

**OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT  
ANALYSIS/MODEL COVER SHEET**

1. QA: QA

Page: 1 of 38

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Describe use:		
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REV01

Revised to change the predictive relationship for diffusion, and to address model validation.

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## 1 PURPOSE

The purpose of this document is described in the *Development Plan for Invert Diffusion Properties Model* (CRWMS M&O 1999b). The purpose is to develop a predictive model for the diffusivity of ions in granular materials in the Engineered Barrier System (EBS). The scope of this document is limited to developing a model showing how resistivity and diffusivity can be estimated as a function of water content and temperature. The *Development Plan for the Invert Diffusion Properties Model* (CRWMS M&O 1999b) was prepared which included a completed checklist for the model. The plan documents the AMR Number as E0000 and the corresponding work package as 12012383MX for the *Invert Diffusion Properties Model*. This document specifically applies to the first task of the plan for developing a model. The model is intended to be used to provide input to the EBS Radionuclide Transport Model and the EBS Radionuclide Transport Abstraction. It has been determined that diffusion through the invert is a factor important to the postclosure safety case.

## 2 QUALITY ASSURANCE

This document was prepared in accordance with AP-3.10Q, *Analyses and Models*, and the Development Plan (CRWMS M&O 1999b). A Technical Change Request (T2000-0252) was approved in accordance with AP-3.4Q, *Level 3 Change Control* for this revision.

This technical document has been evaluated (CRWMS M&O 1999c) in accordance with QAP-2-0, *Conduct of Activities*, and has been determined to be subject to the requirements of the *Quality Assurance Requirements and Description* (DOE 2000). The QAP-2-3, *Classification of Permanent Items*, evaluation entitled *Classification of the MGR Ex-Container System* (CRWMS M&O 1999a, p. IV-1) has identified the ex-container system as QL-1, high safety or waste isolation significance. The invert as a diffusive barrier is not specifically classified, but the invert is a component of the ex-container system. For this document, it is assumed that the classification of a diffusive barrier is QL-1.

This model is validated in accordance with Section 5.3 of AP-3.10Q, *Analyses and Models*. Model validation is discussed in Section 6.5. Qualified and accepted input data and references have been identified. Inputs of experimental data are documented in Attachment I of this report in accordance with AP-3.15Q, *Managing Technical Product Inputs*. Results of this model have been submitted to TDMS in accordance with AP-SIII.3Q, *Submittal and Incorporation of Data to the Technical Data Management System*. Computer software and model usage are discussed in Section 3 of this report.

In order to ensure accuracy and completeness of the information generated in this document in accordance with AP-SV.1Q, *Control of the Electronic Management of Data*, access to the information on the personal computer was controlled with password protection. The personal computer file was stored on the network "G" drive, which was backed up daily by the Enterprise Server Team Department per project policy. When the work was completed, the file was transferred to a diskette, appropriately labeled, and verified by examining the file listing. The diskette was then hand-delivered to the Technical Data Management System.

### 3 COMPUTER SOFTWARE AND MODEL USAGE

No software subject to the requirements of the *Quality Assurance Requirements and Description* (DOE 2000) was used in the preparation of this document. The model developed herein is validated in Section 6.5. The developed model is appropriate for the estimation of conductivity and diffusivity. The results of this report are within the range of validation, as discussed in Section 6.5.2.

## 4 INPUTS

### 4.1 DATA AND PARAMETERS

The model inputs consist of formulas, and their inputs for characterizing the conductivity of partially saturated granular media. The model inputs include other formulas that relate the diffusivity to properties of liquid water. It includes measurements of conductivity, and calculations of diffusivity. These data are appropriate for their intended use in this model.

#### 4.1.1 Archie's Formula for Saturated Conditions

Keller and Frischknecht (1966, p. 21) present Archie's Formula for the relationship of the resistivity of a saturated porous material to the resistivity of water, and porosity:

$$\rho_{\text{sat}} = A * \rho_{\text{water}} * \Phi^{-m}$$
$$\rho_{\text{sat}} = \rho_{\text{water}} * \Phi^{-m} \quad (\text{Eq. 1})$$

where:

$\rho_{\text{sat}}$	-Resistivity of saturated material (ohm-cm)
$\rho_{\text{water}}$	-Resistivity of water in the pore space (ohm-cm)
$\Phi$	-Porosity
$m$	-Cementation factor
$A$	-Empirical factor, $A=1$

This equation can also be arrived at by combining the following two equations (Pirson 1963, p. 22; Bear 1988, p. 113):

$$\rho_{\text{sat}} = \rho_{\text{water}} * f \quad (\text{Eq. 2})$$

where:

$\rho_{\text{sat}}$	-Resistivity of saturated material (ohm-cm)
$\rho_{\text{water}}$	-Resistivity of water in the pore space (ohm-cm)
$f$	-Formation factor

and (Pirson 1963, p. 23; Bear 1988, p. 116):

$$f = \Phi^{-m} \quad (\text{Eq. 3})$$

where:

- $\Phi$  -Porosity
- $m$  -Cementation factor

Substituting Equation 3 into Equation 2 yields Equation 1.

#### 4.1.2 Cementation Factor for Unconsolidated Sand

The cementation factor for unconsolidated sand has been widely reported as 1.3 (Bear 1988, p. 116; Pirson 1963, p. 24).

#### 4.1.3 Archie's Formula for Unsaturated Conditions

The formula presented above can be modified for unsaturated conditions that would apply to the Engineered Barrier System (Bear 1988, p. 116; Keller and Frischknecht 1966, p. 28; Pirson 1963, p. 24):

$$\rho = \rho_{\text{sat}} * S_w^{-n} \quad (\text{Eq. 4})$$

where:

- $\rho$  -Resistivity of unsaturated material (ohm-cm)
- $\rho_{\text{sat}}$  -Resistivity of saturated material (ohm-cm)
- $S_w$  -Fractional saturation, volume of water divided by volume of pores
- $n$  -Saturation exponent

#### 4.1.4 Saturation Exponent for Unconsolidated Sand

The saturation exponent for unconsolidated sand has been accepted by the scientific community as 2 (Bear 1988, p. 116; Keller and Frischknecht 1966, p. 28; Pirson 1963, p. 24). Note that the technical basis for the saturation exponent is discussed in Section 6.5.2.

#### 4.1.5 Nernst-Einstein Equation for Diffusivity

The Nernst-Einstein Equation defines a direct proportionality between equivalent conductance and the diffusion coefficient of an ion. Given the equivalent conductance of a solution of ions, the rate of diffusion can be found through the Nernst-Einstein Equation. The Nernst-Einstein Equation (Perry and Chilton 1973, p. 3-235) is as follows:

$$D_0 = 8.931 \times 10^{-10} T_k \left( \frac{l_+^0 \cdot l_-^0}{\Lambda_0} \right) \left( \frac{z_+ + z_-}{z_+ \cdot z_-} \right) \quad (\text{Eq. 5})$$

where:

- $D_o$  -Diffusivity of molecule at infinite dilution (ionic pair), in  $\text{cm}^2 \text{sec}^{-1}$
- $T_k$  -Temperature, in K
- $I_+^0$  -Cationic conductance at infinite dilution, in S/equivalent
- $I_-^0$  -Anionic conductance at infinite dilution, in S/equivalent
- $\Lambda_o$  -Electrolyte conductance at infinite dilution, in S/equivalent
- $z_+$  -Valence of cation (absolute, i.e., no sign)
- $z_-$  -Valence of anion (absolute, i.e., no sign)

and

$$\Lambda_o = I_+^0 + I_-^0 \quad (\text{Eq. 6})$$

It can be shown that the square of the average of two (unique) numbers is always greater than their product (Attachment II). This implies that:

$$\bar{I}^2 \geq I_+^0 \cdot I_-^0$$

where:

- $\bar{I}$  -Average ionic conductance at infinite dilution, in S/equivalent

It is conservative to substitute the square of the average ionic conductance for the product of the cationic and anionic conductance because the resulting diffusion coefficient, if altered, will be made larger (i.e., a faster rate of diffusion). Incorporating this substitution and Equation 6 into Equation 5 yields:

and

$$D = 8.931 \times 10^{-10} T_k \left( \frac{I_+^0 \cdot I_-^0}{\Lambda_o} \right) \left( \frac{z_+ + z_-}{z_+ \cdot z_-} \right) \quad (\text{Eq. 5})$$

$$\Lambda_o = I_+^0 + I_-^0 = 2\bar{I}$$

(Eq. 6)

It follows from Equation II-2:

substituting:

$$D = 8.931 \times 10^{-10} T_k \left( \frac{\bar{I}^2}{2\bar{I}} \right) \left( \frac{2}{1} \right)$$

$$D_* = 8.931 \times 10^{-10} T_k (\bar{I})$$

where the valence of the ions is assumed to be one because this value maximizes the diffusion coefficient denoted by  $D^*$ . Simplifying further.

$$D_* = 8.931 \times 10^{-10} T_k \left( \frac{\Lambda_0}{2} \right) \quad (\text{Eq. 7})$$

where:

$D_*$  - Maximum Diffusivity of molecule at infinite dilution (ionic pair), in  $\text{cm}^2 \text{sec}^{-1}$

The constant in Equation 5 is derived from the universal gas constant and the Faraday constant in the following manner:

$$R_u / F^2 = 8.931 \times 10^{-10} \quad (\text{Eq. 8})$$

where:

$R_u$  - Gas constant,  $R=8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$  (Atkins 1990, front cover)

$F$  - Faraday constant,  $F=96485 \text{ C mol}^{-1}$  (Atkins 1990, front cover)

#### 4.1.6 Equation Relating Equivalent Conductivity and Correlated Concentration

Atkins (1990, p. 750) presents an equation relating the equivalent conductivity to the electrical conductivity:

$$\lambda = \kappa / c \quad (\text{Eq. 9})$$

where:

$\lambda$  - Equivalent conductivity (or molar conductivity), in  $\text{S cm}^2 \text{ mol}^{-1}$

$\kappa$  - Electrical conductivity, in  $\text{S cm}^{-1}$

$c$  - Corrected concentration, in  $\text{mol/L}$

#### 4.1.7 Conductance as a Function of Conductivity and Correlated Concentration

Atkins (1990 p. 750) presents a relationship for the conductivity as a function of conductance:

$$\kappa = G * \Theta \quad (\text{Eq. 10})$$

where:

$\kappa$  - Electrical conductivity, in  $\text{S cm}^{-1}$

$G$  - Measured conductance, in  $\text{S}$

$\Theta$  - Cell constant, in  $\text{cm}^{-1}$

Note:  $G=R^{-1}$  (where  $R$  is resistance) and the conductance is defined as the inverse of resistance ( $\text{S} = \Omega^{-1}$ ) (Atkins 1990, p. 750).

