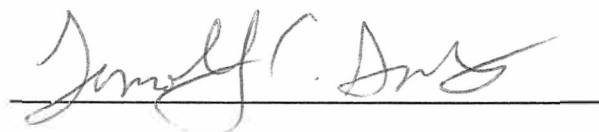


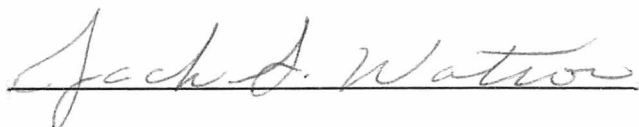
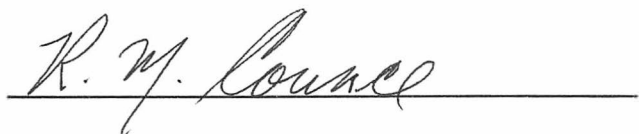
To the Graduate Council:

I am submitting herewith a thesis written by Terry Lee Sams entitled "Sorption Characteristics of Mobile Species in Cement Based Waste Forms Using a Linear Sorption Isotherm." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

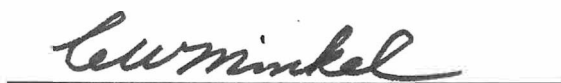
A handwritten signature in cursive script, reading "Timothy C. Scott", written over a horizontal line.

Timothy C. Scott, Major Professor

We have read this thesis
and recommend its acceptance.

A handwritten signature in cursive script, reading "Jack D. Watson", written over a horizontal line.A handwritten signature in cursive script, reading "R. M. Lounce", written over a horizontal line.

Accepted for the Council:

A handwritten signature in cursive script, reading "Lew Minkel", written over a horizontal line.

Associate vice Chancellor

and Dean of The Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment for a Master's degree at The University of Tennessee, Knoxville, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the purposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature



Date

29 Apr 93

**SORPTION CHARACTERISTICS OF MOBILE SPECIES
IN CEMENT BASED WASTE FORMS USING
A LINEAR SORPTION ISOTHERM**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee

TERRY LEE SAMS

MAY 1993

DEDICATION

This thesis is dedicated to my wife, Rebecca. Her caring and understanding were the major driving forces that kept me going while writing this thesis. The majority of this material was written while she was pregnant with our first child and yet she always backed me in my efforts and provided ample opportunity for me to complete my work. Her commitment to education and self-improvement is both inspirational and enviable. I am truly grateful to have such a wonderful wife.

ACKNOWLEDGMENTS

This work was sponsored by the United States Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

I would like to thank my major professor, Dr. Timothy C. Scott, for his guidance and patience. He served as both a friend and an ally during the course of this work. I would also like to thank the other committee members, Dr. Jack Watson and Dr. Robert Counce, for their advice and comments over the course of my work. It has taken several years to complete this thesis and all the committee members kept encouraging me and provided help when needed. I would also like to thank my wife, Rebecca, for everything. She provided strength and guidance constantly. A special acknowledgment is given to Guillermo Daniel Del Cul for all the work he performed in data acquisition and experimental work. His ingenuity and resourcefulness provided the foundation for this work. Finally, a very special thanks is given to my son who provides me with great pleasure and drive just by being my son, Derek.

ABSTRACT

The nuclear industry is constantly striving to achieve cost-effective methods for the responsible disposal of radioactive wastes. Cement-based grouts are the most widely used hosts for the immobilization of low-level liquid radioactive waste. Ultimately, the effectiveness of waste immobilization in grouts is determined by the degree to which the waste form protects the environment from the release of radionuclides contained in the waste. For near-surface and sub-surface monolithic waste forms, the most credible transport pathway to the environment is via groundwater movement. A measure of the waste form's ability to retard the release of radionuclides to the environment is its leachability. Hence, leach data provide the source term for the impact or consequence analyses.

The appropriate model for describing the waste form's leachability and the appropriate tests used to measure the critical parameters have long been topics for debate. This lack of consensus is caused by the diversity and the complexity of the interaction mechanisms coupled with transport phenomena that affect radionuclide release.

The purpose of this research is to extend current immobilized waste form transport models by explicitly including effects of species adsorption to internal surfaces and liquid/solid mass transport resistances. The first phase of the research characterized the dynamic leaching behavior of a cement based waste form taking into account mass transfer resistance due to

macropore diffusion and external fluid film mass transfer. Experiments carried out on cement disks with forced flow were used to assess the relative effects of diffusion and adsorption on control of release. The second phase of the research utilized the results of the first phase in a numerical study of convective/adsorptive transport. The data were regressed using both an ideal plug flow and a dispersed flow model. These models allow for determination of mass transfer resistance due to macropore diffusion and external fluid film mass transfer.

The first analysis assumed ideal plug flow through the sample. The data did not verify this assumption, so a dispersed flow model was assumed. The predictions from this model more closely approximated the data. These predictions were then compared to results obtained from each of the samples to determine if conditions exist where adsorptive behavior dominates the system. Similarities exist for those samples prepared with either simulated waste or additives.

The addition of ionic species in the aqueous phase apparently affects the hydration process as well as increasing the ionic strength of the porewater. The increase in ionic strength of the pore water resulted in an increase in the retention of the adsorbing species. This increased retention could also be due to the increased complexity of the cement matrix and hydration products. As a result, the breakthrough time was increased and the rate of release was decreased.

TABLE OF CONTENTS

CHAPTER	PAGE
1. INTRODUCTION	1
1.1 General Considerations	1
1.2 Research Objectives	2
2. LITERATURE REVIEW	6
2.1 Introduction	6
2.2 Development of ANS 16.1	6
2.3 Factors Affecting Leachability	11
2.3.1 General Considerations	11
2.3.2 Factors Affecting ANS 16.1 Assumptions	14
2.4 Development of Other Models	17
2.4.1 Diffusion/Adsorption Models	18
2.4.1.1 Empirical Methods	19
2.4.1.2 Extrapolation of Small Scale Data to Large Scale Specimens	23
2.4.1.3 Finite Element Model	28
2.4.1.4 Diffusion Through a Semi-Permeable Membrane	31
2.4.1.5 Linear and Nonlinear Sorption Isotherms For One-Dimensional Porous Media	33

2.4.2 Statistical Modelling of a	
One-Dimensional Porous Medium	35
2.4.3 Applications of Diffusion Theory to Permeability . .	38
2.4.4 Use of a Retardation Factor	39
3. EXPERIMENTAL METHODOLOGY AND PROCEDURES	43
3.1 Introduction	43
3.2 Experimental Approach	43
3.3 Materials	45
3.3.1 Cement Matrix Used in Experiments	45
3.3.2 Indian Red Pottery Clay	47
3.3.3 Fly Ash	47
3.3.4 Slag Cement	48
3.4 Apparatus	49
3.5 Experimental Procedure	51
3.5.1 Preparation of Samples	51
3.5.2 Permeability and Porosity Measurements	52
3.5.3 Forced Convective Flow Experiments	55
4. MODEL DEVELOPMENT	57
4.1 Introduction	57
4.2 Packed Bed Adsorption Model	57
4.3 Development of Ideal Plug Flow Model	60
4.4 Development of Dispersed Plug Flow Model	64

5. RESULTS	67
5.1 Introduction	67
5.2 Determination of Fluid Velocity and Porosity	68
5.3 Analysis of Data From Ideal Plug Flow Model	72
5.4 Analysis of Data From Dispersed Plug Flow Model	80
6. CONCLUSIONS AND RECOMMENDATIONS	90
6.1 Conclusions	90
6.2 Recommendations For Future Research	91
LIST OF REFERENCES	93
APPENDICES	101
APPENDIX A. DATA USED IN SECTION 2.4.1.2	102
APPENDIX B. MATERIALS USED IN RESEARCH	104
APPENDIX C. ANALOGY BETWEEN SHERWOOD NUMBER AND j-FACTOR	111
APPENDIX D. ORIGINAL DATA	116
VITA	162

LIST OF TABLES

Table 1.	Factors That Influence Release Rate	13
Table 2.	Experimental Blends Used In Permeability Measurements	69
Table 3.	Operating Parameters Used In Permeability Measurements	70
Table 4.	Data From Permeability And Porosity Measurements	71
Table 5.	Experimental Blends Used In Forced Convection Experiments	77
Table 6.	Parameters Used In Ideal Plug Flow Model	78
Table 7.	Experimental Parameters Used In Ideal Plug Flow Model	79
Table 8.	Parameters Determined From Dispersed Plug Flow Model	81
Table A.1	Data For Section 2.4.1.2	103
Table B.1	Analysis of Type III Portland Cement	105
Table B.2	Analysis of Class F Fly Ash	106
Table B.3	Analysis of Indian Red Pottery Clay	107
Table B.4	Analysis of Blast Furnace Slag	108
Table B.5	Analysis of Simulated Waste	109

LIST OF FIGURES

Figure 1. Scale Effect for Cement Based Waste Forms	26
Figure 2. Scale Effect on Release Rate for Cement Based Waste Forms	27
Figure 3. Schematic Diagram of Experimental Apparatus	50
Figure 4. Schematic Diagram of Sample Holder	53
Figure 5. Graphical Illustration of Sorption Pathways	58
Figure 6. Experimental vs Dispersed Plug Flow Model For Sample 2 . .	82
Figure 7. Experimental vs Dispersed Plug Flow Model For Sample 3 . .	83
Figure 8. Experimental vs Dispersed Plug Flow Model For Sample 4 . .	84
Figure 9. Experimental vs Dispersed Plug Flow Model For Sample 5 . .	85
Figure 10. Experimental vs Dispersed Plug Flow Model For Sample 8 .	86

LIST OF VARIABLES

C_o = initial concentration of the species

δ = dimensionless bed length

R_p = absorbent particle radius

k_f = external fluid film mass transfer coefficient

e_p = porosity of absorbent particle

D_p = pore diffusivity

q^* = equilibrium sorbate concentration of species

c^* = equilibrium sorbate concentration in fluid phase

k = overall mass transfer coefficient

K_n = dimensionless Henry's law adsorption equilibrium constant

D_l = axial dispersion coefficient

c = sorbate concentration in fluid phase

z = distance from column inlet

v = interstitial velocity of fluid

t = time

e = voidage of adsorbent bed

q = average sorbate concentration of species

a_n = mass of species released from specimen during leaching interval, n

A_o = total initial mass of species (after initial wash-off)

$(\Delta t)_n = t_n - t_{n-1}$ duration of the n^{th} leaching interval

V = external volume of specimen

S =geometric surface area of specimen

$T_m = [\frac{1}{2} (t_n^{\frac{1}{2}} + t_{n-1}^{\frac{1}{2}})]^{\frac{1}{2}}$ leaching time, representing the "mean time" of the leaching interval, n

D =intrinsic diffusion coefficient in the porewater

Y =tortuosity, the ratio of actual diffusion path over the shortest geometric distance to the surface

ϵ =porosity, a measure of the volume fraction of the macropores

Φ =constrictivity, a measure of molecular sieve effects in the waste form matrix surrounding the pores

d =net bulk density of the waste form

K_a =physical adsorption or partition coefficient of waste constituents on or in the various phases

L =Leachability Index of species

D_e =effective solid diffusion coefficient of species

Σa_n =cumulative amount of species released through cumulative time

F =mass fraction of species released

D_e' =modified solid diffusion coefficient

K =equilibrium constant

x =space distance or sample thickness

τ =dimensionless time parameter

Sh = Sherwood number

D_m = molecular diffusivity

Sc = Schmidt number

Re = Reynolds number

Pe = Peclet number

Q = flow rate

μ = viscosity

K_p = Darcy permeability

ΔP = pressure gradient

S_a = adsorbed concentration of species

θ = volumetric moisture content

D_{ij} = component of the dispersion tensor D

a_t = transverse dispersivity

a_l = longitudinal dispersivity

δ_{ij} = Kronecker delta

a_m = molecular diffusion coefficient

T = tortuosity

$|V|$ = magnitude of the velocity vector

V_i = i^{th} component of velocity vector

V_j = j^{th} component of velocity vector

M = source term for the species of interest

R = retardation factor

v_w = velocity of groundwater

v_n = velocity of species of interest

ρ_b = porous media bulk density

ϕ_ϵ = effective porosity of media

K_d = distribution coefficient

L_r = rate of radionuclide leaching

λ_d = radioactive decay constant

J = flux of ion

V_2 = volume of solution in compartment 2

A = cross-sectional area

C_1 = concentration of species in compartment 1

C_2 = concentration of species in compartment 2

q_v = specific discharge or Darcy velocity

K_{hc} = hydraulic conductivity

ψ = groundwater head

S_t = source term

u = horizontal velocity

D_L = longitudinal diffusivity

D_T = transverse diffusivity

t_b' = breakthrough time from model

t_b = breakthrough time from data

L_c = lysimeter cap thickness

D_c = molecular diffusivity of lysimeter cap

D_s = molecular diffusivity of lysimeter monolith

CHAPTER 1

INTRODUCTION

1.1 General Considerations

The nuclear industry is constantly striving to achieve cost-effective methods for the responsible disposal of radioactive wastes. Cement-based grouts are the most widely used hosts for the immobilization of low-level radioactive waste (LLW) streams for a variety of reasons. These include: 1) low material cost; 2) processes run at low temperatures; 3) utilization of standard equipment; 4) adaptability to a wide variety of disposal scenarios; 5) the resulting waste forms are resistant to chemical, biological, thermal, and radiation degradation; and 6) high waste loadings are achieved with a minimum waste volume increase when the grout formulas are waste-stream specific (1).

Ultimately, the effectiveness of waste immobilization in grouts is determined by the degree to which the waste form protects the environment from the release of radionuclides contained in the waste. For near-surface and sub-surface monolithic waste forms, the most credible transport pathway to the environment is via groundwater movement (2). A measure of the waste form's ability to retard the release of radionuclides to the environment is its leachability. Hence, leach data provide the source term for the impact or consequence analyses.

The appropriate model for describing the waste form's leachability and the appropriate tests used to measure the critical parameters have long been

topics for debate. This lack of consensus is caused by the diversity and the complexity of the interaction mechanisms coupled with transport phenomena that affect radionuclide release. These include: 1) adsorption and desorption, 2) coprecipitation, 3) encapsulation, 4) geochemical interaction between the waste form and the groundwater, and 5) the rate of groundwater movement. Coupled with the complexity of these interactions are influences such as site-specific geochemistry and groundwater flow patterns.

Most expressions used for prediction of long-term leach rates assume that diffusion through the solid is the rate limiting process. These expressions normally fit mid-range data taken during the experiment but often do not fit short times and/or long times. Most cement-based waste forms are still active chemically because of the long-term hydration of the cement matrix. Because of these chemical reactions and/or the dissolution of the matrix, it is most probable that expressions based on diffusion alone will not accurately account for long-term leach behavior.

1.2 Research Objectives

The research discussed will extend the current transport model by explicitly including the effects of species adsorption to internal surfaces and liquid/solid mass transport resistances. This thesis investigates the idea that adsorption may be an important, or controlling, effect in the leaching process. The approach is to model species transport in immobilized waste forms in the

same manner as the movement of the species within an adsorption system such as a packed bed. This approach allows for the determination of mass transfer resistance due to macropore diffusion and external fluid film mass transfer. The results could be compared to results obtained from other sources such as the American Nuclear Society 16.1 leach test. This study can be used to better interpret long range leaching studies and provides qualitative reasons for any unusual observed behavior.

This study is comprised of two basic parts. The first part involves experimental mass transport measurements of forced species flow through immobilized waste forms while the second part is a mathematical description of convective/adsorptive transport as it relates to industrial waste forms. This research is based on the premise that diffusion, adsorption, and convection are all potentially important in the transport of species through the waste form. Thus, the research focuses on convective experiments in order to minimize "diffusive" effects and determine the order of magnitude difference that typical adsorption phenomena can make in these systems.

Phase one of the research characterizes the dynamic leaching behavior of a cement based waste form taking into account mass transfer resistance due to macropore diffusion and external fluid film mass transfer. Experiments carried out on cement disks with forced flow were used to assess the relative effects of diffusion and adsorption on control of release. The disks were prepared using materials routinely used in cement-based waste forms. These

materials include Portland cement, fly ash, Indian Red pottery clay, and slag cement. The materials are blended together prior to the addition of simulated waste or an appropriate amount of water. Experiments involved preparation of samples from various cement based blends that are representative of waste forms currently used for disposal of low-level radioactive liquid waste streams. Liquid streams containing various concentrations of the model species were forced through the samples thus allowing the species of interest to interact with the internal portions of the specimen. Various overpressures of inert gas were used to drive the convective process. Breakthrough curves for species transport through the samples were determined using a step change in cesium-137 concentration. This "flow through" approach is more representative of the conditions that exist on large waste forms exposed to groundwater movement. These experiments were designed to examine effects primarily due to adsorption without significant interference from diffusion. In addition, experiments were run to determine the physical properties, such as permeability, and characterize the cement based matrices.

The second phase of the research utilizes the results of the first phase in a mathematical model of convective/adsorptive transport. The data are regressed using the models described in chapter 4. This model allows for determination of mass transfer resistance due to macropore diffusion and external fluid film mass transfer. These predictions were then compared to results obtained from each of the samples to determine if conditions exist

where adsorptive behavior dominates the system. The conclusions derived from this study can be used to better interpret long range leaching studies and to suggest qualitative reasons for any observed unusual behavior.

The next chapter contains a review of the pertinent literature followed by a description of the experimental methods employed, development of the descriptive model, and chapters on analysis of results and future recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This literature survey examines the models presently used in the United States to predict long-term leachability of solid waste forms. The predominant model is the American Nuclear Society 16.1 leach test (2). This model assumes that the leach process is diffusion-controlled. This chapter addresses the various assumptions implied by this type of model as well as associated problems and consequences. Several other theoretical models are also discussed along with basic assumptions and relevance to the accurate prediction of long term leach behavior. A summary of the types of approaches carried out to date on leaching studies serves to highlight unique features of the work in this thesis.

2.2 Development of ANS 16.1

Many experimental studies have been conducted to characterize the leachability of radionuclides from solidified waste forms (3-6). Unfortunately, these studies are limited to the early stages of the leaching process, typically lasting less than ninety days. Diffusive transport is thought to be the driving force in these early stages (7) particularly if the solidified waste form has a permeability less than 10^{-3} times that of the surrounding geologic media (8). If the waste form is assumed to be a semi-infinite slab with an initial condition

in which the concentration of a less mobile form of a species, C_l , is directly proportional to the concentration of the more mobile form of a species, C , then the following equation can be written (9,10).

$$C_l = (K \times C) \quad (1)$$

where K is an equilibrium constant.

Taking a differential section of the waste form and doing a mass balance yields

$$\frac{\partial C_l}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial t} \quad (2)$$

where

D_e = effective solid diffusion coefficient of the species,

t = time, and

x = distance into the slab.

Initial and boundary conditions are

$x > 0, t = 0, C = C_o,$

$x = 0, t > 0, C = 0,$ and

$x = \infty, t > 0, C = C_o.$

The solution to the differential mass balance equation is (9,11)

$$C = C_o \operatorname{erf} \left[\frac{x}{2} \sqrt{\frac{(1+K)}{e^t}} \right] \quad (3)$$

where

$$\text{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-\beta^2} d\beta \quad (4)$$

If the total mass fraction released is less than 0.2, it can be assumed that the finite specimen approximates a semi-infinite specimen and the differential mass balance reduces to (11,12)

$$F = \frac{a_n}{A_0} = 2 \frac{S}{V} \sqrt{D_e' \frac{t}{\pi}} \quad (5)$$

where

F = mass fraction of species released, dimensionless,

a_n = mass of species contained in leachate, mg,

A_0 = mass of species contained in waste form, mg,

S = waste form surface area, cm^2 ,

V = waste form volume, cm^3 ,

D_e' = modified solid diffusion coefficient, cm^2/s ,

t = leaching interval, s.

