THE EFFECTS OF MOLECULAR DIFFUSION ON GROUNDWATER
SOLUTE TRANSPORT THROUGH FRACTURED TUFF

by
Gary Robert Walter

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF HYDROLOGY AND WATER RESOURCES
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
WITH A MAJOR IN HYDROLOGY

In the Graduate College
THE UNIVERSITY OF ARIZONA

1985
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Gary Robert Walter entitled The Effects of Molecular Diffusion on Groundwater Solute Transport through Fractured Tuff and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Date

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Dissertation Director
STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: [Signature]

[Signature]
ACKNOWLEDGMENTS

A large portion of the work presented in this dissertation was performed with funds provided by Los Alamos National Laboratory, Order No. 4L11-3951V-1 to the University of Arizona, Dr. G. M. Thompson, Principal Investigator. I wish to thank Carmen Parada for her help in performing and improving the diffusion experiments, Randy Golding for the tracer characterization work, Steve Jensen for performing the bacteriophage assays, and Zonge Engineering for performing measurements of rock electrical properties. I also wish to thank Hydro Geo Chem, Inc. for supporting preparation of the manuscript and Sarah Adams for translating my scribbles into text. Lastly, I would like to thank my wife, Peggy, for keeping me on the fire escape after my dissertation defense.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xi</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2. PHYSICAL AND CHEMICAL FACTORS AFFECTING MATRIX DIFFUSION</td>
<td>4</td>
</tr>
<tr>
<td>Transport Processes</td>
<td>4</td>
</tr>
<tr>
<td>Rock Properties</td>
<td>15</td>
</tr>
<tr>
<td>Chemical Factors Affecting Matrix Diffusion</td>
<td>21</td>
</tr>
<tr>
<td>3. EXPERIMENTAL INVESTIGATIONS</td>
<td>23</td>
</tr>
<tr>
<td>Porosity and Pore-Size Distributions</td>
<td>23</td>
</tr>
<tr>
<td>Diffusion Experiments</td>
<td>32</td>
</tr>
<tr>
<td>Electrical Properties of the Tuff</td>
<td>47</td>
</tr>
<tr>
<td>Discussion of Experimental Results</td>
<td>62</td>
</tr>
<tr>
<td>Porosity</td>
<td>63</td>
</tr>
<tr>
<td>Constrictivity and Tortuosity</td>
<td>65</td>
</tr>
<tr>
<td>4. NUMERICAL MODEL OF MULTICOMPONENT MATRIX DIFFUSION</td>
<td>68</td>
</tr>
<tr>
<td>Multicomponent Diffusion Equations</td>
<td>68</td>
</tr>
<tr>
<td>Numerical Model of Multicomponent Matrix Diffusion</td>
<td>78</td>
</tr>
<tr>
<td>5. MULTICOMPONENT EFFECTS IN THE DIFFUSION CELL EXPERIMENTS</td>
<td>89</td>
</tr>
<tr>
<td>6. EXPERIMENTAL VERIFICATION OF MATRIX DIFFUSION IN FRACTURED TUFF</td>
<td>107</td>
</tr>
<tr>
<td>Experimental Procedure</td>
<td>107</td>
</tr>
<tr>
<td>Results and Interpretation</td>
<td>111</td>
</tr>
<tr>
<td>Conclusions</td>
<td>133</td>
</tr>
<tr>
<td>7. SUMMARY AND CONCLUSIONS</td>
<td>135</td>
</tr>
<tr>
<td>APPENDIX A: REDUCTION OF GENERALIZED FORCES AND FLUXES TO AN EXPERIMENTALLY TRACTABLE SET</td>
<td>138</td>
</tr>
</tbody>
</table>
### TABLE OF CONTENTS—Continued

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>DEFINITION OF THE EFFECTIVE DIFFUSION COEFFICIENT AND GOVERNING PARTIAL</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>DIFFERENTIAL EQUATIONS IN A POROUS MEDIUM</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>TRACER CHARACTERIZATION</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>Acid Dissociation Constants</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>Free Aqueous Diffusion Coefficients</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>Sorption Properties of the Fluorobenzoate Tracers</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>F2 Bacteriophage Tracer</td>
<td>159</td>
</tr>
<tr>
<td>D</td>
<td>LITHOLOGY AND MINERALOGY OF THE TUFF SAMPLES</td>
<td>160</td>
</tr>
<tr>
<td>E</td>
<td>IONIC AND COMBINE DIFFUSION COEFFICIENT MATRICES FOR VARIOUS AQUEOUS SYSTEMS</td>
<td>164</td>
</tr>
<tr>
<td>F</td>
<td>COMPUTATION OF AQUEOUS CHEMICAL EQUILIBRIUM</td>
<td>168</td>
</tr>
<tr>
<td>G</td>
<td>MODEL VERIFICATION</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>REFERENCES</td>
<td>182</td>
</tr>
</tbody>
</table>
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Conceptual model of matrix diffusion from a single fracture</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Initial and boundary conditions assumed in the matrix diffusion solution</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>of Grisak and Pickens (1981)</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic drawing of the mercury infusion porosimeter</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>Blank run P-V curve of the mercury infusion porosimeter</td>
<td>28</td>
</tr>
<tr>
<td>3.3</td>
<td>Log of pore diameter versus cumulative percent of total porosity determined</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>for tuff samples</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Log-probability plot of pore diameter versus cumulative percent of total porosity for tuff samples</td>
<td>34</td>
</tr>
<tr>
<td>3.5</td>
<td>Plexiglas diaphragm diffusion cell</td>
<td>36</td>
</tr>
<tr>
<td>3.6</td>
<td>Schematic drawing of the pumping and detection system</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>used in the diffusion experiments</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>Schematic drawing of the data acquisition system</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>used in the diffusion experiments</td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>Typical diffusion test results for NaBr using:</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>A) Br⁻ electrode, B) conductivity bridge, and</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C) conductivity detector</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>Schematic drawing of the apparatus used for induced-polarization measurements</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>(Zonge, 1972)</td>
<td></td>
</tr>
<tr>
<td>3.10</td>
<td>Ratio of d-c impedance to a-c impedance versus frequency for tuff samples</td>
<td>53</td>
</tr>
<tr>
<td>3.11</td>
<td>Conceptual model of reduced anion mobility zones in a porous rock</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>(after Marshall and Madden, 1959)</td>
<td></td>
</tr>
<tr>
<td>3.12</td>
<td>Theoretical changes in a-c impedance with frequency for a typical NTS tuff</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>sample</td>
<td></td>
</tr>
<tr>
<td>3.13</td>
<td>Average effective diffusion coefficients plotted versus total porosity</td>
<td>64</td>
</tr>
</tbody>
</table>
**LIST OF ILLUSTRATIONS—Continued**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.14</td>
<td>Average effective diffusion coefficient plotted versus greater than 0.1 μm porosity</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic diagram of the integrated finite difference grid</td>
</tr>
<tr>
<td>5.1</td>
<td>Structure, boundary and initial conditions used in the IFDM model of the diffusion experiments</td>
</tr>
<tr>
<td>5.2</td>
<td>Comparison of computed and observed diffusion results using I^- for G1-2840A (2/24/82)</td>
</tr>
<tr>
<td>5.3</td>
<td>Computed relative concentration of Na^+ compared to computed relative concentration of I^-</td>
</tr>
<tr>
<td>5.4</td>
<td>Computed concentrations of component ions across the tuff disc for NaI diffusion test on G1-2804A</td>
</tr>
<tr>
<td>5.5</td>
<td>Comparison of computed and observed diffusion results using PFB^- for G1-2840A (5/11/85)</td>
</tr>
<tr>
<td>5.6</td>
<td>Computed relative concentration of Na^+ compared to computed relative concentration of PFB^-</td>
</tr>
<tr>
<td>5.7</td>
<td>Computed concentrations of component ions across the tuff disc for NaPFB diffusion test on G1-2804A</td>
</tr>
<tr>
<td>6.1</td>
<td>Schematic drawing of the apparatus used for the fracture flow experiment</td>
</tr>
<tr>
<td>6.2</td>
<td>Measured tracer concentrations versus volume eluted in the fracture flow experiment</td>
</tr>
<tr>
<td>6.3</td>
<td>Boundary and initial conditions in the matrix diffusion model of Grisak and Pickens (1981)</td>
</tr>
<tr>
<td>6.4</td>
<td>Comparison of observed and simulated tracer breakthrough curves for ( \theta ) equal 0.24 and various values of ( D_e )</td>
</tr>
<tr>
<td>6.5</td>
<td>Comparison of observed and simulated tracer breakthrough curves for ( D_e = 4.5 \times 10^{-7} ) cm(^2)/s and various values of ( \theta )</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>6.6</td>
<td>123</td>
</tr>
<tr>
<td>6.7</td>
<td>124</td>
</tr>
<tr>
<td>6.8</td>
<td>128</td>
</tr>
<tr>
<td>6.9</td>
<td>131</td>
</tr>
<tr>
<td>C.1</td>
<td>150</td>
</tr>
<tr>
<td>C.2</td>
<td>154</td>
</tr>
<tr>
<td>C.3</td>
<td>158</td>
</tr>
<tr>
<td>G.1</td>
<td>178</td>
</tr>
<tr>
<td>G.2</td>
<td>180</td>
</tr>
<tr>
<td>G.3</td>
<td>181</td>
</tr>
</tbody>
</table>

**Figure 6.6** Comparison of observed and simulated phage breakthrough curve.

**Figure 6.7** Relative PFB concentration versus relative SCN concentration observed in the fracture flow experiment.

**Figure 6.8** Simulated effect of multicomponent diffusion (distilled water) on the fracture flow breakthrough curves.

**Figure 6.9** Simulated effect of multicomponent diffusion (J-13 water) on the fracture flow breakthrough curves.

**Figure C.1** Apparatus for performing pH titrations under nitrogen atmosphere.

**Figure C.2** Schematic drawing of apparatus used for electrical conductivity measurements.

**Figure C.3** Apparatus for filling and degassing tuff samples used in batch sorption tests.

**Figure G.1** Grid used for IFD model verification.

**Figure G.2** Comparison of computed and analytic solutions to 1-D problem.

**Figure G.3** Correlation of numerical solution to single salt diffusion problem with analytic solution for $t_D = 0.0665$. 
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Correspondence between phenomenological coefficients and common transport coefficients</td>
</tr>
<tr>
<td>3.1</td>
<td>Grain density, porosity, and median pore diameters of tuff samples</td>
</tr>
<tr>
<td>3.2</td>
<td>Experimentally determined diffusion coefficients</td>
</tr>
<tr>
<td>3.3</td>
<td>Tortuosities of selected tuff samples computed from bulk resistances (pore–fluid resistance) $\rho_o = 13.5 , \text{ohm-m}$</td>
</tr>
<tr>
<td>3.4</td>
<td>Summary of rock properties affecting matrix diffusion in NTS tuffs</td>
</tr>
<tr>
<td>5.1</td>
<td>Composition of J-13 water used to compute diffusion coefficient matrices</td>
</tr>
<tr>
<td>5.2</td>
<td>Ion diffusion coefficient matrix for NaI and NaPFB in pure water</td>
</tr>
<tr>
<td>5.3</td>
<td>Ion diffusion coefficient matrix for NaI in J-13 water</td>
</tr>
<tr>
<td>5.4</td>
<td>Ion diffusion coefficient matrix for NaPFB in J-13 water</td>
</tr>
<tr>
<td>6.1</td>
<td>Tracer data from the single fracture flow experiment</td>
</tr>
<tr>
<td>6.2</td>
<td>Ion diffusion coefficient matrix for NaSCN and NaPFB in pure water</td>
</tr>
<tr>
<td>6.3</td>
<td>Ion diffusion coefficient matrix for a solution of NaSCN and NaPFB in pure water</td>
</tr>
<tr>
<td>6.4</td>
<td>Ion diffusion coefficient matrix for NaSCN and NaPFB in J-13 water</td>
</tr>
<tr>
<td>C.1</td>
<td>Measured and reported pKa's for fluorobenzoic acids</td>
</tr>
<tr>
<td>C.2</td>
<td>Limiting ionic conductances for benzoate and fluoro-benzoates with computed diffusion coefficients ($D_o$)</td>
</tr>
<tr>
<td>D.1</td>
<td>Lithologies and mineralogies of tuff samples</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>E.1</td>
<td>Ion and combine diffusion coefficient matrices for the system Li–K–Cl</td>
</tr>
<tr>
<td>E.2</td>
<td>Ion and combine diffusion coefficient matrices for the system H–Na–SO₄</td>
</tr>
</tbody>
</table>
ABSTRACT

Theoretical and experimental studies of the chemical and physical factors which affect molecular diffusion of dissolved substances from fractures into a tuffaceous rock matrix have been made on rocks from G Tunnel and Yucca Mountain at the Nevada Test Site (NTS).

Although a number of physical/chemical processes may cause nonadveative transport of dissolved species from fractures into the tuff matrix, diffusion in these rocks is controlled by the composition of the groundwater through multicomponent effects and several rock properties.

The effective molecular diffusion coefficient of a particular species in the tuff can be related to its free aqueous diffusion coefficient by \( D_e = \phi_m (\alpha/\tau^2) D_0 \) where \( \phi_m \) is matrix porosity, \( \alpha \) is the constrictivity, and \( \tau \) is the tortuosity.

The porosities of the samples studied ranged from 0.1 to 0.4. The parameter \( (\alpha/\tau^2) \) ranged from 0.1 to 0.3, and effective matrix diffusion coefficients were measured to be between 2 to 17. \( \times 10^{-7} \) cm\(^2\)/s for sodium halides and sodium pentafluorobenzoate.

Total porosity was found to be the principle factor accounting for the variation in effective diffusion coefficients. The constrictivity-tortuosity factor was found to have a fair correlation with the median pore diameters measured by mercury intrusion. Measurements of bulk rock electrical impedance changes with frequency indicate that the constrictivity factor, \( \alpha \), has a maximum value of 0.8 to 1, but may be
smaller. If the larger values are correct, then the diffusion paths in tuff are more tortuous than in granular media.

The diffusion coefficient matrix computed for various tracers in J-13 well water from the NTS indicates coupling of the diffusion fluxes of all ionic species. Multicomponent diffusion is a second order effect, however, which does not significantly affect experimental results.

The results of a bench-scale fracture flow experiment revealed that the transport of ionic tracers (SCN⁻ and pentafluorobenzoate) was affected by diffusion into the tuff matrix. The transport of a particulate tracer did not appear to be affected by diffusion.
CHAPTER 1

INTRODUCTION

Molecular diffusion is a mechanism for transporting dissolved substances from pores or fractures where advective transport dominates into a rock or soil matrix of much lower permeability. The importance of this mechanism has been discussed for some time in the fields of ore geochemistry, marine geochemistry, and soil chemistry (Garrels, Dreyer and Howland, 1949; Lerman, 1975; Norton and Knapp, 1977; and van Genuchten and Wierenga, 1976). Molecular diffusion may also be the rate controlling step in various sorption and ion exchange processes (van Genuchten and Wierenga, 1976). Interest in molecular diffusion as a solute-dispersing mechanism in groundwater flow through fractured rocks has been motivated recently by the theoretical and experimental studies of Grisak and Pickens (1980a, 1980b), Bibby (1981), Barker and Foster (1981), Neretnieks, Eriksen and Tahtinen, (1982), and Bradbury, Lever and Kinsey (1982).

These studies, in particular that of Grisak and Pickens (1980a), indicate that matrix diffusion (diffusion from a fracture into a block of porous rock) may be a very significant process in retarding movement of solutes and attenuating their concentrations. Various sensitivity studies (for example, Grisak and Pickens, 1980a and Tang, Frind and Sudicky, 1981) have shown that the most important factors affecting diffusional transport in fractured rocks are the groundwater
velocity through the fracture, the aperture of the fracture, the effective diffusion coefficient of the solute in the matrix, and the porosity of the matrix.

Although several theoretical studies of the matrix diffusion process have appeared in the literature, at the outset of this study (1980) no definitive field or laboratory study had been made to determine the true importance of matrix diffusion in solute transport through fractured rocks. The laboratory column study reported by Grisak and Pickens (1980b) suggests that matrix diffusion may be observed in fractured till. However, the complex chemistry of the solutions used in these experiments, the unknown fracture pattern and aperture distribution in the test material, and the simple form of the diffusion model leave their results open to interpretation. Recently, the results of matrix diffusion experiments on fractured granites have been reported by groups in Sweden (Neretnieks and others, 1982) and Great Britain (Bradbury and others, 1982). Neretnieks and others (1982) reported fair success in matching the results of single fracture flow experiments using an analytical model including the effects of hydrodynamic dispersion, sorption, and matrix diffusion. Bradbury and others (1982) studied only the effective diffusion coefficient of iodide in static (no advection) experiments.

The present study was commissioned by Los Alamos National Laboratory to evaluate the role that matrix diffusion might play in the transport of radionuclides from a nuclear waste repository which might be located in fractured tuffs at the Nevada Test Site (NTS). Given the high porosities (10 to 30%) of the tuffaceous rocks at the NTS and
their low matrix permeability (on the order of $5 \times 10^{-14} \text{ cm}^2$), they appeared to be perfect candidates for effective attenuation of solutes by matrix diffusion. The purpose of the research described here was three-fold: to identify and measure the most important physical and chemical parameters controlling matrix diffusion in the tuffs, to identify and apply groundwater tracers suitable for use in both field and laboratory tests of matrix diffusion, and to develop a numerical model capable of simulating small scale advection and multicomponent diffusion in fractured tuffs.
CHAPTER 2

PHYSICAL AND CHEMICAL FACTORS AFFECTING MATRIX DIFFUSION

The purpose of this chapter is to present a theoretical background for identifying and measuring those processes which may affect the movement of dissolved substances between a fracture and a porous rock matrix. We begin with a very general description of transport processes based on the laws of irreversible thermodynamics in continuous systems.

Transport Processes

Consider the simple model of a fracture shown in Figure 2.1. In general, we are interested in the case where a solvent (groundwater) containing N-1 components flows parallel to the fracture under a hydraulic gradient. The matrix (unfractured tuff) is assumed to possess some solution saturated porosity through which aqueous phase transport takes place. The interface between the fracture and the matrix may be the unaltered surface of the rock or an altered surface with physical properties different from those of the bulk rock.

If we assume that transport through the fracture is only by advection and hydrodynamic dispersion, then we can apply the principles of irreversible thermodynamics to completely describe the mass fluxes from the fracture into and through the matrix. Based on the linear law postulate of irreversible thermodynamics (Haase, 1969), the mass and
Figure 2.1. Conceptual model of matrix diffusion from a single fracture.
heat fluxes in a system with \( N \) components are completely described by the phenomenological equations

\[
J_i = \sum_{k=1}^{N} L_{ik}^* \vec{x}_k
\]

\[
J_Q = \sum_{k=1}^{N} L_{Qk}^* \vec{x}_k + L_{QQ}^* \vec{x}_Q
\]

where \( J_i \) is the molar flux of the \( i \)th aqueous component

\( i = 1 \) for solvent,

\( L_{ik}^* \) is the phenomenological coefficient relating the \( i \)th flux to the \( k \)th force,

\( \vec{x}_k \) is the \( k \)th generalized force per mole,

\( J_Q \) is the heat flux,

\( \vec{x}_Q \) is the thermal force,

and underlining indicates a vectorial quantity.

The assumption is made that the phenomenological coefficients do not depend on the fluxes and forces, but they can be arbitrary functions of the state variables temperature, pressure, and concentration.

Following the development of Haase (1969), the generalized molar forces, \( \vec{x}_k \), for creeping motions (Reynold's number less than 1) are given by

\[
\vec{x}_k = M_k g - \dot{V}_k \nabla P - \nabla \mu_k + Z_k F \nabla \phi_e
\]

where \( M_k \) is the molecular weight of component \( k \),

\( \dot{V}_k \) is the partial molar volume of \( k \),
\( g \) is gravitational acceleration,

\( P \) is thermodynamic pressure,

\( \mu_k \) is the chemical potential of the \( k^{th} \) component at constant temperature and pressure,

\( \nabla \) is the gradient operator,

\( Z_k \) is the charge on \( k \),

\( F \) is the Faraday constant,

and \( \phi_e \) is the electrical potential.

The thermal force in (2.2) is given by

\[
\mathbf{X}_Q = - \frac{1}{T} \nabla T
\]

where \( T \) is the absolute temperature.

In the remainder of this study, we restrict ourselves to iso-
thermal conditions so that the heat flux and its effect on the other fluxes will be ignored. This is not to say, however, that thermal effects may not be important in some parts of the transport domain.

Combining (2.1) and (2.3) and multiplying each force by the molar concentration of \( j \), \( m_j \), the following flux equations in terms of the force per unit volume are obtained:

\[
J_i = L_{ii}^* (m_i g_i - m_i V_i P) + \sum_{k=2}^{N} L_{ik}^* (m_k g_k - m_k V_k P) + \sum_{k=2}^{N} L_{ik}^* (-m_k \mu_k + m_k Z_k F \nabla \phi_e)
\]

(2.5)
By noting that

\[ m_i M_i = c_i \quad (2.6) \]

and

\[ m_i V_i = n_i \quad (2.7) \]

where \( c_i \) is the mass concentration of \( i \) and \( n_i \) is the volume fraction of \( i \), (2.5) can be rewritten as:

\[
\begin{align*}
J_i &= L^{*}_{1i} (c_i \kappa - n_i \nabla P) - L^{*}_{1i} m_i \nabla \mu_i + L^{*}_{1i} Z_i F \nabla \phi_e \\
&\quad + \sum_{k=2}^{N} L^{*}_{1k} (C_{k \kappa} - n_k \nabla P) \\
&\quad + \sum_{k=2}^{N} L^{*}_{1k} (-m_k \nabla \mu_k + m_k Z_k F \nabla \phi_e) 
\end{align*}
\]

(2.8)

As shown by Groenevelt and Bolt (1969), in order to obtain a set of flux equations whose terms are amenable to experimental measurement, (2.8) should be written in terms of a solution volume flux, a set of mass fluxes, and a current or charge flux. Substituting the identities

\[
\begin{align*}
\bar{J}_v &= \sum_{i=1}^{N} V_i \bar{J}_i \\
\bar{J}_{mi} &= M_i \bar{J}_i \\
\bar{J}_z &= \sum_{i=1}^{N} Z_i \bar{J}_i 
\end{align*}
\]

(2.9) (2.10) (2.11)

into (2.8) gives
\[ J_v = \sum_{i=1}^{N} V_i \sum_{k=1}^{N} L_{ik}^* (c_{k\phi} - n_k \nabla \phi) \]

\[ - \sum_{i=1}^{N} V_i \sum_{k=1}^{N} L_{ik}^* m_k \nabla \mu_k \]  

\[ + \sum_{i=1}^{N} \sum_{k=1}^{N} L_{ik}^* m_k z_k F \nabla \phi_e \]  

(2.12)

\[ J_{mi} = M_i \sum_{k=1}^{N} L_{ik}^* (c_{k\phi} - n_k \nabla \phi) \]

\[ - M_i \sum_{k=1}^{N} L_{ik}^* m_k \nabla \mu_k \]  

\[ + M_i \sum_{k=1}^{N} L_{ik}^* m_k z_k F \nabla \phi_e \]  

(2.13)

and

\[ J_z = \sum_{i=1}^{N} z_i \sum_{k=1}^{N} L_{ik}^* (c_{k\phi} - n_k \nabla \phi) \]

\[ - \sum_{i=1}^{N} z_i \sum_{k=1}^{N} L_{ik}^* m_k \nabla \mu_k \]  

\[ + \sum_{i=1}^{N} z_i \sum_{k=1}^{N} L_{ik}^* m_k z_k F \nabla \phi_e \]  

(2.14)

After some lengthy algebraic manipulation (Appendix A), the cumbersome flux equations represented by (2.12) and (2.13) can be simplified and formulated in terms of familiar forces and phenomenological coefficients:
\[
J_v = L_{vv} \nabla \phi_v + \ldots + L_{vi} \nabla \mu_i + \ldots + L_{vz} \nabla \phi_e
\]
\[
J_{mi} = L_{iv} \nabla \phi_v + \ldots + L_{ii} \nabla \mu_i + \ldots + L_{iz} \nabla \phi_e
\]
\[
J_v = L_{zv} \nabla \phi_v + \ldots + L_{zi} \nabla \mu_i + \ldots + L_{zz} \nabla \phi_e
\]  
(2.15)

where \( \phi_v \) is \((\rho_s g - \nabla P) \) and \( \rho_s \) is the solution density.

A similar set of phenomenological equations was developed by Groenevelt and Bolt (1969) and have been shown to be valid for transport through porous media. Groenevelt and Bolt also pointed out the correspondence between the phenomenological coefficients in (2.15) and more familiar transport coefficients. To see this correspondence, note that the first subscript of each coefficient denotes the quantity transported while the second subscript indicates the potential gradient responsible for that flux. The physical significance of each term in (2.15) is listed in Table 2.1.

The significance of the phenomenological equations for studies of solute transport through fractured tuff is that they summarize all of the processes by which solutes can move from a fracture into the matrix under isothermal conditions. Not only are the familiar advective and diffusive processes included, but also less familiar processes such as electro-osmosis and ion filtration. Although the equations are applicable to both saturated and unsaturated conditions, this study deals only with transport under fully saturated conditions.

Under such conditions, the conceptual models of matrix diffusion presented by most investigators (for example, Grisak and Pickens, 1980a; Neretnieks, 1981; and Tang and others, 1981) have assumed that matrix permeabilities are so small that advective transport from the
Table 2.1. Correspondence between phenomenological coefficients and common transport coefficients.

<table>
<thead>
<tr>
<th>Phenomenological Coefficient</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{vv}$</td>
<td>Darcian flow</td>
</tr>
<tr>
<td>$L_{vi}$</td>
<td>Osmosis</td>
</tr>
<tr>
<td>$L_{vz}$</td>
<td>Electrosmosis</td>
</tr>
<tr>
<td>$L_{iv}$</td>
<td>Ion Filtration</td>
</tr>
<tr>
<td>$L_{ii}$</td>
<td>Diffusion</td>
</tr>
<tr>
<td>$L_{ij}$</td>
<td>Multicomponent diffusion</td>
</tr>
<tr>
<td>$L_{iz}$</td>
<td>Electrophoresis</td>
</tr>
<tr>
<td>$L_{zv}$</td>
<td>Streaming current</td>
</tr>
<tr>
<td>$L_{zi}$</td>
<td>Diffusion current</td>
</tr>
<tr>
<td>$L_{zz}$</td>
<td>Electrical conduction</td>
</tr>
</tbody>
</table>
fracture into the matrix is negligible. That this assumption, with some qualifications, can be applied to the tuffs is seen by a simple calculation.