#### 4.1.8 Concentration Corrected for Activity

Weast (1981, p. F-79) presents a relationship corrected for activity:

$$c = a * M \quad (\text{Eq. 11})$$

where:

- c – Corrected concentration, in mol/L
- a – Activity coefficient, dimensionless.
- M – Concentration, in mol/L

#### 4.1.9 Viscosity of Water at 20 Degrees Celsius

The viscosity of water at 20 °C is 1.002 Centipoise (Weast 1981, p. F-42).

#### 4.1.10 Viscosity of Water as a Function of Temperature

Weast (1981, p. F-42) presents a relationship for the viscosity of water as a function of temperature:

$$\log_{10} \left( \frac{\eta_T}{\eta_{20}} \right) = \frac{1.3272 \cdot (20 - T) - 0.001053 \cdot (T - 20)^2}{T + 105}$$

Rearranging:

$$h_T = 1.002 \times 10^{\left[ \frac{1.3272 \cdot (20 - T) - 0.001053 \cdot (T - 20)^2}{T + 105} \right]} \quad (\text{Eq. 12})$$

where:

- $\eta_T$  – Viscosity of water at temperature T, in Centipoise [gm/cm sec 10<sup>2</sup>]
- $\eta_{20}$  – Viscosity of water at 20 °C, in Centipoise [gm/cm sec 10<sup>2</sup>]
- $\eta_{20} = 1.002$  Centipoise (Section 4.1.9)
- T – Temperature, in Celsius

#### 4.1.11 Electrical Resistivity and Conductivity of 0.1 Molar Potassium Chloride

Robinson and Stokes (1965 p. 462) quote the conductivity of 0.1 molar potassium chloride as 0.012856 S/cm. Since the resistivity ( $\rho$ ) and conductivity ( $\kappa$ ) are inversely related ( $\kappa = \rho^{-1}$ ) (Atkins 1990, p. 750), the resistivity of 0.1 molar potassium chloride is  $(0.012856 \text{ S/cm})^{-1} = 77.7 \text{ ohm-cm}$ .

#### 4.1.12 Activity Coefficient of 0.1 Molar Potassium Chloride

Weast (1981, p. D-146) present the activity coefficient of 0.1 molar potassium chloride is 0.77.

#### 4.1.13 Diffusion Coefficient of Potassium Chloride

Weast (1981, p. F-53) present the diffusion coefficient of potassium chloride in solution is  $1.844 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ . It should be noted that Fetter (1993, page 44) states that the values for molecular diffusion or binary diffusion coefficient are well known, and fall in the range of  $1 \times 10^{-5}$  to  $2 \times 10^{-5} \text{ cm}^2/\text{sec}$ . Further, Freeze and Cherry (1979, p. 103) quotes values within this range for major ions. In conclusion, the value for the diffusion coefficient is reasonable, and falls within the range for ions reported in the literature.

#### 4.1.14 Porosity range

The accepted minimum porosity of unconsolidated sand is 30 % (Bear 1988, p. 46). While it is conceivable that poorly sorted sand may have a lower porosity, this value is considered the lower bound for most samples. The maximum porosity for uniform spherical particles approaches 50 % (Bear 1988, p. 45). The range of porosity used in this model is between 30 % and 50 %.

#### 4.1.15 Effect of Temperature on Diffusion

The diffusivity ( $D$ ) is proportional to temperature ( $T_k$ , in Kelvin) and inversely proportional to viscosity ( $\eta$ ) (i.e.,  $D \propto T / \eta$ ) (Cussler 1997, p. 114).

It follows that if diffusivity ( $D_0$ ) is known at some [ambient] temperature ( $T_{k0}$ ), the diffusivity ( $D$ ) at some [elevated] temperature ( $T_k$ ) can be found by:

$$D = D_0 \cdot \frac{\left( \frac{T_k}{T_{k0}} \right)}{\left( \frac{h}{h_0} \right)} \quad (\text{Eq. 13})$$

Substituting viscosity (Equation 12) for  $\eta$  and  $\eta_0$  [using  $(b * a^x) / (b * a^y) = a^{x-y}$ ]:

$$D = D_0 \cdot \frac{\left( \frac{T + 273}{T_0 + 273} \right)}{10^{\left[ \frac{1.3272 \cdot (20 - T) - 0.001053 \cdot (T - 20)^2}{T + 105} - \frac{1.3272 \cdot (20 - T_0) - 0.001053 \cdot (T_0 - 20)^2}{T_0 + 105} \right]}} \quad (\text{Eq. 14})$$

where:

- $D$  - Adjusted diffusivity, in  $\text{cm}^2/\text{sec}$ , at temperature  $T$ , in degrees Celsius
- $D_0$  - Diffusivity, in  $\text{cm}^2/\text{sec}$ , at temperature  $T_0$ , in degrees Celsius

#### **4.1.16 Diffusion and Flow in Gravel, Soil, and Whole Rock**

Diffusion coefficients (Conca and Wright, 1992) were experimentally determined for gravel, soil, and whole rock using the Unsaturated Flow Apparatus Electrical Conductivity Method (UFA-EC). The UFA consists of an ultracentrifuge with a constant ultralow flow pump that provides fluid to the sample through a rotating seal assembly and microdispersal system. The ultracentrifuge can reach accelerations of up to 20,000 g (CRWMS M&O 1996, Appendix C). The ultracentrifuge was used to establish the range of volumetric moisture contents for a range of moisture potentials for a wide variety of geotechnical materials. The Diffusion coefficient was determined by a direct application of the Nernst Einstein equation (Conca and Wright 1992, p. 9) with electrical conductivity measurements. An electrical conductivity cell (EC), designed for use in the UFA, fits inside the centrifuge sample chamber between two stainless steel electrodes that are 2.5 cm apart. The relationship of diffusion coefficient versus volumetric moisture content data is obtained from this experimental study as documented in DTN MO9810SPA00026.000 entitled Diffusion Coefficient Model for TSPA-VA. The data qualification status are presented in the DIRS and the data are used in Section 6.5.2.

#### **4.1.17 Path Length/Distance(m)**

Path length/Distance (m) is defined as the thickness of the invert material. The thickness of the invert directly below the waste package is 0.606 m (DTN: SN9908T0872799.004). A rounded value of 0.61 m is used for the solid-solid diffusion calculation in Section 6.7

### **4.2 CRITERIA**

No criteria, as defined in AP-3.10Q, were used in the preparation of this document.

### **4.3 CODES AND STANDARDS**

No codes or standards, as defined in AP-3.10Q, were used in the preparation of this document.

## **5 ASSUMPTIONS**

These assumptions are used in the preparation of this model as discussed below. All TBVs for assumptions requiring confirmation are documented in the DIRS.

### **5.1 APPLICATION OF DIFFUSION DATA TO THE STEEL CAGE FILLED WITH GRADED AND CRUSHED TUFF**

Conca and Wright (1992) developed diffusion data for a variety of granular materials. It is assumed that these data apply to the crushed tuff invert at ambient temperature. The technical basis for this assumption is that Conca and Wright (1992) also used the UFA to control volumetric moisture content in their samples, and over a wide range that is relevant to the long-term response of the EBS. Conca and Wright (1992) investigated a wide variety of granular materials including crushed tuff that are applicable to the EBS. This assumption is used

throughout the document, and specifically in Sections 6.5.1 and 6.5.2. This assumption requires confirmation.

## **5.2 UPPER BOUND DIFFUSION LIMIT**

It is assumed that the self-diffusion of water provides a bounding value for the free water diffusion for radionuclides relevant to the EBS. The technical basis for this assumption is explained in the EBS Radionuclide Transport Abstraction AMR (CRWMS M&O 2000, Section 6.4.1.1). This assumption is used in Section 6.5.2.

## **5.3 DEPENDENCE OF DIFFUSIVITY ON POROSITY**

It is assumed that the empirically derived normalized diffusivity relationship depends on porosity through the factor of  $\phi^{-7}/0.5^{0.7}$  as suggested by the application of Archie's Law. The technical basis for this assumption is that the general form of Archie's Law includes a dependence of porosity (Section 4.1.1) with  $m = 1.3$  (Section 4.1.2). This assumption requires confirmation since the empirical linear fit (Section 6.5.2) using transformed data is obtained with volumetric moisture content as the independent variable without consideration to porosity. The assumption can be confirmed through a multiple linear regression analysis in which both porosity and volumetric content are considered.

# **6 ANALYSIS/MODEL**

A model for estimating the diffusivity of electrolytes in saturated and unsaturated porous material is developed in this section. The model has two parts: first, a submodel for estimating the conductivity of a material is presented in Section 6.1. The inputs into this submodel are empirical, and accepted data for clean sand is given as an example. This submodel predicts the conductivity of a material as a function of saturation and porosity.

The second submodel is developed in Section 6.2 and yields a diffusion coefficient based on conductivity (found through direct measurement or through the method in Section 6.1). An additional portion of the submodel is developed in Section 6.3, and allows the adjustment of diffusion coefficients as a function of temperature. The effects of water composition are addressed in a bounding fashion in Section 6.4.

The model is validated by comparison with a collection of measured diffusion coefficients found using traditional techniques. Model validation criteria are developed in Section 6.5.1. Model validation data is developed in Section 6.5.2. A prediction relationship based upon a one sided confidence interval is presented in Section 6.6 that combines the several submodels.

## **6.1 RESISTIVITY AND CONDUCTIVITY OF PARTIALLY SATURATED GRANULAR MATERIALS**

Archie's law is presented as an estimate of the conductivity of a porous material based on saturation, resistance of the saturating solution, and porosity. Combining Equation 1 and

Equation 4 yields an equation for resistivity ( $\rho$ ) as a function of porosity, saturation, and the conductivity of the saturating fluid.

$$\rho = \rho_{\text{water}} \Phi^{-m} S_w^{-n}$$

Invert the relationship for conductivity and simplifying:

$$C = [\rho_{\text{water}} \Phi^{-m} S_w^{-n}]^{-1}$$

$$C = C_{\text{water}} \Phi^m S_w^n$$

(Eq. 15)

where:

- C - Conductivity of partially saturated material (S)
- $C_{\text{water}}$  - Free Water Conductivity of water (S)
- $\Phi$  - Porosity. Parametric range between 0.30 and 0.50
- $S_w$  - Saturation, fraction of pore volume containing water
- m - Empirical cementation factor
- n - Empirical saturation exponent

The calculated conductivity of sand partially saturated with 0.1 molar solution of potassium chloride is shown for ranges of porosity and saturation in Table 1 and Figure 1.