In this method, the modified solid diffusion coefficient is based on incremental data. If more than twenty percent of the contaminant is leached from the waste form, the solid diffusion coefficient is calculated from a shape specific solution of the mass transport equation (13).

Typically, D_e is defined as an effective diffusion coefficient, but this is true only when the release of contaminants is diffusion controlled. For many practical purposes, D_e is modified through the use of a distribution coefficient:

$$D'_e = \frac{D_e}{1+K_d} \quad (6)$$

where K_d is the distribution coefficient and D'_e is the modified effective diffusion coefficient. However, D_e will be used throughout this paper for the modified effective diffusion coefficient. Models based on this theory have been adopted by several regulatory agencies and are used throughout the nuclear industry for determination of waste form leachability (11,12).

Leachability is addressed under Nuclear Regulatory Commission (NRC) regulations by the American Nuclear Society's ANS 16.1 leach test (12). In this test, a right-circular cylindrical sample is leached for a 90-day period with leachant renewal at 2, 7, 24, 48, 72, 96, 120, 456, 1128, and 2136 hours. The resulting data is modeled after equation 5 by:

$$\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) = 2 \sqrt{\frac{D_e}{\pi}} \sqrt{t} \quad (7)$$

where

$\sum a_n$ = cumulative amount of species released through cumulative time

t ,

A_o = original mass of species in the waste form,

V = external volume of waste form,

S = external surface area of waste form, and

D_e = effective solid diffusion coefficient of the species.

This equation for diffusion controlled leaching is based on the following assumptions:

1. The concentration of the species of interest is zero in the solution at the waste form surface.
2. The composition of the leachant is considered constant.
3. The waste form is homogeneous and its chemical and physical characteristics remain relatively constant through-out the leaching process.
4. The geometric surface area remains constant.
5. There are no time dependent interactions between the species of interest, the leachant, and the waste form.
6. The species of interest is present in a single chemical form.
7. The species of interest is effectively mixed by the leachant such that the limiting process is bulk diffusion in the solid.

These seven assumptions form the basis for most leach data modelling.

The experimental procedure is relatively simple and economic. However, there are many discrepancies in the various data that are reported. A variety of factors can influence behavior and thus skew results. The effective diffusion coefficient derived from the above expression lumps together all of the

physical and chemical interactions that may be occurring into a single value. It is this value of the effective solid diffusion coefficient that is most often published when describing the leachability index of a specific waste form.

For convenience, a leachability index is defined as the log of the reciprocal effective solid diffusion coefficient.

$$L = -\log (D_e) \quad (8)$$

where

L = leachability of species, and

D_e = effective solid diffusion coefficient of species, cm^2/s .

Typical leachability indices (averaged from five replicate grout samples) for ^{85}Sr and ^{137}Cs are 11.3 and 10.5, respectively (14). Both of these indices are significantly above the minimum required value of 6. Although this robust model is conservative and is regarded as the industry standard, there is need for improvement when considering a number of complicating factors.

2.3 Factors Affecting Leachability

2.3.1 General Considerations

One of the most important properties of a waste form is the capability to retain the waste within the solid matrix and/or retard the release of the waste to the environment. This important parameter, release rate, is used to define and evaluate the radionuclide source term available for release into the

environment. It is the rate of release of radionuclides into the environment that determines whether a particular waste form can be used for stabilization. Mass transport models use this source term as an input parameter to predict the migration of the radionuclide into the environment. The release rate is influenced by a variety of poorly understood factors and interactions between the waste form and the environment. These factors have been reviewed and evaluated by several researchers (15-17) and categorized with respect to the solid being leached, the leachant, and the leaching system. A summary of these factors are presented in Table 1.

Presently, the most commonly used waste forms for disposal of low-level radioactive waste are cement based. Immobilization of wastes in cement based waste forms is a proven technology used routinely by the nuclear industry. The resulting waste forms are less permeable than the surrounding host soil, are resistant to leaching, and to deterioration resulting from radiation and thermal cycling. The waste form structures also protect against overburden subsidence. Disposal costs can be greatly reduced by large-scale use of these waste forms because commercially available materials and equipment can be utilized (18,19). For this type of waste form, the dominant factors which influence the leachability of constituents from the waste form include the type of cement and its composition, waste to cement ratio, additives used, and cure time (18,19). Other factors which can influence the

Table 1. Factors That Influence Release Rate

Waste Form Factors	Leachant Factors	System Factors
Cement Composition	Composition	Leachant residence time
Waste loading	Complexing agents	Temperature
Surface characteristics	pH	Pressure
Porosity	Eh	Radiation field
Tortuosity	Flow rate	Waste form surface area to leachant volume ratio
Curing time		

leachability are listed in Table 1. Because of the complexity of the mechanisms involved in the leaching process, most experimental tests simulate leach conditions under flooded conditions by employing complete immersion of the specimen for an extended period of time in a large volume of leachate which is renewed at frequent intervals. This is the situation employed by the ANS 16.1 procedure. The leachate is replaced at specified time intervals to represent a dynamic flow system. Another variation of this test is to allow the specimen to remain in the leachate for an extended period of time with aliquots of the leachate taken and analyzed at specific time periods. However, the relevance of the data obtained under these conditions to actual field conditions has not been conclusively established.

2.3.2 Factors Affecting ANS 16.1 Assumptions

Most solid waste forms are disposed at/or below ground level in trenches, vaults, or other containers. It is doubtful that the flow of groundwater around the surface of the waste is sufficiently rapid enough to satisfy the first assumption. That is, the diffused species of interest is swept away fast enough from the waste form surface such that the boundary condition of $C = 0$ at $t > 0$ is met. At a typical burial site, the surrounding host sediment or rock will tend to affect the flow of water around the waste form. Geochemical interactions of the species of interest with the surrounding sediment could result in localized increased concentration of the species, thus

decreasing the concentration gradient. Subsequently, this results in a decrease in the driving force for diffusive release.

After an extended period of time (for example greater than 10,000 years) the species of interest leached from the waste form become somewhat depleted. Hence, the use of a semi-infinite solid, assumption 3, Section 2.2, may result in predicted release rates much higher than the real situation. The semi-infinite slab approach is still often used because of this conservative feature.

It has been reported (20,21) that the release of constituents from a solid waste form is affected by the composition of the leachate. The results of using a leachate solution similar to deep brine resulted in leach rates significantly different than obtained using deionized water as specified by the ANS 16.1 procedure. This could be due to the intrusion of specific chemical species into the solid matrix, thus resulting in a more complex internal pore water chemistry. This could tend to decrease the porosity of the waste form and cause an increased leachability of the species.

It has been proposed that the alkalinity and composition of the pore water within the waste form has a dramatic effect on the leaching of various radionuclide species (22,23). The alkalinity is responsible for precipitation and low solubility of the species. This alkalinity is controlled by the age of the sodium and potassium contents of the cement which in turn affects the pore water alkalinity by variations in the amounts of both sodium and potassium.

This aging factor is a direct result of the hydration process. An increase in the soluble amounts of these two species results in an increased leachability of some radiochemical waste species. This normally occurs at short time periods while at longer time periods the species tend to be less mobile. This is partially attributable to the hydration reactions which occur within the cement matrix.

It has also been found that an increase in the water to cement ratio results in an increased amount of pore water available. The result is an increase in the porosity and the mean pore size. Bulk diffusivities of various radwaste species were found to increase as the water to cement ratio increased (24).

Another observation was the formation of a precipitate on the surface of the waste form samples. This precipitation could be forming a protective barrier and thus decrease the release of contaminants. It could also indicate a deterioration of the surface area and tend to increase the contaminant release. This protective barrier could be the result of increased solubility of calcium, sodium, or potassium. An analysis of this protective barrier indicates that all three species as well as magnesium are precipitating (21,25). Assumption 4, Section 2.2, would not be satisfied in either case.

The majority of leach data analyzed using the previous methods indicate a much faster release during the early leach intervals. Data from later intervals tend to satisfy the linear independence on $\sqrt{t}$ (see Equation 7). There

are several references which discuss leaching experiments that show the initial rapid release (26-30). Data from these studies were analyzed using linear regression to provide a best-fit D_e value from the slope, and an empirical value for the "instantaneous wash off", α , from the intercept at $t = 0$. The modified equation follows:

$$\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) = 2 \sqrt{\frac{D_e}{\pi}} \sqrt{t} + \alpha \quad (9)$$

The actual mechanism or cause of the "instantaneous wash-off" has not been conclusively identified. Numerous postulates have been formed, including surface diffusion and surface pore water removal. It has been observed (30,31) that for a given surface to volume ratio, specimens having a greater surface roughness have higher leach rates. This effect is most pronounced on smaller specimens having the largest surface to volume ratio. The magnitude of this "instantaneous wash-off" relative to the total release tends to decrease with time. Obviously, this decrease is more pronounced for larger specimens. Numerous experiments have thus been performed to provide more reliable models for predicting leachability.

2.4 Development of Other Models

At present, the Nuclear Regulatory Commission requires a Leachability Index greater than 6 for each radionuclide. If the predictive model is in error,

data from these small laboratory samples may substantially misrepresent the release from larger samples typical of those disposed of in trenches or other monolithic waste forms. This particularly can be the case during "initial rate" experiments such as leach tests where rival models may not lead to substantially different initial results.

Long term leachability experiments of large samples of the waste form can not be fully characterized because the response of the waste form to the leaching process is so slow that an extremely long period of time (for example 10,000 years) would be required to complete one test. Performance of such a test is therefore limited by economic and time constraints as well as experimental methodology. Extrapolation of short term data to long term results can be very misleading. This leads to the necessity of developing reliable models to predict long-term leachability from short-term tests. The following sections describe the major classes of models presently utilized to interpret leach data. Each of these approaches has strengths and weaknesses which result from the underlying assumptions in their derivation.

2.4.1 Diffusion/Adsorption Models

The standard dynamic leach test (ANS 16.1) assumes that the process of leaching radionuclides from a waste form is diffusion controlled and one dimensional. This test does not take into account the sorption characteristics of the waste form. The typical solid waste form uses a cement paste as the

binding material (32,33). Various additives are incorporated into the waste form mix to enhance such properties as viscosity, permeability, and cost effectiveness. These types of cement based waste forms are formulated to be many times less permeable than the surrounding host soil. This ensures that the advection (water forced through the waste form under pressure) of percolating water is minimized. Thus, rainwater or groundwater would tend to flow around the waste form rather than through it. Under these conditions, the potential for release of a hazardous constituent would be limited by the diffusion of the constituent to the surface of the waste form. This diffusion controlled mechanism would be limited by the density and permeability of the waste form matrix, tortuosity of the diffusion path, solubility of the constituents, and the distribution coefficients between the waste form porewater and the binder phases. Interfacial distribution results from a combination of ion-exchange, physical and/or chemical adsorption or related phenomena.

2.4.1.1 Empirical Methods

One equation for an effective diffusion coefficient which attempts to take several of these effects into account is given by

$$D_{\theta} = \frac{D}{\left(\frac{\gamma^2}{\Phi}\right) \left[1 + \left(\frac{1-\epsilon}{\epsilon}\right) d K_a\right]} \quad (10)$$

where

D = intrinsic diffusion coefficient in the porewater, cm^2/s ,

γ = tortuosity, the ratio of actual diffusion path over the shortest geometric distance to the surface,

ϵ = porosity, a measure of the volume fraction of the macropores,

Φ = constrictivity, a measure of molecular sieve effects in the waste form matrix surrounding the pores,

d = net bulk density of the waste form, g/cm^3 , and

K_a = physical adsorption or partition coefficient of waste constituents on or in the various phases, cm^3/g .

Typical values for the above physical parameters are 7×10^{-6} , 1.4, 0.28, 0.9, 1.8, and 2, respectively. However, there are numerous paths of mass transport of the species of interest through the complex assembly of phases within the waste form. It is also very difficult to quantitatively measure the parameters needed to solve this equation. These difficulties have led to the prolific use of the ANS 16.1 equation for mass transport.

Other researchers (34-37) have utilized the basic assumption of Fickian diffusion and coupled it with semi-infinite media mass transport theory to

derive various empirical models. All of these models strive to determine a reliable estimate of the quantity, Q , of a radioactive isotope leached from a solid waste form as a function of time, t . The most common empirical model is of the form

$$Q = a\sqrt{t} + bt \quad (11)$$

where a and b are empirically determined constants for a specific leach process involving a specific radioisotope. This equation was developed from studies on the leachability of commercial glasses using aqueous solutions. It appears to be valid only if the glass does not devitrify, as is the case of some phosphate-glass products. To overcome this problem of devitrification, a generalized diffusion equation was first developed:

$$\frac{\partial C}{\partial t} = \alpha \frac{\partial^4 C}{\partial x^4} + \beta \frac{\partial^2 C}{\partial x^2} + h(C_s - C) \quad (12)$$

where α , β , h , and C_s are constants. This led to the development of the following time law implied by the generalized diffusion model for the early stages of leaching (9,15-17):

$$Q = At^{1/4} + Bt^{3/4} \quad (13)$$

The constants A and B are empirically determined constants in terms of the fundamental parameters of the diffusion model. This particular model predicts both larger initial quantities and faster leach rates than the previous empirical model of the same form.

The basic assumption in many models used to predict leach rates is that the rates are diffusion controlled. For this to be true, a plot of $[(\Sigma a_n/A_o) (V/S)]$ versus t must result in a straight line which passes through the origin. Thus a normalization of the data is performed by use of the following equation (19):

$$D_e = \pi \left(\frac{\frac{a_n}{A_o}}{(\Delta t)_n} \right)^2 \left(\frac{V}{S} \right)^2 T_m \quad (14)$$

where

D_e = effective diffusivity of species, cm^2/s ,

a_n = mass of species released from the specimen during leaching interval n ,

A_o = total initial mass of species (after initial wash-off),

$(\Delta t)_n = t_n - t_{n-1}$ duration of the n^{th} leaching interval, s ,

V = volume of specimen, cm^3 ,

S = geometric surface area of specimen, cm^2 , and

$T_m = [\frac{1}{2}(t_n^{\frac{1}{2}} + t_{n-1}^{\frac{1}{2}})]^{\frac{1}{2}}$ leaching time, representing the "mean time" of the leaching interval, n .

This normalization of the data is performed to minimize the effects of the initial "wash-off" period. However, this release of contaminants during the "wash-off" period will occur under normal disposal conditions. Thus, this release of material should be taken into account when predicting long-term release rates.

The release rate calculated from this normalization equation appears to be primarily diffusion controlled. For some radioisotopes, such as cesium, this diffusion-controlled release has some points of inflection which appear to be concentration dependent (26,38). These inflection points may be effected by the build-up of dissolution products. Additional work has revealed that the fraction of material released is either inhibited or depressed if the leachate renewal is conducted less frequently. This frequency variation is more indicative of actual disposal environments where the flow rate of water or its residence time is varied. The rate and direction of groundwater flow needs to be assessed for each disposal site. None of the models discussed can account for this type of behavior.

2.4.1.2 Extrapolation of Small Scale Data to Large Scale Specimens

The scaling parameter, V/S , is the ratio of volume of leachate to surface area of the waste form. It is used to extrapolate data from small scale specimens in order to estimate release rates for full scale waste forms. If a cement-based waste form is being used, it may be necessary to calculate the

effective surface area because of the increased internal pore structure. Numerous studies on large cement based waste forms have been performed and preliminary results indicate a shift in the total fraction of material released (39,40). One such experiment (40) has been proceeding for several years using specimens of 0.2, 2, 20, and 200 liter size blocks. These blocks were initially spiked with the same specific activity of a radioisotope. The blocks were cured for the same time frame and the V/S ratio was constant. The leaching procedure was identical for all specimens.

Several preliminary conclusions have been reached. Among the most important are:

1. An initial leaching period exists for a duration of between 60 to 90 days. It appears to be independent of sample size and is not totally diffusion-controlled.
2. Samples of the same volume but with differing diameter to height ratios have very similar leach rates.
3. Extrapolation of data from the 2 and 20 l samples to the larger 200 liter sample has an error of between 20% to 50%. Data from the smaller sample, 0.2 liter, is out of range for extrapolation.

Differences could be due to thermal gradients which develop during curing resulting in changes in the pore structure. Other possible factors include the distribution of internal micro-cracks and phase changes within the cement matrix.

Some of the results from these tests are reproduced from the literature and presented in Figure 1 (39,40). These specimens were all spiked with cesium-137. Another factor that may be affecting the release rates is that the geometric surface area is used in the calculations instead of the effective surface area. It should also be pointed out that cesium-137 is one of the least reactive radionuclides with respect to Portland cements. Other species, such as strontium, are more reactive and can become incorporated into the cement matrix during curing. Figure 2 contains the results for the effective release rates for the same specimens and time frame. Preliminary examination of the data indicates that the release rates for the blocks are similar. However, it should be noted that the smallest specimen has the slowest release rate and the largest specimen has the next slowest release rate. This relationship of size to release rate is somewhat inconsistent with what was expected. The initial assumption was that the smallest specimen would have the fastest release rate. Additional information is needed before any conclusions can be drawn with regards to the release rate. These experiments are continuing and the data is still being analyzed. Core samples of the blocks are periodically taken to examine the microstructure of the cement matrix. This extended experiment may provide additional information about the internal sorption characteristics of the matrix in the future. Data used for the figures are contained in Appendix A.

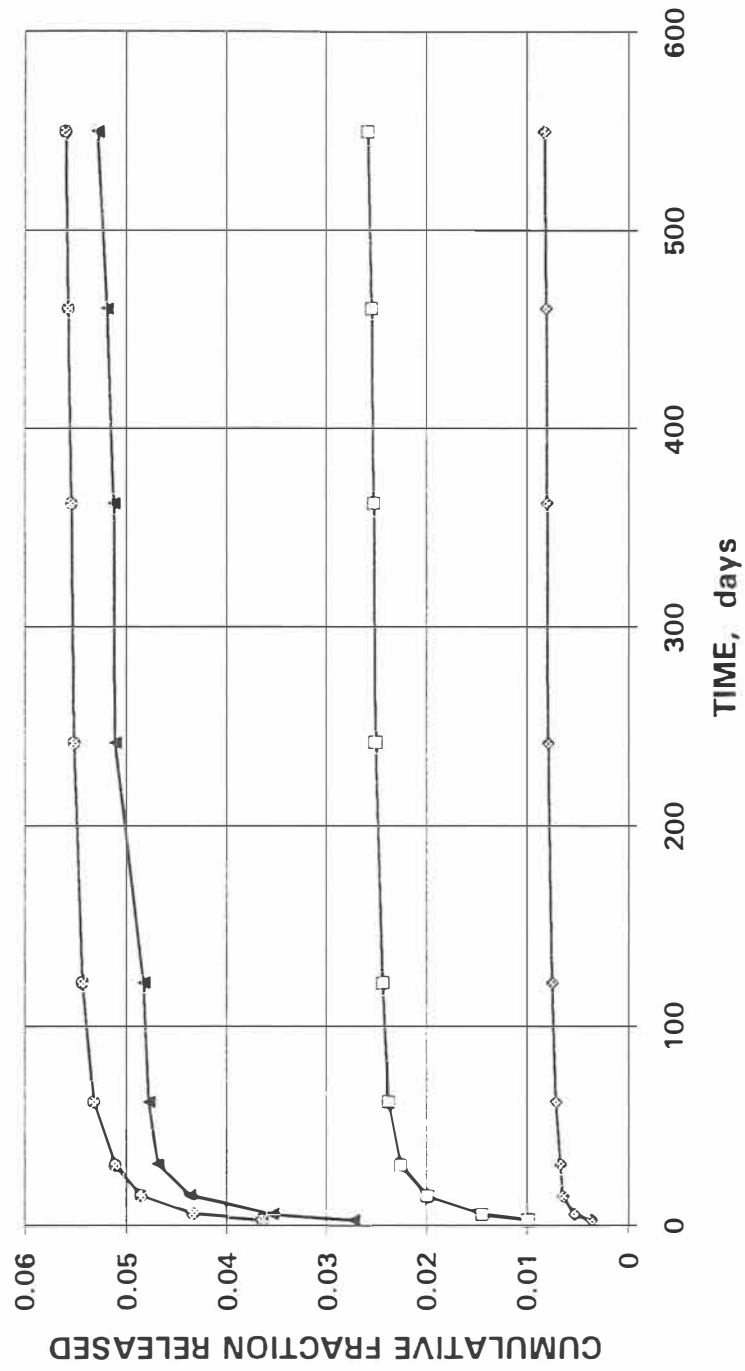


Figure 1. Scale Effect for Cement Based Waste Forms.

