	Trenches	5.2
5.3	Skimmer Wells.....	5.6
5.4	Single- and Dual-Pump Wells.....	5.7

5.4.1	"Small" Drawdown.....	5.12
5.5	Determination of Production Rates for No LNAPL Smearing.....	5.13
5.6	Well Interference	5.15
5.7	Estimation of Recovery Times.....	5.18
5.7.1	Use of Recovery Time Nomograph.....	5.20
5.8	Vacuum-Enhanced Recovery Systems	5.21
5.8.1	Vapor-Phase Mass Removal with Vacuum- Enhanced Recovery	5.23
5.9	Examples on Selection and Design of FPR Systems	5.25
5.9.1	Example 1: Selection and Design of a FPR System	5.26
5.9.1.1	Discussion: Selection of Capture Radius R_c	5.31
5.9.2	Example 2: LNAPL Recovery from Low-Permeability Soil Using Vacuum-Enhanced Systems.....	5.31
5.9.2.1	Discussion: Interpreting Layer Saturation	5.38
5.9.3	Example 3: van Genuchten Model for LNAPL Recovery.....	5.39
Section 6	REFERENCES	6.1
Appendix A:	Effect of Vertical Equilibrium and Capillary Pressure on LNAPL Recovery	A.1
Appendix B:	Maximum LNAPL Rates for Skimmer Pumps and Dual-Pump Wells.....	B.1
Appendix C:	Spreadsheet Calculations of LNAPL Distribution.....	C.1
Appendix D:	Spreadsheet for LNAPL Recovery Analysis.....	D.1
Appendix E:	Technical Note on Use of Scaling Functions in Calculations of Oil Specific Volume and Recovery Time Estimation.....	E.1



List of Tables

<u>Table</u>	<u>Page</u>
2.1.1 Capillary Rise in Soils Having Similar Porosity (0.41) after 72 Days (from Lohman, 1972).....	2.2
3.1.1 Representative LNAPL Density Values (gm/cm ³)	3.4
3.1.2 Representative Dynamic Viscosity Values (centipoise).....	3.5
3.2.1 USDA Particle Size Classification	3.7
3.3.1 Total Porosity of Natural Porous Media.....	3.10
3.3.2 Average Porosity (Standard Deviation) Values Based on Soil Texture	3.11
3.4.1 Interfacial and Surface Tension (dynes/cm) at 20° C	3.12
3.4.2 Descriptive Statistics from Carsel and Parrish (1988) Data Set	3.17
3.5.1 Brooks and Corey Soil Parameters from Carsel and Parrish (1988) Data Set Estimated Using Equation (3.4.7)	3.29
3.5.2 Best Linear Fit for LNAPL Thickness Using Equation (3.5.25).....	3.33
3.6.1 Typical Value of Hydraulic Conductivity (after Marsily, 1986).....	3.36
3.6.2 Hydraulic Conductivity of Different Soil Texture Classes from the Data Set of Carsel and Parish (1988)	3.36
3.9.1 LNAPL Residual Saturation and Volumetric Retention Capacity Values (after Mercer and Cohen, 1990). R is the Volumetric Retention Capacity	3.43
4.5.1 Summary Characteristics of Free-Product Recovery Technologies	4.20
5.8.1 Representative Data for a VER System	5.25

List of Figures

Figure		Page
2.1.1	Generalized Profile of the Subsurface.....	2.3
2.2.1	Pore-Scale View of Subsurface Flow	2.4
2.6.1	Typical Relative Permeability Curve for a Sandy Soil	2.9
2.7.1	Drawdown-Discharge Relationship for an Unconfined Aquifer....	2.12
3.2.1	Typical Grain Size Distribution Curve.....	3.7
3.2.2	USDA Soil Texture Triangle	3.8
3.4.1	Soil Moisture Characteristic Curve	3.14
3.5.1	Liquid Distribution Within the Formation and in a Monitoring Well for Floating Free-Product Hydrocarbon	3.19
3.5.2	Vertical Saturation Distribution of LNAPL (35° API Fuel) in a Sand and Loam Soil Where Both Profiles Have the Same LNAPL Quantity	3.28
3.5.3	LNAPL Thickness for 35° API Fuel in Different Soil Textures	3.30
3.5.4	LNAPL Thickness and Best Linear Model for Sand Soil	3.31
3.5.5	Piecewise Linear Fit for Loam Soil	3.32
3.7.1	Relative Permeability Distribution for a Sand Soil with Monitoring Well Thickness of $b_0 - 1$ m	3.39
3.8.1	Effective LNAPL Layer Relative Permeability, $\bar{k}_{r0}$	3.41
4.1.1	Plan and Section View for Example Trench	4.3
4.1.2	Vertical Cross Section of Section A-A' of Figure 4.1.1	4.4
4.1.3	Vertical Cross Section B'-B of Figure 4.1.1	4.5
4.2.1	Pneumatic Pump Skimming System (from API, 1996)	4.7
4.2.2	Skimmer Well Pump Types (modified from Breslin, 1996)	4.9
4.3.1	Single-Pump Recovery System (from API, 1996)	4.10
4.3.2	Dual-Pump Recovery System (from API, 1996)	4.11
4.3.3	An API Oil/Water Separator	4.14
4.4.1	Vacuum-Enhanced Recovery Systems (from API, 1996).....	4.16



Documents

Document Sharing Hub

5.2.1	LNAPL (35° API Fuel) Recovery from a Trench for a Sand Soil with a Hydraulic Gradient of 0.01	5.4
5.2.2	Flow Pattern on the Upstream Side of a Trench with Water Production of 1 GPM	5.5
5.2.3	Flow Pattern on the Upstream and Downstream Side of a Trench with Water Production of 5 GPM	5.6
5.3.1	LNAPL Recovery Rates from a Skimmer Well for 35° API Fuel in Sand, Loamy Sand and Sandy Loam Soils	5.8
5.3.2	LNAPL Recovery Rates from a Skimmer Well for Gasoline ($\rho_r = 0.7$, $\mu_r = 0.3$) in Sand, Loamy Sand and Sandy Loam Soils	5.9
5.4.1	Distribution of Drawdown with Radial Distance from the Well for the LNAPL and Groundwater Layers	5.10
5.4.2	LNAPL Recovery Rate form Single- and Dual-Pump Wells for 35° API Fuel in Sand Soil	5.11
5.4.3	Percent Error in Using Equation (5.4.3) Instead of the More General Result from Equation (5.4.4) for LNAPL Recovery in an Unconfined Aquifer	5.13
5.5.1	LNAPL and Water Interface for Condition of (a) Upcoming, (b) Drawdown, and (c) No Smearing	5.14
5.5.2	Dimensionless Maximum LNAPL Recovery Rates for Zero-Smearing for Conditions with $R/r_w = 100$	5.15
5.5.3	Dimensionless Maximum Water Recovery Rates for Zero-Smearing for Conditions with $R/r_w = 100$	5.16
5.6.1	Simulation Domain to Investigate Well Interference	5.16
5.6.2	Cumulative Recovery of 35° API Fuel for Different Production Well Spacing	5.17
5.7.1	Recovery of LNAPL Layer	5.18
5.7.2	Recoverable Free-Product LNAPL	5.19
5.7.3	Nomograph for Recovery Times Using Single- and Dual-Pump Systems	5.21
5.8.1	Groundwater Production Rates That Produce LNAPL Quantities Equal Those Produced by a Vacuum of 5 ft (0.15 atmospheres)	5.23
5.8.2	Concentration Boundary Layer Development Above a Floating Free-Product Layer (after Johnson <i>et al.</i> 1990)	5.24
5.9.1	Plan View of LNAPL Lens	5.26

5.9.2	Recovery System with 10 Wells and a Radius of Capture of 75 feet	5.28
5.9.3	Worksheet 1 for Loam Soil	5.32
5.9.4	Worksheet 2 for Loam Soil	5.33
5.9.5	Worksheet for First Set of Computations	5.35
5.9.6	Worksheet for Second Computation Set	5.36
5.9.7	Worksheet for Third Computation Set	5.37
5.9.8	LNAPL Distribution.xls Worksheet for $b_o = 0.239$ m	5.39
5.9.9	LNAPL Thickness Relationship for van Genuchten Model	5.40
5.9.10	Computation Worksheet for First Period – Example 3	5.42
5.9.11	Computation Worksheet for Second Period – Example 3	5.43
5.9.12	Computation Worksheet for Third Period – Example 3	5.44
A-1	Effect of the VE assumption on the Steady-State NAPL Rate after One Year of NAPL Recovery (no capillary pressure)	A.5
A-2	Effect of Capillary Pressure and the VE Assumption on the Steady-State NAPL Rate	A.5
B-1	Steady Incompressible Radial Flow of Oil and Water to a Dual-Pumping Well in a Homogeneous Medium	B.2
B-2	Maximum Dimensionless LNAPL Rate Versus Water Production from a Single- or Dual-Pump Well with $\rho_r = 0.80$, $b_{oDi} = 0.10$, $r_{De} = 1000$	B.6
B-3	Illustration of Volume Smeared Below the Original Water Table	B.6
B-4	Example of Dimensionless Volume of LNAPL Smeared Below the Water Table for a Single- or Dual-Pump Well with $\rho_r = 0.80$, $b_{oDi} = 0.10$, $r_{De} = 1000$	B.7
B-5	Dimensionless Maximum LNAPL Recovery Rates for Zero-Smearing for Conditions with $R/r_w = 10$	B.7
B-6	Dimensionless Maximum Water Recovery Rates for Zero-Smearing for Conditions with $R/r_w = 10$	B.8
B-7	Dimensionless Maximum LNAPL Recovery Rates for Zero-Smearing for Conditions with $R/r_w = 1000$	B.8
B-8	Dimensionless Maximum Water Recovery Rates for Zero-Smearing for Conditions with $R/r_w = 1000$	B.9

C-1	Brooks and Corey Data Entry Worksheet	C.2
C-2	Work Chart Worksheet for Calculating α and β	C.3
C-3	van Genuchten Parameter Worksheet	C.3
C-4	NAPL Saturation and Relative Permeability Distributions	C.4
D-1	LNAPL Recovery Worksheet.....	D.2

Executive Summary

This document addresses the application of proven technologies for recovering free-product petroleum releases to groundwater. An approach is given to optimize free-product recovery for minimal water production and free-product smearing. Information and guidance for design and analysis of free-product recovery systems using trenches, skimmer wells, single- and dual-pump wells, and vacuum-enhanced wells are provided. The principles that govern the distribution and movement of free-product petroleum hydrocarbons near the water table in an unconfined groundwater aquifer are reviewed.