## 6.2 DIFFUSIVITY AS A FUNCTION OF CONDUCTIVITY

Diffusion processes commonly occur within gaseous and liquid phases within granular materials. For diffusion in the soil's liquid phase, the effective diffusion coefficient is generally less than the diffusion in the bulk water (Hillel, 1980 p. 236). In the first place the liquid phase occupies only a fraction of the soil volume; at most, in a state of saturation, its volume fraction equals the porosity. Second the soil's passages are tortuous so that the actual path length of diffusion is significantly greater than the apparent straight line distance. As volumetric moisture content is decreased, the fractional volume available for diffusion in the liquid phase decreases while path length increases.

Traditional steady state measurements of diffusivity in unsaturated media would require inordinate amounts of time to collect. Maintaining boundary conditions over extended time periods is difficult. One indirect method of determining diffusion coefficients at low water content is to use conductivity measurements to calculate diffusion coefficients. The analogy is between the driving forces acting on an ion. In electrical conductivity measurements, the driving force acting on the ions is electrical potential gradient. In diffusion, the driving force acting on the ions is the concentration gradient. These two forces are related through the Nernst-Einstein equation. The following analysis develops the relationship for the diffusivity in a 0.1 molar solution of potassium chloride. The analysis applies to the method of calculation for the diffusivity measurements made by Conca and Wright (1992) as discussed subsequently in Section 6.5.2.

The Conductance Equation is found by combining equations 7, 9, 10, and 11:  
Restating (Eq. 7):

$$D_* = 8.931 \times 10^{-10} T_k \left( \frac{\Lambda_o}{2} \right)$$

Restating (Eq. 9):  $\lambda = \kappa / c$

Restating (Eq. 10):  $\kappa = G * \Theta$

Restating (Eq. 11):  $c = a * M$

Combining Equations 9, 10, and 11:

$$\lambda = (G * \Theta) / (a * M (1L/1000cm^3)) \quad (\text{Eq. 16})$$

Diffusivity is found by combining Equations 7 and 16 (with  $\Lambda_o = \lambda$ ):

$$D_* = 8.931 \cdot 10^{-10} \cdot T_k \cdot \left( \frac{G \cdot \Theta \cdot 10^3}{2 \cdot a \cdot M} \right) \quad (\text{Eq. 17})$$

where:

- $D_*$  -Diffusivity of molecule (ionic pair) at infinite dilution, in  $cm^2 \text{ sec}^{-1}$
- $D$  -Diffusivity of molecule (ionic pair) in concentrated solution, in  $cm^2 \text{ sec}^{-1}$
- $\lambda$  -Conductance, in  $S \text{ cm}^2 \text{ mol}^{-1}$ . Adjusted for concentration effects.
- $\kappa$  -Conductivity, in  $S \text{ cm}^{-1}$
- $c$  -Corrected concentration, in mol/L
- $G$  -Measured conductance, in S
- $\Theta$  -Cell constant, in  $cm^{-1}$
- $a$  -Activity coefficient, dimensionless
- $M$  -Concentration, in mol/L
- $T$  -Temperature, in K
- $\Lambda_o$  -Electrolyte conductance at infinite dilution, in S/equivalent

Equation 15 can be modified to show the diffusivity is found as a function of conductivity:

$$D_* = 8.931 \cdot 10^{-10} \cdot T_k \cdot \left( \frac{C \cdot 10^3}{2 \cdot a \cdot M} \right) \quad (\text{Eq. 18})$$

simplifying:  $D_* = 5.799 \cdot 10^{-6} \cdot T_k \cdot C$  (Eq. 19)

simplifying:  $D_* = 1.728 \cdot 10^{-3} C$  (Eq. 20)

This submodel forms the basis for the calculation of diffusion from the measurement of electrical conductivity for samples of known volumetric moisture content as discussed subsequently in Section 6.5.2. Using the conductivity calculated from Equation 15, diffusivities are calculated in

Table 1: Diffusion Coefficients and Conductivity for 0.1 molar Potassium Chloride

Sw	Vw	Vw	Vw	C	C	C	D	D	D	Dt	Dt	Dt	Dt
Temperature, in degrees Celsius:													
Porosity:	0.30	0.40	0.50	0.30	0.40	0.50	0.30	0.40	0.50	0.40	0.40	0.40	0.40
0.00	0%	0%	0%	2.7E-09	3.9E-09	5.2E-09	4.6E-12	6.8E-12	9.0E-12	5.9E-12	1.2E-11	1.7E-11	2.3E-11
0.00	0%	0%	0%	2.4E-08	3.5E-08	4.7E-08	4.2E-11	6.1E-11	8.1E-11	5.3E-11	1.1E-10	1.5E-10	2.1E-10
0.01	0%	0%	0%	6.7E-08	9.8E-08	1.3E-07	1.2E-10	1.7E-10	2.3E-10	1.5E-10	3.0E-10	4.3E-10	5.8E-10
0.01	0%	0%	0%	1.3E-07	1.9E-07	2.6E-07	2.3E-10	3.3E-10	4.4E-10	2.9E-10	5.8E-10	8.4E-10	1.1E-09
0.01	0%	0%	1%	2.7E-07	3.9E-07	5.2E-07	4.6E-10	6.8E-10	9.0E-10	5.9E-10	1.2E-09	1.7E-09	2.3E-09
0.03	1%	1%	2%	2.4E-06	3.5E-06	4.7E-06	4.2E-09	6.1E-09	8.1E-09	5.3E-09	1.1E-08	1.5E-08	2.1E-08
0.05	2%	2%	3%	6.7E-06	9.8E-06	1.3E-05	1.2E-08	1.7E-08	2.3E-08	1.5E-08	3.0E-08	4.3E-08	5.8E-08
0.07	2%	3%	4%	1.3E-05	1.9E-05	2.6E-05	2.3E-08	3.3E-08	4.4E-08	2.9E-08	5.8E-08	8.4E-08	1.1E-07
0.10	3%	4%	5%	2.7E-05	3.9E-05	5.2E-05	4.6E-08	6.8E-08	9.0E-08	5.9E-08	1.2E-07	1.7E-07	2.3E-07
0.13	4%	5%	7%	4.5E-05	6.6E-05	8.8E-05	7.9E-08	1.1E-07	1.5E-07	1.0E-07	2.0E-07	2.9E-07	3.9E-07
0.15	5%	6%	8%	6.0E-05	8.8E-05	1.2E-04	1.0E-07	1.5E-07	2.0E-07	1.3E-07	2.7E-07	3.9E-07	5.2E-07
0.17	5%	7%	9%	7.8E-05	1.1E-04	1.5E-04	1.3E-07	2.0E-07	2.6E-07	1.7E-07	3.4E-07	4.9E-07	6.7E-07
0.20	6%	8%	10%	1.1E-04	1.6E-04	2.1E-04	1.9E-07	2.7E-07	3.6E-07	2.4E-07	4.8E-07	6.9E-07	9.3E-07
0.30	9%	12%	15%	2.4E-04	3.5E-04	4.7E-04	4.2E-07	6.1E-07	8.1E-07	5.3E-07	1.1E-06	1.5E-06	2.1E-06
0.40	12%	16%	20%	4.3E-04	6.3E-04	8.4E-04	7.4E-07	1.1E-06	1.4E-06	9.4E-07	1.9E-06	2.7E-06	3.7E-06
0.50	15%	20%	25%	6.7E-04	9.8E-04	1.3E-03	1.2E-06	1.7E-06	2.3E-06	1.5E-06	3.0E-06	4.3E-06	5.8E-06
0.70	21%	28%	35%	1.3E-03	1.9E-03	2.6E-03	2.3E-06	3.3E-06	4.4E-06	2.9E-06	5.8E-06	8.4E-06	1.1E-05
0.90	27%	36%	45%	2.2E-03	3.2E-03	4.2E-03	3.8E-06	5.5E-06	7.3E-06	4.8E-06	9.7E-06	1.4E-05	1.9E-05

Notes:

(Sw) Saturation (Sw) is a parametric value ranging between 0.1% and 100%

(Vw) Volumetric Water Content (Vw) is the product of porosity and saturation.

(C) = (0.012856 \* (Porosity)<sup>1.3</sup> \* (Saturation)<sup>2</sup>). Source: Equation 15 with C<sub>water</sub> = 0.012856 ( See Section 4.1.11).(D) = 2.222 \* 10<sup>-5</sup> \* ((Porosity)<sup>1.3</sup> \* (Saturation)<sup>2</sup>). Source: Equation 22.(Dt) = (7.455 \* 10<sup>-8</sup> \* (Temp. in K) \* (porosity)<sup>1.3</sup> \* (Sw)<sup>2</sup>) / [10<sup>4</sup> \* ((-1.3172 \* (20 - Temp in °C)) - 0.001053 \* ((Temp in °C - 20)<sup>2</sup>) / (Temp in °C + 105) + 0.051)]

Source: Equation 27.

While saturation (Sw) and volumetric water content (Vw) are displayed as percentages, the fractional values are used in calculations.