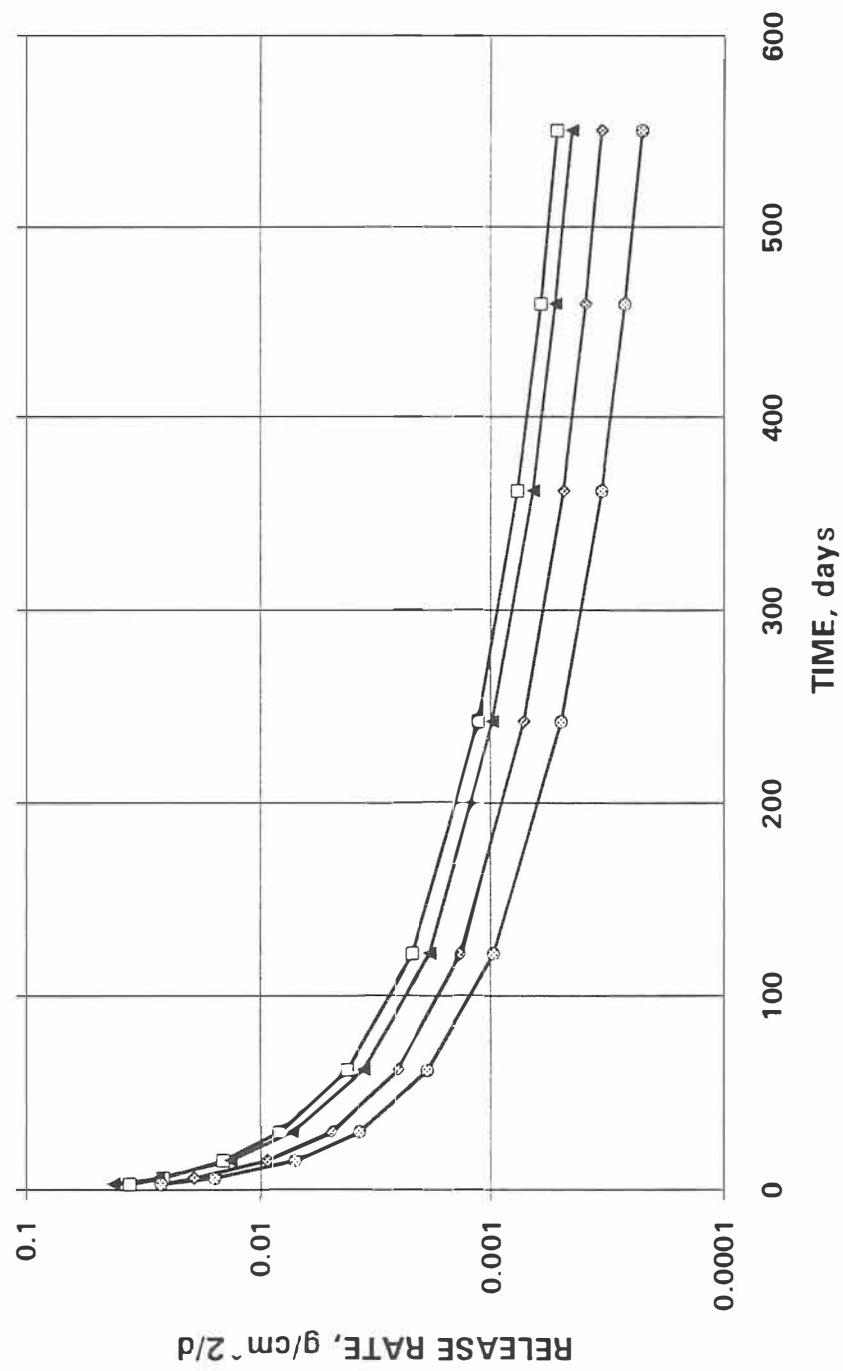


Figure 2. Scale Effect on Release Rate for Cement Based Waste Forms.

2.4.1.3 Finite Element Model

The ANS 16.1 leaching procedure is based on a semi-infinite specimen and that the total mass fraction of material leached is less than 0.2. Numerous laboratory studies have been conducted on small scale leach specimens (41-45) and the results analyzed using the semi-infinite model assumptions as previously discussed. Samples from pilot-scale monoliths have also been characterized by this method with good results (46). The majority of laboratory specimens have been spiked with various radionuclides such as cesium 137 and strontium 85. The pilot scale monolith contained no radionuclides but core samples from the monolith were tested to determine the relative leaching resistance of major cations and to determine the homogeneity of the monolith. All of this data is intended for extrapolation of larger monolithic waste forms containing relatively lower concentrations of the various radionuclides.

An alternate test method is the use of field lysimeters. The basic design for a lysimeter is that of a conical shaped monolith with leachate collection at various points around its perimeter and at the bottom. The resultant leachate is collected and analyzed for species concentration. The lysimeter can also have a clay cap which is representative of larger capped monoliths. The cap is designed to channel precipitation away from the monolith so as to minimize water penetration into the waste form, thus reducing advective transport near the monolith surface. A great deal of effort

has been spent modelling the release rates from these lysimeters. One approach is the use of a finite element model (47). The transport of a solute in the absence of adsorption was modelled in two-dimensions by the following general relation.

$$\epsilon \frac{\partial c}{\partial t} + \frac{\partial}{\partial x}(\phi c u) + \frac{\partial}{\partial y}(\phi c v) = \frac{\partial}{\partial x} \left(\phi D_L \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left(\phi D_T \frac{\partial c}{\partial y} \right) + S_t \quad (15)$$

where

c = concentration,

S_t = source term,

ϵ = porosity,

u = horizontal velocity,

v = vertical velocity,

D_L = longitudinal diffusivity, and

D_T = transverse diffusivity.

The longitudinal and transverse dispersivities and the hydraulic conductivities are taken into account in the diffusivity terms. The specific discharge q_v is defined by Darcy's Law as

$$q_x = -K_{hc} \frac{\partial \psi}{\partial x} ; q_y = -K_h \frac{\partial \psi}{\partial y} \quad (16)$$

where

q_v = specific discharge or Darcy velocity,

K_{hc} = hydraulic conductivity, and

ψ = groundwater head.

If the surrounding media is homogeneous then K_h is constant. Then from the equation for conservation of mass

$$\frac{\partial^2 \bar{\psi}}{\partial x^2} + \frac{\partial^2 \bar{\psi}}{\partial y^2} = 0 ; \bar{\psi} = K_h \psi \quad (17)$$

An analytical solution was then used to model the flux out of the uncapped lysimeter and is as follows:

$$q = 6.023 \sqrt{\frac{D_s}{\pi t}} \quad (18)$$

where D_s is the molecular diffusivity of the monolith and t is time. A separate analytical solution was derived for the flux out of the capped lysimeter.

$$q = 6.023 \sqrt{\frac{D_s}{\pi t}} \left[2 \sum_{n=0}^{\infty} (-1)^n e^{-\frac{L_c^2 (1+2n)^2}{4D_c t}} \right] \quad (19)$$

where L_c is the cap thickness and D_c is the molecular diffusivity of the cap.

The model results from the two lysimeter tests agreed quite well with the actual field data. The data also verified the shielding effect from the cap placed on one of the lysimeters. The results from these experiments illustrate

that a finite element model, using simple assumptions for groundwater flow and transport, could successively predict the release rates from a waste form.

2.4.1.4 Diffusion Through a Semi-Permeable Membrane

Cement based waste forms are constantly being studied to determine their durability and their leaching characteristics. These tests are often designed to identify the role of the various components of the waste form in the retention of hazardous material. Other variables, such as porosity, water to cement ratio, and cement type, have been shown to be important factors in both durability and leachability (48-54). The principal variable studied in most leaching experiments is the diffusion coefficient. The diffusion coefficient is then used to predict the leachability of the waste form.

The diffusion of ions through hardened cement pastes has been investigated using a semi-permeable membrane approach (55,56). Apparatus similar to that used for this research was used to determine the diffusion of anions such as chlorine through the hardened cement paste. The specimen was clamped between two chambers of liquid of known volume. One chamber contained a solution of the diffusing ion being studied. Concentration of the diffusing ion was measured as a function of time. The variables studied were: 1) water to cement ratio, 2) curing time, 3) curing conditions, 4) temperature, and 5) types of porous material. The flux of a

diffusing ion from compartment one of the cell to compartment two is given by the following equation:

$$J = \frac{V_2}{A} \frac{dC_2}{dt} = \frac{D}{x} (C_1 - C_2) \quad (20)$$

where

J = flux of ion (mole/cm²/s),

D = diffusion coefficient (cm²/s),

V_2 = volume of solution in compartment 2 (cm³),

A = cross-sectional area (cm²),

x = thickness of sample (cm),

C_1 = concentration of species in compartment 1 (mole/cm³), and

C_2 = concentration of species in compartment 2 (mole/cm³).

The assumption was that effective diffusivity was independent of concentration. The solution concentrations are assumed to be equal to the surface activities and thus the effective diffusivity can be calculated from the following:

$$\text{for } t > t_0, C_1 > C_2: D = \frac{C_2 V x}{A C_1 (t - t_0)} \quad (21)$$

A rectilinear plot of concentration, C_2 , versus time, t , can thus be used to determine the effective diffusivity.

2.4.1.5 Linear and Nonlinear Sorption Isotherms For One-Dimensional Porous Media

Most batch-sorption experiments are performed on either crushed material or small samples in order to obtain data within a reasonable time frame. This approach could damage the internal pore structure of the waste form thus disrupting the actual sorption behavior. One approach has been to prepare intact samples similar to the ones used in this research except that geologic rock was used (53,57,58). The assumption was that the experiment could be described in terms of a one-dimensional, single porosity medium in which the pore water diffusion coefficient is constant in both time and space. Taking a differential section and performing a mass balance yields the following equation.

$$\frac{\partial}{\partial t} \left(C + \rho \frac{S}{\epsilon} \right) = D \frac{\partial^2 C}{\partial x^2} \quad (22)$$

where

ρ = bulk density,

ϵ = porosity,

S = mass of solute in the solid phase per unit mass of porous medium,

C = concentration of solute in the liquid phase, and

D = diffusion coefficient.

It was further assumed that the adsorption was instantaneous and could be described by a power function isotherm:

$$S = KC^N \quad (23)$$

where K and N are constants.

The distribution ratio R_D is defined as the ratio of S to C and is given by

$$R_D = KC^{N-1} \quad (24)$$

Combining the previous equations yields the following governing equation used for the experiments:

$$\frac{\partial C}{\partial t} = \frac{D_e}{\alpha} \frac{\partial^2 C}{\partial x^2} \quad (25)$$

where D_e is equal to ϵD and is the effective diffusion coefficient and

$$\alpha = \epsilon + \rho NR_D \quad (26)$$

The following boundary conditions were applied.

$$C = C_0 \text{ at } x = 0 \text{ and } C = 0 \text{ at } x = L.$$

By choosing the value of N , the radionuclides can be assumed to be absorbing in linear ($N = 1$) or nonlinear fashion ($N \neq 1$). The solution for the nonlinear case must be solved numerically. For the linear case, the solution is given by:

$$\frac{C_t VL}{AC_o} = D_e t - \frac{\alpha L^2}{6} \quad (27)$$

2.4.2 Statistical Modelling of a One-Dimensional Porous Medium

A statistical model assumes that the leaching characteristics of a test system remain constant through-out the leaching process. The assumption is that the data are normally distributed with random errors. In other words, the characteristics observed during an experimental leach test will remain the same as if the entire leaching process were continually observed. Based on this assumption, a mathematical formula could be developed based on a statistical study of observed experimental data. Such a model could then be used to predict the long-term leachability of a waste form (59,60).

The initial assumptions were that the leaching process is one-dimensional and the response of the desorption process was much faster than that of the diffusion process. In other words, the desorption process maintains its equilibrium state at all times. It was also assumed that the species of radionuclide being leached is comprised of the species of interest and the stable isotopes of the same element. A one-dimensional mass

balance was then written and the distribution coefficient and retardation factor were substituted into the equation. The resultant equation was a linear combination of the mass balance relationship between the radionuclide and the stable nuclide. These components were analyzed independently and the mass balance relationship for the radionuclide became:

$$\frac{\partial C}{\partial t} = \frac{D_e}{\epsilon R} \frac{\partial^2 C}{\partial x^2} - \lambda_d C \quad (28)$$

where

C = concentration of the species of interest in the aqueous phase,

t = time,

D_e = effective diffusivity,

R = retardation factor,

ϵ = porosity of the solid waste form,

x = space coordinate, and

λ_d = radioactive decay constant.

Equation 28 is the basic differential equation used to describe the change in radionuclide concentration. It is very similar to previously described models except that the diffusion coefficient has been replaced by a term expressed in a ratio of hydrodynamic diffusion coefficient and the product of porosity and retardation factor. If the concentration of the radionuclide in the

aqueous solution of the solidified waste form is known, then a leach rate can be obtained from the following equation:

$$L_r = Da \left(\frac{\partial C}{\partial x} \right)_{x=0} \quad (29)$$

where

L_r = rate of radionuclide leaching,

a = cross-sectional area of solid, and

$(\partial C / \partial x)_{x=0}$ = gradient of radionuclide concentration at boundary of waste form.

The following dimensionless terms were then defined:

$$C' = \frac{C}{C_0}, \quad x' = \frac{x}{X}, \quad t' = \frac{Dt}{\epsilon R X^2} \quad (30)$$

where X denotes the thickness or length of the waste form. The assumption was made that leaching only occurs from one end of the waste form. The solution to the partial derivative in equations 28 and 29 could only be found once the boundary conditions were defined. After the partial derivative was solved and substitution of equation 30 into 28 and 29, the result was manipulated so as to obtain the following dimensionless terms for the leaching number and the leaching rate, respectively:

$$\bar{L} = \frac{\lambda_d \epsilon R X^2}{D} \quad (31)$$

$$\bar{L}_r = \frac{\epsilon R X^2 L}{A_o D} \quad (32)$$

The leaching constant can be determined from a dynamic leaching test and is defined as:

$$\bar{L}_c = \frac{D}{\epsilon R X^2} \quad (33)$$

A normalized leaching diagram was obtained by plotting the dimensionless leaching rate as a function of dimensionless time. This diagram could be used to predict the leaching rate of a waste form once the leaching constant has been determined. It is presumed that the leaching constant can be determined from a shortened leaching test.

2.4.3 Applications of Diffusion Theory to Permeability

When evaluating a cement based waste form for its effectiveness in retarding the release of hazardous constituents, it sometimes becomes necessary to determine the coefficient of permeability. The methods employed for this determination can generally be divided into two groups: 1) the output method where a steady outflow of water through a specimen is monitored, and 2) the input method where the depth of water penetration into

the specimen is measured. Both of these methods have disadvantages (55) but the input method is more widely used. This method usually employs an overpressure of inert gas to force the water into the specimen. The resulting second order differential equation has been solved by numerical computer analysis and formulas have been developed for calculating the coefficient of permeability (55,56). Numerical solutions are also presented for the output method. It was concluded that diffusion theory can be used as a basis for a computer analysis for both methods. The results obtained from the computer analysis are in fairly good agreement with literature values and with values obtained by direct application of Darcy's Law.

2.4.4 Use of a Retardation Factor

The major pathway for the release of radionuclides to the environment from a waste form is through water. This pathway can be percolated water, that is, water moving in an upward direction as a result of site conditions, groundwater, precipitation, or other means of water transport. The relative mobility of a species is influenced by the water velocity, properties of the species, and transport properties of the disposal site. Typically, adsorption is quantified by measuring the distribution of the adsorbate between the solid phase and the liquid phase. This value is referred to as the distribution coefficient and is often denoted by a " K_d ", " D ", or " R_d ". Adsorption refers to conditions that have reached equilibrium and generally requires reversibility.

That is, desorption occurs at the same rate and yields the same equilibrium ratio of adsorbate between the solid and the liquid phases.

Often it is assumed that the distribution coefficient, K_d , is constant. That is, the distribution of the species of interest between the solid adsorbent and the solution is a constant value. However, changing environmental conditions, such as pH and dissolved-solids content in groundwater, can affect the value of the distribution coefficient (57-60,61). One approach utilized to attempt to account for these effects is the use of a retardation factor, R . The basic equation used to model contaminant transport for porous media is derived from mass balance considerations and is of the form:

$$R \frac{\partial C}{\partial t} = \nabla \cdot \theta D \nabla C - \nabla \cdot VC + M \quad (34)$$

where

$$\theta D_{ij} = a_t |V| \delta_{ij} + (a_t - a_l) \frac{V_i V_j}{|V|} + \theta a_m T \gamma_{ij} \quad (35)$$

where

C = concentration of species of interest (mass of solute/volume of porous media),

t = time (sec),

S_a = adsorbed concentration (mass of species adsorbed/mass of porous media),

θ = volumetric moisture content,

D_{ij} = component of the dispersion tensor D (area/time),

a_t = transverse dispersivity (length),

a_l = longitudinal dispersivity,

δ_{ij} = Kronecker delta,

a_m = molecular diffusion coefficient (area/time),

T = tortuosity,

$|V|$ = magnitude of the velocity vector (volume of flow/area/time),

V_i = i^{th} component of velocity vector (volume of flow/area/time),

V_j = j^{th} component of velocity vector (volume of flow/area/time), and

M = source term for the species of interest (mass/volume/time).

The retardation factor for porous flow is defined as:

$$R = \frac{V_w}{V_n} = 1 + \frac{\rho_b}{\phi_\epsilon} K_d \quad (36)$$

where

R = retardation factor (dimensionless),

v_w = velocity of groundwater (length/time),

v_n = velocity of species of interest (length/time),

ρ_b = porous media bulk density (mass/length³),

ϕ_ϵ = effective porosity of media (dimensionless), and

K_d = distribution coefficient (length³/mass).