This manual is useful for evaluating remediation options at sites where free product is present at the water table of an unconfined aquifer or perched on a confining bed. It assumes that the reader has a basic understanding of hydrogeology and is aware of subsurface complexities (e.g., heterogeneity and water table fluctuation) that complicate estimates of free-product recovery. As an introduction to the design approach, the manual briefly reviews the basic principles of flow of lighter-than-water nonaqueous phase liquids in porous media. Physical/chemical parameters that are essential in the design and analysis of free-product recovery systems are discussed. Information and data for parameter estimation are also provided.

A description of remediation technologies associated with free-product recovery is provided. This includes basic design information for systems using trenches, skimmer wells, single- and dual-phase-type pumping methods, and vacuum enhancement. The relative merits of each method are described and summarized, and guidance towards selection of free-product recovery technology for application at a particular site is given. The manual provides and explains equations and nomographs for determining recovery rates, total volumes recovered, and recovery times. Several examples are offered to illustrate how to perform these design and analysis calculations.

Two computer spreadsheets are available to implement the calculations described in this document for free-product recovery using single- and dual-pump wells and vacuum-enhanced systems. These spreadsheets are described in Appendix C and Appendix D, and their use is shown by example in Section 5.9.

SECTION 1 – INTRODUCTION

1.1 Purpose and Scope

This publication provides an overview of proven technologies for recovering free-product petroleum releases to groundwater. An approach is given to optimize free-product recovery (FPR) for minimal water production and free-product smearing. Information and guidance for design and analysis of free-product recovery systems using trenches, skimmer wells, single and dual-pump wells, and vacuum-enhanced wells are provided. The principles that govern the distribution and movement of free-product petroleum hydrocarbons near the water table in an unconfined groundwater aquifer are reviewed. Information and data for parameter estimation are also provided.

This publication does not address the methods, procedures and equipment to be used in site assessment for locations of free-product releases. It does not address issues of efficiency of free-product recovery in relating recovery amounts to reduction in risk to groundwater receptors. Tools for characterizing petroleum hydrocarbon distribution are discussed only if they relate to design and analysis of free-product recovery systems. This publication does not address alternative remediation methods for petroleum-impacted soils and groundwater such as soil vapor extraction, bioventing, air sparging, pump-and-treat, or intrinsic bioremediation.

Discussion of petroleum hydrocarbon liquids in the subsurface environment involves the use of certain terminology. Petroleum hydrocarbon liquids generally are less dense than water. This implies that such liquids would float on the water table of an unconfined groundwater aquifer. This contrasts with liquids such as chlorinated solvents that have density greater than water, resulting in the potential to sink to the base of an aquifer. Petroleum hydrocarbons are an example of a "light" nonaqueous phase liquid (LNAPL), which means that they are lighter than and immiscible with water. If LNAPL is present in sufficient quantity, it will move in response to impressed forces. This condition of free-product or mobile LNAPL contrasts with the condition of residual product where the hydrocarbon liquid is present as discontinuous globules within the porous matrix. Residual LNAPL cannot be skimmed or pumped from a well.

1.2 Background

Petroleum hydrocarbons may be accidentally released to the subsurface through spills, leaking pipelines, leaking underground or above ground storage tanks, or other sources. The released hydrocarbon liquids migrate downward through the vadose zone, primarily because of gravity. If only small volumes of petroleum hydrocarbon liquids are released, they may become entirely trapped in the vadose zone by capillary forces. If greater amounts of petroleum hydrocarbons are released, then the hydrocarbon liquids may migrate completely through the unsaturated zone to accumulate within the capillary fringe. If enough hydrocarbon liquids accumulate within the capillary fringe, they will depress the water table and develop pressure gradients that will cause the resulting hydrocarbon liquid lens to spread laterally across the water table.

In some cases petroleum hydrocarbon releases are identified at the time of the spill or through inventory monitoring. In other cases, such releases are only identified after the hydrocarbon liquids or their constituents appear in surface waters or groundwater wells. Once the release has been identified, its magnitude and extent must be determined, the hydrogeologic characteristics of the release area identified, and potential pathways for human and ecological exposures must be assessed. After the environment and potential exposures have been characterized, decisions can be made on how to best manage the release. Best management decisions could include monitoring of intrinsic bioremediation or application of engineered remediation technologies such as pump-and-treat, hydrocarbon liquid recovery, or soil vapor extraction. The purpose of this manual is to provide guidance for selection, design and operation of hydrocarbon liquid recovery systems.

When a site investigator detects separate phase petroleum hydrocarbon (aka free-product LNAPL) in a monitoring well, he or she must determine how much (if any) of this LNAPL is recoverable from the formation. This requires measurement and estimation of the critical parameters to determine the potential free-product recovery rate and expected cumulative recoverable volume. The investigator must also use this information to decide which of the available free-product techniques are appropriate for the site conditions.

Many of the free-product recovery systems in operation today employ either single- or dual-pump recovery wells. Applying a vacuum to the well has enhanced the efficiency of some of these systems. Only limited guidance is currently available regarding how best to operate these systems for optimum long-term free-product LNAPL recovery. As a result, recovery wells may not be operating efficiently, thus prolonging remediation times or causing unnecessary expenditures for additional recovery wells. Although these techniques are in widespread use, few guidelines are available on the potential (optimal) pumping rates for removing both groundwater and free hydrocarbon.

Given the operational constraints for a facility, an optimal pumping rate can be determined. While low pumping rates may lengthen remediation times, high rates may cause other problems. For example, excessive groundwater pumping causes hydrocarbon to be smeared into deeper soils below the original water table, into soils that were originally uncontaminated. When this occurs, there is an increase in the volume of soils with residual hydrocarbon contamination and a resulting reduction in the volume of recoverable free-product LNAPL. This may increase long-term remediation costs. Excessive pumping also produces larger volumes of water that must be treated and discharged.

Optimal recovery of separate phase hydrocarbon must be defined in the context of the remediation goals of the site risk management program. It could be defined as a means to minimize the amount of residual hydrocarbon left in the formation. However, sometimes this may result in low rates of recovery over an extended time frame. In some cases it may be desirable (or required by regulation) to accelerate the rate of free-hydrocarbon removal even though this may result in a reduction in the ultimate recovery of hydrocarbon from the formation. Capital and operations and maintenance costs must also be considered. This publication provides quantitative information that can help the decision-maker select the best free-product recovery system for his or her site conditions and operational constraints.

1.3 Organization

This manual should be used in cases where it has been determined that free product is present at the water table of an unconfined aquifer or perched on a confining bed.

Section 2 briefly reviews the basic principles of LNAPL flow. The basic concepts and definitions that relate to multiphase fluid flow in the subsurface are presented, with emphasis placed on flow out of a formation into a well or trench.

Section 3 contains a discussion of physical/chemical parameters that are significant in the design and analysis of free-product recovery systems. Methods for parameter estimation are presented.

Section 4 provides a description of remediation technologies associated with free-product recovery. The relative merits of each method are described and summarized, and guidance towards selection of free-product recovery technology for application at a particular site is provided.

Section 5 presents basic design information for free-product recovery systems using trenches, skimmer wells, single- and dual-phase-type pumping methods, and vacuum-enhanced systems. Recovery rates, total volumes recovered, and recovery times are discussed. Several examples are provided to illustrate how to perform these design and analysis calculations.

1.4 Supplementary References

A comprehensive guide to assessment and remediation of underground LNAPL releases is presented in:

- 1) A Guide to the Assessment and Remediation of Underground Petroleum Releases, API Publication 1628, Third Edition, July 1996.

Supplements to this guide are:

- 2) Natural Attenuation Processes, API Publication 1628A, July 1996.
- 3) Risk-Based Decision Making, API Publication 1628B, July 1996.
- 4) Optimization of Hydrocarbon Recovery, API Publication 1628C, July 1996.
- 5) In-Situ Air Sparging, API Publication 1628D, July 1996.
- 6) Operation and Maintenance Considerations for Hydrocarbon Remediation Systems, API Publication 1628E, July 1996.