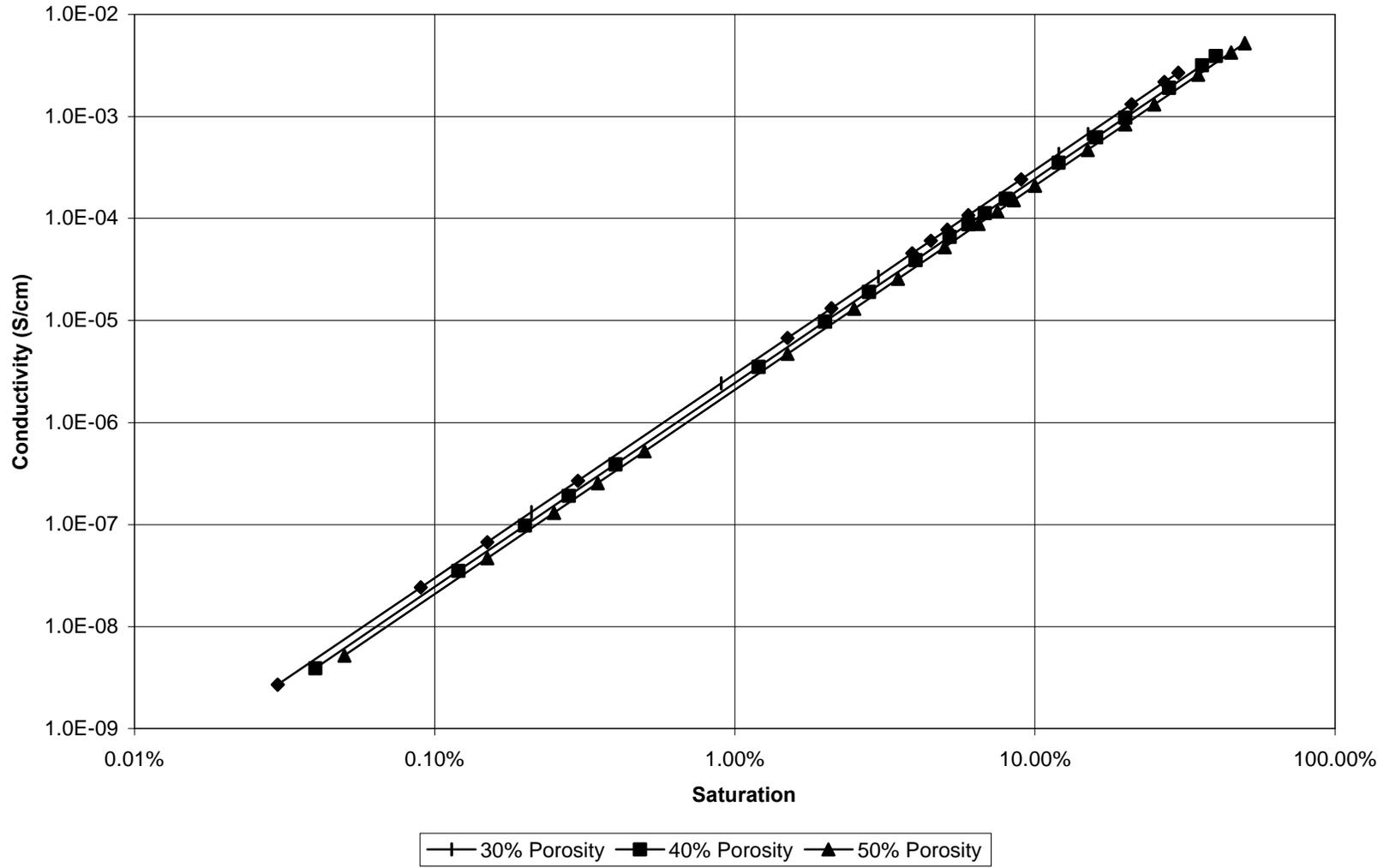


Figure 1. Plot of Conductivity vs. Saturation

Table 1 for a range of porosities and saturation levels. Substituting for C from Equation 15, and assuming the temperature to be 25 °C (Section 5.1):

$$D_* = 1.728 \cdot 10^{-3} \cdot C_{\text{water}} \Phi^m S_w^n \quad (\text{Eq. 21})$$

Simplifying: 
$$D_* = 2.222 \cdot 10^{-5} \Phi^m S_w^n \quad (\text{Eq. 22})$$

The parametric values in Equation 18 through 22 are as follows:

- a = 0.77
- M = 0.1 mol/liter
- T<sub>k</sub> = Temperature, in K. In this example T=298 K (25 °C)
- C<sub>water</sub> = 0.012856 S/cm in 0.1 molar potassium chloride.(4.1.11)
- m = 1.3 for sand
- n = 2.0 for sand

It should be noted that the derivation of Equation 22 as presented above is consistent with relationships presented in the literature for the dependence of diffusivity on volumetric moisture content (Hillel 1980, p. 236 and Jury et al. 1991 p. 221) In these relationships, the tortuosity factor is an empirical parameter smaller than unity that expresses the ratio of the straight line length of a sample of granular material to the average path length through the water-filled pores for a diffusing molecule or ion. The tortuosity has been found to depend on both the fractional water volume, and the geometric configuration of the water phase (Hillel 1980, p. 236). The diffusivity is found to be strongly dependent through a nonlinear relationship to volumetric moisture content.

### 6.3 TEMPERATURE EFFECTS ON CONDUCTIVITY AND DIFFUSION

The diffusivity of ions in solution is proportional to temperature and inversely proportional to viscosity ( See Section 4.1.15).

Restating (Eq. 14):

$$D = D_0 \cdot \frac{\left( \frac{T + 273}{T_0 + 273} \right)}{10^{\left[ \frac{1.3272 \cdot (20 - T) - 0.001053 \cdot (T - 20)^2}{T + 105} - \frac{1.3272 \cdot (20 - T_0) - 0.001053 \cdot (T_0 - 20)^2}{T_0 + 105} \right]}}$$

Restating (Eq. 17) at the reference temperature:

$$D_* = 8.931 \cdot 10^{-10} \cdot T_{k0} \cdot \left( \frac{G \cdot \Theta \cdot 10^3}{2 \cdot a \cdot M} \right)$$

for T<sub>0</sub> = 25 °C, the viscosity exponent is:

$$\frac{1.3272 \cdot (20 - T_0) - 0.001053 \cdot (T_0 - 20)^2}{T_0 + 105} = -0.051 \quad (\text{Eq. 23})$$

Substituting Equation 17 and Equation 23 into Equation 14 and converting to Kelvin ( $T_0$  cancels out of the numerator):

$$D_* = \frac{\left( 8.931 \cdot 10^{-10} \cdot T_k \cdot \left( \frac{G \cdot \Theta \cdot 10^3}{2 \cdot a \cdot M} \right) \right)}{10^{\left[ \frac{1.3272 \cdot (20 - (T_k - 273)) - 0.001053 \cdot ((T_k - 273) - 20)^2}{(T_k - 273) + 105} + 0.051 \right]}}$$

simplifying:

$$D_* = \frac{\left( 8.931 \cdot 10^{-10} \cdot T_k \cdot \left( \frac{G \cdot \Theta \cdot 10^3}{2 \cdot a \cdot M} \right) \right)}{10^{\left[ \frac{1.3272 \cdot (293 - T_k) - 0.001053 \cdot (T_k - 293)^2}{T_k - 168} + 0.051 \right]}} \quad (\text{Eq. 24})$$

Equation 24 is the general equation for calculating the diffusivity. It can be simplified for 0.1 molar potassium chloride with conductance measured at temperature  $T_{k0}$ , in Kelvin:

Equation 19: 
$$D_0 = 5.799 \cdot 10^{-6} \cdot T_{k0} \cdot C$$

Substituting Equation 19 and Equation 23 into Equation 14 and converting to Kelvin:

$$D_* = \frac{\left( 5.799 \cdot 10^{-6} \cdot T_k \cdot C \right)}{10^{\left[ \frac{-1.3272 \cdot (T_k - 293) - 0.001053 \cdot (T_k - 293)^2}{T_k - 168} + 0.051 \right]}} \quad (\text{Eq. 25})$$

Substituting Equation 15 for C:

$$D_* = \frac{\left( 5.799 \cdot 10^{-6} \cdot T_k \cdot (C_{water} \cdot \Phi^m \cdot S_w^n) \right)}{10^{\left[ \frac{-1.3272 \cdot (T_k - 293) - 0.001053 \cdot (T_k - 293)^2}{T_k - 168} + 0.051 \right]}} \quad (\text{Eq. 26})$$

For sand partially saturated with 0.1 molar potassium chloride:

$$D_* = \frac{(7.455 \cdot 10^{-8} \cdot T_k \cdot \Phi^{1.3} \cdot S_w^2)}{10^{\left[ \frac{-1.3272(T_k - 293) - 0.001053(T_k - 293)^2}{T_k - 168} + 0.051 \right]}} \quad (\text{Eq. 27})$$

Using Equation 27, diffusion coefficients based upon Archie's Law are calculated in Table 1 as a function of temperature.

## 6.4 EFFECTS OF WATER COMPOSITION ON DIFFUSION AND CONDUCTION

The activity coefficient of an ion in a single salt solution is generally higher than the activity coefficient of an ion in solution with many other ions. This statement is corroborated by Stumm and Morgan (1981, p. 411), where activity coefficients in single salt solutions are compared with activity coefficients measured in seawater. The use of activity for single salt solutions is conservative and bounding.

## 6.5 MODEL VALIDATION

Validation requires review of model calibration parameters for reasonableness and consistency with all relevant data. The invert diffusion properties model is validated in Section 6.5.2 by comparing the validation data (Section 4.1.16) with the validation criteria presented in Section 6.5.1.

### 6.5.1 Validation Procedure

The submodels include the conductivity prediction and the diffusion prediction. The conductivity submodel was presented in Sections 6.1 for liquids and is well established. The prediction of conductivity for geologic materials requires an assessment of the empirical cementation and saturation exponents as outlined below.

The second submodel relates to the prediction of the diffusion coefficient as a function of porosity, saturation, and temperature from the normalized diffusion relationship to volumetric moisture content, and how this prediction compares with measured data. Conca and Wright (1992) performed measurements for the diffusion coefficient for unsaturated soil, gravel, bentonite, and rock over a broad range of water contents (DTN: MO9810SPA00026.000). The measurements were performed using the Unsaturated Flow Apparatus- Electrical Conductivity (UFA-EC). These measured data are used to validate the basic diffusion relation presented in Equation 22. The statistical approach is to:

- (1) Transform the data for cohesionless materials from Conca and Wright (1992) for diffusion coefficient versus volumetric moisture content to obtain a linear relationship between these variables. Volumetric moisture content is defined as the saturation times the porosity.

- (2) Evaluate the valid range for volumetric moisture content, and select this range for analysis.
- (3) Perform linear regression analysis (Natrella 1963, p. 5-25) to obtain the slope of the regression line, and variance on the slope.
- (4) For a given  $(1-\alpha)$  confidence interval estimate the confidence interval for predicting future values (Natrella 1963, p. 5-24), and compare this result from the prediction obtained from Equation (22). The empirically determined relationship with given confidence interval is determined to be valid if the confidence interval brackets the prediction from Equation (22) for the range of porosities presented in Section 4.1.14.

Note that regarding validation of the temperature effects submodel the analysis is well established, and is based upon the well established temperature correction for viscosity as discussed previously in Section 6.3.

### 6.5.2 Validation Results

The data (Section 4.1.16) showing the relationship of diffusion coefficient to volumetric moisture content for various granular materials is presented in Figure 2. These data include measurements for a variety of geologic materials including soils from the locations of exploratory boreholes G-1, G-3, and G-4; various gravels, and various sands. Also, the data includes crushed tuff with gradations from 2-4 mm and 6.3 to 9.5 mm respectively; crushed basalt with gradations from 6.3 to 9.5 mm and 12.5 to 15 mm respectively; and crushed granite with a gradation from 6.3 to 9.5 mm. The results show a linear relationship between the log of the volumetric moisture content and the log of the diffusivity over the range of 1.5% to 66.3%. The results do not show any significant trends in terms of mineralogic composition of the parent materials nor with regard to gradation and porosity. This data can be applied to crushed tuff (Section 5.1).

Conca and Wright (1992) do not provide a detailed discussion of measurement error through the use of the Nernst-Einstein equation. The sources of error from the relation presented by Conca and Wright (1992, p. 9) include the measurement of temperature (T), the measurement of the cell constant( $\Theta$ ), the transference of the  $i$ th ion, the charge number( $Z_i$ ), and the measured conductance (G). Nevertheless, Figure 2 shows a departure from linearity for volumetric moisture contents less than 1.5%. This departure from linearity may be caused in fact by the systematic measurement error at very low moisture contents. The valid range for the measured data is estimated to be from a volumetric moisture content of 1.5% to 66.3 %.