The term on the left of the equality symbol in equation 34 represents the rate of mass accumulation per unit volume in both the liquid and the solid phase. The terms on the right of the equality symbol represent the net material accumulation or loss per unit volume due to dispersion, diffusion, advection, and sources. The mass balance assumes a linear relationship between the amount of material in the dissolved phase to that adsorbed on the solid phase.

When the retardation factor, R , is used in conjunction with a constant distribution coefficient, K_d , each layer or segment of the porous medium is assumed to have a constant retardation factor. Using this assumption provides an easy solution to the transport equation and the determination of species concentration as a function of time and distance. However, most geologic pathways for groundwater migration are not homogeneous throughout the various layers. Thus the retardation factor does not remain constant within each individual layer.

CHAPTER 3

EXPERIMENTAL METHODOLOGY AND PROCEDURES

3.1 Introduction

The purpose of this research is to extend current immobilized waste form transport models by explicitly including effects of species adsorption to internal surfaces and liquid/solid mass transport resistances . This study is comprised of two basic parts. The first part involves experimental mass transport measurements of forced species flow through immobilized waste forms while the second part utilizes a mathematical model of convective/adsorptive transport as it relates to industrial waste forms. This research is based on the premise that diffusion, adsorption, and convection are all potentially important in the transport of species through the waste form. Thus the research focuses on convective experiments in order to minimize "diffusive" effects and determine the order of magnitude difference that typical adsorption phenomena can make in these systems.

3.2 Experimental Approach

Phase one of the research characterized the dynamic leaching behavior of a cement based waste form taking into account mass transfer resistance due to macropore diffusion and external fluid film mass transfer. Experiments involved preparation of samples from various cement based blends that are representative of waste forms currently used for disposal of low-level

radioactive liquid waste streams. Liquid streams containing various concentrations of the model species were forced through the samples thus allowing the species of interest to interact with the internal portions of the specimen. Various overpressures of inert gas were used to drive the convective process. Breakthrough curves for species transport through the samples were determined using a step change in cesium-137 concentration. This "flow through" approach is more representative of the conditions that exist on large waste forms exposed to groundwater movement. These experiments were designed to examine effects primarily due to adsorption without significant interference from diffusion. In addition, experiments were run to determine the physical properties and characterize the cement based matrices.

The second phase of the research utilizes the results of the first phase in a numerical study of convective/adsorptive transport. The data are regressed using the models described in chapter 4. These models allow for determination of mass transfer resistance due to macropore diffusion and external fluid film mass transfer. These predictions were then compared to results obtained from each of the samples to determine if conditions exist where adsorptive behavior dominates the system.

The conclusions derived from this study can be used to better interpret long range leaching studies and to suggest qualitative reasons for any observed unusual behavior.

3.3 Materials

The nuclear industry is constantly striving to develop methods for the long-term disposal of low-level radioactive waste. One of its main objectives is to develop methods that are cost effective and pose little or no risk to public health and safety. Cement based waste forms, grouts, are the most widely used method for the treatment and ultimate disposal of both chemical and radioactive waste because of their low processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and regulatory requirements. The mechanical, chemical, and physical properties of the waste form are greatly dependent on both the cement blend and the waste.

Portland cement based technologies involve adding a mixture of water, Portland cement, and often a pozzolanic material, such as cement kiln dust and/or fly ash from fossil fuel power plants, to the waste. Other materials such as clay, gypsum, or calcium chloride may be added to control the setting reaction rate or to produce a residual with special characteristics. Appendix B contains the chemical analyses of the materials used in this study.

3.3.1 Cement Matrix Used In Experiments

An acceptable waste form must have certain physical properties that meet or exceed performance and processing criteria. These physical properties of the hardened and the wet waste form are partially determined

by the amount of cement in the blend. The amount of cement used is typically described in the waste-to-cement ratio (w_s/c). In general, a w_s/c of only 0.25 is required for complete hydration of ordinary Portland cement, with additional water serving to fluidize the mix and thus making it more processible. The cement serves as the binder, solidifying materials during the formation of hydration products within the waste form. This hydration occurs over a period of time and produces a solid matrix of material.

Portland cement chemistry is complex, and there have been few studies on the reaction processes when wastes and other materials are added to the cement mixture. The dry constituents of Portland cement include, in order of concentration by weight, CaO , SiO_2 , Al_2O_3 , Fe_2O_3 , SO_3 , and MgO . Portland cement reactions primarily involve the hydration of tricalcium aluminate, tricalcium silicate, and water to form a product mixture primarily of calcium silicate hydrate and calcium hydroxide. The chemical and physical processes by which radionuclides and chemical wastes are bound and fixated in the cement mixture is not completely understood. However, several hypotheses for the stabilization mechanism have been proposed. The cement used in these studies was obtained from Ash Grove Cement West in Durkee, OR. Various types of cement were used and are identified with each of the individual experiments. Types I, II, and III are the most commonly used cements for waste forms. Factors such as cost, hydration rates, heat of

hydration, and alkalinity of the cement must be considered prior to selecting a particular type.

3.3.2 Indian Red Pottery Clay

Indian Red Pottery Clay (IRPC) is added solely as an ion-exchange medium primarily to retain ^{137}Cs (62-64). With an exchange capacity of 0.1 meq ^{137}Cs per gram of clay, only small quantities should be used in an actual waste form containing low-level radioactive waste. However, experience in waste form formulation and development has shown that the pottery clay content needs to be 8 wt % of the dry solids blend to insure intimate contact with the ^{137}Cs . In addition, it has been shown that minor variations in the pottery clay content have a negligible impact on the waste form's physical properties. The IRPC utilized in these studies was obtained from the American Art Clay Company in Indianapolis, IN.

3.3.3 Fly Ash

Fly ash is a byproduct of the combustion of coal and is typically regarded as a waste. The use of fly ash in waste form formulation is primarily as a cement extender. The physical characteristics of fly ash are such that it improves the fluid properties of the wet grout as well as the adsorption of water. Its use as an extender should be maximized due to its low cost compared to other types of extenders. It has also been shown that fly ash

decreases the leachability of strontium by incorporating it into the cementitious matrix. The fly ash used in these studies was obtained from the Ross Island Sand and Gravel Company in Portland, WA.

3.3.4 Slag Cement

Slag cement is a by-product of the iron-making process. When quenched with water and rapidly chilled, it forms a glassy granulated material of sand-like consistency. It has a high calcium content and thus excellent cementitious properties. Slag cement sets in a manner similar to cement when it is finely ground and mixed with a suitable activator. The ground blast furnace slag is normally substituted for 25 to 75% of the Portland cement in general concrete applications.

When slag cement is combined with Type I or Type II Portland cement, its hydraulic properties are activated in the presence of alkalis and calcium hydroxide to produce dense cementing compounds similar to Portland cement. The combination of slag cement and Portland cement provides the following benefits: increased workability of the plastic mix at lower water to cement ratios, increased resistance to alkali and sulfate caused deterioration, increased density of the hardened mix which reduces the permeability, and increased compressive strength at age due to its pozzolanic nature. The slag used in this study was obtained from Ash Grove Cement West, Inc. in Seattle, WA.

3.4 Apparatus

The experimental apparatus is schematically shown in Figure 3. The sample specimen was clamped between the two chambers. Chamber 2 was connected to a Cole-Palmer peristaltic pump and a 1.5 liter reservoir of saturated $\text{Ca}(\text{OH})_2$ solution. This large volume of solution was used in order to minimize any substantial change in radionuclide concentration. The reservoir was spiked with the appropriate radionuclide prior to the beginning of each experiment simulating a step change in concentration. A detector was placed in-line with the reservoir so as to monitor the concentration of the solution. Chamber 1 was also connected to a peristaltic pump and a volume of 0.035 liter of saturated $\text{Ca}(\text{OH})_2$ solution was continually swept by the surface of the specimen.

The cumulative buildup of the radioisotope in chamber 1 was measured with time via a titanium window, NaI(Tl) detector, and a multichannel analyzer-data acquisition system made by Hewlett-Packard. The concentration in chamber 2 was also measured with time via a titanium window, NaI(Tl) detector, and the multichannel analyzer-data acquisition system. The detectors are standard laboratory equipment purchased from Fisher-Scientific Company. The concentration was measured in counts per minute and recorded on computer disk for subsequent analysis. The detectors were standard pieces of equipment and were factory calibrated. The radionuclide used in the experiments was a research grade radioisotope. The

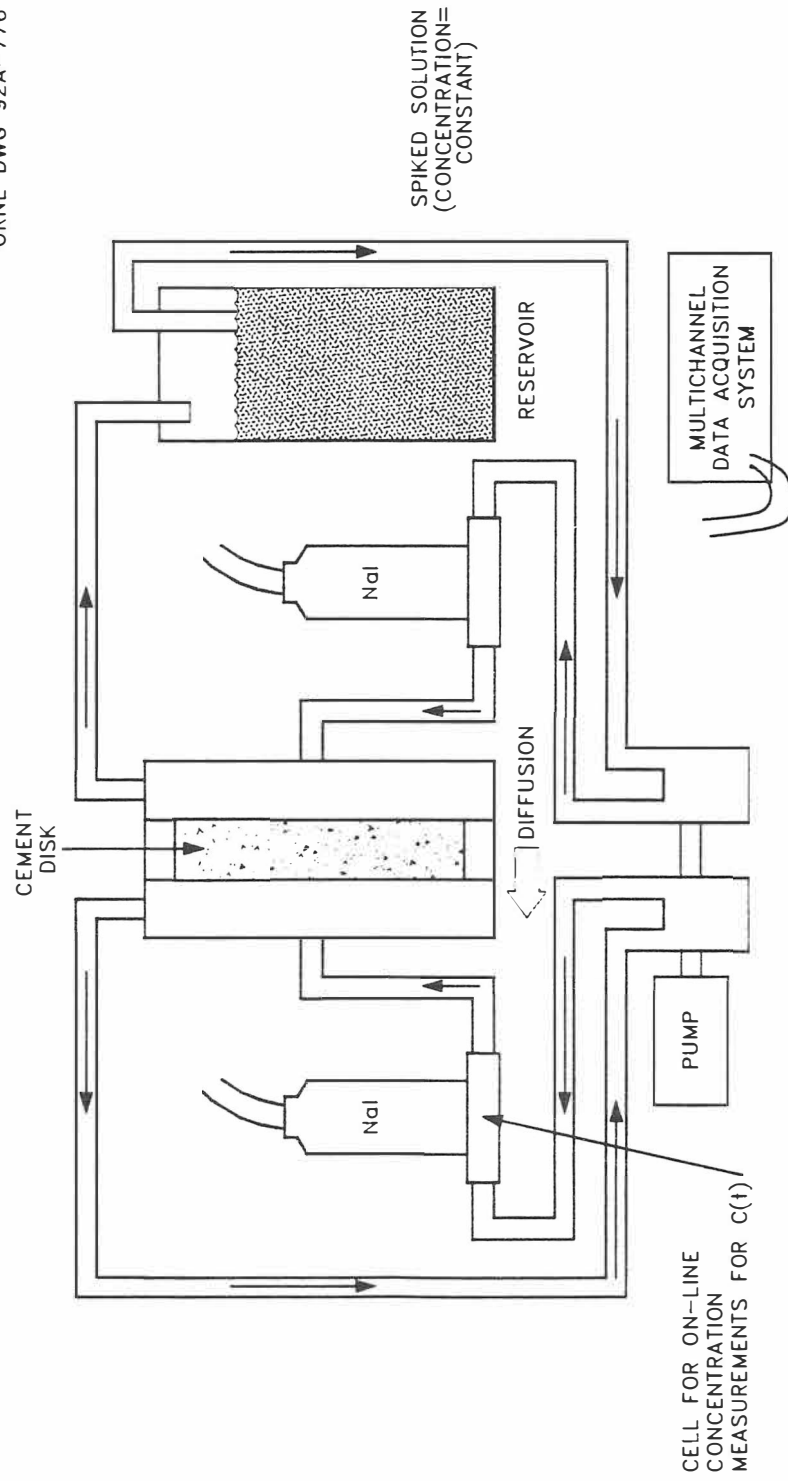


Figure 3. Schematic Diagram of Experimental Apparatus.

specific activity level was calculated for each experiment using standard decay rates and half-lives for the radionuclide of interest. All data was collected and stored on an International Business Machine (IBM) AT personal computer. Appendix C contains a listing of all the data obtained.

3.5 Experimental Procedure

3.5.1 Preparation of Samples

The dry solids blend is typically comprised of cement, fly ash, IRPC, slag cement in various combinations. The dry materials are blended in 5.0 Kg lots for 23 h at 30 rpm in a 7.6 liter Patterson-Kelly twin shell V-blender prior to mixing with the aqueous solution. The appropriate amount of dry materials and liquid are then mixed in a Hobart model N-50 mixer with a wire loop whip mixer blade. Mixing is accomplished by adding solids to liquid during an 8-15 s interval while stirring at low speed for a total of 30 s. Mixing is then continued at medium speed for a total mixing time of 60 s.

The specimens were various mixtures of the components described in the previous section. The dry components were thoroughly mixed with a proportionate amount of water. This proportionality is referred to as the mix ratio, or the amount of dry material to waste. The ratio of dry materials to waste is a key variable in waste form development. This research used mix ratios and dry solids blends that are similar to ones commonly used at the Department of Energy's Savannah River Site and the Hanford Site. The

mixture was then poured into stainless steel rings of 9.0 cm outside diameter and 7.8 cm inside diameter or 3 inch Schedule 40 pipe. The height of the rings was typically either 0.7 cm or 0.3 cm. These rings had previously been attached to a sheet of teflon with silicone rubber. The sample and holder was then placed in a heated humidity cabinet and cured for 28 days at 100% humidity and 23°C or 60°C. After curing, the specimens were soaked in the appropriate solution for the intended test to assure complete liquid saturation of the grout pores and ionic and chemical equilibrium with the test environment. A solution of 0.1 N CsCl saturated with Ca(OH)_2 was normally used for the sorption experiments. The sample was immersed for a period of five days. Specimens of 3 mm thickness were prepared in this manner for the sorption experiments and 7 mm thick for the permeability measurements. The specimens remained inside the stainless steel rings for subsequent testing. The assembly was then clamped between the two chambers of the experimental apparatus using neoprene rubber gaskets. A schematic representation of the specimen assembly and the connecting piping is shown in Figure 4.

3.5.2 Permeability and Porosity Measurements

Permeability measurements were taken using a different experimental set-up. The samples were prepared as previously described. After curing, the specimens were clamped between a liquid reservoir and a grooved metal plate

ORNL DWG 92A-777

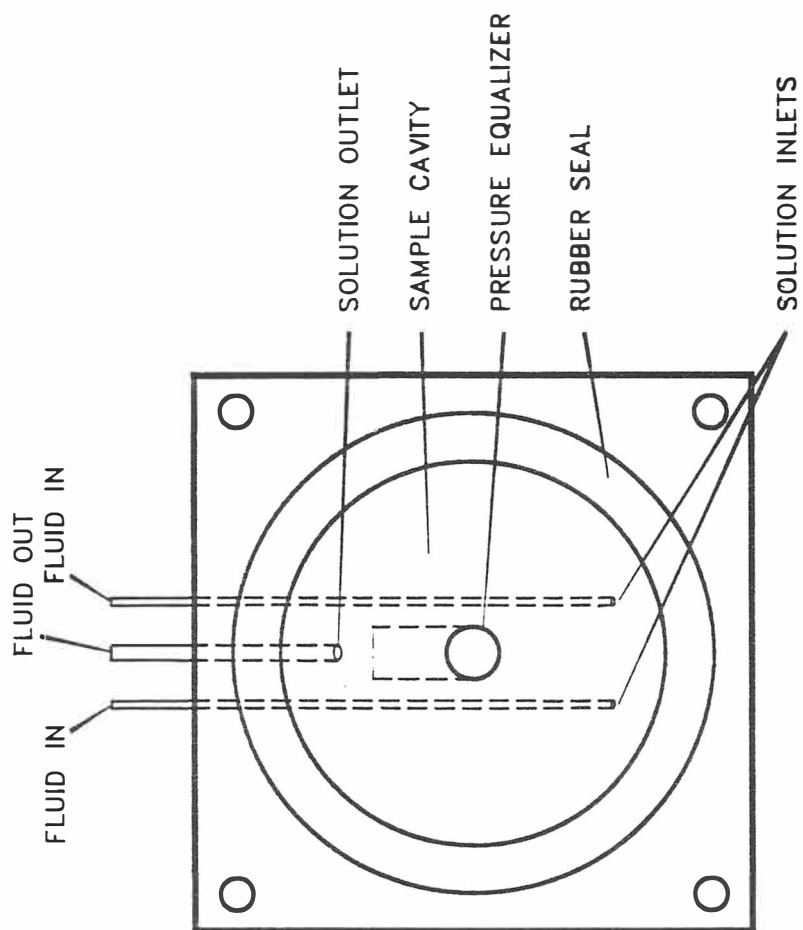


Figure 4. Schematic Diagram of Sample Holder

which allowed for collection of water as well as support for the specimen. The grooves fed a capillary tube where the amount of solution permeating the specimen was measured. A 0.1 mL volumetric pipette was used to determine the amount of permeate. The permeating solution was a saturated solution of $\text{Ca}(\text{OH})_2$. The driving force for permeation was either an overpressure of inert gas such as nitrogen or the head of solution above the disk or a combination. An overpressure of 5 or 8 lbs/in² was typically used. The large surface area to thickness ratio allowed for rapid measurements of permeability.

The following equation was used to analyze the data from the permeability experiments.

$$Q = \frac{K_p \Delta P A}{\mu x} \quad (37)$$

where,

Q = flow rate, cm³/s,

μ = viscosity of fluid, cp,

K_p = permeability, Darcy,

ΔP = pressure gradient, lbs/in²,

x = length of specimen, cm, and

A = area of specimen, cm².

The above equation was rearranged to yield an expression for the permeability. The volumetric flow rate measured was then used to determine the velocity of fluid through the specimen using the following:

$$v = \frac{Q}{A} \quad (38)$$

where v is the velocity in cm/s. These are the velocities used in the determination of the mass transfer characteristics of the specimens.

The same apparatus was used for the determination of accessible porosity of the cement disks. Two or three sample volumes of tert-butyl alcohol were permeated through the cement disk using overpressures of 5 or 8 lbs/in². The permeated alcohol was then measured for water content via Fischer reagent titration. The results for the permeability and the porosity are presented in Chapter 5.

3.5.3 Forced Convective Flow Experiments

The samples were prepared as previously described in section 3.5.1. The assembly was then clamped between the two chambers of the experimental apparatus using neoprene rubber gaskets. Figure 3 illustrates the system that was used for these experiments. A schematic representation of the specimen assembly and the connecting piping is shown in Figure 4. The same solution (0.1 N CsCl saturated with Ca(OH)₂) was continuously flowed past both surfaces of the sample using peristaltic pumps. The solution on the

large reservoir side was spiked at time zero with Cs^{137} and the cumulative buildup of the radioisotope on the other side was measured with time via a titanium window, NaI(Tl) detector, and a multichannel analyzer-data acquisition system. The total volume in Chamber 1 was 1500 mL. Thus the addition of the spike of radioisotope simulated a step change. The volume in Chamber 2 was 35 mL. The correlation between the isotope flux through the sample and the activity was close to instantaneous. The detector count time was typically 5 or 10 minutes per measurement for experiments which lasted one to five weeks. A pressure differential of 5 or 8 lbs/in² was used to cause flow of liquids through the samples. Chapter 5 contains all the relevant data for these experiments.