U.S. Environmental Protection Agency information and guidance on free-product recovery is contained in

- 7) Ground Water Issue, Light Nonaqueous Phase Liquids, Newell, C. J., Acree, S.D., Ross, R.R., and S.G. Huling, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, EPA/540/S-95/500, July 1995.
- 8) How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites, Solid Waste and Emergency Response, U.S. Environmental Protection Agency, EPA 510-R-96-001, September 1996.

SECTION 2 – SUBSURFACE MIGRATION OF LNAPL AND GROUNDWATER

When an LNAPL is released to the subsurface environment it will migrate through a porous medium leaving behind a trail of LNAPL-globules trapped by capillary forces. In addition, chemical constituents of the LNAPL will partition to the multiple phases (soil, water and air) that are present. This section provides an overview of the subsurface environment and the basic principles of LNAPL and groundwater flow.

2.1 Subsurface Environment

The porous media that are of interest include natural soils, cemented sediments, and fractured and karst rock. Natural soils are granular materials containing amorphous mineral and organic matter. Based on their particle-size distribution, natural soils are classified into various textures as will be discussed in Section 3. Most of the locations where crude oil or petroleum products are handled lie over natural soils or cemented sediments. The presence of fractured or karst rock beneath a facility greatly complicates the efforts at site characterization, and possibly those associated with recovery of LNAPL. This document focuses on porous media consisting of granular materials or cemented sediments.

Porous media consist of solid material and void or pore space. Air and water, and possibly LNAPL, occupy the pore space. The natural distribution of subsurface water is especially important for describing and analyzing free-product recovery systems. Figure 2.1.1 provides a schematic view of the regions that make up the subsurface profile. The vadose zone (1), also called the unsaturated or partially saturated zone, constitutes all of the subsurface media above the water table. The vadose zone contains a varying amount of water depending on its soil texture and infiltration from rainfall or surface water bodies. Except for the upper few meters that are influenced by plants and their root systems, the vadose zone retains a significant amount of soil water held by capillary forces. The capillary fringe (2) is a region of the subsurface profile that is nearly saturated with water pulled upward from the underlying saturated zone by capillary forces. Table 2.1.1 shows the capillary rise in soils of varying texture. The thickness of the capillary fringe varies from a few inches or

centimeters in coarse-grained soils to a few feet or meters in fine-grained soils such as silts and clays. The capillary fringe is sometimes called the tension-saturated zone since the pore space is nearly filled with water and the water pressure is less than atmospheric pressure (Freeze and Cherry, 1979). The water table (3), otherwise known as the phreatic surface, is the elevation within the subsurface profile at which the water pressure is the same as the atmospheric pressure. This corresponds to the water elevation that is observed in a monitoring well since the diameter of such a well is so large that capillary forces are unimportant. The saturated zone (4) is that part of the subsurface profile where water pressure is greater than atmospheric pressure. In this region water or other liquids generally fill the pore space, though under conditions with a fluctuating water table, some air may be temporarily trapped within the pore space. Water in the saturated zone is called groundwater, and depending on the storage and permeability characteristics of the formation, this region can form an aquifer (in this case an unconfined aquifer because of the presence of the water table).

**Table 2.1.1 Capillary Rise in Soils Having Similar Porosity (0.41)
after 72 Days (from Lohman, 1972)**

Material	Grain Size (mm)	Capillary Rise (cm)
Fine gravel	5-2	2.5
Very coarse sand	2-1	6.5
Coarse sand	1-0.5	13.5
Medium sand	0.5-0.2	24.6
Fine sand	0.2-0.1	42.8
Silt	0.1-0.05	105.5
Silt	0.05-0.02	200 ¹

¹ Still rising after 72 days

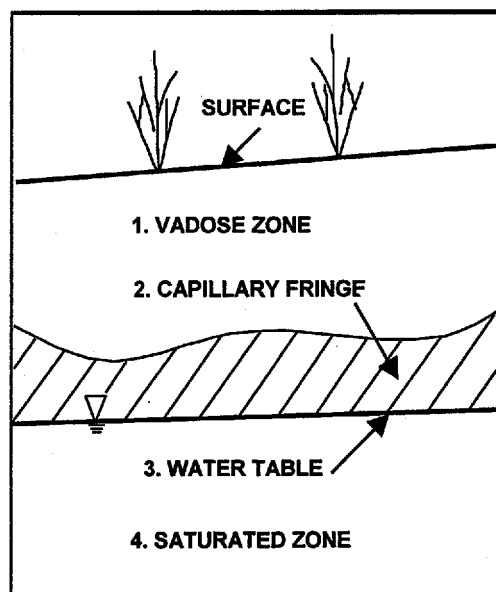


Figure 2.1.1 Generalized Profile of the Subsurface

2.2 Description of Subsurface Flow

A fluid particle moving through a porous medium can travel along a complex path, such as shown schematically in Figure 2.2.1. Other fluid particles passing through the same porous medium can encounter a multitude of different conditions and thus take different pathways. Because of the complexity of describing flow on the pore-size scale, a practical method of describing fluid flow in porous media has been developed that relies on a macroscopic or “average” description of conditions over a larger volume. The parameters that are used in this macroscopic description of porous media flow attempt to incorporate many of the pore-scale phenomena. Because of the potential variability in soil texture and other properties over short distances, these parameters are spatially variable and difficult to accurately measure.

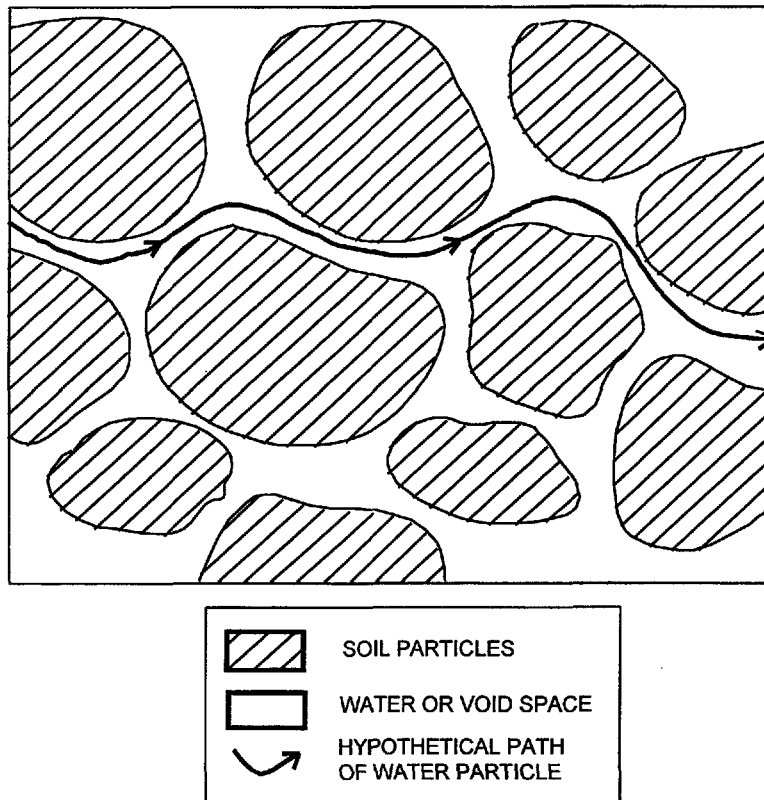


Figure 2.2.1 Pore-Scale View of Subsurface Flow

2.3 Fluid Saturation and Capillary Pressure

For a representative volume of a porous media, the fraction of the total volume that is occupied by pore space is called the *porosity*, and the fraction of the pore space that is occupied by a given fluid phase is called the phase *saturation*. Below the water table and in the absence of LNAPL, the water saturation is nearly one (1) and the air saturation is nearly zero (0). As one moves from the saturated region to the capillary fringe, the water saturation decreases from 1 to a value that represents the amount of water that is held within the medium by capillary forces. This corresponds to the *specific retention* of the porous media for water. (In hydrology, the specific retention is the fraction of the total volume of porous media that is occupied by water retained by capillary forces, rather than the fraction of the pore space.)

When the representative volume of porous media is occupied by more than one fluid phase (i.e., air, water and LNAPL), there are interfaces within the pore space across which the fluids are in contact. The interface between two fluids has associated with it an excess interfacial energy that is represented by the property called surface or *interfacial tension*. If the interface between two fluids within the pore space is curved, then there exists a pressure difference between the two phases. This pressure difference is called the *capillary pressure* between the two phases; its magnitude increases with the interfacial tension and it increases as the radii of curvature of the interface decreases.

Another property that is related to the interfacial energy between two fluids and a solid surface is *wettability*. Wettability is a measure of the tendency of one fluid to spread and coat a solid surface in the presence of another fluid with which it is immiscible. The fluid that preferentially spreads and coats the solid surface is called the wetting fluid. The other fluid is said to be non-wetting. Wettability is a function of both fluids and the nature of the solid surface. Mineral soils (i.e., soils composed of sand, silt, clay and some organic matter) are water-wet compared with both air and LNAPL. LNAPL is generally the non-wetting fluid when compared with water and the wetting fluid when compared with air. Wettability is important in describing the distribution of fluids at the pore scale. For a mineral soil, water will tend to occupy the smallest sized pores, air will tend to occupy the largest pores and LNAPL will occupy the intermediate sized pore spaces.