Consider an extreme flow situation where a hydraulic gradient perpendicular to the wall of a fracture acts to advect solute into the matrix while a concentration gradient exists which causes diffusion into the matrix. The relative importance of advection to diffusion in this case can be estimated by computing the molecular flux ratio

\[ R_{DA} = \frac{J_D}{J_A} \]  

(2.16)

where \( J_D \) is the flux due to molecular diffusion and \( J_A \) is the flux due to advection.

For a single salt, the diffusion flux is given by Fick's Law:

\[ J_D = -D_e \frac{dM}{dx} \]  

(2.17)

where \( D_e \) is the effective diffusion coefficient in the rock and \( M \) is the molar concentration (see Appendix B for the definition of \( D_e \) used in this study). The advective flux is given by

\[ J_A = Mq = -MK \frac{dh}{dx} \]  

(2.18)

where \( q \) is the Darcian velocity and \( h \) is the hydraulic head.

Combining (2.17) and (2.18) we have

\[ R_{DA} = \frac{D_e \frac{dM}{dx}}{MK \frac{dh}{dx}} = \frac{2.3 D_e d(\log M)}{K dh} \]  

(2.19)
A typical effective diffusion coefficient for a simple salt such as NaCl is approximately $1.5 \times 10^{-11}$ m$^2$/s (Feenstra and others, 1984). For a hydraulic conductivity of $1 \times 10^{-11}$ m/s typical of the NTS tuff (Daniels and others, 1982), $R_{DA}$ becomes

$$R_{DA} = 3.5 \text{ meters } d(\log M)/dh \quad (2.20)$$

Obviously, the transport ratio in (2.20) depends on the relative gradients in the driving forces. For a unit change in hydraulic head ($dh = 1 \text{ m}$), the diffusion flux will exceed the advective flux if $d(\log m)$ is greater than $1/3.5$, or approximately $0.3$. This calculation indicates that for the diffusion flux to exceed the advective flux the molar concentration need change by only a factor of 2 for every meter change in head. Because large concentration gradients are more likely to exist in a repository environment than large hydraulic gradients under steady state flow conditions, molecular diffusion must be considered an important transport process.

A qualification to this statement is that if the tuffs possess membrane or ion selective properties, osmotic pressure gradients may exist or be created which will cause a volume flux into the matrix. Kemper and van Schaik (1966) and Kemper and Rollins (1966) have examined these effects in soils. Experimental evaluation of this possibility in the tuffs will be presented later.

Even if the advective flux terms can be ignored, other non-advevtive flux terms remain which have not been considered in previous matrix diffusion studies. First, previous models of matrix diffusion have considered only diffusion of a single component.
Equation (2.15), however, indicates that to some extent the diffusion fluxes of all the dissolved components are coupled. For ionic components, Lasaga (1979) and Anderson and Graf (1978) have shown that in natural water the off-diagonal phenomenological coefficients and related diffusion coefficients are not zero and cannot be ignored. Single component diffusion applies only in the case of true tracer diffusion where a concentration gradient exists only for an isotope of the species of interest (that is, no chemical concentration gradients). It may be closely approximated by some neutral species, for example, noble gases. The theoretical importance of multicomponent diffusion effects on transport in the tuffs is discussed in a later section and related to the results of laboratory experiments.

Lastly, the importance of the charge fluxes must be considered. Throughout this study, the assumption will be made that no macroscopic electrical potentials exist and that the net charge flux is zero. The possibility exists, however, that naturally occurring electrolytic reactions or corrosion reactions involving metallic materials placed in the tuffs might give rise to electrical potentials and currents. In such a case, the current fluxes and the coupled electrophoretic mass fluxes would need to be considered. Such a consideration was outside the scope of this study.

In summary, this study deals primarily with experimental and theoretical consideration of multicomponent diffusional transport through the tuff. Experiments were conducted, however, to evaluate the membrane properties of the tuffs.
Rock Properties

The extent to which matrix diffusion is effective in dispersing a given solute depends on a number of rock properties. The sensitivity analysis by Grisak and Pickens (1980a) indicated that the effective diffusion porosity of the matrix, the fracture aperture, and the advective velocity through the fracture are the principal physical factors controlling matrix diffusion.

The roles of these parameters can readily be seen by examining an analytical solution for transport through a semi-infinite fracture under the initial and boundary conditions shown in Figure 2.2. For the simple case of no hydrodynamic dispersion and a uniform concentration across the fracture, the governing equations for solute transport in the matrix and in the fracture are:

\[ \phi_m D \frac{\partial M_m}{\partial t} = D_e \frac{\partial^2 M_m}{\partial y^2} \] (2.21)

and

\[ b \left( \frac{\partial M_f}{\partial t} + v_f \frac{\partial M_f}{\partial x} \right) = D_e \frac{\partial M_f}{\partial y} \] (2.22)

where \( b \) is the half aperture of the fracture,
\( \phi_m D \) is the total diffusion porosity of the matrix,
\( M_m \) is the molar concentration in the matrix,
\( M_f \) is the molar concentration in the fracture.

Equations (2.21) and (2.22) are subject to the initial and boundary conditions:
Figure 2.2. Initial and boundary conditions assumed in the matrix diffusion solution of Grisak and Pickens (1981).
\[ M_f(x,y) = M_m(x,y) = 0 \quad ; \ t=0 \]  
(2.23a)

\[ M_f(0,0) = M_m(0,0) = M_0 \quad ; \ t>0 \]  
(2.23b)

\[ M_f(x,0) = M_m(x,0) \quad ; \ x>0, \ t>0 \]  
(2.23c)

The solution to this problem given by Grisak and Pickens (1981) for the relative concentration of solute in the fracture is:

\[ \frac{M_f}{M_0} = 1 - \text{erf} \left[ \frac{[D_e/vb] x}{2[(t-x/v)D_e/\theta_m]^{1/2}} \right] \]  
(2.24)

The attenuating effects of matrix dispersion can be seen in (2.24) to be directly proportional to the effective matrix diffusion coefficient and matrix porosity, and inversely proportional to the fracture flow velocity and fracture aperture. \( D_e \) in (2.24) is not the diffusion coefficient within a pore, which may be approximated by the free aqueous diffusion coefficient in large pores, but includes at least the effects of the tortuosity of the pores and the total porosity. Additional factors controlling the magnitude of the matrix diffusion will be discussed later.

Numerous models have been presented to describe the functional relationship between free aqueous or free gas diffusion coefficients and effective diffusion coefficients in natural or artificial porous media. Excellent reviews of these models are those of Olsen and Kemper (1968), and van Brakel and Heertjes (1974). For fully saturated materials, most of the models take the form of

\[ D_e = (\theta_m a / \tau^2) D_0 \]  
(2.25)
where $\varrho_{\text{me}}$ is the effective diffusion porosity of the matrix,

$\alpha$ is a constructivity factor,

$\tau$ is a tortuosity factor,

and $D_0$ is the free aqueous diffusion coefficient.

More complex relationships have been observed in unsaturated materials where $\varrho_{\text{me}}$ becomes the volumetric moisture content (Porter and others, 1966; Saxena and others, 1974).

As used in (2.25), the tortuosity factor is taken to be the ratio of the average distance traveled by the diffusion species through the porous medium to the macroscopic distance over which concentration gradients are measured.

If the pores in a medium are relatively large (greater than about 10 $\mu$m), then surface interactions with the solid phase may have a negligible effect on diffusion, and the ratio of the effective matrix diffusion coefficient to the free aqueous diffusion coefficient is primarily a function of tortuosity and porosity. The tortuosity factor is squared because it is applied as a correction both to the concentration gradient and to the cross-sectional area perpendicular to the diffusion gradient (Porter and others, 1966). Tortuosity can be estimated from the pore geometry, experimental measurements of the effective diffusion coefficient, or from electrical measurements on the porous medium.

Wyllie and Spangler (1952) described the relationship between the tortuosity and the formation factor, $F_m$, used by the petroleum industry, and so tortuosity can be estimated from bulk electrical conductivity or resistivity measurements of a rock. The electrical
conductivity of the medium is a function of tortuosity because the conductivity measurement requires that ions migrate through the medium in response to an imposed electrical potential. The movement of the ions is impeded directly as a function of the tortuosity.

The discussion above applies only to large pores. For pores with diameters less than 10 μm, the effective diffusion coefficient decreases to an extent which cannot be explained solely in terms of a geometric tortuosity factor, hence the need for the constrictivity term in (2.22). Surface effects due to the presence of the solid phase may act to decrease the effective diffusion coefficient. Kemper (1960), Kemper, Maasland and Porter (1964), and Saxena and others (1974) have suggested that water near mineral surfaces has a higher viscosity than that of the bulk fluid resulting in slower diffusion in this zone. A more important surface effect may be the interaction of ionic species with the electrical field extending from individual mineral surfaces (Kemper and Rollins, 1966).

In most natural waters, silicate mineral surfaces have a negative electrical charge (Parks, 1967). The potential field associated with this charge penetrates some distance into the fluid phase before it is neutralized by positive charges in the solution. Anions do not penetrate as deeply into this field as do cations. The exclusion of anions from part of the cross-sectional pore area can result in a decrease in the effective diffusion coefficient. This effect becomes particularly important in very small pores where the electrical fields of adjacent minerals overlap. Graham-Bryce (1963) attributed anomalously low tracer-diffusion coefficients for iodide in clays to this
phenomenon. Banin (1972) and Blackmore (1976) have also explained seemingly irreversible diffusion in soil aggregates and clay pastes to this "salt-sieving" effect.

The concept of reduced mobility of anions in small pores has also been the basis of several explanations of the frequency dependence of bulk-rock electrical impedance (induced polarization effects) (Marshall and Madden, 1959; Anderson and Keller, 1964; Arulanandan and Mitchell, 1968). The theory of Marshall and Madden will be discussed in detail in a later chapter as it relates to the determination of tortuosity and constrictivity factors for the tuff.

Van Brakel and Heertjes (1974) have explained the constrictivity factor in terms of the variation of cross-sectional pore area along pore segments. Viewed in this way, it can be related to the ratio of the maximum to the minimum cross-sectional pore area along a pore segment. Estimates of the magnitude of the geometric constrictivity factor for various pore geometries indicate that $\alpha$ can vary from 1 (no constrictions) to about 0.2 (80% constriction) (Michaels, 1959; Petersen, 1959).

Based on the above examination of the rock properties controlling the effective matrix diffusion coefficient, the following properties were experimentally evaluated for tuff samples from the NTS:

1) total and interconnected porosity,
2) pore size distribution,
3) effective diffusion coefficients,
4) bulk electrical impedance at varying frequencies.
Details of the experimental procedures and the results are presented in the next chapter.

**Chemical Factors Affecting Matrix Diffusion**

Chemical processes may limit or enhance matrix diffusion in several ways. To see this, consider Fick's Law for an isothermal, multicomponent, aqueous solution:

\[
I_i = - \sum_{j=1}^{N} D_{ij} \nabla N_j \tag{2.26}
\]

or in matrix form

\[
\vec{I} = - \tilde{D} \nabla \vec{N} \tag{2.27}
\]

where a single bar superscript indicates a column matrix, a single bar subscript a vector, and a tilde superscript a second order matrix.

The diffusion coefficients in (2.26) and (2.27) depend on the ionic strength and composition of the solution. Also, the off-diagonal coefficients, \( D_{ij} \) where \( i \) is not equal to \( j \), which couple the flux of one component to the gradients of the other components, are not generally zero. Thus, to predict the diffusion flux of a given ionic species requires a knowledge of the effect of solution composition and ionic strength on the diffusion coefficients, as well as the direction and magnitude of the concentration gradients of the coupled species. Sorption or ion exchange reactions with the rock matrix also affect diffusion by modifying the gradients, but do not affect the aqueous phase diffusion coefficients.
In the general case of multicomponent ionic solutions containing weak electrolytes, the causes of the diffusional coupling are both electrostatic interactions between cations and anions, and the formation of complex species due to ion association and complexation reactions (Wendt, 1965). In Chapter 4, multicomponent diffusion equations based on the work of Wendt (1965), Toor (1964a, 1964b), and Anderson and Graf (1978) are derived which are suitable for numerical computation of these multicomponent effects. The data required to solve these equations are: ionic conductances, equilibrium constants for the complex species, and activity coefficients for all the species. These data are generally available for most naturally occurring species, but were lacking at the outset of this study for several of the tracers considered for use in laboratory experiments. These unknown parameters were measured as part of this study and the results are reported in Appendix C.
CHAPTER 3

EXPERIMENTAL INVESTIGATIONS

In order to evaluate the physical and chemical parameters which affect solute transport from fractures into the tuff matrix, various laboratory investigations were undertaken. The methods and results of this work are described in this chapter.

Laboratory measurements were made of the total and interconnected porosity and pore-size distributions in samples of the tuff from "G" tunnel in Rainier Mesa and from two drill holes on Yucca Mountain at the Nevada Test Site. In addition, numerous measurements of the effective diffusion coefficients of samples of the tuff using various solutes were performed. Measurements of bulk electrical resistivity and induced electrical polarization were also made on selected samples to support the diffusion studies. These measurements were used to evaluate the effects of tortuosity and constrictivity factors on the effective diffusion coefficients.

Porosity and Pore-Size Distributions

The porosity of interest in this study is the effective diffusion porosity of the tuff matrix. The diffusion porosity consists primarily of interconnected pores formed between mineral grains and rock aggregates, but may include intracrystalline spaces in zeolite minerals. Inasmuch as diffusion into the latter type of pore is generally considered as part of the kinetics of ion exchange, only the
intergranular porosity is considered here. A number of more or less standard techniques exist for measuring the various types of porosity of rock samples, but none is totally free from interpretational problems. Manger (1966) has discussed the various method dependent errors associated with total and interconnected porosity measurements in tuff from the NTS.

For the purpose of this study, we are interested not only in the total diffusion porosity, but also the size distribution of the pores. Four basic methods exist for estimating both porosity and pore-size distributions. These are nitrogen-adsorption techniques, mercury-infusion porosimetry (Gregg and Sing, 1967), successive granulation (Norton and Knapp, 1977), and microscopic examination using both optical and scanning electron microscopy. The mercury-infusion technique was used in this study because it is well suited to the range of porosity and pore-sizes present in the tuffs. Even though the meaning of pore sizes measured using mercury porosimetry is open to interpretation, the technique is so widely used that it provides an operational standard for comparing pore size measurements for a wide variety of materials. Grain density measurements were used to estimate the total porosity of the samples.

The mercury-infusion measurements were made on a specially constructed porosimeter. A schematic of the mercury-infusion apparatus is shown in Figure 3.1. The porosimeter was constructed by modifying a Ruska mercury pump and pycnometer for use as a porosimeter by adding a mercury level observation tube to the top of the pycnometer and the necessary pressure/vacuum regulation and measurement system. Infusion
Figure 3.1. Schematic drawing of the mercury infusion porosimeter.
pressures were measured using a Setra 0-2000 psig pressure transducer and digital readout. The transducer also measured partial vacuums. The porosimeter was capable of operating from pressures ranging from about 1.3 Pascal (Pa) (1 mm of Hg) to $1.4 \times 10^5$ Pa (2000 psig). The porosimeter was thus capable of measuring pores with theoretical diameters ranging from about 0.1 cm to $10^{-5}$ cm. A thermistor temperature probe was installed in the mercury reservoir and temperature was monitored with a digital thermometer because temperature variations in the laboratory were found to cause incorrect volume measurements.

Porosity and pore-size distribution measurements were made by first evacuating the pycnometer to less than 1 mm Hg, forcing the mercury level to a hairline on the observation tube and setting the volume indicator of the mercury pump to zero. A dried and weighed sample of tuff was then placed in the pycnometer and evacuated to less than 1 mm Hg for at least one hour before the experiment. The mercury pump was used to force mercury to the hairline and the volume measured to 0.001 cm$^3$. The volume displaced from the zero position gave the sample bulk volume because at 1 mm Hg virtually none of the mercury would infuse into the sample. The volume indicator was then reset to zero and the pressure on the pycnometer was increased stepwise by releasing the vacuum and applying $N_2$ gas pressure. After each step change in pressure, the system was maintained at a constant pressure for several minutes to allow the mercury to infuse into the sample. The cumulative volume change was then measured by bringing the mercury level back to the hairline with the pump. Typically, 10 to 20 steps were used per order of magnitude change in pressure.
The pressure-volume data were analyzed by subtracting the system volume expansion at each pressure from the cumulative volume change during the sample run. The system expansion correction was determined at low pressure using a semilogarithmic regression of volume versus pressure from a blank run made with no sample in the pycnometer. Above about 50 psia, a linear regression was used for the system expansion correction. A pressure-volume plot with the linear regression line for a typical blank run is shown in Figure 3.2.

The theoretical pore diameters were calculated from the corrected pressure-volume data using the Washburn equation (Gregg and Sing, 1967):

\[ d_t = \frac{4\tau_s \cos\theta}{P} \]  

where \( d_t \) is the theoretical pore diameter,
\( \tau_s \) is the surface tension of mercury,
\( \theta \) is the contact angle for mercury,
and \( P \) is the pressure.

Grain densities were determined using the pycnometer procedure described in Procedure ASTM D 854-58 (American Society for Testing and Materials, 1973). Briefly, the procedure consisted of crushing a sample of tuff to a fine powder in a mortar and pestle, and drying it at approximately 95°C for several days prior to testing. The crushed sample was then placed in a preweighed 25 ml glass pycnometer. The wetting fluid (distilled water or kerosene) was then added to the pycnometer until the sample was completely covered. The pycnometer was
Figure 3.2. Blank run P-V curve of the mercury intrusion porosimeter.
then attached to a vacuum pump and evacuated for several hours to remove trapped air. The pycnometer was then filled and weighed. The specific gravity, $SpG$, of the sample was computed from

$$SpG = \frac{W_o}{[W_o + (W_a - W_b)]}$$

(3.2)

where $W_o$ is the weight of the oven-dry sample,

$W_a$ is the weight of the pycnometer filled with only fluid,

and $W_b$ is the weight of the pycnometer filled with fluid and sample.

The specific gravities were corrected for temperature and fluid density to obtain the grain densities.

The total porosities were computed using the grain density of the crushed sample and the bulk volume of the sample determined from the mercury infusion measurement.

The grain density, total porosity, porosity for pores greater than 0.1 μm diameter, and median pore diameter for samples used in the diffusion experiments are listed in Table 3.1. Except where noted, the porosity values are from mercury-infusion measurements made on the samples actually used in the diffusion tests. The measurements were performed after the diffusion experiments had been completed. Because of the destructive nature of the grain density measurement and the irreversibility of mercury infusion, both measurements could not be made on the same sample of tuff. Due to heterogeneities in the samples from the same section of core, an intrinsic uncertainty exists in the total porosity value.
Table 3.1. Grain density, porosity, and median pore diameters of tuff samples.

<table>
<thead>
<tr>
<th>LANL SAMPLE</th>
<th>UA SAMPLE</th>
<th>GRAIN DENSITY (MEAN) (gm/cm³)</th>
<th>FLUID</th>
<th>TOTAL POROSITY</th>
<th>&gt;0.1 μm POROSITY</th>
<th>MEDIAN PORE DIAM.(μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U12G RNM 9</td>
<td>D(GT)-2A</td>
<td>(2.62)</td>
<td>-</td>
<td>0.42</td>
<td>0.07</td>
<td>0.04*</td>
</tr>
<tr>
<td>0.8-1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U12G RNM 9</td>
<td>D(GT)-2B</td>
<td>(2.62)</td>
<td>-</td>
<td>0.45</td>
<td>0.12</td>
<td>0.05*</td>
</tr>
<tr>
<td>0.8-1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U12G RNM 9</td>
<td>D(GT)-1</td>
<td>(2.62)</td>
<td>-</td>
<td>0.45</td>
<td>0.17</td>
<td>0.03*</td>
</tr>
<tr>
<td>5.9-6.4 SIDE B</td>
<td>D(GT)-4A</td>
<td>2.74 KERO 2.50 WATER (2.62)</td>
<td></td>
<td>0.48</td>
<td>0.17</td>
<td>0.03*</td>
</tr>
<tr>
<td>16.2-17.5'</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1-2290A</td>
<td>D(YM)-7</td>
<td>2.35 KERO 2.59 KERO 2.65 KERO (2.53)</td>
<td></td>
<td>0.24</td>
<td>0.09</td>
<td>0.03*</td>
</tr>
<tr>
<td>G1-2290B</td>
<td>D(YM)-10</td>
<td>(2.53)</td>
<td></td>
<td>0.34</td>
<td>0.15</td>
<td>0.07*</td>
</tr>
<tr>
<td>G1-2333B</td>
<td>D(YM)-6</td>
<td>2.65 KERO 2.61 KERO (2.63)</td>
<td></td>
<td>0.24</td>
<td>0.17</td>
<td>0.36</td>
</tr>
<tr>
<td>G1-2698</td>
<td>D(YM)-12</td>
<td>2.29 KERO 0.01</td>
<td></td>
<td>0.22</td>
<td>0.01</td>
<td>0.008*</td>
</tr>
<tr>
<td>G1-2840A</td>
<td>D(YM)-3A</td>
<td>2.65 KERO 2.61 KERO (2.63)</td>
<td></td>
<td>0.24</td>
<td>0.17</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Table 3.1—Continued

<table>
<thead>
<tr>
<th>LANL SAMPLE</th>
<th>UA SAMPLE</th>
<th>GRAIN DENSITY (MEAN) (gm/cm³)</th>
<th>FLUID</th>
<th>TOTAL POROSITY</th>
<th>&gt;0.1 µm POROSITY</th>
<th>MEDIAN PORE DIAM. (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1-2901</td>
<td>D(YM)-2</td>
<td>2.50</td>
<td>KERO</td>
<td>0.19</td>
<td>0.16</td>
<td>0.35</td>
</tr>
<tr>
<td>G1-4750</td>
<td>D(YM)-14</td>
<td>2.55</td>
<td>KERO</td>
<td>0.13</td>
<td>0.10</td>
<td>1.0</td>
</tr>
<tr>
<td>YM-45</td>
<td>D(YM)-4</td>
<td>2.55</td>
<td>KERO</td>
<td>0.21</td>
<td>0.20</td>
<td>1.66</td>
</tr>
</tbody>
</table>

NOTE: (2.65) indicates mean value
<2.62> indicates grain density taken from sample U12G RNM 9 16.2-17.5
* indicates median pore diameter from linear extrapolation of pore size distribution curve to 50%
The uncertainty due to variations in grain density within the same section of core is not great because the standard error of the mean grain density for all of the G1 samples (Yucca Mountain) is only 0.11 gm/cm$^3$. This reduces to 0.05 if the anomalously low value for G1-2698 is not included. The mean grain density for all the samples is 2.55 g/cm$^3$. The low value for G1-2698 is probably due to a higher percentage of clinoptilolite (30-60%, Appendix D) in this sample than in the others. The density of clinoptilolite is about 2.1 g/cm$^3$ (Dana, 1964). Manger (1966) reported similarly low grain densities for non-zeolitized, non-devitrified tuff samples from subunit T of the bedded tuffs of the Paintbrush Tuff.

Data on the pore size distributions are shown in Figure 3.3. In this figure, the common logarithm of the pore diameter in microns is plotted versus the cumulative percent of the total porosity. Log-probability plots for the same samples are shown in Figure 3.4. The log-probability plot was used because many rock properties appear to have log-normal distribution. Figure 3.4 is useful for estimating the statistical properties of the pore size distributions because a log-normal distribution will appear as a straight line on the log-probability plot. As can be seen, most of the size distribution curves approach a log-normal distribution as the pore size decreases.

**Diffusion Experiments**

Direct measurements of the effective diffusion coefficients of various ionic species through samples of the tuff were made using a diaphragm diffusion cell modified from the original design of Stokes
Figure 3.3. Log of pore diameter versus cumulative percent of total porosity determined for tuff samples.
Figure 3.4. Log-probability plot of pore diameter versus cumulative percent of total porosity for tuff samples.
A drawing of the diaphragm diffusion cell is shown in Figure 3.5. The diffusion experiments were performed by cementing with epoxy a one inch diameter by $1/4$ inch thick disc of tuff in the membrane-holding disc of the cell. A solution of high concentration of the diffusing species was placed in the lower reservoir and a solution of lower concentration was placed in the upper reservoir. The resulting concentration gradient caused molecular diffusion through the tuff disc. All the solutions were prepared using water from the J-13 test well near Yucca Mountain as the solvent.

Two techniques were used for monitoring the concentration in the upper reservoir. In the first technique, the concentration of the diffusing species was continuously monitored in the upper reservoir using the pumping and detection system shown in Figure 3.6. For some of the sodium bromide, sodium iodide, and sodium thiocyanate tests, the detector consisted of a Plexiglas flow-through cell into which a Graphic Controls ion-selective electrode and a reference electrode were inserted. The electrode potential was measured with a Beckman Model PHI 81 pH/millivolt meter. In later tests, and tests using other species, a Wescan flow-through conductivity meter and detector were used. The upper reservoir solution was pumped through the cell using a peristaltic pump. The data acquisition system used to monitor the tests is shown in Figure 3.7. The output from the detector was sent to a signal scanner which sequentially switched the output from up to three detectors, or two detectors and a digital thermometer, to a Hewlett-Packard 3390A peak integrator. The scanning rate was such that a given diffusion cell was sampled once every 3 to 5 minutes, with a 30 second "on"
Figure 3.5. Plexiglas diaphragm diffusion cell.
Figure 3.6. Schematic drawing of the pumping and detection system used in the diffusion experiments.
Figure 3.7. Schematic drawing of the data acquisition system used in the diffusion experiments.
When the output from a given detector was switched on, the peak integrator perceived the signal as a chromatographic peak which it integrated and stored. The relationship between the peak area and the detector output and solution concentration was determined by calibrating the system with solutions of known concentration.

The integrator transmitted the stored peak areas and run times to a Hewlett-Packard 85A microcomputer where they were stored on magnetic tape. All data reduction and computation of diffusion coefficients was then performed by programs written for the HP 85A.