CHAPTER 4

MODEL DEVELOPMENT

4.1 Introduction

The research project discussed in this paper extends the current transport model by explicitly including effects of species adsorption to internal surfaces and liquid/solid mass transport resistances. It is speculated that as soon as the waste form is immersed in the leachate, desorption may occur. The desorption process can be driven by either dissolution or ion exchange or a combination. Movement towards equilibrium between the sorbed species and the dissolved species results in a net driving force for the desorption process (65). The following section describes the model used for the data analysis.

4.2 Packed Bed Adsorption Model

The approach taken in this research is to examine the adsorption effects separately from diffusion. This research is based on the idea that adsorption may be an important, or controlling, effect. The approach was to model species transport in waste forms in the same manner as the movement of the species within an adsorption system such as a packed bed (66-68). Transporting species are allowed to adsorb and desorb on the waste forms internal surfaces and diffuse in the liquid phase as fluid convection takes place within the waste form (67). Figure 5 provides a schematic illustration of this

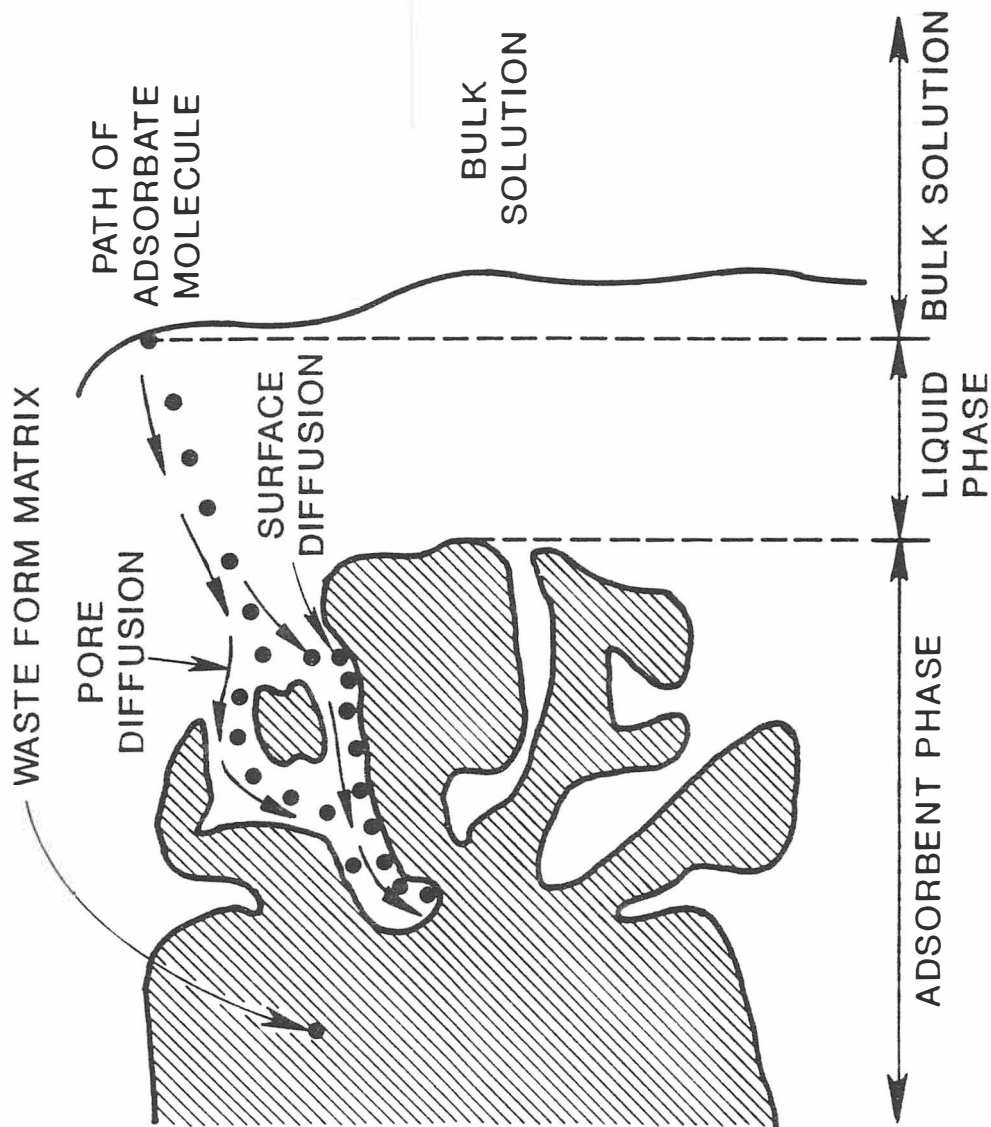


Figure 5. Graphical Illustration of Sorption Pathways.

type of behavior. The differential fluid phase mass balance for an element of an adsorbable species in this situation can be represented by (68)

$$D_l \frac{\partial^2 c}{\partial z^2} + \frac{\partial(vc)}{\partial z} + \left(\frac{\partial c}{\partial t} \right) + \left(\frac{1-e}{e} \right) \left(\frac{\partial \bar{q}}{\partial t} \right) = 0 \quad (39)$$

where

D_l = axial dispersion coefficient,

c = sorbate concentration in fluid phase,

z = distance from column inlet,

v = interstitial velocity of fluid,

t = time,

e = voidage of adsorbent bed, and

$\bar{q}$ = average sorbate concentration of species, where

$$\bar{q} = \left(\frac{3}{R^3} \right) \int_0^{R_p} R^2 q dR \quad (40)$$

This assumes that the flow pattern through the column can be represented as plug flow with a term for axial dispersion. The first term in the equation represents dispersion and goes to zero as ideal plug flow is approached. The second term represents concentration gradients due to convection, the third term is concentration as a function of time, and the fourth term is the volume averaged sorbate concentration within the bed or a group of particles at a given position in the bed as a function of time.

4.3 Development of Ideal Plug Flow Model

The dynamic behavior of a convective/diffusive system with adsorption will be affected by the form of the adsorption equilibrium relationship and the fluid/solid mass transfer characteristics. This study was initially based on the following assumptions:

1. plug flow - axial dispersion is initially neglected thus the first term of equation 39 is assumed to be zero,
2. linear adsorption isotherm, and
3. mass transfer resistance is due to series contributions of fluid film and macropore resistances.

This leads to the following expression for the sorbate term in equation 39.

$$\frac{\partial \bar{q}}{\partial t} = k(q^* - q) = kK_h(c - c^*) \quad (41)$$

where,

q^* = equilibrium sorbate concentration of species,

c^* = equilibrium sorbate concentration in fluid phase,

k = the equivalent rate constant, and

K_h = dimensionless Henry's law adsorption equilibrium constant.

The initial and boundary conditions for an adsorption system which is initially sorbate free are

$$t < 0, \quad q(R, 0, z) = c(0, z) = 0$$

$$t > 0, \quad c(t, 0) = c_o$$

These conditions apply when the system is subjected to a step change in sorbate concentration at the inlet at time equals zero. The forced convection experiments were conducted using a step change in sorbate concentration.

The mass transfer coefficient, k , can be defined as:

$$\frac{1}{kK_h} = \frac{R_p}{3k_f} + \frac{R_p^2}{15e_p D_p} + \frac{r_c^2}{15K_h D_c} \quad (42)$$

where,

R_p = absorbent "particle radius",

k_f = external fluid film mass transfer coefficient,

e_p = porosity of absorbent particle,

D_p = pore diffusivity,

r_c = microparticle radius, and

D_c = intracrystalline diffusivity.

The mass transfer constants are based on the assumption that the resistances include mass transfer from the bulk liquid to the particle surface and mass transfer in the macropores of the adsorbent material.

For the simple system involving a linear rate equation with plug flow, such as the one assumed in this research, the following model for the breakthrough curve is reproduced from the literature (68).

$$\frac{C}{C_o} = \exp^{-\delta} \int_0^{\tau} \exp^{-u} I_0(2\sqrt{\delta u}) du + \exp^{-(\tau-\delta)} I_0(2\sqrt{\delta \tau}) \quad (43)$$

where,

C_o = initial concentration of the species,

δ = dimensionless bed length, and defined as

$$\delta = \left(\frac{kK_h z}{v} \right) \left(\frac{1-e}{e} \right) \quad (44)$$

τ = dimensionless time parameter, and defined as

$$\tau = k \left(t - \frac{z}{v} \right) \quad (45)$$

where

k = overall mass transfer coefficient,

K_h = dimensionless Henry's law adsorption equilibrium constant, and

I_o = hyperbolic Bessel function.

For the simple case of a linear, isothermal trace component system with plug flow, the following analytic solution is given for the breakthrough curve (68):

$$\frac{C}{C_o} = \frac{1}{2} \operatorname{erfc}(\sqrt{\delta} - \sqrt{\tau}) \quad (46)$$

Following is the expression used for the error function calculation:

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n(2n+1)} \quad (47)$$

where

$$x = \sqrt{\delta} - \sqrt{\tau} \quad (48)$$

and

$$\text{erfc}(x) = 1 - \text{erf}(x) \quad (49)$$

The error function is also an odd function and the following identity was used when the value of x was negative.

$$\text{erf}(x) = -\text{erf}(-x) \quad (50)$$

The model equations for a linear rate system with plug flow are written in terms of dimensionless variables and the fluid mass balance assumes the form:

$$\frac{\partial \phi}{\partial \delta} + \frac{\partial \psi}{\partial \tau} = 0 \quad (51)$$

where

$\phi = C/C_0$ (dimensionless fluid concentration parameter), and

$\psi = \bar{q}/q_0$ (dimensionless sorbate concentration parameter).

The dimensionless rate equation becomes:

$$\frac{\partial \psi}{\partial \tau} = \phi - \psi \quad (52)$$

The dimensionless bed length, δ , and time parameter, τ , have previously been described. These equations are analogous to the heat transfer equations for a packed bed system.

It is noteworthy that because of the linear nature of the adsorption isotherm, this simple analytical solution can take multiple mass transfer resistances into account.

4.4 Development of Dispersed Plug Flow Model

Flow through a packed bed can be represented by equation 39. This model lumps together the effects of all mechanisms which contribute to axial mixing into a single effective axial dispersion coefficient, D_l . The axial dispersion coefficient is used to define the Peclet number for a particle as follows:

$$Pe = \frac{2vR_p}{D_l} \quad (53)$$

where

Pe = the Peclet number for a particle,

v = velocity,

R_p = particle radius, and

D_l = the effective axial dispersion coefficient.

The Peclet number can also be defined in terms of the Reynolds number and the Schmidt number as follows:

$$Pe = ReSc \quad (54)$$

The Peclet number for liquids is usually less than 1 for Reynolds numbers less than 100, and approaches the theoretical limit of 2 in the high Reynolds numbers region (67,68). This increase in dispersion as been attributed to the effect of the greater hold-up of liquid in the laminar boundary layer surrounding the particle. This combined with small random fluctuations in the flow can lead to greatly increased axial mixing. If adsorption within the particle is sufficiently strong and rapid, the concentration profile through the particle becomes asymmetrical. This can lead to a significant contribution to axial dispersion arising from direct transport through the solid. This effect is only important at low Reynolds numbers. This effect becomes most significant when all adsorption occurs at the outside of the particle such as occurs during the initial stages of the uptake. A limiting expression for such a system has been suggested (68) and was rearranged to yield the following definition for the axial dispersion coefficient:

$$D_I = \left(\frac{20}{\epsilon} \right) D_m + \left(\frac{2vR_p}{2} \right) \quad (55)$$

where,

D_l = axial dispersion coefficient,

e = bed voidage,

D_m = molecular diffusivity,

R_p = adsorbent particle radius, and

v = interstitial velocity of fluid.

This indicates that for strongly adsorbed species under laminar flow conditions, axial dispersion may be very important. Dispersed plug flow is thus assumed as well as finite mass transfer resistance. Assuming a linear equilibrium isotherm and dispersed plug flow, the following analytic expression for the breakthrough curve is reproduced (68).

$$\frac{C}{C_o} = \frac{1}{2} \operatorname{erfc} \left(\frac{1 - t/\bar{t}}{2 \left[\frac{D_l}{vZ} \left(\frac{t}{\bar{t}} \right) \right]^{0.5}} \right) \quad (56)$$

where the mean retention time, $\bar{t}$, of the adsorbing species is defined as

$$\bar{t} = \frac{Z}{v} \left(1 + K \left[\frac{1 - e_p}{e_p} \right] \right) \quad (57)$$

Equation 56 is the asymptotic form for the breakthrough curve for $k \rightarrow \infty$.

Equations describing the error function have already been presented. Analysis of the experimental data using the analytic solution for both plug and dispersed flow is presented in Chapter 5.

CHAPTER 5

RESULTS

5.1 Introduction

The removal of cesium-137 from the cement disks by forced convective flow has been modelled by use of equation 43 and equation 56. These models for the breakthrough curve are for a simple system involving a linear rate equation with either ideal plug flow or dispersed plug flow. The cement matrix was thus modelled as a packed bed comprised of spheres with diameters in the range of $1.2 - 1.3 \times 10^{-3}$ cm (56). The accessible porosity was determined as described in Section 3.5.2. It was initially assumed that water traverses through the cement disk in a plug-flow fashion. This assumption proved invalid and a dispersed plug flow model was then assumed. The flow rates used in this research are very low and are assumed to simulate the movement of groundwater and percolated water around a monolithic waste form. They are also representative of the flow of rainwater around the waste form.

The mass transfer coefficient for the spheres in the packed bed was conservatively calculated by setting the Sherwood number equal to 2.0. This is the lower limit which might be expected because all the convection terms have been neglected. This calculation has embedded in it a parallel resistance representation for film diffusion and macromolecular pore diffusion. The following sections describe the data regression techniques and calculations.

5.2 Determination of Fluid Velocity and Porosity

The permeability measurements were used in another area of research as well as providing a method for the determination of fluid velocity through the specimens. The volumetric flow rate was measured as a function of time for each of several specimens. This flow rate was then used to calculate the fluid velocity through the disks using equation 38. A sample calculation follows for Sample 392-1.

$$Q = 7.87 \times 10^{-4} \text{ cm}^3/\text{sec}$$

$$A = 35 \text{ cm}^3$$

$$v = Q/A = 2.249 \times 10^{-6} \text{ cm/sec}$$

The driving force for this experiment was an overpressure of 5.7 lbs/in² (0.388 atm). Table 2 contains the data for the blends used in this series of experiments. Type I,II cement and class F fly ash were used in all the blends. The quantities of cement, fly ash, and Indian Red pottery clay were varied for the permeability measurements. The data indicate that as the amount of cement is increased the porosity and the permeability decrease. It is assumed that this is a result of increased hydration products from the cement. Since the amount of fly ash is decreased, the percent of pores should decrease also. This is due to the fact that fly ash is much slower to react in this type of environment and thus accessible porosity should decrease. Tables 3 and 4 contain the data from the experiments performed. The velocities were

Table 2. Experimental Blends Used In Permeability Measurements

Sample	Cement, wt%	Fly ash, wt%	Indian Red pottery clay, wt%	Mix ratio, lb/gal
392-1	45	45	10	8
392-2	45	45	10	8
393-1	50	42	8	8
393-2	50	42	8	8

Table 3. Operating Parameters Used In Permeability Measurements

Sample	ΔP (atm.)	A (cm ²)	L (cm)	Q (cm ³ /s)
392-1	0.388	35.0	0.7	7.87×10^{-5}
392-2	0.388	35.0	0.7	7.38×10^{-5}
393-1	0.590	35.0	0.7	7.35×10^{-6}
393-2	0.590	35.0	0.7	8.23×10^{-6}

Table 4. Data From Permeability and Porosity Measurements

Sample	Velocity, cm/sec	Porosity, vol%	Permeability, darcy/cp
392-1	2.249×10^{-6}	26.6	4.1×10^{-6}
392-2	2.109×10^{-6}	26.4	3.8×10^{-6}
393-1	2.100×10^{-7}	not measured	2.4×10^{-7}
393-2	2.351×10^{-7}	16.9	2.8×10^{-7}

calculated using the previous equation. Table 4 also contains the permeability and porosity measurements for each of the specimens. The very low velocities used in these experiments simulate the flow of groundwater and percolated water around a monolithic waste form. These velocities are also representative of the flow of rainwater around the monolith.

5.3 Analysis of Data From Ideal Plug Flow Model

The cement based disks used in this research were modelled as a packed bed comprised of $1.2 - 1.3 \times 10^{-3}$ centimeter diameter spheres (56). It was initially assumed that the liquid phase traversed through the specimen in a plug flow manner. Porous spherical particles generally have two internal diffusional resistances to mass transfer in addition to the external film resistance (66,68). Depending on the particular system, any one of the three potential resistances can be controlling. For this research project, the intracrystalline resistance was assumed negligible. The sorption rate appears to be somewhat dependent on the particle size of the cement matrix. This is evident between samples 3 and 8. The crystal structure of the cement matrix is relatively small and thus micropore diffusion would be extremely slow. Hence, it was assumed that the external fluid film mass transfer resistance and the macropore mass transfer resistances were the important factors.

The appropriate dimensionless group characterizing the external film mass transfer is the Sherwood number, Sh (68). It is defined by the following:

$$Sh = \frac{2k_f R_p}{D_m} = 2.0 + 0.6 Sc^{1/2} Re^{1/2} \quad (58)$$

where,

Sh = Sherwood number,

k_f = external fluid film mass transfer coefficient,

R_p = adsorbent particle radius,

D_m = molecular diffusivity,

Sc = Schmidt number, defined as

$$Sc = \frac{\mu}{\rho_f D_m} \quad (59)$$

and

Re = Reynolds number, defined as,

$$Re = \frac{\rho_f v e_p (2R_p)}{\mu} \quad (60)$$

Equation 58 implies that the Sherwood number approaches a limiting value of 2.0 at low velocities, as in the case of an isolated sphere. This conservative approach was used in the calculations of the overall mass transfer coefficient.

Setting the Sherwood number equal to 2.0 and letting the Reynolds

number approach zero, the following expression is derived from Equation 58 for the determination of the external fluid film mass transfer coefficient.

$$k_f = \frac{D_m}{R_p} \quad (61)$$

Verification that the Reynolds number, Re , is low enough that the second term in Equation 58 can be neglected was accomplished by using the following data.

$$\rho_f = 1.0 \text{ g/cm}^3,$$

$$\nu = 2.249 \times 10^{-6} \text{ cm/sec},$$

$$e_p = 0.265,$$

$$R_p = 1.3 \times 10^{-3} \text{ cm, and}$$

$$\mu = 1.0 \text{ cp}.$$

Using equation 60 yields a Reynolds number of 1.55×10^{-7} . The Schmidt number was calculated from equation 59 using a D_m of $2.1 \times 10^{-5} \text{ cm}^2/\text{sec}$ (26). This yields a Schmidt number of 4.762×10^2 . Using the values of the Reynolds and the Schmidt numbers in equation 58 yields a Sherwood number of 2.005. This is not significantly different from the assumption of 2.0 as was used in the determination of the external film mass transfer coefficient.

