### DESIGN, CONSTRUCTION, AND EVALUATION OF CLAY LINERS FOR WASTE MANAGEMENT FACILITIES

ROX

233758

CBA 007 0892

by

L.J. Goldman and L.I. Greenfield NUS Corporation Gaithersburg, Maryland 20878

A.S. Damle, G.L. Kingsbury C.M. Northeim, and R.S. Truesdale Research Triangle Institute Research Triangle Park, North Carolina 27709

EPA Contract No. 68-01-7310

### Project Officer

M.H. Roulier Waste Minimization, Destruction and Disposal Research Division Risk Reduction Engineering Laboratory Cincinnati, Ohio 45268

OFFICE OF SOLID WASTE AND EMERGENCY RESPONSE U.S. ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, DC 20460

RISK REDUCTION ENGINEERING LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY. CINCINNATI, OHIO 45268

### TABLE OF CONTENTS

| Chapter |                              |                        |  | Раде               |
|---------|------------------------------|------------------------|--|--------------------|
|         | -                            |                        |  | <u>i ugc</u>       |
|         | Fore<br>Pref<br>Abst<br>Figu | eword<br>face<br>tract | •                    | iii<br>iv<br>v     |
|         | Tab1<br>Ackr                 | es                     | ents   | xiv<br>xix<br>xxii |
| 1       | Intr                         | oduction               | -<br>-   |                    |
| -       | 1.1                          | Scope                  | •                    | 1-1                |
|         | 1.2                          | Summary<br>1.2.1       | y of Current Practices<br>Investigation of Site Conditions | 1-3                |
|         |                              | 1.2.2                  | (Field)<br>Material Selection and Characterization         | 1-3                |
|         |                              | 1.2.3                  | (Laboratory)<br>Develop Liner Design/Construction<br>Plans | 1-4                |
| · .     |                              | 1.2.4                  | Pilot Construction Test (Test Fill)                        | 1-5                |
|         |                              | 1.2.5                  | Construction   | 1-5                |
|         | 1.3                          | Analysi                | s of Current Practices                                     | 1-7                |
|         |                              | 1.3.1                  | Liner Material   | 1-7                |
|         |                              | 1.3.3                  | Water Content  | 1-7                |
|         |                              | 1.3.4                  | Pilot Construction (Test Fill)                             | 1-8                |
|         | 1.4                          | Summary                |  | 1-0                |
|         | 1.5                          | Referen                | ice  | 1-9                |
| 2       | Clav                         | Sati                   |  |                    |
| -       | 2.1                          | Clav Mi                | nerals   | 2-1                |
|         |                              | 2.1.1                  | Clav Mineral Structure                                     | 2-2                |
|         |                              | 2.1.2                  | Clay Mineral Groups  | 2-2                |
|         |                              |                        | 2.1.2.1 Kaolinite Minerals                                 | 2-4                |
|         |                              |                        | 2.1.2.2 Illite Minerals                                    | 2-9                |
|         |                              |                        | 2.1.2.3 Chlorite Minerals                                  | 2-10               |
| •       | 2.2                          | Clav Fo                | 2.1.2.4 Smectite Minerals                                  | 2-13               |
|         |                              | 2.2.1                  | Clav Mineral Paragenesis                                   | 2-14               |
|         |                              | 2.2.2                  | Clay Soil Formation and Occurrence                         | 2-14               |
|         |                              |                        | 2.2.2.1 Fluvial Soils                                      | 2-15               |
|         |                              |                        | 2.2.2.2 Glacial Soils                                      | 2-17               |
|         | 2.3                          | Clav Ch                | 2.2.2.3 Residual Soils                                     | 2-17               |
| ,       | 2.0                          | 2.3.1                  | Flectrical Double Lavon Theory                             | 2-18               |
|         |                              | 2.3.2                  | Cation-Exchange Canacity and Cation                        | 2-18               |
|         |                              |                        | Affinity   | 2_20               |
|         |                              | 2.3.3                  | Significance of the Electrical Double                      | 2-20               |
|         |                              |                        | Layer to Clay Liners                                       | 2_22               |

CBA 007 0893

٧i

· 6

| <u>Chapter</u> |      |                  |   | Page         |
|----------------|------|------------------|---|--------------|
|                | 2.4  | Clay So<br>2.4.1 | il Fabric and Hydraulic Conductivity<br>Soil Porosity and Hydraulic | 2-24         |
|                |      |                  | Conductivity  | 2-24         |
|                |      |                  | Porosity<br>2.4.1.2 Soil Macrostructure and Secondary               | 2-24         |
|                |      | 2.4.2            | Soil Structure and Hydraulic  | 2-27         |
|                | 2.5  | Referen          | ces   | 2-32<br>2-38 |
| 3              | Test | Methods          | and Soil Properties   | 3-1          |
|                | 3.1  | Introdu          | ction   | 3-1          |
|                | 3.2  | Fundame          | ntal Relationships  | 3-2          |
|                |      | 3.2.1            | Water Content   | 3-2          |
|                |      | 3.2.2            | Density   | 3-2          |
|                |      | 3.2.3            | Specific Gravity  | 3-2          |
| •              |      | 3.2.4            | Unit Weight   | 3-5          |
|                |      | 3.2.5            | Void Ratio  | 3-5          |
|                |      | 3.2.6            | Porosity  | 3-5          |
|                |      | 3.2.7            | Degree of Saturation  | 3-6          |
|                | 3.3  | Atterbe          | rg Limits   | 3-6          |
|                | 3.4· | Soil Cl          | assification  | 3-10         |
|                |      | 3.4.1            | Grain Size Analysis   | 3-10         |
|                |      | 3.4.2            | The Unified Soil Classification System                              | 3-15         |
|                |      |                  | 3.4.2.1 Field Classification  | 3-15         |
|                |      |                  | 3.4.2.2 Laboratory Classification                                   | 3-17         |
|                |      |                  | 3.4.2.3 Field Identification Procedures for                         |              |
|                |      |                  | Fine-Grained Soils or Fractions                                     | 3-19         |
|                | 3.5  | Compact          | ion   | 3-20         |
|                |      | 3.5.1            | Fundamentals of Compaction  | 3-20         |
|                |      | 3.5.2            | Compaction and Permeability   | 3-25         |
|                | 3.6  | Field M          | easurement of Density and Moisture                                  | 0 20         |
|                |      | Content          |   | 3-25         |
|                |      | 3.6.1            | Traditional Methods   | 3-25         |
|                |      | 3.6.2            | Nuclear Methods   | 3-28         |
|                |      |                  | 3.6.2.1 Nuclear Density Gauge                                       | 3-28         |
|                |      |                  | 3.6.2.2 Nuclear Moisture Gauge                                      | 3-31         |
|                | 3.7  | Testing          | for Shear Strength  | 3-33         |
|                | 3.8  | Hydraul          | ic Conductivity Testing   | 3-35         |
|                |      | 3.8.1            | Darcy's Law   | 3_36         |
|                |      | 3.8.2            | Hydraulic Gradient  | 3-38         |
|                |      | 3.8.3            | Permeability Measurement and Factors                                | J-JU         |
|                |      |                  | That Influence Test Results   | 3_20         |
|                |      |                  | 3.8.3.1 Sample Selection Size and                                   | 2-22         |
|                |      |                  | Prenaration   | 2 40         |
|                |      |                  | 3.8.3.2 Hydraulic Gradient  | 3-40         |
| •              |      |                  | 3833 Sample Saturation  | 3-40         |
|                |      |                  |   | 5-4/         |

| <u>Chapter</u> | -           |   |   | Page   |
|----------------|-------------|---|---|--|
| ų              |             | 3.8.4   | 3.8.3.4Permeant Characteristics3.8.3.5Test DurationLaboratory Permeability Tests3.8.4.1Pressure Cell3.8.4.2Compaction Permeameter3.8.4.3Triaxial Cells                          | 3-49<br>3-49<br>3-50<br>3-50<br>3-50<br>3-55         |
|                |             | 3.8.5   | 3.8.4.4Consolidation CellsField Permeability Tests3.8.5.1Bore Hole Tests3.8.5.2Porous Probes3.8.5.3Air Entry Permeameter3.8.5.4The Guelph Permeameter3.8.5.5Ring Infiltrometers | 3-57<br>3-57<br>3-57<br>3-61<br>3-63<br>3-66<br>3-69 |
|                | 3.9         | Referen                                       | ces   | 3-73   |
| 4              | Clay<br>4.1 | -Chemica<br>Paramet                           | 1 Interactions and Soil Permeability<br>ers Determined in Permeability  | 4-1  |
|                | 4.2         | Clay-Ch<br>Rermeab                            | emical Interactions that Influence  | 4-2  |
|                |             | 4.2.1<br>4.2.2<br>4.2.3<br>4.2.4              | Soil Fabric and Permeability<br>Dissolution by Strong Acids or Bases<br>Precipitation of Solids<br>Effect of Microorganisms   | 4-3<br>4-4<br>4-11<br>4-11<br>4-11                   |
|                | 4.3         | Measuri<br>Through<br>4.3.1<br>4.3.2<br>4.3.3 | ng Clay-Chemical Compatibility<br>Permeability Testing<br>Measurement Devices<br>Test Setup<br>Compatibility of Materials With Test   | 4-12<br>4-12<br>4-13                                 |
|                |             | 4.3.4<br>4.3.5                                | Effect of Backpressure<br>Effect of Hydraulic Gradient  | 4-14<br>4-14   |
|                | 4.4<br>4.5  | 4.3.6<br>Summary<br>Permeab                   | Criteria for Concluding a Test<br>of Available Research Data<br>ility Studies To Investigate Clay-Chemical  | 4-15<br>4-16   |
| •<br>• • • •   |             | Interac<br>results<br>4.5.1                   | tions (test methods, data, and discussion of<br>for 23 individual studies)<br>Observations by Macey (1942) on   | 4-16   |
|                |             | 1 5 2   | Effects of Organics on Fireclay   | 4-16   |
|                |             | 4.5.2   | Solvents by Michaels and Lin (1954)   | 4-26   |
|                |             | 4.5.3   | of Naphtha on Montmorillonite   | 4-29   |
|                |             | · • • • • • • •                               | of the Effect of Electrolyte<br>Concentration on Permeability of a  |  |
|                |             |   | Sodic Soil  | 4-29   |

viii

5 .....

#### Chapter

#### Tests by van Schaik and Laliberte (1968) 4.5.5 of Permeability of Soils to a Liquid 4-31 Hydrocarbon ..... Study by Everett (1977) of Permeability 4.5.6 of Lacustrine Clay to Four Liquid Wastes ..... 4-32 Tests by Sanks and Gloyna (1977) of 4.5.7 Permeability of Lacustrine Clay to 4-33 Liquid Waste ..... Investigation of the Effect of 4.5.8 Organic Solvents on Clays by Green, Lee, and Jones (1979) ..... 4-35 Anderson's Study (1981) of the Effects 4.5.9 of Organics on Permeability ..... 4-39 Schramm's Study (1981) of the 4.5.10 Permeability of Soil to Organic Solvents ..... 4-54 Evaluation by Monserrate (1982) 4.5.11 of the Permeability of Two Clays to 4-59 Selected Electroplating Wastes ..... Research by Brown, Green, and Thomas 4.5.12 (1983) on the Effect of Two Organic Hazardous Wastes on Simulated Clay Liners ..... 4-60 Study by Brown, Thomas, and Green (1984) of the Effect of Dilutions 4.5.13 of Acetone and Mixtures of Xylene and Acetone on Permeability of a 4-64 Micaceous Soil ..... Tests by Brown, Thomas, and Green 4.5.14 (1984) to Determine the Permeability of Micaceous Soil to Petroleum Products ..... 4-64 Study by Brown and Thomas (1984) of 4.5.15 the Permeability of Commercially 4-70 Available Clays to Organics ..... Studies Conducted for EPA by Daniel 4.5.16 (1983) and Foreman and Daniel (1984) 4-72 at the University of Texas, Austin ..... Tests Conducted for Chemical 4.5.17 Manufacturers Association by Daniel and Liljestrand (1984) ..... 4-73 4.5.18 Study by Dunn (1983) of the Effects of Synthetic Lead-Zinc Tailings Leachate on Clay Soils ..... 4-81 Studies by Acar and Others (1984) on the 4.5.19 Effect of Organics on Kaolinite ..... 4-82 Finding by Olivieri (1984) of 4.5.20 Impermeability of Montmorillonite to 4-83 Benzene ..... Study of Permeability of Clays to 4.5.21 Simulated Inorganic Textile Wastes by Tulis (1983) ..... 4-84

CBA 007 0896

Page

| <u>Chapter</u> |     |          |  | Page         |
|----------------|-----|----------|--|--------------|
|                |     | 4.5.22   | Tests Conducted by Engineering<br>Consulting Firms for Specific Applica- |              |
|                |     |          | tion (unpublished data)  | A 0A         |
|                |     | 4.5.23   | Tests Reported by Bentonite Companies                                    | 4-04         |
|                | 4.6 | Refere   | nces   | 4-98         |
| 5              | Cur | rent Pra | ctices. Clay Liner Design and Installation                               |              |
| _              | 5.1 | Desian   | the besign and installation  | 5-1          |
|                |     | 5.1.1    | Site Investigation   | 5-1          |
|                |     | 5.1.2    | Liner Material Selection and   | 5-2          |
| ,              |     |          | Characterization   | 5-6          |
|                |     |          | 5.1.2.1 Native Soils   | 5-13         |
|                |     |          | 5.1.2.2 Admixed Soils  | 5-14         |
|                |     | 5.1.3    | Facility Design  | 5-16         |
|                |     |          | 5.1.3.1 Configuration  | 5-16         |
|                |     |          | 5.1.3.2 Foundation Design  | 5-16         |
|                |     |          | 5.1.3.2.1 Settlement   | 5-16         |
|                |     |          | 5.1.3.2.2 Seepage  | 5-17         |
|                |     |          | 5 1 3 2 4 Sidouall Decise  | 5-18         |
|                |     |          | 5 1 3 2 5 Rottom Docion  | 5-21         |
|                |     |          | 5.1.3.3 liner Design   | 5-27         |
|                |     |          | 5.1.3.4 Special Design Considerations                                    | 5-2/         |
|                |     |          | 5.1.3.4.1 Control of Frosion   | 5-32         |
|                |     |          | 5.1.3.4.2 Control of Scouring  | 5-32         |
|                |     |          | 5.1.3.4.3 Cold Climate Design  | 5-34         |
|                |     |          | 5.1.3.4.4 Control of Piping  | 5-34         |
|                |     |          | 5.1.3.4.5 Control of Desiccation   | 5-35         |
|                |     |          | 5.1.3.4.6 Seismic Design   | 5-35         |
|                |     |          | 5.1.3.4.7 Intergradient Facility   |              |
|                |     | 511      | Design   | 5-39         |
|                |     | 5.1.5    | Design Case Studion  | 5-40         |
|                | 5.2 | Clav I i | ner Construction: Nethodology  | 5-42         |
|                |     | and Equ  | ipment   | 5 40         |
|                |     | 5.2.1    | Preinstallation Activities   | 5-40         |
|                |     |          | 5.2.1.1 Foundation Preparation   | 5-40<br>5-46 |
| , t            |     |          | 5.2.1.2 Groundwater Control  | 5-40         |
|                |     |          | 5.2.1.3 Leak Detection System Installation                               | 5-48         |
|                |     | 5.2.2    | Clay Liner Installation  | 5-48         |
|                |     |          | 5.2.2.1 Natural Soil Liners  | 5-48         |
|                |     |          | 5.2.2.1.1 Liner Material   |              |
|                |     |          | Emplacement  | 5-49         |
|                |     |          | 5.2.2.1.2 Clod Size Reduction  | 5-49         |
|                |     |          | 5.2.2.1.3 Moisture Control   | 5-52         |
|                |     |          | 5.2.2.2 Admixed Pentential Line  | 5-55         |
|                |     |          | 5.2.2.3 Climatic Efforte   | 5-70         |
|                |     | 5.2.3    | Postinstallation Activition  | 5-75         |
|                |     |          | Constantation Activities   | 5-80         |

ا معدورين .

| Chapter |             |   | Page                                 |
|---------|-------------|---|--------------------------------------|
|         | 5.3         | Quality Assurance and Quality Control<br>5.3.1 Key Terms<br>5.3.2 Personnel<br>5.3.3 Observations and Tests<br>5.3.4 Documentation                    | 5-82<br>5-83<br>5-86<br>5-88<br>5-98 |
|         | 5.4         | Clay Liner Design and Construction: Problems<br>and Preventive Measures   | 5-109                                |
|         | 5.5         | References  | 5-112                                |
| 6       | Fail<br>6.1 | ure Mechanisms<br>Desiccation Cracks<br>6.1.1 Description<br>6.1.2 Studies of Cracking  | 6-1<br>6-1<br>6-2                    |
|         | 6.2         | Slope Instability<br>6.2.1 Description  | 6-3<br>6-3<br>6-4                    |
|         | 6.3         | Settlement  | 6-5<br>6-5<br>6-5                    |
|         | 6.4         | Piping<br>6.4.1 Description<br>6.4.2 Studies of Piping  | 6-6<br>6-6<br>6-6                    |
|         | 6.5         | Penetration<br>6.5.1 Description<br>6.5.2 Studies of Penetration  | 6-8<br>6-8<br>6-9                    |
|         | 6.6         | Erosion<br>6.6.1 Description  | 6-9<br>6-9                           |
|         | 6.7         | Cold Climate Operations   | 6-9<br>6-11                          |
|         | 6.0         |   | 6-15                                 |
|         | 6.10        | Failures from Design or Construction Errors   | 6-16                                 |
|         | 6.11        | References  | 6-17                                 |
| 7       | Clay        | Liner Performance   | 7-1                                  |
|         | /.1         | Case Studies (physical description: startum date:   | /-1                                  |
|         | /•2         | geology and hydrology; waste type; liner description,   |                                      |
|         |             | installation, and performance for 17 clay-lined   | 71                                   |
| •       |             | facilities) for Site Selection  | 7-1                                  |
|         |             | 7.2.1 Uniteria for Site Selection $\dots \dots \dots$ | 7-5                                  |
|         |             | 7.2.3 Site B  | , c<br>7-7                           |
|         |             | 7.2.4 Site C  | 7-9,                                 |
|         |             | 7.2.5 Site D  | 7-14                                 |
|         |             | 7.2.6 Site E  | 7-18                                 |
|         |             | 7.2.7 Site F  | 7-21                                 |
|         |             | 7.2.8 Site G  | 1-20                                 |
|         |             | /.2.9 ,5100 H   | 7-20                                 |
|         |             | 7.2.10 JILE 1   | 7-38                                 |

<u>Chapter</u>

| <u>Chapter</u> |            |   | Page       |
|----------------|------------|---|------------|
|                |            | 7.2.12 Site K                                   | 7-42       |
|                |            | 7.2.13 Site L                                   | 7-46       |
|                |            | 7.2.14 Site M                                   | 7-49       |
|                |            | 7.2.15 Site N                                   | 7-55       |
|                |            | 7.2.16 Site 0                                   | 7-59       |
|                |            | 7.2.17 Site P                                   | 7-62       |
|                |            | 7.2.18 Site Q                                   | 7-67       |
|                | 7.3        | Liner Types                                     | 7-70       |
|                |            | 7.3.1 Unlined Facilities                        | 7-71       |
|                |            | 7.3.2 Recompacted Soil Liners                   | 7-72       |
|                |            | 7.3.3 Admixed Liners                            | 7-72       |
|                | 7.4        | Site Characterization                           | 7-73       |
|                |            | 7.4.1 Case Studies                              | 7-74       |
|                | 7.5        | Installation of Clay Liners                     | 7-74       |
|                |            | 7.5.1 Installation Methods                      | 7-75       |
|                |            | 7.5.2 Quality Assurance/Quality Control -       |            |
|                |            | for Clay Liners                                 | 7-76       |
|                | 7.6        | Waste Types                                     | 7-77       |
|                |            | 7.6.1 Free Liquids                              | 7-77       |
|                |            | 7.6.2 Stabilized or Solidified Liquids          | 7-78       |
|                |            | 7.6.3 Sludges and Solid Wastes                  | 7-78       |
|                |            | 7.6.4 Waste Compatibility                       | 7-79       |
|                | /./        | Performance Monitoring                          | 7-81       |
|                |            | 7.7.1 Unsaturated Zone Monitoring               | 7-82       |
|                |            | 7.7.2 Groundwater Monitoring                    | 7-84       |
|                |            | 7.7.3 Leachate Level and Quality                |            |
|                | 7 0        | Monitoring                                      | 7-85       |
|                | 7.0        |   | 7-85       |
|                | /.9        |   | 7-86       |
| 8              | Pred       | iction of Clay Liner Performance                | ~ .        |
| Ū              | 8.1        | Introduction                                    | 8-1        |
|                | 8.2        | Background Considerations                       | 8-1        |
|                | 012        | 8.2.1 Performance Criteria                      | 8-1        |
|                |            | 8.2.2 Clay Liner System                         | 8-1        |
|                |            | 8.2.3 General Equations                         | 0-2        |
| •              | 8.3        | Transit Time Prediction Methods                 | 8-6        |
|                |            | 8.3.1 Simple Transit Time Fountion              | 8-6        |
|                |            | 8.3.2 Modified Transit Time Equation            | 8_8        |
|                |            | 8.3.3 Green-Ampt Wetting Front Model            | 8-0        |
|                | •          | 8.3.4 Transient Linearized Infiltration         | 00         |
|                |            | Equation  | 8-10       |
|                | _          | 8.3.5 Numerical Solutions                       | 8-12       |
|                | 8.4        | Comparison of Different Approaches              | 8-14       |
|                | 8.5        | Batch-Type Absorption Procedures for Estimating |            |
|                | . ·        | Clay Liner Performance                          | 8-14       |
|                | 8.6        | References                                      | 8-16       |
|                |            |   | - <b>.</b> |
| Appendix       | <b>.</b> . |   |            |
| A              | Test       | Method Descriptions                             | A-1        |
|                |            |   | -          |

x11

0899

CBA 007

## FIGURES

| Number         |   | Page |
|----------------|---|------|
| 1-1            | Cross section of an idealized clay liner system                 | 1-2  |
| 2-1            | Clay mineral tetrahedral sheet structure                        | 2-3  |
| 2-2            | Clay mineral octahedral sheet structure                         | 2-3  |
| 2-3            | Kaolinite group minerals  | 2-7  |
| 2-4            | Illite clay minerals  | 2-11 |
| 2-5            | Chlorite and smectite clay minerals                             | 2-12 |
| 2=0            | Electrical double laver   | 2-19 |
| 2-0            | Effect of solution of on clay mineral surface                   |      |
| _ 2-1          | charge (EDM)  | 2-21 |
| 2 0            | Comparisons of clay mineral sizes and surface areas             | 2-23 |
| 2-0            | Comparisons of cray mineral sizes and currect a construction    | 2-25 |
| 2-9            | Uldy SUIT TADITUS   | 2-28 |
| 2-10           | Fractures in glacial till                                       | 2-29 |
| 2-11           | ROOT CASE IN GIACIAL CITL                                       | 2-30 |
| 2-12           | Permeable strata in glacial till deposittest                    | 2-33 |
| 2-13           | Compaction curve from a standard compaction test                | 2 00 |
| 2-14           | Compaction curves for different compactive errores              | 2-34 |
|                | applied to a silty clay   | 2 04 |
| 2-15           | Permeability as a function of molding water content             |      |
|                | for samples of silty clay prepared to constant                  | 2-36 |
|                | density by kneading compaction                                  | 2-30 |
| 2-16           | The effect of dispersion on hydraulic conductivity              | 2-37 |
| 2-17           | Effect of method of compaction on the permeability              | 2-30 |
|                | (hydraulic conductivity) of a silty clay                        | 2-33 |
| 3_1            | Schematic representation of soil illustrating the               |      |
| 5-1            | fundamental relationships among the solid. liquid.              |      |
|                | and air constituents  | 3-4  |
| 2 2            | Consistency limits of cohesive soils                            | 3-6  |
| 2-2            | Device for determining the liquid limits of a                   |      |
| 2-2            | cohorive soil. The dish contains a grooved sample               | 3-7  |
| 2 /            | Clay cample being grooved for liquid limit test                 | 3-7  |
| 3-4            | Dolling a clay sample for plastic limit test                    | 3-9  |
| 3-5            | Rolling a clay sample for plastic finite cese totototototototo  |      |
| 3-0            | the plastic limit   | 3-9  |
| 27             | Tunical relationships between the liquid limit                  |      |
| 3-1            | and the placticity index for various soils                      | 3-11 |
| 2 0            | Identical entricle size distribution curves for                 |      |
| 3-8            | idealized particle size distribution curves for                 | 3-14 |
| 2.0            | Weil-graded, poorly-graded, and gap-graded sorro for the terror | 3-16 |
| 3-9            | Tuning soil compaction curve illustrating maximum               | • •• |
| 3-10           | Typical Soll compaction curve infusciating maximum              | 3-21 |
| <b>•</b> • • • | ary density and optimum water content                           | 0    |
| 3-11           | compaction curves for affective compactive efforts              | 3-23 |
|                | applied to a silty clay found from                              | 5 25 |
| 3-12           | Four types of compaction curves found from                      | 3_21 |
|                |   | 5-24 |
| 3-13           | Permeability as a function of molding water concent             |      |
|                | for samples of silty clay prepared to constant density          | 3 25 |
|                | by kneading compaction  | 5-20 |

### xiii

FIGURES (continued)

| Num          | her   |            |
|--------------|---|------------|
| <u>Itani</u> | <u>.</u>  |            |
| 3-1          | 14 Influence of   | Page       |
|              | Dermonte of the method of compaction on the   | <u> </u>   |
| 3-1          | 15 Schematic of silty clay  |            |
| -            | for O toot  | 3-27       |
| 3-1          | 6 Effect of have  |            |
|              | Sasumua alackpressure on permeability to unter  | 3-34       |
| 3-1          | 7 Apparatus for   |            |
| 3-1          | 8 Modified come cell method   | 3-48       |
| 3-1          | 9 Detail of the | 3-51       |
| 3-20         | Schematic of the base plate for a double-ring and   | 3-53       |
| 3-21         | Consolidation a constant head triaxial coll permeameter   | 3-54       |
| 3-22         | Two-stage to permeameter  | 3-56       |
|              | Derick looc   | 3-58       |
| 3-23         | Installed news  |            |
| 3-24         | Modified air and probe (Daniel, 1987)   | 3-59       |
| 3-25         | Schematic discutty permeameter  | 3-62       |
| 3-26         | Double-ring in the of Guelph permeameter  | 3-64       |
| 3-27         | Sealed double militrometer  | 3-67       |
|              | double-ring infiltrometer   | 3-70       |
| <u>4-1</u>   | Change in a new in  | 3-72       |
|              | permeability income ter (400%) corresponding to a   |            |
| 4-2          | Distribution of increase of 25,600%   |            |
| _            | according to the adjacent to a clay surface   | -5         |
| 4-3          | Intrinsic permashility of the diffuse double laws   |            |
|              | (e) measured for differences as a function of void space 4  | -7         |
| 4-4          | Coefficient of permeants  |            |
| 4 5          | various chemicals   | -28        |
| 4-5          | Permeability of the four all  |            |
| 1 6          | (0.01N CaSO4) 4.  | -40        |
| 4-0          | Permeability of the four clauses  | 12         |
| 4-/          | Permeability and breakthrough soils to acetic acid  | .4.5       |
| 4-8          | Clay soils treated with aniling   | 44         |
| 4-9          | Permeability of the four clay coils   |            |
| 4-10         | Permeability of the four clay soils to ethylene glycol  | 45         |
| . 10         | and the four clay soils to acetone  | 40         |
|              | mixed astimute for the methanol   | +/         |
| 4-11         | Permonhalitic clay soil   |            |
|              | illitic all of the methanol-treated mined   | 19         |
| 4-12         | Permeability soil at two hydraulic gradients  | <i>,</i> 0 |
|              | Clay soils treakthrough curves of the factor 4-4  | 9          |
| 4-13         | Permeability and with xylene  | 5          |
|              | Clay soils treakthrough curves of the faust   | 0          |
| 4-14         | Variation of interior with heptane  | -          |
|              | for each soil   | 1          |
| 4-15         | Permeability of University of Solvent   | -          |
|              | sulfate chromie Store clay to 0 01 N and 4-56   | 3          |
|              | (1 molar) as a c acid (1 molar), and zing chiaring  | -          |
|              | as a runction of moisture at compact  |            |
|              | 4-61  |            |