The second technique for monitoring the concentration in the upper reservoir involved discrete measurements using an Altex RC-20 conductivity bridge or a Schoeffel ultraviolet absorption detector. The conductivity bridge was used as a check on the results from the flow-through conductivity detector. The UV detector was used to selectively monitor the concentrations of the fluorobenzoate tracers.

Diffusion experiments were performed using solutions of various sodium salts dissolved in J-13 well water. Salts used in the experiments were sodium bromide, sodium iodide, sodium thiocyanate, and sodium pentafluorobenzoate (PFB). Prior to the tests, the tuff discs were soaked in the tracer solution for several days. To start the tests, the lower reservoir was filled with the tracer solution and the tuff sealed in place in the diffusion cell. Vacuum was then applied to the lower reservoir to degas the solution to prevent bubbles from forming during the tests. For discs not previously saturated, vacuum was then applied to the upper reservoir to remove air from the disc and to initiate a flow of solution through the disc. Several hours were
required to draw a few milliliters of solution through the discs. The cell was then placed in a constant temperature bath at 25 ± 0.1°C or 30 ± 0.1°C for several hours prior to the test. This procedure was designed to assure that the fluid in the disc was in thermal equilibrium with the solution in the lower reservoir at the start of the test. The tests were initiated by placing a known volume of either J-13 water or a solution with 1% of the lower reservoir concentration in the upper reservoir.

The resulting time-concentration data were analyzed using the so-called steady state method (Robinson and Stokes, 1959). This method uses only the data after a sufficient time has elapsed for an approximately linear concentration gradient to be established across the disc. When such a gradient has been established, the time-averaged diffusion coefficient is given by

\[
D_{ea} = \frac{At(1/V_U + 1/V_L)}{L} \ln \Delta C^* \tag{3.3}
\]

where \(D_{ea}\) is the time averaged diffusion coefficient,
\(A\) is the surface area of the disc,
\(L\) is the thickness of the disc,
\(V_U\) is the volume of the upper reservoir,
\(V_L\) is the volume of the lower reservoir,
\(\Delta C^* = (C_L(0) - C_U(0))/(C_L(t) - C_L(t))\)

\(C_U(0)\) and \(C_L(0)\) are the concentrations in the upper and lower reservoirs respectively when a linear concentration gradient begins to exist,

and \(C_U(t)\) and \(C_L(t)\) are the concentrations at time \(t\).
To compute $D_{ea}$, both the upper and lower reservoir concentrations must be known. The upper reservoir concentration was measured and the lower reservoir concentration was computed from the change in upper reservoir concentration. Due to its large volume (approximately 320 ml), the lower reservoir concentration changed by less than 1% during the course of a typical experiment.

To apply the steady state method, a time must be selected after which a linear concentration gradient exists across the disc. This time was determined by plotting $\ln \Delta C^*$ versus time as shown in Figure 3.8 for sample U12G RNM 9. In this case the curve becomes linear in time after about 400 minutes. Regression analysis was then used to compute $D_{e}$ from the slope of the linear portion of the curve. The error in the diffusion coefficient was computed from the variance of the regression slope. Admittedly the selection of the linear portion of the curve was somewhat subjective. The data-analysis program was written so that the operator could interactively perform the regression on various portions of the curve until the error in the computed diffusion coefficient was minimized. Usually about three tries were needed to select a linear portion after which no further improvement in the regression could be made.

Typical results of the diffusion experiments are shown in Figure 3.8. Figure 3.8a shows results of a test using the Br-selective electrode. Figure 3.8b shows a result using the conductivity bridge and Figure 3.8c the result for the same sample using the flow-through conductivity detector. The tests usually lasted between 24 and 48 hours, but some were as short as 12 hours and others as long as 5 days.
Figure 3.8. Typical diffusion test results for NaBr using: 
A) Br\textsuperscript{-} electrode, B) conductivity bridge, and 
C) conductivity detector.
Approximately 60 diffusion experiments were performed on 15 different samples of tuff from "G" Tunnel at Rainier Mesa, and the USW-G1 and UE24a-1 test holes near Yucca Mountain. Many of the tests were unsuccessful, either because of failures in the detection system or because the resulting time-concentration curve was clearly not the result of diffusion. In the latter case, the anomalous results were usually traced to a failure in the cement sealing the tuff disc into the membrane holding disc. The results of tests which were considered to be successful on the basis that the time-concentration curves were consistent with molecular diffusion, are listed in Table 3.2.

Although the results of the diffusion experiments will be discussed in detail later in this chapter, a few comments on the quality of the results are now in order. As can be seen from Table 3.2, the effective diffusion coefficients range from $21.3 \times 10^{-7}$ down to $2.2 \times 10^{-7}$ cm$^2$/s. In general, these results fall within the range of values that would be expected based on reasonable, prior estimates of tortuosity and constrictivity (such as those given by van Brakel and Heerjtes, 1974).

As for the results for individual rocks on which multiple diffusion experiments were performed, reproducibility was a persistent problem. For example, tests on U12G RNM 9(0.8-1.0') using NaBr gave a mean diffusion coefficient of $8.4 \times 10^{-7}$ cm$^2$/s, but ranged from $4.7 \times 10^{-7}$ to $10.5 \times 10^{-7}$. Similar scatter can be seen in the values for other samples. An exhaustive search for the causes of these inconsistencies indicated that they were associated with the diffusion apparatus or the tuff itself, not with the detection and data acquisition.
### Table 3.2. Experimentally determined diffusion coefficients.

<table>
<thead>
<tr>
<th>LANL SAMPLE #</th>
<th>DIFFUSION COEFFICIENT (× 10⁻⁷ cm²/s)</th>
<th>DETECTOR*</th>
<th>SALT</th>
<th>DATE MEASURED</th>
</tr>
</thead>
<tbody>
<tr>
<td>U12G</td>
<td>4.7 ± .1</td>
<td>IS</td>
<td>NaBr</td>
<td>7/17/81</td>
</tr>
<tr>
<td>RNM 9</td>
<td>10.5 ± .03</td>
<td>CD</td>
<td>NaBr</td>
<td>7/22/82</td>
</tr>
<tr>
<td>0.8-1.</td>
<td>10. ± 1.</td>
<td>IS</td>
<td>NaBr</td>
<td>7/26/82</td>
</tr>
<tr>
<td>U12G</td>
<td>13.3 ± .04</td>
<td>CD</td>
<td>NaBr</td>
<td>5/27/82</td>
</tr>
<tr>
<td>RNM 9</td>
<td>12.2 ± .1</td>
<td>CD</td>
<td>NaBr</td>
<td>6/11/82</td>
</tr>
<tr>
<td>0.8-1.</td>
<td>14.4 ± .1</td>
<td>CD</td>
<td>NaBr</td>
<td>7/01/82</td>
</tr>
<tr>
<td>U12G</td>
<td>11.3 ± .02</td>
<td>IS</td>
<td>NaBr</td>
<td>10/10/81</td>
</tr>
<tr>
<td>RNM 9</td>
<td>3.73 ± .02</td>
<td>CD</td>
<td>NaBr</td>
<td>6/03/82</td>
</tr>
<tr>
<td>5.9-6.4</td>
<td>5.12 ± .02</td>
<td>CD</td>
<td>NaBr</td>
<td>6/25/82</td>
</tr>
<tr>
<td>SIDE B</td>
<td>5.12 ± .02</td>
<td>CD</td>
<td>NaBr</td>
<td></td>
</tr>
<tr>
<td>U12G</td>
<td>10.8 ± .3</td>
<td>IS</td>
<td>NaI</td>
<td>10/08/81</td>
</tr>
<tr>
<td>RNM 9</td>
<td>21.3 ± .1</td>
<td>CD</td>
<td>NaBr</td>
<td>5/24/82</td>
</tr>
<tr>
<td>16.2-</td>
<td>20.0 ± .1</td>
<td>CD</td>
<td>NaBr</td>
<td>5/31/82</td>
</tr>
<tr>
<td>G1-2290</td>
<td>3.3 ± .2</td>
<td>IS</td>
<td>NaBr</td>
<td>8/04/82</td>
</tr>
<tr>
<td>G1-2290</td>
<td>3.53 ± .05</td>
<td>CD</td>
<td>NaBr</td>
<td>7/29/82</td>
</tr>
<tr>
<td></td>
<td>4.0 ± 1.</td>
<td>IS</td>
<td>NaBr</td>
<td>8/02/82</td>
</tr>
<tr>
<td>G1-2333A</td>
<td>11. ± 2.</td>
<td>CD</td>
<td>NaBr</td>
<td>3/17/82</td>
</tr>
<tr>
<td></td>
<td>13.7 ± .2</td>
<td>CD</td>
<td>NaBr</td>
<td>7/09/82</td>
</tr>
<tr>
<td>G1-2333B</td>
<td>16.8 ± .1</td>
<td>CD</td>
<td>NaBr</td>
<td>3/11/82</td>
</tr>
<tr>
<td>G1-2698</td>
<td>4.99 ± .02</td>
<td>CD</td>
<td>NaBr</td>
<td>7/19/82</td>
</tr>
<tr>
<td>G1-2840A</td>
<td>2.5 ± .4</td>
<td>IS</td>
<td>NaBr</td>
<td>2/18/82</td>
</tr>
<tr>
<td></td>
<td>5.45 ± .02</td>
<td>CD</td>
<td>NaI</td>
<td>2/24/82</td>
</tr>
<tr>
<td></td>
<td>6.3 ± .2</td>
<td>CB</td>
<td>NaSCN</td>
<td>4/01/82</td>
</tr>
<tr>
<td></td>
<td>2.48 ± .01</td>
<td>CD</td>
<td>NaPFB</td>
<td>5/01/82</td>
</tr>
<tr>
<td></td>
<td>2.2 ± .1</td>
<td>UV</td>
<td>NaPFB</td>
<td>5/11/82</td>
</tr>
<tr>
<td>G1-2840B</td>
<td>3.98 ± .04</td>
<td>CD</td>
<td>NaI</td>
<td>2/18/82</td>
</tr>
<tr>
<td></td>
<td>4.46 ± .07</td>
<td>CB</td>
<td>NaBr</td>
<td>4/08/82</td>
</tr>
<tr>
<td></td>
<td>5. ± 1.</td>
<td>CB</td>
<td>NaPFB</td>
<td>4/14/82</td>
</tr>
<tr>
<td></td>
<td>5.01 ± .04</td>
<td>CB</td>
<td>NaSCN</td>
<td>4/20/82</td>
</tr>
<tr>
<td></td>
<td>5.37 ± .01</td>
<td>CD</td>
<td>NaBr</td>
<td>4/28/82</td>
</tr>
<tr>
<td></td>
<td>5.68 ± .01</td>
<td>CD</td>
<td>NaBr</td>
<td>4/29/82</td>
</tr>
<tr>
<td>LANL SAMPLE</td>
<td>DIFFUSION COEFFICIENT (x $10^{-7}$ cm$^2$/s)</td>
<td>DETECTOR*</td>
<td>SALT</td>
<td>DATE MEASURED</td>
</tr>
<tr>
<td>-------------</td>
<td>---------------------------------------------</td>
<td>-----------</td>
<td>------</td>
<td>---------------</td>
</tr>
<tr>
<td>G1-2901</td>
<td>3.1 ± .05</td>
<td>CB</td>
<td>NaBr</td>
<td>3/03/82</td>
</tr>
<tr>
<td></td>
<td>4.92 ± .04</td>
<td>CD</td>
<td>NaN</td>
<td>3/11/82</td>
</tr>
<tr>
<td></td>
<td>2.82 ± .06</td>
<td>CB</td>
<td>NaPFB</td>
<td>4/28/82</td>
</tr>
<tr>
<td>G1-4750</td>
<td>2.91 ± .07</td>
<td>CD</td>
<td>NaBr</td>
<td>7/21/82</td>
</tr>
<tr>
<td>YM-45A</td>
<td>4.79 ± .04</td>
<td>CD</td>
<td>NaBr</td>
<td>6/03/82</td>
</tr>
<tr>
<td></td>
<td>5.40 ± .03</td>
<td>CD</td>
<td>NaBr</td>
<td>6/07/82</td>
</tr>
<tr>
<td></td>
<td>4.6 ± .2</td>
<td>CD</td>
<td>NaBr</td>
<td>6/14/82</td>
</tr>
<tr>
<td></td>
<td>4.94 ± .02</td>
<td>CD</td>
<td>NaI</td>
<td>7/09/82</td>
</tr>
<tr>
<td></td>
<td>2.92 ± .05</td>
<td>IS</td>
<td>NaI</td>
<td>7/13/82</td>
</tr>
<tr>
<td>YM-45</td>
<td>6.7 ± .2</td>
<td>IS</td>
<td>NaBr</td>
<td>7/28/82</td>
</tr>
</tbody>
</table>

* IS - Ion selective electrode
CD - Conductivity detector
CB - Conductivity bridge
UV - UV absorbance detector
system. The differences are too large to be accounted for by errors in the calibration of the detector or other uncertainties in the data. Although leaks in the cement holding the tuff discs in the membrane holding disc were a possible source of anomalously high values, the resulting time-concentration curves are linear which is consistent with diffusional rather than advective transport. In addition, such leaks, when present, could usually be detected before the tests were begun by visual inspection of the membrane holding disc with a hand lens. During such inspections, gaps in the epoxy cement were revealed by a lack of optical continuity between the Plexiglas disc and the rock.

Three other possible sources of error were incomplete or changing degrees of water saturation of the discs, swelling of montmorillonitic clays in some of the samples, and gradual dissolution of the sample. The extent to which changing saturation may have affected the results is difficult to evaluate. As for incomplete saturation, it would result in a lower effective diffusion coefficient and could explain the anomalously low diffusion coefficients measured on samples U12G RNM 9(0.8-1.0')A and U12G RNM 9(16.2-17.5) because these values were determined from the first tests performed on these samples. Later tests were performed after the samples had been soaked in J-13 water for several months. This explanation cannot account for the high value for U12G RNM 9(5.9-6.4')B obtained from the first test on this sample.

As for the effect of swelling clay on the variance in the effective diffusion coefficients, montmorillonite has been found in some of the G1 samples, but not in the YM or U12G samples (Appendix D).
Tests on the G1 samples generally resulted in more consistent values of the effective diffusion coefficient.

Lastly, some dissolution of the samples probably occurred during the course of the experiments. Tests of the stability of the detector system performed by soaking the samples in about 30 ml of J-13 water and monitoring the change in conductivity of the water showed a detectable increase in the dissolved salt content of the water. Although this drift was not sufficient to affect the results of any particular diffusion test, it does indicate that the rocks were not in chemical equilibrium with the J-13 water. This disequilibrium implies that the tuff discs may have changed their properties after months of soaking in J-13 water. A gradual increase in porosity due to mineral dissolution may have caused the gradual increase in diffusion coefficients shown for G1-2840B.

**Electrical Properties of the Tuff**

The fundamental similarity between molecular diffusion and electrical conductance through electrolyte solutions allows the use of measurements of the electrical resistivity of the water saturated tuffs as a check on the results of the diffusion experiments. In addition, some properties of the tuff which affect ionic diffusion can be measured more effectively using electrical measurements. For these reasons, six tuff discs used in the diffusion experiments were sent to Zonge Engineering of Tucson, Arizona for measurement of their direct current resistivity and alternating current impedance.
Prior to measurement of their electrical properties, the tuff discs were soaked in J-13 water for several weeks. Most of the samples had already been used in diffusion experiments and were already saturated with J-13 water. The electrical measurements were performed using procedures described by Zonge (1972). Briefly, the procedure consists of placing the rock sample in the sample holder shown in Figure 3.9 where each end of the rock is in contact with water presumed to be typical of the pore fluid. A constant current square wave of alternating polarity is then passed through the rock and the induced polarization effect computed from the impedance change and phase shift of the wave as modified by its passage through the sample.

The measured values of bulk-rock resistivity ($\rho_b$) determined from the impedance at 0.01 or 0.1 Hz are shown in Table 3.3. These values are practically equivalent to the direct current resistivity. The changes in impedance with increasing frequency are shown in Figure 3.9 in terms of the ratio of the impedance at lowest frequency measured to that at each increasing frequency.

The bulk resistivities listed in Table 3.3 provide an independent check on the parameter $\alpha/\tau^2$ which was introduced as an empirical coefficient, along with porosity, to relate the effective diffusion coefficient to the free aqueous diffusion coefficient. For a rock which does not contain highly conductive minerals and is fully saturated, the bulk-rock resistivity can be related to the resistivity of the pore fluid ($\rho_f$) by (Wyllie and Spangler, 1952)

$$\rho_b = (\tau^{1/2}/\theta) \rho_f$$ (3.4)
Figure 3.9. Schematic drawing of the apparatus used for induced-polarization measurements (Zonge, 1972).
where $T$ is an empirical parameter often called "tortuosity" but not necessarily identical to $\tau$. To the extent that the same factors which control ionic diffusion through the tuffs also control electrical conduction, $T$ in (3.4) can be related to the geometric factor $\tau^2/a$ in (2.22).

This correspondence can be seen by considering Ohm's Law (Gartenhaus, 1975)

$$J_z = \sigma \Delta \phi_e$$  \hspace{1cm} (3.5)

where $J_z$ is the electrical current (charge flux),

$\sigma$ is the electrical conductivity,

$\Delta \phi_e$ is the electrical potential difference.

Remembering that resistivity, $\rho$, is the inverse of conductivity, $\sigma$, and that both are normalized for a unit length of material, (3.5) can be written in terms of a resistance, $R$, and a potential gradient as

$$J_z = R^{-1} \frac{d\phi_e}{dx}$$  \hspace{1cm} (3.6)

If (3.6) describes the charge flux in an aqueous solution, then the flux through a porous medium can be described by correcting (3.6) for the porosity, tortuosity, and constrictivity of the medium, as is done with diffusion fluxes. Applying these corrections to (3.6) gives

$$J'_z = \left(\frac{a\phi}{\tau^2}\right) R^{-1} \frac{dE}{dx}$$  \hspace{1cm} (3.7)

where $J'_z$ is the flux through the porous medium.
Following the argument of Porter and others (1966) that \( \tau \) appears as a correction to both the gradient and the cross-sectional area of flow, (3.7) may be written as

\[
J'_z = \frac{a\phi}{\tau R} \frac{d \phi}{d \tau dx}
\]  

(3.8)

Now, comparing (3.4) and (3.8), the following identity can be seen:

\[
\frac{\tau^{1/2}}{a} = \tau/\alpha
\]  

(3.9)

Using (3.8), the measured bulk resistivities, and the porosities, the apparent tortuosities, \( T \), can be computed for the tuff samples used in the diffusion experiments. These values are shown in Table 3.3. In making these calculations, the pore fluid in the disc was assumed to have the same resistivity as J-13 water (13.5 ohm-m).

The change in impedance with frequency (Figure 3.10) also yields additional insight into the factors affecting conduction and diffusion though the tuffs. Marshall and Madden (1959) proposed a model describing induced polarization effects in rock containing no metallic minerals based on the membrane properties of the rock. Their model is based on the assumption that a porous rock contains zones where the mobility of anions is less than that of cations due to the electrical interaction of the anions with the negative surface charge on the mineral grains.

A schematic drawing of these zones in a granular rock is shown in Figure 3.11 where the constrictions between the grains are zones of low ion mobility due to overlapping electrical double layers. As
Table 3.3. Tortuosities of selected tuff samples computed from bulk resistances (pore-fluid resistance) $\rho_0 = 13.5$ ohm-m.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Bulk Resistance (ohm-m)</th>
<th>Total Porosity</th>
<th>Tortuosity (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U12G–RNM 9</td>
<td>43.3</td>
<td>0.42</td>
<td>1.82</td>
</tr>
<tr>
<td>0.8 ft to 1.0 ft (sample A)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U12G–RNM 9</td>
<td>60.2</td>
<td>0.45</td>
<td>4.03</td>
</tr>
<tr>
<td>5.9 ft to 6.4 ft (side B)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U12G–RNM 9</td>
<td>31.7</td>
<td>0.45</td>
<td>1.12</td>
</tr>
<tr>
<td>16.2 ft to 17.5 ft (sample A)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1–2290</td>
<td>133.7</td>
<td>0.24</td>
<td>5.65</td>
</tr>
<tr>
<td>G1–2333</td>
<td>60.4</td>
<td>0.36</td>
<td>2.59</td>
</tr>
<tr>
<td>(sample 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G–2901</td>
<td>134.5</td>
<td>0.19</td>
<td>3.58</td>
</tr>
</tbody>
</table>
Figure 3.10. Ratio of d-c impedance to a-c impedance versus frequency for tuff samples.
Figure 3.11. Conceptual model of reduced anion mobility zones in a porous rock (after Marshall and Madden, 1959).
discussed previously, the reduced anion mobility in the constrictions is at least one factor contributing to the constrictivity factor $a$.

Based on this conceptual model, Marshall and Madden developed the following expression for the impedance of the rock at a given frequency and a pore solution containing a single monovalent salt:

$$
\begin{align*}
  z_i & = \frac{\Delta x^H}{F_{\mu \nu}} \left[ t_p^H + \frac{B}{A} t_p^L ight] \\
  & + \frac{(S^L - S^H)^2}{\varepsilon_H \varepsilon_S} \left[ \frac{A}{B} \frac{\varepsilon S^L}{t_p^L (t_p^H)^2 \tanh \varepsilon_H} \right] \\
  & + \frac{(S^L - S^H)^2}{(t_p^L)^2 (t_p^H)^2 \tanh \varepsilon_L} \\
  & + \frac{(S^L - S^H)^2}{(t_p^L)^2 (t_p^H)^2 \tanh \varepsilon_H} \\
\end{align*}
$$

(3.10)

where $D_p^L$, $D_p^H$ are the diffusion coefficients of the cation in the low and high mobility zones, respectively

$F$ is the Faraday Constant

$m$ is the total molar salt concentration

$\varepsilon_H = (i\omega/(2D_p^H t_p^H)^{1/2} \cdot \Delta x^H/2$

$\varepsilon_L = (i\omega/(2D_p^L t_p^L)^{1/2} \cdot \Delta x^L/2$

$t_p^H, t_p^L$ are the transport numbers for the cation in the high and low mobility zones, respectively

$t_n$ is the transport number of the anion

$z_i$ is the impedance at the $i^{th}$ frequency

$A = \Delta x^L/\Delta x^H$

$B = \frac{D_p^L}{D_p^H}$

$S^H = t_p^H/t_p^H$

$S^L = t_p^L/t_p^L$

$\omega$ is the angular frequency
\[i = (-1)^{1/2}\]

and \(\mu_{p}^{H}\) is the mobility of the cation in the ion selective zone.

For the steady state direct-current conductance, Marshall and Madden have also derived the following equation:

\[
\sigma_{DC} = \frac{F_{\mu}^{H} p m [\frac{1}{t_n} + \frac{A}{B} \frac{t_n^H}{t_n^L}]}{\Delta X_H^H [S_H^H(1+\frac{B}{A}) + S_L^L(1+\frac{A}{B})]} \tag{3.11}
\]

Multiplying (3.10) and (3.11) and taking the inverse gives the induced polarization response at each frequency:

\[
\frac{z_{DC}}{z_i} = \frac{S_H^H(1 + \frac{B}{A}) + S_L^L(1 + \frac{A}{B})}{S_H^L S_L^L \left[\frac{1}{t_n^L} + \frac{A}{B} \frac{t_n^L}{t_n^H}\right]} \cdot \left[\frac{t_n^N + \frac{B t_n^L}{A}}{t_p^N + \frac{t_n^N}{t_p^N} + \frac{\frac{\varepsilon_{H}^H}{\varepsilon_{L}^L} (t_n^N)^2 \tanh L}{(t_n^N)^2 \tanh c_H^L} + \frac{A}{B} \frac{\varepsilon_{L}^L}{\varepsilon_{H}^H} \frac{t_n^N}{t_p^N} \tanh c_H^L}\right]^{-1} \tag{3.12}
\]

To simplify further discussion, it is convenient to replace the transport numbers by diffusion coefficients using the following definition (Moore, 1972):

\[t_p = \lambda_p / (\lambda_p + \lambda_n) = D_p / (D_p + D_n) \tag{3.13}\]

where \(\lambda_p\), \(\lambda_n\) are the limiting ionic conductances of the cation and anion, respectively.

Substituting (3.13) into (3.12) then gives
The model described above has the property that as the frequency increases, the impedance decreases. This effect is attributed to the fact that when the frequency becomes sufficiently high, the distance traveled by an ion during a half cycle is comparable to or less than the length of the high mobility zone. At and above this frequency, the anions no longer "see" the effect of the constrictions and the impedance decreases very rapidly.

Figure 3.12 shows this effect in a set of impedance curves computed from (3.14) for a range of parameters applicable to the tuffs. Both the high and low mobility zone lengths were assumed to be 0.1 µm. Note also that the free aqueous diffusion coefficients were used rather than the effective diffusion coefficients so that the induced polarization could be compared to the observed curves in Figure 3.10 to estimate zone lengths and transport numbers for the tuffs. Obviously, the measured curves do not match any of the theoretical curves. This is due to the fact that the model assumes a uniform zone length, while each tuff sample contains a wide range of zone lengths. This nonuniformity spreads the impedance effect over a broad range of frequencies. Nevertheless, the frequency effects predicted by the model using reasonable estimates of the zone length and diffusion coefficients support
Figure 3.12. Theoretical changes in a-c impedance with frequency for a typical NTS tuff sample.
the proposition that the observed frequency effects are caused by restricted ion mobility in the necks of pores.