The relationship between phase saturation and capillary pressure is a characteristic property of a soil (for the air and water system it is called the *soil moisture characteristic curve*). This relationship can be measured in the laboratory using standard methods. Empirical methods have also been developed that allow one to estimate the soil moisture characteristic from data on soil texture and composition. These methods are discussed in detail in Section 3.

The soil moisture characteristic curve may be used as a guide to understanding the vertical distribution of fluid saturation. Under vertical equilibrium conditions the pressure in each phase is determined by the hydrostatic pressure equation (see equation 2.4.3). If the fluids have different densities then they will have different vertical pressure gradients. Thus the capillary pressure will vary linearly

with elevation. The soil moisture characteristic curve determines the phase saturation from the capillary pressure. Estimation of the vertical distribution of saturation is described more fully in Section 3. In the analysis of free-product recovery systems it is often assumed that the vertical distribution of fluids under conditions of vertical equilibrium hold even when the fluids are migrating laterally. This *vertical equilibrium* assumption is discussed in Sections 3 and 5, and in Appendix A.

2.4 Hydraulic Gradient

Fluids move through the subsurface in response to changes in energy content. Neglecting osmotic effects and other factors that are unimportant to free-product recovery, the energy content is the sum of pressure and gravitational potentials. For liquids that are considered incompressible (such as water and LNAPL under normal environmental conditions) this is conveniently expressed through the *hydraulic head* for the fluid phase:

$$h_i = \frac{p_i}{\rho_i g} + z \quad (2.4.1)$$

In equation (2.4.1) h_i is the hydraulic head (energy per unit weight) for phase i (either water or LNAPL), p_i is the phase pressure, ρ_i is the phase density, g is the gravitational acceleration constant and z is the elevation measured positive in the upward direction. Differences in head correspond to differences in energy per unit weight of fluid, and the hydraulic head gradient corresponds to the driving force (per unit weight) that causes fluid movement. Since the fluid energy content may vary in all three directions within a porous media, the *hydraulic gradient* is expressed as a vector quantity.

$$\vec{J}_i = -\nabla h_i = -\left[\frac{\partial h_i}{\partial x} + \frac{\partial h_i}{\partial y} + \frac{\partial h_i}{\partial z} \right] \quad (2.4.2)$$

Vertical equilibrium corresponds to the vertical component of the hydraulic gradient vanishing $\left(\frac{\partial h_i}{\partial z} = 0\right)$. This is equivalent to the hydrostatic pressure equation for phase i:

$$\frac{\partial p_i}{\partial z} = -\rho_i g \quad (2.4.3)$$

When equation (2.4.3) holds, the fluid is in vertical equilibrium, even if horizontal pressure gradients do not vanish.

2.5 Darcy's Law

Darcy's law expresses linear relations between the volume flux for phase i and its hydraulic gradient.

$$\bar{q}_i = K_i \bar{J}_i \quad (2.5.1)$$

In equation (2.5.1) $\bar{q}_i$ is the *volume flux* of phase i, which is the volume of phase i that crosses a unit area per unit time. The volume flux has units of L/T (velocity); it is also called the *Darcy velocity* or the *specific discharge*. The proportionality constant between the hydraulic gradient and the volume flux is called the hydraulic conductivity for phase i, K_i . The hydraulic conductivity is more generally expressed as a second order tensor to address preferential directions for flow within the porous medium, though for simplicity we consider K_i a scalar quantity with all directions having the same capacity for flow.

The *hydraulic conductivity* is a function of fluid and porous media properties. This is expressed by

$$K_i = \frac{\rho_i g k}{\mu_i} \quad (2.5.2)$$

where the intrinsic permeability k is a property of the porous media and μ_i is the dynamic (or absolute) viscosity of phase i. As long as the fluid phase i does not

change the pore structure of the porous medium (i.e., shrinking or swelling) then the value of k is the same whether the pore space is occupied by water or LNAPL. This allows one to estimate the LNAPL hydraulic conductivity, K_o , from the more easily measured water hydraulic conductivity by using equation (2.5.2).

$$K_o = \frac{\rho_o}{\rho_w} \frac{\mu_w}{\mu_o} K_w \quad (2.5.3)$$

The water hydraulic conductivity, fluid density and dynamic viscosity are discussed in Section 3.

2.6 Relative Permeability

In steady multiphase (air, water, LNAPL) flow, different fluids flow practically independently of each other, as the interfacial boundaries between them are mostly situated in pores where there is no flow. Hence, neither fluid influences the flow behavior of the other one, and each fluid flows in the pore network allotted to it, just as if it were the only fluid present (Dullien, 1992). The result is that the fluid sees only an effective permeability k_{ei} that is less than k . It is customary to express the effective permeability as a fraction of the intrinsic permeability of the medium. This defines the *relative permeability* for phase i as

$$k_{ri} = \frac{k_{ei}}{k} \quad (2.6.1)$$

Darcy's law for multiphase flow may be written

$$\bar{q}_i = K_i k_{ri} \bar{J}_i \quad (2.6.2)$$

Equation (2.6.2) simply states that for the same driving force $\bar{J}_i$, the Darcy velocity (volume flux) under multiphase flow conditions (with $k_{ri} < 1$) is smaller than that for the case where only a single fluid occupies the pore space by an amount equal to the relative permeability for the phase.

The relative permeability for a fluid phase is a function of the saturation of the phases that are present. A typical two-phase relative permeability curve for a sandy soil is shown in Figure 2.6.1. This figure shows the relative permeability for LNAPL and water as a function of water saturation in a sand medium that contains only LNAPL and water ($S_o + S_w = 1$).

Figure 2.6.1 suggests several observations. First, a minimum phase saturation must be present before its relative permeability is non-zero. For the wetting phase this is called the irreducible water saturation and for the non-wetting phase the minimum saturation for flow is called the residual LNAPL saturation. This observation means that once a fluid is present at saturation above the minimum level, it must remain present at or above this minimum saturation to flow unless components in the fluid are transferred to another phase (i.e., volatilization of LNAPL in the vadose zone). The dashed curves shown in the figure correspond to the extrapolated relative permeability curves for saturations less than the minimum. Such values do not naturally occur.

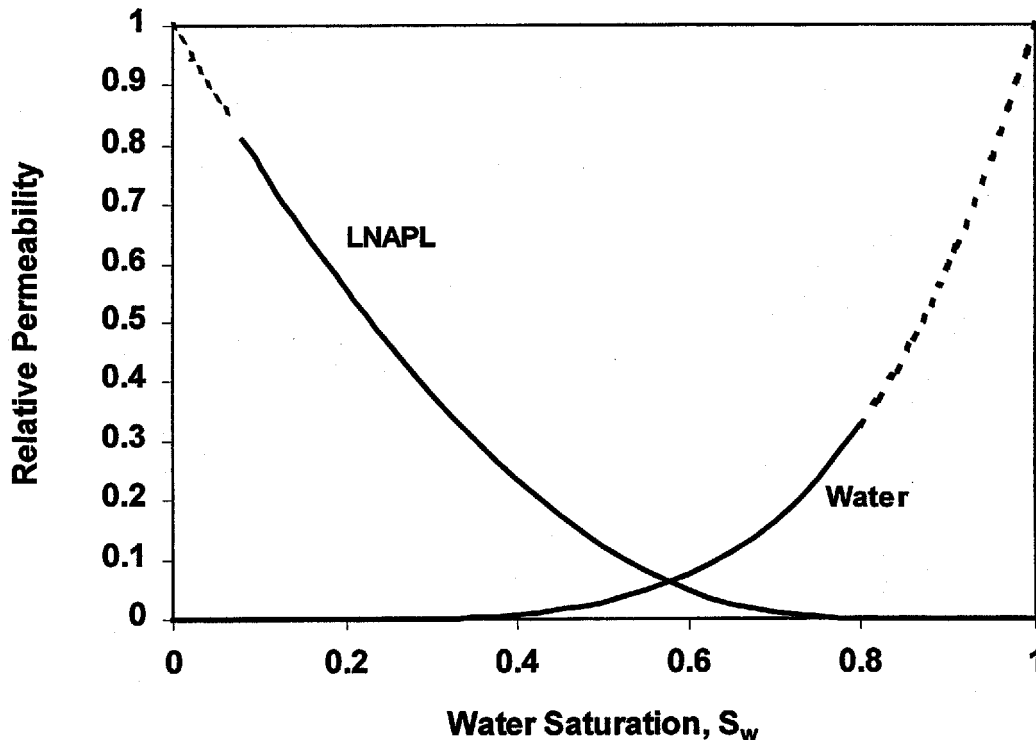


Figure 2.6.1 Typical Relative Permeability Curve for a Sandy Soil

A second feature to note is that the sum of the fluid relative permeability values is not unity. The presence of another fluid within the porous media (e.g., air or NAPL) decreases the area available for flow and the overall capability of the media to allow fluid flow.

A third feature shown in Figure 2.6.1 is that the relative permeability increases with saturation faster for LNAPL than for water. This is because LNAPL is the non-wetting fluid for this pair of fluids, and the non-wetting fluid tends to occupy the centers of the larger pore spaces because of wettability considerations.

A fourth feature is that a fluid can be present at saturations exceeding its minimum value for flow and still have a very small relative permeability. This is shown most clearly for water that has a minimum saturation value of 0.075 for flow, and yet has a relative permeability value near zero up to saturation of almost 0.4. This larger magnitude corresponds more closely to the concept of water being held by capillary forces and not migrating in response to water table fluctuations. In hydrology the corresponding parameter is called the *specific retention* while the volume fraction that will drain is called the *specific yield*.