## FIGURES (continued)

## Number

## Page

| 4-16       | Hydraulic conductivity versus pore volume for                        |                          |
|------------|--|--------------------------|
|            | kerosene at a hydraulic gradient of 91                               | 4-65                     |
| 4-17       | Hydraulic conductivity versus pore volume for                        |                          |
|            | laboratory-compacted micaceous soil exposed to                       | 1 66                     |
|            | diesel fuel at a hydraulic gradient of 91                            | 4-00                     |
| 4-18       | Hydraulic conductivity versus pore volume for                        |                          |
|            | laboratory-compacted micaceous soll exposed to                       | <b>4-67</b> <sup>.</sup> |
| 4 10       | parattin oil at a nyurauric gradient of si                           |                          |
| 4-19       | laboratory-compacted micaceous soil exposed to                       |                          |
|            | pasoline at a hydraulic gradient of 91                               | 4-68                     |
| 4-20       | Hydraulic conductivity versus pore volume for                        |                          |
|            | laboratory-compacted micaceous soil exposed to                       |                          |
|            | motor oil at a hydraulic gradient of 91                              | 4-69                     |
| 4-21       | Permeability versus number of pore volumes of flow                   |                          |
|            | for kapinite permeated with methanol at a hydraulic                  | 4-74                     |
|            | gradient of 250 or 300 bydraulic gradient for kaplinite              | т / т                    |
| 4-22       | permeability versus hydraulic gradient for kaorinite                 | 4-75                     |
| 1-23       | Permeability versus hydraulic gradient for kaolinite                 |                          |
| 4-23       | permeated in consolidation cell permeameters                         | 4-76                     |
| 4-24       | Permeability versus hydraulic gradient for kaolinite                 |                          |
|            | permeated in compaction mold cell                                    | 4-77                     |
| <b>г</b> 1 | Compared alow suboff soal  | 5-19                     |
| 5-1        | Dike components and typical configurations                           | 5-20                     |
| 5-2        | Methods of liner sidewall compaction                                 | 5-22                     |
| 5-4        | Liner design for collection system pipes and sump                    | 5-28                     |
| 5-5        | Methods of keying-in liner segments                                  | 5-30                     |
| 5-6        | Liner material emplacement   | 5-50                     |
| 5-7        | Emplacement of liner material over foundation                        | F F1                     |
|            | excavation underneath a collection pipe                              | 2-21                     |
| 5-8        | Use of pulvi-mixer for clod size reduction                           | 5-54                     |
| 5-9        | Moisture addition to liner material pilot to                         | 5-56                     |
| 5-10       | loints and seenage along lift boundaries                             | 5-61                     |
| 5-10       | Sketches of different types of roller feet                           | 5-65                     |
| 5-12       | Various compacting rollers   | 5-67                     |
| 5-13       | Compaction on a 2(H) to 1(V) slope with a towed                      |                          |
|            | sheepsfoot roller  | 5-69                     |
| 5-14       | Central plant mixing of bentonite and soil                           | 5-/2                     |
| 5-15       | Truck-loaded bentonite spreader                                      | 5-/3                     |
| 5-16       | Pneumatically fed bentonite spreader                                 | 5-70                     |
| 5-17       | Blending bentonite with soil Using a disk harrow                     | 5_70                     |
| 5-18       | Joil Stabilizer mixing benconfile in place                           | 5-81                     |
| 5-19       | Initialable dulie over a hazardous waste failurer                    | 5-10                     |
| 5-20       | Statictical analysis of CAC test data                                | 5-104                    |
| 3-21       | JURIJUI ANALYSIS VI VVV LEST VALA ********************************** |                          |

0902 CBA 007

# FIGURES (continued)

| Number    |   | Page |
|-----------|---|------|
| 6-1       | Location of past destructive earthquakes in the     |      |
| • •       | United States                                       | 6-12 |
| 6-2       | Differences in propagation of damage for eastern    |      |
|           | and western earthquakes                             | 6-12 |
| 7-1       | Plan view of site A                                 | 7-6  |
| 7-2       | Plan view of site B                                 | 7-8  |
| 7-3       | Plan view of site C                                 | 7-10 |
| 7-4       | Cross-sectional view of site C (vertical            |      |
|           | dimensions are to scale)                            | 7-12 |
| 7-5       | Plan view of site D                                 | 7-15 |
| 7-6       | Cross-sectional view of site D liner                | 7-17 |
| 7-7       | Plan view of site E                                 | 7-19 |
| 7-8       | Cross-sectional view of site F                      | 7-22 |
| 7-9       | Plan view of site G                                 | 7-26 |
| 7-10      | Plan view of site H                                 | 7-29 |
| 7-11      | Cross-sectional view of site H liner showing        |      |
|           | details of leachate collection system and lysimeter |      |
|           | construction  | 7-30 |
| 7-12      | Plan view of site I                                 | 7-36 |
| 7-13      | Cross section of liner at site I                    | 7-37 |
| 7-14      | Plan view of site J                                 | 7-39 |
| 7-15      | Cross-sectional view of site J liner                | 7-41 |
| 7-16      | Cross-sectional view of site K liner                | 7-43 |
| 7-17      | Cross section of containment system at site L       | 7-47 |
| 7-18      | Cross section of site M                             | 7-50 |
| /-19      | Plan view of site M leachate collection and leak    |      |
| 7 00      | detection systems                                   | 7-51 |
| 7-20      | Plan view of site N                                 | 7-57 |
| /-21      | Cross-sectional view of site N liner and leachate   |      |
| 7 00      | management systems                                  | 7-58 |
| /-22      | Cross section of site P showing relationship of     |      |
| . 7 . 0.0 | liner and dikes                                     | 7-63 |
| 7-23      | Detailed cross section of site P liner              | 7-64 |
| /-24      | cross section of site Q liner                       | 7-69 |
| 8-1       | Flow domain for leachate flow                       | 0 7  |
| ,         |   | 9-3  |

xvi

CBA 007 0903

1 40.00 \$

### TABLES

| <u>No.</u>   |  | Page           |
|--------------|--|----------------|
| 2-1          | Clay Mineral Characteristics   | 2-5            |
| 3-1          | Soil Tests Summarized in Appendix A  | 3-3            |
| 3-2          | U.S. Standard Sieve Sizes and Their Corresponding<br>Open Dimension                      | 3-13           |
| 3-3<br>3-4   | Z/A of Various Soil Components   | 3-30           |
| J-4          | Permeability Tests on Saturated Soil   | 3-41           |
| 3-5          | Permeability of Compacted Clay Liners  | , .<br>, , , , |
| 3-6          | from Laboratory Tests<br>Test Results Showing Effect of Sample                           | 3-42           |
| 00           | Diameter on Permeability Measurements  | 3-45           |
| 4-1          | Results of Permeability Tests With Organic Chemicals                                     | 4-17<br>4-24   |
| 4-2<br>4-3   | Void Ratio and Coefficient of Permeability   | 7 67           |
|              | Relationships for Calcium- and Sodium-<br>Montmorillonite Permeated by Water and Naphtha | 4-30           |
| 4-4          | Summary of Soil Permeability With Soltrol C and Water                                    | 4-30           |
| 4-0          | Exposed to Water and Waste Liquids   | 4-34<br>4-36   |
| 4-6<br>4-7   | Classification of Clay-Organic Solvent Systems   | 4 00           |
| °<br>4-8     | According to Swell Properties  | 4-37           |
| 1_0          | Organic Liquids and Water And Properties   | 4-38           |
| 4-5          | of the Four Clay Soils   | 4-41           |
| 4-10<br>4-11 | Permeability Coefficients (cm/s) Determined  | 4 57           |
| 4-12         | in Soils Tested With Organic Solvents  | 4-5/           |
| 4-13         | Tested (Brown and Thomas, 1984)<br>Properties of Clav Soils Tested by Daniels and        | 4-71           |
| , <u> </u>   | Liljestrand (1984)   | 4-79<br>4-80   |
| 4-14         | Permeability Test Results (Pennsylvania Case A)  | 4-87           |
| 4-16<br>4-17 | Chemical Characteristics of Waste Permeants, Project E                                   | 4-00           |
| 4-18<br>4-19 | Results of Permeability Tests, Project E   | 4-92<br>4-95   |
| 4-20         | Initial and Final Permeabilities Determined  | 4-95           |
| 4-21         | Effect of Concentrated Organics on a Treated   |                |
| 4-22         | Bentonite Seal<br>Permeability (cm/s) of a Treated Bentonite                             | 4-9/           |
|              | Seal to Kerosene   | 4-97           |

# TABLES (continued)

| No.  |   |       |
|------|---|-------|
|      |   | Page  |
| 5-1  | Accessible Methods of Subsurface Exploration            | F 7   |
| 5-2  | Nonaccessible Methods of Subsurface Exploration         | 5-/   |
| 5-3  | Properties of Soils Used To Construct Soil Liners       | 5-9   |
| 5-5  | Factors Controlling Statistic Construct Soil Liners     | 5-12  |
|      | in Some Problem Soils                                   |       |
| 5-6  | Relative Volume Change of a Soil on Taking              | 5-25  |
|      | by Plasticity Index and Other Parameters                |       |
| 5-7  | Soil Volume Change as Indicated by Liquid Limit and Out | 5-36  |
|      | Size Grain  |       |
| 5-8  | Effect of Clod Size on Permeability of Laboratory       | 5-36  |
| 5.0  | Compacted Clay  | 5 53  |
| 5-3  | Compaction Equipment and Related Specifications for     | 5-53  |
| 5-10 | Compaction Equipment                                    | 5-58  |
| 5-11 | Current OA Practices for Claudia                        | 5-63  |
| 5-12 | Recommendations for Construction                        | 5-99  |
|      | of Clay-Lined Landfills by the Wisconsin Documentation  |       |
|      | of Natural Resources                                    |       |
| 5-13 | Elements of a Construction Documentation Report         | 5-101 |
| 5-14 | Potential Clay Liner Design and Installation            | 5-102 |
|      | Problems and Preventive Measures                        | E 110 |
| 7-1  | Clay-Linod Englisher in a                               | 5-110 |
| 7-2  | General Occurrence of Chamination                       | 7-3   |
|      | Groundwater at Site C                                   | / 3   |
| 7-3  | Lysimeter (L) and Leachate Collocation Cont             | 7-13  |
|      | Liquid Volumes (gal) at Site H                          |       |
| 7-4  | Monitoring Data for Site H                              | 7-32  |
| /-5  | Heavy Metal Content and Percent Solids of Lime          | 7-34  |
| 7-6  | Sludge Disposed at Site M                               | 7 50  |
| /-0  | Site M  | /-52  |
| 7-7  | leachate Analysia at all                                | 7-54  |
| 7-8  | Leachate Volumes at Site M                              | 7-56  |
| 7-9  | Water Sample Analysis: Bop Cop Tatal O the              | 7-57  |
| 4    | and Fecal Coliform                                      |       |
| • •  |   | 7-60  |
| 8-1  | Comparison of Transit Time Predictions                  | • • - |
|      |   | 8-15  |

xviii

TABLE 4-1. RESULTS OF PERMEABILITY TESTS WITH ORGANIC CHEMICALS

ALIPHATIC AND AROMATIC HYDROCARBONS

Heptane

Fixed-wall permeameter tests at high gradient with four clays showed rapid permeability increases and breakthrough. The increase in permeability was more than 3 orders of magnitude in an illite clay. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. (Anderson, 1981)

Benzene

The flow rate of benzene through fireclay was of an enormously higher order of magnitude than the flow rate for water. (Macey, 1942)

In a column test under a head of 701 cm (23 feet), signs of full penetration throughout the clay material were observed after 36 days; in a similar column with water as the permeant fluid the liquid level dropped less than 2.54 cm (1 inch) over a 100-day period. Samples were 91 cm in height and 2.54 cm in diameter. (White, 1976, unpublished data)

Following an initial decrease in permeability (compared to permeability to deionized water established in a similar sample), total breakthrough occurred on the eighth day of testing when Ranger shale was exposed to benzene in a fixed-wall permeameter under low hydraulic gradient. (Green et al., 1979)

Benzene did not penetrate compacted Ca-montmorillonite that was first saturated with 0.01 N calcium sulfate even at hydraulic gradients as high at 150. (Olivieri, 1984)

In flexible-wall tests with a Georgia kaolinite, permeability decreased until the tests were terminated. The final value was approximately 2 orders of magnitude lower than the initial permeability. (Acar et al., 1984a)

Xylene

Following an initial decrease in permeability, total breakthrough occurred on the 25th day of testing when fireclay was tested in a fixed-wall permeameter under low hydraulic gradient. In Ranger shale, a slight decrease in permeability was observed and remained steady until the test was terminated at 40 days. In Kosse kaoline, a slight decrease in permeability was followed by an increase to about the initial level, which persisted until the test was terminated at day 36; changes did not exceed half an order of magnitude. (Green et al., 1979)

In column tests under very low gradient, intrinsic permeabilities were higher than permeability to water by at least 1 order of magnitude in samples of Lake Bottom, Nicholson, Fanno, Chalmers, and Canelo clays. Permeabilities

(continued)

4-17

#### Xylene (con.)

were slightly higher than for water in three other soils. The samples (5.8 cm in diameter and 5 cm in height) were presaturated with xylene. (Schramm, 1981)

Fixed-wall tests at high gradient with four clays showed permeability increases and breakthrough followed by nearly constant permeabilities roughly 2 orders of magnitude higher than baseline permeabilities. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. (Anderson, 1981)

In fixed-wall permeameter tests at high gradient, the permeability of an unsaturated micaceous soil was 4 orders of magnitude higher when exposed to xylene than when tested with 0.01 N calcium sulfate. (Brown et al., 1984)

#### Xylene/Acetone

In fixed-wall permeameter tests at high gradient, the permeability of an unsaturated micaceous soil to either pure acetone or pure xylene was greater than the permeability determined for mixtures of the two solvents. The permeability of a mixture of 87.5 percent xylene and 12.5 percent acetone was lower by 3 orders of magnitude than the permeability measured with pure xylene (though still higher than the permeability to 0.01 N calcium sulfate). When the acetone component was increased to 75 percent, the permeability was approximately the same as that determined with pure acetone (i.e., about 1.5 orders of magnitude greater than the permeability to 0.01 N calcium sulfate). (Brown et al., 1984)

Kerosene (a mixture of aliphatics and aromatics)

In column tests under very low gradient, intrinsic permeabilities were higher than permeability to water by approximately 1 order of magnitude in samples of Lake Bottom, Nicholson, Fanno, Chalmers, and Canelo clays. Permeabilities were slightly higher than for water in three other soils. The samples (5.8 cm in diameter and 5 cm in height) were presaturated with kerosene. (Schramm, 1981)

In fixed-wall permeameter tests at high gradient, the permeability of an unsaturated micaceous soil increased by 3 to 4 orders of magnitude compared to the permeability determined with 0.01 N calcium sulfate. (Brown et al., 1984)

#### Naphtha

The permeabilities of two clays (Na-saturated and Ca-saturated montmorillonite) to naphtha were greater by several orders of magnitude than their permeabilities to water. (Buchanan, 1964)

(continued)

CBA 007 0907

. معرف (

### Soltrol C (a light hydrocarbon liquid)

Intrinsic permeabilities for samples tested with the light hydrocarbon were significantly higher than the permeabilities measured in similar samples exposed to water. (van Schaik, 1970)

Diesel Fuel

Fixed-wall permeaneter tests at high gradient with an unsaturated micaceous illite produced highly variable data inconsistent with the pattern of permeability changes seen with other liquid hydrocarbons. Permeability was greater by 1 to 2 orders of magnitude than the permeability measured with 0.01 N calcium sulfate in a similar sample. (Brown et al., 1984)

### Paraffin Oil

In fixed-wall permeameter tests at high gradient with an unsaturated micaceous illite, permeability was greater by about 1 order of magnitude than the permeability measured with 0.01 N calcium sulfate in a similar sample. Maximum values were obtained after the passage of one pore volume. (Brown et al., 1984)

#### Gasoline

In fixed-wall permeameter tests at high gradient with an unsaturated micaceous illite, permeability was greater by 1 to 2 orders of magnitude than the permeability measured with 0.01 N calcium sulfate in a similar sample. (Brown et al., 1984)

#### Motor 011

In fixed-wall permeameter tests at high gradient with an unsaturated micaceous illite, permeability increased by about 1 to 2 orders of magnitude as 2.5 pore volumes of fluid were passed through the sample. (Brown et al., 1984)

#### **ETHERS**

Dioxane

Kaolinite initially packed and permeated with water was permeated with anhydrous dioxane until complete displacement of the water was achieved. Replacement of water by dioxane was accompanied by about a 20- to 30-percent increase in intrinsic permeability. This permeability was much lower, however, than the values determined for kaolinite beds initially prepared with dioxane. (Michaels and Lin, 1954)

(continued)

4-19

TABLE 4-1 (continued)

#### **KETONES**

Acetone

In fixed-wall permeameter tests under low hydraulic gradient, three clays showed slight decreases in permeability (compared to permeability to deionized water established in a similar sample). All tests were concluded before 40 days. Less than 0.5 pore volumes were passed through the sample. (Green et al., 1979)

Fixed-wall permeability tests at high gradient with four clays showed initial permeability decreases followed by increases compared to baseline. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. Extensive shrinking and cracking in the soils were observed after permeation. (Anderson, 1981)

In flexible-wall tests with a Georgia kaolinite, an immediate decrease in permeability was followed by an increase, the final value stabilizing at approximately double the initial permeability (Acar et al., 1984)

Acetone (high and low concentration)

An increase over baseline permeability (established with 0.01 N calcium sulfate in similar samples) was seen in an unsaturated micaceous soil for solutions where the acetone concentration was 75 or 100 percent. Samples tested with lower concentrations of acetone did not show appreciable changes in permeability compared to the 0.01 N calcium sulfate. Tests were carried out in fixed-wall permeameters at high gradient. (Brown et al., 1984)

Acetone (low concentration)

Permeability decreased slightly in a Georgia kaolinite clay tested in a flexible-wall permeameter with a solution containing a low concentration of acetone (i.e., below 0.1 percent) prepared in 0.01 N calcium sulfate. (Acar et al., 1984a)

ALCOHOLS, GLYCOLS, PHENOL

Methanol

Permeability decreased slightly (compared to permeability to deionized water established in a similar sample) when Ranger shale was exposed to methanol under low hydraulic gradient in a fixed-wall permeameter. The test was terminated after 30 days. (Green et al., 1979)

Fixed-wall permeameter tests at high gradient with four clays showed steady permeability increases compared to baseline. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. Examination of the methanol-treated samples revealed development of large pores and cracks. (Anderson, 1981)

(continued)

### Methanol (con.)

Test results with Lufkin clay in flexible-wall cells showed essentially no change in permeability with time when samples were permeated with methanol. The permeability to methanol was virtually the same as with 0.01 N calcium sulfate. (Daniel, 1983)

At high hydraulic gradients, kaolinite was found to have a higher conductivity to methanol than to water regardless of the permeameter types; fixedwall, flexible-wall, and consolidation permeameters were used. In the flexible-wall and consolidation permeameters, kaolinite is about twice as permeable to methanol as to water. (Foreman and Daniel, 1984)

Isopropyl Alcohol

In column tests under very low gradient, intrinsic permeabilities were higher than permeability to water by almost 1 order of magnitude in samples of Nicholson, Fanno, and Canelo clays. Permeability values were the same or slightly higher than baseline in five other soils. The samples (5.8 cm in diameter and 5 cm in height) were presaturated with the alcohol. (Schramm, 1981)

Glycerol

Permeability decreased slightly (compared to permeability to deionized water established in a similar sample) when Ranger shale was exposed under low hydraulic gradient to glycerol in a fixed-wall permeameter. The test was terminated after 36 days. (Green et al., 1979)

Ethylene Glycol

Fixed-wall permeameter tests at high gradient showed permeability decreases compared to baseline followed by increases in three clays; a smectitic clay showed an initial rapid increase followed by a slower but continuous increase in permeability. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution (Anderson, 1981)

In column tests under very low gradient, intrinsic permeabilities were an order of magnitude lower than permeabilities to water in Chalmers clay, Mohave clay, and River Bottom sand. Values were slightly lower in Lake Bottom, Nicholson, Canelo, and Anthony clays and slightly higher in Fanno clay. The samples (5.8 cm in diameter and 5 cm in height) were presaturated with the ethylene glycol. (Schramm, 1981)

(continued)

CBA 007 0910

4-21

and the second of the second second

TABLE 4-1 (continued)

Phenol (949 mg/L)

In column tests with a lacustrine clay (packed to discharge 2 mL/day), no significant effect on permeability was noted when deionized water was replaced by the phenol solution as the permeant fluid. (Sanks and Gloyna, 1977)

Phenol (low concentration)

Permeability decreased slightly in a Georgia kaolinite clay tested in a flexible-wall permeameter with a solution containing a low concentration of phenol (i.e., below 0.1 percent) prepared in 0.01 N calcium sulfate. (Acar et al., 1984a)

Phenol (high concentration)

In flexible-wall tests with a Georgia kaolinite and a high-strength phenol solution, an immediate decrease in permeability was followed by an increase, the final value stabilizing at approximately double the initial permeability. (Acar et al., 1984a)

AMINES

Aniline

Fixed-wall permeability tests at high gradient with four clays showed permeability increases and breakthrough. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. Extensive structural changes in the upper half of the soil columns were observed following permeation with aniline. The aggregated structure was characterized by visible pores and cracks on the surface of the soils. (Anderson, 1981)

Pyridine

The flow rate of pyridine through fireclay was of an enormously higher order of magnitude than the rate of flow for water. (Macey, 1942)

CHLORINATED ALIPHATICS

Carbon Tetrachloride

Permeability decreases slightly (compared to permeability to deionized water established in a similar sample) when Ranger shale was tested under low hydraulic gradient in a fixed-wall permeameter. The test was terminated after 14 days. (Green et al., 1979)

(continued)

CBA 007 0911

2.4

TABLE 4-1 (continued)

#### Trichloroethylene

Permeability decreased slightly (compared to permeability to deionized water established in a similar sample) when fireclay was tested under low hydraulic gradient in a fixed-wall permeameter. The test was terminated after 36 days. (Green et al., 1979)

#### OTHER

Acetic Acid

Tests at high gradient in fixed-wall permeameters showed continuous permeability decreases to baseline in two clays. Tests with smectitic and illite clays showed permeability increases after initial decreases. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. The permeability decreases were attributed to partial soil dissolution and migration of particles, which temporarily clogged the fluid conducting pores. Progressive soil piping eventually caused the increase in permeability. (Anderson, 1981)

#### Nitrobenzene

The flow rate of nitrobenzene through fireclay was of an enormously higher

In flexible-wall tests with a Georgia kaolinite, permeability decreased until the tests were terminated. The final value was approximately 2 orders of magnitude lower than the initial permeability (Acar et al., 1984a) "Xylene Waste" (paint solvent containing xylene with 25 percent paint pigments and trace amounts of water)

In fixed-wall permeameter tests, the permeability of three clay soils, presaturated with 0.01 N calcium sulfate, increased rapidly upon exposure to xylene waste after the cumulative flow exceeded 0.2 to 0.4 pore volume. Permeabilities were 2 to 4 orders of magnitude greater than permeabilities measured with 0.01 N calcium sulfate. Highest permeabilities measured on initially unsaturated samples were greater by 1 to 2 orders of magnitude than for samples that were initially saturated with the calcium sulfate. (Brown et al., 1983)

"Acetone Waste" (a chemical manufacturing waste containing 91.7 percent acetone, 4 percent benzene, and 0.6 percent phenol)

In fixed-wall permeameter tests, the permeability of three clay soils, presaturated with 0.01 N calcium sulfate, initially decreased (minimum permeability at approximately 0.5 pore volume) and then steadily increased. Permeabilities were 2 to 4 orders of magnitude greater than permeabilities measured with 0.01 N calcium sulfate. Highest permeabilities measured on initially unsaturated samples were greater by 1 to 2 orders of magnitude than for samples that were initially saturated with the calcium sulfate. (Brown et al., 1983)

Perchloroethylene Waste

There is evidence that a perchloroethylene waste, which formed a separate, denser than water phase, contributed to the failure of a clay liner at a surface impoundment. (Personal communication, 1984)

"Acid Prowl" (pesticide wash of very low pH; higher viscosity than water)

After several days of exposure to a lacustrine clay packed in a fixed-wall column, the water reacted with the soil to produce chlorine gas. Over a 5-week period, the flow of liquid from the column was irregular due to clogging of pores by the gas. (Everett, 1977)

"Acid Wash" (42 percent sulfuric acid with about 5 percent organics; higher viscosity than water)

Permeability of a lacustrine clay packed in shrink tubing increased by about 1 order of magnitude over a period of 19 days. The permeability was lower, however, than values obtained when the soil sample was exposed to water. (Everett, 1977)

(continued)

TABLE 4-2 (continued)

"Mother Liquor" (an acid wash with pH of 0.37; higher viscosity than water)

Permeability of a lacustrine clay packed in shrink tubing was lower than the value obtained when the soil sample was exposed to water. The waste may have reacted with the soil, liberating gases and increasing pore pressures and clogging flow. (Everett, 1977)

"Hydrazo Benzene" (33 percent methanol, 12.8 percent sodium hydroxide, 15.5 percent sodium formate, and 1.5 percent hydroazobenzene and azobenzene; more viscous than water)

Permeability of a lacustrine clay packed in shrink tubing was slightly lower than the value obtained when the soil sample was exposed to water. Tests were carried out for 34 days under low gradient (less than 100 cm). (Everett, 1977)

"Acid Waste" (100 mM HC1/L)

Due to reaction with carbonates, much higher permeabilities were observed in tests with lacustrine clay compared to permeabilities determined with deionized water. (Sanks and Gloyna, 1977)

"Basic Waste" (100 mM NaOH/L)

meabilities in a lacustrine clay decreased compared to the values measured with deionized water. (Sanks and Gloyna, 1977)

4-25

#### CHAPTER 4

# CLAY-CHEMICAL INTERACTIONS AND SOIL PERMEABILITY

It has been known for many years that the permeability of clay soils may be drastically altered by chemicals present in the permeating liquid. Apart from the many recent studies stemming from concern over the effects of hazardous waste and waste leachates on clay liners, much research has been carried out over the last several decades to determine the effects of various chemicals on agricultural soils or on geological formations important for oil production. The potential effects of certain organic fluids on clay permeability were recognized as early as 1942, when Macey's experiments with fireclay showed that the rates of flow for certain organic liquids through clay were "of an enormously higher order than for water" (Macey, 1942). Since Macey's experiments, many researchers have investigated the effects of the observed changes in permeability.

The current state of the knowledge in this area is complicated by the dilemma of how to measure the permeability changes that appear to be caused by clay-chemical interactions. The question of what types of permeameters give valid measures of clay-chemical compatibility remains an important issue. Because permeability studies with different fluids have been carried out with different test protocols, different test devices, and different clays, quantitative data comparisons cannot be made except in a few of the more recent studies. Much can be learned from a review of the research that ing the behavior of certain clays in the presence of many types of fluids. Unifying theories of soil physics that explain the reported findings have been advanced by several researchers. Such theories are useful for predicting clay-chemical incompatibilities that could lead to performance failures in clay-lined hazardous waste disposal facilities.

This chapter presents the experimental findings that pertain to the effects of chemicals on clay barrier permeability as well as the theories and mechanisms proposed to explain the observed effects. Section 4.1 defines the terms most important in clay-chemical compatibility testing-- permeability (or, if the permeating liquid is water, hydraulic conductivity) and intrinsic permeability. Section 4.2 is a discussion of the clay-chemical interactions that influence soil permeability. A summary of the relevant permeability studies is presented in Section 4.3. Approaches that have been used in different test methods are addressed in Section 4.4. Section 4.5 reviews in more detail permeability testing efforts that have been carried out to measure clay-chemical interactions.

# 4.1 PARAMETERS DETERMINED IN PERMEABILITY TESTING FOR COMPATIBILITY

When results of clay-chemical compatibility tests are compared, it is important to understand the parameters that are being measured and calculated. The parameter usually determined in compatibility tests is permeability,  $\underline{K}$ , which is defined by Darcy's Law as expressed in Equation (4.1):

$$K = Q/Ai$$

where

 $Q = volumetric flow rate (L^3/t)$ 

A = cross-sectional area of flow (L<sup>2</sup>)

i = hydraulic gradient (dimensionless).

K has units of length per unit time (e.g., cm/s). The density and viscosity of the permeating liquid as well as the pore size distribution within the soil matrix will influence the value of K. Hydraulic conductivity refers to the value of K when the permeating fluid is water. Darcy's Law is limited to saturated soil conditions and to laminar flow conditions.

In order to separate the effects of the liquid properties (viscosity and density) from those of the medium (pore size distribution), a different parameter, the <u>intrinsic permeability</u>, should be used. Intrinsic permeability, usually referred to as k, is a property of the medium that is dependent on the shape, size, and continuity of the pore spaces. Intrinsic permeability is "a measure of the relative ease with which a porous medium can transmit a liquid under a potential gradient. It is a property of the medium alone and is independent of the nature of the liquid and of the force field causing movement" (Lohman et al., 1972).

Intrinsic permeability, k, has units of length squared (e.g.,  $cm^2$ ) and is related to permeability, K, by Equation (4.2):

 $K = k \frac{\rho}{\mu} g$  or  $k = K \frac{\mu}{\rho g}$ 

where

 $\rho$  = density of the fluid (M/L<sup>3</sup>)

 $\mu$  = dynamic viscosity of the fluid (M/Lt)

g = acceleration due to gravity  $(L/t^2)$ .

In clay-chemical compatibility testing, the value of K for a clay soil permeated by a certain chemical is determined from measurements of the fluid inflow or outflow. A change or lack of change in the value of K (when compared to K for water or other baseline fluid) may be due to a combination of two factors--

(4.1)

(4.2)

- Difference in the permeant fluid viscosity and density (compared to baseline permeant fluid)
- Change in porous medium characteristics as a result of clay-chemical interactions.

In order to separate these effects, it is usually necessary to report the results of the tests in terms of intrinsic permeability (k) both for the tests with the baseline permeant fluid and for the tests with the chemical permeant fluid in question. In practice, most researchers report and discuss their test results in terms of permeability (K) rather than intrinsic permeability (k). Provided the density and viscosity of the test fluid (at the test temperature) are known, one could calculate k to correspond to each K value reported. In general, only substantial permeability changes are meaningful in clay-chemical compatibility testing. When large changes in permeability are measured during the course of a test, the clay-chemical interaction is apparent regardless of whether the k values are computed and plotted.