Despite the failure of the model to match the observed impedance curves, some information can still be gleaned from these data. In theory, when the frequency becomes very high, the impedance will reach a plateau value after which the effect of the constrictions on ion mobility will no longer be seen. At this point, the apparent tortuosity, $T$, in (3.4) should approach the true tortuosity, $\tau$. Assuming that the constrictivity, $\alpha$, goes to 1 as the frequency increases, the bulk resistance at high frequency is related to the pore-fluid resistivity by

$$\rho_{AC} = (\tau/\theta)\rho_c$$  \hspace{1cm} (3.15)

while the direct-current resistivity (from (3.9)) is related to the pore fluid resistivity by

$$\rho_{DC} = \tau/(\alpha\theta)\rho_c$$  \hspace{1cm} (3.16)

Combining (3.15) and (3.16) then allows the constrictivity to be computed from the relative impedance at high and low frequencies:

$$Z_{AC}/Z_{DC} = \alpha$$  \hspace{1cm} (3.17)

Using (3.17), the minimum contribution of restricted anion mobility to the constrictivity factor was computed from the maximum frequency effect measured for the tuff samples. The values of $\alpha$ computed in this way are listed in Table 3.4. These values range from 0.88 to 0.99 and are an estimate of the maximum value of the
<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity</th>
<th>Median Diameter (μm)</th>
<th>D_{Avg}</th>
<th>a/τ²</th>
<th>α</th>
<th>τ</th>
<th>log δd</th>
</tr>
</thead>
<tbody>
<tr>
<td>U12GRNM 9 (0.8-1.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE A</td>
<td>0.42</td>
<td>0.04</td>
<td>10.3</td>
<td>0.98</td>
<td>0.99</td>
<td>1.0</td>
<td>0.88</td>
</tr>
<tr>
<td>U12GRNM 9 (0.8-1.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE B</td>
<td>0.45</td>
<td>0.05</td>
<td>13.3</td>
<td>0.74</td>
<td>0.99</td>
<td>1.16</td>
<td>-</td>
</tr>
<tr>
<td>U12GRNM 9 (5.9-6.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIDE B</td>
<td>0.45</td>
<td>0.03</td>
<td>4.4</td>
<td>0.17</td>
<td>0.94</td>
<td>2.4</td>
<td>0.45</td>
</tr>
<tr>
<td>U12GRNM 9 (16.2-17.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE A</td>
<td>0.48</td>
<td>0.03</td>
<td>20.7</td>
<td>0.81</td>
<td>0.99</td>
<td>1.1</td>
<td>1.96</td>
</tr>
<tr>
<td>G1-2290 SAMPLE A</td>
<td>0.24</td>
<td>0.09</td>
<td>3.3</td>
<td>0.24</td>
<td>0.88</td>
<td>1.9</td>
<td>2.03</td>
</tr>
<tr>
<td>G1-2290 SAMPLE B</td>
<td>0.34</td>
<td>0.07</td>
<td>3.8</td>
<td>0.17</td>
<td>0.88</td>
<td>2.28</td>
<td>2.5</td>
</tr>
<tr>
<td>G1-2333 SAMPLE A</td>
<td>0.36</td>
<td>0.27</td>
<td>1.0</td>
<td>12.4</td>
<td>0.31</td>
<td>0.93</td>
<td>1.7</td>
</tr>
<tr>
<td>G1-2698 SAMPLE A</td>
<td>0.22</td>
<td>0.01</td>
<td>0.008</td>
<td>4.99</td>
<td>&gt;1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sample</td>
<td>Porosity total</td>
<td>&gt;.1µm</td>
<td>Median pore Diameter (µm)</td>
<td>$d_{Avg}$</td>
<td>$a/\tau^2$</td>
<td>$a$</td>
<td>$\tau$</td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
<td>-------</td>
<td>---------------------------</td>
<td>-----------</td>
<td>------------</td>
<td>----</td>
<td>-------</td>
</tr>
<tr>
<td>GL-2840</td>
<td>0.24</td>
<td>0.17</td>
<td>0.36</td>
<td>4.65</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE A</td>
<td>0.19</td>
<td>0.16</td>
<td>0.33</td>
<td>4.01</td>
<td>0.17</td>
<td>0.88</td>
<td>2.3</td>
</tr>
<tr>
<td>YM-45</td>
<td>0.21</td>
<td>0.20</td>
<td>1.66</td>
<td>4.93</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE A</td>
<td>0.21</td>
<td>0.20</td>
<td>1.66</td>
<td>4.93</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average $a/\tau^2$  
"G" Tunnel: 0.84 ± 0.25  
Yucca Mountain: 0.21 ± 0.05

Average $a$  
"G" Tunnel: 0.97 ± 0.06  
Yucca Mountain: 0.89 ± 0.06

Average $\tau$  
"G" Tunnel: 1.09 ± 0.16  
Yucca Mountain: 1.97 ± 0.64
constrictivity factor because the maximum frequency effect had not been reached at 100 Hz.

**Discussion of Experimental Results**

The primary purpose of the experimental measurements described above was to measure the rock properties which must be known to model matrix diffusion in the tuffs. In addition, the experimental results provide a basis for evaluating the extent to which effective matrix diffusion coefficients can be predicted from free aqueous diffusion coefficients and the properties of the rock as defined by

\[
D_e = (\theta a/\tau^2)D_0
\]  

(3.18)

The properties of samples for which porosity, pore-size distribution, effective diffusion coefficients, and resistance measurements have been made are listed in Table 3.4. The mean effective diffusion coefficients listed in this table were computed from the diffusion coefficients measured for all of the halide and pseudo-halide (SCN⁻) salts using conductivity techniques. The values for the geometric factor \((a/\tau^2)\) were computed by dividing the effective diffusion coefficient by the greater than 0.1 μm porosity \((\theta_{0.1})\) and a free aqueous diffusion coefficient of \(1.5 \times 10^{-5} \text{ cm}^2/\text{s}\) typical of sodium halide salts. The reasons for computing the geometric factor from \(\theta_{0.1}\) rather than from the total porosity will be explained later. The use of a single sodium halide diffusion coefficient is justified because the sodium salts of halides and pseudo-halides have free aqueous diffusion coefficients which differ by less than 5% (Robinson and Stokes, 1959).
The values of tortuosity (τ) listed in Table 3.4 were computed using the constrictivity values (α) determined from the induced polarization tests and the geometric factors determined from the diffusion experiments.

Porosity

The average effective diffusion coefficients are plotted versus total porosity in Figure 3.13. As would be expected, the diffusion coefficients show a positive correlation with the total porosity, although the correlation is far from perfect. The regression lines shown in this figure are subject to considerable uncertainty despite the relatively high correlation coefficients. This uncertainty is due not only to experimental error in the diffusion coefficients, but also to the limited amount of data and the influence of factors other than porosity on the effective diffusion coefficients.

An interesting feature of these results is the positive x-intercept of the regression lines. Clearly, the regression lines should pass through the origin when the porosity is zero. This observation probably cannot be explained by experimental error because most sources of error (such as leakage around the tuff disc, detector drift) result in overestimates of the diffusion coefficient. Such overestimates would, in turn, result in a finite value of the diffusion coefficient at zero porosity (positive y-intercept). We take these data to imply that the effective diffusion porosity is less than the total porosity due to occluded pores or ion exclusion from small pores. For the "G" tunnel samples, the effective porosity may be as little as
Figure 3.13. Average effective diffusion coefficients plotted versus total porosity.
15% of the total porosity. In the Yucca Mountain samples, the effective porosity may be as little as 35% of the total.

To test this hypothesis, the effective diffusion coefficients were plotted versus the porosity measured for pores greater than 0.1 μm diameter determined by mercury porosimetry (Figure 3.14). As can be seen, this change in independent variable has relatively little effect on the slopes of the regression lines, but moves the x-intercept closer to zero for both the "G" tunnel and Yucca Mountain samples. Use of $\Phi_{0.1}$ in equation (3.18) is therefore more appropriate than using the total porosity.

Constrictivity and Tortuosity

The geometric rock properties, other than porosity, controlling the effective diffusion coefficients are the constrictivity and tortuosity factors. The combined geometric factor, $\alpha/\tau^2$, can be directly computed from the effective diffusion coefficients and the effective porosity using (3.18). For the "G" Tunnel samples, excluding U12G RNM 9(5.9-6.4'), the mean geometric factor is $0.84 \pm 0.25$ at the 95% confidence level. The geometric factor for the Yucca Mountain samples (excluding G1-2698 which had an anomalously low $\Phi_{0.1}$) was $0.21 \pm 0.05$.

The maximum constrictivity factors, computed independently from the electrical measurements, also differ between the "G" Tunnel and Yucca Mountain samples. The "G" Tunnel samples showed very little induced polarization (IP) response (Figure 3.10) and consequently have $\alpha$'s very close to 1 ($\bar{\alpha} = 0.97 \pm 0.06$) whereas the Yucca Mountain samples had a greater IP response and smaller $\alpha$'s ($\bar{\alpha} = 0.89 \pm 0.06$).
Figure 3.14. Average effective diffusion coefficient plotted versus greater than 0.1 μm porosity.
Likewise, the mean tortuosity factor ($\tau$) for the "G" Tunnel samples is less than that of the Yucca Mountain samples by almost a factor of 2 (1.1 compared to 2.0). Within each of these groups, the variance of the geometric factor is largely due to variations in the tortuosity.

The differences in the geometric factors and effective diffusion coefficients between the "G" Tunnel and Yucca Mountain samples described above can largely be explained by the lithologic differences between the sites. The "G" Tunnel samples are all non-welded tuffs with a very uniform matrix disrupted only by occasional zeolite phenocrysts. This visual uniformity is supported by the relatively small graphic standard deviations ($\delta d$) for the pore size distribution shown in Table 3.4. The median pore diameter for the "G" Tunnel samples is also relatively small. The Yucca Mountain samples, on the other hand, are moderately to densely welded, contain abundant lithic fragments, and are much more heterogeneous in appearance. This heterogeneity is also revealed in their larger graphic standard deviations. The Yucca Mountain samples also have larger median pore diameters than the "G" Tunnel samples. The greater heterogeneity of the Yucca Mountain samples probably accounts for their greater constrictivity and tortuosity than the "G" Tunnel samples. Their larger median pore diameter, however, accounts for a greater fraction of the porosity being effective.
CHAPTER 4

NUMERICAL MODEL OF MULTICOMPONENT MATRIX DIFFUSION

As discussed in Chapter 2, multicomponent diffusion effects add a complexity to the problem of matrix diffusion which has not been addressed in previous work. The purpose of this chapter is to develop multicomponent diffusion flux equations in a form suitable for incorporation into a numerical model of matrix diffusion of reactive, ionic species.

Multicomponent Diffusion Equations

Consider a dilute, isothermal aqueous solution defined by \( n = 1, 2, \ldots, N \) thermodynamic component ions. The component ions may combine to form \( m = 1, 2, \ldots, M \) complex aqueous species according to the generalized reaction for the \( m^{th} \) complex species:

\[
(C_1^{\nu_{m1}} C_2^{\nu_{m2}} \cdots C_J^{\nu_{mJ}} A_1^{\nu_{m1}} A_2^{\nu_{m2}} \cdots A_K^{\nu_{mK}})^{z_m}
\]

\[\mp \sum \nu_{mj} C_j + \sum \nu_{mk} A_k \quad (4.1)\]

where \( C_j ; j = 1 \) to \( J \) are cationic component ions,

\( A_k ; k = 1 \) to \( K \) are anionic component ions,

\( N = J + K, \)

\( \nu_{mj}, \nu_{mk} \) are the stoichiometric coefficients of the component ions in the \( m^{th} \) reaction,

\( z_m \) is the charge of the \( m^{th} \) complex species.
Although diffusion in such a solution could be modeled by computing the diffusion fluxes of all the \( N + M \) diffusing species, this direct approach is numerically inconvenient because of the potentially large number of equations which must be solved. Because the composition of the solution is completely defined by the component ions, the computational effort can be reduced by considering only the total fluxes of the component ions. The purpose of this section is to develop these total component diffusion equations.

Assuming that the mole fraction of \( \text{H}_2\text{O} \) is constant and following the development of Wendt (1965), the chemical potentials of the complex species are given by

\[
\mu_m = \sum_{n=1}^{N} \nu_{mn} \mu_n
\]  

(4.2)

or in matrix notation

\[
\mu_C = \tilde{\nu} \mu_I
\]  

(4.3)

where \( \mu_C \) is the column matrix of chemical potentials of the aqueous complexes, 

\( \mu_I \) is the column matrix of chemical potentials of the ionic components, 

and \( \tilde{\nu} \) is a matrix of stoichiometric coefficients for the component ions.

Using (4.3), the potential gradients of the complexes are related to the gradients of the component ions by
\[ \nabla \mu_C = \nabla \mu_I \]  

(4.4)

For conservation of charge, we also require that

\[ z_C = \nabla z_I \]  

(4.5)

The molar diffusion fluxes of all the species (component ions and complexes) in the solvent-fixed reference frame are given by (Wendt, 1965)

\[ \mathbf{J}^* = \tilde{L}^* ( \nabla \bar{\mu}^* + \bar{z}^* f \mathbf{E} ) \]  

(4.6)

where \( \mathbf{J}^* \) is the column matrix of species diffusion fluxes,

\( \tilde{L}^* \) is the matrix of phenomenological coefficients,

\( f \) is \( 10^7 \) times Faraday's constant,

\( \bar{\mu}^* \) is the column matrix of species chemical potentials,

\( \mathbf{E} \) is the local electrical field,

and \( \bar{z}^* \) is the column matrix of species charges.

For the case of no external electrical fields, the condition for no net electrical current is

\[ \bar{z}^T \mathbf{J}^* = 0 \]  

(4.7)

where the T superscript indicates the transpose of a matrix.

Multiplying both sides of (4.6) by \( \bar{z}^T \) gives

\[ \bar{z}^T \mathbf{J}^* = \bar{z}^T \tilde{L}^* \nabla \bar{\mu}^* + f \mathbf{E} \bar{z}^T \tilde{L}^* \bar{z}^* \]  

(4.8)

and by (4.7)
0 = \bar{z}^* \bar{I}^* \nabla \mu^* + fE \bar{z}^* \bar{T}^* \bar{I}^* z^* \nabla \mu^* \tag{4.9}

By rearranging (4.9) we obtain

\[ fE = \frac{-z^* \bar{I}^* \bar{T}^* \nabla \mu^*}{\bar{z}^* \bar{T}^* \bar{I}^* z^*} \tag{4.10} \]

Substituting (4.10) into (4.6) then gives

\[ \bar{I}^* = \bar{L}^* \left( \nabla \mu^* - \frac{z^* \bar{z}^* \bar{I}^* \bar{T}^* \nabla \mu^*}{z^* \bar{T}^* \bar{I}^* z^*} \right) \tag{4.11} \]

Applying the distributive law to the last term in (4.11) yields

\[ \bar{I}^* = \left[ \bar{L}^* - \frac{\bar{L}^* \bar{z}^* z^* \bar{T}^* \nabla \mu^*}{z^* \bar{T}^* \bar{I}^* z^*} \right] \nabla \mu^* \tag{4.12} \]

which is a relatively simple form for the species fluxes. This equation defines the fluxes of all the species actually existing in the solution, whether they be aqueous forms of the component ions or complex species.

In order to reduce the number of flux equations which must be solved, we wish to rearrange (4.12) to obtain the total fluxes of the component ions. By conservation of mass, the total fluxes of the component ions are given by

\[ \bar{I}_T = \bar{I}_I + \bar{v}^t \bar{I}_C \tag{4.13} \]

where column matrices \( \bar{I}_I \) and \( \bar{I}_C \) have the form
The column matrix of species fluxes, \( \mathbf{\bar{J}} \), can then be written in terms of the ionic component fluxes, \( \mathbf{\bar{J}}_I \), and the complex species fluxes, \( \mathbf{\bar{J}}_C \):

\[
\mathbf{\bar{J}}^* = \mathbf{\bar{J}}_I + \mathbf{\bar{J}}_C
\]

and

\[
\mathbf{\bar{J}}^* - \mathbf{\bar{J}}_I = \mathbf{\bar{J}}_C
\]

By similarly filling out \( \nabla \mu_I \) and \( \nabla \mu_C \) so that \( \nabla \mu^* = \nabla \mu_I + \nabla \mu_C \), (4.12) can be rewritten as

\[
\mathbf{\bar{J}}^* = \mathbf{\bar{L}}^* - \mathbf{\bar{L}}^* \frac{z^* z^T \mathbf{\bar{L}}^*}{z^T \mathbf{\bar{L}}^* z^*} \nabla \mu_I
\]

\[
+ \left[ \mathbf{\bar{L}}^* - \mathbf{\bar{L}}^* \frac{z^* z^T \mathbf{\bar{L}}^*}{z^T \mathbf{\bar{L}}^* z^*} \right] \nabla \mu_C
\]

In the absence of any complex formation, (4.16) becomes

\[
\mathbf{\bar{J}}^* = \mathbf{\bar{J}}_I = \left[ \mathbf{\bar{L}}^* - \tilde{\beta} \right] \nabla \mu_I
\]

where

\[
\tilde{\beta} = \left[ \frac{\mathbf{\bar{L}}^* z^* z^T \mathbf{\bar{L}}^*}{z^T \mathbf{\bar{L}}^* z^*} \right]
\]
The first term on the right hand side of (4.16) can now be substituted into (4.13) for \( \overline{J}_I \) and the second term for \( \overline{J}_C \) to give

\[
\overline{J}_T = (\overline{L}^* - \overline{\beta}) \overline{\nabla \mu}_I + \overline{\nabla} \left[ (\overline{L}^* - \overline{\beta}) \overline{\nabla \mu}_C \right] \tag{4.18}
\]

The chemical potentials in (4.18) can be then eliminated by the transformation (Cullinan, 1965)

\[
\overline{\mu}_I = \eta \overline{\nabla M}_I
\]

\[
\overline{\mu}_C = \eta \overline{\nabla M}_C
\]

where \( \overline{M}_I \) and \( \overline{M}_C \) are the column matrices of the molar concentrations of the ionic components and complex species, respectively. Equation (4.15) can now be written in terms of molar concentration gradients as

\[
\overline{J}_T = (\overline{L}^* - \overline{\beta}) \eta \overline{\nabla M}_I + \overline{\nabla} \left[ (\overline{L}^* - \overline{\beta}) \eta \overline{\nabla M}_C \right] \tag{4.20}
\]

The molarities of the complexes can then be related to the component ion molarities by

\[
\overline{\nabla M}_C = \lambda \overline{\nabla M}_I \quad ; \quad \lambda_{kj} = (\partial M_j / \partial M_k)_{T,P,M_k} \quad ; \quad k \neq j \tag{4.21}
\]

Substituting (4.21) into (4.20) yields

\[
\overline{J}_T = \left[ (\overline{L}^* - \overline{\beta}) \eta \right] \overline{\nabla M}_I + \overline{\nabla} \left[ (\overline{L}^* - \overline{\beta}) \eta \lambda \right] \overline{\nabla M}_I \tag{4.22}
\]

or

\[
\overline{J}_T = \tilde{D} \overline{\nabla M}_I \tag{4.23}
\]

where \( \tilde{D} \) is the diffusion coefficient matrix for the component ions defined from (4.22) as
\[ \tilde{\Gamma} = \{ [\tilde{L}^* - \tilde{\beta}] \tilde{\eta} + \tilde{\gamma} \} \{ [\tilde{L}^* - \tilde{\beta}] \tilde{\eta} \tilde{\lambda} \} \]

The terms in \( \tilde{\eta} \) can be derived from the definition of the chemical potential for the \( i \)th ion (Haase, 1969):

\[ \mu_i = \mu_i^0 + RT \ln(y_iM_i) \]  \hspace{1cm} (4.24)

where \( y_i \) is the activity coefficient of the \( i \)th ion,
\( \mu_i^0 \) is the chemical potential of the \( i \)th ion in its standard state,
and \( R \) is the gas constant.

Differentiating (4.24), gives

\[ d\mu_i = \left( \frac{RT}{y_i} \right) d\gamma_i + \left( \frac{RT}{M_i} \right) dM_i \]  \hspace{1cm} (4.25)

and taking the partial with respect to \( M_j \) yields

\[ \left( \frac{\partial \mu_i}{\partial M_j} \right)_{T,P,M_k} = RT \left( \frac{\partial \ln \gamma_i}{\partial M_j} \right)_{T,P,M_k} \]
\[ + \frac{RT}{M_i} \left( \frac{\partial M_i}{\partial M_j} \right)_{T,P,M_k} \]  \hspace{1cm} (4.26)

where \( k \neq i,j \).

The first term on the right hand side of (4.26) can be evaluated for dilute solution by using the Debye–Huckel equation:

\[ \ln \gamma_i = \frac{-\frac{1}{2} A_{ij} \frac{I^{1/2}}{1 + a_iB I^{1/2}}}{I^{1/2}} \]  \hspace{1cm} (4.27)

where \( I \) is the ionic strength of the solution, and \( A_i, a_i, \) and \( B \) are constants. The ionic strength is defined as
\[
I = \frac{1}{2} \sum (M_k z_k^2)
\]

where the summation is taken over all of the aqueous species.

Differentiating (4.27) gives

\[
d \ln \gamma_i = \left[\frac{-2 A z_i^2}{I^{1/2} (1 + a_i B I^{1/2})^2}\right] dI
\]

(4.28)

From the definition of \( I \) when the concentrations of all the species but the \( j \)th are constant, the derivative of \( I \) is

\[
dI = \frac{1}{2} z_j^2 dM_j
\]

(4.29)

Substituting (4.29) into (4.28) and rearranging gives

\[
(\partial \ln \gamma_i / \partial M_j) = \frac{-2 A z_i^2 z_j^2}{I^{1/2} (1 + a_i B I^{1/2})^2}
\]

(4.30)

For very dilute solutions, (4.30) can be approximated by

\[
(\partial \ln \gamma_i / \partial M_j) = \frac{-Az_i z_j^2}{I^{1/2}}
\]

(4.31)

and so

\[
(\partial \ln \gamma_i / \partial M_j) = (\partial \ln \gamma_j / \partial M_i)
\]

(4.32)

because the partial derivative is a constant and depends only on the charges of the \( i \)th and \( j \)th species.

Now considering the second term on the right hand side of (4.26), \( M_i \) is the actual molar concentration of the \( i \)th ionic component.
(and not its stoichiometric or analytic concentration), therefore $M_i$ is not a function of $M_j$ and

$$\left(\frac{\partial M_i}{\partial M_j}\right) = 0 ; \left(\frac{\partial M_i}{\partial M_i}\right) = 1$$  \hspace{1cm} (4.33)

Thus, the components of $\tilde{\eta}_I$ are determined from (4.31) and (4.33) to be:

$$\eta_{ij} = \delta_{ij} \frac{RT}{M_i} - A_{ij}^2 \frac{z_i^2}{I^{1/2}}$$  \hspace{1cm} (4.34)

where $\delta_{ij}$ is the Kronecker delta (1 if $i=j$, 0 if $i\neq j$).

The terms in $\lambda$ in (4.22) can be derived from the mass action equation for the $k^{th}$ complex species written in terms of the component ions:

$$M_k = \frac{1}{\gamma_k} K \prod_{n=1}^{N} (\gamma_n M_n)^{\nu_{kn}}$$  \hspace{1cm} (4.35)

where $K$ is the equilibrium constant.

Differentiating (4.35) with respect to each $M_j$ gives the components of $\tilde{\lambda}$ (Wendt, 1965):

$$\frac{\partial M_k}{\partial M_j} = \frac{K}{\gamma_k} \nu_{kj} M_j \prod_{n=1}^{N} (\gamma_n M_n)^{\nu_{kn}} n \neq j$$  \hspace{1cm} (4.36)

The use of equation (4.22) to compute the diffusion fluxes is useful only if the phenomenological coefficients are known or can be computed. Anderson and Graf (1978) reviewed and tested various methods for computing the components of $\tilde{L}$. In particular, they reviewed and refined the models of Lane and Kirkaldy (1966) and Wendt (1965). Although the kinetic models of Lane and Kirkaldy proved to be more accurate than Wendt's model, Anderson and Graf doubted that the
site-exchange mechanism postulated by Lane and Kirkaldy is applicable to solutions of weak electrolytes. For this reason, the simpler method of Wendt was used for computing the phenomenological coefficients.

Assuming that the off-diagonal coefficients of $\hat{L}^*$ are zero (Wendt, 1965), then the diagonal terms for the charged species are given by

$$L^*_i = \Gamma_i M_i / (|z_i| f)$$  \hspace{1cm} (4.37)

where $\Gamma_i$ is the limiting ionic conductivity of the $i^{th}$ charged species.

The phenomenological coefficients for neutral complex species are computed directly from their tracer diffusion coefficients by

$$L^*_i = D'_i M_i / RT$$

where $D'_i$ is the tracer diffusion coefficient of the $i^{th}$ uncharged species.

Equation (4.22) describes the free-aqueous multicomponent diffusion fluxes, but is not appropriate for describing the macroscopic diffusion fluxes through a porous medium. As discussed in the previous chapters, numerous models have been proposed to describe the relationship between the free-aqueous diffusion coefficients and the effective diffusion coefficients in a saturated porous medium. The relationship adopted in this work is given in Chapter 2, equation (2.22) as

$$D_o = (\theta_m a / \tau^2) D_o$$  \hspace{1cm} (4.38)
Although the porosity and tortuosity terms may be regarded as properties only of the porous medium, the constrictivity term, \( a \), may be dependent on both the medium and on the colligative and compositional properties of the solution. If we assume that \( a \) affects the limiting ionic conductances of the charged species in the same way that it affects the diffusion coefficients, then we can compute phenomenological coefficients in the porous medium using (4.38) and letting \( L_{mii}^* = a_i L_{ii}^* \) where \( L_{mii}^* \) is the coefficient in the porous medium. The ionic flux equations for the porous medium then become

\[
\bar{J}_T = \left( \bar{L}_m^* - \bar{\beta}_m \right) \bar{\eta} + \bar{v}^T \left( \bar{L}_m^* - \bar{\beta}_m \right) \bar{\eta} \lambda \ \nabla m \_I \quad (4.39)
\]

**Numerical Model of Multicomponent Matrix Diffusion**

A numerical model was developed to investigate the importance of multicomponent diffusion effects in porous media. Although the numerical model was developed to include the effects of advection, hydrodynamic dispersion, molecular diffusion in the rock matrix, and equilibrium aqueous phase chemical reactions, only the diffusion and chemical equilibrium capabilities of the model were utilized in this research. The other capabilities of the model have not been fully verified and will not be discussed. The integrated finite-difference method (Narasimhan and Witherspoon, 1976) was chosen to solve the governing partial differential equations.

The mathematical problem to be solved is governed by the following continuity equation for transport in a porous medium:
\[
\bar{C} \frac{\partial \bar{M}_T}{\partial t} = \nabla \cdot \bar{I}_{TD} + \bar{S}_T
\]  
(4.40)

where \( \bar{I}_{TD} \) is the column matrix of total diffusion fluxes of the components,

\( t \) is time,

\( \bar{S}_T \) is the column matrix of total component source/sink terms,

and \( \bar{C} \) is the column matrix of capacity terms which relate the change in mass per unit matrix volume to the change in concentration.