The residual LNAPL saturation has important implications for the transport and fate of LNAPL releases. When LNAPL moves through a region of the subsurface it will leave behind an amount that is trapped by capillary forces. In addition, as LNAPL drainage occurs and its saturation decreases, the drainage rate also decreases and LNAPL appears to be held at saturation values above residual. Thus a finite release can only migrate a certain distance before its capability for flow is depleted. This same feature means that free-product recovery cannot capture all of the LNAPL near the water table. A significant fraction will be left behind, unable to migrate to the recovery system.

2.7 Groundwater Recovery by Wells

Groundwater production is often used to enhance the flow of LNAPL to a recovery well. There are two simple relationships that are useful for describing the flow of a liquid to a well. First, if the saturated thickness of the layer of liquid

(e.g., water or LNAPL) is spatially uniform then the *Thiem equation* is appropriate (Bear, 1979).

$$s_i = \frac{Q_i}{2\pi K_i \bar{k}_i \bar{b}_i} \ln\left(\frac{R}{r_w}\right) \quad (2.7.1)$$

In equation (2.7.1) s_i is the drawdown of the liquid layer which is the decrease in head from that at a radius R from the well (called the *radius of influence*), where the liquid head is not impacted by well production, and the head at the well which has radius r_w . The variables $\bar{k}_i$ and $\bar{b}_i$ are the liquid layer's average or effective relative permeability and thickness, respectively. The essential feature of the Thiem equation is that the saturated thickness of the liquid layer remains constant during radial flow towards the well.

In an unconfined aquifer, drawdown of the water table during groundwater production results in a decreasing saturated thickness of the water layer with distance towards the well. The *Dupuit equation* accounts for this changing saturated thickness of the water layer (Bear, 1979).

$$b_w^2 - h_w^2 = \frac{Q_w}{\pi K_w} \ln\left(\frac{R}{r_w}\right) \quad (2.7.2)$$

In equation (2.7.2) b_w is the water-layer saturated thickness at the radius of influence R and h_w is the water-layer saturated thickness at the well of radius r_w . Q_w and K_w are the water production rate and the hydraulic conductivity of the aquifer for water, respectively. This equation expresses the response of the unconfined aquifer to water production. If free-product LNAPL is present near the water table, it will also experience the head distribution caused by water pumping, and move towards the well.

Equation (2.7.2) may be written in a form that expresses the drawdown, $s_w = b_w - h_w$, around a well as a function of water production rate and water-layer saturated thickness far from the well (Charbeneau and Chiang, 1995):

$$s_w = \frac{Q_w \ln\left(\frac{R}{r_w}\right)}{\pi K_w b_w \left(1 + \sqrt{1 - \frac{Q_w}{\pi K_w b_w^2} \ln\left(\frac{R}{r_w}\right)}\right)} \quad (2.7.3)$$

Equation (2.7.3) is useful for analyzing and designing free-product recovery systems, as will be discussed in Section 5. It is shown graphically in Figure 2.7.1, where the fraction discharge is defined by

$$\Gamma = \frac{Q_w}{\pi K_w b_w^2} \ln\left(\frac{R}{r_w}\right) \quad (2.7.4)$$

The fraction discharge is the ratio of the well discharge to the maximum possible well discharge when the aquifer is pumped dry ($h_w = 0$). When $s_w/b_w = 1$, $\Gamma = 1$.

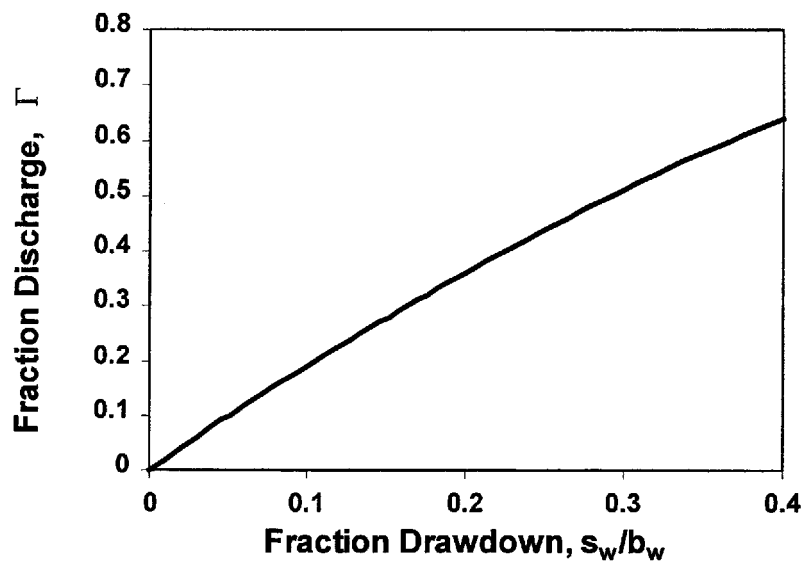


Figure 2.7.1 Drawdown-Discharge Relationship for an Unconfined Aquifer

2.8 Air Flow to a Well

Applying a vacuum to a well may enhance free-product recovery. The flow of air through porous media is usually modeled in terms of pressure gradients (rather than head) since the density of air is small. However, as air moves through a media and its pressure changes, so will its density according to the ideal gas law. The relationship between air production from a well and pressure may be represented by (Johnson *et al.*, 1990)

$$\frac{Q_a}{L_w} = \frac{\pi k \bar{k}_{ra}}{\mu_a} \frac{p_{atm}^2 - p_w^2}{p_w \ln(R/r_w)} \quad (2.8.1)$$

In equation (2.8.1) Q_a is the air discharge, L_w is the well screen length open to air flow, p_{atm} is the (absolute) atmospheric pressure, and p_w is the suction pressure ($p_w < p_{atm}$) applied to the well. Equation (2.8.1) is analogous to the Dupuit equation for the flow of water to a well. For most applications of vacuum-enhanced recovery, the suction pressure head does not differ too much from atmospheric pressure ($p_w = 0.7$ to $0.9 p_{atm}$). For these conditions the following approximation applies

$$\frac{p_{atm}^2 - p_w^2}{p_w} = \frac{(p_{atm} + p_w)(p_{atm} - p_w)}{p_w} \cong 2(p_{atm} - p_w)$$

and equation (2.8.1) may be approximated as

$$s_a = \frac{Q_a}{2\pi K_w \bar{k}_{ra} L_w} \frac{\mu_a}{\mu_w} \ln\left(\frac{R}{r_w}\right) \quad (2.8.2)$$

In equation (2.8.2) s_a is the equivalent water drawdown (head) developed by the vacuum system

$$s_a = \frac{p_{atm} - p_w}{\rho_w g} \quad (2.8.3)$$

Equation (2.8.2) proves to be useful for analyzing and designing free-product recovery systems, as will be discussed in Section 5.

SECTION 3 – SIGNIFICANT VARIABLES AND PARAMETERS

There are several parameters that must be determined to design a free-product recovery system. Many parameters can be estimated from knowledge of soil properties. Estimation of other parameters can be more difficult and require interpretation of site data. This section describes the significant parameters that are used in Section 5 to predict the performance of free-product recovery systems. Guidance on parameter estimation is also provided.

Methods for parameter estimation normally take one of two different routes. Direct laboratory and field testing of the subsurface constitutes one method. Problems associated with direct measurement techniques can include high costs, lengthy time requirements, and possible errors in testing methods.

The second route to parameter estimation is based on past research and summary literature tabulations. This method is primarily based on soil texture information and fluid properties. Estimations of this type require minimal site investigation, costs are normally lower, and parameter estimation is quicker when compared to individual laboratory tests. Inaccuracies associated with this method can be large. Nevertheless, the relative benefits gained by this method can outweigh the increased uncertainty, especially in screening calculations when minimal site characterization data are available. For this reason parameter estimation based on literature summaries of past research is stressed.

The parameters that are discussed in this section and their corresponding sub-section numbers are given below:

- 3.1 LNAPL Fluid Properties: Density and Viscosity
- 3.2 Soil Texture
- 3.3 Porosity and Fluid Saturation
- 3.4 Capillary Pressure Relationships
- 3.5 Formation Free Product "Thickness" Under Vertical Equilibrium
- 3.6 Hydraulic Conductivity and Intrinsic Permeability
- 3.7 Relative Permeability
- 3.8 Effective LNAPL Layer Saturation and Relative Permeability
- 3.9 Residual LNAPL Saturation
- 3.10 Water Table Fluctuations and Vertical Equilibrium

3.1 LNAPL Fluid Properties: Density and Viscosity

As noted in Section 1, the fluids of interest in free-product recovery are less dense than water. They are LNAPLs. However, the liquids of interest can be either more or less viscous than water. The LNAPL fluid properties density and viscosity are discussed in this section.

3.1.1 Fluid Density

The *density* of a fluid (ρ) is its mass per unit volume. The usual engineering units are kg/m^3 or slugs/ft^3 . However, the unit gm/cm^3 may be preferable if one wishes to compare the density of the LNAPL with that for water. Water has an approximate density of 1.0 gm/cm^3 , therefore the ratio of the LNAPL density to the water density has the same magnitude as the LNAPL density in gm/cm^3 . The *relative LNAPL density* is

$$\rho_r = \frac{\rho_o}{\rho_w} \quad (3.1.1)$$

where ρ_o and ρ_w are the LNAPL and water density, respectively. The relative LNAPL density is also known as the liquid's *specific gravity*.