The data are normalized to a diffusivity of 0.1 molar potassium chloride (Section 4.1.13). From Equation (22) at a saturation of 100%, and a porosity of one, the diffusivity is  $2.22 \times 10^{-5}$  cm<sup>2</sup>/sec. Noting that saturation  $S_w$  is equal to the ratio of volumetric moisture content to the saturated (maximum) volumetric moisture content:

$$\theta = \phi \cdot S_w \cdot 100 \tag{Eq. 28}$$

where:

- $\theta$  - Volumetric Moisture Content (%)
- $\phi$  - Porosity
- $S_w$  - Degree of saturation

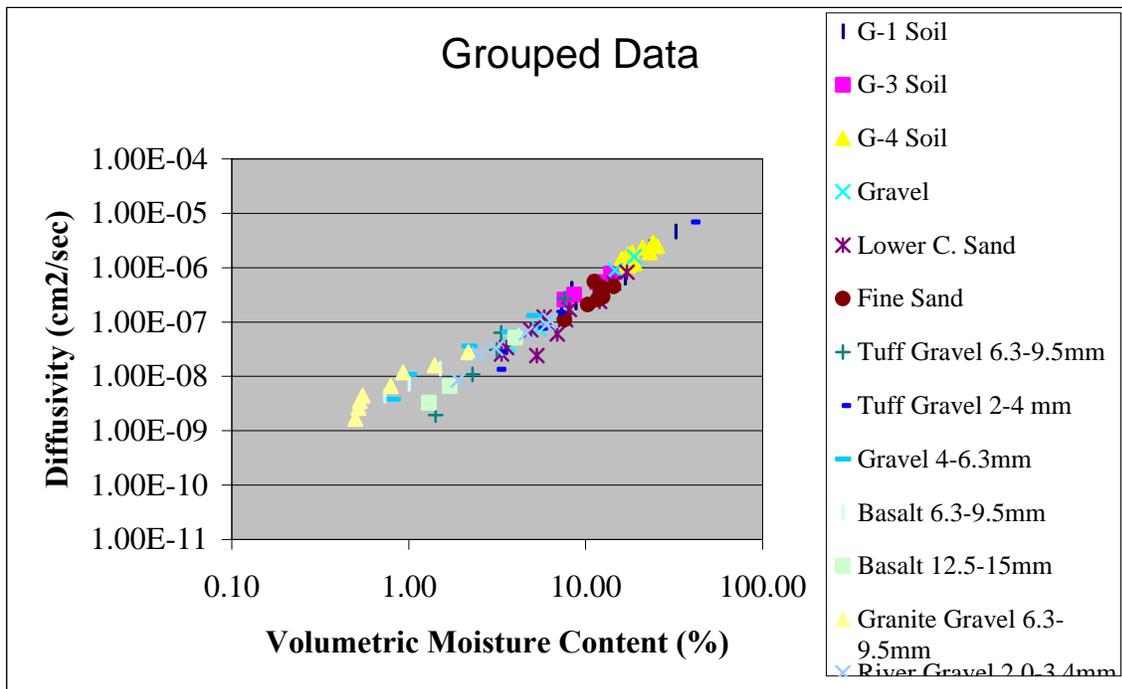
Solving for the saturation ( $S_w$ ) as a function of volumetric moisture content( $\theta$ ):

$$S_w = \frac{1}{100} \cdot \frac{\theta}{\phi} \tag{Eq. 29}$$

Substituting this relation into Equation 22 and normalizing to the free water diffusivity of 0.1 molar solution of KCl at a temperature 25 °C:

$$D_n = D_* / 2.22 \cdot 10^{-5} = \frac{\theta^2}{10000 \cdot \phi^{.7}} \tag{Eq. 30}$$

with  $m = 1.3$  (Section 4.1.2) and  $n = 2.0$  (Section 4.1.4).



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Figure 2. Relationship of Diffusivity to Volumetric Moisture Content for Various Granular Materials

Transform the data (Section 4.1.16) to the log plane (Attachment I). As discussed by Natrella, (1963, p. 5-30), a linearizing transformation can be performed, and the statistics that apply to these linear relations can then be used to estimate expectation and variance. The linearizing transformation for the new variables X and Y are as follows:

$$Y = \log(D/D_0)$$

$$X = \log(\theta) - 2$$

(Eq. 31)

where:

- Y -Transformed Variable for the Normalized Diffusivity
- X -Transformed Volumetric Moisture Content, and
- D<sub>0</sub> -Diffusivity of 0.1 molar potassium chloride at 25 °C.

Note that curvefitting is performed on the transformed data for a functional relationship in which the intercept is known to be zero (Natrella, 1963, p. 5-25). This ensures that the relationship between X and Y passes through the origin. This follows from Equations 22 and 28. When the porosity ( $\phi$ ) and saturation ( $S_w$ ) are 1, Equation 22 shows that the diffusivity equals the free water diffusivity so that  $Y = \text{Log}(1) = 0$ . Equation 28 shows that the volumetric moisture content  $\theta$ , is 100% when  $\phi = 1$ , and  $S_w = 1$ , so that  $X = \log(100) - 2 = 0$ . Therefore, the X-Y relationship must pass through the origin. Use the basic worksheet for a relationship with a zero intercept (Natrella 1963, p. 5-25). The resulting sums for the transformed values for X and Y for the diffusivity data are presented in Attachment I. Note that the steps and the formulas presented below correspond to the steps in the worksheet for the case that the intercept is known to be zero (Natrella 1963, p. 5-25):

$$S_X := \sum_{i=0}^{124} X_i$$

(Eq. 32)

The result is:

$$S_X = -119.982$$

$$S_Y := \sum_{i=0}^{124} Y_i$$

(Eq. 33)

The result is:

$$S_Y = -217.547$$

Calculate the following second moments for the data (Step (2)-(4)) (Natrella 1963, p. 5-25):

$$S_{XX} := \sum_{i=0}^{124} (X_i)^2$$

(Eq. 34)

The result is:

$$S_{XX} = 129.565$$

$$S_{XY} := \sum_{i=0}^{124} X_i \cdot Y_i$$

(Eq. 35)

The result is:

$$S_{XY} = 239.592$$

Step (3)

$$S_{YY} := \sum_{i=0}^{124} (Y_i)^2$$

(Eq. 36)

The result is:

$$S_{YY} = 449.213$$

The result for the slope ( $b_1$ ) of the X-Y relationship is (Step (4)):

$$b_1 := \frac{\sum_{i=0}^{124} X_i \cdot Y_i}{\sum_{i=0}^{124} X_i \cdot X_i}$$

(Eq. 37)

$$b_1 = 1.849$$

For Steps (5-7), the results are:

$$S_y := \sqrt{\frac{S_{YY} - \frac{S_{XY}^2}{S_{XX}}}{n-1}}$$

(Eq. 38)

$$S_y = 0.223$$

Note that  $S_y$  represents the standard deviation of the data points in the X-Y plane from the linear fit. Estimate standard deviation of the slope (Natrella 1963 p. 5-25):

$$S_{b1} := \sqrt{\frac{S_y^2}{\sum_{i=0}^{124} X_i \cdot X_i}}$$

(Eq. 39)

The result is:

$$S_{b1} = 0.02$$

Use Worksheet from Natrella (1963, p. 5-19) with modifications for the zero intercept relationship (Natrella 1963, p. 5-25) to estimate the confidence interval estimate for a single (future) value corresponding to a chosen value of X. The steps are:

(1) Choose the desired confidence level for the 95 % confidence level:

$$\alpha := 0.05$$

$$1 - \alpha = 0.95$$

(2) Obtain  $S_y$  from the above calculations (Eq. 38):

$$S_y = 0.223$$

(3) Look up  $t_{1-\alpha/2}$  for  $n-2$  degrees of freedom in Table A-4 (Natrella 1963, p. T-5):

$$t := 1.98$$

(4) Define the functions by choosing  $X'$ , the value of  $X$  at which to make an interval estimate of a single value of  $Y$ .

(5) Compute the 95 % confidence level envelopes for the case of a line with zero intercept (Natrella 1963, p. 5-24):

$$Y_h(x) := b_1(x) + t \left( \sqrt{S_y^2 + x^2 (S_{b_1^2})} \right) \quad (\text{Eq. 40a})$$

$$Y_l(x) := b_1(x) - t \left( \sqrt{S_y^2 + x^2 (S_{b_1^2})} \right) \quad (\text{Eq. 40b})$$

The calculations (Eqs. 40a-40b) for the upper and lower bound curves for the two sided confidence interval for future values of diffusivity are repeated for a range of volumetric moisture contents. The results of the analysis are presented in Figures 3. The results show that the prediction from Archie's Law (Eq. 22) falls within the confidence interval, and that the criterion for validation as outlined above is satisfied. The empirical relationship predicted by Archie's Law in Equation 22 in terms of volumetric moisture content with a cementation factor of 1.3 (Section 4.1.2), and a saturation exponent of 2 falls within the 95 % confidence interval for the data (Conca and Wright (1992) represented by Equations 40a and 40b. It is determined that these models are validated for their intended use in the EBS Radionuclide Transport Model and the EBS Radionuclide Transport Abstraction Model.

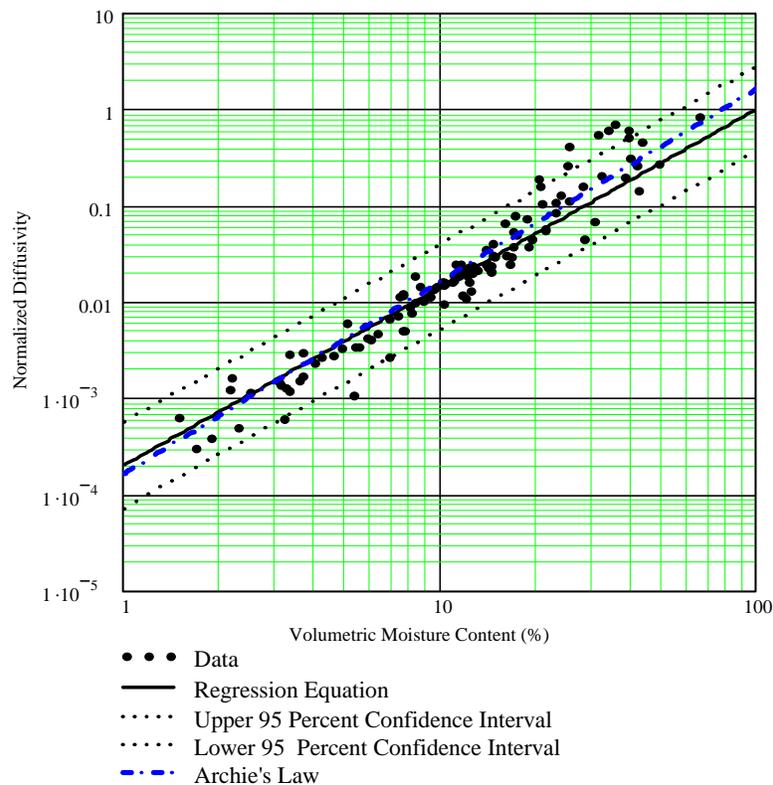
Note that the data applied to a 0.1 molar solution of potassium chloride at 25 °C. However, since the dependence of diffusivity relates to the physical structure of the pore space (Hillel 1980, pp. 236-237), the normalized relationships can be applied to other radionuclides.