As discussed in the previous section, the total diffusion fluxes are given by

\[
\bar{I}_{TD} = -(\phi_{meu}/\tau^2) \bar{D}_M \nabla \bar{M}_I = -\bar{D}_e \nabla \bar{M}_I
\]  
(4.41)

Because we wish to solve (4.40) for the total ionic concentrations, the actual concentration gradients in (4.41) are related to the total concentrations by

\[
\bar{M}_i = B_{ii} \bar{M}_T \bar{i}
\]  
(4.42)

or

\[
\bar{M}_I = \bar{B} \bar{M}_T
\]  
(4.43)

where \( \bar{M}_T \) is the total or analytic concentration of the \( i \)th component,

\( \bar{M}_i \) is the actual concentration of the \( i \)th species,

\( B_{ii} \) is \( M_i/M_T \)

and \( \bar{B} \) is a diagonal matrix.
Substituting (4.41) into (4.40) gives

\[ \bar{C} \frac{\partial \bar{M}_T}{\partial t} = -\nabla \cdot \bar{D}_0 \nabla \bar{M}_T + \bar{S}_T \]  (4.44)

Equation (4.44) governs the movement of the N ionic components of which one flux is completely determined by the electroneutrality constraints

\[ z^T \bar{J}_{TD} = 0 \]  (4.45)

and

\[ z^T \bar{M}_T = 0 \]  (4.46)

so that only N-1 conservation equations need to be solved.

Although equation (4.44) could be solved directly, a further simplification and reduction in computational effort can be achieved by diagonalizing the diffusion coefficient matrix. Toor (1964a, 1964b) and Cullinan (1965) have shown that if \( \bar{D} \) is independent of concentration and if the Onsager relationships hold, then a nonsingular matrix \( \bar{T} \) exists such that

\[ \bar{T}^{-1} \bar{D} \bar{T} = \bar{D}_\psi \]  (4.47)

where \( \bar{D}_\psi \) is a diagonal matrix of "combine" diffusion coefficients. The columns of \( \bar{T} \) are the components of the eigenvectors of \( \bar{D} \) and the combine diffusion coefficients are the eigenvalues of \( \bar{D} \). In the case of N nonreactive ionic components, this transformation results in a combine diffusion coefficient matrix of the form (see Appendix E for further examples).
and the combines diffuse independently of each other. In this case, both the ionic diffusion coefficients and the combine diffusion coefficients vary little with concentration.

For the case of reactive components, that is, those that form complexes or ion pairs, a closed form proof that the resulting diffusion coefficient matrix can be diagonalized has not been presented in the literature. Toor (1964a, 1964b), however, discusses diagonalization of such matrices in passing. In practice, all of the diffusion coefficient matrices for reactive components considered in this study could be diagonalized, even though the resulting matrix is slightly different from that of the nonreactive case.

Typically, the reactive combine matrices have the form

\[
\tilde{D} = \begin{bmatrix}
D\psi_1 & 0 & 0 & 0 \\
0 & D\psi_2 & 0 & 0 \\
0 & 0 & D\psi_3 & 0 \\
0 & 0 & 0 & D\psi_N
\end{bmatrix}
\]

where one of the diagonal terms represents the diffusional coupling due to reactions between the components. Also, in contrast to the
nonreactive case, both the ionic and combine diffusion coefficients are much more sensitive to concentration.

The diagonalization procedure is applied to the governing transport equation by multiplying both sides of (4.44) by $\tilde{T}^{-1}$ to yield

$$C \frac{\partial (\tilde{T}^{-1} \tilde{m}_T)}{\partial t} = -\nabla \cdot \tilde{T}^{-1} \tilde{D}_c \nabla \tilde{T}^{-1} \tilde{B} \tilde{m}_T + \tilde{T}^{-1} \tilde{S}_T$$  \hspace{1cm} (4.48)

A new set of combine concentrations can be defined as

$$\tilde{\psi}_T = \tilde{T}^{-1} \tilde{m}_T$$  \hspace{1cm} (4.49)

and

$$\tilde{\psi} = \tilde{T}^{-1} \tilde{m}_I = \tilde{B} \tilde{\psi}_T$$  \hspace{1cm} (4.50)

and the combine source terms as

$$\tilde{S}_\psi = \tilde{T}^{-1} \tilde{S}_T$$  \hspace{1cm} (4.51)

Using (4.49) and (4.51), (4.48) can be rewritten as

$$C \frac{\partial \tilde{\psi}_T}{\partial t} = -\nabla \cdot \tilde{B}_\psi \nabla \tilde{\psi}_T + \tilde{S}_\psi$$  \hspace{1cm} (4.52)

where we note that $\tilde{B}_\psi$ is the identity matrix for nonreactive components, but is a full matrix if aqueous chemical reactions are present. The terms in $\tilde{B}_\psi$ are computed from the total concentrations of the components and the equilibrium constants of the appropriate aqueous complexation reactions using the algorithm described in Appendix F.

Equation (4.52) is discretized using the integrated finite-difference method and solved using an adaptive implicit-explicit point iterative algorithm adapted from Edwards (1972) and Neuman and
Narasimhan (1977). The integrated finite-difference method (IFDM) has also been used by Rasmussen, Narasimhan and Neretnieks (1982) to study similar problems of matrix diffusion in fractured rocks.

Application of IFDM to (4.52) involves dividing the transport domain into a finite number of polyhedral cells and solving a set of mass balance equations for each cell. Following the development of Narasimhan and Witherspoon (1976), the mass balance equations for the diffusive fluxes are formulated by first integrating equation (4.52) over a finite subregion, \( V \), of the transport domain:

\[
\int_V \nabla \cdot \mathbf{D} \nabla \bar{\psi} T - \bar{S} \psi \, dV = 0
\]  

(4.53)

Assuming \( \bar{\psi} T \) to be constant over \( V \), (4.53) can be rewritten as

\[
CV \frac{\partial \bar{\psi} T}{\partial t} = \int_V \left[ -\nabla \cdot \mathbf{D} \nabla \bar{\psi} T + \bar{S} \psi \right] dV
\]  

(4.54)

Applying the divergence theorem, we can convert the right hand side of (4.53) to an integral expression over the surface, \( \Gamma \), of \( V \):

\[
CV \frac{\partial \bar{\psi} T}{\partial t} = \int_\Gamma \mathbf{D} \nabla \bar{\psi} T \cdot \mathbf{n} \, d\Gamma + \bar{S} \psi \, V
\]  

(4.55)

where \( \mathbf{n} \) is the unit vector normal to \( \Gamma \).

In practice, the finite subregion is represented by a polyhedral cell, such as shown in Figure 4.1, which in the current version of the model can have up to six sides. The centroid of the mth cell is represented by the node point \( m \). In Figure 4.1, the node point
Figure 4.1. Schematic diagram of the integrated finite difference grid.
m is associated with node points for the four surrounding cells \((n = 1 \text{ to } 4)\).

For cell \(m\), the mass balance equation for the \(i\)th combine given by (4.55) is discretized as

\[
C_{i,m} V_m \frac{\Delta \psi_{i,m}}{\Delta t} = \sum_n \left[ D_{i,mn} \left( \sum_{j \neq 1} B_{i,j,n} \psi_{j,n} - \sum_{j \neq 1} B_{i,j,m} \psi_{j,m} \right) + D_{i,mn} (B_{i,i,n} \psi_{i,n} - B_{i,i,m} \psi_{i,m}) \right] A_{mn} / L_{mn} + S_{i,m} V_m \tag{4.56}
\]

where \(D_{i,mn}\) is the harmonic mean diffusion coefficient for combine \(i\) across the interface between \(m\) and \(n\),

\(A_{mn}\) is the area of the interface between \(m\) and \(n\),

\(L_{mn}\) is the distance between nodes \(m\) and \(n\).

For sufficiently small time steps, \(\Delta t\), equation (4.56) can be rearranged to give an explicit solution for \(\Delta \psi_{i,m}\) (assuming that all other \(\psi_{j,m}, j \neq i\) are constant for \(\Delta t\)):

\[
\Delta \psi_{i,m} = \frac{\Delta t}{C_{i,m} V_m} \left[ S_{i,m} V_m \right. \\
+ \sum_n \frac{D_{i,mn} A_{mn}}{L_{mn}} \left( \sum_{j \neq 1} B_{i,j,n} \psi_{j,n}^0 - \sum_{j \neq 1} B_{i,j,m} \psi_{j,m}^0 \right) \\
+ \sum_n \frac{D_{i,mn} A_{mn}}{L_{mn}} (B_{i,i,n} \psi_{i,n}^0 - B_{i,i,m} \psi_{i,m}^0) \right] \tag{4.57}
\]

where \(\psi_{i,n}^0\) and \(\psi_{i,m}^0\) are the combine potentials at the beginning of the time step.
Based on the physical arguments given by Neuman and Narasimhan (1977), the maximum time step for which the explicit solution given by (4.57) is stable is

\[ \Delta t_{\text{stab}} \leq C_m V_m \left\{ \sum_n [D_{i,mn} (\sum_j B_{ij,n} \psi^*_j,n) - \sum_j B_{ij,m} \psi^*_j,m] + D_{i,mn} B_{ii,n} \frac{A_{mn}}{L_{mn}} \right\}^{-1} \]  

(4.58)

An implicit solution for (4.56) can also be formulated. In order to simplify future notation, let us drop the subscript for the ith combine and define

\[ G_{mn} = \frac{D_{i,mn} A_{mn}}{L_{mn}} \]  

(4.59)

Letting \( \psi_m = \psi^*_m + \Delta \psi_m \) and \( \psi_n = \psi^*_n + \Delta \psi_n \), (4.56) can be rewritten as

\[ \Delta \psi_m = \frac{\Delta t}{C_m V_m} \{S_m V_m + \sum_n G_{mn} (\sum_j B_{ij,n} \psi^*_j,n) - \sum_j B_{ij,m} \psi^*_j,m \] 

\[ + \sum_n G_{mn} [B_n (\psi^*_n + \Delta \psi_n) - B_m (\psi^*_m + \Delta \psi_m)] \} \]  

(4.60)

Introducing the weighting factor, \( \theta \), (4.60) can be rearranged to give
\[ \Delta \psi_m = \frac{\Delta t}{C_{m}V_{m}} \left\{ S_{m}V_{m} + \sum_{n} G_{mn} \left[ \sum_{j} B_{ij,n} \psi_{j,n} - \sum_{j} B_{ij,m} \psi_{j,m} \right] 
\right.
+ \sum_{n} \left[ G_{mn}B_{n} \psi_{n}^{o} - G_{mn}B_{m} \psi_{m}^{o} \right] \n
+ \Theta \sum_{n} \left[ G_{mn}B_{n} \Delta \psi_{n} - G_{mn}B_{m} \Delta \psi_{m} \right] \] (4.61)

Following the development of Neuman and Narasimhan (1977), the point iterative algorithm is developed by making the following substitutions into (4.61):

\[ \Delta \psi_m \text{ (left side) } \rightarrow \Delta \psi_m^{k+1} \]
\[ \Delta \psi_m \text{ (right side) } \rightarrow (1 + g)\Delta \psi_m^{k+1} - g\Delta \psi_m^k \]
\[ \Delta \psi_n \text{ (right side) } \rightarrow \Delta \psi_n^k \]

where \( k \) is the iteration number and \( g \) is the acceleration factor.

Making these substitutions and combining terms, (4.61) now becomes

\[ \Delta \psi_m^{k+1} = \frac{\Delta t}{C_{m}V_{m}} \left\{ \left(\sum_{n} G_{mn} \left( \sum_{j \neq m} B_{ij,n} \psi_{j,n} - \sum_{j \neq m} B_{ij,m} \psi_{j,m} \right) \right) \n+ \sum_{n} \left( G_{mn}B_{n} \psi_{n}^{o} - G_{mn}B_{m} \psi_{m}^{o} \right) \n
+ \Theta \sum_{n} \left( G_{mn}B_{n} \Delta \psi_{n}^k - gG_{mn}B_{m} \Delta \psi_{m}^k \right) \n
- (1 + g) \Theta \sum_{n} G_{mn}B_{n} \Delta \psi_{n}^{k+1} + S_{m}V_{m} \right\} \] (4.62)

Solving (4.62) for \( \Delta \psi_m^{k+1} \) gives the following iterative algorithm:
\[ \Delta \psi_{m}^{k+1} = \left[ \frac{\Delta t}{C_{m}V_{m}} \left( \sum_{n} G_{mn} \left( \sum_{j \neq 1}^{} B_{ij,n} \psi_{j,n}^{0} - \sum_{j \neq 1}^{} B_{ij,m} \psi_{j,m}^{0} \right) \right) \right] + \sum_{n} \left( G_{mn}B_{n}^{\Delta} \psi_{n}^{k} - G_{mn}B_{m}^{\Delta} \psi_{m}^{k} \right) + \Theta \sum_{n} \left( G_{mn}B_{n}^{\Delta} \psi_{n}^{k} - gG_{mn}B_{m}^{\Delta} \psi_{m}^{k} \right) \]

+ \frac{S_{m} \Delta t}{C_{m}V_{m}} \left[ 1 + \frac{\Delta t}{(1 + g) \Theta \sum_{n} G_{mn}B_{m}} \right] \quad (4.63) \]

Equation (4.63) represents an unconditionally stable, iterative algorithm when \( 0.5 \leq \Theta \leq 1.0 \). The convergence of (4.63) to the correct value for the change in the concentration of the \( i \)th combine is conditioned on the assumption that the term

\[ \sum_{j \neq 1}^{} B_{ij,n} \psi_{j,n}^{0} - \sum_{j \neq 1}^{} B_{ij,m} \psi_{j,m}^{0} \]

can be taken as constant during the time step. This term represents the coupling of diffusional fluxes for reactive components but is zero for nonreacting components where coupling is caused only by electrostatic interactions. In the computer code in which this algorithm is implemented, the time step size is controlled so that the magnitude of the reaction term is less than a user-specified value. In this way, the accuracy of the solution is controlled by the time step size.

Verification of the IκDM solution for a one-dimensional diffusion problem is given in Appendix G.
CHAPTER 5

MULTICOMPONENT EFFECTS IN THE DIFFUSION CELL EXPERIMENTS

As discussed in Chapter 2, multicomponent diffusion effects arise because of the coupling of the diffusion fluxes in multicomponent solutions. The coupling is caused by electrostatic interactions between free ions and by aqueous phase reactions whereby the ionic components combine to form ion pairs or complexes. The purpose of this chapter is to evaluate the extent to which multicomponent diffusion may have affected the results of the diffusion experiments using the multicomponent diffusion model described in Chapter 4. In particular, the possibility that small differences in the experimentally determined diffusion coefficients when selective and non-selective detectors were used were due to differential diffusion of the tracer cation and anion will be examined. This evaluation will focus on the results of a series of diffusion experiments performed on sample G1-2840A using NaI and Na pentafluorobenzoate (PFB).

To evaluate the extent to which simple electrostatic coupling may have resulted in differential diffusion of sodium and either iodide or PFB in the experiments on G1-2840A, the free aqueous diffusion coefficient matrices for these two salts in both distilled water and in J-13 water were computed using the theory presented in Chapter 4. The first case represents simple diffusion of a binary salt where complete coupling exists between the cation and anion. The second case
represents multicomponent diffusion. The calculations for J-13 water were performed assuming that its composition was that reported by Wolfsberg and others (1979) with the chloride content adjusted to assure electrical neutrality of the solution. The J-13 water composition used in the calculations is shown in Table 5.1.

The computed ion diffusion coefficient matrices for NaI and NaPFB in pure water are shown in Table 5.2. The corresponding diffusion coefficient matrices in J-13 water are shown in Tables 5.3 and 5.4. The computed combine diffusion coefficient matrices are also given in these tables. In both cases the diffusion coefficients were computed assuming that all of the ionic components were free ions and using limiting ionic conductances at 25°C reported in Landolt-Bornstein (1969) except of PFB which was experimentally determined (see Appendix C). In the binary case (pure water), the diagonalization process results in a combine diffusion coefficient which is equivalent to the mean salt diffusion coefficient of NaI. In the multicomponent case, a direct correspondence between the combine diffusion coefficients and standard salt diffusion coefficients does not exist.

The simulations of the diffusion cell experiments were performed using the IrD model described in Chapter 4 and a one-dimensional grid. The grid consisted of 17 cells and nodes distributed as shown in Figure 5.1. Cell 1 represented the upper reservoir of the diffusion cell and the computed concentration at node 1 as taken as the concentration in the upper reservoir. The simulations were performed by setting the volume of cell 1 equal to the volume of fluid added to the
Table 5.1. Composition of J-13 water used to compute diffusion coefficient matrices.

<table>
<thead>
<tr>
<th>Species</th>
<th>Total Molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>$2.09 \times 10^{-3}$</td>
</tr>
<tr>
<td>K</td>
<td>$1.20 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ca</td>
<td>$3.20 \times 10^{-4}$</td>
</tr>
<tr>
<td>Mg</td>
<td>$8.00 \times 10^{-5}$</td>
</tr>
<tr>
<td>Cl</td>
<td>$2.10 \times 10^{-4}$</td>
</tr>
<tr>
<td>HCO$_3$</td>
<td>$2.38 \times 10^{-3}$</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>$2.10 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Table 5.2. Ion diffusion coefficient matrix for NaI and NaPFB in pure water.

<table>
<thead>
<tr>
<th>NaI DIFFUSION COEFFICIENTS (1 x 10^{-5} cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>I</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COMBINE DIFFUSION COEFFICIENTS 1 x 10^{-5} cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

NOTE: Zero values in the above matrix are values less than 1 x 10^{-19}

<table>
<thead>
<tr>
<th>NaPFB DIFFUSION COEFFICIENTS (1 x 10^{-5} cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>PFB</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COMBINE DIFFUSION COEFFICIENTS (1 x 10^{-5} cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

NOTE: Zero values in the above matrix are values less than 1 x 10^{-19}
Table 5.3. Ion diffusion coefficient matrix for NaI in J-13 water.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Cl</th>
<th>HCO₃</th>
<th>SO₄</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>.8076</td>
<td>-.7710</td>
<td>-.6109</td>
<td>-.5561</td>
<td>.8013</td>
<td>.4667</td>
<td>.8442</td>
<td>.7971</td>
</tr>
<tr>
<td>K</td>
<td>-.0018</td>
<td>1.953</td>
<td>-.0021</td>
<td>-.0019</td>
<td>.0027</td>
<td>.0016</td>
<td>.0029</td>
<td>.0027</td>
</tr>
<tr>
<td>Ca</td>
<td>-.0038</td>
<td>-.0056</td>
<td>.7805</td>
<td>-.0040</td>
<td>.0058</td>
<td>.0034</td>
<td>.0061</td>
<td>.0058</td>
</tr>
<tr>
<td>Mg</td>
<td>-.0009</td>
<td>-.0013</td>
<td>-.0010</td>
<td>.7042</td>
<td>.0013</td>
<td>.0008</td>
<td>.0014</td>
<td>.0013</td>
</tr>
<tr>
<td>Cl</td>
<td>.0032</td>
<td>.0047</td>
<td>.0038</td>
<td>.0034</td>
<td>2.028</td>
<td>-.0029</td>
<td>-.0052</td>
<td>-.0049</td>
</tr>
<tr>
<td>HCO₃</td>
<td>.0213</td>
<td>.0313</td>
<td>.0251</td>
<td>.0226</td>
<td>-.0325</td>
<td>1.165</td>
<td>-.0343</td>
<td>-.0324</td>
</tr>
<tr>
<td>SO₄</td>
<td>.0034</td>
<td>.0050</td>
<td>.0040</td>
<td>.0036</td>
<td>-.0052</td>
<td>-.0030</td>
<td>1.066</td>
<td>-.0052</td>
</tr>
<tr>
<td>I</td>
<td>.0765</td>
<td>.1123</td>
<td>.0901</td>
<td>.0809</td>
<td>-.1167</td>
<td>-.0680</td>
<td>-.1230</td>
<td>.8615</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.0000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1.619</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1.189</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.073</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.956</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.7062</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.7896</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.033</td>
</tr>
</tbody>
</table>

NOTE: Zero values in the above matrix are values less than $1 \times 10^{-19}$. 
Table 5.4. Ion diffusion coefficient matrix for NaPFB in J-13 water.

<table>
<thead>
<tr>
<th>ION DIFFUSION COEFFICIENTS (1 x 10^{-5} cm^2/s)</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Cl</th>
<th>HCO_3</th>
<th>SO_4</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>.4999</td>
<td>-1.222</td>
<td>-.9813</td>
<td>-.8815</td>
<td>1.271</td>
<td>.7400</td>
<td>1.339</td>
<td>.4507</td>
</tr>
<tr>
<td>K</td>
<td>-.0028</td>
<td>1.952</td>
<td>-.0033</td>
<td>-.0030</td>
<td>.0043</td>
<td>.0025</td>
<td>.0045</td>
<td>.0015</td>
</tr>
<tr>
<td>Ca</td>
<td>-.0060</td>
<td>.0088</td>
<td>.7779</td>
<td>-.0064</td>
<td>.0092</td>
<td>.0054</td>
<td>.0097</td>
<td>.0033</td>
</tr>
<tr>
<td>Mg</td>
<td>-.0014</td>
<td>-.0020</td>
<td>-.0016</td>
<td>.7037</td>
<td>.0021</td>
<td>.0012</td>
<td>.0022</td>
<td>.0007</td>
</tr>
<tr>
<td>Cl</td>
<td>.0051</td>
<td>.0075</td>
<td>.0060</td>
<td>.0054</td>
<td>2.025</td>
<td>-.0046</td>
<td>-.0082</td>
<td>-.0028</td>
</tr>
<tr>
<td>HCO_3</td>
<td>.0338</td>
<td>.0496</td>
<td>.0398</td>
<td>.0358</td>
<td>-.0516</td>
<td>1.154</td>
<td>-.0543</td>
<td>-.0183</td>
</tr>
<tr>
<td>SO_4</td>
<td>.0054</td>
<td>.0079</td>
<td>.0064</td>
<td>.0057</td>
<td>-.0082</td>
<td>-.0048</td>
<td>1.062</td>
<td>-.0029</td>
</tr>
<tr>
<td>I</td>
<td>.4326</td>
<td>.6346</td>
<td>.5094</td>
<td>.4576</td>
<td>-.6597</td>
<td>-.3843</td>
<td>-.6952</td>
<td>.4871</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COMBINE DIFFUSION COEFFICIENTS (1 x 10^{-5} cm^2/s)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.0000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2.030</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1.954</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.191</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.076</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.9230</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.7827</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.7052</td>
</tr>
</tbody>
</table>

NOTE: Zero values in the above matrix are values less than 1 x 10^{-19}. 
Figure 5.1. Structure, boundary and initial conditions used in the IFDM model of the diffusion experiments.
upper reservoir at the start of the diffusion experiment. The initial concentration at node 1 was set to the measured initial concentration in the upper reservoir.

Cell 17 represented the lower reservoir of the diffusion cell. The simulations were started with the volume and concentration in cell 17 equal to those in the lower reservoir. The concentration in cell 17 was allowed to vary, however, just as the concentration in the lower reservoir of the diffusion cell could vary slightly during the actual experiments. The remaining 15 cells and nodes in the grid represented the tuff sample. The initial concentration in these cells was set equal to the initial concentration in the lower reservoir to correspond to the initial condition established during the diffusion cell experiments described in Chapter 3.

The results of numerical simulations of the 2/24/82 diffusion experiment on G1-2840A using NaI as the tracer are shown in Figure 5.2. The detector in this test was an iodide selective electrode so that only the change in iodide concentration was monitored.

The open circles in Figure 5.2 represent the iodide concentration measured in the upper reservoir divided by the initial iodide concentration in the lower reservoir which was 0.050 M. The sudden offset in the observed concentration occurring between 4 and 6 hours is an artifact believed to be caused by diurnal fluctuations in line voltage to the laboratory. Although these shifts did not affect the calculation of the effective diffusion coefficient (which is based on the slope of the curve), they do distort the comparison between the experimental and simulated diffusion curves. To facilitate this
Figure 5.2. Comparison of computed and observed diffusion results using I\(^-\) for G1-2840A (2/24/82).
comparison, each of the observed data points after 6 hours have been
shifted upward (as indicated by the arrows) by a constant relative con-
centration of 0.001.

The solid curve in Figure 5.2 is the simulated diffusion curve
for NaI in distilled water, that is, without multicomponent effects.
This simulation was performed using the ratio of the effective to the
free aqueous diffusion coefficient ($D_e/D_0$) of 0.036 actually computed
from the experimental results, but an total interconnected porosity of
0.135. The experimentally determined total porosity for this sample
was 0.24 and the greater than 0.1 micron porosity was 0.17. The lower
porosity used in the simulations was needed to properly match the early
time data and is consistent the discussion of effective diffusion
porosity in Chapter 3.

The dashed curve in Figure 5.2 is the simulated result when
multicomponent diffusion of the major constituents in J-13 water was
considered using the same $D_e/D_0$ ratio and porosity. As can be seen,
the multicomponent simulation differed substantially from both the
experimental curve and the single component simulation. In order to
match the experimental results in the multicomponent simulation, the
$D_e/D_0$ had to be reduced to 0.033. Using the reduced $D_e/D_0$ caused the
multicomponent simulation to coincide almost exactly with the single
component result.

The reason for this substantial multicomponent effect is not
fully understood. It does not appear to be a numerical artifact of the
model because essentially the same results were obtained when the maxi-
mum change in concentration per time step was reduced from 0.001 to
0.0001 which resulted in a doubling of the number of time steps and presumably an increase in accuracy of the numerical solution. Neither did changing the convergence criterion of the iterative solution cause any significant change in the results. In all the simulations, the charge balance error was less than $10^{-12}$ of the total ionic strength.

Despite the relatively strong multicomponent effect observed in these simulations, the simulated concentrations of $\text{Na}^+$ and $\text{I}^-$ in the upper reservoir were nearly identical, as shown in Figure 5.3. The simulated concentrations of the other constituents remained essentially constant in both the upper and lower reservoirs. This behavior implies that monitoring concentration changes with either an ion selective detector or a non-selective detector should give essentially the same experimental result.