The *specific weight* (γ) of a fluid is its weight (not mass) per unit volume. Density and specific weight are related by equation (3.1.2)

$$\gamma = \rho g \quad (3.1.2)$$

where g is the gravitational acceleration constant ($g = 9.81 \text{ m/s}^2 = 32.2 \text{ ft/s}^2 = 981 \text{ cm/s}^2$).

The hydrocarbon specific gravity may be expressed on the basis of the following empirical equation (Perry and Chilton, 1973):

$$^\circ\text{API} = \frac{141.5}{\rho_r} - 131.5 \quad (3.1.3)$$

The degree API is a scale measurement adopted by the American Petroleum Institute (API). It ranges from 0.0 (equivalent to a specific gravity 1.076) to 100.0 (equivalent to a specific gravity 0.6112). Hydrocarbon fractions commonly found beneath refineries and other petroleum manufacturing sites range from °API 30 to 40, representing light paraffin oil to kerosene. These fractions present challenges to remediation because they are light enough to float on the water table, but not volatile enough to be easily remediated by the *in situ* vapor extraction processes (Charbeneau and Chiang, 1995).

Fluid density varies with pressure and temperature. Liquid densities are normally inversely proportional to temperature and proportional to pressure. Temperature ordinarily has more of a pronounced effect on liquid density than does pressure (Young, 1992; Bear, 1972). The specific gravity of most LNAPLs range from 0.75 to 0.99 (EPA, 1995). Density, being somewhat temperature dependent, causes some liquids (i.e., some coal tar residues) to be light oils at higher temperatures and dense oils at lower temperatures (Newell *et al.*, 1994). Representative LNAPL density values are shown in Table 3.1.1.

3.1.2 Fluid Viscosity

Viscosity is a measure of the friction between molecules within a fluid. The *dynamic (or absolute) viscosity* (μ) is defined as the ratio of the shear stress to the strain rate for a Newtonian fluid. The *kinematic viscosity* (ν) is the ratio of the dynamic viscosity and density for a fluid. The standard SI system unit for dynamic viscosity is Newton-second/square meter (N-s/m²), which is the same as Pascal-second (Pa-s). Another commonly used unit for dynamic viscosity is the poise. One poise = 10⁻² N-s/m². Because of the magnitude of the dynamic viscosity of most fluids of interest in free-product recovery, dynamic viscosity values are usually reported in centipoise (cp), that is, 10⁻² poise. Water has a dynamic viscosity of approximately 1 cp. The *relative LNAPL viscosity* has a magnitude equal to the LNAPL dynamic viscosity measured in cp:

$$\mu_r = \frac{\mu_o}{\mu_w} \quad (3.1.5)$$

where μ_o and μ_w are the LNAPL and water dynamic viscosity, respectively.

Table 3.1.1 Representative LNAPL Density Values (gm/cm³)

Fluid Type	Temp. 0 °C	Source	Temp. 15 °C	Source	Temp. 20 °C	Source	Temp. 25 °C	Source
Water	1.000	C	0.998	C	0.998	C	0.996	C
Automotive Gasoline	0.746	A	0.729	A				
Automotive Diesel	0.838	A	0.827	A				
Kerosene	0.842	A	0.839	A			0.835	A
Jet Fuel (JP-3)					0.800	B		
Jet Fuel (JP-5)			0.844	A	0.820	B		
Fuel Oil #2	0.874	A	0.866	A	0.840	A		
Fuel Oil #4	0.914	A	0.904	A	0.900	B	0.898	A
Fuel Oil #5	0.932	A	0.923	A			0.917	A
Fuel Oil #6 or Bunker C	0.986	A	0.974	A			0.964	A
Electrical Lubricating Oil	0.882	A	0.974	A				
Electrical Lubricating Oil – used	0.883	A	0.874	A				
Electrical Insulating Oil	0.892	A	0.882	A				
Electrical Insulating Oil – used	0.878	A	0.867	A				
Norman Wells Crude	0.845	A	0.832	A			0.829	A
Avalon Crude	0.846	A	0.839	A			0.834	A
Alberta Crude	0.850	A	0.840	A			0.832	A
Transmountain Blend Crude	0.865	A	0.855	A				
Bow River Blend Crude	0.900	A	0.893	A			0.885	A
Prudhoe Bay Crude	0.915	A	0.905	A			0.900	A
Atkinson Crude	0.922	A	0.911	A			0.905	A
La Rosa Crude	0.923	A	0.914	A			0.908	A

Source: A-API, 1996; B-Mercer and Cohen, 1990; C-Vennard and Street, 1982

Viscosity values are temperature dependent, with liquid viscosity values decreasing as temperature increases. Viscosity values for oil tend to increase with age in the subsurface as the lower viscosity more volatile constituents evaporate or dissolve (EPA, 1995). A representative listing of dynamic viscosity values useful for free-product recovery design is provided in Table 3.1.2.

Other characteristics of petroleum hydrocarbon liquids are discussed in API (1996). An extensive catalog of crude oil and petroleum product properties is contained in Jokuty *et al.* (1996).

Table 3.1.2 Representative Dynamic Viscosity Values (centipoise)

Fluid Type	Temp. 0 °C	Source	Temp. 15 °C	Source	Temp. 20 °C	Source	Temp. 25 °C	Source
Water	1.79	B	1.14	B	1.00	B	0.89	B
Automotive Gasoline	0.75	A	0.62	A				
Automotive Diesel	3.90	A	2.70	A				
Kerosene	3.40	A	2.30	A			2.20	A
Jet Fuel (JP-3)								
Jet Fuel (JP-5)								
Fuel Oil #2	7.74	A			4.04	A		
Fuel Oil #4			47.2	A	22.7	A		
Fuel Oil #5			215	A			122	A
Fuel Oil #6 or Bunker C	7.E+07	A					3180	A
Electrical Lubricating Oil	350	A	144	A				
Electrical Insulating Oil	37.8	A	18.8	A				
Norman Wells Crude	8.76	A	5.05	A			3.93	A
Avalon Crude	575	A	11.4	A				A
Alberta Crude	17.6	A	6.43	A			4.22	A
Transmountain Blend Crude	650	A	10.5	A				
Bow River Blend Crude	88.4	A	33.7	A			23.7	A
Prudhoe Bay Crude	577	A	68.4	A			35.3	A
Atkinson Crude	136	A	57.3	A			35	A
La Rosa Crude	640	A	180	A			104	A

Source: A-API, 1996; B-Vennard and Street, 1982

3.2 Soil Texture

Soil texture is one of the most important properties describing a porous medium, and one that is most readily available for a site. Other physical properties related to the distribution and mobility of LNAPL are related to soil texture. For screening level analyses, soil texture and monitoring well data may be sufficient to characterize the subsurface at a particular site.

Soil texture refers to the size range of particles in the soil. As such, the term carries both qualitative and quantitative connotations. Qualitatively, it represents the “feel” of the soil material, whether coarse and gritty or fine and smooth. Quantitatively, soil texture denotes the measured distribution of particle sizes or the proportions of the various size ranges of particles that occur in a given soil. It is a permanent, natural attribute of the soil that is often used to characterize its physical makeup (Hillel, 1982). Three broad texture-based groups include sand, loam and clay (Brady, 1974).

Grain size distribution is closely related to soil texture. A grain size distribution gives the relative percentage of grain sizes. For coarser material the grain size distribution is determined by sieving a sample of dry soil through a series of successively smaller screens and measuring the percent mass retained. For fine-grained material the grain size distribution is determined by the rate of settlement in an aqueous suspension. Figure 3.2.1 shows a typical grain size distribution curve. The x-axis represents the particle diameter and the y-axis represents the percent passing or percent retained. Percent passing represents the amount of soil that is smaller than that specific grain size. ASTM D422-63 and many introductory geology and geotechnical engineering textbooks contain methods for analyzing grain size.

Many different organizations have established soil classification standards for use in different disciplines. The United States Department of Agriculture’s (USDA) system is one of the most widely used within the groundwater and environmental industry. Table 3.2.1 shows the USDA particle size classification system.

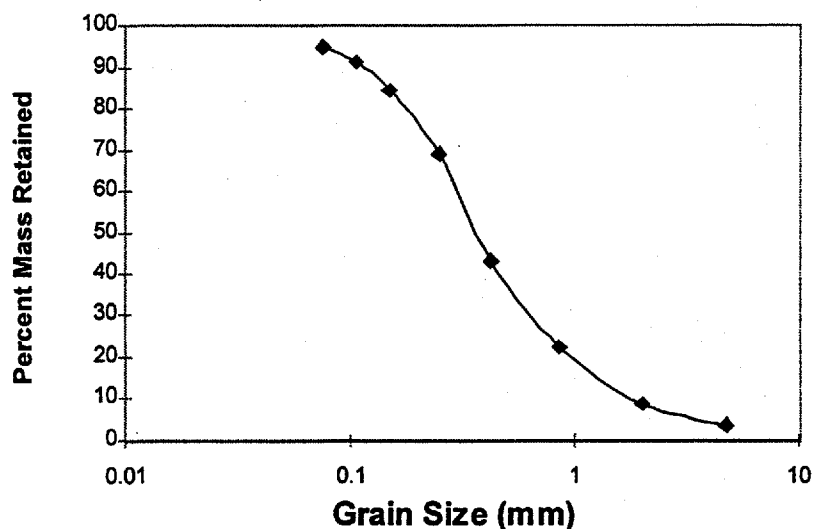


Figure 3.2.1 Typical Grain Size Distribution Curve

Table 3.2.1 USDA Particle Size Classification

Particle Sizes for U.S.D.A. Textural Classification System	
Particle Designation	Particle Diameters, mm
gravel	> 2.00
sand	0.05 to 2.0
very coarse	1.0 to 2.0
coarse	0.5 to 1.0
medium	0.25 to 0.5
fine	0.10 to 0.25
very fine	0.05 to 0.10
silt	0.002 to 0.05
clay	< 0.002

The grain size determines the particle size classification. The relative mass percentages of different particle sizes determine the soil texture for a soil sample. The USDA standard classification is provided by the soil texture triangle shown in Figure 3.2.2.