Note that for the predicted power relationship presented above, the residual values or the difference between the predicted and actual values of  $Y$  ( $Y_{p_i} - Y_i$ ) should follow the normal law of error. This means that positive errors occur nearly as frequently as negative errors, and that small magnitude errors occur more frequently than large magnitude errors. Figure 4 presents a histogram of the transformed data points, and shows qualitatively that the distribution of residuals follows the normal law of error.

## 6.6 UPPER BOUND MODEL PREDICTIONS

Consider the one sided confidence interval at the 95 % confidence level. In this case, the one sided confidence interval is calculated by using the  $t_{95} = 1.658$  column in Table A-4 (Natrella 1963, p. T-5) for 120 degrees of freedom. Note that the  $t_{95}$  statistic for 120 degrees of freedom is used because the statistics are only tabulated to 120 degrees, and it is conservative to use this value.

Eq. 40a and Eq. 22 are combined to account for porosity effects. The analysis presented in Figure 5 suggests scaling to a porosity of 50 % (Section 5.3).



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Figure 3. Relationship of Diffusivity to Volumetric Moisture Content

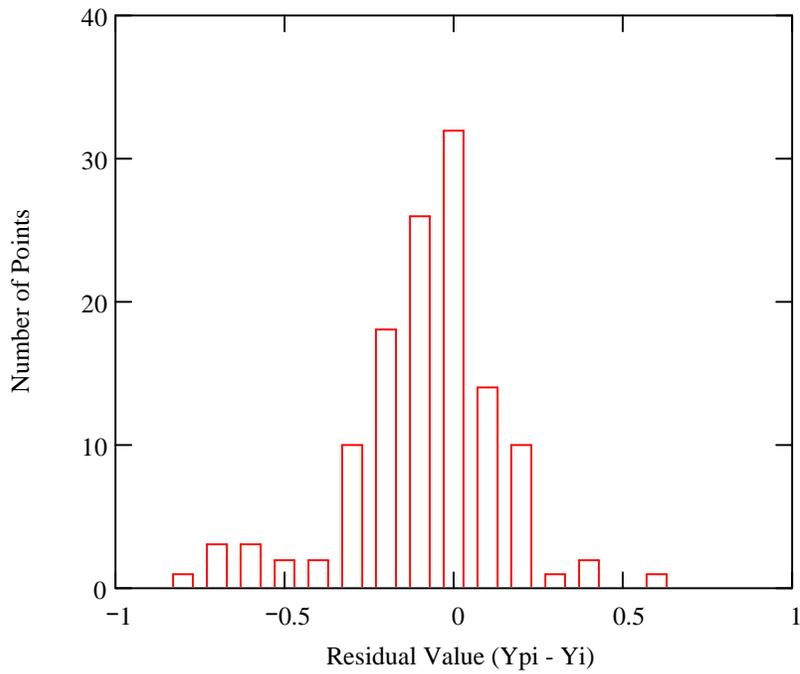
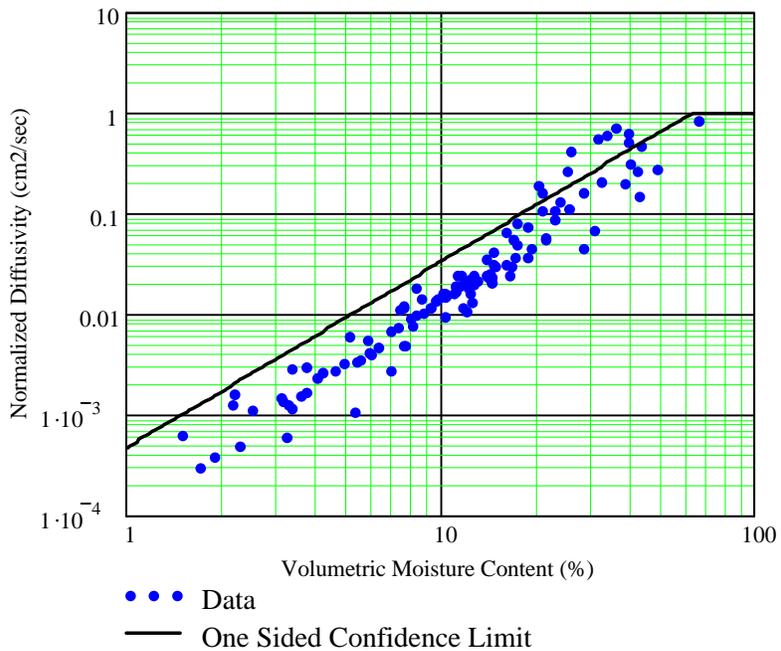


Figure 4. Histogram of the Residuals for the Power Relationship



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Figure 5. One Sided Confidence Limit for Normalized Diffusivity (Based upon Equation 40)

The empirical relation for the one sided confidence interval can be modified as suggested by Eq. 22 that takes into account the assumption (Section 5.3) that accounts for the dependence of diffusivity on porosity:

$$Y_h(\theta, \phi) = b_1 \cdot (\log(\theta) - 2) + \sqrt{S_y^2 + (\log(\theta) - 2)^2 \cdot S_{b1}^2}$$

$$\frac{D_*(\theta, \phi)}{D_0} = 10^{Y_h(\theta, \phi)} \cdot \frac{\phi^{-.7}}{0.5^{-.7}}$$

(Eq. 41)

Note that the volumetric moisture content is expressed as a percent while the porosity is expressed as a ratio between 0 and 1. It should be further noted that the self diffusion of water represents an upper bound to the normalized diffusion relationship (Section 5.2):

$$\frac{D_*(\theta, \phi)}{D_0(\theta, \phi)} = \text{if} \left( \frac{D_*(\theta, \phi)}{D_0(\theta, \phi)} > 1.0, 1.0, \frac{D_*(\theta, \phi)}{D_0(\theta, \phi)} \right)$$

(Eq. 42)

Apply the correction for temperature. From Equation 14. The relationship presented above applies to the case of ambient temperature  $T_0$  or  $T_{k0}$ . The following equation is obtained that combines the several submodels.

$$D_*(\mathbf{q}, \mathbf{f}, T) = D_*(\mathbf{q}, \mathbf{f}) \cdot \frac{\left( \frac{T + 273}{T_0 + 273} \right)}{10^{\left( \frac{(1.3272 \cdot (20 - T) - 0.001053 \cdot (T - 20)^2)}{(T + 105)} \right) - (-0.0512)}}$$

(Eq. 43)

Expressing the equation in degrees Kelvin, the following relationship is obtained for future calculations:

$$D(\theta, \phi, T_k) = D_*(\theta, \phi) \cdot \frac{\frac{T_k}{T_0}}{10^{\left( \frac{(1.3272 \cdot (293.15 - T_k) - 0.001053 \cdot (293.15 - T_k)^2)}{T_k - 168.15} \right) - (-0.0512)}}$$

(Eq. 44)

Eq. 43 represents an empirically derived bounding relationship for predicting the normalized diffusivity as a function of volumetric moisture content, porosity, and temperature. Figure 6 is a semilog plot of normalized diffusivity as a function of moisture content based upon Eq. 41. Figure 7 is a semilog plot of normalized diffusivity as a function of temperature for a material at a porosity of 50%. As can be seen from Figures 6 and 7, the diffusivity is a weak function of porosity, and is more dependent on temperature.

## 6.7 SOLID-SOLID DIFFUSION

As volumetric moisture content is reduced, the paths for diffusion become more tortuous and, it is possible that liquid films might become discontinuous. In this situation, transport would not be governed by diffusion through liquid films. Fernandez et al. (1988 pp. 171-172) developed analysis for solid- solid diffusion. The scenario considered a conservative case of the exposure of bare waste adjacent to rock which could be inferred to apply to the invert. Using the one dimensional solution to Fick's Law, Freeze and Cherry (1979, p. 393) present the solution for solid-solid diffusion:

$$\frac{C}{C_0} = \text{erfc}\left(\frac{x}{2\sqrt{D \cdot t}}\right)$$

(Eq. 45)

where:

- C -Concentration at time t
- C<sub>0</sub> -Initial concentration
- Erfc -Complementary error function
- x -Pathlength
- t -time
- D -Solid-Solid Diffusivity

Find the value of the argument to the error function corresponding to 99 % of the concentration. From Freeze and Cherry 1979, p. 539, the tabulated values are presented for reference in Table 2.

Table 2: Tabulated Complementary Error Function

$\beta$	$\text{Erfc}(\beta)$
0.0	1.00000
0.05	0.943628

Using linear interpolation, the value for the argument  $\beta$  of the error function is:

$$\frac{0.05 - 0.0}{0.943628 - 1.0} \cdot (0.99 - 1.0) + 0.0 = 8.8697 \times 10^{-3}$$

Bird et al. (1960 p. 505) discuss experimental diffusivities in the solid state for several substances. The mass diffusivity for a binary system is a function of temperature, pressure, and composition. Values are presented over the range from  $10^{-15} \text{ cm}^2/\text{sec}$  to  $10^{-30} \text{ cm}^2/\text{sec}$ . If the diffusion coefficient of  $10^{-15} \text{ cm}^2/\text{sec}$  ( $10^{-19} \text{ m}^2/\text{sec}$ ) is selected, the breakthrough time for 99 % of the concentration across an invert 0.61m in thickness is calculated as follows from Equation 45:

$$\frac{0.61\text{-m}}{2 \cdot \sqrt{10^{-19} \cdot \frac{\text{m}^2}{\text{sec}} \cdot t}} = 8.869710^{-3}$$

Rewriting the expression:

$$\sqrt{10^{-19} \cdot \frac{\text{m}^2}{\text{sec}} \cdot t} = \frac{(0.61\text{-m})^2}{4} \cdot \frac{1}{(8.869710^{-3})^2}$$

Solving for the time:

$$t = \frac{(0.61\text{-m})^2}{4} \cdot \frac{1}{(8.869710^{-3})^2} \cdot \frac{1}{\left(10^{-19} \cdot \frac{\text{m}^2}{\text{sec}}\right)}$$

$$t = 1.18 \cdot 10^{22} \text{ secs} = 3.74 \cdot 10^{14} \text{ yrs}$$

Therefore, solid-solid diffusion is a very slow process, and would provide a lower bound to the rate of diffusion through liquid films in a porous media. In conclusion, it might be expected that for very low moisture contents where liquid films might become discontinuous, that lower values of diffusivity might occur than what is predicted by the empirical power law fit presented above.