As for concentration profiles within the rock itself, changes in the concentrations of the components other than $\text{Na}^+$ and $\text{I}^-$ were produced in the simulations (Figure 5.4), although none of the component concentrations changed by more than 1% after 25 hours into the simulation. Figure 5.4 also shows that the concentration gradients of $\text{Na}^+$ and $\text{I}^-$ were linear at the end of the test as was assumed when the experimental diffusion coefficients were computed.

The simulated and experimental results for the 5/11/83 test on the same rock sample using NaPFB and a ultraviolet absorption detector are shown in Figure 5.5. As in the previous example, the experimentally determined $D_e/D_0$ ratio worked well in the simulation but the porosity needed adjustment to match the early time data. In this case, the porosity had to be raised to 0.33 although the total porosity for
Figure 5.3. Computed relative concentration of $\text{Na}^+$ compared to computed relative concentration of $\Gamma^-$. 
Figure 5.4. Computed concentrations of component ions across the tuff disc for NaI diffusion test on G1-2804A.
Figure 5.5. Comparison of computed and observed diffusion results using PFB$^-$ for G1-2840A (5/11/85).
this sample measured by mercury infusion after the diffusion experiment was only 0.24. The high apparent porosity value needed in the simulations could be due to experimental error in the early time data.

In contrast to the NaI results, little difference can be seen between the single component and multicomponent simulations for PFB− shown in Figure 5.5. Subtle multicomponent effects were revealed, however, by the numerical simulations. First, noticeable differences were produced in the concentrations of Na+ and PFB− in the upper reservoir. Figure 5.6 shows that Na+ and PFB− did not diffuse exactly in unison and that the Na+ concentration increased more rapidly in the upper reservoir than did the PFB− concentration. The excess Na+ flux was compensated by a counter diffusion of the other cations, primarily Ca+2 and Mg+2, toward the lower reservoir. The deficit in PFB− in the upper reservoir was countered by a buildup of SO4−2. The simulated changes in concentrations of the other components in the upper reservoir were too small to imply that any differences would be observed in the experimental results using a selective detector or a non-selective detector.

The simulated concentration changes within the rock sample are shown in Figure 5.7. Much larger changes were observed in these simulations than in the previous case. Changes in concentration of up to 5% were observed for the divalent species. Similar changes were not observed in the upper and lower reservoirs because of the large water-rock ratio in the experimental apparatus. Although this result does not affect the interpretation of the diffusion experiments, it is interesting because it implies that measurable multicomponent effects
Figure 5.6. Computed relative concentration of Na, compared to computed relative concentration of PFB. 

Relative Concentration of Na in J-13

Relative Concentration of PFB in J-13
Figure 5.7. Computed concentrations of component ions across the tuff disc for NaPFB diffusion test on G1-2804A.
might be observed in diffusion experiments if concentration within the porous medium could be measured.

The results of these numerical simulations of the multicomponent effects in the diffusion cell experiments indicate that the simple electrostatic coupling between the tracer ions and the other native ions has little effect on the interpretation of the experimental results. They also show that either selective or non-selective detectors should yield similar effective diffusion coefficients. The small but measureable diffusion fluxes observed for ionic species with no initial concentration gradients are an interesting secondary observation. Although these secondary fluxes have no effect on the interpretation of the experiments, they could be important in special cases where small concentration changes would result supersaturation of some mineral phases.
CHAPTER 6

EXPERIMENTAL VERIFICATION OF MATRIX DIFFUSION IN FRACTURED TUFF

The range of values of the effective matrix diffusion coefficients and porosities reported in Chapter 3 and the limited multicomponent effects evaluated in Chapter 5 all suggest that matrix diffusion should be an important process affecting the transport of simple ionic species through the fractured tuffs at the NTS. To test this hypothesis, a fracture flow experiment was performed on a section of core from Yucca Mountain containing a single natural fracture.

Experimental Procedure

The fracture flow experiment was performed at Los Alamos National Laboratory using core segment G1-2540 from the USW-G1 test hole at Yucca Mountain. This segment of core contained a natural fracture along which the core had split. The two halves of the core had been repositioned as nearly as possible and the exterior of the core had been sealed with epoxy by Los Alamos National Laboratory Personnel. Prior to the experiment reported here, the core had been soaked in J-13 water for several months and a fracture flow experiment using tritium and technetium had been performed by Robert Rundberg of LANL. The results of this previous experiment are not currently available. The experiment reported here was performed using sodium thiocyanate
(NaSCN), sodium pentafluorobenzoate (NaPFB), and the F2 bacteriophage as tracers.

The experimental apparatus, shown in Figure 6.1, consisted of a 12 cm long by 6.35 cm diameter section of the G1-2540 core. The fracture ran roughly along the longitudinal mid-plane of the core. The circumference of the core had been sealed and plexiglas fluid distribution channels epoxied along the exposed surface of the fracture at each end of the core. Teflon tubing (0.5mm ID) was attached to the plexiglas channels at each end of the core. Flow through the fracture was induced using a low speed peristaltic pump and samples of the effluent were collected in glass sample tubes using an automatic sampler.

The fracture flow experiment was performed using a tracer solution consisting of 485 mg/l of NaSCN (5.99 x 10^-3 M), 203 mg/l NaPFB (2.84 x 10^-3 M), and 10^7 plaque forming units (PFU) per liter of the F2 bacteriophage. The phage was prepared by Mr. Steve Jensen of the University of Arizona who assisted in this experiment. J-13 water was used as the solvent. The tracer test was started by inserting the intake of the peristaltic pump into the tracer solution and speeding-up the pump to move the tracer solution rapidly to the entrance of the fracture. The pump was then slowed to its normal pumping rate which was 0.78 ± 0.1 ml/hr. The tracer solution was pumped into the fracture at a constant rate for approximately sixteen hours after which the intake tube was removed from the tracer solution and inserted into a container of pure J-13 water which was then pumped into the rock.

Samples of the effluent from the fracture were collected by an automatic sampler which collected the samples in glass tubes. The
Figure 6.1. Schematic drawing of the apparatus used for the fracture flow experiment.
sampler functioned by optically counting the number of drops collected in a given sample tube and switching tubes after a prescribed number of drops had fallen into a tube. The time associated with each sample was determined by periodically counting the number of drops falling from the effluent tube in a fixed period of time. Prior to the test, every tenth sample tube had been weighed to the nearest 0.01 g. The pumping rate was determined by reweighing these tubes after the test to determine the mass of sample solution which each contained and converting the tracer mass to volume. By knowing the number of drops in each tube and the drop rate, the flow rate was determined. The number of drops per sample ranged from 10 when sampling was frequent to 50 toward the end of the test.

Analyses of SCN\(^{-}\) and PFB\(^{-}\) were performed by high performance liquid chromatography (HPLC) using procedures described in Appendix C. Because of the small sample volume and the need to stabilize the phage prior to culturing, 0.500 ml of a special phage buffer was added to each sample. The analytical tracer concentration for each sample was converted to the true effluent concentration by correcting for the sample dilution. The need to dilute the samples, however, introduced some error into the analyses.

An additional source of error was inconsistent injection volume by the automatic sampling and injection system in the HPLC. This problem was detected by inconsistent chromatograms produced by duplicate injections of the same sample. Inspection of the chromatograms revealed a persistent extraneous peak which previous experience indicated was due to the relatively high concentration of nitrate in the
J-13 water (approximately 15 mg/l). The nitrate in the J-13 water was therefore used as an internal standard to which the tracer concentrations could be related. By thus relating the chromatographic peak heights of the tracers to the peak height of the nitrate, much of the error due to the inconsistent injection volume was removed. The corrected tracer concentrations and sample times are listed in Table 6.1.

Counting of the bacteriophage tracer was performed independently by Mr. Steve Jensen using facilities provided by Dr. Charles Gerba of the University of Arizona Microbiology Department. The phage concentrations reported by Mr. Jensen are also listed in Table 6.1. Phage concentrations exceeding the injectate solution concentration, $C_o$, are assumed to be due to contamination or to errors introduced by the serial dilutions necessary to bring the sample phage concentration down to countable levels.

**Results and Interpretation**

The resulting tracer breakthrough curves for $\text{SCN}^-$, $\text{PFB}^-$, and the F2 phage are plotted versus cumulative volume eluted in Figures 6.2. Before proceeding with a quantitative evaluation of these breakthrough curves, the rationale behind and problems with the experimental design deserve some discussion. First, the experimental apparatus was designed by LANL personnel who graciously allowed us to use it. Ideally, an experimental apparatus should be designed so that the initial and boundary conditions present in the experiment approximate as closely as possible those of the mathematical model which will be used to analyze the results. The experiment described here does not
Table 6.1. Tracer data from the single fracture flow experiment.

<table>
<thead>
<tr>
<th>Cum. Volume (ml)</th>
<th>Time (hrs)</th>
<th>SCN C/C₀</th>
<th>PFB C/C₀</th>
<th>PHAGE C/C₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.64</td>
<td>-</td>
<td>-</td>
<td>nd</td>
</tr>
<tr>
<td>0.75</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
<td>nd</td>
</tr>
<tr>
<td>1.00</td>
<td>1.28</td>
<td>-</td>
<td>-</td>
<td>nd</td>
</tr>
<tr>
<td>1.25</td>
<td>1.60</td>
<td>-</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>1.50</td>
<td>1.92</td>
<td>nd</td>
<td>nd</td>
<td>0.01</td>
</tr>
<tr>
<td>1.75</td>
<td>2.24</td>
<td>nd</td>
<td>nd</td>
<td>0.63</td>
</tr>
<tr>
<td>2.00</td>
<td>2.56</td>
<td>-</td>
<td>-</td>
<td>0.79</td>
</tr>
<tr>
<td>2.25</td>
<td>2.88</td>
<td>nd</td>
<td>nd</td>
<td>-</td>
</tr>
<tr>
<td>2.50</td>
<td>3.21</td>
<td>0.01</td>
<td>0.01</td>
<td>1.4</td>
</tr>
<tr>
<td>2.63</td>
<td>3.37</td>
<td>0.24</td>
<td>0.25</td>
<td>1.1</td>
</tr>
<tr>
<td>2.88</td>
<td>3.69</td>
<td>0.32</td>
<td>0.32</td>
<td>0.89</td>
</tr>
<tr>
<td>3.00</td>
<td>3.85</td>
<td>0.45</td>
<td>0.47</td>
<td>-</td>
</tr>
<tr>
<td>3.25</td>
<td>4.17</td>
<td>0.54</td>
<td>0.69</td>
<td>0.90</td>
</tr>
<tr>
<td>3.75</td>
<td>4.81</td>
<td>0.62</td>
<td>0.66</td>
<td>3.1</td>
</tr>
<tr>
<td>3.88</td>
<td>4.97</td>
<td>0.55</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>4.13</td>
<td>5.29</td>
<td>0.65</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>4.25</td>
<td>5.45</td>
<td>-</td>
<td>-</td>
<td>0.80</td>
</tr>
<tr>
<td>4.53</td>
<td>5.81</td>
<td>0.50</td>
<td>0.46</td>
<td>3.1</td>
</tr>
<tr>
<td>5.53</td>
<td>7.09</td>
<td>0.74</td>
<td>0.77</td>
<td>-</td>
</tr>
<tr>
<td>11.03</td>
<td>14.14</td>
<td>0.86</td>
<td>0.86</td>
<td>-</td>
</tr>
<tr>
<td>13.03</td>
<td>16.71</td>
<td>0.87</td>
<td>0.88</td>
<td>-</td>
</tr>
<tr>
<td>15.03</td>
<td>19.26</td>
<td>0.86</td>
<td>0.88</td>
<td>-</td>
</tr>
<tr>
<td>16.03</td>
<td>20.55</td>
<td>0.81</td>
<td>0.79</td>
<td>-</td>
</tr>
<tr>
<td>17.03</td>
<td>21.83</td>
<td>0.92</td>
<td>0.94</td>
<td>-</td>
</tr>
</tbody>
</table>

ND  none detected
-  not analyzed
Figure 6.2. Measured tracer concentrations versus volume eluted in the fracture flow experiment.
strictly meet this criterion because its boundary and initial conditions were determined by the pre-existing experimental apparatus and do not exactly match those of any available analytical solution for the single fracture, matrix diffusion problem (such as, Grisak and Pickens, 1981; Tang and others, 1981; or Sudicky and Frind, 1982). Although the boundary and initial conditions could be very closely duplicated by a numerical model, use of a numerical model would complicate interpretation of the experiment due to the possibility of numerical dispersion. As will be discussed later, the boundary conditions in the experiment approximate those assumed in the relatively simple analytical model of Grisak and Pickens (1981) and, therefore, were analyzed using this model.

Second, the experiment was performed with multiple tracers, despite the possibility of introducing multicomponent effects. We had hoped to separate the effects of matrix diffusion from other effects such as dispersion or multiple, discrete flow paths by observing the differences in breakthrough times for the tracers with different free aqueous diffusion coefficients. Obtaining ionic tracers which have significantly different diffusion coefficients and yet are good tracers is difficult because the free aqueous diffusion coefficients of most inorganic ions vary by only a factor of two. This fact was expressed by Cussler (1976) as Toor's Law: All ionic diffusion coefficients are the same. Fortunately, two excellent groundwater tracers, SCN$^-$ and PFB$^-$, were available which have diffusion coefficients of about $1.5 \times 10^{-5}$ cm$^2$/s and $0.9 \times 10^{-5}$ cm$^2$/s, respectively. The bacteriophage was used because it provided a tracer with a much lower diffusion
coefficient than any ionic species. Although the free aqueous diffusion coefficient of the F2 phage is not precisely known, it can be estimated from its size using the Stokes–Einstein equation (Bird, Stewart and Lightfoot, 1960):

\[ D_0 = \frac{kT}{6\pi \eta r} \quad (6.1) \]

where \( D_0 \) is the free aqueous diffusion coefficient
- \( k \) is the Boltzmann constant equal to \( 1.38 \times 10^{-16} \, \text{g cm}^2 \, \text{s}^{-1} \, \text{°K}^{-1} \),
- \( T \) is absolute temperature,
- \( r \) is the radius of the particle,
and \( \eta \) is the dynamic viscosity of water.

Although (6.1) assumes a spherical particle, it may be applied approximately to the phage which is a tailess, symmetrical polyhedron (Appendix C) with a diameter of about \( 3.0 \times 10^{-6} \, \text{cm} \). The free aqueous diffusion coefficient computed from (6.1) is thus about \( 7.3 \times 10^{-8} \, \text{cm}^2/\text{s} \) or about two orders of magnitude less than those of the ionic tracers.

The resulting tracer breakthrough curves were interpreted by matching them to breakthrough curves computed using the analytical solution of Grisak and Pickens (1981). Although the initial and boundary conditions of this model have been described in Chapter 2, they will be repeated here so that they can be compared to the experimental conditions. The initial and boundary conditions assumed by their model are shown in Figure 6.3. Their solution assumes a single fracture contained in a matrix extending to infinity in the direction perpendicular to the fracture plane. The fracture and matrix are assumed to be
Figure 6.3. Boundary and initial conditions in the matrix diffusion model of Grisak and Pickens (1981).
initially free of tracer and the upstream surface of the fracture and
the matrix are assumed to be kept at constant tracer concentration
equal to $C_0$. The tracer concentration across the fracture is further
assumed to be uniform and equal to the tracer concentration in matrix
immediately across the interface between the fracture and the matrix.
The tracer flux is assumed to be purely advective in the fracture and
purely diffusive in the matrix. Given these conditions, the solutions
for the tracer concentration in the fracture and in the matrix are:

$$
\frac{C_f}{C_0} = \text{erfc} \left\{ \frac{[D_e/vb] x}{2[(t-x/v)D_e/\theta_{me}]^{1/2}} \right\} \tag{6.2}
$$

$$
\frac{C_m}{C_0} = \text{erfc} \left\{ \frac{[D_e/vb] x + y}{2[(t-x/v)D_e/\theta_{me}]^{1/2}} \right\} \tag{6.3}
$$

where $C_f$ is the concentration in the fracture,

$C_m$ is the concentration in the matrix,

$C_0$ is the input tracer concentration,

$D_e$ is the effective diffusion coefficient in the matrix,

$v$ is the average fluid velocity in the fracture,

$b$ is the half aperture of the fracture,

$x$ is the distance along the fracture,

$y$ is the distance into the matrix from the fracture wall,

$t$ is time,

$\theta_{me}$ is the effective diffusion porosity of the matrix,

and erfc is the complementary error function.
The experimental conditions approximate, but do not exactly match the assumptions of the model. First, the matrix is obviously not infinite. The finite dimensions of the core could cause deviations from the analytical model. Because of the limited extent of the matrix perpendicular to the fracture, as the tracer concentration in the matrix builds-up with time, the outflow concentration will be greater than that predicted by the model. Estimates of the concentration of tracers in the matrix at the end of the experiment using (6.3) and reasonable estimates of the parameters indicates that the tracer concentrations should be less than 1% of the $C_0$ at 1 centimeter into the matrix even at the head of the column. This calculation shows that the limited extent of the matrix should cause little deviation from the breakthrough curves predicted by Grisak and Pickens model.

Secondly, the upstream surface of the core was not maintained at constant concentration during the course of the experiment, rather the flux of tracer into the fracture was maintained constant. Gershon and Nir (1969) have evaluated the model dependent error introduced by assuming such a constant concentration boundary condition rather than a more accurate flux boundary condition for the case of advective-dispersive transport. They found the error to be minimal at large Brenner numbers ($\nu_l/D_H$). Given that hydrodynamic dispersion and longitudinal diffusion along the fracture studied here appear to be negligible, the constant concentration boundary condition is probably acceptable.

Lastly, the solution of Grisak and Pickens assumes that the concentrations in the fracture and in the matrix are equal across their
interface. This assumption may not be appropriate if the interface has physical properties different than that of the matrix. A more appropriate boundary condition was used by Tang and others (1981) and Sudicky and Frind (1982) who assumed only that the tracer flux across the interface was constant. This boundary condition adds complexity to the analytical solution and makes it more difficult to compute. As will be seen, the solution of Grisak and Pickens quite accurately describes the experimental results and seems adequate given nature and purpose of the experiment.

Because independent measurements of the effective diffusion coefficient and porosity had not been made on samples of G1-2540, the first attempt to match the experimental breakthrough curve was made by assuming an effective matrix diffusion coefficient of $4.5 \times 10^{-7}$ cm$^2$/s typical of the Yucca Mountain samples and an effective porosity of 0.24 which was measured for sample G1-2840. The fracture aperture ($2b$) was computed from the time of first appearance of the ionic tracers, the flow rate and the core dimensions. The aperture computed in this way was $3.2 \times 10^{-1}$ cm. As shown in Figure 6.4, this choice of parameters resulted in an excellent match to the observed breakthrough curves for both SCN$^-$ and PFB$^-$ and further attempts to improve the fit were not judged to be worthwhile. The fact that these two tracers have different diffusion coefficients and should have different breakthrough curves will be discussed later. In order to judge the sensitivity of the match to changes in the effective diffusion coefficient and the effective porosity, the results of additional simulations performed by doubling and halving each of these parameters are also shown in Figures
Figure 6.4. Comparison of observed and simulated tracer breakthrough curves for \( \phi \) equal 0.24 and various values of \( D_e \).
6.4 and 6.5. This range of parameters corresponds to the ranges observed in the independent measurements of diffusion coefficients and effective porosity described in Chapter 3.

The phage breakthrough curve was somewhat more difficult to match due to the scatter in the data and to the uncertainty in an appropriate effective diffusion coefficient and porosity for this particulate tracer. By ignoring the data which were greater than the injectate phage concentration, a fairly good match was obtained using an effective diffusion coefficient of $9 \times 10^{-8}$ cm$^2$/s, a porosity of 0.16, and a fracture aperture of $2 \times 10^{-1}$ cm (Figure 6.6).

The excellent agreement between the experimental breakthrough curves and those computed from the Grisak and Pickens model using independently determined effective diffusion coefficients and porosities is strong support for the hypothesis that matrix diffusion is an important transport process in the fractured tuffs at the NTS. Two troublesome anomalies in the experimental results remain to be explained, however. The first is the nearly identical behavior of the SCN$^-$ and PFB$^-$ despite their different free aqueous diffusion coefficients. The second is the early breakthrough of the phage.

The nearly identical breakthrough of SCN$^-$ and PFB$^-$ can be clearly seen in Figure 6.7 were the relative PFB$^-$ concentration is plotted versus the relative SCN$^-$ concentration. Although the PFB concentrations are higher in some cases, the slope of the regression line for these data is almost exactly one and the two concentrations are identical within analytical error.
Figure 6.5. Comparison of observed and simulated tracer breakthrough curves for $D_e = 4.5 \times 10^{-7}$ cm$^2$/s and various values of $\Phi$. 

- Computed
- SCN
- FF
- Phage
- △ Indicates $>Co$
Figure 6.6. Comparison of observed and simulated phage breakthrough curves.
Figure 6.7. Relative PFB concentration versus relative SCN concentration observed in the fracture flow experiment.
Simple multicomponent diffusion effects do not seem to explain the observed behavior. To illustrate this, the theoretical breakthrough curves for the independent diffusion of NaPFB and NaSCN, coupled diffusion of PFB$^-$ and SCN$^-$ in a solution of NaPFB and NaSCN, and diffusion of PFB$^-$ and SCN$^-$ in J-13 water at the concentrations used in the fracture flow experiment were computed using the theory described in Chapter 4 and the analytic solution of Grisak and Pickens (1981). The resulting free aqueous diffusion coefficient matrices are listed in Tables 6.2 and 6.3. The simulations were performed using the Grisak and Pickens analytical model and the independent combine diffusion coefficients. The simulated breakthrough curves for NaSCN in pure water, NaPFB in pure water, and a solution of NaSCN and NaPFB in pure water are shown in Figure 6.8.

As can be seen, the simulated breakthrough curve for NaSCN only is identical to the best fit curve shown in Figure 6.4, as it should be because the independent diffusion coefficient of NaSCN is $1.5 \times 10^{-5}$ cm$^2$/s. The curve for the independent diffusion of NaPFB is slightly above the best fit because of the slightly lower independent diffusion coefficient of NaPFB ($0.94 \times 10^{-5}$ cm$^2$/s). Contrary to expectation, the simulation for the simultaneous diffusion of NaPFB and NaSCN resulted in more diffusion of SCN$^-$ and less diffusion of PFB$^-$ into the matrix thus worsening the fit to the experimental curve. Similar calculations for NaPFB and NaSCN in J-13 water (Table 6.4 and Figure 6.9) resulted in breakthrough curves nearly identical to those for the solution of NaPFB and NaSCN.
Table 6.2. Ion diffusion coefficient matrix for NaSCN and NaPFB in pure water.

|               | NaSCN DIFFUSION COEFFICIENTS (1 x 10^{-5}\text{ cm}^2/\text{s}) | \begin{array}{cc} 
<table>
<thead>
<tr>
<th>Na</th>
<th>SCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>.7427</td>
</tr>
<tr>
<td>SCN</td>
<td>.7427</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>.0000</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>1.485</td>
<td></td>
</tr>
</tbody>
</table>
| NaPFB DIFFUSION COEFFICIENTS (1 x 10^{-5}\text{ cm}^2/\text{s}) | \begin{array}{cc} 
<table>
<thead>
<tr>
<th>Na</th>
<th>PFB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>.4680</td>
</tr>
<tr>
<td>PFB</td>
<td>.4680</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>.9359</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

**NOTE:** Zero values in the above matrix are values less than 1 x 10^{-19}\text{ cm}^2/\text{s}.
Table 6.3. Ion diffusion coefficient matrix for a solution of NaSCN and NaPFB in pure water

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>SCN</th>
<th>PFB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>.7354</td>
<td>.9305</td>
<td>.3233</td>
</tr>
<tr>
<td>SCN</td>
<td>.6316</td>
<td>1.092</td>
<td>-.3416</td>
</tr>
<tr>
<td>PFB</td>
<td>.1039</td>
<td>-.1617</td>
<td>.6649</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.0000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1.706</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>.7867</td>
</tr>
</tbody>
</table>

NOTE: Zero values in the above matrix are values less than $1 \times 10^{-19}$ cm$^2$/s.
Figure 6.8. Simulated effect of multicomponent diffusion (distilled water) on the fracture flow breakthrough curves.
<table>
<thead>
<tr>
<th>ION</th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>Cl</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>H₂PO₄⁻</th>
<th>SCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.7730</td>
<td>-0.8217</td>
<td>-0.6596</td>
<td>-0.3925</td>
<td>0.8541</td>
<td>0.4975</td>
<td>0.8999</td>
<td>0.3030</td>
</tr>
<tr>
<td>Ca</td>
<td>-0.0090</td>
<td>1.943</td>
<td>-0.0106</td>
<td>-0.0095</td>
<td>0.0138</td>
<td>0.0080</td>
<td>0.0145</td>
<td>0.0049</td>
</tr>
<tr>
<td>Mg</td>
<td>-0.0193</td>
<td>-0.0283</td>
<td>-0.7622</td>
<td>-0.0204</td>
<td>0.0295</td>
<td>0.0172</td>
<td>0.0310</td>
<td>0.0105</td>
</tr>
<tr>
<td>Cl</td>
<td>-0.0043</td>
<td>-0.0064</td>
<td>-0.0051</td>
<td>-0.0016</td>
<td>0.0066</td>
<td>0.0039</td>
<td>0.0070</td>
<td>0.0023</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.0164</td>
<td>0.0241</td>
<td>0.1593</td>
<td>0.0174</td>
<td>0.0146</td>
<td>0.0264</td>
<td>0.0089</td>
<td>0.0256</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.1083</td>
<td>0.1589</td>
<td>0.1276</td>
<td>0.1146</td>
<td>1.0847</td>
<td>1.0882</td>
<td>1.7411</td>
<td>0.0586</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>0.0173</td>
<td>0.0254</td>
<td>0.0204</td>
<td>0.0183</td>
<td>0.0154</td>
<td>1.0431</td>
<td>0.0094</td>
<td>0.0269</td>
</tr>
<tr>
<td>SCN</td>
<td>0.7872</td>
<td>0.1155</td>
<td>0.0927</td>
<td>0.0833</td>
<td>0.0833</td>
<td>1.2665</td>
<td>0.6785</td>
<td>1.2265</td>
</tr>
</tbody>
</table>

Table 6.4. Ion diffusion coefficient matrix for NaSCN and NaF in J-18 water.
### Table 6.4—Continued

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.0000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2.035</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1.959</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.766</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.208</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.081</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.8210</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.7509</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.7063</td>
</tr>
</tbody>
</table>

**NOTE:** Zero values in the above matrix are values less than $10^{-19}$ cm$^2$/s.
Figure 6.9. Simulated effect of multicomponent diffusion (J-13 water) on the fracture flow breakthrough curves.
Although the multicomponent effects displayed in the fracture flow simulations are consistent with those observed in the diffusion cell simulations, that is an increase in the diffusion of the pseudo-halide SCN and slight decrease in the diffusion of PFB, they do not help explain the observed results. Unexpectedly similar diffusion of SCN\(^-\) and PFB\(^-\) was also observed in some of the diffusion cell experiments, such as in the tests on G1-2840B. Although PFB\(^-\) was found to have a lower effective diffusion coefficient than the halides and SCN in other tuff samples, the overall scatter in the effective diffusion coefficients is such that the possibility that SCN\(^-\) and PFB\(^-\) have very similar diffusion coefficients in either the J-13 water or in the tuffs cannot be ignored.