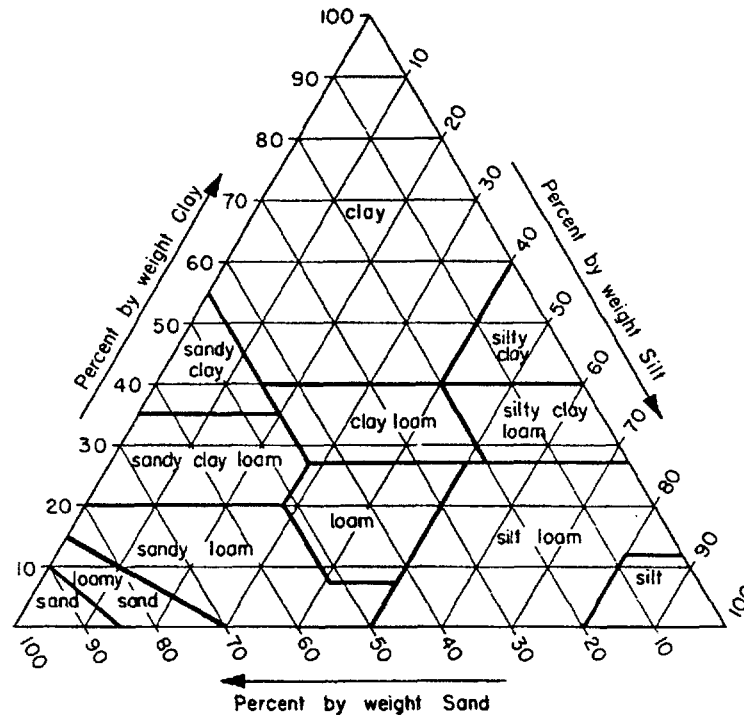


Figure 3.2.2 USDA Soil Texture Triangle

3.3 Porosity and Fluid Saturation

Two physical properties that significantly affect fluid movement through natural porous media are porosity and permeability. The permeability of soils is discussed in Section 3.6. The porosity and fluid saturation of natural porous media are briefly described in this section.

3.3.1 Porosity

The *porosity* (n) of a porous medium is the ratio of the volume of void space to the total volume of the medium. It may be defined either as a fraction or a percent of void space. The definition of porosity as a fraction is

$$n = \frac{\text{Volume of Void Space}}{\text{Bulk Volume of Material}} \quad (3.3.1)$$

As noted in Section 3.2, natural unconsolidated and consolidated porous media consist of particles with a range of sizes. Particles can be loosely packed, tightly packed and cemented, or anywhere in between. Porosity depends on many different factors, the most important of which are the particle size distribution, the shape and packing of the particles, and the degree of cementation. In general, a wider range in particle sizes results in a smaller porosity because the void space between larger particles can be filled by smaller particles. Angular and plate-like particles do not pack into as small a volume as well-rounded particles, resulting in a larger porosity. Increasing cementation results in a smaller porosity, other things being equal.

The porosity n refers to the total porosity of the medium. The porosity of the material upon deposition is called the *primary porosity*. Through diagenesis the total porosity may either increase or decrease. Post-depositional cementation results in a decrease in total porosity. Fractures may develop in consolidated clays, and both fractures and solution cavities may form in rock. Such alterations through which fluids may migrate are known as *secondary porosity*. Secondary porosity may also develop through animal burrows and plant root openings. The *effective porosity* refers to the volume of interconnected pore space through which fluids can flow. The term *kinematic porosity* is also used to describe the pore space through which fluid flow occurs (Marsily, 1985). In unconsolidated coarse-grained soils, the effective porosity and total porosity are nearly the same. However, in clays the effective porosity may be substantially less than the total porosity.

Representative values of the total porosity are presented in Table 3.3.1. Investigators have correlated measured porosity values with soil texture. For example, see the discussion of agricultural soils presented by Rawls *et al.* (1993). Table 3.3.2 shows the average porosity values for different soil textures presented by Carsel and Parish (1988). For a brief discussion of the data set from which Table 3.3.2 was derived, see Section 3.4.

Table 3.3.1 Total Porosity of Natural Porous Media

(Bear, 1972)		(Freeze and Cherry, 1978)	
Sedimentary Materials / Soil Type	Porosity Value in %	Unconsolidated Deposits	Porosity Value in %
Peat Soils	60 to 80	Gravel	25 to 40
Soils	50 to 60	Sand	25 to 50
Clay	45 to 55	Silt	35 to 50
Silt	40 to 50	Clay	40 to 70
Medium to Coarse Mixed Sands	35 to 40	Rocks	
Uniform Sand	30 to 40	Fractured Basalt	5 to 50
Fine to Medium Mixed Sands	30 to 35	Karst Limestone	5 to 50
Gravel	30 to 40	Sandstone	5 to 30
Gravel and Sand	30 to 35	Limestone Dolomite	0 to 20
Sandstone	10 to 20	Shale	0 to 10
Shale	1 to 10	Fractured Crystalline Rock	0 to 10
Limestone	1 to 10	Dense Crystalline Rock	0 to 5

3.3.2 Fluid Saturation

The void space of a natural porous medium affected by an LNAPL release is filled with water, air and LNAPL. The fraction of the pore space of a representative volume of material that is occupied by a particular fluid 'i' is called the *fluid saturation*, S_i .

$$S_i = \frac{\text{volume of fluid } i}{\text{volume of void space}} \quad (3.3.2)$$

In equation (3.3.2), i can be either w , a or o , standing for water, air and LNAPL, respectively. The fact that all of the pore space is filled means that the sum of the fluid saturation values must equal unity.

$$S_w + S_a + S_o = 1 \quad (3.3.3)$$

The fluid saturation for any phase can range from 0 to 1.

**Table 3.3.2 Average Porosity (Standard Deviation)
Values Based on Soil Texture**

Soil Type	Porosity (n)
Clay	0.38 (0.09)
Clay Loam	0.41 (0.09)
Loam	0.43 (0.10)
Loamy Sand	0.41 (0.09)
Silt	0.46 (0.11)
Silt Loam	0.45 (0.08)
Silty Clay	0.36 (0.07)
Silty Clay Loam	0.43 (0.07)
Sand	0.43 (0.06)
Sandy Clay	0.38 (0.05)
Sandy Clay Loam	0.39 (0.07)
Sandy Loam	0.41 (0.09)

(Source: Carsel and Parrish, 1988)

3.4 Capillary Pressure Relationships

When more than one fluid is present within the void space of a porous medium, then an interface exists separating the fluid phases. Molecules located near the interface have a greater energy than molecules of the same fluid located within the bulk volume due to adhesive forces between molecules. The excess energy associated with the interface results in an *interfacial tension* (σ_{ow}) between different fluids and *surface tension* between a liquid and its vapor (σ_{ao}).

Laboratory measurements show that the values of both the surface and the interfacial tensions of a crude oil extend over a wide range of values, from 2 dyne/cm to 30 dyne/cm. A value of 25 dyne/cm is commonly used for both surface and interfacial tensions of a crude oil. In addition, measurements show that for an unleaded gasoline with 7% MTBE, the interfacial tension is 35.1 dyne/cm (Charbeneau and Chiang, 1995). Typical values of the interfacial tension between a hydrocarbon liquid and water and surface tension are shown in Table 3.4.1. In the laboratory the surface tension for water in contact with air is $\sigma_{aw} = 72$ dyne/cm. In soil, some chemicals will accumulate at the interface between water and air, reducing the surface tension, and an effective air-water surface tension of 65 dyne/cm is often assumed.

Table 3.4.1 Interfacial and Surface Tension (dynes/cm) at 20° C

Chemical Name	Interfacial Tension	Surface Tension
Benzene	35	28.9
Ethylbenzene	35.5	29.3
Toluene	36.1	28.5
o-Xylene	36.1	30.3
Crude Oil	no data	24-38
Diesel Fuel	50	25
Gasoline	50	21
Naptha (BTX mixture)	45	20
Fuel Oil No. 1	48	27
Jet Fuel JP-4/5	50	25
Petroleum Distillates	50	21

Source: Mercer and Cohen (1990)

If the interface separating two phases is curved, then a pressure difference exists between the phases. This pressure difference is called the *capillary pressure* (p_c), and it is defined as the pressure in the non-wetting phase minus the pressure in the wetting phase (see the discussion in Section 2.3 with regard to wettability). For most natural porous media, water is the wetting phase, air is the non-wetting phase, and LNAPL is generally non-wetting compared with water and wetting compared with air. Wettability is important for multiphase flow

because it dictates that water will occupy the smallest pore spaces, air will occupy the largest pore spaces, and LNAPL will occupy the intermediate size pore spaces.