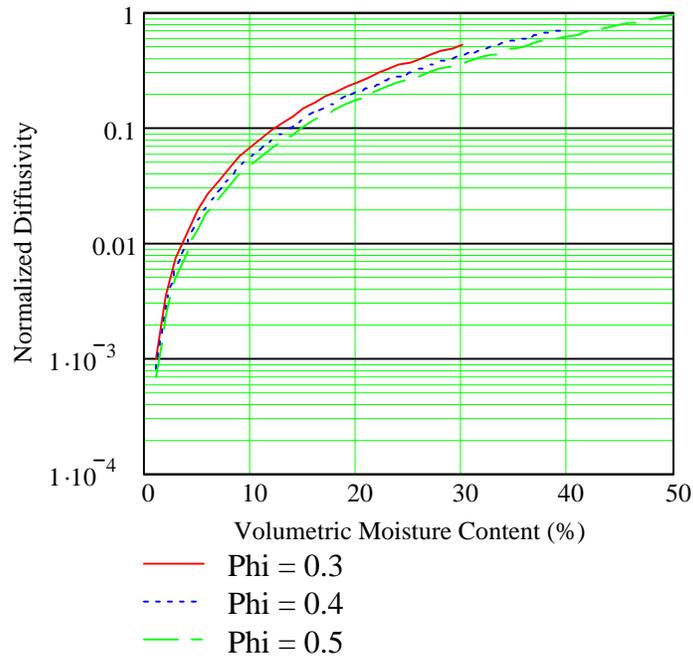


Figure 6. Relationship of Normalized Diffusivity to Volumetric Moisture Content with Variations in Porosity

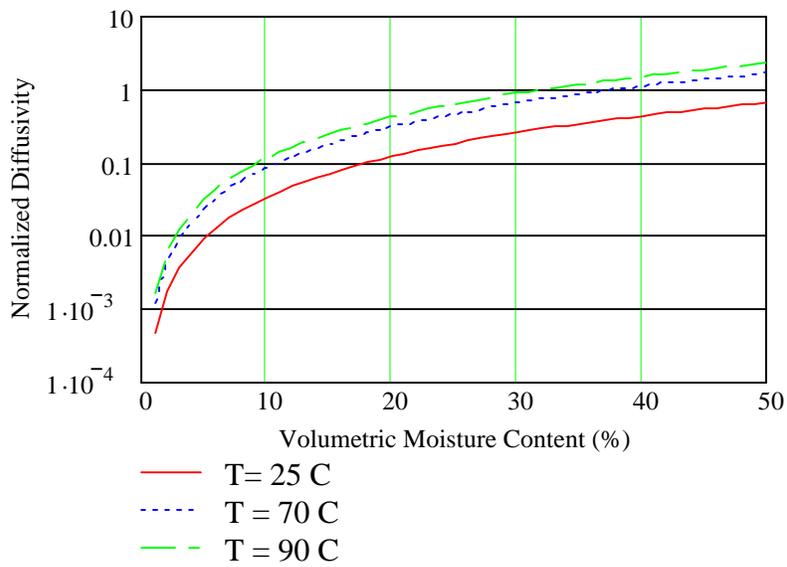


Figure 7. Relationship of Normalized Diffusivity to Volumetric Moisture Content at Elevated Temperature for a Porosity of 50%

## 7 CONCLUSIONS

The diffusivity of a granular material can be predicted from electrical conductivity measurements or from basic material properties, using two empirical constants that is in basic agreement with Archie's Law.

The model validation (Section 6.5.2) includes a comparison of the formula for Archie's Law with data from measurements (Section 4.1.16) and with a statistical fit to these data (Section 6.5.2). It is determined that these models are validated for their intended use. The results of the model (DTN: MO0007MWDIDD31.001) have been submitted to the TDMS in accordance with APSIII.3Q for submittal and incorporation of data to the Technical Data Management System.

The impact of uncertainty is addressed in this section through the statistical analysis of 95 % confidence level based upon the data from DTN: MO9810SPA00026.000. Changes to these inputs will require recalibrating this model. This document may be affected by technical product input information that requires confirmation. Any changes to the document that may occur as a result of completing confirmation activities will be reflected in subsequent revisions. The status of the input information quality may be confirmed by review of the Document Input Reference System database. Based upon these caveats, the conclusions are:

1. A submodel estimated the electrical conductivity of a granular material (Section 6.1). The inputs into this model are empirical, and accepted data for granular materials with clean sand was given as an example. This model predicts the conductivity of a material as a function of saturation and porosity.
2. A submodel (Section 6.2) yields the diffusion coefficient based upon the conductivity submodel and the application of the Nernst-Einstein Equation. This equation relates the electrical conductivity for ions in an electrical potential gradient to the diffusion of ions due to a concentration gradient. This submodel forms the basis for the measurement of diffusion from the measurement of electrical conductivity for samples of known volumetric moisture content as discussed subsequently in Section 6.5.2.
3. A submodel (Section 6.3) is developed that accounts for temperature effects on the diffusivity. This submodel is based upon the well established relation (Section 4.1.15) for the dependence of diffusivity on temperature and liquid viscosity that in turn is dependent on temperature.
4. The model uses the activity for single salt solutions, which is conservative and bounding (Section 6.4).
5. Validation criteria are presented for the several submodels. The conductivity submodel presented in Section 6.1 is well established. Also, the temperature effects submodel is reasonable, and is based upon well known and accepted facts. For validating the

submodel that relates diffusion to volumetric moisture content for granular materials, a statistical approach is outlined in Section 6.5.1. For a 95% confidence interval, the confidence interval for predicting future values (Natrella 1963, p. 5-19) were estimated, and were compared to the result from the prediction obtained from Equation (22). The empirically determined relationship with a given confidence interval was determined to be valid because the confidence interval brackets the prediction from Equation (22) for the range of porosities presented in Section 4.1.14.

6. An upper bound model prediction (Eq. 44) relation was developed that combines the several submodels. This is a bounding relationship that predicts the normalized diffusivity as a function of volumetric moisture content, porosity, and temperature for use in the EBS Radionuclide Transport Model and EBS Radionuclide Transport Abstraction. In summary, this relationship is based upon:
  - The diffusivity of the invert is a function of volumetric moisture content, porosity and temperature.
  - The one sided confidence interval for the diffusion data (Section 4.1.16) from Conca and Wright (1992).
  - The temperature correction is based upon Equation (13).
  
7. As volumetric moisture content is reduced, and paths for diffusion become more tortuous, it is possible that liquid films might become discontinuous, and diffusion would not be governed by diffusion through liquid films. Fernandez et al. (1989 pp. 171-172) developed an analysis for solid-solid diffusion. A calculation (Section 6.7) is developed for solid-solid diffusion, and shows that this is a very slow process, and provides a lower bound to the rate of diffusion through liquid films in a porous media. In conclusion, it might be expected that for very low moisture contents where liquid films might become discontinuous, that lower values of diffusivity might occur than what is predicted by the empirical power law fit presented above.

Three TBVs are identified as listed in the DIRS. The diffusion data (Section 4.1.16) is used for the empirically determined relationship. It is expected to have minimal impact on the results since the data are in agreement with Archie's Law. The data used are various geotechnical materials, and are applied to crushed tuff (Section 5.2). It is expected that this TBV will have minimal impact. Finally, the TBV in using the factor for scaling the porosity (Section 5.3) is expected to have minimal impact because of the weak dependence of the diffusivity on porosity.

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### **8.3 SOURCES OF DATA**

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## 9 ATTACHMENTS

	<b>Pages</b>
Attachment I: Diffusion Data for Granular Materials from Conca and Wright (1992) for Volumetric Moisture Content between 1.5% and 66.3% .....	I-1 to I-5
Attachment II: Mathematical Proof .....	II-1 to II-2

**ATTACHMENT I**

**DIFFUSION DATA FOR GRANULAR MATERIALS  
FROM CONCA AND WRIGHT (1992)  
FOR VOLUMETRIC MOISTURE CONTENT BETWEEN 1.5% AND 66.3%**

TABLE I-1: DIFFUSION DATA

Sample	Volumetric Moisture Content (%)	Diffusion Coefficient (cm <sup>2</sup> /sec)	X	Y	X*X	Y*Y	X*Y
1	1.50E+00	1.39E-08	-1.824	-3.204	3.327	10.264	5.843
2	1.70E+00	6.60E-09	-1.770	-3.527	3.131	12.441	6.242
3	1.90E+00	8.60E-09	-1.721	-3.412	2.963	11.643	5.873
4	2.17E+00	2.77E-08	-1.664	-2.904	2.767	8.435	4.831
5	2.20E+00	3.63E-08	-1.658	-2.787	2.748	7.766	4.619
6	2.29E+00	1.09E-08	-1.640	-3.309	2.690	10.952	5.428
7	2.50E+00	2.50E-08	-1.602	-2.949	2.567	8.695	4.724
8	3.10E+00	3.30E-08	-1.509	-2.828	2.276	7.999	4.267
9	3.14E+00	3.06E-08	-1.503	-2.861	2.259	8.185	4.300
10	3.20E+00	1.35E-08	-1.495	-3.216	2.235	10.345	4.808
11	3.27E+00	2.79E-08	-1.485	-2.901	2.207	8.417	4.310
12	3.33E+00	6.35E-08	-1.478	-2.544	2.183	6.472	3.759
13	3.34E+00	2.60E-08	-1.476	-2.932	2.179	8.595	4.328
14	3.57E+00	3.37E-08	-1.447	-2.819	2.095	7.947	4.080
15	3.70E+00	3.70E-08	-1.432	-2.779	2.050	7.720	3.978
16	3.70E+00	6.60E-08	-1.432	-2.527	2.050	6.387	3.618
17	4.00E+00	5.22E-08	-1.398	-2.629	1.954	6.912	3.675
18	4.20E+00	5.94E-08	-1.377	-2.573	1.895	6.620	3.542
19	4.60E+00	6.21E-08	-1.337	-2.554	1.788	6.521	3.415
20	4.90E+00	7.20E-08	-1.310	-2.489	1.716	6.197	3.261
21	5.10E+00	1.32E-07	-1.292	-2.226	1.670	4.956	2.877
22	5.30E+00	2.40E-08	-1.276	-2.967	1.627	8.800	3.784
23	5.40E+00	7.60E-08	-1.268	-2.466	1.607	6.081	3.126
24	5.51E+00	7.68E-08	-1.259	-2.461	1.585	6.058	3.099
25	5.83E+00	1.23E-07	-1.234	-2.257	1.524	5.093	2.786
26	5.90E+00	9.30E-08	-1.229	-2.378	1.511	5.656	2.923
27	6.00E+00	8.92E-08	-1.222	-2.396	1.493	5.743	2.928
28	6.30E+00	1.06E-07	-1.201	-2.321	1.442	5.389	2.787
29	6.90E+00	6.00E-08	-1.161	-2.569	1.348	6.598	2.983
30	6.93E+00	1.50E-07	-1.159	-2.171	1.344	4.712	2.516
31	7.30E+00	1.60E-07	-1.137	-2.143	1.292	4.591	2.435
32	7.40E+00	2.50E-07	-1.131	-1.949	1.279	3.798	2.204