The external film mass transfer coefficient was calculated using equation 61 and these values were then used to determine the mass transfer coefficient, k , as defined by equation 42. These values were then used in the determination of the Henry's constant, K_h , in an iterative process using a

personal computer spreadsheet. All of the original data have been tabulated and are included in Appendix C. The value of K_h was varied until a breakthrough of material occurred. This process was repeated for all the samples. An example calculation for the mass transfer coefficients follows. Data from sample 2 was used for this example.

$$k_f = \frac{D_m}{R_p} = \frac{7.56 E-2 \frac{cm^2}{hr}}{1.3 E-3 cm} = 58.15 \frac{cm}{hr} \quad (62)$$

The value calculated from equation 62 is then substituted into equation 42. The last term in equation 42 is dropped because it is assumed that micropore mass transfer is negligible.

$$\frac{1}{kK_h} = \frac{R_p}{3k_f} + \frac{R_p^2}{15 e_p D_p} \quad (42)$$

where,

R_p = absorbent "particle radius", 1.3×10^{-3} cm,

k_f = external fluid film mass transfer coefficient, 58.15 cm/hr,

e_p = porosity of absorbent particle, 0.169,

D_p = pore diffusivity, 7.56×10^{-2} cm²/hr.

Substitution of these values into the above equation yields the following:

$$\frac{1}{kK_h} = 0.00124 \text{ hr} \Rightarrow k = \frac{805.14}{K_h} \frac{1}{\text{hr}} \quad (64)$$

Equation 42 has now been reduced to a one parameter model in terms of the Henry's Law constant. This parameter, equation 64, is then substituted into equations 44 and 45. The resultant expression for the parameter is then substituted into equation 46.

Table 5 contains a listing of the various blends used in this research. Descriptions of each of the components were presented in Chapter 3. The experimental procedure was also described in Chapter 3. The resultant model obtained by substitution as described above, was then analyzed by means of an iterative procedure to find the initial breakthrough of material. Table 6 contains the data for the experimental breakthrough time, t_b , as well as other parameters. Table 7 contains the parameters that were determined using this iterative process. The breakthrough time, t_b' , obtained from the model is much greater than the experimental breakthrough time, t_b . In every case, material was coming through the sample well before a plug flow front would reach the other side of the sample. The breakthrough time, t_b , for sample 2 was determined experimentally to be 4 hours. The plug flow breakthrough time, t_b' , was determined to be 86.4 hours. The experimental data were compared to the theoretical breakthrough curve for the ideal plug flow model. The breakthrough curve generated from the model could be represented by a step increase in concentration. The various parameters used in the model, K_h

Table 5. Experimental Blends Used In Forced Convection Experiments

Sample	Cement type and wt%	Fly ash, wt%	Indian Red pottery clay, wt%	Mix ratio, lb/gal
2	I, 38.5	53.5	8.0	10
3 ¹	II, 38	54	8	8
4	II, 45	45	10	8
5 ²	II, 45	45	10	8
8 ³	Slag, 100	0	0	7

¹ Simulated waste was used instead of water. See Appendix B for composition.

² Aluminum nitrate was added at 1 wt%

³ Simulated waste was used instead of water. See Appendix B for composition.

Table 6. Parameters Used In Ideal Plug Flow Model

Sample	R_p , cm	t_b^4 , hr	e_p	z , cm	v^5 , cm/hr	k_f^6 , cm/hr
2	1.3E-3	4.0	0.169	0.7	0.175	58.15
3	1.3E-3	16	0.169	0.7	0.04375	58.15
4	1.3E-3	12	0.265	0.7	0.05833	58.15
5	1.2E-3	34	0.169	0.7	0.02059	63
8	1.2E-3	1.6	0.265	0.3	0.1875	63

⁴Time for breakthrough from experimental data

⁵velocity necessary for t_b to be attained

⁶From equation 52

Table 7. Experimental Parameters Used In Ideal Plug Flow Model

Sample	δ^7	K_h^8	k^9, hr^{-1}	$t_b'^{10}, \text{hrs}$
2	15836	0.035	23004	86.4
3	63344	0.0539	14938	824
4	41877	0.01535	81968	824
5	157975	0.00302	312888	824
8	6553	0.0953	15495	37

⁷From equation 44⁸From equation 42⁹From equation 42¹⁰Breakthrough time calculated from z/v

and k , were varied repeatedly in an effort to better correlate the experimental data to the theoretical breakthrough curve. The two sets of data could never be made to even come close to matching. Thus, this analysis invalidated the initial assumption of ideal plug flow. The subsequent analysis assumed dispersed plug flow and a discussion follows.

5.4 Analysis of Data From Dispersed Plug Flow Model

This section presents the subsequent analysis of the experimental data assuming dispersed plug flow. This was necessary after the initial assumption of ideal plug flow was invalidated as described in section 5.3. The same experimental data was used and the model equations, equations 56 and 57, were analyzed using a iterative procedure on a personal computer spreadsheet. The dispersed plug flow model is a single parameter model in terms of K_h . Once the effective dispersion coefficient was determined by equation 55, the value of K_h was varied so that the residual sum of squares was minimized. The resultant parameter values are presented in Table 8. The data are presented in graphical format in Figures 6 - 10. As can be seen from the fit of the dispersed plug flow model to the actual experimental data, this approach appears to be more valid. The data from samples 3 and 5 fit the dispersed flow model quite well. One common factor between the two samples is the assumption that there is an increase in the ionic strength of the porewater. Sample 3 was prepared with a simulated waste and thus a

Table 8. Parameters Determined From Dispersed Plug Flow Model

Sample	Peclet number	D_l , cm ² /hr	K_h
2 ¹¹	3.690×10^{-5}	8.947	795
3	3.872×10^{-6}	8.947	1475
4	6.071×10^{-6}	8.947	1879
5	3.872×10^{-6}	8.947	4460
8	5.785×10^{-5}	5.706	12.8