#### 4.2 CLAY-CHEMICAL INTERACTIONS THAT INFLUENCE PERMEABILITY

Mechanisms whereby the chemical nature of a permeant fluid may alter clay soil permeability and theories to predict clay-chemical interactions have been described by several researchers, among them Mitchell (1976), Brown and Anderson (1980), Acar and Field (1982), Evans, Chaney, and Fang (1981), Anderson and Jones (1983), Daniel (1982, 1983), Daniel and Liljestrand (1984), Dunn (1983), Monserrate (1982), Peirce (1984), and Griffin and Roy (1985). In addition to laboratory and field permeability tests, methods such as X-ray diffraction, shrink-swell measurements, settling tests, and other techniques have been used to investigate the clay-chemical interactions that influence permeability.

Changes in the permeability of clay soils due to chemical interactions may result from--

- Alterations in soil fabric stemming from chemical influences on the diffuse double layer surrounding clay particles
- Dissolution of soil constituents by strong acids or bases
- Precipitation of solids in soil pores
- Soil pore blockage due to the growth of microorganisms.

The permeability of a soil may also be affected by the pore fluid velocity; high velocities can displace small particles in the soil matrix. The fluid flow velocity can also influence chemical interactions that depend on the time of contact between the soil and some chemical component of the permeating fluid. Thus, permeability and fluid flow velocity are interrelated characteristics of a soil-permeant fluid system.

4-3

#### 4.2.1 Soil Fabric and Permeability

The permeability of any soil depends upon the geometric characteristics of the area available for fluid flow. Influencing factors are the size, shape, tortuosity, and degree of interconnection between the pore spaces. The geometric arrangement of the soil particles will determine these pore space characteristics.

The term "fabric" refers to the arrangement of particles, particle groups, and pore spaces in a soil. Modes of particle association orientation in clay suspensions were described by van Olphen (1963) as "dispersed," "aggregated," "flocculated," or "deflocculated" (see discussion in Section 2). Particle associations corresponding to these descriptors are illustrated in Figure 2-10. Dispersion and flocculation represent the extremes in soil fabric classification, and a chemical present in the permeating liquid may influence the permeability of a clay soil by altering the soil fabric toward either of these extremes. Figure 4-1 illustrates how a change in pore diameter can drastically alter permeability.

A dispersed deflocculated soil fabric tends to have a large number of very small pore spaces; with flocculation, relatively large-sized interparticle and interaggregate pores are formed. These large diameter pores can cause drastic changes in the permeability of the clay soil since the flow rate is proportional to the square of the diameter of the flow channel.

The pulling together of groups of clay particles into aggregates results when cohesive forces between individual clay particles outweigh the repulsive forces. The forces of attraction result from London-van der Waals forces and do not vary significantly with the chemistry of the pore water. Attractive forces are strongest close to the clay surface and diminish rapidly with increasing distance from the surface.

The forces of repulsion between adjacent clay surfaces, however, are primarily electrostatic and are influenced by the clay surface charge and the chemistry of liquid adjacent to the clay surfaces. Interparticle spacing is a function of the thickness of the diffuse double-layer cationic clouds that form the Gouy layer of the diffuse double layer (Anderson and Jones, 1983). (See also Section 2.3 and discussion below). In theory, the direction of change in permeability associated with varying pore fluid chemistry could be predicted if the variables that affect the thickness of the diffuse double layer are known (Acar and Seals, 1984). However, the heterogeneous mineral composition and wide particle-size distribution common in many soils along with the complicated nature of chemical-soil interactions make this difficult to accomplish in practice.

#### 4.2.1.1 Diffuse Double-Layer Theory--

The theory of the diffuse double layer (also called the electrical double layer) has evolved from the studies of colloid chemistry directed at the description of surface interactions of small particles in a waterelectrolyte system. The description that follows is excerpted from Mitchell (1976, pp. 112-113).



Source: Anderson, 1981

Figure 4-1. Change in a pore diameter (400%) corresponding to a permeability increase of 25,600%.

In a dry clay, adsorbed cations are tightly held by the negatively charged clay surfaces. Cations in excess of those needed to neutralize the electronegativity of the clay particles and their associated anions are present as salt precipitates. When the clay is placed in water the precipitated salts go into solution. Because the adsorbed cations are responsible for a much higher concentration near the surfaces of particles, there is a tendency for them to diffuse away in order to equalize concentrations throughout. Their freedom to do so, however, is restricted by the negative electric field originating in the particle surfaces . . The negative surface and the distributed charge in the adjacent phase are together termed the DIFFUSE DOUBLE LAYER . . .

The distribution of cations adjacent to a negatively charged clay particle in suspension (the diffuse double layer) is depicted in Figure 4-2 (see also Figure 2-6). The distribution for a particular soilwater-electrolyte system results from a balance between the tendency of the cations to escape due to diffusion and the opposing electrostatic attraction of the clay surface for the cations. The Gouy-Chapman theory of the diffuse double layer (Gouy, 1910; Chapman, 1913) is widely recognized, and mathematical descriptions of the diffuse double layer have been formulated for both planar and spherical surfaces.

Despite the fact that the Gouy-Chapman theory does not account for all the factors that can influence the behavior of the soil-water-electrolyte system, it has been useful as a generalized model for explaining claychemical interactions that affect permeability. Since the thickness of the double layer influences the level of interlayer and interparticle repulsion, system variables that influence the double-layer thickness consequently affect the physical interactions among clay particles.

The nature and thickness of the double layers, and thus the repulsive forces, depend upon characteristics of clay particles and the pore fluid. In general, the tendency for particles in suspension to flocculate decreases with increased thickness of the double layer. An approximate quantitative indication of the relative influences of several factors on the thickness of the double layer is given by Equation (4.3) below (see Mitchell, 1976, p. 118):

$$H = \frac{DkT}{8\pi n_0 e^2 v^2}$$

where

H = thickness of the double layer

D = dielectric constant of the medium

k = Boltzman constant (1.38 x  $10^{-16}$  erg/K)

T = temperature in degrees Kelvin

(4.3)



Figure 4-2. Distribution of ions adjacent to a clay surface according to the concept of the diffuse double layer.

### 4-7

CBA 007

0921

 $n_0 =$  electrolyte concentration

e = unit electric charge, 16 pvp 10<sup>-6</sup> coulomb

v = valence of cations in the pore fluid.

The thickness varies inversely with the valence of the cations present and inversely with the square root of the concentration; the thickness increases with the square root of the dielectric constant and the temperature, other factors remaining constant. Based on the Gouy-Chapman model, Lambe (1958) noted that the following variables in the soil-water system affect double-layer thickness and colloidal stability: dielectric constant, electrolyte concentration, temperature, ionic valence, size of hydrated ions present, pH, and anion adsorption.

It has been found that attractive forces exceed repulsive forces when interlayer spacing is about 0.5 nm (Yong and Warkentin, 1975). Thus, a sufficient reduction in repulsive forces (i.e., reduced double-layer thickness) could "transform a massive, structureless, and slowly permeable clay barrier into an aggregated, structured, and more permeable barrier" (Anderson and Jones, 1983).

4.2.1.1.1 <u>Dielectric Constant</u>--The dielectric constant is a measure of the ease with which molecules can be polarized and oriented in an electric field (Mitchell, 1976, p. 113). It represents the ability of a fluid to transmit a charge. Quantitatively, the static dielectric constant is defined by D in Coulomb's equation (Equation 4.4), where F is the force of electrostatic attraction between two charges, Q and Q', separated by a distance d.

$$F = \frac{QQ'}{Dd^2}$$

As the dielectric constant decreases, the fluid film surrounding the clay that contains positive cations must be thinner for the negative surface charge on the clay to be neutralized. For a constant surface charge, the surface potential function will increase as the dielectric constant decreases. Since most organic liquids have dielectric constants substantially lower than water, it is to be expected that the double-layer thickness would be reduced (with an associated tendency toward flocculation) when an organic liquid rather than water surrounds the clay particle. Due to the effects of dielectric constant on the electrical double layer, there is a relationship between the dielectric constant of an adsorbed fluid and interlayer spacing exhibited by clay particles. In general, interlayer spacing decreases with a decrease in the dielectric constant, although this apparent relationship can be complicated by the other factors that affect interlayer spacing.

4.2.1.1.2 <u>Electrolyte Concentration</u>--As the electrolyte concentration in the pore fluid increases, the thickness of the double layer tends to decrease, promoting flocculation. An analysis of the effect of electrolyte concentration on the double layer indicates that an increase in concentration

(4.4)

reduces the surface potential for the condition of constant surface charge. Also, the decay of potential with distance is more rapid with increased electrolyte concentration. In essence, the double layer is suppressed by an increase in electrolyte concentration. Interparticle interactions extend to much greater particle spacings for a low electrolyte concentration (e.g.,  $0.83 \times 10^{-4}$  M NaCl) than a higher concentration (e.g.,  $0.83 \times 10^{-2}$  M NaCl) (Mitchell, 1976, p. 122). The effect of salt concentration on the behavior of clays has been discussed by Anderson (1981):

As salt concentration in interparticle spaces increases, the cationic cloud is compressed closer to the clay surface, resulting in a decrease in electrostatic repulsion and interlayer spacing. Weiss (1958) noted the direct relationship between salt concentration and interparticle spacing in smectitic clay minerals in a study using distilled water and several concentrations of sodium chloride in water. Both distilled water and 0.01 N NaCl gave infinite interlayer spacing values (the clay was completely dispersed), while 1.0, 3.0, and 5.0 N NaCl gave interlayer spacings of 0.93, 0.61, and 0.58 nm, respectively.

4.2.1.1.3 <u>Temperature</u>-An increase in temperature causes an increase in double-layer thickness with a corresponding tendency toward dispersion. However, the value of the dielectric constant for various fluids is also affected by temperature, generally decreasing with increased temperature. For water, the value of the product DT (Equation 4.3) is reasonably constant, and temperature effects tend to cancel out.

4.2.1.1.4 <u>Ionic Valence</u>--The cation valence affects both the surface potential and the thickness of the double layer. For solutions of the same molarity and a constant surface charge, increasing the cation valence will cause a decrease in the thickness of the double layer and a tendency toward flocculation. It is also shown that an increase in valence will suppress the midplane concentrations between parallel plates, leading to a decrease in interplate repulsion (Mitchell, 1976, p. 122).

4.2.1.1.5 <u>Size of Hydrated Ions</u>--The smaller the size of the hydrated ion, the closer it can approach the surface of the clay particle (Lambe, 1958). Thus, for a given cation valence, the thickness of the double layer will tend to decrease with decreasing hydrated radii of double-layer cations.

4.2.1.1.6 <u>pH</u>--Changes in pH can affect the thickness of the double layer in several ways. The electrolyte concentration as well as the net negative charge on the clay particle are influenced by the solution pH. The formation of stable suspensions or dispersions of clay particles often require high pH conditions. There are two ways in which pH can change the surface charge that results from chemical reaction at the surface of the clay particles. First, a high pH can cause dissociation of hydroxyl groups at the edge of clay particles, increasing the net charge and expanding the double layer. The dissociation reaction is given below:

$$SiOH \xrightarrow{H_2O} SiO^- + H^+$$

(4.5)

CBA 007 0923

4-9

The higher the pH, the greater the tendency for the H<sup>+</sup> to dissociate and the greater the effective negative charge. Low pH discourages this dissociation, lowering the surface charge, reducing the thickness of the double layer, and promoting flocculation (Evans et al., 1981; Mitchell, 1976, p. 127).

Second, pH affects alumina exposed at the edges of clay particles. Alumina ionizes positively at low pH and negatively at high pH. Thus, in an acid environment, positive double layers may develop at the edges of clay particles with H<sup>+</sup> serving as the potential determining ion (Mitchell, 1976, p. 126).

Changes in pH do not significantly affect surface charge resulting from isomorphous substitution of the crystal lattice of the clay mineral. Thus, clays with most of their surface charge attributed to isomorphous substitution (e.g., smectites and illites) are less affected by changes in pH than the kaolinite minerals, which have most of their surface charge resulting from surface chemical reactions (see Section 2.3).

4.2.1.1.7 <u>Anion Adsorption</u>--Adsorption of anions (e.g.,  $Cl^-$ ,  $PO_4^{-3}$  and certain surfactants) by the clay particle can increase the net negative charge and increase the double-layer thickness. Dispersion can occur as a result.

## 4.2.1.2 Displacement of Water--

If adsorbed water within clay particles is displaced by a fluid with a different dielectric constant or electrolyte concentration, the result may be a change in the interlayer spaces of the clay. Such changes can cause the clays to shrink and crack. This can result in the formation of large conducting channels through the soil along with drastic increases in the permeability. Desiccation of clays by certain organic fluids has been reported by Anderson (1981) and others.

### 4.2.1.3 Cation Exchange--

Cations adsorbed in the diffuse double layer are exchangeable with other cations in solution. In general, the affinity of a cation for a clay increases with cation valence and decreases with increasing ionic radius within an element group. (See Section 2.2.)

Cation exchange will usually result in a change in double layer thickness. The thickness of the double layer decreases with increasing cation valence for montmorillonite; replacement of Na<sup>+</sup> with Ca<sup>++</sup> results in a reduction of interlayer basal spacing from over 4 nm to about 1.9 nm. For montmorillonite, only two layers of water are incorporated between layers when calcium is the adsorbed cation; with sodium, the number of water layers between layers is practically unlimited. Thus, cation exchange can cause double-layer collapse, desiccation and shrinkage, flocculation, and increased permeability for certain clays.

Theng (1974) has summarized the importance of cation exchange in clay-organic complexes:

CBA 007

0924

. . . Since uncharged polar organic molecules are adsorbed essentially by replacement of the interlayer water, the behavior of such molecules is likewise strongly influenced by the exchangeable cation. Evidence is accumulating to show that, at least at low water contents, cation-dipole interactions are of paramount importance in their effect on the adsorption of polar organic species by clay materials.

# 4.2.2 Dissolution by Strong Acids or Bases

Both organic and inorganic acids react with and dissolve aluminum, iron, and silica in the crystal lattice of clay minerals. Strong bases can have a similar effect. This dissolution can result in a release of mineral fragments that may migrate from their original position and leave enlarged pore spaces for conducting the permeant fluid through the clay. Anderson and Jones (1983) have pointed out that "whether the permeability of the clay barrier increases or decreases will depend on the fate of the migrating particles." The increase in conducting pore size may give rise to an increased permeability if the particles migrate through the clay mass. If the particles lodge in pore constrictions, clogging the conducting pore spaces, a decrease in permeability may result (Anderson and Jones, 1983).

Data originally reported by Pask and Davies (1945) show that sulfuric acid dissolves 3, 11, and 89 percent of the aluminum present in kaolinite, illite, and smectite. Other studies also suggest that kaolinite is less soluble than smectite in strong acids (Grim, 1953).

## 4.2.3 Precipitation of Solids

The precipitation of solids in the soil-water system is controlled by ionic concentration and equilibrium solubility. If the concentration of certain ions exceeds the solubility limits, minerals such as gypsum (CaSO4 2H<sub>2</sub>O) or jarosite (KFe<sub>3</sub>(SO4)<sub>2</sub>(OH)<sub>6</sub>) may precipitate from solution (Shepard, 1981; Dunn, 1983). Formation of such precipitates can clog pore spaces in the soil matrix.

# 4.2.4 Effect of Microorganisms

The presence of microorganims can affect the mobility of fluids through the soil. Fuller (1974) classified activity of microorganisms in terms of three classes of chemical reactions: (1) oxidation and reduction, (2) mineralization and immobilization, and (3) reactions with organic constituents. In certain circumstances, the attenuation of contaminants in soils attenuation of contaminants by microorganisms. Processes that can contribute to 1974; Dunn, 1983):

- Degradation of carbonaceous wastes
- Transformation of cyanide to mineral nitrogen and denitrification to nitrogen gas

- Oxidation-reduction reactions with metal ions
- Reduction of sulfate to sulfide
- Production of carbon dioxide from organic molecules
- Production of simple organic acids
- Production of humic and fumaric acids that can react with trace contaminants
- Production of organic species on which trace contaminants can be adsorbed.

Apart from the benefits of attenuation, the physical presence of the microorganisms as well as the gases produced as a result of the reactions listed above can cause blockage in the conducting pore spaces within soils, reducing the area for flow and decreasing permeability. This effect has been noted in permeability tests, particularly when the permeant fluid is conducive to the growth of microorganisms.

#### 4.3 MEASURING CLAY-CHEMICAL COMPATIBILITY THROUGH PERMEABILITY TESTING

Permeability is a highly variable engineering property of soils, and slight changes in the measurement technique or test equipment can cause order of magnitude changes in the values determined (Mitchell et al., 1965). Because one is always dealing with orders of magnitude in permeability testing, it is unrealistic to expect test results to agree within less than several hundred percent (Zimmie et al., 1981). Bryant and Bodocsi (1986) have also examined precision and reliability that can be achieved in laboratory permeability measurements. No widely accepted method exists for measuring clay-chemical compatibility through permeability testing. Thus, a variety of equipment and techniques have been employed in this area of research. Some of the variables in test methods are described in this section, and advantages and disadvantages are highlighted. For additional information and recommendations see Bowders et al. (1986).

#### 4.3.1 Measurement Devices

The permeability of clay soils to various liquids is usually determined in either constant head or falling head tests in fixed-wall, flexiblewall, or consolidation permeameters. Each category of test device can have many variations. Fixed-wall permeameters that have been used in claychemical compatibility testing include stainless steel permeameters, plexiglass permeameters, thick-walled pyrex glass permeameters, glass cylinders, PVC (polyvinyl chloride) tubes, and shrink tubing. Shrink tubing may, in fact, lend to fixed-wall tests a major desirable feature of flexible-wall tests--reduction in the possibility of sidewall leakage.

Tests with water and other solutions that do not interact with clays have shown that comparable permeability measurements may be obtained through different types of test devices. Everett (1977) measured the permeability of Lacustrine clays in falling head tests over a 2-month test period in three types of fixed-wall permeameters. Test results showed almost equivalent permeability readings in all test devices. Values measured were 9.0 x  $10^{-9}$  cm/s in a commercial metal permeameter, 6.9 x  $10^{-9}$  cm/s in PVC pipe, and 8.3 x  $10^{-9}$  cm/s in shrink tubing.

Permeability tests performed in both fixed-wall and flexible-wall tests at Duke University (Peirce, 1984; Peirce and Peel, 1985) also indicate that comparable data can be obtained from the different devices. Test fluids used in the Duke investigation did not significantly alter the soil permeabilities as compared to baseline permeabilities obtained with 0.01 N calcium sulfate. More than 100 tests were carried out. The reproducibility of the permeability results suggests that side-wall leakage in fixed-wall devices can be virtually eliminated through careful quality control during sample preparation, compaction, and testing if the permeant fluid does not alter the clay that is tested.

Test results may differ somewhat with different types of permeameters when the test fluid is other than water (or comparable baseline fluid). Daniel (1983) found that methanol in tests with kaolinite in three types of permeameters produced similar curves (permeability versus pore volumes passed through sample) but with compaction mold permeabilities somewhat higher than values measured in flexible-wall or consolidation cells.

### 4.3.2 Test Setup

ALL ALL MADE

Whether permeability tests are carried out as constant head or falling head should not affect the validity of the test results. Effectively, one is doing the same thing in both tests. In the constant head test, readings are converted to a flow rate; in the falling head test, readings are converted to changes in head. Most of the permeability tests described in this section are essentially constant head tests because of the very low permeabilities of compacted clay soils. Test results reported by Monserrate (1982), however, were computed as falling head permeabilities.

Buettner and Haug (1983) noted that leakage is the controlling factor on how low a permeability can be measured. They measured total leakage from their flexible-wall permeameter setup by placing a solid metal block in the cell and monitoring the changes in inflow and outflow. Volume change indicators with an accuracy of  $\pm 0.005$  cm<sup>3</sup> were used to determine the leakage rate and also enabled the researchers to measure the change in volume of clay soils due to consolidation or swelling. Buettner and Haug found that if leakage is not corrected for, the potential error at low permeabilities (less than  $10^{-12}$  cm/s) can be as high as 2 orders of magnitude.

#### 4.3.3 <u>Compatibility of Materials with Test Fluids</u>

A problem that has become apparent in testing organic fluids in triaxial cells is the incompatibility between the commonly used latex membranes and the fluid to be tested (Acar et al., 1984a; Foreman and Daniel, 1984). Excessive deformations (i.e., wrinkling and expansion) in the membrane may occur with possible effects on the test results. One technique used by
Acar et al. (1984a) to alleviate problems resulting from incompatibility was to wrap the samples with two rounds of 0.03-mm sheet Teflon<sup>®</sup>. After place ment around the wrapped samples, the membranes were coated with a contaminant-resistant (silicon base) grease to decrease chemical diffusion. Even with these provisions, however, acetone used as the test fluid was found to diffuse through the membrane into the cell water. A procedure and apparatus that can be used to test the membrane-permeant fluid compatibility have been described by Rad and Acar (1984).

Foreman and Daniel (1984) also found a workable technique to be wrapping the soil sample along with the top cap and base pedestal with two or three revolutions of 15-cm (6-inch) -wide Teflon<sup>®</sup> tape before placement of the latex membrane. Long-term flexible-wall tests with heptane have been carried out successfully with this method.

Materials compatibility has also been a problem in fixed-wall tests with corrosive test fluids. Stainless steel permeameters and pressure fittings were damaged in tests with chronic acid (Monserrate, 1982). Several researchers have used plexiglass devices with Teflon<sup>®</sup> fittings to avoid such problems.

#### 4.3.4 Effect of Backpressure

Slight deviations from full saturation have been shown to significantly affect measured permeability values (Mitchell et al., 1965). Recognizing this, some researchers include in the test method a saturation step involving backpressuring. Zimmie et al. (1981) noted that many permeability determinations are made using backpressure to promote complete saturation and then releasing or lowering the backpressure during the permeability test. When this is done, dissolved gases immediately begin to come out of solution, causing the measured permeability values to decrease. Zimmie et al. (1981) concluded, "The maximum, fully saturated permeability value should be determined. It is necessary to utilize backpressure to properly saturate the specimen whether or not the actual permeability test utilizes backpressure."

#### 4.3.5 Effect of Hydraulic Gradient

Mitchell, Hooper, and Campanela (1965), in tests with a silty clay, found evidence that rapid infiltration of water could cause migration of fine particles that tended to plug conducting pore spaces and reduce flow rates. Mitchell and Younger (1967) measured permeability to water of a compacted silty clay as a function of hydraulic gradient. A gradual increase in the gradient from 0 to 17 over 26 days resulted in a corresponding increase in permeability from less than 5 pvp  $10^{-7}$  to 5.4 x  $10^{-6}$  cm/s. The increase was approximately linear in the region of gradients of about 4 to 10, the curve of permeability versus hydraulic gradient tending to flatten at the lower and higher gradients. The nonlinear behavior at the higher gradients may have been the result of movement of fine soil particles. Other researchers-Olsen (1965) and Hamilton (1979)--have reported data

that show no significant effect of hydraulic gradient on either discharge velocity or permeability to water.

Under a cooperative agreement with the U.S. Environmental Protection Agency (EPA), Daniel (1982) investigated the effect of hydraulic gradient on permeability. Water (actually 0.01 N calcium sulfate) as well as other wall cells, fixed-wall permeameters, and consolidation cells. The permeability of kaolinite to water did not vary with hydraulic gradient in any test device. Changes in hydraulic gradient caused a slight increase in permeability for kaolinite permeated with methanol in flexiblewall permeameters and consolidation cells, however, the trend was permeability with decreasing gradient in tests with methanol. Due to large variations in the test data obtained for fixed-wall permeameters, the results of the tests were somewhat inconclusive.

In other research funded by the EPA, Brown, Thomas, and Green (1984) studied the effects of hydraulic gradient on the permeability of three clay soils to two organic wastes--a xylene waste and an acetone waste. It was concluded that hydraulic gradients of 31, 91, and 181 did not greatly affect the permeabilities in either presaturated or unsaturated samples.

## 4.3.6 Criteria for Concluding a Test

Clay-chemical compatibility tests should be continued until all changes in permeability resulting from the interaction of the chemical with the clay have been observed. To satisfy this condition, compatibility tests should be concluded only if the slope of the permeability versus time curve does not vary significantly from zero (steady-state permeability has been reached) and at least one pore volume of fluid has passed through the clay. If the first condition is not met, there is no assurance that reactions of the chemical with the clay are complete. If the second condition is not met, there is no order to satisfy the above conditions, it is necessary to determine the chemistry of both the influent and effluent (to detect breakthrough) and report pore volumes through samples as well as real time. (Conclusion from a workshop on Permeability Testing, Atlanta, GA, January 1984, unpublished.)

A statistical procedure was developed at Duke University (Monserrate, 1982; Peirce and Witter, 1986) to determine when a test should be concluded. Readings of column level and time are taken at certain intervals throughout the test. The hydraulic conductivity is computed for each time interval. From this set of data the first 10 points are taken and a linear regression analysis is performed to determine the slope of the hydraulic conductivity on the other end. The first point is then dropped and another value is added beginning of the test this slope will be fairly large, but as the test progresses it will decrease and approach zero when steady-state is obtained.

The criteria for when steady-state is obtained will be taken when two

- When the slope at the curve does not vary significantly from zero at the 95-percent confidence level, and
- At least one pore-volume of the liquid is passed through the sample (Peirce, 1984).

## 4.4 SUMMARY OF AVAILABLE RESEARCH DATA

Numerous studies pertaining to the effects of chemicals on clay soil permeabilities have been carried out by researchers at universities and by private firms across the country during the last few decades. Research has been sponsored by the EPA, the Army Corps of Engineers, the Chemical Manufacturers Association, and others. Among the classes of compounds that have been tested are aliphatic hydrocarbons, chlorinated aliphatics, aromatic hydrocarbons, alcohols, glycols, ketones, carboxylic acids, amines, and solutions, many studies have been carried out using complex chemical mixtures. In tests involving actual wastes or leachates (obtained by passing water through wastes), the exact composition of the fluid is usually not known although major components and important parameters are usually identified and quantified.

The results of some of the most significant permeability tests involving specific organic solvents are presented in Table 4-1. The results of permeability tests involving wastes are presented in Table 4-2.

Some of the studies summarized here and in more detail in Section 4.5 have shown that certain pure, concentrated organics can drastically alter the permeability of clay soils under the conditions of the laboratory test. These test results have led to widespread concern over the possible seepage of wastes into the environment from clay-lined disposal facilities. It should be emphasized that clay liners in disposal facilities are most often in contact with leachate having much lower organic solvent concentrations than the test solutions associated with the drastic permeability increases seen in some laboratory studies. Laboratory studies performed with less concentrated test solutions (either actual wastes or leachates or dilutions prepared in the laboratory) do not appear to produce such effects.

Because of the wide variations in the soils used in clay liners and the leachates to which they will be exposed during service, testing of the actual liner/leachate system is necessary to confirm compability.

4.5 PERMEABILITY STUDIES TO INVESTIGATE CLAY-CHEMICAL INTERACTIONS

The major findings of various research efforts to investigate effects on permeability of clay-chemical interactions are presented in this section.