Sample	Volumetric Moisture Content (%)	Diffusion Coefficient (cm <sup>2</sup> /sec)	X	Y	X*X	Y*Y	X*Y
33	7.60E+00	2.60E-07	-1.119	-1.932	1.253	3.732	2.162
34	7.60E+00	1.10E-07	-1.119	-2.305	1.253	5.315	2.580
35	7.60E+00	2.69E-07	-1.119	-1.917	1.253	3.675	2.145
36	7.70E+00	1.10E-07	-1.114	-2.305	1.240	5.315	2.567
37	8.00E+00	1.98E-07	-1.097	-2.050	1.203	4.203	2.249
38	8.10E+00	1.70E-07	-1.092	-2.116	1.191	4.479	2.310
39	8.32E+00	4.10E-07	-1.080	-1.734	1.166	3.007	1.872
40	8.35E+00	2.15E-07	-1.078	-2.014	1.163	4.057	2.172
41	8.60E+00	3.20E-07	-1.066	-1.842	1.135	3.391	1.962
42	8.80E+00	2.30E-07	-1.056	-1.985	1.114	3.940	2.095
43	9.24E+00	2.55E-07	-1.034	-1.940	1.070	3.764	2.007
44	9.24E+00	2.55E-07	-1.034	-1.940	1.070	3.764	2.007
45	9.56E+00	3.00E-07	-1.020	-1.870	1.039	3.495	1.906
46	9.64E+00	3.07E-07	-1.016	-1.860	1.032	3.458	1.889
47	9.75E+00	3.20E-07	-1.011	-1.842	1.022	3.391	1.862
48	1.01E+01	3.51E-07	-0.996	-1.801	0.991	3.245	1.794
49	1.01E+01	3.62E-07	-0.996	-1.788	0.991	3.197	1.780
50	1.02E+01	3.54E-07	-0.991	-1.798	0.983	3.232	1.782
51	1.02E+01	3.30E-07	-0.991	-1.828	0.983	3.342	1.813
52	1.03E+01	3.34E-07	-0.987	-1.823	0.974	3.323	1.800
53	1.03E+01	2.10E-07	-0.987	-2.025	0.974	4.099	1.999
54	1.04E+01	3.40E-07	-0.983	-1.815	0.966	3.295	1.784
55	1.09E+01	3.62E-07	-0.963	-1.788	0.927	3.197	1.721
56	1.11E+01	3.72E-07	-0.955	-1.776	0.911	3.155	1.696
57	1.11E+01	4.22E-07	-0.955	-1.721	0.911	2.963	1.643
58	1.11E+01	4.27E-07	-0.955	-1.716	0.911	2.946	1.639
59	1.12E+01	4.19E-07	-0.951	-1.725	0.904	2.974	1.640
60	1.12E+01	5.48E-07	-0.951	-1.608	0.904	2.586	1.529
61	1.14E+01	4.27E-07	-0.943	-1.716	0.889	2.946	1.619
62	1.14E+01	4.12E-07	-0.943	-1.732	0.889	2.999	1.633
63	1.16E+01	5.40E-07	-0.936	-1.614	0.875	2.606	1.510
64	1.17E+01	2.60E-07	-0.932	-1.932	0.868	3.732	1.800
65	1.18E+01	4.80E-07	-0.928	-1.666	0.861	2.774	1.546
66	1.20E+01	2.40E-07	-0.921	-1.967	0.848	3.867	1.811

Sample	Volumetric Moisture Content (%)	Diffusion Coefficient (cm <sup>2</sup> /sec)	X	Y	X*X	Y*Y	X*Y
67	1.20E+01	4.47E-07	-0.921	-1.696	0.848	2.878	1.562
68	1.22E+01	4.09E-07	-0.914	-1.735	0.835	3.010	1.585
69	1.23E+01	5.05E-07	-0.910	-1.643	0.828	2.701	1.496
70	1.23E+01	4.40E-07	-0.910	-1.703	0.828	2.901	1.550
71	1.23E+01	3.60E-07	-0.910	-1.790	0.828	3.206	1.629
72	1.23E+01	4.50E-07	-0.910	-1.694	0.828	2.868	1.541
73	1.25E+01	2.90E-07	-0.903	-1.884	0.816	3.551	1.702
74	1.27E+01	4.37E-07	-0.896	-1.706	0.803	2.911	1.529
75	1.27E+01	4.90E-07	-0.896	-1.657	0.803	2.744	1.485
76	1.27E+01	5.32E-07	-0.896	-1.621	0.803	2.627	1.453
77	1.31E+01	4.77E-07	-0.883	-1.668	0.779	2.783	1.473
78	1.39E+01	5.39E-07	-0.857	-1.615	0.734	2.609	1.384
79	1.39E+01	7.80E-07	-0.857	-1.455	0.734	2.116	1.247
80	1.41E+01	5.12E-07	-0.851	-1.637	0.724	2.681	1.393
81	1.42E+01	5.52E-07	-0.848	-1.605	0.719	2.575	1.360
82	1.44E+01	4.50E-07	-0.842	-1.694	0.708	2.868	1.425
83	1.44E+01	5.20E-07	-0.842	-1.631	0.708	2.659	1.372
84	1.44E+01	4.50E-07	-0.842	-1.694	0.708	2.868	1.425
85	1.46E+01	6.82E-07	-0.836	-1.513	0.698	2.289	1.264
86	1.47E+01	9.00E-07	-0.833	-1.393	0.693	1.939	1.160
87	1.48E+01	6.54E-07	-0.830	-1.531	0.688	2.344	1.270
88	1.60E+01	1.47E-06	-0.796	-1.179	0.633	1.391	0.939
89	1.61E+01	6.82E-07	-0.793	-1.513	0.629	2.289	1.200
90	1.65E+01	5.45E-07	-0.783	-1.610	0.612	2.593	1.260
91	1.67E+01	6.60E-07	-0.777	-1.527	0.604	2.332	1.187
92	1.70E+01	1.20E-06	-0.770	-1.268	0.592	1.607	0.975
93	1.71E+01	8.20E-07	-0.767	-1.433	0.588	2.053	1.099
94	1.73E+01	1.76E-06	-0.762	-1.101	0.581	1.213	0.839
95	1.75E+01	1.10E-06	-0.757	-1.305	0.573	1.704	0.988
96	1.88E+01	1.60E-06	-0.726	-1.143	0.527	1.306	0.829
97	1.89E+01	8.19E-07	-0.724	-1.433	0.524	2.055	1.037
98	1.94E+01	9.89E-07	-0.712	-1.352	0.507	1.827	0.963
99	2.04E+01	4.19E-06	-0.690	-0.725	0.477	0.525	0.500
100	2.08E+01	3.58E-06	-0.682	-0.793	0.465	0.629	0.541

Sample	Volumetric Moisture Content (%)	Diffusion Coefficient (cm <sup>2</sup> /sec)	X	Y	X*X	Y*Y	X*Y
101	2.10E+01	2.34E-06	-0.678	-0.978	0.459	0.956	0.663
102	2.15E+01	1.23E-06	-0.668	-1.257	0.446	1.580	0.839
103	2.16E+01	1.29E-06	-0.666	-1.236	0.443	1.528	0.823
104	2.31E+01	2.40E-06	-0.636	-0.967	0.405	0.934	0.615
105	2.31E+01	1.90E-06	-0.636	-1.068	0.405	1.141	0.680
106	2.40E+01	2.90E-06	-0.620	-0.884	0.384	0.782	0.548
107	2.53E+01	5.82E-06	-0.597	-0.582	0.356	0.339	0.347
108	2.54E+01	2.50E-06	-0.595	-0.949	0.354	0.900	0.565
109	2.57E+01	9.26E-06	-0.590	-0.380	0.348	0.145	0.224
110	2.82E+01	3.50E-06	-0.550	-0.803	0.302	0.644	0.441
111	2.85E+01	1.00E-06	-0.545	-1.347	0.297	1.814	0.734
112	3.09E+01	1.51E-06	-0.510	-1.168	0.260	1.364	0.596
113	3.17E+01	1.23E-05	-0.499	-0.257	0.249	0.066	0.128
114	3.23E+01	4.60E-06	-0.491	-0.684	0.241	0.468	0.336
115	3.38E+01	1.34E-05	-0.471	-0.220	0.222	0.048	0.103
116	3.58E+01	1.57E-05	-0.446	-0.151	0.199	0.023	0.067
117	3.85E+01	4.33E-06	-0.415	-0.710	0.172	0.504	0.294
118	3.93E+01	1.36E-05	-0.406	-0.213	0.165	0.045	0.086
119	3.95E+01	1.13E-05	-0.403	-0.294	0.163	0.086	0.118
120	4.00E+01	6.90E-06	-0.398	-0.508	0.158	0.258	0.202
121	4.20E+01	5.80E-06	-0.377	-0.583	0.142	0.340	0.220
122	4.25E+01	3.22E-06	-0.372	-0.839	0.138	0.704	0.312
123	4.34E+01	1.02E-05	-0.363	-0.338	0.131	0.114	0.123
124	4.90E+01	6.09E-06	-0.310	-0.562	0.096	0.316	0.174
125	6.63E+01	1.83E-05	-0.178	-0.084	0.032	0.007	0.015
Sums			-119.982	-217.547	129.565	449.213	239.592

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**ATTACHMENT II**  
**MATHEMATICAL PROOF**

The square of the average of two numbers is always greater than their product. Consider two non-negative numbers A and B. Since the square of any real number is always greater than or equal to zero:

$$(A - B)^2 \geq 0 \quad (\text{Eq. II-1})$$

$$A^2 - 2 \cdot A \cdot B + B^2 \geq 0 \quad (\text{Eq. II-2})$$

Adding 4AB to both sides of the equation

$$A^2 + 2 \cdot A \cdot B + B^2 \geq 4 \cdot A \cdot B \quad (\text{Eq. II-3})$$

$$(A + B)^2 \geq 4 \cdot A \cdot B \quad (\text{Eq. II-4})$$

or factoring (Eq. II-4)

$$\frac{(A + B)}{2} \cdot \frac{(A + B)}{2} \geq A \cdot B \quad (\text{Eq. II-5})$$