These results imply either an increase in the effective diffusion coefficient of PFB\(^-\) over that predicted by its free aqueous diffusion coefficient and the rock geometric factor, \(a/\tau^2\), or a decrease in the effective diffusion coefficient of SCN\(^-\). Because no evidence exists that PFB\(^-\) or SCN\(^-\) form any aqueous phase complexes with the dominant species in the J-13 water and tests have shown that PFB\(^-\) does not sorb on the tuff matrix, the simplest explanation of the observed diffusion behavior of these two species is that SCN\(^-\) experiences more ion exclusion due to surface charge interactions. Like the true halides, SCN\(^-\) is a small anion with a high charge density. PFB\(^-\) is a larger ion with a more diffuse surface charge. For these reasons, if anion exclusion occurs in the tuff matrix, the SCN\(^-\) should experience more exclusion and display a lower effective diffusion coefficient. That this exclusion should result in identical effective
diffusion coefficients for SCN$^-$ and PFB$^-$ would seem fortuitous, however.

The second anomaly in the fracture flow experiment is the early breakthrough of the phage. Such early breakthrough has been observed in field tracer tests using particulate tracers such as yeast (Walter and Thompson, unpublished data). In order to match the phage breakthrough curve using the matrix diffusion model, the fracture aperture had to be reduced to $2.0 \times 10^{-2}$ cm from $3.2 \times 10^{-2}$ cm. The simplest explanation for this behavior is that the phage, being much larger than the ionic species, has access to a reduced volume of the fracture. Although the average fracture aperture is much larger than the phage, asperities on the fracture surfaces would certainly exclude the phage from some percentage of the total fracture volume. To determine whether or not this excluded volume could be as large as one-third of the total volume would require a knowledge of the surface structure of the fracture.

Conclusions

The ability to match, in general, the observed fracture flow breakthrough curves using the Grisak and Pickens model of matrix diffusion and independently determined values for the effective diffusion coefficients and porosity is strong support for the conclusion that matrix diffusion was observed during these tests. Although certain anomalous details of the experimental results are troublesome, such as the similar behavior of SCN$^-$ and PFB$^-$, they are not inconsistent with results observed in diffusion cell experiments. These anomalies are
interesting but do not invalidate the general conclusion about the importance of matrix diffusion.
CHAPTER 7

SUMMARY AND CONCLUSIONS

In theory, the various physical/chemical transport processes may cause non—advective solute transport from fractures into the unfractured tuff matrix at the NTS. In the absence of artificially induced electrical or thermal potential gradients, molecular diffusion appears to be the dominant process.

Measurements of the total porosity and pore—size distribution have revealed that the tuff porosities vary from about 10 to 40%. Much of this porosity is present as pores less than 1 μm in diameter. In some samples, the median pore diameter is less than 0.1 μm. The pore diameter and size distribution seem to affect the effective matrix—diffusion coefficients.

The effective matrix—diffusion coefficients determined from static diffusion cell experiments using sodium halide salts range from about 2 x 10^-7 to 17 x 10^-7 cm^2/s. These values are in a range which would be predicted from an educated guess about the porosity and constrictivity/tortuosity factor for the tuffs. The data in this report basically support a relationship between the effective diffusion coefficient and the free aqueous—diffusion coefficient of the form

\[ D_e = \phi (a/\tau^2) D_0 \]  

(7.1)
The correlation between the total porosity and the effective diffusion coefficient for the samples studied was very good \((r = 0.90)\), and the total porosity accounts for most of the variation in diffusion coefficients from sample to sample. A fair correlation \((r = 0.75)\) was found between the constrictivity/tortuosity factor and the median pore diameter. The reasons for the correlation are not certain but may be due to ion exclusion from the smaller pores. These results indicate that reasonably accurate effective matrix diffusion coefficients may be made based on porosity and pore-size distributions. Electrical measurements such as bulk-rock resistance and changes in bulk impedance with current frequency may also be used to estimate the effective diffusion coefficients.

The results of the experimental work all indicate that the tuffaceous rocks from the NTS have sufficient porosity and large enough effective diffusion coefficients to make matrix diffusion an important transport process. For some species, such as those which form ion pairs or complexes, multicomponent diffusion effects may complicate the simple single-component diffusion models on which previous theoretical studies have been based (e.g., Neretniks, 1981; Grisak and Pickens, 1981). The multicomponent diffusion coefficients reported here are certainly large enough to cause coupled ionic fluxes under some conditions.

The results of a bench-scale experiment performed by inducing a flow of solution containing three tracers (NaSCN, Na pentafluorobenzoate (PFB), and F-2 bacteriophage) down a single fracture in a tuff core were successfully interpreted using the single fracture matrix
diffusion model of Grisak and Pickens (1981) and independent estimates of the effective diffusion coefficient and effective porosity. The fracture flow results failed to show any difference in the breakthrough curves for SCN and PFB, although their free aqueous diffusion coefficients differ by almost a factor of two. The F-2 phage tracer, being a particulate, showed almost no diffusion effects, but broke through much earlier than the ionic tracers. This result implies that the effective fracture aperture for the particulate tracer is lower than that for the ionic species.
APPENDIX A

REDUCTION OF GENERALIZED FORCES AND FLUXES TO AN EXPERIMENTALLY TRACTABLE SET

In order to rewrite equations (2.12), (2.13), and (2.14) in terms of an experimentally tractable set of forces and fluxes, consider first the case where \( \nabla u_k = 0 \), \( F = 0 \), and \( (c_k g - n_k \nabla P) = 0 \) for the same \( k \). We then have

\[
J_v = \sum_{i=1}^{N} \sum_{k=1}^{N} L_{ik}^* (c_k g - \hat{n}_k \nabla P) \quad (A.1)
\]

\[
J_{mi} = M_i \sum_{k=1}^{N} L_{ik}^* (c_k g - \hat{n}_k \nabla P) \quad (A.2)
\]

\[
J_z = \sum_{i=1}^{N} z_i \sum_{k=1}^{N} L_{ik}^* (c_k g - \hat{n}_k \nabla P) \quad (A.3)
\]

We can rewrite (A.1), (A.2), and (A.3) as

\[
J_v = \sum_{i=1}^{N} V_i L_{ii}^* (c_i g - \hat{n}_i \nabla P) + \sum_{i=1}^{N} \sum_{k \neq i} V_i L_{ik}^* (c_k g - \hat{n}_k \nabla P) \quad (A.4)
\]

\[
J_{mi} = M_i L_{ii}^* (c_i g - \hat{n}_i \nabla P) + M_i \sum_{k \neq i} L_{ik}^* (c_k g - \hat{n}_k \nabla P) \quad (A.5)
\]
\[ J_z = \sum_{i=1}^{N} z_i L_i^* (c_i \varphi - \hat{n}_i \varphi P) + \sum_{i=1}^{N} z_i \sum_{k \neq i}^{N} L_{ik} (c_k \varphi - \hat{n}_k \varphi P) \] (A.6)

Now, in (A.4) we add and subtract

\[ \sum_{i=1}^{N} \bar{V}_i L_{ii} \sum_{k \neq i}^{N} (c_k \varphi - \hat{n}_k \varphi P) \] (A.7)

to the right-hand side to obtain

\[ J_v = \sum_{i=1}^{N} \bar{V}_i L_i^* (c_i \varphi - \hat{n}_i \varphi P) + \sum_{i=1}^{N} \bar{V}_i L_i^* \sum_{k \neq i}^{N} (c_k \varphi - \hat{n}_k \varphi P) + \sum_{i=1}^{N} \bar{V}_i \sum_{k \neq i}^{N} L_{ik} (c_k \varphi - \hat{n}_k \varphi P) - \sum_{i=1}^{N} \bar{V}_i L_i^* \sum_{k \neq i}^{N} (c_k \varphi - \hat{n}_k \varphi P) \] (A.8)

Then rearranging (A.8) we obtain

\[ J_v = \sum_{i=1}^{N} \bar{V}_i L_i^* \sum_{k=1}^{N} (c_k \varphi - \hat{n}_k \varphi P) + \sum_{i=1}^{N} \bar{V}_i \sum_{k \neq i}^{N} (L_{ik}^* - L_{ii}^*) (c_k \varphi - \hat{n}_k \varphi P) \] (A.9)
Consider the summation over $k$ in the first term of (A.9). Inasmuch as

$$
\sum_{k=1}^{N} c_k g = \rho_s g \tag{A.10}
$$

where $\rho$ is the density of the solution (total mass of solution per unit volume) and

$$
\sum_{k=1}^{N} \dot{n}_k \dot{\gamma} = \dot{\gamma} \tag{A.11}
$$

(remembering that $\dot{n}_k$ is the volume fraction of $k$ and the sum of $\dot{n}_k$ over all the components is 1), then (A.9) can be written in terms of the total external force potential per unit volume and a sedimentation term (Groenevelt and Bolt, 1969) as

$$
\mathcal{J}_v = \sum_{i=1}^{N} \dot{v}_i \mathbf{L}_{ii}^* (\rho_s \mathbf{g} - \dot{\gamma} \mathbf{P}) + \sum_{i=1}^{N} \dot{v}_i \sum_{k \neq i}^{N} (\mathbf{L}_{ik}^* - \mathbf{L}_{ii}^*) (c_k g - \dot{n}_k \dot{\gamma} \mathbf{P}) \tag{A.12}
$$

Groenevelt and Bolt have shown that when gravity is the only external force, the sedimentation term is negligible for dissolved species and for the present discussion we will ignore it.

We can now perform similar rearrangements of (A.5) and (A.6) to obtain
\[ J_{mi} = M_i \sum_{k=1}^{N} (c_k g - \hat{\eta}_k \nabla P) + M_i \sum_{k \neq i}^{N} (L_{ik}^* - L_{ii}^*) [c_k g - \hat{\eta}_k \nabla P] \]  
(A.13)

and

\[ J_z = \sum_{i=1}^{N} z_i L_{ii}^* (\rho_s g - \nabla P) + \sum_{i=1}^{N} z_i \sum_{k \neq i}^{N} (L_{ik}^* - L_{ii}^*) [c_k g - \hat{\eta}_k \nabla P] \]  
(A.14)

where the sedimentation terms in (A.13) and (A.14) are also negligible.

Now, ignoring the sedimentation terms in (A.12), (A.13), and (A.14), these equations can be rewritten as

\[ J_v = L_{vv} (\rho_s g - \nabla P) \]

\[ J_{mi} = L_{iv} (\rho_s g - \nabla P) \]  
(A.15)

\[ J_z = L_{zv} (\rho_s g - \nabla P) \]

where \( L_{vv} \) is the coefficient relating the volume flux to the external force per unit volume (permeability), \( L_{iv} \) relates the flux of \( i \) to the volume force (filtration coefficient), and \( L_{zv} \) relates the charge flux to the volume force (streaming coefficient).

Now consider the case where \( (c_i g - \nabla P) = 0 \) for all \( i \) and \( F = 0 \), then from (A.9), (A.10), and (A.11), we have

\[ J_v = \sum_{i=1}^{N} \sum_{k=1}^{N} L_{ik}^* (-m_k \nabla u_k) \]  
(A.16)

\[ J_{mi} = M_i \sum_{k=1}^{N} L_{ik}^* (-m_k \nabla u_k) \]  
(A.17)
If we rearrange (A.16) by switching the order of summation, we obtain

\[
J_z = \sum_{i=1}^{N} \sum_{k=1}^{N} z_i L_{ik}^* \left( -m_{ik} \nu_{uk} \right)
\]  
(A.18)

or

\[
J_z = \sum_{k=1}^{N} v_k L_{k1}^* \left( -m_{1k} \nu_{1k} \right) + \ldots + \left( \sum_{k=1}^{N} v_k L_{k1}^* \right) \left( -m_{1N} \nu_{1N} \right)
\]  
(A.19)

where each \( L_{vi} \) relates the total volume flux to the diffusion force of component \( i \) (osmotic coefficients). Rewriting (A.17) without rearranging gives

\[
J_{\nu} = \nu_1 \left( -m_{11} \nu_{11} \right) + \ldots + \nu_i \left( -m_{1i} \nu_{1i} \right) + \ldots + \nu_N \left( -m_{1N} \nu_{1N} \right)
\]  
(A.20)

or

\[
J_{\nu} = -M_{i1}^* \nu_{11} - \ldots - M_{i1}^* \nu_{11} - M_{i1}^* \nu_{1N} - M_{i1}^* \nu_{1N} - \ldots - M_{i1}^* \nu_{1N} - M_{i1}^* \nu_{1N}
\]  
(A.21)

or

\[
J_{\nu} = -L_{i1}^* \nu_{11} - \ldots - L_{i1}^* \nu_{11} - L_{i1}^* \nu_{1N} - L_{i1}^* \nu_{1N}
\]  
(A.22)
where each \( L_{ik} \) relates the diffusion flux of \( i \) to the diffusion force of \( k \).

Lastly, rearranging the charge flux given by (A.18) as we did for the volume flux gives

\[
\frac{J_z}{z} = \left( \sum_{k=1}^{N} z_k L_{ik}^* \right) (-m_i \nabla \mu_i) + \ldots + \left( \sum_{k=1}^{N} z_k L_{ik}^* \right) (-m_i \nabla \mu_i) \\
+ \ldots + \left( \sum_{k=1}^{N} z_k L_{ik}^* \right) (-m_N \nabla \mu_N)
\]

(A.23)

or

\[
\frac{J_z}{z} = L_z (-m_i \nabla \mu_i) + \ldots + L_{zi} (-m_i \nabla \mu_i) + \ldots + L_{zN} (-m_N \nabla \mu_N)
\]

(A.24)

where each \( L_{zi} \) relates the total charge flux to the diffusion force of \( i \).

Now consider the case where \((c_{ik} - \nabla P) = 0\) for all \( k \) and \( \nabla \mu_k = 0 \) for all \( k \), but \( F \neq 0 \). The resulting fluxes are

\[
J_v = \sum_{i=1}^{N} V_i \sum_{k=1}^{N} L_{ik}^* m_k z_k F \nabla E
\]

(H.25)

\[
J_{mi} = M_i \sum_{k=1}^{N} L_{ik}^* m_k z_k F \nabla E
\]

\[
\frac{J_z}{z} = \sum_{i=1}^{N} z_i \sum_{k=1}^{N} L_{ik}^* m_k z_k F \nabla E
\]
Without rearrangement we can write

\[
\begin{align*}
J_v &= L_{vz} V E \\
J_{mi} &= L_{iz} V E \\
J_z &= L_{zz} V E
\end{align*}
\]

(A.26)

where \( L_{vz} \) relates the volume flux to the electric field strength (electro-osmotic permeability), \( L_{iz} \) relates the mass flux of \( i \) to the field strength (electrophoretic coefficient) and \( L_{zz} \) is the electrical conductance.
DEFINITION OF THE EFFECTIVE DIFFUSION COEFFICIENT AND GOVERNING PARTIAL DIFFERENTIAL EQUATION IN A POROUS MEDIUM

As noted by Bradbury and others (1982), a certain ambiguity exists in the scientific literature with regard to the definition of the "effective" matrix diffusion coefficient. The definition of this term affects both the values of the effective diffusion coefficients reported in the literature and the form of the governing partial differential equation. As examples only from the references cited in this study, Grisak and Pickens (1980a, 1980b, and 1981), Porter and others (1966), and Tang and others (1981) refer to an "effective" diffusion coefficient which includes the effects of matrix pore geometry on the free aqueous diffusion coefficient, \( D_0 \), but not the effects of porosity. Saxena and others (1974) refer to this same coefficient as the "actual" diffusion coefficient in the porous medium, while Bradbury and others (1982) call it the "apparent" diffusion coefficient. Defined in this way, the relationship between the "effective" diffusion coefficient, \( D_e' \), in a saturated porous medium and the free aqueous diffusion coefficient is generally written as

\[
D_e' = \frac{a}{\tau^2} D_0
\]

where \( a \) is a "constrictivity" factor and \( \tau \) is the tortuosity. The resulting governing PDE for diffusion in the porous medium is
\[ \frac{\partial m}{\partial t} = D_e \frac{\partial m}{\partial x} \quad (B.2) \]

where \( m \) is the molar concentration of \( m \) in the pore solution.

An alternative definition of the "effective" diffusion coefficient is often found in the chemical engineering and material science literature. For example, van Brakel and Heertjes (1974) define the relationship between the effective diffusion coefficient and the free aqueous diffusion coefficient as

\[
D_e = \bar{\phi} \frac{\alpha}{\tau^2} D_0 \quad (B.3)
\]

where \( \bar{\phi} \) is the total porosity of the porous medium. Defined in this way, the effective diffusion coefficient is consistent with the "porous system" diffusion coefficient used by Kemper and van Shaik (1966), the "diffusion coefficient in the porous medium" used by Olsen and Kemper (1968), and the "intrinsic" diffusion coefficient of Bradbury and others (1982).

This definition of the effective diffusion coefficient has been used in this study primarily because it is consistent with the diffusion coefficients directly computed from the results of the membrane diffusion experiments reported in Chapter 3. This definition also allows a straightforward development of the governing PDE for diffusion in a porous medium (Olsen and Kemper, 1968). Following Olsen's development in the nomenclature of this study, the modified form of Fick's Law for one dimensional diffusion in a saturated porous medium is

\[
\frac{dN}{dt} = -\theta \frac{dx \ dy \ \alpha}{\tau^2} D_0 \frac{dN}{dx} \quad (B.4)
\]
where \( dN \) is the number of moles diffusing in time \( dt \) through the area \( \theta dx \ dy \). The molar flux is then given by

\[
J = -\theta a/c^2 \ D_0 \ dM/dx \tag{B.5}
\]

or

\[
J = -D_e \ dM/dx \tag{B.6}
\]

Using the continuity equation to derive the rate of change in mass (moles) per infinitesimal volume of pore solution, gives

\[
dN/dt = [J_{in} - J_{out}] \ dydz = -D_e \ [dM/dx - (dM/dx + \partial(dM/dx)/\partial x \ dx)] \ dydz \tag{B.7}
\]

Substituting

\[
N = M \ \theta dx dy dz
\]

into (B.7) gives

\[
\theta \ \partial m/\partial t = -D_e \ \partial^2 M/\partial x^2 \tag{B.8}
\]

Equation (B.8) is the form of the governing PDE used in this study.
APPENDIX C

TRACER CHARACTERIZATION

In addition to evaluating the diffusion properties of the tuff, an important aspect of this work was to characterize the physical and chemical properties of tracer to be used in matrix diffusion experiments. Experiments were conducted to determine the acid dissociation constants of fluorobenzoic acid tracers, their free aqueous diffusion coefficients, and their sorption behavior with respect to the tuffs. The author was greatly assisted in the measurements by Mr. Randal Golding.

Acid Dissociation Constants

The dissociation constants of five fluorinated benzoic acid tracers were determined by potentiometric titrations using an Altex PHI 71 pH meter and double-junction glass-membrance electrode. All titrations were performed using a 9.700 x 10^{-3} M NaOH solution prepared with water distilled over KMnO₄ and degassed with nitrogen. Potassium chloride was added to the solution to adjust the ionic strength to 0.1. The base solution was stored in a 5 liter polyethylene bottle wrapped with aluminum foil and stored under a nitrogen atmosphere. Solution of primary-standard potassium acid phthalate and the fluorinated benzoic acids were prepared in a similar manner and their ionic strengths adjusted to 0.1 using KCl. The concentrations of the acids ranged from
4 \times 10^{-3} \text{ M} \text{ for the weakest and least soluble acid to } 10^{-2} \text{ M} \text{ for the strongest and most soluble.}

The titrations were performed under a nitrogen atmosphere using the apparatus shown in Figure C.1. The pH electrode was standardized with Curtin Matheson pH 4 and pH 7 buffer solutions. The base solution was standardized against the potassium acid phthalate solutions.

The dissociation constants for the acids were then determined from the titration curves using the following mass balance and mass action equations:

\[
K_a = \frac{aH^+ \cdot aA^-}{aHA}
\]

\[
M_{HA} = F_{HA} - M_{H^+} + M_{OH^-} - F_{B^-}
\]

\[
M_{A^-} = F_{B^-} + M_{H^+} - M_{OH^-}
\]

\[
a = \gamma M
\]

where \( a \) is the activity,

\( m \) is the molarity,

\( F \) is the formal concentration,

\( \gamma \) is the activity coefficient,

\( HA \) is the undissociated acid,

\( H^+ \) is the hydrogen ion,

\( A^- \) is the acid anion,

\( B^- \) is the base,

and \( OH^- \) is the hydroxide ion.

Equations (C.1) through (C.4) are combined to give
Figure C.1. Apparatus for performing pH titrations under nitrogen atmosphere.
The activity coefficients $\gamma_H^+$, $\gamma_A^-$, and $\gamma_{HA}$ used in the calculations were 0.83, 0.77, and 1.0, respectively (Kielland, 1937). The dissociation constants were determined by solving (C.5) for four to five points in the buffer region of the titration curve. The computed pKa's are given in Table C.1 with their standard errors and the reported values, where available. The pKa of pentafluorobenzoic acid is lower than previously reported possible because of poor standardization of the electrode below pH 4. The reproducibility of values at different points in the titrations was less than for the weaker acids. The only explanation for the disagreement between the reported and measured value of orthofluorobenzoic acid is impurities in the acid.

**Free Aqueous Diffusion Coefficients**

Given the accuracy with which the effective matrix diffusion coefficients could be determined for the diffusion cell experiments, calculation of the free aqueous diffusion coefficients of the fluorobenzoate tracers from their limiting ionic conductances was judged to be sufficiently accurate. At the pH's and concentrations under consideration (pH > 6), the fluorobenzoates are completely dissociated and behave as strong 1:1 electrolytes. Based on data and calculations given by Robinson and Stokes (1959) and our own calculations, free aqueous diffusion coefficients computed from ionic conductances differ by no more than 5% from directly measured diffusion coefficients.
Table C.1. Measured and reported pKa's for fluorobenzoic acids.

<table>
<thead>
<tr>
<th>Acid</th>
<th>pKa Reported (25°C)</th>
<th>pKa Measured (23°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzonic</td>
<td>4.19&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.18 ± 0.01</td>
</tr>
<tr>
<td>p-fluorobenzoic</td>
<td>4.04&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.13 ± 0.01</td>
</tr>
<tr>
<td>m-fluorobenzoic</td>
<td>3.85&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.82 ± 0.01</td>
</tr>
<tr>
<td>o-fluorobenzoic</td>
<td>2.90&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.42 ± 0.02</td>
</tr>
<tr>
<td>m-trifluoromethylbenzoic</td>
<td>-</td>
<td>3.79 ± 0.01</td>
</tr>
<tr>
<td>pentafluorobenzoic</td>
<td>1.73&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.49 ± 0.02</td>
</tr>
</tbody>
</table>

<sup>a</sup> Chemical Rubber Company (1980).
<sup>b</sup> Kuhn and Wasserman (1928).
<sup>c</sup> Ryan and Berner (1969).
The limiting ionic conductance of an ion is defined as its equivalent ionic conductance at infinite dilution. These values for the fluorobenzoate anions were determined by measuring the molar conductances of their sodium and potassium salts at various concentrations. For strong electrolytes such as these, the molar conductance is described by the empirical equation (Moore, 1972)

\[
\lambda = \lambda_0 - k_c M^{1/2}
\]  

(C.6)

where \(\lambda\) is the molar conductance,

\(\lambda_0\) is the molar conductance at infinite dilution,

\(k_c\) is an experimental constant,

and \(M\) is the molar concentration.

The sodium and potassium salts of the fluorobenzoic acids were prepared by titrating the acids with the appropriate base to the equivalence points. The resulting salt solution was then used to prepare more dilute solutions. The conductivities of these solutions were measured using the apparatus shown in Figure C.2. The temperature bath was set at \(25 \pm 0.05^\circ C\) and the values of \(\theta_0\) for the salt solutions were determined by linear regression. The limiting ionic conductance of the anion was then computed from Kohlrausch’s Law of the Independent Migration of Ions (Moore, 1972):

\[
\lambda_0 = \lambda_0^+ + \lambda_0^-
\]  

(C.7)

where \(\lambda_0^+\) for sodium and potassium ions are known.
Figure C.2. Schematic drawing of apparatus used for electrical conductivity measurements.
The resulting values for the limiting ionic conductances are listed in Table C.2. Based on the differences between the measured values and the published values for benzoate and p-fluorobenzoate, the error in the other measured values may be about 7%. The source of this error is not known, but this level of accuracy seems adequate for the purposes of this study. The resulting values for the free aqueous diffusion coefficients at infinite dilution are also shown in Table C.2. These values were computed using the Nernst equation (Robinson and Stokes, 1959):

\[ D_0 = \frac{RT\gamma_0}{ZF^2} \]  

(C.8)

where \( R \) is the gas constant,

\( T \) is the absolute temperature,

\( \gamma_0 \) is the limiting ionic conductance,

\( Z \) is the ionic charge,

and \( F \) is Faraday's constant.