The magnitude of the capillary pressure is determined through the Laplace Equation (Adamson, 1978)

$$p_c = \frac{2\sigma}{r_c} \quad (3.4.1)$$

In equation (3.4.1), r_c is the mean radius of curvature of the interface separating the two fluids with interfacial tension σ .

Capillary pressure is a function of the saturation of the fluid phases that are present. This follows from equation (3.4.1). Consider the case where the wetting phase (water) is present only in small quantities so that its saturation is low. Since the wetting phase will occupy the smallest pore openings, the interface separating the wetting and non-wetting phases must be present within the small pore space and the corresponding radius of curvature will be small. Equation (3.4.1) shows that for this case the capillary pressure must be large. The opposite situation occurs when the wetting phase saturation is large. Then the interface is located in larger pore openings and the radius of curvature is large with a corresponding small capillary pressure.

The relationship between capillary pressure and saturation, $p_c(S_w)$, is determined by the pore size distribution of the porous media. When the two fluids are water and air, the relationship is called the soil moisture characteristic curve (Hillel, 1982), or simply the soil characteristic curve. Typical soil moisture characteristic curves for sand and clay soils are sketched in Figure 3.4.1. The sand has a large number of pores of roughly the same size. Thus a small change in capillary pressure can result in dewatering many pores with a resulting large decrease in water saturation. At very large capillary pressures the water becomes isolated at contact points between grains and in films that coat the soil. Further increases in the capillary pressure will not cause further appreciable decreases in the water saturation. The limiting saturation is called the *irreducible water saturation* (S_{wr}). While S_{wr} is thought to be a characteristic of a soil, it may also be viewed as a

fitting parameter when capillary pressure and saturation data are fit to mathematical models.

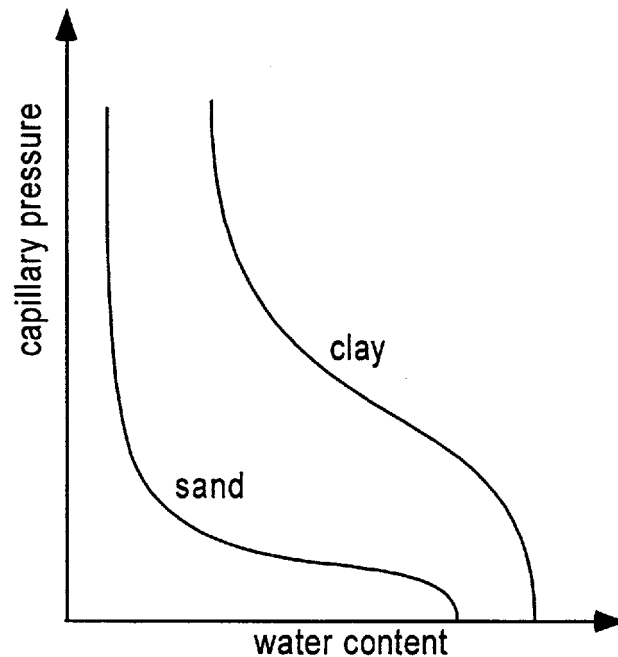


Figure 3.4.1 Soil Moisture Characteristic Curve

The clay soil shown in Figure 3.4.1 has a large range of pore sizes and many smaller pores. Thus larger capillary pressures are necessary to displace water from the largest pores, and the corresponding decrease in saturation with increasing capillary pressure is smaller than for the sand soil.

Soil characteristic curves are often measured in the laboratory. To compare different soils, the characteristic curves are fit to mathematical models, and the best-fit model parameters are compared. Many different models have been suggested in the soil science and engineering literature. The two models that are currently most widely used are the power-law relations of Brooks and Corey (1964) and the model suggested by van Genuchten (1980). These models represent the reduced saturation (θ) of water as a function of the capillary pressure head (Ψ). The reduced saturation is scaled so that it will range from 0 to 1.

$$\Theta_w = \frac{S_w - S_{wr}}{1 - S_{wr}} \quad (3.4.2)$$

The capillary pressure head is generally defined by

$$\Psi = \frac{P_c}{\Delta \rho g} \quad (3.4.3)$$

where $\Delta \rho$ is the density difference between the two fluids. For the air and water system $\Delta \rho = \rho_w$.

The Brooks and Corey model takes the form

$$\begin{aligned} \Theta &= 1, \quad \Psi \leq \Psi_b \\ \Theta &= \left(\frac{\Psi_b}{\Psi} \right)^\lambda, \quad \Psi > \Psi_b \end{aligned} \quad (3.4.4)$$

There are two parameters that appear in the Brooks and Corey model. Ψ_b is called the displacement or *bubbling capillary pressure head*. It is related to the size of the largest void spaces in the porous media. Again, refer to equation (3.4.1). A minimum capillary pressure must be applied before the interface between the wetting and non-wetting fluids is displaced from the largest pore spaces. Until this minimum capillary pressure is applied, the wetting phase saturation does not change. The bubbling capillary pressure head corresponds to the minimum capillary pressure. The second Brooks and Corey model parameter is called the *pore size distribution index*, λ . Large values of λ correspond to a narrow range of pore sizes while small λ values correspond to a wide range in pore sizes.

Van Genuchten (1980) presented the second model that is widely used. For $\Psi > 0$ this model takes the form

$$\Theta = \left(\frac{1}{1 + (a\Psi)^N} \right)^M \quad (3.4.5)$$

where M , N and 'a' are constants. Van Genuchten further suggests that the parameters M and N be related through $M = 1 - 1/N$ or $N = 1/(1-M)$. This model results in a continuous soil characteristic curve throughout the range $\Psi > 0$. On one hand, this is convenient for numerical modeling purposes. On the other hand, this model predicts that the non-wetting fluid can enter a porous medium at zero capillary pressure, and one might question the zero non-wetting phase entry pressure because of the limited size of even the largest pores.

For large capillary heads, the Brooks and Corey and the van Genuchten models become identical if

$$\lambda = N - 1$$

$$\Psi_b = \frac{1}{a}$$
(3.4.6)

Equation (3.4.6) is useful for relating the parameters of the two models. Alternately, Lenhard *et al.* (1989) suggest that throughout the range of water contents a better relationship is found from

$$\lambda = \frac{M}{1-M} (1 - 0.5^{1/M})$$

$$\Theta_* = 0.72 - 0.35 e^{-N^4}$$

$$\Psi_b = \frac{\Theta_*^{1/\lambda}}{a} (\Theta_*^{-1/M} - 1)^{1-M}$$
(3.4.7)

where the parameter Θ_* is defined by the second of Eq. (3.4.7).

Extensive studies have been undertaken by the U.S. Department of Agriculture, the U.S. Environmental Protection Agency, and other organizations to determine the soil water retention parameters for the Brooks and Corey model and the van Genuchten model. Carsel and Parrish (1988) used a database for the 12 Soil Conservation Service (SCS) textural classifications obtained from measurements for all soils reported in SCS Soil Survey Information Reports. These reports

(published by state by the Natural Resource Conservation Service, formerly the Soil Conservation Service) generally contain soil data for the predominant soil series within a state. A total of 42 books representing 42 states were used to develop the database. They used a multiple regression equation developed by Rawls and Brakensiek (1985) to estimate the retention parameters for the Brooks and Corey model, and estimated the corresponding van Genuchten model parameters from these using the asymptotic equations (3.4.6). Table 3.4.2 shows the mean and standard deviation Brooks and Corey model parameters determined from their study. For different soil texture classes, this table provides guidance to representative magnitudes of the respective parameters and their relative variability.

Table 3.4.2 Descriptive Statistics from Carsel and Parrish (1988) Data Set

Tabulated Values: Mean (Standard Deviation)

Soil Type	Residual Saturation, S_{wr}	Bubbling Pressure Head, Ψ_b (m) *	Pore Size Distribution Index, λ
Clay	0.18 (0.089)	1.25 (1.88)	0.09 (0.09)
Clay loam	0.23 (0.024)	0.53 (0.42)	0.31 (0.09)
Loam	0.18 (0.030)	0.28 (0.16)	0.56 (0.11)
Loamy sand	0.14 (0.037)	0.081 (0.028)	1.28 (0.27)
Silt	0.074 (0.022)	0.62 (0.27)	0.37 (0.05)
Silty loam	0.15 (0.033)	0.50 (0.30)	0.41 (0.12)
Silty clay	0.19 (0.064)	2.0 (2.0)	0.09 (0.06)
Silty clay loam	0.21 (0.021)	1.0 (0.6)	0.23 (0.06)
Sand	0.10 (0.023)	0.069 (0.014)	1.68 (0.29)
Sandy clay	0.26 (0.034)	0.37 (0.23)	0.23 (0.19)
Sandy clay loam	0.26 (0.015)	0.17 (0.11)	0.48 (0.13)
Sandy loam	0.16 (0.041)	0.13 (0.066)	0.89 (0.17)

*Carsel and Parrish (1988) report mean and standard deviation of van Genuchten's 'a' parameter. Using Eq. (3.4.6) and a first-order expansion, the standard deviation of Ψ_b is approximated by $\sigma_{\Psi_b} \cong \frac{\sigma_a}{a^2}$.