## 4.5.1 Observations by Macey (1942) on Effects of Organics on Fireclay

As a result of permeability experiments with fireclay, Macey (1942) concluded that the rates of flow of benzene, nitrobenzene, and pyridine

TABLE 4-1. RESULTS OF PERMEABILITY TESTS WITH ORGANIC CHEMICALS

#### ALIPHATIC AND AROMATIC HYDROCARBONS

Heptane

Fixed-wall permeameter tests at high gradient with four clays showed rapid permeability increases and breakthrough. The increase in permeability was more than 3 orders of magnitude in an illite clay. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. (Anderson, 1981)

#### Benzene

The flow rate of benzene through fireclay was of an enormously higher order of magnitude than the flow rate for water. (Macey, 1942)

In a column test under a head of 701 cm (23 feet), signs of full penetration throughout the clay material were observed after 36 days; in a similar column with water as the permeant fluid the liquid level dropped less than 2.54 cm (1 inch) over a 100-day period. Samples were 91 cm in height and 2.54 cm in diameter. (White, 1976, unpublished data)

Following an initial decrease in permeability (compared to permeability to deionized water established in a similar sample), total breakthrough occurred on the eighth day of testing when Ranger shale was exposed to benzene in a fixed-wall permeameter under low hydraulic gradient. (Green et al., 1979)

Benzene did not penetrate compacted Ca-montmorillonite that was first saturated with 0.01 N calcium sulfate even at hydraulic gradients as high at 150. (Olivieri, 1984)

In flexible-wall tests with a Georgia kaolinite, permeability decreased until the tests were terminated. The final value was approximately 2 orders of magnitude lower than the initial permeability. (Acar et al., 1984a)

#### Xylene

Following an initial decrease in permeability, total breakthrough occurred on the 25th day of testing when fireclay was tested in a fixed-wall permeameter under low hydraulic gradient. In Ranger shale, a slight decrease in permeability was observed and remained steady until the test was terminated at 40 days. In Kosse kaoline, a slight decrease in permeability was followed by an increase to about the initial level, which persisted until the test was terminated at day 36; changes did not exceed half an order of magnitude. (Green et al., 1979)

In column tests under very low gradient, intrinsic permeabilities were higher than permeability to water by at least 1 order of magnitude in samples of Lake Bottom, Nicholson, Fanno, Chalmers, and Canelo clays. Permeabilities

(continued)

#### Xylene (con.)

were slightly higher than for water in three other soils. The samples (5.8 cm in diameter and 5 cm in height) were presaturated with xylene. (Schramm, 1981)

Fixed-wall tests at high gradient with four clays showed permeability increases and breakthrough followed by nearly constant permeabilities roughly 2 orders of magnitude higher than baseline permeabilities. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. (Anderson, 1981)

In fixed-wall permeameter tests at high gradient, the permeability of an unsaturated micaceous soil was 4 orders of magnitude higher when exposed to xylene than when tested with 0.01 N calcium sulfate. (Brown et al., 1984)

#### Xylene/Acetone

In fixed-wall permeameter tests at high gradient, the permeability of an unsaturated micaceous soil to either pure acetone or pure xylene was greater than the permeability determined for mixtures of the two solvents. The permeability of a mixture of 87.5 percent xylene and 12.5 percent acetone was lower by 3 orders of magnitude than the permeability measured with pure xylene (though still higher than the permeability to 0.01 N calcium sulfate). When the acetone component was increased to 75 percent, the permeability was approximately the same as that determined with pure acetone (i.e., about 1.5 orders of magnitude greater than the permeability to 0.01 N calcium sulfate). (Brown et al., 1984)

Kerosene (a mixture of aliphatics and aromatics)

In column tests under very low gradient, intrinsic permeabilities were higher than permeability to water by approximately 1 order of magnitude in samples of Lake Bottom, Nicholson, Fanno, Chalmers, and Canelo clays. Permeabilities were slightly higher than for water in three other soils. The samples (5.8 cm in diameter and 5 cm in height) were presaturated with kerosene. (Schramm, 1981)

In fixed-wall permeameter tests at high gradient, the permeability of an unsaturated micaceous soil increased by 3 to 4 orders of magnitude compared to the permeability determined with 0.01 N calcium sulfate. (Brown et al., 1984)

#### Naphtha

The permeabilities of two clays (Na-saturated and Ca-saturated montmorillonite) to naphtha were greater by several orders of magnitude than their permeabilities to water. (Buchanan, 1964)

(continued)

## Soltrol C (a light hydrocarbon liquid)

Intrinsic permeabilities for samples tested with the light hydrocarbon were significantly higher than the permeabilities measured in similar samples exposed to water. (van Schaik, 1970)

Diesel Fuel

Fixed-wall permeaneter tests at high gradient with an unsaturated micaceous illite produced highly variable data inconsistent with the pattern of permeability changes seen with other liquid hydrocarbons. Permeability was greater by 1 to 2 orders of magnitude than the permeability measured with 0.01 N calcium sulfate in a similar sample. (Brown et al., 1984)

#### Paraffin Oil

In fixed-wall permeameter tests at high gradient with an unsaturated micaceous illite, permeability was greater by about 1 order of magnitude than the permeability measured with 0.01 N calcium sulfate in a similar sample. Maximum values were obtained after the passage of one pore volume. (Brown et al., 1984)

#### Gasoline

In fixed-wall permeameter tests at high gradient with an unsaturated micaceous illite, permeability was greater by 1 to 2 orders of magnitude than the permeability measured with 0.01 N calcium sulfate in a similar sample.

#### Motor Oil

In fixed-wall permeameter tests at high gradient with an unsaturated micaceous illite, permeability increased by about 1 to 2 orders of magnitude as 2.5 pore volumes of fluid were passed through the sample. (Brown et al., 1984)

**ETHERS** 

Dioxane

Kaolinite initially packed and permeated with water was permeated with anhydrous dioxane until complete displacement of the water was achieved. Replacement of water by dioxane was accompanied by about a 20- to 30-percent increase in intrinsic permeability. This permeability was much lower, however, than the values determined for kaolinite beds initially prepared with dioxane. (Michaels and Lin, 1954)

(continued)

#### **KETONES**

#### Acetone

In fixed-wall permeameter tests under low hydraulic gradient, three clays showed slight decreases in permeability (compared to permeability to deionized water established in a similar sample). All tests were concluded before 40 days. Less than 0.5 pore volumes were passed through the sample. (Green et al., 1979)

Fixed-wall permeability tests at high gradient with four clays showed initial permeability decreases followed by increases compared to baseline. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. Extensive shrinking and cracking in the soils were observed after permeation. (Anderson, 1981)

In flexible-wall tests with a Georgia kaolinite, an immediate decrease in permeability was followed by an increase, the final value stabilizing at approximately double the initial permeability (Acar et al., 1984)

Acetone (high and low concentration)

An increase over baseline permeability (established with 0.01 N calcium sulfate in similar samples) was seen in an unsaturated micaceous soil for solutions where the acetone concentration was 75 or 100 percent. Samples tested with lower concentrations of acetone did not show appreciable changes in permeability compared to the 0.01 N calcium sulfate. Tests were carried out in fixed-wall permeameters at high gradient. (Brown et al., 1984)

Acetone (low concentration)

Permeability decreased slightly in a Georgia kaolinite clay tested in a flexible-wall permeameter with a solution containing a low concentration of acetone (i.e., below 0.1 percent) prepared in 0.01 N calcium sulfate. (Acar et al., 1984a)

ALCOHOLS, GLYCOLS, PHENOL

Methanol

Permeability decreased slightly (compared to permeability to deionized water established in a similar sample) when Ranger shale was exposed to methanol under low hydraulic gradient in a fixed-wall permeameter. The test was terminated after 30 days. (Green et al., 1979)

Fixed-wall permeameter tests at high gradient with four clays showed steady permeability increases compared to baseline. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. Examination of the methanol-treated samples revealed development of large pores and cracks. (Anderson, 1981)

(continued)

Methanol (con.)

Test results with Lufkin clay in flexible-wall cells showed essentially no change in permeability with time when samples were permeated with methanol. The permeability to methanol was virtually the same as with 0.01 N calcium sulfate. (Daniel, 1983)

At high hydraulic gradients, kaolinite was found to have a higher conductivity to methanol than to water regardless of the permeameter types; fixedwall, flexible-wall, and consolidation permeameters were used. In the flexible-wall and consolidation permeameters, kaolinite is about twice as permeable to methanol as to water. (Foreman and Daniel, 1984)

#### Isopropyl Alcohol

In column tests under very low gradient, intrinsic permeabilities were higher than permeability to water by almost 1 order of magnitude in samples of Nicholson, Fanno, and Canelo clays. Permeability values were the same or slightly higher than baseline in five other soils. The samples (5.8 cm in diameter and 5 cm in height) were presaturated with the alcohol. (Schramm, 1981)

#### Glycerol

Permeability decreased slightly (compared to permeability to deionized water established in a similar sample) when Ranger shale was exposed under low hydraulic gradient to glycerol in a fixed-wall permeameter. The test was terminated after 36 days. (Green et al., 1979)

#### Ethylene Glycol

Fixed-wall permeameter tests at high gradient showed permeability decreases compared to baseline followed by increases in three clays; a smectitic clay showed an initial rapid increase followed by a slower but continuous increase in permeability. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution (Anderson, 1981)

In column tests under very low gradient, intrinsic permeabilities were an order of magnitude lower than permeabilities to water in Chalmers clay, Mohave clay, and River Bottom sand. Values were slightly lower in Lake Bottom, Nicholson, Canelo, and Anthony clays and slightly higher in Fanno clay. The samples (5.8 cm in diameter and 5 cm in height) were presaturated with the ethylene glycol. (Schramm, 1981)

(continued)

Phenol (949 mg/L)

In column tests with a lacustrine clay (packed to discharge 2 mL/day), no significant effect on permeability was noted when deionized water was replaced by the phenol solution as the permeant fluid. (Sanks and Gloyna, 1977)

Phenol (low concentration)

Permeability decreased slightly in a Georgia kaolinite clay tested in a flexible-wall permeameter with a solution containing a low concentration of phenol (i.e., below 0.1 percent) prepared in 0.01 N calcium sulfate. (Acar et al., 1984a)

Phenol (high concentration)

In flexible-wall tests with a Georgia kaolinite and a high-strength phenol solution, an immediate decrease in permeability was followed by an increase, the final value stabilizing at approximately double the initial permeability. (Acar et al., 1984a)

AMINES

Aniline

Fixed-wall permeability tests at high gradient with four clays showed permeability increases and breakthrough. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. Extensive structural changes in the upper half of the soil columns were observed following permeation with aniline. The aggregated structure was characterized by visible pores and cracks on the surface of the soils. (Anderson, 1981)

Pyridine

The flow rate of pyridine through fireclay was of an enormously higher order of magnitude than the rate of flow for water. (Macey, 1942)

CHLORINATED ALIPHATICS

Carbon Tetrachloride

Permeability decreases slightly (compared to permeability to deionized water established in a similar sample) when Ranger shale was tested under low hydraulic gradient in a fixed-wall permeameter. The test was terminated after 14 days. (Green et al., 1979)

(continued)

4-22

#### Trichloroethylene

Permeability decreased slightly (compared to permeability to deionized water established in a similar sample) when fireclay was tested under low hydraulic gradient in a fixed-wall permeameter. The test was terminated after 36 days.

#### OTHER

Acetic Acid

Tests at high gradient in fixed-wall permeameters showed continuous permeability decreases to baseline in two clays. Tests with smectitic and illite clays showed permeability increases after initial decreases. Baseline permeabilities were established in the same sample with 0.01 N calcium sulfate prior to introducing the test solution. The permeability decreases were attributed to partial soil dissolution and migration of particles, which temporarily clogged the fluid conducting pores. Progressive soil piping eventually caused the increase in permeability. (Anderson, 1981)

#### Nitrobenzene

The flow rate of nitrobenzene through fireclay was of an enormously higher prder of magnitude than the flow rate for water. (Macey, 1942)

In flexible-wall tests with a Georgia kaolinite, permeability decreased until the tests were terminated. The final value was approximately 2 orders of magnitude lower than the initial permeability (Acar et al., 1984a)

"Xylene Waste" (paint solvent containing xylene with 25 percent paint pigments and trace amounts of water)

In fixed-wall permeameter tests, the permeability of three clay soils, presaturated with 0.01 N calcium sulfate, increased rapidly upon exposure to xylene waste after the cumulative flow exceeded 0.2 to 0.4 pore volume. Permeabilities were 2 to 4 orders of magnitude greater than permeabilities measured with 0.01 N calcium sulfate. Highest permeabilities measured on initially unsaturated samples were greater by 1 to 2 orders of magnitude than for samples that were initially saturated with the calcium sulfate. (Brown et al., 1983)

"Acetone Waste" (a chemical manufacturing waste containing 91.7 percent acetone, 4 percent benzene, and 0.6 percent phenol)

In fixed-wall permeameter tests, the permeability of three clay soils, presaturated with 0.01 N calcium sulfate, initially decreased (minimum permeability at approximately 0.5 pore volume) and then steadily increased. Permeabilities were 2 to 4 orders of magnitude greater than permeabilities measured with 0.01 N calcium sulfate. Highest permeabilities measured on initially unsaturated samples were greater by 1 to 2 orders of magnitude than for samples that were initially saturated with the calcium sulfate. (Brown et al., 1983)

Perchloroethylene Waste

There is evidence that a perchloroethylene waste, which formed a separate, denser than water phase, contributed to the failure of a clay liner at a surface impoundment. (Personal communication, 1984)

"Acid Prowl" (pesticide wash of very low pH; higher viscosity than water)

After several days of exposure to a lacustrine clay packed in a fixed-wall column, the water reacted with the soil to produce chlorine gas. Over a 5-week period, the flow of liquid from the column was irregular due to clogging of pores by the gas. (Everett, 1977)

"Acid Wash" (42 percent sulfuric acid with about 5 percent organics; higher viscosity than water)

Permeability of a lacustrine clay packed in shrink tubing increased by about 1 order of magnitude over a period of 19 days. The permeability was lower, however, than values obtained when the soil sample was exposed to water. (Everett, 1977)

(continued)

4-24

"Mother Liquor" (an acid wash with pH of 0.37; higher viscosity than water)

Permeability of a lacustrine clay packed in shrink tubing was lower than the value obtained when the soil sample was exposed to water. The waste may have reacted with the soil, liberating gases and increasing pore pressures and clogging flow. (Everett, 1977)

"Hydrazo Benzene" (33 percent methanol, 12.8 percent sodium hydroxide, 15.5 percent sodium formate, and 1.5 percent hydroazobenzene and azobenzene; more viscous than water)

Permeability of a lacustrine clay packed in shrink tubing was slightly lower than the value obtained when the soil sample was exposed to water. Tests were carried out for 34 days under low gradient (less than 100 cm).

"Acid Waste" (100 mM HC1/L)

Due to reaction with carbonates, much higher permeabilities were observed in tests with lacustrine clay compared to permeabilities determined with deionized water. (Sanks and Gloyna, 1977)

"Basic Waste" (100 mM NaOH/L)

ermeabilities in a lacustrine clay decreased compared to the values measured with deionized water. (Sanks and Gloyna, 1977)

through clay are "of an enormously higher order than for water." Analytical reagent-grade organics were used. All the organic liquids passed through the clay at flow rates 100,000 to 1,000,000 times greater than the flow rate of water through the same clay. The high rates of flow produced experimental difficulties because of the high resistance to flow of the testing apparatus, and the experiments were finally abandoned. Differences between the viscosities of the organic fluids and of water are not sufficient to account for the very large permeability changes that were observed.

#### 4.5.2 <u>Tests With Kaolinite and Organic Solvents by Michaels and Lin (1954)</u>

Michaels and Lin (1954) measured the permeability of high-purity kaclinite to nitrogen gas, cyclohexane, acetone, dioxane, methanol, and distilled water. Tests were also conducted to determine the effect of replacement of one permeant liquid by another. The investigation was one part of a broad program of fundamental research sponsored by the U.S. Army Corps of Engineers and by industrial contributions and was carried out at the Massachusetts Institute of Technology (MIT) Soil Stabilization Laboratory.

#### 4.5.2.1 Test Method--

Permeability tests were conducted in a 5.1-cm (2-inch) -diameter fixedwall permeameter cell. Bed thickness was 1.1 to 1.8 cm. The base-exchange capacity of the kaolinite was determined to be  $5.0 \pm 0.5 \text{ meq}/100 \text{ g}$ . Samples were dried for 24 hours at  $160^{\circ}$ C prior to saturation by the organic liquids for the permeability test.

Prior to permeability testing, each sample was submerged in the fluid to be tested (either organic liquid or water). The wetted samples containing known amounts of clay were poured into the permeability cell, entrapped air was removed, and the sample was consolidated by means of a confining piston. Samples were consolidated to several void ratios (volume of voids/volume of solid) for each test fluid. Void space was determined through column bulk density and the true density of kaolinite.

For the permeability tests, a hydrostatic head not exceeding 10 percent of the compaction pressure was maintained. Permeabilities were determined for each void ratio. Permeability coefficients determined for separate clay samples prepared with a given fluid and compacted to essentially the same void ratio were found to be reproducible to within 10 percent.

The effect of change of fluid medium on the permeability of a confined clay was determined through a series of desolvation experiments. Kaolinite initially packed and permeated with water was subsequently permeated with dioxane until the water was completely displaced (as evidenced by constant permeability to dioxane). The dioxane was then displaced with acetone under similar conditions. Finally, warm, dry nitrogen was passed through the sample until the bed was solvent-free. Beds initially tested with the organic liquids (methanol, dioxane, acetone, and cyclohexane) were similarly treated with dry nitrogen until all solvent was removed.

The permeability to nitrogen of the desolvated samples was then determined and compared to the permeability with the original permeant fluid.

#### 4.5.2.2 Test Results--

The intrinsic permeabilities  $(cm^2)$  of samples packed at different void ratios, measured for organic solvents and for nitrogen, are shown in Figure 4-3. Predictably, the permeabilities increased with increasing void ratio. The data also indicate that permeability at any given void ratio decreases with increasing polarity of the permeant.

As a result of the desolvation experiments, the authors concluded that:

Whatever specific effects these permeant liquids exert on the kaolinite persist when the clay is thoroughly dried in the confined state. The reduced permeabilities of kaolinite to these liquids relative to the values observed for this clay to gas when packed in the dry state apparently cannot be ascribed to adsorbed liquid films, abnormally high liquid viscosities, or electro-osmotic effects. . . It seems most probable, therefore, that the lower permeabilities of kaolinite to these liquids than to nitrogen are caused by improved dispersion, and possibly more orderly packing of the solids in more polar media.

Results of the desolvation experiments show the effect of replacement of permeant fluid on the permeability of the kaolinite. For samples sedimented from and initially permeated with methanol, dioxane, acetone, or cyclohexane and then exhaustively permeated with warm, dry, nitrogen gas, the final gas permeability is found to be equal, within the limits of experimental accuracy, to the permeability to the initial permeant liquid at the corresponding void ratio. This is particularly true at low void ratios. An increase in permeability upon drying is observed if the initial void ratio is high.

Specific observations by Michaels and Lin include the following:

- Replacement of water by dioxane is, in all cases, accompanied by about a 20- to 30-percent increase in permeability; the dioxane permeabilities through these beds are, however, much lower than the values determined for kaolinite beds prepared initially in dioxane.
- Replacement of the dioxane with acetone leads to a small additional permeability increase approximately when water is the initial permeant fluid.
- Displacement and evaporation of the acetone with dry nitrogen is accompanied by a great increase in permeability; the magnitude of this increase is greatest for kaolinite samples confined initially at high void ratios.

|      |    |                       |        | $ \begin{array}{rcl} x & - & Watt \\ 0 & - & N_2 \\ \hline & - & Cyc \\ \Delta & - & Acc \\ \hline \Delta & - & Dicz \\ + & - & Meti \end{array} $ | er<br>Iohexane<br>tone<br>kane<br>hanol |  |            |
|------|----|-----------------------|--------|--|---|--|------------|
|      |    |                       |        |  |   |  |            |
|      |    |                       |        |  |   |  |            |
|      |    |                       |        |  |   |  |            |
|      |    |                       |        |  | 2                                       |  | • •        |
| 1.0  |    |                       |        | $ \rightarrow $  |   | ·····  |            |
|      |    |                       |        | $\angle \angle$  |   |  |            |
|      |    |                       |        |  |   |  |            |
|      |    |                       | 14-1-1 |  |   |  |            |
|      |    |                       |        |  |   |  |            |
|      |    |                       |        |  |   | · · · · · · · · · · · · · ·                        |            |
|      |    | 9 <del>7 - 7</del> 7  |        |  | ••••••••••••••••••••••••••••••••••••••  |  |            |
|      | /  |                       | /      | <u> </u>   |   | • • •  |            |
|      |    |                       |        |  |   |  |            |
| , ,  |    |                       |        |  |   | · · ·  |            |
|      | -/ |                       | ·····  | · · · · · · · · · · · · · · · · ·  |   |  |            |
| ·    | 1  |                       |        |  |   |  |            |
|      | i  |                       |        | . +  | • : <del>*</del> :                      |  |            |
|      |    |                       |        |  |   |  | - <b>-</b> |
|      |    |                       |        |  |   | - · <del>· · · · · · · · · · · · · · · · · ·</del> |            |
|      |    |                       |        |  |   |  |            |
|      |    |                       |        |  |   |  |            |
|      |    |                       |        |  |   |  |            |
| ===7 |    |                       |        |  |   |  |            |
| ).01 |    | 18                    |        |  |   |  |            |
|      |    |                       |        |  |   |  |            |
|      |    | · <del>7 33 · ·</del> |        | TTRA P   | <u>e ::: +f ci</u>                      | - 121-A ) -  |            |
|      |    |                       |        |  |   |  |            |

Permeants

Source: Michaels and Lin, 1954

Figure 4-3. Intrinsic permeabilities as a function of void space (e) measured for different permeants.

#### 4.5.2.3 Discussion--

Intrinsic permeabilities reported by Michaels and Lin cannot be directly compared with permeability data from other tests because the measurement procedure is unique. No information is provided about the amount of fluid passed through the sample in determining each of the reported permeabilities.

While samples used in permeability tests are usually air-dried, the clay samples used by Michaels and Lin were dried for 24 hours at 160°C, a condition that could cause irreversible changes in clays and organic matter. It is possible that the adsorptive properties of the kaolinite were permanently altered by this drying procedure. The kaolinite mineral, halloysite, will not rehydrate if the interlayer water is removed.

#### 4.5.3 Study by Buchanan (1964) of the Effect of Naphtha on Montmorillonite

Buchanan (1964) at Texas A&M University studied permeabilities of sodiumand calcium-saturated montmorillonite when these clays were permeated by water and naphtha. Permeabilities of the two clays to naphtha were greater by several orders of magnitude than their permeabilities to water, even with reductions in void ratios for the samples treated with naphtha. The data also suggest that the permeability of the sodium-saturated clay is more dramatically affected by the naphtha. Permeability differences were thought to be at least partially due to the inability of naphtha to form an immobilized liquid film on the clay mineral surfaces. Buchanan's data are summarized in Table 4-3.

#### 4.5.4 <u>Study by Reeve and Tamaddoni (1965) of the Effect of Electrolyte</u> <u>Concentration on Permeability of a Sodic Soil</u>

Reeve and Tamaddoni (1965) of the U.S. Department of Agriculture studied the effects of high-salt, high-sodium solutions on the permeability of a highly sodic soil. California Waukena clay loam containing about 15 percent of expanding lattice-type clay was tested in the laboratory and in the field.

#### 4.5.4.1 Test Method--

Solutions of varying concentrations but with constant sodium adsorption ratio (SAR) were used in the tests. Test solutions were prepared from sodium chloride (NaCl) and calcium chloride (CaCl<sub>2</sub>) at SAR levels of 0 (100 percent CaCl<sub>2</sub>), 80 (a partially reclaiming solution), 180 (the equilibrium solution of the natural soil), and  $\infty$  (100 percent NaCl). For each SAR level, seven ionic concentrations (63, 125, 250, 500, 1,000, 2,000, and 4,000 meq/L) were tested in a selected sequence. Laboratory tests were carried out in fixed-wall 5.4-cm (2.125-inch) ID cylinders.

#### 4.5.4.2 Test Results--

The test results indicate that permeability is a function of both the absolute concentration and the SAR of the initial solution. Permeability increased with increasing SAR value and ionic concentration. The permeability-concentration relationship was found to depend markedly on the initial solution concentration (i.e., if the initial solution concentration

#### TABLE 4-3. VOID RATIO AND COEFFICIENT OF PERMEABILITY RELATIONSHIPS FOR CALCIUM- AND SODIUM-MONTMORILLONITE PERMEATED BY WATER AND NAPHTHA<sup>a</sup>

|                               |               | Water                   | Naphtha       |                        |  |
|-------------------------------|---------------|-------------------------|---------------|------------------------|--|
| Clay                          | Void<br>ratio | Permeability<br>(cm/s)  | Void<br>ratio | Permeability<br>(cm/s) |  |
| Calcium-saturated<br>smectite | 1.72          | 1.6 x 10-9              | 1.52          | 6.4 x 10 <sup>-5</sup> |  |
| Sodium-saturated smectite     | 3.75          | 5.2 x 10 <sup>-11</sup> | 1.31          | 3.8 x 10 <sup>-5</sup> |  |

<sup>a</sup>Data from Buchanan (1964).

TABLE 4-4. SUMMARY OF SOIL PERMEABILITY WITH SOLTROL C AND WATER<sup>a</sup>

| Soil<br>(bulk density in g/cm <sup>3</sup> )   | Intrinsic<br>permeability (um <sup>2</sup> )<br>Water Oil |      | <u>Permeability, K (cm/s)</u><br>Water Oil |                        |
|--|---|------|--|------------------------|
| Cavendish loamy sand<br>(bulk density:<br>1.44 g/cm <sup>3</sup> ;<br>6 percent clay)  | 4.94  | 9.38 | 4.8 x 10 <sup>-3</sup>                     | 3.0 x 10 <sup>-3</sup> |
| Chin sandy clay loam<br>(bulk density:<br>1.25 g/cm <sup>3</sup> ;<br>18 percent clay) | 0.73  | 5.45 | 7.1 x 10 <sup>-4</sup>                     | 5.1 x 10 <sup>-3</sup> |
| Chin sandy clay loam<br>(bulk density:<br>1.38 g/cm <sup>3</sup> ;<br>18 percent clay) | 0.22  | 2.53 | 2.1 x 10 <sup>-4</sup>                     | 1.4 x 10 <sup>-3</sup> |
| Lethbridge clay loam<br>(bulk density:<br>1.22 g/cm <sup>3</sup> ;<br>37 percent clay) | 0.51  | 6.10 | 5.0 x 10 <sup>-4</sup>                     | 3.3 x 10 <sup>-3</sup> |

<sup>a</sup>Data from van Schaik (1970).

4-30

was low, the range of permeability values with varying solution concentrations was lower than if the initial solution concentration was high, and vice versa.) Apparently the degree of flocculation or dispersion that occurred with the application of the initial solution influenced the magnitude of the permeability.

In some of the tests a large change in solution concentration (e.g., from 125 to 1,000 meq/L) was accompanied by a large increase in outflow due to sidewall leakage as a consequence of the contraction of the previously swollen mass.

In the test series in which initially low concentrations (63 meq/L) were increased stepwise to 4,000 meq/L and then reduced to the initial concentration, reproducibility of permeability values as a function of concentration was good. These results suggested that a reversible swelling process was occurring. In the test series in which initial concentrations of 1,000 meq/L were increased to 4,000 meq/L and then reduced to 63 meq/L, results showed a gradual decrease in permeability with a given solution concentration. This was attributed to slaking or particle rearrangement that led to permeability decreases that progressed with time.

The permeability of the Waukena soil to a saturated calcium sulfate (CaSO4) solution was an order of magnitude lower than the lowest values measured with the test solutions.

Test results showed that intake rates measured in the field at high electrolyte concentrations were approximately three times as great as corresponding permeabilities measured in the laboratory. However, the fractional change was essentially the same at equal electrolyte concentrations.

#### 4.5.5 <u>Tests by van Schaik and Laliberte (1968) of Permeability of Soils</u> to a Liquid Hydrocarbon

Permeability data are reported by van Schaik (1970) for three soils tested with tap water and with a light hydrocarbon liquid (trade name Soltrol C). Permeability measurements were made on samples that had been vacuum-saturated. The intrinsic permeabilities with the oil were first reported by van Schaik and Laliberte (1968).

#### 4.5.5.1 Test Results--

The saturated intrinsic permeability of the three samples varied between 0.22 and 4.94  $\mu$ m<sup>2</sup> for water. For oil, the values ranged between 2.53 and 9.38  $\mu$ m<sup>2</sup>. The data are summarized in Table 4-4.

#### 4.5.5.2 Discussion--

The test apparatus used in the study was designed to measure properties of unsaturated porous media. The number of pore volumes displaced by the test fluid during the permeability determination was not reported. Details of the test procedure used also were not given in the references cited. In spite of these limitations, the intrinsic permeabilities are useful for

comparing the relative permeabilities of the various soils to water and oil. The increased permeabilities of the soils when exposed to the oil are consistent with the later findings by Anderson (1981).

#### 4.5.6 <u>Study by Everett (1977) of Permeability of Lacustrine Clay to Four</u> Liquid Wastes

Everett (1977) investigated the permeability of lacustrine clays from Bay County, Michigan, to four liquid wastes. The purpose of the study was to establish the feasibility of a hazardous waste landfill in Bay County. Three types of permeability test devices were used. The results of the comparative tests with water show no significant differences in the permeabilities measured in the different devices.

The predominant mineral in the soil was quartz, estimated to be 40 to 50 percent. Clay minerals present were illite and chlorite, each at about 10 to 15 percent. Other important constituents were dolomite (20 to 25 percent) and calcite (10 to 15 percent). The clay fraction was reported to average 18.1 percent. The mean cation exchange capacity of the soil (determined with ammonium acetate solution) was low.

Wastes used in the compatibility tests were "Acid Prowl," "Acid Wash," "Mother Liquor," and "Hydrazo Benzene." "Acid Prowl" is a pesticide wash of very low pH. The "Acid Wash" was about 42 percent sulfuric acid in water and also contained about 5 percent organics including dichlorobenzidine, orthochloroaniline, and tars. The waste labeled "Hydrazo Benzene" actually contained about 1.5 percent hydroazobenzene and azobenzene. Other components were methanol (33 percent), sodium hydroxide (12.8 percent), sodium formate (15.5 percent), and water (36.7 percent). The waste has a pH of 12.10. The "Mother Liquor" was an acid wash (pH of 0.37) of unknown use. All waste samples were more viscous than water.

#### 4.5.6.1 Test Method--

Permeability to water was measured in three different test devices-commercial Soil Test<sup>®</sup> units (fixed-wall, 10.2-cm [4-inch] diameter, 10.2-cm [4-inch] sample height), PVC pipe (10.3-cm [4-inch] diameter, 15.2-cm [6-inch] sample height), and shrink tubing (10.2-cm [4-inch] diameter, 15.2-cm [6-inch] length). Samples tested in the Soil Test units and the shrink tubing were prepared in a standard Proctor mold according to ASTM specifications for modified Proctor compaction (D-1557-70). The objective of preparing the samples was to obtain uniform packing. The PVC pipe was packed in a different manner, not specified.