¹¹e_p = 0.265

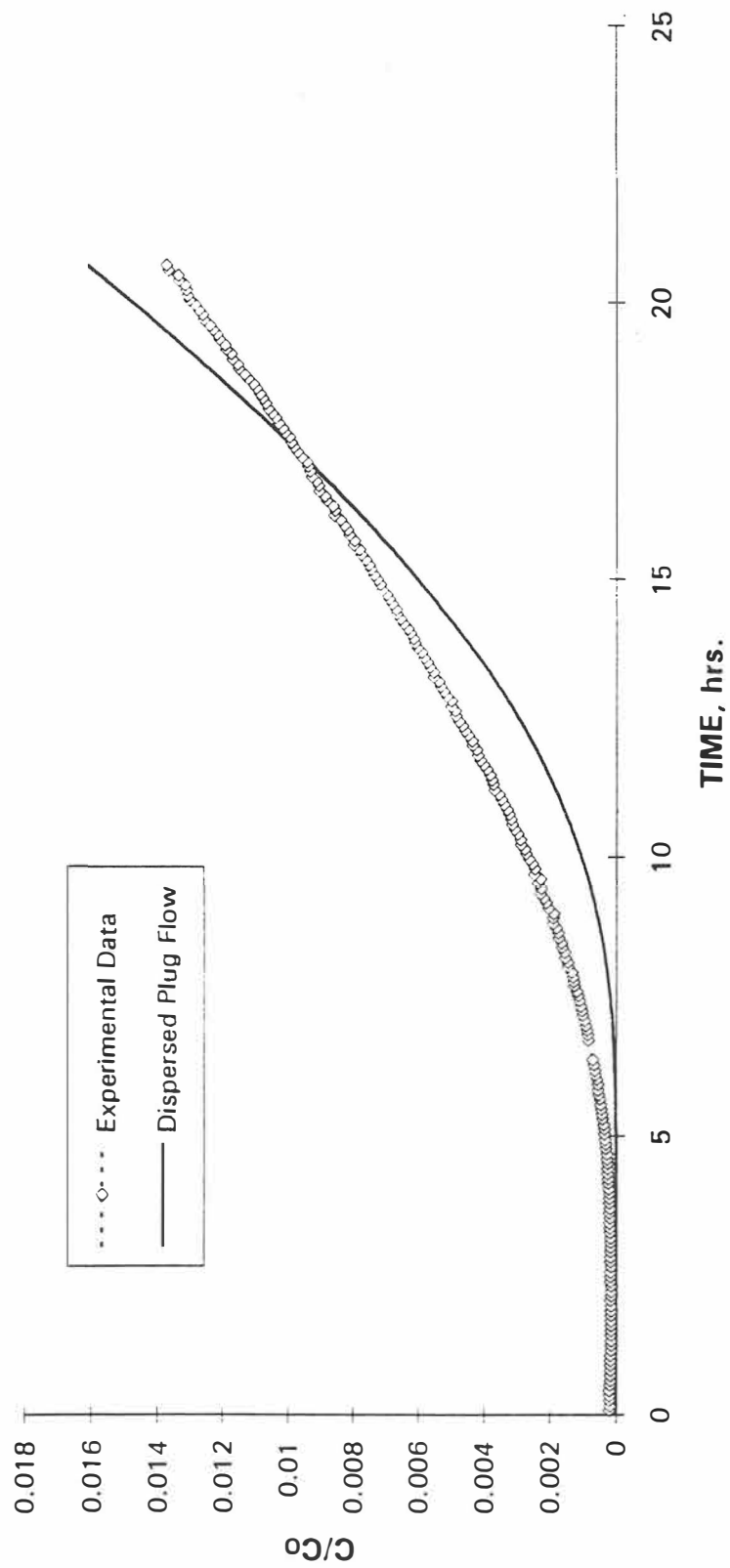


Figure 6. Experimental vs Dispersed Plug Flow Model For Sample 2

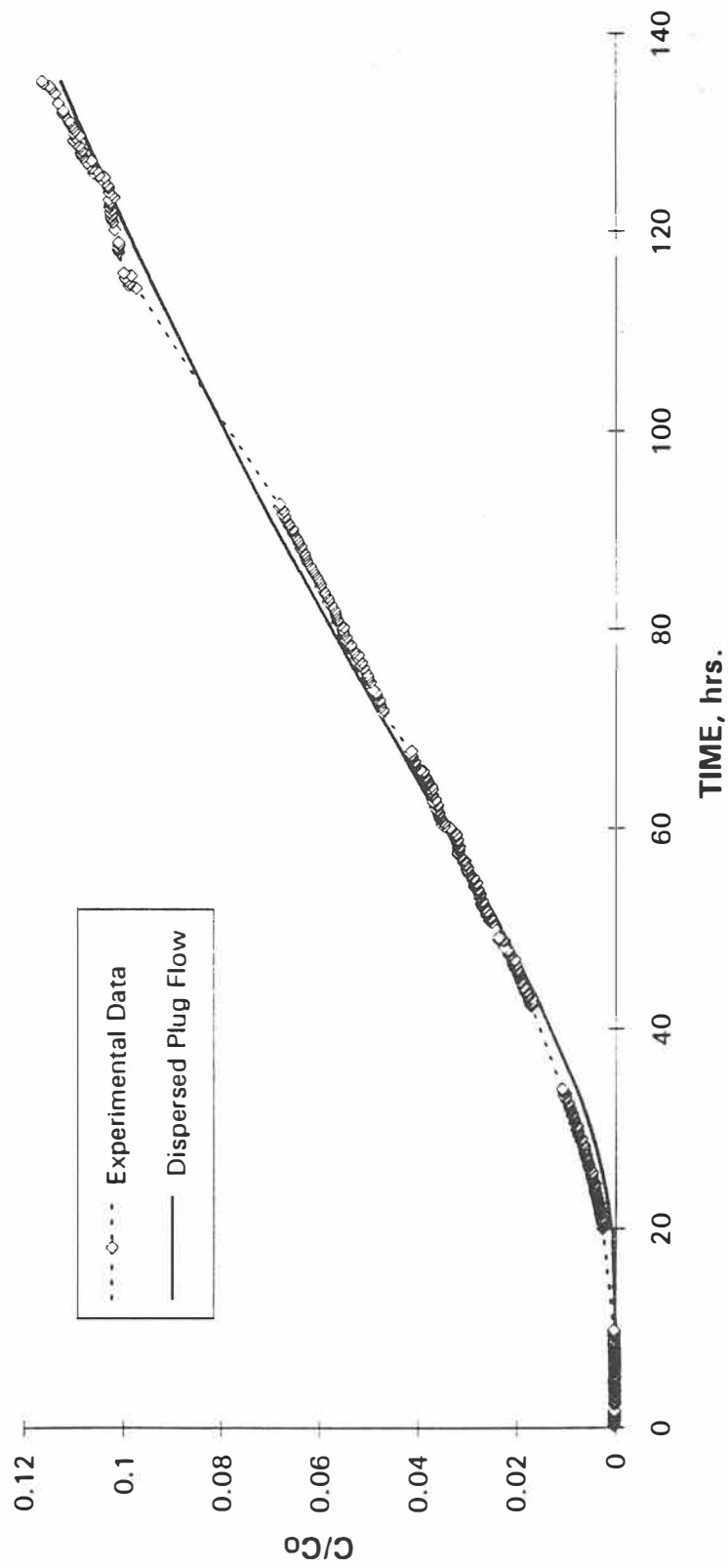


Figure 7. Experimental vs Dispersed Plug Flow Model For Sample 3

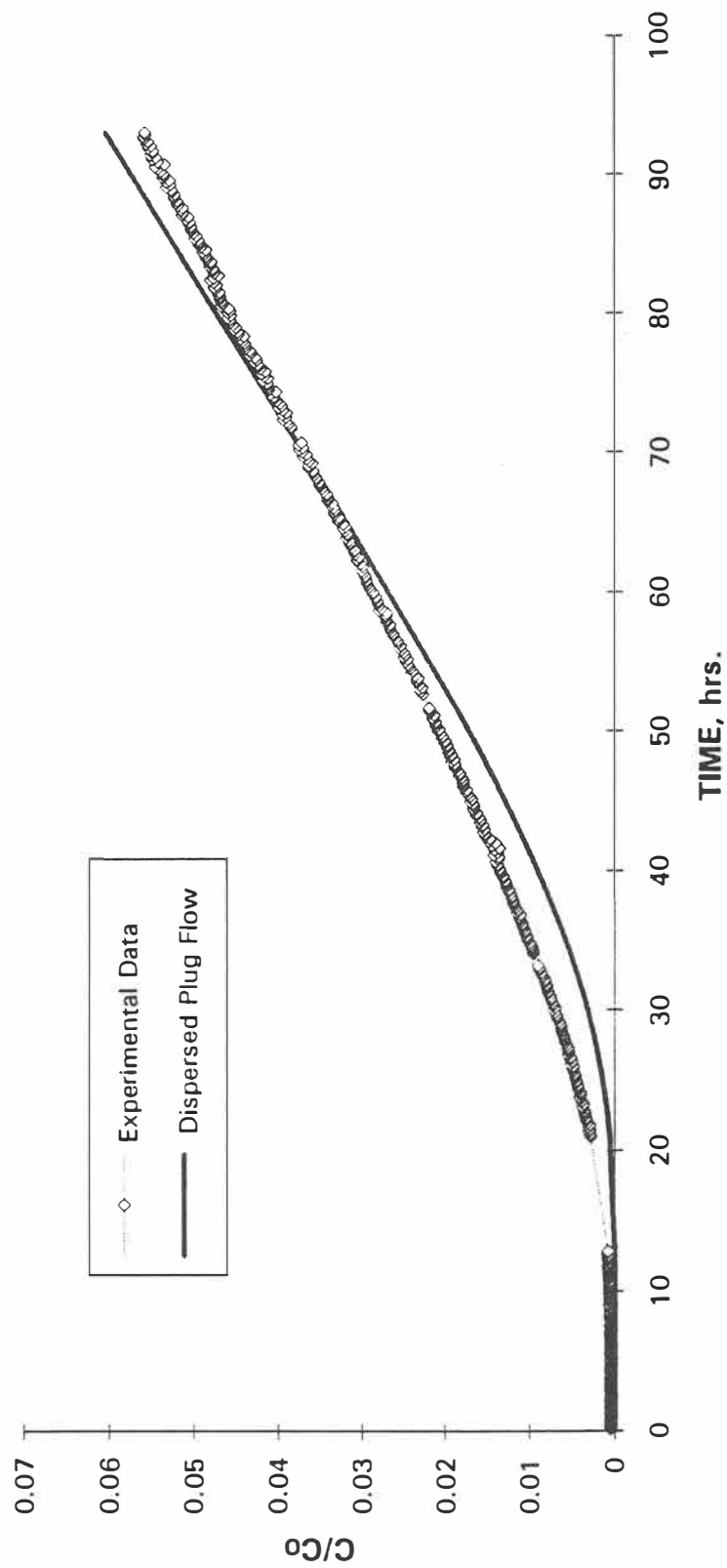


Figure 8. Experimental vs Dispersed Plug Flow Model For Sample 4

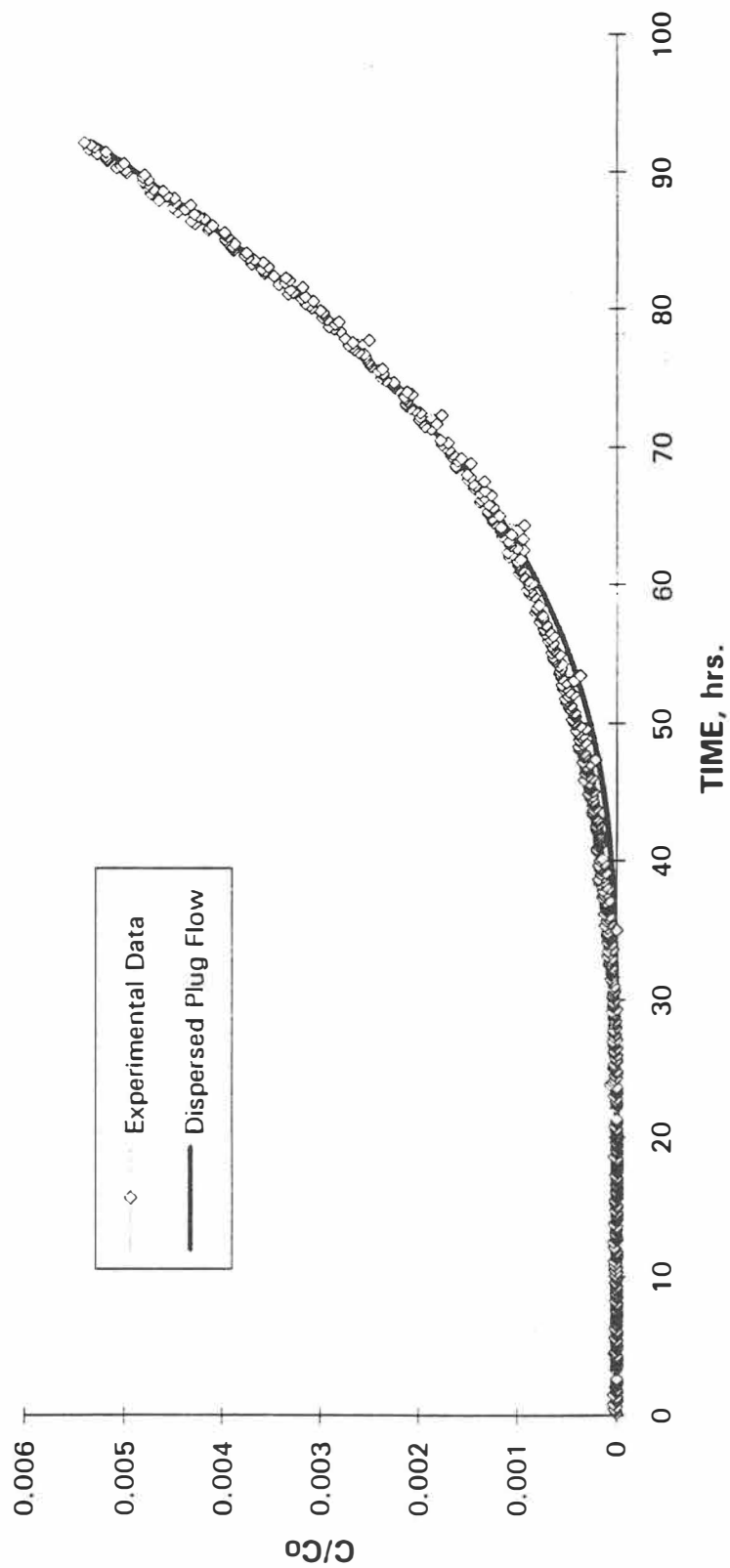


Figure 9. Experimental vs Dispersed Plug Flow Model For Sample 5

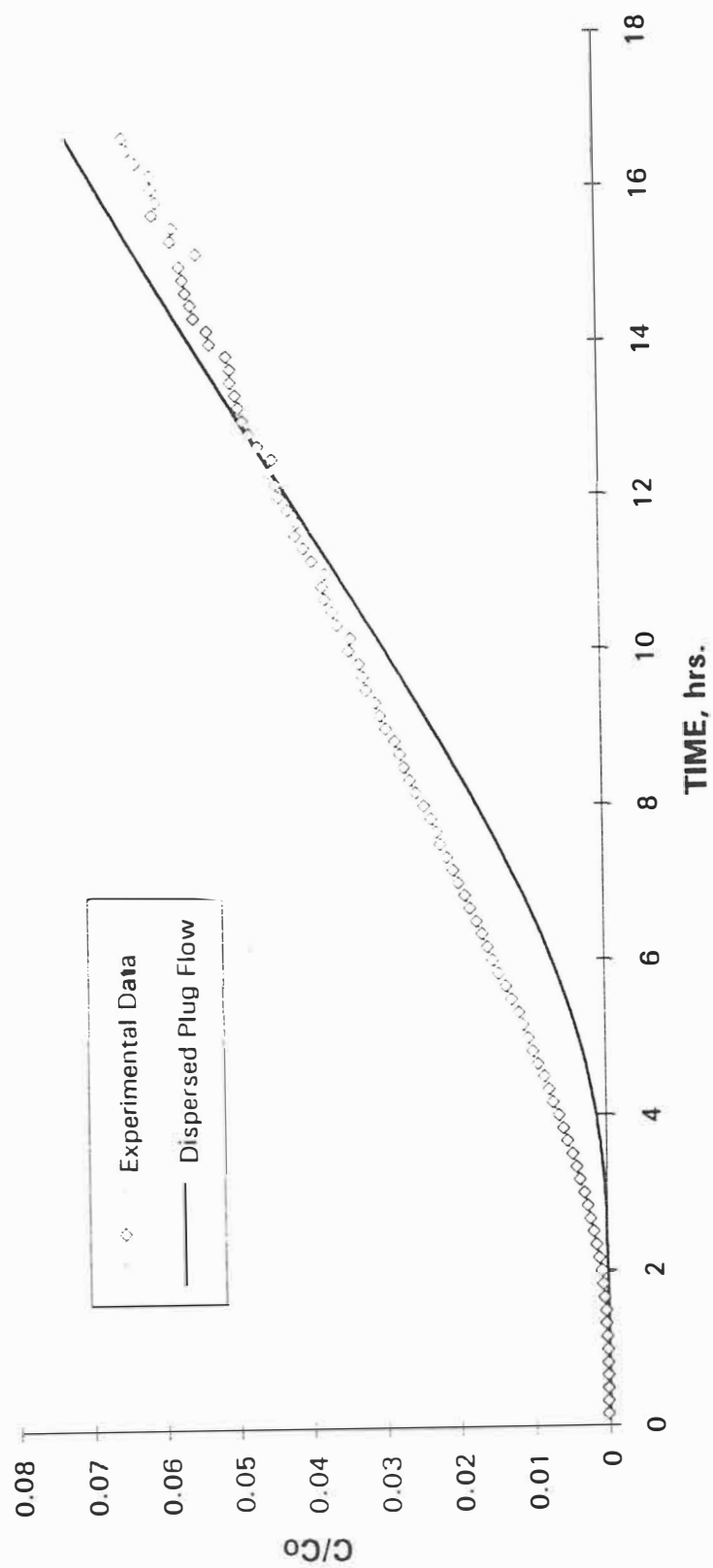


Figure 10. Experimental vs Dispersed Plug Flow Model For Sample 8

multitude of ions were present in the porewater of the matrix. Sample 5 was prepared using aluminum nitrate as an additive in the mixture. Aluminum nitrate is readily soluble and thus would be present in the porewater. This increase in ionic strength is speculated to enhance the complex chemical reactions that take place within the cement matrix. The porosity could subsequently be decreased as well as an increased affinity for the sorbing species. This would help to explain some of the differences between the values of K_h for similar samples. Samples 2 and 3 are essentially the same blend of dry material and samples 4 and 5 are also the same blend of materials. The differences in the two pairs of samples are in the use of additional ions in the sample preparation.

A comparison of Samples 2 and 3, Figures 7 and 8, shows that the addition of simulated waste instead of water increased the time necessary for species breakthrough. This could be due to increased complexity in the hydration products resulting in an increased affinity for the adsorbing species. Since a simulated waste was used in sample 3, it is more representative of actual waste forms used in the disposal of low level radioactive waste. A very good fit was obtained for the dispersed plug flow model for sample 3. This indicates a strongly adsorbed species which would result in a skewed concentration front. It is therefore concluded that the dispersed plug flow model could be used for determining breakthrough times for these types of waste forms.

Simulated waste was also used in sample 8, Figure 10. However, this specimen was comprised of only granulated blast furnace slag cement. The dispersed plug flow model correlates well with the experimental data. It should be noted that the breakthrough time for the species was rapid compared to other samples. This implies weaker adsorption and/or increased pathways for the species to flow through such as would occur with channeling. Comparing the behavior of sample 8 with sample 3 when C/Co is approximately 0.06 shows that the time required is substantially larger for sample 3. It took only 16 hrs for this quantity to elude from sample 8 as compared to 83 hrs for sample 3. Sample 2 which used distilled water, retarded the release of Cs^{137} for longer periods of time as compared to sample 8. It is concluded that granulated blast furnace slag does not retard the elution of Cs^{137} as well as the other blends used in this study.

Samples 4 and 5, Figures 8 and 9, are essentially the same material with the exception that sample 5 has aluminum nitrate added at 1 wt%. Other researchers (18) have utilized various aluminum compounds to retard the release of radionuclides. The data from sample 5 indicate that the addition of aluminum nitrate does decrease the release of Cs^{37} from the waste form. The value of C/Co at a time of approximately 92 hrs is ten times smaller for sample 5 as compared to sample 4. The value of C/Co was approximately 0.05 for sample 4 and approximately 0.005 for sample 5 at this elution time. It is concluded that the addition of aluminum nitrate does

increase the retention of Cs^{137} . Both sets of experimental data were reasonably well described by the dispersed plug flow model. This analysis of the data validates the assumption of dispersed flow through the specimens. The assumption of $\text{Sh} = 2$ is also valid for this flow system. It should also be noted that the longer elution times are better described by the dispersed plug flow model. This is evident when the model goodness of fit for samples 2, 3 and 5 is compared to samples 2 and 8.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The experimental data were analyzed using two distinct flow models. These models for the breakthrough curve are for a simple isothermal trace component system involving a linear rate equation with either ideal plug flow or dispersed plug flow. The cement matrix was thus modelled as a packed bed comprised of spheres. It was initially assumed that water transverses through the cement disk in a plug-flow fashion. This assumption proved invalid and a dispersed plug flow model was then assumed. The mass transfer coefficient for the spheres in the packed bed was conservatively calculated by setting the Sherwood number equal to 2.0. This is the lower limit which might be expected because all the convection terms have been neglected. This calculation has embedded in it a parallel resistance representation for film diffusion and macromolecular pore diffusion.

The dispersed plug flow model is a single parameter model in terms of K_h . Once the effective dispersion coefficient was determined by equation 55, the value of K_h was varied so that the residual sum of squares was minimized. The resultant parameter values are presented in Table 8. The data are presented in graphical format in Figures 6 - 10. As can be seen from the fit of the dispersed plug flow model to the actual experimental data, the assumption of convective dispersion is more valid. It is also evident that the

addition of agents which alter the ionic environment of the cement and the porewater can lead to much greater interaction between the cement and adsorbing species. It is also evident that this change in the ionic character of the waste form matrix can enhance the retention performance of the waste form by orders-of-magnitude.

6.2 Recommendations For Future Research

This research indicates that there is a need for long term studies of the leaching characteristics of cement based waste forms. Small sample thickness, such as the ones used in this research, are appropriate because of the relatively short time for breakthrough. Samples with smaller thicknesses could be used but they are very fragile and break easily. Additional studies also need to be performed on independent determination of the adsorption and chemical characteristics for the various materials used in this research. Also a better determination of the physical characteristics of these cement matrices needs to be carried out. Cement hydration is a complex mechanism and various assumptions have to be made as to the pore structure and pore chemistry.

Future experiments should also be conducted on the flow characteristics of the waste form. These studies should concentrate on one particular blend of materials and one simulated aqueous waste. Various material thicknesses should be used as well as various pressures. An

experiment with no flow should also be conducted to aid in the determination of the true dispersive behavior of the waste form. Another series of experiments should involve the determination of the porewater chemistry and its effect on the adsorption of various species. This should involve the use of various additives and one blend of material for the waste form. Scanning electron microscopy would be needed to determine the crystalline structure of the matrix. A method to determine the porewater chemistry would need to be developed. This could necessitate the dissection of the sample and collecting the porewater at various intervals during the experiment. These experiments would enhance the understanding of the complex behavior of cement hydration and its ability to retain adsorbable species. The last series of experiments that should be conducted involves the determination of the Henry's law equilibrium constant, K_l . Each of the various waste form components would be tested to determine this important parameter. The constant would also be determined for various mix ratios of the blended material in combination with a simulated waste.

LIST OF REFERENCES

LIST OF REFERENCES

- (1) Sams, Terry L.; Gilliam, T. Michael, "Systematic Approach for the Design of Pumpable Cement-Based Grouts for Immobilization of Hazardous Wastes", Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes, ASTM STP 1033, P. L. Cote and T. M. Gilliam, Eds., American Society for Testing and Materials, Philadelphia, 1989.
- (2) Gilliam, T. M.; Dole, L. R., "Determining Leach Rates of Monolithic Waste Forms", Presented at the Boston Summer AIChE Meeting, August 24-27, 1986.
- (3) Goto, Seishi; Roy, Della M., "Diffusion of Ions Through Hardened Cement Pastes", Cement and Concrete Research, Vol. II, 1981.
- (4) Sullivan, T. M., "Prediction of the Migration of Radionuclides to the Boundary of a Shallow Land Burial Trench", Presented at Waste Management '88, 1988.
- (5) Sullivan, T. M.; Kempf, C. R.; Suen, C. J.; Nughabghab, S. M.; "Development of a General Model to Predict the Rate for Radionuclide Release (Source Term) from a Low-Level Waste Shallow Land Burial Facility", Presented at the Waste Management "88, 1988.
- (6) Cohen, Donald S., Leaching of Radioactive Isotopes from Waste Solids, EPA 520/8-81-001, January, 1981.
- (7) Godbee, H. W.; Compere, E. L.; Joy, D. S.; Kibbey, A. H.; Moore, J. G.; Nestor, Jr., C. W.; Nielson, Jr., R. M.; "Application of Mass Transport Theory to the Leaching of Radionuclides from Waste Solids", Nuclear and Chemical Waste Management, Vol. 1, 1980.
- (8) Godbee, H. W.; Ander, O. U.; Nielson, Jr., R. M., "Application of Mass Transport Theory to the Leaching of Radionuclides from Waste Solids", Nuclear and Chemical Waste Management, 1:29-35.
- (9) Cohen, D. S., "Leaching of Radioactive Isotopes from Waste Solids", EPA, Washington, D. C.
- (10) Godbee, H. W.; Joy, D. S., "Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment", Part I: Background and Theory, Oak Ridge National Laboratory, ORNL-TM-4333, 1974.

- (11) Gilliam, T. M.; Sams, T. L.; Pitt, W. W., "Testing Protocols for Evaluating Monolithic Waste Forms Containing Mixed Waste", Advances in Ceramics, Vol. 20, 1986.
- (12) American Nuclear Society Standards Committee, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure", American Nuclear Society, August 6, 1986.
- (13) Nester, Jr., C. W., "Diffusion from Solid Cylinders", ORNL/CSD/TM-84, January 1980.
- (14) Sams, T. L.; McDaniel, E. W.; Gilliam, T. M., "Immobilization of Neutralized Cladding-Removal Waste in a Cement-Based Grout", Oak Ridge National Laboratory, Second International Conference, Canadian Nuclear Society, Winnipeg, Canada, September, 1986.
- (15) Cahn, J. W., "Spinodal Decomposition", The 1967 Institute of Metals Lecture, Trans. Metallurgical Society of AIME, 242, 1968, 166-180.
- (16) Cahn, J. W., "Spinodal Decomposition", Acta Metallurgical, 9, 1961, 795-801.
- (17) Cahn, J. W., "The Later Stages of Spinodal Decomposition and the Beginnings of Particle Coarsening", Acta Metallurgical, 14, 1966, 1685-1692.
- (18) Sams, T. L.; McDaniel, E. W.; Tallent, O. K.; Francis, C. L.; Washburn, F. A., Formulation Studies and Grout Development for Fixation of Variable Phosphate/Sulfate Waste, Milestone 195, ORNL/TM-10291/R1, February, 1988.
- (19) Sams, T. L.; McDaniel, E. W.; Gilliam, T. M., "Immobilization of Neutralized Cladding-Removal Waste in a Cement-Based Grout", Second International Conference on Radioactive Waste Management, ISBN:0-919784-08-9, Canadian Nuclear Society, September, 1986.
- (20) Gilliam, T. M.; Loflin, J. A., Leachability Studies of Hydrofracture Grouts, Milestone 2.A, FTP/A ONLWN14, 1987.
- (21) Serne, R. J.; Martin, W. J.; Lokken, R. O.; LeGore, V. L.; Lindenmeier, C. W.; Martin, P. F. C., "Leach and EP Toxicity Tests on Grouted Waste From Tank 106-AN", Hanford Grout Technology Program, Pacific Northwest Laboratory, September 1989.

- (22) Glasser, F. P.; Angus, M. J.; McCulloch, C. E.; MacPhee, D.; Rahman, A. A., "The Chemical Environment in Cements", Materials Research Society Symposium Proceedings, Vol. 44, 1985.
- (23) Koster, H.; Odler, I., "Investigations on the Structure of Fully Hydrated Portland Cement and Tricalcium Silicate Pastes. Part I. Bound Water, Chemical Shrinkage and Density of Hydrates", Cement and Concrete Research, Vol. 16, pp. 207-214, 1986.
- (24) Langton, C. A., "Physical Properties of Saltstone: A Savannah River Plant Waste Form", Materials Research Society Symposium Proceedings, Vol. 44, 1985.
- (25) Serne, R. J.; Martin, W. J.; LeGore, V. L.; Lindenmeier, C. W.; McLaurine, S. B.; Martin, P. F. C.; Lokken, R. O., "Leach Tests on Grouts Made with Actual and Trace Metal-Spiked Synthetic Phosphate/Sulfate Waste", Pacific Northwest Laboratory, October, 1989.
- (26) Dayal, R.; Arora, H.; Morcos, N., Estimation of Cesium-137 Release from Waste/Cement Composites Using Data from Small-Scale Specimens, NUREG/CR-3382, Nuclear Regulatory Commission, Washington, D.C., July 1983.
- (27) Serne, R. J.; Martin, W. J.; LeGore, V. L.; Lindenmeier, C. W.; McLaurine, S. B.; Martin, P. F. C.; Lokken, R. O., "Leach Tests on Grouts Made with Actual and Trace Metal-Spiked Synthetic Phosphate/Sulfate Waste", Pacific Northwest Laboratory, Richland, WA, April, 1988.
- (28) Matsuzuru, H.; Ito, A., "Effects of Dimension of Specimen on Amounts of ^{137}Cs , ^{90}Sr and ^{60}Co Leached from Matrix of Hardened Cement Grout", Journal of Nuclear Science and Technology, 15:296-301.
- (29) Matsuzuru, H.; Moriyama, N., "Leaching Radionuclides from a Cement Composite Incorporating Evaporatory Concentrates Generated at the Pressurized Water Reactor Nuclear Power Plant." Nuclear Science and Engineering, 80:14-25.
- (30) Piciulo, P. L.; Adams, J. W.; Davis, M. S.; Milian, L. W.; Anderson, C. I., "Release of Organic Chelating Agents from Solidified Decontamination Wastes", Brookhaven National Laboratory, Upton, NY, July, 1986.

- (31) Machiels, A. J.; Pescatore, C., "The Functional Dependence of Leaching on the Surface-To-Solution Volume Ratio", Sixth International Symposium on the Scientific Basis for Nuclear Waste Management, Boston, Mass., 1982.
- (32) McDaniel, E. W.; Tallent, O. K.; Sams, T. L.; Delzer, D. B., "Basis for Selecting Cement-Based Waste Forms for Immobilizing Radioactive Waste", Proceedings of the Twelfth International Symposium on the Scientific Basis for Nuclear Waste Management, Internationales Congress Centrum, Berlin, (West) Germany, October 10-13, 1988.
- (33) McDaniel, E. W.; Weeren, H. O.; Delzer, D. B.; Sams, T. L.; Tallent, O. K., "Materials Used in Low-Level Liquid Waste Reprocessing/Treatment Studies at Oak Ridge National Laboratory", Proceedings of the Conference on Nuclear Fuel Reprocessing and Waste Management (RECOD 87), Paris, France, August 24-28, 1987.
- (34) "Development and Application of a Risk Assessment Method for Radioactive Waste Management", Vol. I: Generic Description of AMRAW-A Model, U.S. EPA, 520/6-78-005, 1978.
- (35) Alfrey, T.; Grunee, E. F.; Lloyd, W. G., "Diffusion in Glassy Polymers", J. Polymer Science: Part C, 12, 1966, 249-261.
- (36) Frisch, H. L.; Wang, T. T.; Kwei, T. K., "Diffusion in Glassy Polymers", J. Polymer Science: Part A-2, 7, 1969, 879-887.
- (37) Wang, T. T.; Frisch, H. L., "Diffusion in Glassy Polymers", III, J. Polymer Science, Part A-2, 1969, 2019-2028.
- (38) Arora, H.; Dayal, R., "Leaching Studies of Cement-Based Low-Level Radioactive Waste Forms", Topical Report, Long Island, NY, October, 1986.
- (39) Bernard, A.; Nomine, J. C.; Cornec, G.; Bonnet, A.; Farges, L., "Long-Term Leaching Tests on Full-Scale Blocks of Radioactive Wastes", Nuclear and Chemical Waste Management, Vol. 3, 1982.
- (40) Nomine, J. C.; Billon, A., "Experience Acquired in the Field of Long-Term Leaching Tests on Blocks of Radioactive Waste", Environmental Aspects of Stabilization/Solidification of Hazardous and Radioactive Wastes, Atlanta, GA, May, 1987.