**Sorption Properties of the Fluorobenzoate Tracers**

The adsorption of benzoate, m-trifluoromethylbenzoate, pentfluorobenzoate, bromide, and o-, m-, and p-fluorobenzoate on tuff sample U12G RNM#9 (15.2-17.9') was investigated using a batch technique. The adsorption studies were performed by placing 14 g of tuff, ground and sieved through a 270 mesh screen, in 50 ml jars with screw cap lids. The void space was then evacuated and 30 mls of a 8.3 x 10^{-5} M tracer solution in J-13 water was added to the jar under low vacuum
Table C.2. Limiting ionic conductances for benzoate and fluoro-
benzoates with computed diffusion coefficients ($D_0$).

<table>
<thead>
<tr>
<th>Species</th>
<th>Published $\lambda_0$ cm$^2$/ohm-eq.</th>
<th>Measured $\lambda_0$ cm$^2$/ohm-eq.</th>
<th>$D_0$ cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzoate</td>
<td>32.28</td>
<td>30.8</td>
<td>$0.82 \times 10^{-5}$</td>
</tr>
<tr>
<td>p-fluorobenzoate</td>
<td>33.00</td>
<td>35.0</td>
<td>$0.93 \times 10^{-5}$</td>
</tr>
<tr>
<td>m-fluorobenzoate</td>
<td>-</td>
<td>30.0</td>
<td>$0.80 \times 10^{-5}$</td>
</tr>
<tr>
<td>o-fluorobenzoate</td>
<td>-</td>
<td>30.5</td>
<td>$0.81 \times 10^{-5}$</td>
</tr>
<tr>
<td>m-trifluoromethylbenzoate</td>
<td>-</td>
<td>27.9</td>
<td>$0.74 \times 10^{-5}$</td>
</tr>
<tr>
<td>pentafluorobenzoate</td>
<td>-</td>
<td>27.1</td>
<td>$0.72 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
(4 inches of mercury). The apparatus used for this addition is shown in Figure C.3. Each jar was then shaken and a 1/2 ml sample was withdrawn, filtered, and analyzed by high performance liquid chromatography (HPLC). The sample was injected through a 10 μl sample loop. The liquid chromatography column was a 25 cm x 1/4 inch packed with Partisil-10 SAX. The detector was a Hitachi UV absorption detector Model 1040 at 200 nm wavelength. The mobile phase was a 0.01 M H₃PO₄, H₂PO₄ buffer at pH 4.

Two batch solutions were used. One contained p-, m- and pentafluorobenzoate and the other contained bromide, benzoate, o-fluorobenzoate, and m-trifluoromethylbenzoate. Each batch was compared to an identical solution which had not contacted the tuff after each analysis. Samples were collected and analyzed 10, 100, 1000, and 10,000 minutes after addition of the tracer solution. Excluding the first sampling, each solution was shaken thoroughly for 30 minutes before sampling.

No changes in concentrations greater than the reproducibility of the analytical technique were observed indicating that no absorption of any of the tracers occurred during the experiments. An increase in the peak area of the first eluting peak relative to the blank was observed for each batch. This is attributed to increase background salt concentrations in the solution which contacted the tuff. Peak heights above the corrected baseline remained constant. The pH was observed to be constant during the tests.
Figure C.3. Apparatus for filling and degassing tuff samples used in batch sorption tests.
F2 Bacteriophage Tracer

Bacteriophages are viruses which infect specific host bacteria. Their use as hydrologic tracers has been reviewed by Keswick and others (1982). The F2 bacteriophage was selected for use in this study because of its small size (0.03 µm) and longevity (several days at pH between 7 and 8). Sand column tests (Steven Jensen, personal communication) had also shown that this virus does not sorb onto soil materials because it carries a negative surface charge in the pH range 7 to 8.
APPENDIX D

LITHOLOGY AND MINERALOGY OF THE TUFF SAMPLES

The samples of tuff used in these studies came from three different locations in the thick sequence of Tertiary volcanic rocks forming most of the mesas at the Nevada Test Site. All of the samples were collected and supplied to the author by Los Alamos National Laboratory.

The samples labeled U12G RNM#9 came from a single core taken from the "Tunnel Beds" in G tunnel in Ranier Mesa. G Tunnel is a tunnel complex used for underground testing of nuclear devices. The Tunnel Beds are part of the Ranier Mesa Member of the Timber Mountain Tuff (Byers and others, 1976).

The sample labeled G1 were cut from cores collected from the USW-G1 drill hole on Yucca Mountain. The appended sample number represents the depth below land surface (in feet) of the sample (Waters and Carrol, 1981). Samples G1-2290 and G1-2333 represent the Bullfrog Member of the Crater Flat Tuff. The samples from between 2698 and 2901 feet came from the Tram Tuff member of the Crater Flat Tuff. Sample G1-4750 is from the Lithic-Rich Tuff. All samples were collected from the saturated zone.

The sample labeled YM-45 was cut from core collected at 588.4 meters below land surface in the UE25a-1 drill hole near Yucca Mountain.
(Sykes, Heiken and Smyth, 1979). This sample represents the Prow Pass Member of the Crater Flat Tuff and was collected from the saturated zone.

The lithologies and dominant mineralogy of these samples are summarized in Table D.1.
Table D.1. Lithologies and mineralogies of tuff samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Rock Type</th>
<th>Degree of Welding</th>
<th>Dominant Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>U12G-RNM 9</td>
<td>zeolitized</td>
<td>none</td>
<td>70-90 Cpt</td>
</tr>
<tr>
<td>0.8 ft to 1.0 ft (sample A)</td>
<td>ash flow</td>
<td></td>
<td>5-10 Ill/ mica</td>
</tr>
<tr>
<td>U12G-RNM 9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>5.9 ft to 6.4 ft (side B)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U12G-RNM 9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>16.2 ft to 17.5 ft (sample A)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1-2290</td>
<td>zeolitized</td>
<td>none</td>
<td>30-50 Cpt</td>
</tr>
<tr>
<td></td>
<td>ash flow</td>
<td></td>
<td>30-50 Mrd</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10-20 AF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-5 Mntm</td>
</tr>
<tr>
<td>G1-2333</td>
<td>devitrified</td>
<td>moderate</td>
<td>20-40 Crist</td>
</tr>
<tr>
<td></td>
<td>ash flow</td>
<td></td>
<td>20-40 AF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15-30 Qtz</td>
</tr>
<tr>
<td>G1-2698</td>
<td>zeolitized</td>
<td>slight</td>
<td>30-60 Cpt</td>
</tr>
<tr>
<td></td>
<td>ash flow</td>
<td></td>
<td>20-30 AF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10-20 Qtz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5-10 Mntm</td>
</tr>
<tr>
<td>G1-2840</td>
<td>devitrified</td>
<td>moderate</td>
<td>40-60 Qtz</td>
</tr>
<tr>
<td></td>
<td>ash flow</td>
<td></td>
<td>30-50 AF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0-10 Crist</td>
</tr>
<tr>
<td>G1-2901</td>
<td>devitrified</td>
<td>moderate</td>
<td>20-40 Qtz</td>
</tr>
<tr>
<td></td>
<td>ash flow</td>
<td></td>
<td>20-40 AF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10-30 Anal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5-10 Cpt</td>
</tr>
<tr>
<td>Sample #</td>
<td>Rock Type</td>
<td>Degree of Welding</td>
<td>Dominant Minerals</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>-------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>G1-4750</td>
<td>zeolitized ash flow</td>
<td>moderate</td>
<td>25-40 Qtz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20-30 AF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10-20 Anal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10-20 Mntm</td>
</tr>
<tr>
<td>YM-45</td>
<td>devitrified</td>
<td>dense</td>
<td>70 Ab</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 Anal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5 Or</td>
</tr>
</tbody>
</table>

Ab  - Albite  
AF  - Alkaline feldspars  
Anal - Analcime  
Cpt - Clinoptilolite  
Crist - Cristobolite  
Ill - Illite  
Mntm - Montmorillonite  
Mrd - Mordenite  
Or - Orthoclase  
Qtz - Quartz
APPENDIX E

IONIC AND COMBINE DIFFUSION COEFFICIENT MATRICES
FOR VARIOUS AQUEOUS SYSTEMS

The diffusion coefficient matrix diagonalization procedure described in Chapter 4 was applied to two types of aqueous systems. The type A system represents solutions of strong electrolytes which do not form aqueous complexes at low concentration, such as the system Li$^+$ — K$^+$ — Cl$^-$. The type B system represents solutions of weaker electrolytes in which aqueous complexes or ion pairs may exist, such as H$^+$ — Na$^+$ — SO$_4^{2-}$.

For the Li—K—Cl system the ion diffusion coefficient matrix computed using limiting ionic conductances from Robinson and Stokes (1959) is shown in Table E.1. The resulting combine diffusion coefficient matrix (also shown in Table E.1) is diagonal with two non-zero terms even though the original diffusion coefficient matrix was full with some negative off-diagonal terms. That the combine matrix contains only two non-zero terms reflects the fact that diffusion in this system can be completely described in terms of two diffusing salts, LiCl and KCl. The combines are not equivalent to these two salts, however.

The type B system, represented by H—Na—SO$_4$, differs from the type A system in that these ionic components combine in solution, even
Table E.1. Ion and combine diffusion coefficient matrices for the system Li–K–Cl.

<table>
<thead>
<tr>
<th>Component</th>
<th>Molarity</th>
<th>Ionic Conductance (ohm⁻¹ cm²/gm-equiv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2.5 x 10⁻²</td>
<td>38.7</td>
</tr>
<tr>
<td>K</td>
<td>2.0 x 10⁻²</td>
<td>73.5</td>
</tr>
<tr>
<td>Cl</td>
<td>4.5 x 10⁻²</td>
<td>76.4</td>
</tr>
</tbody>
</table>

**Ion Diffusion Coefficient Matrix**  
(1 x 10⁻⁵ cm²/s)

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>K</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.86</td>
<td>-0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>K</td>
<td>-0.26</td>
<td>1.47</td>
<td>0.51</td>
</tr>
<tr>
<td>Cl</td>
<td>0.60</td>
<td>1.15</td>
<td>0.84</td>
</tr>
</tbody>
</table>

**Combine Diffusion Coefficient Matrix**  
(1 x 10⁻⁵ cm²/s)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1.19</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1.98</td>
</tr>
</tbody>
</table>
at relatively low concentrations, to form complex species. For this case, we consider only the reaction

\[ H^+ + SO_4 \rightleftharpoons HSO_4 \]

Wendt (1965) gives a value of 0.36 for the equilibrium constant for this reaction. The ion and combine diffusion coefficient matrices for this system are given in Table E.2. As with the type A system, the ionic diffusion coefficient matrix is full and the combine diffusion coefficient matrix is diagonal. Contrary to the type A system, however, the combine matrix contains three non-zero terms. This result reflects the fact that even though the reactive system can be defined by two thermodynamic components, \( \text{Na}_2\text{SO}_4 \) and \( \text{H}_2\text{SO}_4 \), diffusion involves three diffusion quantities.
Table E.2. Ion and combine diffusion coefficient matrices for the system H—Na—SO₄

<table>
<thead>
<tr>
<th>Component</th>
<th>Molarity</th>
<th>Activity Coefficient</th>
<th>Ionic Conductance (ohm⁻¹ cm²/gm-equiv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.0 x 10⁻²</td>
<td>0.93</td>
<td>38.7</td>
</tr>
<tr>
<td>H</td>
<td>9.98 x 10⁻²</td>
<td>0.93</td>
<td>73.5</td>
</tr>
<tr>
<td>SO₄</td>
<td>9.98 x 10⁻²</td>
<td>0.74</td>
<td>76.4</td>
</tr>
<tr>
<td>HSO₄</td>
<td>2.03 x 10⁻⁶</td>
<td>0.93</td>
<td>51.2</td>
</tr>
</tbody>
</table>

Ion Diffusion Coefficient Matrix (1 x 10⁻⁵ cm²/s)

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>H</th>
<th>SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.21</td>
<td>-0.83</td>
<td>0.19</td>
</tr>
<tr>
<td>H</td>
<td>-0.83</td>
<td>3.50</td>
<td>1.33</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.19</td>
<td>1.33</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Combine Diffusion Coefficient Matrix (1 x 10⁻⁵ cm²/s)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.27</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0.005</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>4.20</td>
</tr>
</tbody>
</table>
APPENDIX F

COMPUTATION OF AQUEOUS CHEMICAL EQUILIBRIUM

Consider an aqueous solution containing $N$ cationic components and $M$ anionic components which may combine to form $S$ ion pairs or complexes. Further assume that the total molarity of each component is known. The $j$th complexation reaction can be represented by

$$v_{j1}C_1 + \ldots + v_{jN}C_N + v_{jN+1}A_1 + v_{jN+M}A_M = S_j \quad (F.1)$$

where $v_{ij}$ are the stoichiometric coefficients of the $i$th reactant (component) in the $j$th reaction and in the $j$th complex species. For each reaction there is a thermodynamic constant defined as

$$K_j = \frac{\gamma_i^m}{\prod_{i=1}^{N+M} v_{ji} \gamma_i^m_i} \quad (F.2)$$

where $m_i$ is the molar concentration of the $i$th component and $\gamma_i$ is the activity coefficient of component $i$. This is the mass-action constraint.

To handle redox equilibria, we adopt the convention that all redox reactions are defined by the appropriate reduction half-reactions (Stumm and Morgan, 1970) written in terms of the an oxidized component, electrons, and a reduced product species. Thus, the general reduction half-reaction is
jth reduction: \[ \sum_{j=1}^{N+M-1} \nu_{ji} c_i + \nu_{jN+M} e = R_j \] (F.3)

and the corresponding mass-action equation is

\[ K_j = \frac{\gamma_{jN+M}^{m_{jN+M}}}{\left( \prod_{i=1}^{N+M-1} (\gamma_{i}^{m_{i}})^{\nu_{ji}} \right)^{\alpha_e}} \] (F.4)

Note that this convention requires that the fictitious free electron be treated as a component. In the remainder of this section, the free electrons are treated in a manner exactly analogous to the treatment of free protons ($H^+$) (Stumm and Morgan, 1970).

Because the total molarity of the components is assumed to be known, we can also write a mass-balance constraint as

\[ m_i^T = m_i + \sum_{j=1}^{S} \nu_{ji} m_i \] (F.5)

where $m_i^T$ is the total or analytic concentration of component $i$. An additional constraint on the system is that the solution must be electrically neutral so that

\[ \sum_{i=1}^{N+M} z_i m_i + \sum_{j=1}^{S} z_j m_j = 0 \] (F.6)

Equations (F.2) through (F.6) are sufficient to completely define the actual distribution of aqueous species in the solution and
our purpose here is to solve this system of equation for the molar concentrations of these species. Following the method of Wolery and Walters (1975), we solve (F.2) for the concentration of the $j$th complex so that

$$m_j = \frac{1}{\gamma_j} K_j \prod_{i=1}^{N+M} (\gamma_i m_i)^{\nu_{ji}}$$

(F.7)

and substituting (F.7) into (F.5) we obtain

$$m_j^T = m_i + \sum_{j=1}^{S} \frac{\nu_{ji}}{\gamma_j} K_j(\gamma_j m_j)^{\nu_{ji}} = \prod_{k=1}^{N+M} (\gamma_k m_k)^{\nu_{jk}}$$

(F.8)

which is the mass-balance constraint expressed entirely in terms of the components. Also note that in (F.8) the subscript $k$ is simply a dummy subscript for $i$ and that $\gamma_k$, $m_k$, and $\nu_{jk}$ all refer to the components. We wish to solve (F.8) for the unknown concentration of $i$, $(m_i)$. Dividing (F.8) by $m_i$ gives

$$\frac{m_j^T}{m_i} = 1 + \sum_{j=1}^{S} \frac{\nu_{ji}}{\gamma_j} K_j(\gamma_j m_j)^{\nu_{ji}} - 1 \prod_{k \neq i}^{N+M} (\gamma_k m_k)^{\nu_{jk}}$$

(F.9)

and rearranging (F.9) gives

$$m_j = m_i^T \left[ 1 + \sum_{j=1}^{S} \frac{\nu_{ji}}{\gamma_j} K_j(\gamma_j m_j)^{\nu_{ji}} - 1 \prod_{k \neq i}^{N+M} (\gamma_k m_k)^{\nu_{jk}} \right]^{-1}$$

(F.10)
Using (F.10) we can define an iterative solution algorithm for \( m_i \) by writing

\[
\begin{align*}
    m_i^{(z+1)} &= m_i^T \left[ 1 + \sum_{j=1}^{N+M} \frac{\nu_{ji}}{\gamma_j} K_{ji} \gamma_i(\omega) m_i(\omega)^{\nu_{ji}-1} \right]^{-1} \\
               &\quad \cdot \prod_{k=1}^{N+M} (\gamma_k^i m_k(\omega)^{\nu_{jk}})
\end{align*}
\]

where the superscript \( z \) denotes the value at the \( z \)th iteration. Wolery and Walters (1975) have shown that this iterative procedure is convergent for physically meaningful values of the variables.

As written, (F.11) has the form of a point Jacobi iteration in that the new values of the vector \( \bar{m}^{z+1} \) are computed from the values of \( \bar{m} \) at the previous iteration. We wish to consider the possibility of using a Gauss-Seidel iteration, that is, updating the values of \( m_k \) as soon as they are available during an iteration. In this way (F.11) becomes

\[
\begin{align*}
    m_i^{(z+1)} &= m_i^T \left[ 1 + \sum_{j=1}^{N+M} \frac{\nu_{ji}}{\gamma_j} K_{ji} \gamma_i(\omega) m_i(\omega)^{\nu_{ji}-1} \right]^{-1} \\
               &\quad \cdot \prod_{k=1}^{i-1} (\gamma_k^i m_k(\omega)^{\nu_{jk}}) \cdot \prod_{k=i+1}^{N+M} (\gamma_k^i m_k(\omega)^{\nu_{jk}})
\end{align*}
\]
Let us evaluate the convergence of (F.12) by following the procedure used by Wolery and Walters (1975). First, by differentiating (F.12) with respect to any $m_p$ where $p \neq i$, we obtain

\[
\frac{\partial m_i^{(z+1)}}{\partial m_p} = - \frac{(m_i^{(z+1)})^2}{m_i^j} \left[ \sum_{j=1}^{S} \frac{\gamma_{ij}^{(z)}}{\gamma_j^{(z)}} K_{ji} (m_i^{(z)})^{\gamma_{ji}^{(z)} - 1} \right. \\
\left. \cdot (\gamma_p^{(z)} m_p^{(z)})^{\gamma_{jp}^{(z)} - 1} \cdot (\gamma_j^{(z)} m_i^{(z+1)})^{\gamma_{jk}^{(z)}} \prod_{k=1}^{i-1} (\gamma_{jk}^{(z)} m_k^{(z+1)})^{\gamma_{jk}^{(z)}} \prod_{k=i+1}^{N+M} (\gamma_k^{(z)} m_k^{(z)})^{\gamma_{jk}^{(z)}} \right]^{-1}
\]

(F.13)

From (F.13) we have (because the summation term is cannot be negative)

\[
\frac{\partial m_i^{(z+1)}}{\partial m_p} \leq 0
\]

(F.14)

If we differentiate (F.13) with respect to $m_i^{(z)}$ we obtain
\[ \frac{\Delta m_i^{(z+1)}}{\Delta m_i^{(z)}} = - \left( \frac{m_i^{(z+1)}}{m_i} \right)^2 \left[ \sum_{j=1}^{S} \frac{\nu_{ji}}{\gamma_j} K_{ji}(\nu_{ji} - 1) \right] \]

\[ = (\gamma_i m_i^{(z)})^2 \nu_{ji} - 2 \cdot \prod_{k=1}^{i-1} (\gamma_k m_k^{(z+1)})^\nu_{jk} \cdot \prod_{k=i+1}^{N+M} (\gamma_k m_k^{(z)})^\nu_{jk} \right]^{-1} \]

so that

\[ \frac{\Delta m_i^{(z+1)}}{\Delta m_i^{(z)}} \leq 0 \quad \text{if} \quad \nu_{ji} \geq 1 \quad \text{for at least one reaction} \]  \hspace{1cm} (F.16)

Now consider the approximation to \( m_i \) obtained from the iterative solution of (F.12). Letting the initial estimate of \( \bar{m} \) be \( \bar{m}^T \) and representing the right hand side of (F.12) by \( \phi(\bar{x}^{(1)}) \) we have

\[ \phi(0) = \bar{m}^T > \bar{m}^* \]  \hspace{1cm} (F.17)

where \( \bar{m}^* \) is the exact solution. Equation (F.17) holds because of the decreasing nature of \( \phi \) and the identity
\[ m_1^{(1)} = \phi(x^0) = \phi(-m^T) \tag{F.18} \]

Inasmuch as \( x^0 > m^* \), the negative slope of \( \phi \) (required by the nonpositive partial derivatives) requires that

\[ m_1^{(1)} < m_i^* \tag{F.19} \]

Similarly, for the second step

\[ m_1^{(2)} = \phi(m_1^{(1)}, \ldots, m_{i-1}, m_i^T, \ldots, m_T^{N+M}) \tag{F.20} \]

and by the negative partial derivatives,

\[ m_1^{(2)} > m_i^* \tag{F.21} \]

By induction

\[ m(0) \geq m(2) \geq m(4) \ldots \geq m^* \]

\[ \geq \ldots \geq m(3) \geq m(1) \tag{F.22} \]

The sequences

\[ \bar{m}(0), \bar{m}(2), \ldots \]

and

\[ \bar{m}(1), \bar{m}(3), \ldots \]

are bounded monotone sequences by (F.22) and are, therefore, convergent by the same arguments given in Wolery and Walters (1975).
The calculation of pH by the iterative procedure described above is accomplished by writing the proton balance as

\[ m^T_H = m^\circ_H - \sum_{j=1}^{S} \nu_j m_j^H + m_{OH} \]  

(F.23)

where \( m_{OH} \) accounts for the production of protons by the dissociation of water and \( m_{OH} \) is computed from

\[ a_{H^+} a_{OH^-} = K_w \]  

(F.24)

By rearranging (F.23) in a manner similar to that described for the other components, the same iterative procedure can be used. Convergence of the iterative procedure was found to be very slow for weak acids if the initial guess for the proton concentration is taken as

\[ m^T_H = m^\circ_H \]  

(F.25)

with \( m^T_H \) computed from the stoichiometry of any acids in solution. Convergence is greatly enhanced in this case if the initial estimates for the conjugate bases are used.

If required, activity coefficients are computed before each iteration using the extended Debye-Hückel equation if the ionic strength is less than 0.1 and the mean salt method if the ionic strength is greater than 0.1.
APPENDIX G

MODEL VERIFICATION

The accuracy of the ItDM solution of algorithm was verified against an analogous one-dimensional analytical solution for transient heat flow in a slab bounded by surfaces of constant temperature given by Carslaw and Jaeger (1959, p. 100). The verification model assumes a region extending from \(-1 < x < 1\) with zero initial potential (hydraulic head or concentration) and with the surfaces at \(x = \pm 1\) kept at constant potential for \(t > 0\). Both concentrations are governed by the diffusion equation

\[
\frac{\partial \phi}{\partial t} = \alpha \frac{\partial^2 \phi}{\partial t^2}
\]

where \(\phi\) is the normalized potential, either temperature, \(T/T_0\),

or concentration, \(C/C_1\)

\(t\) is time

and \(\alpha\) is the diffusivity or the diffusion coefficient, \(D\)

subject to the initial and boundary conditions

\[
\phi(x) = 0; \quad -1 < x < 1; \quad t = 0
\]

\[
\phi(\pm 1) = 1; \quad t \geq 0
\]

According to Carslaw and Jaeger (1959), the solution to this problem is

176
\[
\phi(x, t) = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\frac{(2n+1)^2 \pi^2 T}{4}\right) \cdot \cos\left((2n+1)\pi \xi / 2\right)
\]

where
\[
t_D = at/l^2
\]
\[
\xi = x/l
\]

The diffusion solution algorithms were verified using the one-dimensional grid shown in Figure G.1. The grid consisted of 23 nodes distributed over the region from \(x/l = 0\) to \(1\). The node at \(x/l = 0\) was held at constant potential.

Verification of the basic algorithm was performed for diffusion of a simple, hypothetical salt, CA, composed of monovalent ions, C and A (2 ionic components). The limiting ionic conductances of the two ions were assumed to be equal so that the resulting ionic diffusion coefficient matrix was

\[
D = \begin{bmatrix}
0.333 & 0.333 \\
0.333 & 0.333
\end{bmatrix}
\]

The diagonalized combine diffusion coefficient matrix was then

\[
\tilde{D} = \begin{bmatrix}
0.6665 & 0.0000 \\
0.0000 & 0.0000
\end{bmatrix}
\]

The single, non-zero combine diffusion coefficient results from the complete coupling of the diffusion fluxes of the two ionic species and
Figure G.1. Grid used for IBD model verification.
represents the effective diffusion coefficient of the neutral salt component CA.

The numerical solution was tested using values of $\Delta t_0$ equal to 0.001 and 0.0001, and values of $\Delta C_{\text{max}}$ equal to 0.1 and 0.01. The results of a simulation using $\Delta t_0 = 0.001$ and $\Delta C_{\text{max}} = 0.1$ are shown in Figure G.2 for values of $t_D$ ranging from 0.0133 to 0.0665. The numerical solution for $t_D = 0.665$ is plotted versus the analytic solution in Figure G.3. The agreement is very good and was found to improve with smaller values of $\Delta C_{\text{max}}$. 
Figure G.2. Comparison of computed and analytic solutions to 1-D problem.
Figure G.3. Correlation of numerical solution to single salt diffusion problem with analytic solution for $t_D = 0.0665$. 
REFERENCES


Waters, A. C., and P. R. Carroll, Editors. 1981. Preliminary stratigraphic and petrologic characterization of core samples from USW—G1, Yucca Mountain, Nevada. Los Alamos National Laboratory, LA-8840—MS.


Wolfsberg, K., and others. 1979. Sorption—desorption studies on tuff. I. Initial studies with samples from the J—13 drill site, Jackass Flats, Nevada. Los Alamos Scientific Laboratory, LA-7480—MS.
Wolery, T. J., and L. J. Walters. 1975. Calculations of equilibra-
tions distributions of chemical species in aqueous solutions by 

Wyllie, M. O. J., and M. B. Spangler. 1952. Application of electrical 
resistivity measurements to problems of fluid flow in porous 

Zonge, K. L. 1972. Electrical properties of rocks as applied to geo-