Samples were saturated by backwashing with water for more than 2 weeks before permeability data were recorded. Readings were taken over a 2-month period to determine the permeability of the samples to water. After testing with water, three shrink tube columns and the PVC pipe columns were tested with wastes. Samples were allowed to saturate by backwashing with the waste until the effluent showed the presence (by color or pH) of the waste.

The tests were all conducted in falling head setups with a head of less than 100 cm (39.37 inches). The metal test units were not used for testing the wastes because of the corrosive nature of the wastes.

4.5.6.2 Test Results--

"Acid Prowl" was tested in the PVC column. After several days of contact with the soil, chlorine gas became noticeable at the outlet pipe. After 2 weeks, the gas was no longer apparent, and liquid flow from the permeameter ceased. The column was allowed to stand with the waste fluid head for 3 more weeks. During this time the fluid reacted irregularly. This behavior was attributed to clogging of pores by chlorine gas generated with the sample.

"Acid Wash," "Mother Liquor," and "Hydrazobenzene" were tested in shrink tubes. The permeabilities measured with the wastes were lower than the corresponding permeabilities to water. This may be due in part to the higher viscosity of the wastes compared to water. Values obtained after 19 days of testing with "Acid Wash" showed a slight increase in permeability (about 1 order of magnitude) compared to the initial value. For "Mother Liquor," test data with the waste showed permeability to be lower by more than 2 orders of reacted with the soil-liberating gases, which would increase pore pressures permeability values were slightly lower than values obtained with water. Permeability data are compared in Table 4-5.

## 4.5.6.3 Discussion--

Although the compatibility tests were carried out for approximately 1 month, the volumes of liquid forced through the columns under the low gradients had to be very small. The number of pore volumes displaced was not specified. Sufficient data were not presented to determine quantitatively the effect attributable to the viscosity of the wastes.

4.5.7 <u>Tests by Sanks and Gloyna (1977) of Permeability of Lacustrine</u>

Sanks and Gloya (1977) tested five simulated liquid wastes with three clays in column tests to determine effects on permeability. The aqueous waste solutions tested were chosen to be representative of materials that acid, base, and heavy metals. Clays tested contained large percentages of charge 2 mL/day of distilled water at 152-cm (5-ft) head with an allowable and refilled with the waste fluid to be tested.

Permeabilities with deionized water ranged from 4 x  $10^{-8}$  to 1.2 x  $10^{-7}$  cm/s. Much higher permeabilities were observed when the acid waste (100 mM HC1/L) was passed through the columns due to reaction with carbonates. Permeabilities decreased in tests with the basic waste (100 mM NaOH/L). Phenol at 10 mM/L (940 mg/L) appeared to have little effect on permeability.

| Day of<br>test data | <u></u>                               | Permeability (cm/s      | 5)                       |
|---------------------|---------------------------------------|-------------------------|--------------------------|
|                     | ···· ·· · · · · · · · · · · · · · · · | With water              |                          |
| 1                   | $3.4 \times 10^{-10}$                 | 6.7 x 10 <sup>-7</sup>  | 4.0 x $10^{-7}$          |
| 3                   | $1.3 \times 10^{-9}$                  | 6.5 x 10 <sup>-7</sup>  | 6.0 x 10 <sup>-7</sup>   |
| 5                   | 1.5 x 10 <sup>-9</sup>                | 5.7 x 10 <sup>-7</sup>  | 5.1 x 10-7               |
|                     | With<br>"acid wash"                   | With<br>"mother liquor" | With<br>"hydrazobenzene" |
| 15                  | 7.1 x 10-11                           | 9.0 x 10-10             | 9.0 x 10 <sup>-8</sup>   |
| 19                  | No flow                               | $1.0 \times 10^{-9}$    | 7.8 x 10 <sup>-8</sup>   |
| 29                  | 2.9 x $10^{-10}$                      | 8.3 x 10-10             | No reading               |
| 32                  | 5.8 x 10-10                           | 2.1 x $10^{-9}$         | 1.3 x 10 <sup>-7</sup>   |
| 34                  | 6.9 x 10-10                           | 3.1 x 10-10             | 1.3 x 10 <sup>-7</sup>   |

# TABLE 4-5.PERMEABILITIES MEASURED WITH LACUSTRINE CLAY<br/>EXPOSED TO WATER AND WASTE LIQUIDSa

<sup>a</sup>Data from Everett (1977).

4-34

Heavy metals tested, HgCl<sub>2</sub> at 30 mM/L (8,100 mg/L) and ZnSO<sub>4</sub> x  $7H_2O$  at 30 mM/L (8,610 mg/L), showed no effect except for one anomaly.

## 4.5.8 Investigation of the Effect of Organic Solvents on Clays by Green, Lee, and Jones (1979)

Under a grant from EPA's Kerr Environmental Laboratory, Ada, Oklahoma, to the University of Texas at Dallas, Green, Lee, and Jones (1979) studied the impacts of organic solvents on the shrink/swell behavior and permeability of four clay soil materials--Ranger shale, fire clay, Kosse kaoline, and Parker soil. The test results were compared to results with water. The studies included extensive soil characterization. Soil properties are carbon tetrachloride, trichlorethylene, methanol, and glycol (Green et al., 1981, 1983).

## 4.5.8.1 Test Methods--

Swell properties of the clays in contact with water, the organic solvents, and various solvent mixtures were investigated. The swell properties were measured with a 6.4-cm-diameter consolidometer. Care was taken to prevent evaporation. Clay core samples used in the tests were compacted at optimum moisture content. In the consolidometer, samples were flooded with the test fluid and measurements of the swell or shrink behavior were made as a function of time.

Permeability data were collected on 15 clay/solvent systems. Test durations ranged from 8 to 40 days. Fixed-wall permeameters used in the study were thick-walled Pyrex glass, and all joints were Teflon<sup>®</sup>-lined. The test procedure was adapted from an ASTM method. Samples were compacted at optimum moisture conforming to standard compaction procedures before transfer to the permeameters. The test fluid was then introduced, the liquid level being adjusted in an 8-mm graduated standpipe. Equilibrium permeabilities were estimated from curves of K(cm/s) versus time. The number of pore volumes of permeant fluid passed through the samples was not reported.

## 4.5.8.2 Test Results--

Each of the clay soils swelled to a greater extent when exposed to deionized water than with any of the pure solvents tested. The shrink/swell behavior of the various clays in water and in organic solvents is described in Table 4-7. The final percent swells for the samples are listed in Table 4-8.

Based on the swelling data for both pure solvents and for mixtures, the authors concluded that "in mixtures of solvents, a clay will tend to swell as though it were immersed in the component of higher dielectric constant only" (Green et al., 1979).

When Ranger shale was presented with benzene, breakthrough occurred on the eighth day of testing. Breakthrough occurred at about day 25 in the fire clay sample presented with xylene.

CBA 007

0949

|  | Clays                |                              |                             |                              |  |  |
|--|----------------------|------------------------------|-----------------------------|------------------------------|--|--|
| Properties   | Ranger<br>shale      | Fire<br>clay                 | Kosse<br>kaoline            | Parker<br>soil               |  |  |
| Particle size distribution (wt. %)                             |                      | ·····                        |                             |                              |  |  |
| Clay<br>Silt<br>Sand   | 40<br>59<br>1        | 44<br>55<br>1.5              | 53<br>47<br>0               | 10.5<br>70.5<br>19           |  |  |
| Total carbon (%)   | 0.60                 | 0.03                         | 0.12                        | 3.18                         |  |  |
| Carbonate (%)  | 0.32                 | 0                            | 0                           | 0.42                         |  |  |
| Cation exchange capacity                                       | 54.4                 | 11.2                         | 13.4                        | 14.1                         |  |  |
| Atterberg limits   |                      |                              |                             |                              |  |  |
| Plastic limit (moisture %)<br>Liquid limit (moisture %)        | 36<br>46             | 31<br>32                     | 38<br>50                    | 22<br>26                     |  |  |
| Optimum moisture content (%)                                   | 17.5                 | 16                           | 31                          | 18                           |  |  |
| Corresponding dry density<br>(g/cm <sup>3</sup> )              | 1.73                 | 1.81                         | 1.36                        | 1.86                         |  |  |
| Mineralogy (% of clay<br>fraction)                             |                      |                              |                             |                              |  |  |
| Kaolinite<br>Quartz<br>Illite/mica<br>Chlorite-montmorillonite | 24<br>28<br>24<br>10 | 78<br>16<br>10<br>Negligible | 85<br>10<br>5<br>Negligible | 14<br>Negligible<br>37<br>49 |  |  |

TABLE 4-6. PROPERTIES OF SOILS TESTED<sup>a</sup>

<sup>a</sup>Data from Green et al., 1979.

120

# TABLE 4-7. CLASSIFICATION OF CLAY-ORGANIC SOLVENT SYSTEMS ACCORDING TO SWELL PROPERTIES<sup>a</sup>

| Swelling<br>only   | Swelling then shrinking   | Shrinking then<br>swelling         | Shrinking<br>only                              |
|--|---|------------------------------------|--|
| RS/H <sub>2</sub> O<br>RS/glycerol<br>RS/methanol<br>RS/CCl <sub>4</sub><br>RS/TCE<br>KK/water<br>KK/acetone<br>FC/water | RS/acetone<br>KK/xylene<br>FC/acetone<br>FC/TCE<br>FC/xylene (NS) | RS/benzene<br>KK/TCE<br>FC/benzene | RS/xylene (NS)<br>KK/CC14 (NS)<br>FC/CC14 (NS) |
| RS = Ranger sha<br>FC = Fire clay<br>NS = Net shrink   | ale   | KK = Kosse kao<br>TCE = Trichloro  | line<br>ethylene                               |

observed unless indicated otherwise)

aReproduced from Green, Lee, and Jones, 1979.

| Clay-soil     | Solvent                            | Percent swell <sup>b</sup> |
|---------------|------------------------------------|----------------------------|
| Ranger shale  | Benzene                            | 0.05                       |
|               | Benzene/acetone (3:1) <sup>C</sup> | 5.75                       |
|               | Xylene                             | -0.11                      |
|               | Carbon tetrachloride               | 1.1                        |
|               | Trichloroethylene                  | 1.0                        |
|               | Acetone                            | 4.0                        |
|               | Acetone/benzene (3:1) <sup>C</sup> | 4.6                        |
|               | Acetone/water (1:1)d               | 11.0                       |
|               | Methanol                           | 11.4                       |
|               | Glycerol                           | 5.3                        |
|               | Water                              | 11.7                       |
| Kosse kaoline | Xvlene                             | 0.16                       |
|               | Acetone                            | 8.7                        |
|               | Water                              | 11.7                       |
| Fire clav     | Xvlene                             | -0.25                      |
|               | Carbon tetrachloride               | -0.6                       |
|               | Acetone                            | 3.6                        |
|               | Water                              | 8.2                        |

## TABLE 4-8. PERCENT SWELL FOR CLAY SOILS IN CONTACT WITH ORGANIC LIQUIDS AND WATER<sup>a</sup>

<sup>a</sup>Adapted from Green et al., 1979. <sup>b</sup>Negative value indicates net shrinkage. <sup>c</sup>Mole percent. dvolume percent.

For organic solvents other than benzene, a decrease in permeability of Ranger shale was observed for 5 to 10 days. This decrease was followed by stable readings at a minimum value. The permeability coefficients reported are shown in Figure 4-4. Although there is some scatter in the measurements characteristic of normal experimental error, the decreasing permeability trends over the duration of the test period are evident. The largest decrease in permeability compared to water is seen with glycerol. With carbon tetrachloride, the decrease in permeability was followed by an increase that continued to the end of the test period.

#### 4.5.8.3 Discussion--

The authors based their final conclusion, an empirical relationship for estimating the coefficient of permeability from dielectric constant of the permeant and packed bulk clay density, on what they judged to be final permeabilities. Their data do not indicate that stable permeabilities were reached, however, in all of the solvent clay systems tested. Certainly the permeabilities measured just prior to breakthrough could not be classified as permeability.

# 4.5.9 Anderson's Study (1981) of the Effects of Organics on Permeability

Anderson (1981) at Texas A&M University studied seven organic fluids in comparative permeability tests. Four native clay soils were tested--two with predominantly montmorillonite (smectitic) clay minerals but different chemical properties, one with predominantly kaolinite minerals, and one with predominantly illite. Each soil contained a minimum of 35 percent by weight clay minerals and exhibited a baseline permeability of less than  $1 \times 10^{-7}$  cm/s when compacted at optimum water content. Organic solvents tested were reagent grade ethylene glycol, acetone, heptane, xylene (mixed isomers), aniline, glacial acetic acid and methanol. The control fluid used to establish the baseline permeability for each soil was a standard aqueous solution of calcium sulfate (0.01 N CaSO<sub>4</sub>). (Although it was not noted in the initial publication of this research, the methanol used in the experiment contained 20 percent water [Anderson 1982].)

Characteristics of the four soils used in the tests are presented in Table 4-9. The percentage of soil voids filled with water at compaction at optimum moisture content was approximately 75 percent for the two smectitic clays and approximately 90 percent for the other two samples. The minimum permeability for each sample occurred at or just above the optimum moisture content (Anderson et al., 1981; Brown and Anderson, 1983).

### 4.5.9.1 Test Method--

Permeability was measured in constant head tests on soil cores compacted at or above optimum water content. Pressurized compaction permeameters with an air-induced elevated hydraulic gradient were used. For two montmorillonite clays, a gradient of 361.6 (equivalent to a hydraulic head of 42.2 m of water) was used. For the illite and kaolinite clay soils, a hydraulic gradient of 61.6 (equivalent to a hydraulic head of 7 m of water) was imposed. No signs of particle migration or turbulent flow resulted from the elevated gradients.







| TABLE 4-9. | GRAIN SIZE | DISTRIBUTION, | MINERALOGY,        | AND | PROPERTIES |
|------------|------------|---------------|--------------------|-----|------------|
|            | OF         | THE FOUR CLAY | SOILS <sup>a</sup> |     |            |

| Clay soil<br>description  | Non-<br>calcareous<br>smectite | Calcareous<br>smectite       | Mixed<br>cation<br>kaolinite                  | Mixed<br>cation<br>illite |
|---|--------------------------------|------------------------------|---|---------------------------|
| % Sand (>50 nm)   | 35-37                          | 7-8                          | 39-41   | 14-15                     |
| % Silt (50-2.0 nm)  | 26-28                          | 42-44                        | 17-18   | 38-39 <sup>1</sup>        |
| % Clay (<2.0 nm)  | 36-38                          | 48-50                        | 42  | 47                        |
| Coarse clay (2.0-0.2 nm)<br>% of total<br>Mineralogy <sup>b</sup> | 16<br>QZ-1<br>KK-2<br>MI-2     | 25<br>MT-1<br>KK-2<br>QZ-3   | 33<br>KK-1<br>QZ-2                            | 61<br>I-1<br>QZ-2         |
| Fine clay (<0.2 nm)<br>% of total<br>Mineralogy <sup>b</sup>      | 84<br>MT-1                     | 75<br>MT-1<br>KK-3           | 67<br>KH-1<br>MT-3                            | 39<br>I-1<br>MT-2         |
| Cation exchange capacity<br>(meq/100 g)                           | 24.2                           | 36.8                         | 8.6   | 18.3                      |
| Total alkalinity (meq/100 g)                                      | 3.3                            | 129.2                        | 0.8   | 4.2                       |
| Fe <sub>2</sub> 0 <sub>3</sub> (%)                                | 0.42                           | 0.2                          | 13.2  |                           |
| Organic matter (%)  | 0.9                            | 3.0                          | 0.6   | -                         |
| CaCO <sub>3</sub> Equiv. (%)                                      | -                              | 33                           | Trace   | <u> </u>                  |
| Shrink-swell potential  | Very high                      | Very high                    | Moderate                                      | Moderate                  |
| Liquid limit  | 51-67                          | 58-98                        | 41-60   | ~46                       |
| Plasticity index  | 30-45                          | 34-72                        | 18-30   | ~27                       |
| ,<br>Optimum water content <sup>C</sup>                           | 20.0                           | 21.5                         | 20.0  | 19.0                      |
| Maximum density (kN m <sup>-3</sup> )                             | 15.0                           | 14.4                         | 16.3  | 16.6                      |
| <sup>a</sup> Adapted from Anderson, 1981.                         | •                              |                              |   |                           |
| <sup>b</sup> Key to mineralogy: MT = Sme<br>KK = Kac<br>I = Ill   | ectite 1<br>Dinite 2<br>ite 3  | = >40%<br>= 10-40%<br>= <10% | QZ = Quartz<br>MI = Mica or<br>KH = Halloysil | illite<br>ce              |
| <sup>C</sup> Percent by dry weight.                               |                                |                              |   |                           |

Special precautions were taken to minimize several sources of error that occur frequently in permeability testing. At least one pore volume of the CaSO4 solution was passed through the soil cores to minimize trapped air. Before the permeameter was pressurized, the top of the soil sample was exposed to 10 cm of standard CaSO4 solution for 48 hours. This procedure helps to prevent channel formation and bulk flow and promotes sealing of the permeameter sidewalls. Provision was made to view the effluent passing through the soil sample so that trapped air or evidence of piping could be monitored. Care was taken to minimize evaporative losses from the collected effluent. Teflon fittings were used wherever possible to avoid deterioration from exposure to the organic solvents.

After seating the soils at low pressure, the selected gradient was applied to the permeameter fluid chamber until stable permeability values were obtained with the standard  $CaSO_4$  solution. At this point, pressure was released and permeameters were disassembled. Soil that had expanded out of the mold was removed and additional standard leachate was passed through the remaining sample in the permeameter. Percent swelling was determined for each soil. At this point, the soil sample was assumed to be completely saturated.

After the saturation step to ensure stable baseline permeability, the remaining standard CaSO4 solution was removed and replaced with one of the organic solvents to be tested. The selected gradient was imposed and between 0.5 and 2.0 pore volumes of fluid were passed through the sample in the permeameter. The permeameters were then depressurized, disassembled, and the cores removed and examined for evidence of structural changes. Following the permeability tests of the noncalcareous smectite clay soil with aniline, methanol, and ethylene glycol (all highly water-soluble), water was reintroduced to the test columns and permeabilities were again determined.

During the permeability tests, effluent was carried to an automatic fraction collector, which separated the samples obtained from 10 permeameters during specific time increments. The percentage of organic fluid in the effluent samples was determined to develop breakthrough curves. A permeability value, leachate volume, and time increment were obtained on each volume of fluid passed through a sample.

#### 4.5.9.2 Test Results--

ALC: NOT

Baseline permeability (two pore volumes) for the four soils is depicted in Figure 4-5. Permeability data obtained for the various organics tested are presented in Figures 4-6 through 4-13 (Anderson, 1981; Anderson et al., 1981; Brown and Anderson, 1983). Findings as described by the authors are excerpted below:

<u>Acetic Acid (glacial)</u>--All four clay soils permeated with acetic acid showed initial decreases in permeability . . . thought to be due to partial dissolution and subsequent migration of soil particles. These migrating particle fragments could lodge in the fluid-conducting pores, thus decreasing cross-sectional area available for fluid flow.



Source: Anderson, 1981

Figure 4-5. Permeability of the four clay soils to water  $(0.01N CaSo_4)$ .



Source: Anderson, 1981

Figure 4-6. Permeability of the four clay soils to acetic acid.



Source: Anderson, 1981

Figure 4-7. Permeability and breakthrough curves of the four clay soils treated with aniline.



Source: Anderson, 1981

Figure 4-8. Permeability of the four clay soils to ethylene glycol.

4-46



Source: Anderson, 1981.

Figure 4-9. Permeability of the four clay soils to acetone.

CBA 007 0961

4-47



Source: Anderson, 1981

Figure 4-10. Permeability of the four clay soils to methanol and the breakthrough curve for the methanol-treated mixed cation illitic clay soil.



Source: Anderson, 1981




Source: Anderson, 1981



0964

CBA 007



Source: Anderson, 1981

F

Figure 4-13. Permeability and breakthrough curves of the four clay soils treated with heptane.

Two of the soils treated with acetic acid (calcareous smectite and mixed cation kaolinite) showed continuous permeability decreases throughout the test period. After passage of approximately 20 percent of a pore volume, the acid treated kaolinitic clay generated a dark red-colored effluent . . . probably due to dissolution of iron oxides. The acid treated calcareous smectite began passing cream-colored foamy effluent after passage of about 28 percent of a pore volume. . . The creamy material was probably dissolved calcium, while the foam was the result of CO<sub>2</sub> liberation from the dissolved carbonates.

Both noncalcareous smectite and the mixed cation illite eventually showed permeability increases after . . . passage of 39 percent and 62 percent of a pore volume, respectively. . . Permeability increases with both of these soils were probably due to progressive soil piping that eventually cleared initially clogged pores.

Aniline--Both noncalcareous smectite and mixed cation illite had breakthrough of aniline with concurrent permeability increases at pore volume values (below 0.5). . . Aniline broke through after passage of one pore volume for the kaolinitic soil. The calcareous smectite . . . permeability increased rapidly at first, but showed substantial decrease concurrent with aniline breakthrough. After the permeability decrease, this soil exhibited a slow but steady permeability increase. There were no signs of migrating soil particles in any effluent samples. . . Apparently, aniline is too weak a base to cause significant dissolution of clay soil components. However, . . . the organic base caused extensive structural changes in the upper half of the soil cores. The massive structure of the four soils . . . was altered by aniline into an aggregated structure characterized by visible pores and cracks in the surface of the soils.

<u>Ethylene Glycol</u>-- . . . Permeability values indicated that it was the ability of ethylene glycol to alter the soil fabric that was the dominating influence on permeability. Three of the clay soils treated with ethylene glycol showed initial permeability decreases. The kaolinitic clay soil continued to undergo permeability decreases as long as it was being tested. The illitic clay soil began showing a permeability increase after passage of 0.5 pore volumes. In contrast, the calcareous smectite followed its initial permeability decrease with a substantial increase, a second decrease, and finally reached a nearly constant value that continued until the end of the test period.

The noncalcareous smectitic clay soil treated with ethylene glycol showed an initial rapid increase in permeability and a slower but continuous increase after passage of 0.5 pore volume.

<u>Acetone</u>--All soils treated with acetone had initial permeability decreases. These decreases continued until passage of approximately 0.5 pore volume. During passage of the next 0.5 pore volume, however, the soils underwent large permeability increases. One possible explanation for this sequence of permeability changes is as follows:

- 1. The higher dipole moment of acetone caused initial increase in interlayer spacing between adjacent clay particles as compared to water only.
- 2. As more acetone passed through the soil cores, more water layers were removed from clay surfaces. Due to its larger molecular weight, however, fewer acetone layers were adsorbed than had adsorbed when water was the only fluid present. This resulted in a larger effective cross-sectional area available for fluid flow.

While acetone can displace water from clay surfaces due to its higher dipole moment, it cannot form as many adsorbed fluid layers as water due to its higher molecular weight.

Examination of the soil after acetone treatment showed extensive shrinkage and cracking. Such soil shrinkage is usually associated with dehydration, indicating that acetone had extracted water from soil particle surfaces.

Methanol--Unlike soils treated with acetone, methanol-treated soils underwent no initial permeability decrease.

Percent methanol in the effluent from the illitic clay soil paralleled an increase in permeability of the soil. After passage of 1.5 pore volumes, the hydraulic gradient was reduced from 61.1 to 1.85 and another pore volume of methanol passed. After an initial decrease, permeability of the soil steadily increased at the lower hydraulic gradient. . . No particle migration was detected in effluent from methanol-treated cores, and therefore soil piping was discounted as a mechanism for observed permeability increases. Examination of methanol-treated soil cores revealed development of large pores and cracks visible on the soil surface. The lower dielectric constant of methanol may have caused a decrease in interlayer spacing of the clay minerals present in the soils and thereby promoted the structural changes.

<u>Xylene</u>--Xylene-treated soils showed rapid permeability increases followed by nearly constant permeabilities roughly two orders of magnitude greater than their permeabilities to water. Permeability increases may be caused by . . . structural changes in the xylene-treated soils, exemplified by massive structure before treatment and blocky structure after the soils were treated with xylene.

<u>Heptane</u>--Permeability patterns for the heptane cores closely approximated those shown by the xylene-treated cores (i.e., large initial permeability increases). Following these initial large increases, rate of permeability increase slowed until nearly constant permeability values were observed.

Only the calcareous smectitic clay showed . . . permeability to heptane well below its permeability to xylene. The constant permeability values eventually reached by the neutral nonpolar treated cores were probably related to the limited ability of these fluids to penetrate interlayer spaces of the clay minerals.

#### 4.5.9.3 Reintroduction of Water--

When the standard calcium sulfate solution was reintroduced to the noncalcareous smectite test columns permeated with aniline, methanol, and ethylene glycol, a subsequent decrease in the permeability (roughly 1 order of magnitude) was observed. The final permeability (after one pore volume of standard solution) remained well above the baseline permeability measured prior to introduction of the organic solvents (Anderson, 1981).

#### 4.5.9.4 Discussion--

Viscosity and density differences between the organic fluid and water do not account for the large changes in permeability observed in the tests. The data from these permeability tests illustrate the importance of passing multiple pore volumes of fluid through the soil samples in order to determine the effects of solvents on permeability. The work by Anderson has been criticized as being "unrepresentative of real conditions" because pure organic solvents (rather than waste leachate) were used in the permeability tests (Gray and Stoll, 1983). The test results stand, however, as a demonstration of potential effects on clay liners should they come in contact with certain types of undiluted organic liquids.

The high gradients used in the tests have also been questioned (Zoeller, 1982; Gray and Stoll, 1983) since it is unlikely that gradients as high as 361 would be encountered in the field. The use of elevated gradients in laboratory testing in order to reduce testing time is not uncommon. Although the gradients used by Brown and Anderson were higher than those used by most researchers, the permeability changes observed cannot be attributed to the elevated gradients. Conditions were maintained well within the laminar flow regime (i.e., Reynolds number was below 10) so that Darcy's Law for computing the permeabilities remained valid. In general, the trends observed in these tests are consistent with data from other researchers, and explanations can be linked to the findings from clay-chemical complex studies.

Complete saturation in the compaction permeameter without backpressure cannot be ensured. It is possible that air introduced with the permeant fluids could have influenced the test results to some extent, but probably by no more than 1 order of magnitude.

Finally, the use of fixed-wall permeameters for these studies has been criticized (because of the potential for sidewall leakage) by advocates of triaxial test methods. As there are advantages and disadvantages with either method, the argument as to which test is most meaningful is finally a matter of opinion.

Acetic acid, a weak organic acid, has a dissociation constant of  $1.75 \times 10^{-5}$  in aqueous solution (pKa = 4.75) at  $25^{\circ}$ C. Since glacial acetic acid was used, the extent of ionization was a fraction of this. The permeability decreases observed probably would have been followed by sharp increases in permeability due to dissolution of the basic soil components if a dilution had been used rather than glacial acetic acid. Progressive soil piping, as pointed out by Brown and Anderson, follows the soil dissolution and eventually results in large pores with an associated increase in

This effect (i.e., increased permeability) is to be expected with carboxylic acids or sulfonic acids in general. This is of particular significance since carboxylic acids are among the biological degradation products of a wide range of organic compounds. Soils that are high in carbonates are most affected by acids (even weak acids such as acetic acid), but other soil constituents such as  $Fe_2O_3$  are also susceptible.

# 4.5.10 <u>Schramm's Study (1981) of the Permeability of Soil to Organic</u>

Schramm (1981) evaluated permeabilities for eight soils tested with kerosene, isopropyl alcohol, ethylene glycol, and mixed xylenes. Permeability with water was also measured. A total of 211 column tests were run to determine saturated permeabilities to the various test fluids. The research was performed at the University of Arizona. Clay content in the soils ranged from 1 percent in River Bottom sand to 70 percent in Lake Bottom clay. Characteristics of the soils are presented in Table 4-10.

# 4.5.10.1 Test Method--

Permeabilities were obtained in glass or plexiglass cylinders through the falling head method. Cylinders 5.8 cm in diameter were used in the tests with soil packed to a depth of 5 cm. Soil was retained in the cylinders by a galvanized screen glued to the cylinder. Prior to testing, samples were immersed overnight in the test solvent. During the test, the height of the solvent column above the soil surface varied between 6 and 2 cm. Six replicates were tested for every solvent-soil combination. Experiments were varied from 1-1/2 minutes to several weeks. An analysis of variance was performed to evaluate differences between intrinsic permeability for the various soils and solvents.

# 4.5.10.2 Test Results--

A summary of the saturated permeability values (expressed in cm/h) obtained from these tests is given in Table 4-11. It is notable that with each soil tested the highest permeabilities were obtained with the non-polar organics, kerosene, and xylene. (Kerosene is a mixture of  $C_{12}$ - $C_{18}$  compounds and includes both alignatics and aromatics.)

Intrinsic permeabilities were also calculated to take into account differences in viscosity and density for the various permeant fluids. Analysis of the intrinsic permeability values included a one-way variance test to determine if the intrinsic permeability varies significantly with solvents or with soils. The intrinsic permeabilities for a given soil are expected to be constant unless there is interaction between the soil and the permeating liquid. The differences in intrinsic permeability with the different solvents are shown in Figure 4-14 for five soils. The trend for increased intrinsic permeability is readily apparent.

The analysis also shows rather uniform behavior of intrinsic permeability for solvents in the different soil types, the Fanno, Mohave, and River Bottom Sand having highest relative intrinsic permeabilities with all organic solvents.

From the data summary and analysis of variance, Schramm (1981) concluded that:

Calculated values of intrinsic permeability vary for the same soil depending on solvent. However, the variation is relatively minor compared to variation due to differences in soil properties among several soils...

Since intrinsic permeability values vary for the same soil depending on solvent, the soil and solvents are interacting.

| Soil name         | Soil<br>order | C1 ay<br>% | Silt<br>% | Sand<br>% | Soil<br>paste<br>pH | Cation<br>exchange<br>capacity<br>(meq/100 g) | Electrical<br>conductivity<br>of saturated<br>extract<br>( <sup>e</sup> mho/cm) | Column<br>bulk<br>density<br>(g/cm <sup>3</sup> ) | Soil<br>surface<br>area<br>(m <sup>2</sup> /g) | Predominant<br>clay<br>minerals |
|-------------------|---------------|------------|-----------|-----------|---------------------|---|---|---|--|---------------------------------|
| Lake Bottom clay  | Entisol       | 70.6       | 24.0      | 5.4       | 7.7                 | 34.7  | 1,111   | 1.52  | 142.0  | Illite<br>Kaolinite             |
| Nicholson         | Alfisol       | 49.0       | 47.0      | 3.0       | 6.7                 | 37.0  | 176   | 1.53  | 120.5  | Vermiculite                     |
| Fanno             | Alfisol       | 46.0       | 19.0      | 35.0      | 7.0                 | 33.0  | 392   | 1.48  | 122.1  | Montmorillonite<br>Mica         |
| Chalmers          | Mollisol      | 31.0       | 52.0      | 14.0      | 6.6                 | 22.0  | 288   | 1.53  | 95.6   | Montmorillonite<br>Vermiculite  |
| Canelo            | Alfisol       | 28.0       | 28.6      | 43.4      | 5.6~                | 5.76  | 240   | 1.72  | 35.0   |                                 |
| Anthony           | Entisol.      | 15.0       | 14.0      | 71.0      | 7.8                 | 10.0  | 328   | 1.87  | 49.8   | Montmorillonite<br>Mica         |
| Mohave            | Aridisol      | 11.1       | 37.0      | 52.0      | 7.3                 | 10.0  | 615   | 1.78  | 38.3   | Mica<br>Kaolinite               |
| River Bottom sand | Entisol       | 1.0        | 2.0       | 97.0      | 7.2                 | 2.0   | 210   | 1.80  | 3.6  | Kaolinite<br>Mica               |

# TABLE 4-10. CHARACTERISTICS OF SOILS USED IN PERMEABILITY TESTS<sup>a</sup>

<sup>a</sup>Adapted from Schramm (1981).

|   | , | • |
|---|---|---|
| - |   |   |

|                   |                        |                        | Solvent                |                        |                        |
|-------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Soi 1             | Water                  | Kerosene               | Isopropyl<br>alcohol   | Ethylene<br>glycol     | Xylene                 |
| Lake Bottom clay  | 5.0 x $10^{-5}$        | 3.4 x 10 <sup>-4</sup> | $2.1 \times 10^{-4}$   | $1.1 \times 10^{-5}$   | 1.7 x 1(1-3            |
| Nicholson         | 4.2 x 10 <sup>-6</sup> | 9.5 x 10-5             | 2.3 x 10 <sup>-5</sup> | 6.8 x 10 <sup>-7</sup> | $3.5 \times 10^{-4}$   |
| Fanno             | $1.5 \times 10^{-4}$   | 5.2 x 10 <sup>-3</sup> | $3.1 \times 10^{-3}$   | $3.0 \times 10^{-4}$   | 1.8 x 10-2             |
| Chalmers          | 1.8 x 10-5             | 3.8 x 10 <sup>-5</sup> | 2.3 x 10 <sup>-5</sup> | 1.8 x 10-6             | $1.7 \times 10^{-4}$   |
| Canelo            | 5.0 x 10-6             | 5.6 x 10 <sup>-5</sup> | 3.5 x 10 <sup>-5</sup> | $1.4 \times 10^{-6}$   | $1.5 \times 10^{-4}$   |
| Anthony           | 9.9 x 10-5             | 2.0 x $10^{-4}$        | 9.5 x $10^{-5}$        | 5.8 x 10-6             | 4.4 x 10 <sup>-4</sup> |
| Mohave            | 1.9 x 10-3             | 2.6 x $10^{-3}$        | $1.6 \times 10^{-3}$   | 2.0 x $10^{-4}$        | 8.5 x 10-3             |
| River Bottom sand | 1.7 x 10 <sup>-2</sup> | 3.4 x 10 <sup>-2</sup> | 5.8 x 10-3             | 6.4 x $10^{-4}$        | 1.8 x 10 <sup>-2</sup> |

TABLE 4-11. PERMEABILITY COEFFICIENTS (cm/s) DETERMINED IN SOILS TESTED WITH ORGANIC SOLVENTS<sup>a</sup>

<sup>a</sup>Data from Schramm (1981).

4-57



Source: Schramm, 1981

Figure 4-14. Variation of intrinsic permeability with solvent for each soil.

Shield a

#### 4.5.10.3 Discussion--

The test method used by Schramm differed significantly from that employed by Anderson (1981) to measure permeability. Notable differences include the following:

- Gradients imposed on the sample were very low.
- No estimate was made of the pore volumes passed through the test samples.
- Samples were presaturated with the test fluid rather than a standard calcium-sulfate solution.

The impact of the low hydraulic gradient on the test results is not known. The concept of "threshold gradient" has been postulated, although there is no evidence of this effect in the results reported by Schramm.

Although Schramm reports that tests were continued until constant permeability values were obtained, the criterion to establish an acceptable difference in consecutive measurements was not discussed. There is no indication of the number of pore volumes exchanged.

It may be argued that saturating the samples using the test permeant fluid rather than water or a standard permeant solution is representative of conditions typical for a liner in service in a land disposal application.

# 4.5.11 <u>Evaluation by Monserrate (1982) of the Permeability of Two Clays</u> to Selected Electroplating Wastes

Monserrate (1982) at Duke University investigated the permeability of two clays exposed to simulated electroplating wastes. The purpose of the research was to examine the effect of compaction on the permeability response of the two clays. The clays tested were a Wyoming bentonite and a White Store clay from North Carolina. The White Store clay was reported to be an active clay.

The simulated electroplating wastes used as permeant fluids were a 1-molar solution of zinc chloride (ZnCl<sub>2</sub>) (136.3 g/L, pH = 5.5) and a 1-molar solution of chromic acid ( $H_2CrO_4$ ) (100 g/L, pH = 1.5).

4.5.11.1 Test Method--

Standard Proctor tests were conducted on each clay to establish the relationship between water content and compacted density. Procedures outlined in ASTM D-698 Method A (ASTM 1985) were followed. Permeability studies were subsequently conducted at several different moisture contents.

For the permeability tests, the samples were prepared by mixing 0.01 N calcium sulfate with the clay to achieve the desired moisture content. The clays were compacted into either zinc-plated or lucite compaction permeameters using compactive efforts comparable to those used in the standard Procter tests. The compaction permeameters measure 4 inches (10.16 cm) in diameter and 4.6 inches (11.68 cm) in height. Clays were compacted to a depth of 2 inches (5.08 cm). The compaction permeameters were adapted to

allow measurement of flow as the permeant fluid enters the unit. The data were evaluated as a falling head test. A standard solution of deaired 0.01 N calcium sulfate was used to saturate the sample prior to introducing the test permeant fluids. The samples were exposed to the permeant fluids under approximately 75 pounds of air pressure. In the permeability tests, a statistical procedure was used to determine when enough data had been accumulated to make a determination of the k value for a certain claypermeant fluid combination. (See details in Section 4.3).

#### 4.5.11.2 Test Results--

Tests with bentonite showed that at moisture contents in the proximity of the optimal compacted moisture content, permeabilities to calcium sulfate, chromic acid, and zinc chloride were all on the order of  $10^{-10}$ cm/s. At lower moisture contents, the permeability to calcium sulfate was higher by a factor of 2 than the permeability to the chromic acid test solution. At wet-of-optimum water contents, however, the permeabilities determined for the two fluids were nearly identical. The same low water content divergence in permeability was observed for the zinc chloride test fluid, although the magnitude of the difference was less.

The permeability of White Store clay to standard calcium sulfate solution and to the test fluids is shown in Figure 4-15 as a function of the moisture content at compaction. The White Store clay appeared to be more sensitive than the bentonite clay to changes in compacted moisture content. The permeability to the chromic acid test fluid aligns closely with that of calcium sulfate at moisture contents higher than about 20 percent (optimum moisture content = 21.5 percent). At lower than about 20 percent moisture, the permeability to the chromic acid was higher than to calcium sulfate. Zinc chloride test fluid showed permeabilities lower than for calcium sulfate at low moisture.

Monserrate (1982) concluded that for both bentonite and White Store clays, the application of zinc chloride and chromic acid did not alter the clay's permeability response, indicating that the structure of the clay, as compacted, is the predominant influence in determining permeability. She noted that the test results differed markedly from those of Coia (1981) who carried out similar studies at Duke University using the chromic acid.

Monserrate noted that there was extensive corrosion of the steel permeameters and some of the pressure fittings that were exposed to the chromic acid test fluid.

#### 4.5.12 <u>Research by Brown, Green, and Thomas (1983) on the Effect of Two</u> <u>Organic Hazardous Wastes on Simulated Clay Liners</u>

Brown, Green, and Thomas (1983) at Texas A & M University reported results of permeability tests in which clay soil samples representative of three types of simulated clay liners were subjected to a xylene waste and an acetone waste in both laboratory and field studies. The three clay materials tested were predominantly kaolinite, mica, or bentonite. The soils were blended with sandy loam soil to attain permeabilities in the range of  $1 \times 10^{-7}$  to  $1 \times 10^{-8}$ . The laboratory studies in fixed-wall permeameters

March Land Strate of State

3.6 × 10<sup>-7</sup> -II<sub>2</sub>Cr0 CaSO 3.0 × 10<sup>-7</sup> Permeability (cm/s) 2.4 × 10<sup>-7</sup> ĸ 2nCl **H** 1.8 × 10<sup>-7</sup> 1.2 × 10<sup>-7</sup> В 6.0 × 10<sup>-8</sup> 20 20. 1.00 80 82. 24 14 . . 10 12 **Moisture Content at Compaction (%)** 

Source: Monseratte, 1982

Figure 4-15. Permeability of White Store clay to 0.01 N calcium sulfate, chromic acid (1 molar), and zinc chloride (1 molar) as a function of moisture at compaction.

4-61

were directed at determining the influence of different initial moisture contents and elevated gradients on the clay permeabilities. The procedures used in the laboratory tests were similar to those described by Anderson (1981) and Brown and Anderson (1983) in earlier permeability tests with organics. The research was sponsored by the U.S. EPA.

The xylene waste, a paint solvent that was used to clean factory sprayer lines, contained 25 percent paint pigments and trace amounts of water. The acetone waste was a chemical manufacturing waste containing 91.7 percent acetone, 4 percent benzene, 0.6 percent phenol, and 3.7 percent unknown.

#### 4.5.12.1 Test Methods--

For the laboratory tests, soils were compacted wet of optimum to at least 90 percent Proctor density. Prior to exposure to the waste solvents, samples were saturated with 0.01 N calcium sulfate. Unsaturated cores were also subjected to the permeability tests. Pressures of 5, 15, and 30 psi (equivalent to hydraulic heads of 31, 91, and 181) were tested.

Twenty-eight field cells (1.5 m x 1.5 m x 1.8 m inside dimensions) were constructed of reinforced concrete and lined with 100-mil high-density polyethylene to facilitate leachate collection. The clay soils were compacted with a vibratory compactor to 95 percent Proctor in two 7.5-cm-thick lifts. The liquid waste to be tested was introduced into each cell through a standpipe into barrels that were placed above the liners. A head of 1 m of liquid (gradient of 7) was maintained throughout the test. Permeabilities were calculated based on the volume of cell drainage collected during discrete time intervals. Following the permeability tests, each cell was disassembled and subjected to chemical and morphological analysis. The wastes to be tested in the field cells were dyed with Automate Red B and Fluorescent Yellow to facilitate detection within the sample cores.

4.5.12.2 Laboratory Test Results--

To compare the results from the various tests, calculated permeabilities were plotted as a function of the number of pore volumes of effluent that passed through the sample. Permeabilities to standard calcium sulfate solution on similar soils in the laboratory were generally found to be reproducible to within 0.25 order of magnitude. Permeabilities increased, however, when the organic-solvent wastes were substituted as the permeant fluids. Permeability to the organic-solvent wastes was typically 2 to 4 orders of magnitude greater than the permeabilities measured with the calcium sulfate solution. Presaturation with 0.01 N calcium sulfate appeared to retard the effect of the permeant fluids on the samples (i.e., more pore volumes were displaced before breakthrough occurred in the presaturated samples). Highest permeabilities measured on initially unsaturated samples were typically 1 to 2 orders of magnitude greater than for samples that were initially saturated.

Permeability of the clay soils increased rapidly upon exposure to xylene waste after the cumulative flow exceeded 0.2 to 0.4 pore volume. The behavior of acetone was characterized by an initial small decrease in permeability (minimum at approximately 0.5 pore volume), which was followed by a steady increase in permeability. This behavior was explained as follows: acetone first caused swelling of the clay soil with low concentrations initially diffusing into the pores; as more of the water was displaced by the solvent, shrinkage occurred.

Similar increases in permeability were observed for all three soil types. The increase in permeability, however, for the bentonite samples occurred after a larger pore volume was displaced.

If the permeability values calculated from the test data are plotted as a function of pore volumes, the different hydraulic gradients used in the experiments (31, 91, 181) have little influence on either the increase in permeabilities observed or on the final values achieved. (This conclusion holds for both presaturated and unsaturated samples [Brown et al., 1984]).

# 4.5.12.3 Field Test Results--

In the field studies, xylene had penetrated 10 of the 12 clay liners within 12 months after installation; acetone had penetrated 2 of the liners but at a slower rate. Increases in permeability of the bentonite clay soil to xylene were more dramatic (as much as 2 orders of magnitude increase) than of the other soils and occurred after passage of 0.5 pore volume of permeant fluid. Kaolinitic and micaceous soils showed immediate increases in permeability to xylene. Permeability values continued to increase as more pore volumes of fluid passed through the sample. Increases of more than 2 orders of magnitude were observed in some samples after passage of two pore volumes of xylene.

Field tests with the acetone waste exposed to micaceous clay soil showed a permeability decrease with the first 0.5 pore volume. This was followed, however, by an increase in permeability. After two pore volumes had passed through the liner, the permeability was slightly higher than the initial value measured.

Visual inspection of the clay liners following permeation by the liquid wastes was facilitated by the dyes and by the paint pigment in the xylene waste. Dyed surfaces observed throughout the liner indicated that the liquid had moved through the soil through preferential channels rather than in a clearly defined wetting front. Preferential channels were occasionally found to extend from the top to the bottom of the liner. Evidence that xylene moved through cracks in the liner or around blocky subangular structural components was also obtained through chemical analysis of sections of the permeated liners. The channels observed in the clays are attributed to the displacement of water by the chemicals resulting in desiccation that caused the clay to shrink and crack.

# 4.5.12.4 Discussion--

The results of this study, in close agreement with those previously found by Brown and Anderson (1983), indicate that severe permeability increases can occur when certain clay materials are in contact with concentrated organic solvents. Although the hydraulic heads used in the laboratory test procedures are higher than are likely to be encountered in the field, the data suggest that the permeabilities measured are independent of the hydraulic gradient used in the test. These results further support the conclusions by Anderson based on tests involving a gradient of 361. The effect of presaturation with calcium sulfate on the highest permeabilities is significant. Laboratory tests by other researchers (Green et al., 1979; Foreman and Daniel, 1984) have also involved introducing the test permeant fluid onto the unsaturated sample.

# 4.5.13 <u>Study by Brown, Thomas, and Green (1984) of the Effect of Dilutions</u> of Acetone and Mixtures of Xylene and Acetone on Permeability of a Micaceous Soil

To determine the effect of diluting a polar organic solvent with water, Brown, Thomas, and Green (1984) measured the permeability of an unsaturated micaceous compacted soil to several acetone-water dilutions. Samples were tested at a gradient of 91 in laboratory tests with fixed-wall permeameters. Solutions tested were 100, 75, 50, 25, 12.5, and 2 percent acetone. Methods were similar to those used previously by Anderson (1981).

Compared to permeability to water (actually 0.01 N calcium sulfate), an increase in permeability was seen for solutions where the concentration of acetone was 75 percent or 100 percent. Samples permeated with lower concentrations of acetone did not show appreciable changes compared to the permeability to water.

Similar tests were conducted to determine the effect on permeability of mixtures of xylene and acetone (Brown et al., 1984). For 100 percent xylene, the permeability was reported to be 4 orders of magnitude greater than the permeability to water (0.01 N calcium sulfate). When a mixture of 87.5 percent xylene and 12.5 percent acetone was tested, the permeability was dramatically reduced (i.e., more than 3 orders of magnitude below the permeability to pure xylene). Values were comparable for a mixture containing 25 percent acetone and 75 percent xylene and for a 1:1 mixture. When the acetone component was increased to 75 percent, however, the permeability increased to approximately the value obtained in similar tests with pure acetone. This value was about 1.5 orders of magnitude greater than the permeability of the sample to 0.01 N calcium sulfate.

# 4.5.14 Tests by Brown, Thomas, and Green (1984) to Determine the Permeability of Micaceous Soil to Petroleum Products

Brown, Thomas, and Green (1984) also reported permeability tests with five commercial petroleum products. A compacted micaceous soil, unsaturated, was permeated with the test fluids at a gradient of 91. The results of the tests with kerosene, diesel fuel, paraffin oil, gasoline, and motor oil are shown in Figures 4-16 through 4-20, respectively. Conclusions of the tests show that the micaceous soil is more permeable to these petroleum products than to water (0.01 N calcium sulfate).

In tests with kerosene, the permeabilities were 3 to 4 orders of magnitude higher than values measured with 0.01 N calcium sulfate in similar samples. One-half the difference was achieved within the first 0.1 pore volume. The permeability to paraffin oil was about 1 order of magnitude greater than the comparable value to the calcium sulfate solution despite its high viscosity. Maximum values were achieved by the passage of one pore volume.



Figure 4-16. Hydraulic conductivity versus pore volume for laboratory compacted micaceous soil exposed to kerosene at a hydraulic gradient of 91.



Figure 4-17. Hydraulic conductivity versus pore volume for laboratory compacted micaceous soil exposed to diesel fuel at a hydraulic gradient of 91.

CBA 007 0980







Figure 4-19. Hydraulic conductivity versus pore volume for laboratory compacted micaceous soil exposed to gasoline at a hydraulic gradient of 91.



Figure 4-20. Hydraulic conductivity versus pore volume for laboratory compacted micaceous soil exposed to motor oil at a hydraulic gradient of 91.

Test data obtained with diesel fuel were variable and did not appear to increase along the patterns of most organics tested. No explanation is offered for the unpredicted behavior. Values were, however, greater by 1 to 2 orders of magnitude than permeability to water. This was also the case for gasoline. The test with motor oil showed a steady increase in permeability from 2 x  $10^{-7}$  cm/s at 0.5 pore volume to  $1.5 \times 10^{-6}$  cm/s at 3 pore volumes.

4.5.14.1 Discussion--

The data obtained in tests with the commercial petroleum products illustrate the importance of extended permeability tests to allow passage of several pore volumes of fluid. Earlier data indicate that the effects of organic permeant fluids are retarded in tests where the samples are presaturated with water (or 0.01 N calcium sulfate). The tests on unsaturated samples may serve as better estimators of maximum permeabilities that may result when clay liners are exposed to petroleum products.

# 4.5.15 <u>Study by Brown and Thomas (1984) of the Permeability of</u> Commercially Available Clays to Organics

To determine the effect of organic fluids on currently available clays that are sold for sealing and lining impoundments, Brown and Thomas (1984) tested permeabilities of three commercially available clays admixed with sand.

#### 4.5.15.1 Test Method--

Each clay was mixed with sand to obtain a permeability to water of about  $1 \times 10^{-8}$  cm/s. Smectite is the dominant mineral in soil CC1 (blue bentonite) and soil CC2 (a synthetically treated bentonite); a micaceous mineral is dominant in soil CC3 (Ranger Yellow). The soils were compacted at optimum moisture in 10-cm fixed-wall molds using a mechanical compactor as described in ASTM Procedure 698-70.

The compacted soils were exposed to the test fluid without presaturation. Following a 24-hour equilibrium period, a pressure of 15 psi (equivalent to a hydraulic gradient of 91) was applied to the liquid surface. Leachate passed through the samples was collected at intervals to allow calculation of the soil permeability. Fluids tested in replicate were water (0.01 N calcium sulfate), acetone, xylene, kerosene, diesel fuel, gasoline, and used motor oil. A statistical analysis was performed to establish the variance among the data set for each permeant fluid. Means were separated using a Duncan's Multiple Range test at a significance level of P = 0.05.

#### 4.5.15.2 Test Results--

The test results for all permeant fluids are summarized in Table 4-12. All of the organic fluids tested produced dramatic increases over the corresponding permeabilities to water, the increase ranging from 1 to 5 orders of magnitude. Some of the increases, though large, were not statistically significant compared to the permeabilities measured with water due to the large variability seen in the tests. The increases in permeability were significant for all clays permeated with xylene and for both the smectitic clays when permeated by gasoline and kerosene.

| Fluid       | CC1                                    | CC2                        | CC3                       |  |
|-------------|--|----------------------------|---------------------------|--|
| Water       | 3.61 x 10 <sup>-8</sup> b <sup>a</sup> | 2.58 x 10 <sup>-8</sup> b  | 1.57 x 10 <sup>-8</sup> b |  |
| Acetone     | 5.05 x 10 <sup>-5</sup> b              | 1.41 x 10 <sup>-6</sup> b  | 2.51 x 10 <sup>-7</sup> b |  |
| Xylene      | 1.76 x 10 <sup>-4</sup> a              | 7.28 x $10^{-4}$ a         | 1.00 x 10 <sup>-4</sup> a |  |
| Gasoline    | 1.96 x 10 <sup>-4</sup> a              | 9.07 x 10 <sup>-5</sup> a  | 6.19 x 10 <sup>-5</sup> b |  |
| Kerosene    | 1.49 x 10 <sup>-4</sup> a              | 9.10 x 10 <sup>-5</sup> a  | 5.68 x 10 <sup>-5</sup> b |  |
| Diesel fuel | 5.17 x 10 <sup>-5</sup> b              | 4.53 x 10 <sup>-5</sup> ab | 6.29 x 10 <sup>-7</sup> b |  |
| Motor of1   | 6.13 x 10 <sup>-6</sup> b              | 2.13 x 10 <sup>-6</sup> b  | 9.48 x 10 <sup>-7</sup> b |  |

TABLE 4-12.MEAN CONDUCTIVITY OF EACH SOIL TO EACH FLUID TESTED<br/>(Brown and Thomas, 1984)

<sup>a</sup>Values in a given column followed by the same letter do not differ significantly (P = 0.05).

Generally the increase in the micaceous clay permeability was less by 1 order of magnitude than the increases seen in the smectitic clays. The untreated bentonite (CC1) showed the greatest permeability increase in response to each organic test fluid. Since the untreated bentonite is the soil that is most subject to shrinkage and the micaceous soil is least subject to shrinkage, these findings are consistent with the theory that shrinkage resulting in greater spacing between peds is responsible for the changes in soil permeability.

### 4.5.16 <u>Studies Conducted for EPA by Daniel (1983) and Foreman and Daniel</u> (1984) at the University of Texas, Austin

Under a cooperative agreement with EPA, Daniel and others have carried out research to address how the permeability of clay soils is affected by hydraulic gradient and by the test device when the permeant fluid is other than water. Permeability tests were performed using three different types of test devices--flexible-wall cells, fixed-wall compaction mold permeameters, and consolidation cell permeameters--at hydraulic gradients of 10, 50, 100, and 300. The three soils studied were a noncalcareous smectite (Lufkin clay), a mixed-cation illite (from Hoytville, Ohio), and a commercially processed kaolinite (Hydrite R). Fluids tested were water (actually 0.01 N calcium sulfate), methanol, and heptane (Foreman and Daniel, 1984).

#### 4.5.16.1 Test Method--

Most of the tests for the project were flexible-wall tests. The fixedwall and consolidometer tests were performed to allow comparison of the data from the different devices. Soil samples were compacted at or slightly dry of optimum moisture content according to ASTM D-698. Soils were scarified between each lift. Samples to be tested in flexible-wall cells were extruded from the 10.2-cm (4-inch) -diameter compaction mold and trimmed to a height of 9.4 cm (3.7 inches). Similar diameter samples with a height of 11.9 cm (4.7 inches) were tested in the fixed-wall permeameter setup. Samples tested in the consolidation cell were taken from the central portion of a compacted 10.2-cm (4-inch) sample. The sample was trimmed to a height of 1.90 cm (0.75 inch) and a diameter of 6.4 cm (2.5 inches).

Prior to the permeability measurements, the soil samples were saturated with the permeant fluid to be tested. For the flexible-wall tests great care was taken to completely saturate the samples. This was accomplished through soaking under vacuum and backpressuring. During the permeability tests, the backpressure was kept at about 2.8 kg/cm<sup>2</sup> (40 psi) and the cell pressure at 3.87 kg/cm<sup>2</sup> (55 psi). The average effective stress was 1.05 kg/cm<sup>2</sup> (15 psi) for tests at the lower hydraulic gradients; an average effective stress of 1.76 kg/cm<sup>2</sup> (25 psi) was used when the gradient was 300.

#### 4.5.16.2 Test Results--

Test results with Lufkin clay in the flexible-wall cells showed essentially no change in permeability with time when methanol was used as the permeant fluid. Data were obtained for passage of about 0.9 pore volume. The permeability to methanol was virtually the same as with 0.01 N calcium sulfate (Daniel, 1983).

Methanol test results with the kaolinite show that when permeability is plotted as a function of pore volumes of flow, the curves have similar shapes for the three types of permeameters. The compaction mold yields somewhat higher permeability results than the other two test devices. Test data are shown in Figure 4-21.

Permeability values for the kaolinite at different hydraulic gradients were obtained with water and with methanol in the different test devices. The following conclusions were drawn:

- At high hydraulic gradients (values of 150 or larger), kaolinite has a higher conductivity to methanol than to water regardless of permeameter type.
- At high hydraulic gradients, the flexible-wall and consolidationcell permeameters yield similar hydraulic conductivities for both methanol and water; kaolinite is roughly twice as permeable to methanol as to water for these two types of permeameters.
- At high gradients, use of compaction-mold permeameters leads to large sdatter in measured hydraulic conductivity. On the average, compaction-mold devices showed kaolinite to be approximately 10 times more permeable to methanol than to water. The lowest values of K measured with the compaction-mold devices are nearly identical to values measured with the other two devices. It is possible that sidewall leakage contributed to the causes . . .
- With flexible-wall permeameters and two liquids and one soil, hydraulic gradient appears to have little effect on hydraulic conductivity . . .
- With consolidation-cell permeameters, hydraulic gradient has a very substantial effect on hydraulic conductivity. At a hydraulic gradient of 50, K to methanol is only half of K to water, but at gradients of 200 to 300, K to methanol is twice as large as K to water . . . .

Figures 4-22, 4-23, and 4-24 show the effect of hydraulic gradient on tests with kaolinite in flexible-wall cells, consolidation cells, and fixedwall permeameters, respectively. The scatter in the fixed-wall permeameter data does not allow conclusions to be drawn although there appears to be a trend to increased permeability with increased gradient.

4.5.17 <u>Tests Conducted for Chemical Manufacturers Association by Daniel</u> <u>and Liljestrand (1984)</u>

In work sponsored by the Chemical Manufacturers Association (CMA), Daniel and Liljestrand at the University of Texas at Austin carried out a laboratory study of the permeability of five clay soils to six aqueous fluids representative of waste leachates or actual liquid wastes. The purpose of the testing was to determine if dilute organic/water mixtures produced the increases in permeability demonstrated by other researchers using concentrated organic liquids as permeant fluids.



Figure 4-21. Permeability versus number of pore volumes of flow for kaolinite permeated with methanol at a hydraulic gradient of 250 or 300.



Figure 4-22. Permeability versus hydraulic gradient for kaolinite permeated in flexible wall permeameters.



Figure 4-23. Permeability versus hydraulic gradient for kaolinite permeated in consolidation cell permeameters.





The soils studied included Texas Lufkin clay (also used in tests at Texas A&M) and four soils supplied by CMA (identified as S1, S2, S3, and S4) from actual landfill sites. Properties of the clays are listed in Table 4-13. Permeability tests were not performed on the S1 clay since its index properties and mineralogy were similar to those of the S2 clay.

Permeant liquids used in the tests were: a leachate from a solid-waste landfill (L2); two liquids (L1 and L3) from industrial waste impoundments; an aqueous solution containing methanol at 5 percent (50,000 ppm); an aqueous solution saturated with xylene (near 196 ppm); and the leachate, L1, spiked with chloroform (200 ppm) and trichloroethylene (200 ppm) to simulate a landfill leachate contaminated with chlorinated hydrocarbons. Water used to prepare the dilute methanol and xylene solutions was actually 0.01 N calcium sulfate. Characteristics of the leachates L1, L2, and L3 are listed in Table 4-14.

#### 4.5.17.1 Test Method--

Permeability tests were carried out as described previously in Section 4.5.16. All testing was performed using flexible-wall permeameters and hydraulic gradients of 150 or 200. Rates of flow were determined from the rate of inflow for each test chamber.

#### 4.5.17.2 Test Results--

The permeability tests were performed for several months, allowing the passage of more than one pore volume of fluid for most soil/leachate combinations. The permeabilities of the soils S2, S3, S4, and Lufkin clay appear to be related to the plasticity index, the permeability decreasing with increasing plasticity. For any one soil, the permeabilities to the various liquids were all about the same. Permeabilities to the leachates did not differ significantly from the permeability to water (actually 0.01 N calcium sulfate). All permeabilities measured were 1 x  $10^{-8}$  cm/s or lower. In three of the four soils tested, the permeability to 196 ppm xylene was slightly lower than the permeability to the 5 percent methanol. All permeabilities were plotted as a function of pore volumes of fluid passed through the sample.

In addition to the permeability tests, Atterberg limits of the soils were determined using the various test fluids and pure xylene and methanol in place of water. Test fluids L1, L2, L3, and spiked L1 did not significantly alter the plasticity of any of the clay soils during the short-term exposure of the test. Mixing any of the five soils with pure xylene or pure methanol, however, caused a drop in the liquid limit and destruction of the soil's tendency to be plastic. The dilute solutions of methanol and xylene (as used in the permeability tests) had much less significant effects on the plasticity. Only the soil S3 showed a large drop in plasticity when mixed with the 5-percent methanol or the aqueous solution containing 196 ppm xylene.

The significance of Daniel and Liljestrand's findings is that they appear to show that <u>dilute</u> organic/water mixtures are not capable of causing significant changes in the permeability of natural clay liners.

|   |          | •••••••••••••••••••••••••••••••••••••• | · · ·     |                      | · · · · · · · · · · · · · · · · · · · |
|---|----------|--|-----------|----------------------|---------------------------------------|
| Property                                    | S1       | S2                                     | S3        | S4                   | Lufkin clay                           |
| Natural water content (%)                   | 23       | 22                                     | 47        | 32                   | 23                                    |
| Optimum water content (%)                   | 17       | 24                                     | 31        | 18                   | 21                                    |
| Specific gravity                            | 2.73     | 2.81                                   | 2.71      | 2.71                 | 2.66                                  |
| Percent finer than #200 sieve               | 93       | 93                                     | 94        | 87                   | 81                                    |
| Percent sand                                | 7        | 7                                      | 6         | 13                   | 19                                    |
| Dominant minerals                           | Illite   | Chlorite                               | Smectite  | Quartz               | Smectite                              |
| Secondary minerals                          | Chlorite | Smectite,<br>kaolinite                 | Kaolinite | Illite,<br>kaolinite | Kaolinite,<br>illite                  |
| Organic carbon content<br>(% of dry weight) | 1.46     | 0.83                                   | 1.39      | 1.79                 | 0.28                                  |
| Cation exchange capacity<br>(meq/100 g)     | 10       | 20                                     | 40        | 5                    | 25                                    |
| Plasticity index                            | 21       | 32                                     | 59        | 16                   | 42                                    |

TABLE 4-13. PROPERTIES OF CLAY SOILS TESTED BY DANIELS AND LILJESTRAND (1984)

|  | Leachates                         |       |   |  |  |
|--|-----------------------------------|-------|---|--|--|
| or reported  | L1                                | L2    | L3  |  |  |
| Suspended solids (mg/L)  | 465                               | 162   | ` 107   |  |  |
| Dissolved solids (mg/L)  | 20,202                            | 1,043 | 4,593   |  |  |
| Volatile solids (mg/L)   | 5,768                             | 121   | 1,052   |  |  |
| Total organic carbon (TOC)<br>(mg/L)   | 1,440                             | 13    | 82<br>120                                       |  |  |
| Chemical oxygen demand (COD)<br>(mg/L)   | 2,160                             | 12    | 130   |  |  |
| Potential (ORP) (mV)   | 398                               | 268   | 496   |  |  |
| рН   | 6.9                               | 7.1   | 1.5   |  |  |
| Conductivity (µmho/cm)   | 23,700                            | 865   | 4,620   |  |  |
| Metals (mg/L)<br>Cr<br>Cu<br>Pb<br>Ni<br>Zn  | 1.0<br>5.3<br>0.36<br>0.18<br>6.0 | b     | Ъ.  |  |  |
| Organics (mg/L)<br>Ethylbenzene<br>Toluene<br>Nitrotoluene<br>Dinitrotoluene<br>Formaldehyde<br>Dichlorobenzene<br>Aniline<br>Toluenediamine | b                                 | b     | 0.120<br>0.035<br>8<br>117<br>14<br>8<br>4<br>2 |  |  |

# TABLE 4-14. LEACHATE CHARACTERISTICS<sup>a</sup>

<sup>a</sup>Data from Daniel and Liljestrand, 1984. <sup>b</sup>Not reported.

# 4.5.18 <u>Study by Dunn (1983) of the Effects of Synthetic Lead-Zinc Tailings</u> <u>Leachate on Clay Soils</u>

Dunn (1983) evaluated the effects of a synthetic lead-zinc tailings leachate, of low pH and containing large concentrations of heavy metals, on the permeability of two clay soils. The permeability of the clays was shown to be affected by the waste permeant, with cation exchange and precipitation apparently being the most important processes.

The soils used in the testing, Altamont soil and Rockville soil, had been identified as potential liner construction materials. Altamont soil, a "valley alluvium" with moderate plasticity, is a silty clay soil with 1 or 2 percent shale fragments. Montmorillonite is the predominant clay mineral in Altamont soil. Rockville soil, a yellow-brown silty clay with high plasticity, is composed of the fine fraction from a sand and gravel plant. The predominant clay mineral is kaolin. This soil probably contained microorganisms since some evidence of bacterial growth was noted in soil that was stored for several months.

The permeant fluids tested were tap water, distilled water, and the synthetic lead-zinc tailings leachate. Characteristics of this fluid were:

- Conductivity 1,550 µmho/cm
- pH = 2.6
- Lead = 5.8-15.0 mg/L
- Zinc = 200 mg/L.

The leachate was prepared with zinc sulfate, lead sulfate, and lead nitrate. Sulfuric acid was used to attain the desired pH.

Two tests with each clay were conducted with the synthetic leachate. Permeabilities obtained with the test fluid were compared to the results of samples tested with tap water and with distilled water. All the tests were run at a compacted dry density of about 90 percent of maximum dry density and at a water content approximately 1 to 2 percent above optimum. Tap water was used for the molding water. Soil samples were prepared with static compaction since this method was found to be most appropriate for producing replicate samples at approximately the same dry density and water content. The static compaction involves compressing the soil to a known density with applied hydraulic pressure.

Tests were performed in a triaxial cell at a hydraulic gradient of 50. Samples tested were 3.81 cm (1.5 inches) in diameter and 2.54 cm (1 inch) thick. The samples were presaturated (using a backpressure technique) with the fluid to be tested. Prior to permeability testing, the samples were consolidated at 1.5 kg/cm<sup>2</sup> (21.3 psi) effective stress. Permeability measurements were carried out at an effective stress of 1.25 kg/cm<sup>2</sup> (17.8 psi).

The permeability values measured in both soils exposed to the synthetic leachate were higher than those measured with tap water. Values measured with distilled water were lower than permeabilities measured with tap water. The ultimate effect of the synthetic leachate on the permeability to either soil could not be determined from the tests, however, because the permeability values did not reach steady state during the duration of the test (5,000 minutes or 3.5 days). The tests with tap water did appear to reach steady state during this test time.

For one Altamont sample, the measured permeability to the synthetic leachate was approximately 2 orders of magnitude higher than that of tap water. This appeared to correlate with a long curing period (the period of time from compaction to the beginning of the permeability test). Thixotropic alterations of the soil fabric may have occurred during this interval, resulting in the higher K value.

# 4.5.19 <u>Studies by Acar and Others (1984) on the Effect of Organics on</u> <u>Kaolinite</u>

In research funded by EPA, Acar, Olivieri, and Field (Acar et al., 1984b and c) and Acar, Hamidon, Field, and Scott (Acar et al., 1984a) studied the effect of four organic fluids on the saturated permeability of Georgia kaolinite. The fluids tested--benzene, acetone, phenol, and nitrobenzene--were chosen because they represent a wide range of dielectric constants. Comparative tests were performed with 0.01 N calcium sulfate. In addition to the pure solvents, 0.1 percent (1,000 ppm) solutions of acetone and phenol prepared in 0.01 N calcium sulfate solutions were tested. This research was carried out at Louisiana State University, Hazardous Waste Research Center.

# 4.5.19.1 Test Method--

ve izr

The kaolinite was cured at 32 percent moisture for 1 week before compaction in a Harvard miniature mold at a compactive effort corresponding to standard Proctor compaction. Sample dimensions were restricted to 3.55 cm in diameter and 3.8 to 5.1 cm in height.

Tests were conducted in triaxial cells with continuous backpressure. Hydraulic gradients of less than 100 were used. Backpressures of 414 to 449 kPa (60 to 65 psi) were used to fully saturate the samples prior to the permeability testing. Approximately one pore volume of 0.01 N calcium sulfate was passed through the samples to establish the reference permeability value. The influent liquid was then switched to the organic fluid to be tested. Tests were continued until the permeability readings and the effluent concentrations were stable.

A mercury intrusion method was used to characterize the pore size distribution in the samples before and after permeation with the organic test fluids and with the calcium sulfate (Acar et al., 1984b).

A fixed-wall test with acetone as well as flexible-wall tests at variable effective stresses were also carried out in order to evaluate the test scheme. Free-swell and liquid limit tests were conducted with the organic solutions and with the standard calcium sulfate to determine if these properties were affected by the chemicals.

#### 4.5.19.2 Test Results--

All tests with chemicals at low concentrations resulted in slight decreases in permeability. It was found, however, that the chemicals diffused through the flexible latex membrane so that the concentration of the organics that actually permeated the soil sample could not be ascertained.

Reference permeabilities in all kaolinite samples tested with pure organics were between  $5.0 \times 10^{-8}$  cm/s and  $6.0 \times 10^{-8}$  cm/s. When pure organic fluids were introduced into the test cells, an immediate decrease in permeability occurred. For acetone and phenol, this decrease was followed by a permeability increase, the final value stabilizing at approximately double the initial or reference value. In the tests with benzene and nitrobenzene, the permeability decreased until the tests were terminated. Final permeability values measured in these tests were 2 orders of magnitude lower than the reference values.

When acetone was tested in a fixed-wall permeameter, the permeability stabilized at  $2 \times 10^{-6}$  while tests under comparable conditions in flexible-wall cells yielded values between  $6 \times 10^{-8}$  and  $9 \times 10^{-8}$ . The difference in these test results is attributed to sidewall leakage in the fixed-wall test resulting from sample shrinkage during permeation with acetone. The free-swell tests also confirm that shrinkage would occur with acetone permeation.

Both swelling behavior and liquid limit determined with the specific permeant fluid were found to relate to the changes in permeability measured. The liquid limit and free swell were increased significantly with benzene and nitrobenzene, slightly increased with phenol, and decreased with acetone.

Although absolute permeabilities were altered considerably by permeation with the pure organic fluids, the mercury intrusion investigations showed that the size and distribution of pores greater than 80 Å were not significantly affected. Since pores with diameters of less than 80 Å are not expected to contribute appreciably to the total flow, these results suggest that physicochemical properties of the pore fluid close to the clay surfaces lead to variations in flow characteristics.

#### 4.5.20 <u>Finding by Olivieri (1984) of Impermeability of Montmorillonite to</u> Benzene

Olivieri (1984) found that benzene did not penetrate compacted Camontmorillonite that was first fully saturated with 0.01 N calcium sulfate solution even at a hydraulic gradient as high as 150. This finding was attributed to hydraulic pressures being less than the required flow initiation pressure to two-phase flow (Acar and Seals, 1984).

# 4.5.21 <u>Study of Permeability of Clays to Simulated Inorganic Textile</u> Wastes by Tulis (1983)

Tulis (1983) tested Wyoming bentonite, Grolley kaoline, vermiculite, and White Store clay in compaction permeameters with alkaline metal hydroxides. Test solutions were ferrous hydroxide, cupric hydroxide, and manganese hydroxide prepared from 1 N solutions of the respective sulfates by adding sodium hydroxide until a precipitate formed. The final solutions had pH readings as follows: ferrous = 12.9, manganese = 13.0, and cupric = 12.5. Test results show an increase in permeability of the bentonite when it was exposed to the alkaline permeant fluids. The permeability of the kaoline decreased with the application of the bases. Neither the field clay nor the vermiculite showed any significant variation in permeabilities with the test fluid.

Cracks observed in the bentonite indicate that shrinkage was the mechanism responsible for the observed increase in permeability. The decreased permeability of the kaoline was attributed to clogging of the pore space by dispersed clay. All of the leachates from the tests contained silica that had been dissolved by the alkaline solutions.

# 4.5.22 <u>Tests Conducted by Engineering Consulting Firms for Specific</u> <u>Application (unpublished data)</u>

4.5.22.1 Tests Conducted by the Trinity Engineering Testing Corporation--The tests discussed below were performed by the Trinity Engineering Testing Corporation at the request of the Corpus Christi, Texas, City Water Department (White, 1976).

4.5.22.1.1 Soil Characteristics and Test Method--A soil sample from a proposed toxic waste landfill site was subjected to permeability testing with isopropyl alcohol, benzene, and charcoal starter fluid. The material tested was a subsurface clay. Composite samples were compacted at optimum moisture content to a height of approximately 91.4 cm (36 inches) at 95.8 percent standard Proctor density in 2.54-cm (1-inch) inside diameter cylinders. Each of the three organic fluids was added to a level of approximately 61 cm (24 inches) above the compacted soil samples. Water was tested in a fourth sample. A constant pressure head of 7.01 m (23 feet) was imposed with compressed air. Liquid level in each test cylinder was recorded every 4 hours until all the liquid had penetrated the full 91.4-cm (36-inch) column of compacted material.

'4.5.22.1.2 Test Results--In the experiments with isopropyl alcohol and water as the test fluid, the total drop in liquid level was less than 1 inch over a 100-day period. In the column tested with the charcoal starter fluid, liquid began dripping from the bottom of the test cylinder after 122 days. In the benzene test column, signs of full penetration throughout the clay material were observed after 36 days.

In a second experiment series, two 91.4-cm (36-inch) compacted clay soil samples were tested with benzene. The samples differed only in their moisture content (sample A at 10 percent moisture and B at 20 percent moisture). Sample A showed signs of full penetration of the benzene after 20 hours. Full penetration of benzene occurred after 32 days in sample B, and all liquid passed through the sample in 71 days.

The conclusions drawn from the permeability tests are stated below:

- Under optimum compaction, the clays are highly impermeable to domestic water and, conversely, are very permeable to lighter hydrocarbons.
- When properly compacted to a finished thickness of 91.4 cm (3 feet), the clays will serve as a suitable tank liner for domestic water but will not contain the lighter hydrocarbons.
- Under optimum compaction, a 91.4-cm (3-foot) liner of the clay in a tank 7.01 m (23 feet) deep containing benzene can begin to leak within 36 days.

4.5.22.1.3 <u>Discussion</u>--Although the soil sample used in the Trinity Engineering experiments is not adequately characterized, the results of the test clearly indicate potential for large permeability increases resulting from exposure to concentrated nonpolar hydrocarbons. The apparatus and test procedures used differ substantially from those used in permeability tests conducted by other investigators.

The data also illustrate the importance of moisture content during compaction. The performance of clay-soil liner in contact with chemicals such as benzene could be drastically influenced by the uniformity of the moisture content when the liner material was installed and compacted.

4.5.22.2 Test Data Submitted to Pennsylvania Department of Environmental Resources--

The Pennsylvania Department of Environmental Resources has received data pertinent to clay liner/chemical compatibility. The data pertain to specific sites and specific wastes and were submitted to the State by consulting engineers. Testing procedures vary and information needed to evaluate the data is not always provided in the reports. All test results show the clay liner permeabilities to be "within the range required" after exposure to the wastes tested.

Report A deals with tests to evaluate effects on a liner material in contact with a waste comprised of one part oil contaminated soil and four parts water. For the permeability tests, samples were air dried and then recompacted, at +2 percent of optimum moisture content, to 95 percent of maximum dry density. Stainless steel molds 10.2 cm (4 inches) in diameter and 11.7 cm (4.6 inches) in height were used. After trimming, the molded sample was transferred to a constant head permeability device. A backpressure was applied to two of the four samples during saturation with 0.01 N calcium sulfate solution. Permeability measurements with the calcium sulfate showed no significant differences between the results for samples with or without backpressure. Thus, it was concluded that the effect of entrapped air was minimal.

After permeability tests with the standard calcium sulfate, the liner samples were placed in contact with the test fluid, sealed, and placed on a
rocking table for 30 days. Three of the samples were tested with the waste fluid and one with calcium sulfate solution. After 30 days, the samples were drained and the permeability tests repeated. Reported results are shown in Table 4-15.

No discernible color change was observed after a 30-day exposure to the waste fluid. No shrinkage along the sides of the mold was observed, although a change in height of approximately 0.64 cm (0.25 inch) was reported.

The waste tested--one part oil contaminated soil and four parts water-was not characterized further. Neither the extent of the oil contamination nor the characteristics of the contaminated oil were reported. It may be assumed that either tap water or deionized water was used to prepare the waste fluid. The extent to which the oil or its contaminants would be extracted by the water is unknown but probably very small. Although it is not discussed in the report, the waste material in contact with the clay liner sample may have involved three phases, with oil being the lightest phase.

No indication of the length of the permeability testing procedure or pore volumes displaced is given. The hydraulic heads used in the tests also are not reported. These details may be stated in a letter that is referenced in the report. Soil characterization data were not included.

Report B describes the results of a similar investigation in which liner samples from a disposal site were tested with four different wastes. The permeabilities are reported in Table 4-16. All samples showed slight (twofold) increases in permeability after a 30-day exposure to the wastes. It is notable that "control sets" exposed for 30 days to 0.01 N CaSO<sub>4</sub> showed similar increases.

Soil properties are listed below:

Cation exchange capacity: 11.1 meq/100 g soil Predominant exchangeable cation: Calcium Major mineral fraction: Alpha quartz Other minerals (trace to minor): Microcline, Adularia, Muscovite, Kaolinite Percent clay size ( 0.002 mm): 13 Percent silt size (0.002 mm -0.05 mm): 30 Percent sand size (0.05 mm -2.0 mm): 22 Percent larger than 2.0 mm: 35 Liquid limit (percent water): 31 Plastic limit (percent water): 22

Wastes used in the tests were not characterized beyond the description given in the table. Presumably, they were diluted with water as was done in Case A, but this is not stated in the report. The duration of the tests, pore volumes replaced, and hydraulic head are not provided in the report.

Report C provides permeability data on a soil sample tested with chrome ore leachate. The leachate (pH = 13.0) contained 1,400 mg/L total chromium and 1,200 mg/L hexavalent chromium. A constant head test, conducted at a pressure of 20 psi, gave a permeability of  $1.2 \times 10^{-8}$  cm/s. With the falling head method, a permeability of  $2.2 \times 10^{-8}$  cm/s was measured.

| Sample | Coefficier             | nt of permeability (cm/s)                 |
|--------|------------------------|---|
|        | With 0.01 N CaSO4      | After exposure to test fluid <sup>b</sup> |
| Ac     | 1.1 × 10 <sup>-7</sup> | 1.2 x 10-7d                               |
| вс     | 5.9 x 10 <sup>-8</sup> | $3.9 \times 10^{-8}$                      |
| С      | 9.4 x 10 <sup>-8</sup> | $1.1 \times 10^{-7}$                      |
| D      | 1.7 x $10^{-7}$        | Not tested                                |

## TABLE 4-15. PERMEABILITY TEST RESULTSa (Pennsylvania Case A)

<sup>a</sup>Test data reported to Pennsylvania Department of Environmental Resources.

<sup>b</sup>Test fluid was one part oil-contaminated soil to four parts water. <sup>C</sup>Samples under backpressure during initial permeability tests. dControl sample--tested after 30-day exposure to 0.01 N CaSO4.

|            | Coefficient of permeability (cm/s) |                            |  |  |  |  |
|------------|------------------------------------|----------------------------|--|--|--|--|
| Sample     | Before exposure<br>to waste        | After exposure<br>to waste | Waste  |  |  |  |
| <b>A</b> . | 1.4 x 10 <sup>-8</sup>             | 2.0 x 10 <sup>-8</sup>     | Electric furnace<br>baghouse dust                        |  |  |  |
| В          | $1.4 \times 10^{-8}$               | $2.1 \times 10^{-8}$       | Tar decanter sludge<br>(high in organics)                |  |  |  |
| С          | 1.8 x 10 <sup>-8</sup>             | 3.0 x 10 <sup>-8</sup>     | Neutralized pickle<br>liquor rinse water<br>sludge       |  |  |  |
| D          | 1.8 x 10 <sup>-8</sup>             | 3.0 x 10 <sup>-8</sup>     | Hot strip mill recycle<br>system sludge (high in<br>oil) |  |  |  |

# TABLE 4-16. PERMEABILITY TEST RESULTSa (Pennsylvania Case B)

<sup>a</sup>Test data reported to Pennsylvania Department of Environmental Resources.

CBA 007 01002

Sugar 10

Soil characterization and details of the test method were not provided in the brief report.

4.5.22.3 Studies Sponsored by Waste Management, Inc.--

Waste Management, Inc., has sponsored a series of studies to determine compatibility between landfill leachate and in situ clay soil, which functions as the landfill liner. (Weaver and Brissette, Canonie Environmental Services Corporation, 1982). Permeability data were obtained in triaxial devices. Each report includes details of the sampling effort, soil characterization data, and the permeability test results. One important conclusion by Canonie is as follows:

. . . It has been our experience that in concentrations of less than 1 percent organics have no significant impact on soil permeability.

The laboratory permeability results presented in each of the reports indicate that no appreciable change in permeability will occur on soils at the specific sites due to contact with the waste leachate obtained from the facility.

4.5.22.4 Test Data from D'Appolonia Consulting Engineers, Inc.--D'Appolonia Consulting Engineers, Inc. (D'Appolonia), has performed numerous permeability studies involving site-specific soil samples and leachates. Projects have involved slurry trench walls as well as liners for landfills. In 1983 D'Appolonia compiled their permeability test data from 14 projects (D'Appolonia Consulting Engineers, Inc., 1983). Leachates tested in the D'Appolonia projects were frequently high in salts, and some were highly acidic. All data were obtained from triaxial tests. Permeability data from the various projects are summarized below.

Project A--No significant changes were observed in long-term permeability tests on soil samples containing 2 percent or 3 percent commercial bentonite when they were subjected to an aqueous waste fluid of pH 7. The fluid, collected during dredging operations and shipped to D'Appolonia by the client, contained minor concentrations of a number of inorganic salts (sulfate, chloride, fluoride). Specific conductance was reported as 1,710  $\mu$ mho/cm.

The permeability tests involved the exchange of up to 4.7 pore volumes with test times of 24 to 76 days. The hydraulic gradients used varied from 36 to 168; cell pressures were 1.0 to 1.5 kg/cm<sup>2</sup>.

Project B--Extensive permeability tests were performed on reddish-brown clay samples (undisturbed Shelby tube samples) using a stabilized pH 4 fluid. The fluid was prepared in the laboratory using pond water and waste from the site. The most significant characteristic of the stabilized pH 4 fluid was the specific conductance at 94,000  $\mu$ mho/cm at 25<sup>0</sup> C; pH was 3.88. It should be noted that Shelby tube samples may not always be compacted to exactly the same density so that slight deviations in measured permeability are not considered to be significant.

Although all permeabilities measured were below 1 x  $10^{-7}$  cm/s, a trend toward increased permeability was apparent as more pore volumes were exchanged. Changes in soil chracterization were also in evidence as more

pore volumes of test permeant fluid were passed through the samples. Elevated hydraulic gradients 110 and 450 were used for the tests, and cell pressures were 2.5 and 4.5 kg/cm<sup>2</sup>. Test times ranged from 100 to 350 days. In three of the samples, more than 12 pore volumes were exchanged.

<u>Project C</u>--A waste fluid characterized by high salt concentration and high total organic carbon was tested in four soil samples. The samples contained varying proportions of two soils--a fine-to-coarse sand, and a sandy clay with 1 to 3 percent commercial bentonite.

Permeability tests were run at a hydraulic gradient of 20. After initial permeability increases in some samples, the permeabilities decreased. Samples were tested for 692 days. For each sample, between 2 and 13 pore volumes were exchanged. The permeability decrease noted was approximately 1 order of magnitude for a cement bentonite sample. For the other three soil mixtures, permeability decreased by a factor of 2 to 4.

The constituents present in the permeant are not known precisely. Available chemical analysis data indicate that the chemical concentrations in the waste material vary considerably from year to year.

<u>Project D</u>--Slight decreases in permeability were reported for clay-soil samples (with bentonite) exposed to contaminated groundwater samples taken from piezometers. Soil samples were 25 percent flyash, 25 percent uncontaminated clay, 25 percent contaminated clay, and 25 percent silt. Bentonite (1 percent) was added.

Two permeant fluids were tested; pH values were 10.57 (Sample A) and 8.8 (Sample B). Specific conductance was reported at 35,300 and 13,200  $\mu \rm mho/cm$  at 25°C.

Samples were tested at a gradient of 190 with cell pressure at 1.5 kg/cm<sup>2</sup>. Test duration was 90 days with more than three pore volumes exchanged. Final permeabilities were determined to be below 1 x  $10^{-8}$  cm/s.

<u>Project E</u>--Permeability tests were run on a silty clay soil from a proposed facility with four waste leachates as the permeant fluid. Soil samples were compacted in the laboratory (95 percent of standard Proctor density). Chemical characteristics of the waste fluids tested are shown in Table 4-17.

Permeability tests were performed at a hydraulic gradient of 47 and cell pressure of 0.75 kg/cm<sup>2</sup>. Total test time was 40 to 50 days. The results of the permeability tests are given in Table 4-18. All samples were saturated with 0.01 N calcium sulfate solution prior to introduction of the waste fluid.

<u>Project F</u>--Permeability data on undisturbed Shelby tube samples tested with tap water showed permeability values ranging from 6.1 x  $10^{-8}$ to 2.0 x  $10^{-9}$  cm/s with an average of 1.0 x  $10^{-8}$  cm/s. Fifty-seven samples were tested with total test time varying from 6 to 10 days. Hydraulic gradient was 25 to 50, and cell pressure was 3.5 to 5.5 kg/cm<sup>2</sup>.

|   |  | Waste lea   | chate per   | meant flu  | td <sup>b</sup>   |
|---|--|---|---|--|---|
| Parameter   | Units  | No. 3   | No. 4   | Sludge   | Composite<br>leachate   |
| Column test designation   |  | P-1   | P-2   | P-3  | P-4   |
| Ph  | pH units   | 12.63   | 11.23   | 8.37   | 11.23   |
| Specific conductance  | µmho/cm<br>at 25°C   | 20,500  | 11,900  | 10,100   | 11,000  |
| Filterable residue at 180 °C  | mg/L   | 12,100  | 8,620   | 8,720  | 8,380   |
| Acidity   | mg/L CaCO <sub>3</sub>                                       | . 0   | 0   | 0  | 0   |
| Alkalinity  | mg/L CaCO <sub>3</sub>                                       | 4,140   | 130   | 20   | 224   |
| Phenolpthalein<br>alkalinity  | mg/L CaCO <sub>3</sub>                                       | 2,660   | 90  | 2  | 143   |
| Chloride  | mg/L   | 1,600   | 2,300   | 570  | 1,800   |
| Sulfate   | mg/L   | 50  | 2,550   | 500  | 2,250   |
| Cadmium<br>Calcium<br>Chromium (hexavalent)<br>Chromium (total)<br>Iron<br>Lead<br>Magnesium<br>Manganese<br>Nickel | mg/L<br>mg/L<br>mg/L<br>mg/L<br>mg/L<br>mg/L<br>mg/L<br>mg/L | 0.02<br>610<br>450<br>880<br><0.1<br>0.49<br><0.1<br>0.07<br>0.23 | <0.01<br>170<br>14<br>16<br><0.1<br>0.32<br>0.4<br>0.04<br>0.10 | <0.01<br>1,800<br>0.06<br>0.08<br><0.1<br><0.01<br>135<br>0.14<br>0.46 | <0.01<br>505<br>21<br>52<br><0.1<br>0.01<br>2.8<br>0.06<br>0.10 |
| Selenium<br>Sodium<br>Zinc  | mg/L<br>mg/L<br>mg/L   | 1.86<br>945<br>3.82   | 0.196<br>1,860<br>0.12  | <0.001<br>12<br>0.02   | 0.342<br>1,350<br>0.03  |

TABLE 4-17. CHEMICAL CHARACTERISTICS OF WASTE PERMEANTS, PROJECT Ea.

<sup>a</sup>Data from D'Appolonia Consulting Engineers, 1983.

<sup>b</sup>Leachates were generated from various wastes by 1:4 shake extraction of solid waste with water.

<sup>C</sup>Composite leachate obtained by mixing four waste leachates in the following proportion:

No. 3 leachate - 5 percent No. 4 leachate - 75 percent No. 5 leachate - 5 percent (composition not specified) Sludge leachate - 15 percent.

| Sample<br>fluid | Permeant                                    | Pore volumes<br>exchanged                 | Permeability<br>(cm/s)   |
|-----------------|---|---|--|
| P-1             | 0.01 N CaSO <sub>4</sub><br>No. 3 leachate  | -<br>0 - 3.2<br>3.2 - 12.7                | 1.6 x 10 <sup>-7</sup><br>1.7 x 10 <sup>-7</sup><br>1.4 x 10 <sup>-7</sup>                           |
| P-2             | 0.01 N CaSO4<br>No. 4 leachate              | -<br>0 - 8.8                              | 1.1 x 10 <sup>-7</sup><br>1.3 x 10 <sup>-7</sup>   |
| P-3             | 0.01 N CaSO <sub>4</sub><br>Sludge leachate | -<br>0 - 4.7<br>4.7 - 13.5<br>13.5 - 17.2 | 1.4 x 10 <sup>-7</sup><br>1.5 x 10 <sup>-7</sup><br>2.4 x 10 <sup>-7</sup><br>4.2 x 10 <sup>-7</sup> |
| P-4             | 0.01 N CaSO4<br>Composite leachate          | -<br>0 - 0.8<br>0.8 - 5.6                 | 1.1 x 10 <sup>-7</sup><br>1.2 x 10 <sup>-7</sup><br>8.1 x 10 <sup>-7</sup>                           |

TABLE 4-18. RESULTS OF PERMEABILITY TESTS, PROJECT Ea

<sup>a</sup>Data from D'Appolonia Consulting Engineers, Inc., 1983.

<u>Project G</u>--Slurry wall test data were provided for two different leachates identified as low pH or high pH. A commercial bentonite product was added to a clay-sand mix. Sixty-day tests at hydraulic gradients of 170 to 205 and cell pressure at 1.5 kg/cm<sup>2</sup> gave permeability values below 7 x  $10^{-8}$  cm/s. Between 19 and 47 pore volumes were exchanged in the tests.

<u>Project H</u>--Potential clay liner materials were tested with a permeant fluid generated in the laboratory by leaching a young slag from a pilot plant. The pH of the leachate was 4.90; specific conductance was 2.70  $\mu$ mho/cm at 25°C.

Hydraulic gradients of 25 and 100 and cell pressures of 0.75 and 1.5 kg/cm<sup>2</sup> were used in the permeability tests. Distilled water was used to saturate the samples. Small permeability decreases were observed in tests with the slag leachate. Total testing time was approximately 2 to 3 months.

<u>Project I</u>--Groundwater spiked with several chlorinated hydrocarbons was used as the permeant fluid in tests on undisturbed Shelby tubes samples. The total concentration of chlorinated ethanes was 500 ppm. The soil samples tested were comprised of smectite (50 to 75 percent), kaolinite (10 to 25 percent), vermiculite (10 to 25 percent), mica (10 to 25 percent), and quartz (10 to 25 percent).

Permeability tests were conducted at a hydraulic gradient of 150 and a cell pressure of  $1.5 \text{ kg/cm}^2$ . Four samples were tested for up to 140 days with a maximum of 24 pore volumes exchanged. Distilled water was used as the initial permeant fluid. Slight decreases in permeability were observed with the spiked groundwater as permeant fluid.

<u>Project J</u>--Two soil samples were tested with a highly acidic waste fluid (pH = 1.5) that was collected from waste ponds. Other significant characteristics of the fluid were specific conductance = 22,200  $\mu$ mho/cm at 25°C and sulfate = 15,000 ppm.

Slight decreases in permeability were observed after exchange of more than 10 pore volumes. Hydraulic gradients of 20 to 100 were used with cell pressures of 0.7 to 2.0 kg/cm<sup>2</sup>.

<u>Project K</u>--Three waste fluids were tested with a sandy soil mixed with a commerical bentonite product. Significant characteristics of the waste fluids are shown below.

| Parameter  | Waste fluids |           |            |
|--|--------------|-----------|------------|
| pH<br>oK   | 8<br>6.65    | 9<br>7.65 | 10<br>5.00 |
| Specific conductance<br>(umho/cm at 25 <sup>0</sup> C) | 920          | 1,000     | 430        |
| Sulfate (ppm)  | 470          | 460       | 180        |

4-93

No significant change in permeability occurred when the pH 9 fluid was tested with the sandy clay soil. The test involved exchange of 7.4 pore volumes. A slight increase in permeability was noted with the pH 8 fluid tested with the sandy clay soil after 4.7 pore volumes were exchanged. Waste fluid at pH 10 tested with the sandy clay soil mixed with bentonite decreased permeability after exchange of 4.2 pore volumes.

A hydraulic gradient of 22 was used for the tests involving the waste fluids and soil. A hydraulic gradient of 100 was imposed on the soil bentonite tested with pH 10 fluid. Cell pressure was  $1.1 \text{ kg/cm}^2$ . The pH 8 and 9 samples were tested at a hydraulic gradient of 22 and a cell pressure of  $1.0 \text{ kg/cm}^2$ .

<u>Project L</u>--Two waste fluids with neutral pH were used in tests with soil mixed with approximately 1 percent treated bentonite from three vendors. The only notable characteristic of the waste fluids was specific conductance. The permeability data are summarized in Table 4-19. The hydraulic gradient used in the tests was 80 to 90; cell pressure was 1.0 kg/cm<sup>2</sup>.

<u>Project M</u>--Permeability tests were performed on 20 soil samples to determine the effect of a permeant fluid of pH 1.5. The fluid, collected from waste ponds at a disposal site, had a high salt concentration (specific conductance = 22,200  $\mu$ mho cm at 25°C; sulfate = 15,000 ppm).

The only permeability increases noted were for a soil characterized as silt stone and one characterized as sand stone. For these samples, permeability increases were just less than 1 order of magnitude after passage of approximately 12 pore volumes. Hydraulic gradients used in the tests were 15 to 285; cell pressures were 0.75 to 4.00 kg/cm<sup>2</sup>.

<u>Project N</u>--Permeability studies on three composite soil samples were conducted. Three waste leachates used as the permeant fluid were prepared in the laboratory by extracting tailings from a pilot plant. Fluids tested were characterized by pH (3, 6, or 9).

Initial permeabilities were determined with groundwater from the proposed site. The results of the permeability tests are shown in Table 4-20. Permeability increases of approximately 1 order of magnitude were observed in the glacial till samples tested with permeant fluids of pH 6 and 9.

#### 4.5.23 <u>Tests Reported by Bentonite Companies</u>

4.5.23.1 American Colloid Company--

The American Colloid Company produces Volclay<sup>®</sup> soil sealants. These products are a special type of high swelling sodium montmorillonite that has been treated by a proprietary process to render the material unreactive toward most chemical materials. American Colloid Saline Seal 100<sup>®</sup> is a patented product intended for use in containing wastes with high levels of dissolved salts, acids, or alkali.

4-94

|                     | Waste fluid A<br>(1,900 µmho/cm at 25 <sup>0</sup> C) |                          | Waste fluid B<br>(3,800 µmho/cm at 25°C) |                          |
|---------------------|---|--------------------------|--|--------------------------|
|                     | K <sub>max</sub> /K <sub>initial</sub>                | Pore volumes<br>replaced | K <sub>max</sub> /K <sub>initial</sub>   | Pore volumes<br>replaced |
| Cement<br>bentonite | 1.0   | 6                        | 1.0                                      | 13                       |
| Aqua gel            | 2.2   | 8                        | 6.9                                      | 7                        |
| Saline seal         | 1.6   | 7                        | 3.9                                      | 13                       |

TABLE 4-19. RESULTS OF PERMEABILITY TESTS, PROJECT La

<sup>a</sup>Data from D'Appolonia Consulting Engineers, Inc., 1983.

TABLE 4-20. INITIAL AND FINAL PERMEABILITIES DETERMINED IN TRIAXIAL CELL TESTS WITH LEACHATES, PROJECT N<sup>a</sup>

| · · ·                                 | Leachate         | Laboratory permeability @ 20 <sup>0b</sup><br>(cm/s)   |  |  |
|---------------------------------------|------------------|--|--|--|
| Sediment sample                       | permeant<br>pH   | Initial with site groundwater  | Final with<br>waste leachates  |  |
| Glacial till<br>(Composite No. 1)     | 3<br>6<br>9<br>9 | 5.5 x 10-8<br>3.8 x 10-8<br>5.7 x 10-8<br>3.6 x 10-7   | 1.4 x 10-7<br>3.4 x 10-7<br>5.6 x 10-7<br>5.7 x 10-7   |  |
| Stratified drife<br>(Composite No. 2) | 3<br>6<br>9<br>9 | 1.8 x 10 <sup>-5</sup><br>1.5 x 10 <sup>-5</sup><br>1.3 x 10 <sup>-5</sup><br>2.1 x 10 <sup>-5</sup> | 1.3 x 10 <sup>-5</sup><br>1.2 x 10 <sup>-5</sup><br>1.3 x 10 <sup>-5</sup><br>2.1 x 10 <sup>-5</sup> |  |
| 4% Bentonite/till                     | 3                | $1.0 \times 10^{-10}$  | 1.5 x 10 <sup>10<sup>c</sup></sup>   |  |
| Admixture                             | 9                | $1.0 \times 10^{-10}$  | 1.5 x 10 <sup>-10d</sup>   |  |

<sup>a</sup>Data from D'Appolonia Consulting Engineers, Inc., 1983.

<sup>b</sup>Permeability calculations based on final column sample dimensions.

<sup>C</sup>Determined as 83.1 percent saturation based upon final moisture content measurements.

<sup>d</sup>Determined as 83.4 percent saturation based upon final moisture content measurements.

American Colloid has conducted permeability tests of Saline Seal 100<sup>69</sup> with gasoline, kerosene, and 1,1,2-trichloroethane. The trichloroethane tested was waste solvent that had been contaminated with other uncharacterized materials. It was said to be <u>predominantly</u> trichloroethane (Jepsen, 1983).

The American Colloid tests were conducted with a fixed-wall compaction permeameter. Inside walls of the cylinder were coated with a thin film of slurry to provide a barrier against capillary effects along the wall. Samples were compacted to at least 90 percent Proctor. Soil samples were either 5.1 or 10.2 cm (2- or 4-inch) -thick cores and consisted of a uniform standard silica sand mixed with between 6 and 15 percent bentonite (dry weight). Test samples were prehydrated with deionized water for at least 48 hours, and provision was made for deairing. After the test fluid was added to the permeameter, head loss was recorded periodically until stable readings were established. The results of these permeability tests are shown in Table 4-21.

#### 4.5.23.2 Federal Bentonite--

Another major bentonite company, Federal Bentonite, produces, among other bentonite products, petroleum tank farm sealants. The products are made by treating sodium-bentonite with specific polymers in order to obtain the desired sealing characteristics. PPS-21 is a free-flowing granular bentonite product designed to promote an impermeable barrier in the event of failure or leak in petroleum tank farms.

Permeability tests with water and with kerosene were performed on 5.1 cm (2-inch) samples of test soil consisting of PPS-21 mixed with washed beach sand. Samples were prehydrated with deionized water under a 136-cm head prior to introduction of the kerosene. Tests results are summarized in Table 4-22.

#### 4.5.23.3 Discussion--

The behavior of polymer-treated bentonites over a long time period is not demonstrated in the test results presented here. Although the duration of the American Colloid tests exceeded 40 days, only a fraction of a pore volume of fluid was displaced during the tests. The number of pore volumes was not expressed in the data presented by Federal Bentonite.

Suggestions that the polymers in the treated bentonites will degrade after 3 to 4 years have been made, and at least two laboratories claim to have data in support of this time-degradation behavior (Beattie, 1983; Zlamal, 1983). Many applications for the treated bentonites involve shortterm performance requirements. In long-term applications, such as barriers for landfills, the time-degradation issue could have serious implications. The long-term viability of treated bentonite seals needs to be verified.

4-96

| Organic permeant                 | Test duration<br>(days) <sup>b</sup> | Pore volumes<br>displaced | Permeability<br>(cm/s)             |
|----------------------------------|--------------------------------------|---------------------------|------------------------------------|
| Gasoline                         | 68                                   | 0.6                       | 4.7 x 10-7                         |
| Kerosene                         | 40.2                                 | 0.16                      | 4.7 x 10 <sup>-8</sup>             |
| 1,1,2-Trichloroethane<br>(waste) | 71                                   | 0.58                      | 4.2 x 10 <sup>-7<sup>c</sup></sup> |

### TABLE 4-21. EFFECT OF CONCENTRATED ORGANICS UN A TREATED BENTONITE SEAL<sup>a</sup>

<sup>a</sup>Unpublished data on Saline Seal 100<sup>®</sup> from American Colloid Company, personal communication, January 23, 1983.

<sup>b</sup>All tests conducted using a hydraulic head of 76.2 cm (2.5 feet).

<sup>C</sup>Permeability of prehydrated soil was 1.5 x  $10^{-7}$  cm/s prior to addition of organic permeant.

TABLE 4-22. PERMEABILITY (cm/s) OF A TREATED BENTONITE SEAL TO KEROSENE<sup>a,b</sup>

|                         |                 |                                     | and the second sec | ,  |
|-------------------------|-----------------|-------------------------------------|--|--|
| Samp                    | le              | Prior to<br>addition<br>of kerosene | After exposure<br>to kerosene<br>for 7 days  | After exposure<br>to kerosene<br>for 42 days |
| Sample<br>(Prehydrated  | 1:<br>for 24 h) | 5.1 x 10 <sup>-8</sup>              | 3.4 x 10 <sup>-8</sup>   | 2.5 x 10 <sup>-8</sup>                       |
| Sample<br>(Prehydrated) | 2:<br>for 48 h) | 3.2 x 10 <sup>-8</sup>              | 2.2 x 20 <sup>-8</sup>   | 1.5 x 10 <sup>-8</sup>                       |
| Sample<br>(Prehydrated  | 3:<br>for 72 h) | 2.0 x 10 <sup>-8</sup>              | 1.3 x 10 <sup>-8</sup>   | 1.6 x 10-8                                   |
| Sample<br>(Prehydrated) | 4:<br>for 96 h) | 1.3 x 10-8                          | 1.1 x 10 <sup>-8</sup>   | 9.6 x 10 <sup>-9</sup>                       |

<sup>a</sup>Data from Federal Bentonite (1983) on tank farm sealant PPS-21.

<sup>b</sup>Tests conducted under a standard 136-cm head using a falling head permeameter.

4.6 REFERENCES

Acar, Y. B. and R. K. Seals. 1984. Clay Barrier Technology for Shallow Land Waste Disposal Facilities. Hazardous Waste. 1(2):167-181.

Acar, Y. B., A. Hamidon, S. Field, and L. Scott. 1984a. Organic Leachate Effects on Hydraulic Conductivity of Compacted Kaolinite. ASTM Symposium on Impermeable Barriers for Soil and Rock, Denver, Colorado.

Acar, Y. B., and S. D. Field. 1982. Organic Leachate Effects to Hydraulic Conductivity in Fine-Grained Soil, Volume 1. Report NO. GE-82/01, Louisiana State University.

Acar, Y. B., I. Olivieri, and S. D. Field. 1984b. The Effects of Organic Fluids on the Pore Size Distribution of Compacted Kaolinite. ASTM Symposium on Impermeable Barriers for Soil and Rock, Denver, Colorado.

Acar, Y. B., I. Olivieri, and S. D. Field. 1984c. Organic Fluid Effects on the Structural Stability of Compacted Kaolinite. In: Land Disposal of Hazardous Waste: Proceedings of the Tenth Annual Research Symposium at Ft. Mitchell, Kentucky, April 3-5, 1984. EPA-600/9-84-007.

Anderson, D. C. 1981. Organic Leachate Effects on the Permeability of Clay Soils. M.S. Thesis, Soil and Crop Sciences Department, Texas A & M University, College Station, Texas.

Anderson, D. C., 1982. Does Landfill Leachate Make Clay Liners More Permeable? ASCE. pp. 66-69.

Anderson, D. C., K. W. Brown, and J. Green. 1981. Organic Leachate Effects on the Permeability of Clay Liners. National Conference on Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., pp. 223-229.

Anderson, D. C., and S. G. Jones. 1983. Clay Barrier-Leachate Interaction. National Conference on Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., October 31-November 2, 1983.

Anderson, D. C., and S. G. Jones. 1984. Fate of Organic Liquids Spilled on Soil. National Conference on Management of Hazardous Wastes and Environmental Emergencies, Houston, Texas, March 1984. pp. 1-22.

ASTM. 1985. American Society of Testing Materials. Annual Book of ASTM Standards. Vol. 04.08.

Beattie, B. 1983. Federal Bentonite, Montgomery, Illinois, personal communication with Research Triangle Institute.

Bowders, J. J., D. E. Daniel, G. P. Broderick, and H. M. Liljestrand. 1986. Methods for Testing the Compatibility of Clay Liners with Landfill Leachate. In: Hazardous and Industrial Solid Waste Testing: Fourth Symposium, ASTM STP 886, American Society for Testing and Materials, Philadelphia, Pennsylvania, 1986, pp. 233-250.

4-98

- Brown, K. W., and D. C. Anderson. 1980. Effect of Organic Chemicals on Clay Liner Permeability: A Review of the Literature. In: Disposal of Hazardous Waste: Proceedings of the Sixth Annual Research Symposium at Chicago, Illinois, March 17-20, 1980, D. Shultz, ed. EPA-600/9-80-010.
- Brown, K. W., and D. C. Anderson. 1983. Effects of Organic Solvents on the Permeability of Clay Soils. EPA 600/2-83-016. U.S. Environmental Protection Agency, Cincinnati, Ohio.
- Brown, K. W., and J. C. Thomas. 1984. Conductivity of Three Commercially Available Clays to Petroleum Products and Organic Solvents. Hazardous Waste. 1(4):545-553.
- Brown, K. W., J. Green, and J. Thomas. 1983. The Influence of Selected Organic Liquids on the Permeability of Clay Liners. Land Disposal of Hazardous Waste: Proceedings of the Ninth Annual Research Symposium at Ft. Mitchell, Kentucky, May 2-4, 1983. EPA-600/9-83-018.
- Brown, K. W., J. C. Thomas, and J. W. Green. 1984. Permeability of Compacted Soils to Solvents Mixtures and Petroleum Products. In: Land Disposal of Hazardous Waste: Proceedings of the Tenth Annual Research Symposium at Ft. Mitchell, Kentucky, April 3-5, 1984. EPA-600/9-84-007.
- Bryant, J., and A. Bodocsi. 1986. Precision and Reliability of Laboratory Permeability Measurements, EPA-600/2-86-097, U.S. Environmental Protection Agency, Cincinnati, Ohio, 177 pp.
- Buchanan, P. N. 1964. Effect of Temperature and Adsorbed Water on Permeability and Consolidation Characteristics of Sodium and Calcium Montmorillonite. Ph.D. Dissertation, Texas A&M University, College Station, Texas.
- Buelt, J. L., and S. Barnes. 1981. A Comparative Evaluation of Liner Materials for Inactive Uranium-Mill-Tailings Piles. Prepared for the U.S. Department of Energy under Contract No. DE-AC06-76RL0 1830.
- Buettner, W., and M. D. Haug. 1983. Permeability Testing of Fine Grained Soils. In: Potash Technology Mining, Processing, Maintenance, Transportation, Occupational Health and Safety, Environment: Proceedings of the First International Potash Technology Conference, October 3-5, 1983. Saskatoon, Saskatchewan, R. M. McKercher, ed. Pergamon Press, Toronto, Canada.
- Chapman, D. L. 1913. A Contribution to the Theory of Electrocapillarity. Philosophical Magazine. 25(6):475-481.
- Coia, M. F. 1981. The Effect of Electroplating Wastes Upon Clay as an Impermeable Boundary to Leaching. M.S. Thesis, Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina.
- Daniel, D. E. 1982. Effects of Hydraulic Gradient and Field Testing on Hydraulic Conductivity of Soil. U.S. EPA Cooperative Agreement CR 810165 to the University of Texas, Austin.

4-99

- Daniel, D. E. 1983. Third Quarterly Progress Report to the U.S. EPA for the Project: Effects of Hydraulic Gradient and Field Testing on Hydraulic Conductivity of Soil. U.S. EPA Cooperative Agreement CR 810165 to the University of Texas, Austin. For the period February 1983 to May 1983.
- Daniel, D. E., and H. M. Liljestrand. 1984. Effects of Landfill Leachates on Natural Liner Systems. A Report to Chemical Manufacturers Association by Department of Civil Engineering, University of Texas, Austin.
- D'Appolonia Consulting Engineers. 1983. Data Compilation and Presentation for Column Testing Associated with Hazardous Waste Isolation. Prepared for Research Triangle Institute by D'Appolonia Consulting Engineers, Inc., Pittsburgh, Pennsylvania.
- Dunn, R. J. 1983. Hydraulic Conductivity of Soils in Relation to Subsurface Movement of Hazardous Wastes. Ph.D. Dissertation, Department of Civil Engineering, University of California, Berkeley.
- Evans, J. C., R. C. Chaney, and H. Fang. 1981. Influence of Pore Fluid on Clay Behavior. Department of Civil Engineering, Lehigh University, Bethlehem, Pennsylvania. Sponsored by Woodward-Clyde Consultants, Plymouth Meeting, Pennsylvania. Fritz Engineering Laboratory Report No. 383.14, December 4, 1981.
- Everett, E. E. 1977. Suitability of the Lacustrine Clays in Bay County, Michigan for Land Disposal of Hazardous Waste. M. S. Thesis, The University of Toledo, Toledo, Ohio.
- Foreman, D. E., and D. E. Daniel. 1984. Effects of Hydraulic Gradient and Method of Testing on the Hydraulic Conductivity of Compacted Clay to Water, Methanol, and Heptane. In: Land Disposal of Hazardous Waste: Proceedings of the Tenth Annual Research Symposium at Ft. Mitchell, Kentucky, April 3-5, 1984. EPA-600/9-84-007.
- Fuller, W. H. 1974. The "State of the Art" of Migration and Attenuation of Some Potentially Hazardous Polluting Trace and Heavy Metals, Asbestos and Cyanide in Soil. University of Arizona, Tucson, Arizona.
- Gouy, G. 1910. Sur La Constitution de la Charge Electrique a la Surface d'un Electrolyte, Anniue Physique (Paris). 4(9):457-468.

Gray, D. H., and U. U. Stoll. 1983. Readers Write--Leachate Land Liners. ASCE. 52(1):20.

- Green, J., G. Lee, R. Jones, and Ted Palit. 1983. Interaction of Clay Soils with Water and Organic Solvents: Implications for the Disposal of Hazardous Wastes. Environmental Science and Technology. 17:278-282.
- Green, W. J., G. F. Lee, and R. A. Jones. 1979. Impact of Organic Solvents on the Integrity of Clay Liners for Industrial Waste Disposal Pits--Implications for Groundwater Contamination. Final Report to U.S. EPA, Ada, Oklahoma.

Green, W. J., G. F. Lee, and R. A. Jones. 1981. Clay-Soils Permeability and Hazardous Waste Storage. Journal Water Pollution Control Federation. 54(8):1347-1354.

- Griffin, R. A., and W. R. Roy. 1985. Interaction of Organic Solvents with Saturated Soil-Water Systems. Report prepared for the Environmental Institute for Waste Management Studies, University of Alabama by the Illinois State Geological Survey. December 1984.
- Grim, R. E. 1968. Clay Mineralogy (second edition). McGraw-Hill, New York. 596 pp.

Hamilton, J. M. 1979. Measurement of Permeability of Partially Saturated Soils. M.S. Thesis, University of Texas, Austin, Texas, 1979.

- Jepson, C. 1983. American Colloid Company, Skokie, Illinois, personal communication with Research Triangle Institute.
- Lambe, T. W. 1958. The Structure of Compacted Clay. Journal of the Soil Mechanics and Foundations Division, ASCE. 84(SM2):34.

Lohman, S. W., et al. 1972. Definitions of Selected Groundwater Terms--Revisions and Conceptual Refinements. U.S. Geological Survey Water-Supply Paper No. 1988.

- Macey, H. H. 1942. Clay-Water Relationships and the Internal Mechanism of Drying. Transactions of the British Ceramic Society. 41(4):73-95.
- Michaels, A. S., and C. S. Lin. 1954. Permeability of Kaolinite. Industrial and Engineering Chemistry. 46(6):1239-1246.
- Mitchell, J. K. 1976. Fundamentals of Soil Behavior. John Wiley and Sons, Inc., New York, New York.
- Mitchell, J. K., and J. S. Younger. 1967. Abnormalities in Hydraulic Flow Through Fine-Grained Soil. ASTM STP 417. pp. 106-139.
- Mitchell, J. K., D. R. Hooper, and R. G. Campanella. 1965. Permeability of Compacted Clay. Journal of the Soil Mechanics and Foundation Division, ASCE, 91:41-66
- Monserrate, M. L. 1982. Evaluation of the Hydraulic Conductivity of Two Clays Exposed to Selected Electroplating Wastes. M.S. Thesis, Duke University, Durham, North Carolina.
- Olivieri, I. 1984. The Effect of Organic Fluids on the Fabric of Compacted Clay. M.S. Thesis, Department of Civil Engineering, Louisiana State University, Baton Rouge.
- Olsen, H. W. 1965. Deviations From Darcy's Law in Saturated Clay. In: Soil Science Society of America Proceedings, Volume 29. pp. 135-140.

- Pask, J. A., and B. Davies. 1945. Thermal Analysis of Clays and Acid Extraction of Alumina from Clays. U.S. Bureau of Mines, Technical Paper 664. pp. 56-78.
- Peirce, J. J. 1984. Effects of Inorganic Leachates on Clay Liner Permeability. Final Report. U.S. EPA Contract No. 68-03-3149, 24-1. Department of Civil and Environmental Engineering, Duke University. September 28, 1984.
- Peirce, J. J., and T. A. Peel. 1985. Effects of Inorganic Leachates on Clay Soil Permeability. In: Land Disposal of Hazardous Waste: Proceedings of the Eleventh Annual Research Symposium. EPA/600/9-85/013. April.
- Peirce, J. J. and K. A. Witter. 1986. Termination Criteria for Clay Permeability Testing. ASCE Journal of Geotechnical Engineering, September 1986. 112(9):841-854.
- Rad, N. S., and Y. B. Acar. 1984. A Study on Membrane-Permeanto Compatibility. Geotechnical Testing Journal. 7(2).
- Reeve, R. C., and G. H. Tamaddoni. 1965. Effect of Electrolyte Concentration on Laboratory Permeability and Field Intake Rate of a Sodic Soil. Soil Science. 99(4).
- Sanks, R. L., and E. F. Gloyna. 1977. Clay Beds for Storing Solid Industrial Wastes--A Survey. In: Proceedings of the 32nd Industrial Waste Conference, Purdue University, Lafayette, Indiana. Ann Arbor Science, Ann Arbor, Michigan.
- Schramm, M. 1981. Permeability of Soils to Four Organic Solvents and Water. M.S. Thesis, Department of Hydrology and Water Resources, University of Arizona.
- Shepard, T. A. 1981. Geochemical Retardation Processes, Subsurface Contaminant Migration from Mine and Mill Waste Impoundments. Colorado State University.
- Socash, S. M. 1982. Liner Compatibilty Information. Commonwealth of Pennsylvania Department of Environmental Resources, Meadville, Pennsylvania.
- Theng, B. K. G. 1984. The Chemistry of Clay-Organic Reaction. John Wiley and Sons, New York.
- Tulis, D. S. 1983. Response of Clay Permeabilities to Simulated Inorganic Textile Wastes. M. S. Thesis, Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina.
- van Olphen, H. 1963. An Introduction to Clay Colloid Chemistry, Wiley Interscience, New York.

van Schaik, J. C. 1970. Soil Hydraulic Properties Determined with Water and with a Hydrocarbon Liquid. Canadian Journal of Soil Science. 50:79-84. Schaik, J. C., and G. E. Laliberte. 1968. Soil Hydraulic Properties Affected by Saturation Technique. Canadian Journal of Soil Science. 49:95-102.

Weaver, J. W., and R. F. Brissette. 1982. Personal communication with Waste Management, Inc., three reports. A, B, and C.

Weiss, A. 158. Interlamellar Swelling as a General Model of Swelling Behavior. Chem. Ber. 91:487-502.

White, R. 1976. The Permeability of a Clay Material Taken from a Proposed Toxic Waste Landfill Site as Affected by Different Liquids. Personal communication from Trinity Engineering Testing Corp. to the City of Corpus Christi, Texas.

Yong, R. N., and B. P. Warkentin. 1975. Soil Properties and Behavior. Elsevier Scientific Publishing Company, New York.

Zimmie, T. F., J. S. Doynow, and J. T. Wardell. 1981. Permeability Testing of Soils for Hazardous Waste Disposal Sites. In: Proceedings of the Tenth International Conference on Soil Mechanics and Foundation Testing, Vol. 2. Stockholm, Sweden, pp. 403-406.

Zlamal, F. 1983. Slurry Systems Contractors and Consultants, Gary, Indiana, Personal communication with Research Triangle Institute.

Toeller, A. 1982. Review of Texas A&M University Studies on Clay Soils and Organic Reagents. Commonwealth Edison, Chicago. Appendix C to Comments of Utility Solid Waste Activities Group, The Edison Electric Institute and The National Rural Electric Cooperative Association on Sections 3004 and 3005 of the Resource Conservation and Recovery Act of 1976: Permitting Standards for Land Disposal Facilities.

4-103