- (41) Sams, T. L.; McDaniel, E. W., "Development of a Cement-Based Grout for Immobilization of a Low-Level Waste Stream Containing Sodium Sulfate", Waste Management '88 Conference, Tucson, AZ, February-March, 1988.
- (42) Sams, T. L.; Godsey, T. T., Evaluation of Cement-Based Grouts for Stabilization of the S-3 Ponds at the Y-12 Plant, Y/TS-351, November, 1987.
- (43) Gilliam, T. M.; McDaniel, E. W.; Sams, T. L.; Tallent, O. K.; Dole, L. R., "Immobilization of Hanford Facility Decontamination Waste in a Cement-Based Grout", Spectrum '86, American Nuclear Society, September, 1986.
- (44) Gilliam, T. M.; Sams, T. L.; Pitt, W. W., "Testing Protocols for Evaluating Monolithic Waste Forms Containing Mixed Waste", Ceramic Advances, 20, 220, 1986.
- (45) Matsuzuru, H.; Ito, A., "Leaching Behavior of Strontium-90 in Cement Composites", Atomic Energy Research Institute, Tokai, Ibaraki, Japan, April, 1977.
- (46) Lokken, R. O.; Reimus, M. A.; Martin, P. F. C.; Geldart, S. E., "Characterization of Simulated Low-Level Waste Grout Produced in a Pilot-Scale Test", Pacific Northwest Laboratory, February, 1988.
- (47) Pepper, D. W., "Transport of nitrate from a Large Cement Based Waste Form", Savannah River Laboratory, Aiken, SC, December, 1986.
- (48) Smith, P. A., "Modeling of a Diffusion-Sorption Experiment by Linear and Non-Linear Sorption Isotherms" Nuclear Technology, Vol. 92, December, 1990.
- (49) Tallent, O. K.; Sams, T. L.; Tamaura, T.; Godsey, T. T.; Francis, C. L.; McDaniel, E. W., Grout Testing and Characterization for Shallow-Land Burial Trenches at the Idaho National Engineering Laboratory, ORNL/TM-9881, October, 1986.
- (50) Page, C. L.; Short, N. R.; Tarras, A. El, "Diffusion of Chloride Ions Through Hardened Cement Pastes", Cement and Concrete Research, Vol. II, 1981.
- (51) Sewart, G. H.; Farris, W. T.; Huizenga, D. G.; McMakin, A. H.; Streile, G. P.; Treat, R. L.; Long-Term Performance Assessment of Grouted

Phosphate/Sulfate Waste From N Reactor Operations, PNL-6152, April, 1987.

- (52) Serne, R. J.; Martin, W. J.; McLaurine, S. B.; Airhart, S. P.; LeGore, V. L.; Treat, R. L.; Laboratory Leach Tests of Phosphate/Sulfate Waste Grout and Leachate Adsorption Tests Using Hanford Sediment, PNL-6019, December, 1987.
- (53) Serne, R. J.; Relyea, J. F.; "The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program", Waste/Rock Interactions Technology Program, April, 1982.
- (54) Raber, E.; Garrison, J.; Oversby, V., "The Sorption of Selected Radionuclides on Various Metal and Polymeric Materials", Radioactive Waste Management and the Nuclear Fuel Cycle, Vol. 4(1), September, 1983.
- (55) Vuorinen, J.; "Applications of Diffusion Theory of Permeability Tests on Concrete Part I: Death of Water Penetration into Concrete and Coefficient of Permeability", Magazine of Concrete Research; Vol. 37, September, 1985.
- (56) Vuorinen, J.; "Applications of Diffusion Theory of Permeability Tests on Concrete Part II: Pressure-Saturation Test on Concrete and Coefficient of Permeability", Magazine of Concrete Research; Vol. 37, September, 1985.
- (57) Erdal, B. R.; Aguilar, R. D.; Bayhurst, B. P.; Daniels, W. R.; Duffy, C. J.; Lawrence, F. O.; Maestas, S.; Oliver, P. Q.; Wolfsberg, K.; "Sorption-Desorption studies on Granite: I. Initial Studies of Strontium, Technetium, Cesium, Barium, Cerium, Europium, Uranium, Plutonium, and Americium, February, 1979.
- (58) Barney, G. S.; Navratil, J. D.; Schultz, W. W., Eds.; "Geochemical Behavior of Disposed Radioactive Waste", American Chemical Society, Seattle, WA, March, 1983.
- (59) Sullivan, T. M., "Prediction of the Migration of Radionuclides to the Boundary of a Shallow Land Burial Trench", Waste Management '88 Meeting, Tucson, AZ, 1988.
- (60) Hung, Cheng Y., "Prediction of Long-Term Leachability of a Solidified Radioactive Waste from a Short-Term Leachability Test by a Similitude

Law for Leaching Systems", Nuclear and Chemical Waste Management, Vol. 3, 1982.

- (61) Serne, R. J.; Criscenti, L. J.; Strachan, D. M.; "Comparison of Geochemical Code Predictions and Laboratory Test Results for Uranium Leaching/Adsorption from Cement", Mitsubishi Metal Corporation, Tokyo, Japan, March, 1987.
- (62) Tamura, T.; Jacobs, D. G., "Structural Implications in Cesium Sorption," Health Physics, 2, 395-98, 1960.
- (63) Tamura, T.; Jacobs, D. G., "Improving Cesium Selectivity of Bentonite by Heat Treatment," Health Physics, 5, 149-154, 1961.
- (64) Tamura, T.; Jacobs, D. G., "Development and Applications of Minerals in Radioactive Waste Disposal," Proc. Intern. Clay Conf., 1, 425-439, 1966.
- (65) Crank, J.; Park, G. S., Diffusion in Polymers, New York, Academic Press, 1968.
- (66) Karger, Barry L.; Snyder, L. R.; Horvath, C., An Introduction to Separation Science, New York, John Wiley & Sons, 1973.
- (67) Crank, J., The Mathematics of Diffusion, Oxford University Press, Second Edition, 1975.
- (68) Ruthven, D. M., Principles of Adsorption and Adsorption Processes, New York, John Wiles & Sons, 1984.

APPENDICES

APPENDIX A

DATA OBTAINED FROM LONG TERM EXPERIMENTS SECTION 2.4.1.2

Table A.1 Data For Section 2.4.1.2

French Data for thesis						
		volume	200 liter	20 liter	2 liter	0.2 liter
		time,days	Total rel.			
		3	0.003595	0.009868	0.02731	0.03645
		6	0.005233	0.01432	0.0355	0.04336
		15	0.006375	0.01986	0.04371	0.04854
		30	0.006675	0.02256	0.04689	0.05113
		62	0.007106	0.02378	0.04778	0.0532
		122	0.007462	0.02432	0.04827	0.05434
		242	0.007883	0.02506	0.05112	0.05512
		362	0.007971	0.02522	0.05126	0.0554
		460	0.0081	0.02544	0.0519	0.05571
		550	0.008273	0.0258	0.05283	0.05595
		volume- >	200	20	2	0.2
		time,days	release rate			
		3	0.02647	0.03606	0.04229	0.0265
		6	0.01926	0.02617	0.02749	0.01576
		15	0.009386	0.01452	0.01354	0.007058
		30	0.004914	0.008244	0.007263	0.003717
		62	0.002531	0.004204	0.003581	0.001871
		122	0.001351	0.002185	0.001838	0.0009715
		242	0.0007194	0.001135	0.000982	0.0004968
		362	0.0004863	0.0007638	0.000658	0.0003338
		460	0.0003889	0.0006062	0.000524	0.0002641
		550	0.0003322	0.0005142	0.000446	0.0002219

APPENDIX B

MATERIALS USED IN RESEARCH

Table B.1. Analysis of Type III Portland Cement¹

Chemical Composition	Weight Per Cent
Silicon dioxide (SiO ₂)	21.78
Aluminum oxide (Al ₂ O ₃)	3.45
Ferric oxide (Fe ₂ O ₃)	2.65
Magnesium oxide (MgO)	1.10
Sulfur trioxide (SO ₃)	3.25
Loss on ignition	1.40
Insoluble residue	0.20
Tricalcium silicate (C ₃ S)	65.7
Tricalcium aluminate (C ₃ A)	4.7
Total alkalies (as Na ₂ O)	0.47

¹Purchased from Ash Grove Cement West, Inc., Durkee, OR.

Table B.2. Analysis of Class F Fly Ash¹

Chemical Composition	Weight Per Cent
Silicon dioxide (SiO ₂)	44.99
Magnesium oxide (MgO)	2.04
Calcium oxide (CaO)	11.12
Aluminum oxide (Al ₂ O ₃)	22.30
Ferric oxide (Fe ₂ O ₃)	5.46
Sulfur trioxide (SO ₃)	0.65
Sodium oxide (Na ₂ O)	4.76
Potassium oxide (K ₂ O)	3.76
Phosphorus pentoxide P ₂ O ₅	0.96
Titanium dioxide (TiO ₂)	4.39
Moisture	0.08
Loss on ignition	0.51
Density (g/cm ³)	2.348
Surface area (m ² /g)	0.663

¹Purchased from Ross Island Sand and Gravel Co., Portland, WA.

Table B.3. Analysis of Indian Red Pottery Clay¹

Chemical Composition	Weight Per Cent
Silicon dioxide (SiO ₂)	64.27
Ferric oxide (Fe ₂ O ₃)	7.04
Aluminum oxide (Al ₂ O ₃)	16.41
Titanium dioxide (TiO ₂)	1.06
Phosphorus pentoxide (P ₂ O ₅)	0.17
Calcium oxide (CaO)	0.23
Magnesium oxide (MgO)	1.55
Sodium oxide (Na ₂ O)	0.40
Potassium oxide (K ₂ O)	4.07
Loss on ignition	4.78

¹Purchased from American Art Clay Company, Inc., Indianapolis, IN.

Table B.4. Analysis of Blast Furnace Slag¹

Chemical Composition	Weight Per Cent
Silicon dioxide (SiO ₂)	31.78
Aluminum oxide (Al ₂ O ₃)	15.06
Ferric oxide (Fe ₂ O ₃)	0.66
Calcium oxide (CaO)	41.05
Magnesium oxide (MgO)	7.27
Sulfur trioxide (SO ₃)	1.98
Total alkalies (as Na ₂ O)	0.13
Potassium oxide (K ₂ O)	0.24
Sulfide as sulfur	0.72

¹Purchased from Ash Grove Cement West, Inc., Seattle, WA.

Table B.5. Analysis of Simulated Waste¹

Chemical Composition	g/L
As_2O_3	0.39993
BaCO_3	0.07422
$\text{Cd}(\text{NO}_3)_2 \bullet 4\text{H}_2\text{O}$	0.06635
$\text{Cr}(\text{NO}_3)_2 \bullet 9\text{H}_2\text{O}$	0.01107
$\text{Pb}(\text{NO}_3)_2$	0.07159
$\text{Hg}(\text{NO}_3)_2 \bullet \text{H}_2\text{O}$	0.09884
SeO_2	0.04222
AgNO_3	0.01880
$\text{CuSO}_4 \bullet 4\text{H}_2\text{O}$	0.02738
$\text{Fe}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$	1.0010
$\text{Fe}_2(\text{SO}_4)_3$	0.13516
$\text{MnSO}_4 \bullet 4\text{H}_2\text{O}$	0.08720

¹Waste composition based on actual low level waste stream (18).

Table B.5(cont.) Analysis of Simulated Waste¹

Chemical Composition	g/L
$\text{Al}(\text{NO}_3)_3 \bullet 9\text{H}_2\text{O}$	0.24217
KNO_3	0.0209
CaSO_4	0.06811
$\text{ZnSO}_4 \bullet 7\text{H}_2\text{O}$	0.03268
$\text{Ni}(\text{NO}_3)_2 \bullet 6\text{H}_2\text{O}$	0.09315
NaF	0.02622
NaCl	0.03675
$\text{Ca}(\text{NO}_3)_2 \bullet 4\text{H}_2\text{O}$	0.01536

¹Waste composition based on actual low level waste stream (18).

APPENDIX C

ANALOGY BETWEEN SHERWOOD NUMBER AND j-FACTOR

The data generated during this research were analyzed according to the methods detailed in Chapter 5. However, a comparison of expressions for the Sherwood number, Sh , and the j -factor, j_D , needs to be performed to validate the assumptions outlined in Chapter 5. The j -factor is typically used to represent the mass transfer coefficient when there is constant surface composition and low mass transfer rates. A limited empirical analogy for j_D states that it is a function of the Reynolds number, Re , geometry, and boundary conditions¹². This expression is the usual form of the Chilton-Coburn analogy for flow through packed beds. The following equation can be written for mass transfer around a sphere in a packed bed:

$$j_D = Sh Re^{-1} Sc^{-\frac{1}{3}} \quad (D.1)$$

This expression have been used for a variety of flow systems such as flow through a packed bed and in pipes at high Reynolds numbers. The corresponding equation for heat transfer is as follows:

$$j_H = Nu Re^{-1} Pr^{-\frac{1}{3}} \quad (D.2)$$

where Pr is the Prandl number.

The analogy between j_H for heat transfer and j_D for mass transfer is as follows:

¹²T. H. Chilton and A. P. Colburn, Ind. Eng. Chem., 26, 1183, 1934.

$$j_H = j_D = 0.91 Re^{-0.51} \Psi \quad \text{for } (Re < 50) \quad (D.3)$$

where Ψ is the empirical shape factor. The empirical shape factor for spheres in a packed bed is 1.00. This correlation for the j-factor, j_D , is useful for a number of flow situations, such as transverse flow over cylinders, flow through packed beds, and flow in pipes at high Reynolds numbers.

The relationship between the friction factor, f , and the j-factor has been defined by the following.

$$j_H = j_D = \frac{f}{2} \quad (D.4)$$

This relationship is valid only for turbulent flow, $Re > 10,000$. This equation also agrees closely with boundary-layer theory for a flat plate when Pr and Sc exceed 0.5. However, for flow around curved boundaries, form-drag occurs and $f/2$ will exceed j_D considerably. This implies that equation D.1 should be used for flow around spheres.

Consider the heat-transfer correlation for forced convection around a sphere of diameter D :¹³

¹³R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, John Wiley & Sons, New York, NY, 1960.

$$Nu = 2.0 + 0.60 Re^{\frac{1}{2}} Pr^{\frac{1}{3}} \quad (D.5)$$

Nu is the Nusselt number and the variables have previously been defined. Substitution of the corresponding mass-transfer quantities into the above equation yields:

$$Sh = 2.0 + 0.6 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \quad (D.6)$$

Equations D.5 and D.6 hold for constant surface temperature and composition, respectively, and for small mass transfer rates. However, the Chilton-Colburn analogy, equation D.1, does not hold for this flow system, except as an approximation when Nu and Sh are much larger than 2.0. Using the same approach as used in chapter 5 to verify that the Reynolds number, Re , is low enough that the second term in Equation D.6 can be neglected was accomplished by using the following data.

$$\rho_f = 1.0 \text{ g/cm}^3,$$

$$\nu = 2.249 \times 10^{-6} \text{ cm}^2/\text{sec},$$

$$e_p = 0.265,$$

$$R_p = 1.3 \times 10^{-3} \text{ cm}, \text{ and}$$

$$\mu = 1.0 \text{ cp}.$$

Using equation 60 yields a Reynolds number of 1.55×10^{-7} . The Schmidt number was calculated from equation 59 using a D_m of $2.1 \times 10^{-5} \text{ cm}^2/\text{sec}$

(26). This yields a Schmidt number of 4.762×10^2 . Using the values of the Reynolds and the Schmidt numbers in equation 58 yields a Sherwood number of 2.005. This is not significantly different from the assumption of 2.0 as was used in the determination of the external film mass transfer coefficient.

Substitution of these values into equation D.3 yields the following results:

$$j_D = 0.91 (1.55 \times 10^{-7})^{-0.51} (1) = 2704$$

Thus the value for j_D , 2704, is extremely large for a system with very low concentrations of species. Thus the assumption of setting Sh equal to 2.0 has validity and illustrates that equation D.1 can not be used as a predictor of the mass transfer resistances for this system. Although the mass transfer rate is very small, the Reynolds number is far too small for this approximation. The flow of fluid through this system is more closely approximated by stagnant flow.

APPENDIX D

ORIGINAL DATA

Sample 2			
Thickness = 0.7 cm			
	Co =	cps	22275
Time(min)	c.p.m	Time(hrs)	C/Co
10	12.48	0.08	0.000211862
20	13.28	0.17	0.000197715
30	13.55	0.27	0.000207298
40	12.58	0.35	0.00020262
50	13.68	0.43	0.000209922
60	12.9	0.53	0.000184024
70	12.31	0.62	0.000166797
80	12.34	0.70	0.00017136
90	13.66	0.80	0.000167253
100	11.27	0.88	0.000167481
110	11.05	0.97	0.000164287
120	13.27	1.05	0.000171588
130	13.074	1.15	0.000154475
140	12.57	1.23	0.000157099
150	12.93	1.32	0.000155844
160	12.65	1.42	0.000154133
200	13.14	1.50	0.000157784
210	12.87	1.58	0.000157784
220	11.64	1.67	0.000150482
230	12.7	1.77	0.000155616
240	11.66	1.85	0.000158582
250	12.63	1.93	0.000156643
260	12.95	2.03	0.000162233
270	13.61	2.12	0.000158126
280	13.25	2.20	0.000159381
290	12.5	2.30	0.000158468
300	12.64	2.38	0.00016577
310	13	2.47	0.000177521
320	13.2	2.55	0.000162119
330	12.23	2.65	0.000156301
340	13.33	2.73	0.000167824
350	12.51	2.82	0.000172273
360	12.73	2.92	0.00017832
370	12.02	3.00	0.000168166
380	13.36	3.08	0.00017832
390	12.54	3.17	0.000174098

400	13.11	3.27	0.00019144
410	12.78	3.35	0.000192923
420	13.13	3.43	0.00021768
430	12.27	3.53	0.00019395
440	12.55	3.62	0.000202506
450	12.28	3.70	0.00019954
460	13.17	3.80	0.000201822
470	12.2	3.88	0.000211063
480	12.85	3.97	0.000213687
490	11.63	4.05	0.000223042
500	13.24	4.15	0.000238672
510	11.71	4.23	0.000251222
520	12.92	4.32	0.000263087
530	13.19	4.42	0.000265027
540	12.49	4.50	0.000275979
550	13.06	4.58	0.000279516
560	12.82	4.67	0.000294575
		4.77	0.000322983
		4.85	0.000330171
		4.93	0.000344888
		5.03	0.000367249
		5.12	0.00036531
		5.20	0.000390295
		5.30	0.000416421
		5.38	0.000433877
		5.47	0.000462627
		5.55	0.000486814
		5.65	0.000503242
		5.73	0.000530738
		5.82	0.000553897
		5.92	0.000555951
		6.00	0.000601472
		6.08	0.000624518
		6.17	0.000653953
		6.27	0.000672549
		6.35	0.00070438
		6.70	0.000837634
		6.80	0.000853379
		6.88	0.000889316
		6.97	0.000928449
		7.05	0.000968493
		7.15	0.001005002

		7.23	0.001037859
		7.32	0.001071629
		7.42	0.001120345
		7.50	0.001152403
		7.58	0.001191193
		7.68	0.001268089
		7.77	0.00127984
		7.85	0.001301402
		7.93	0.001350802
		8.03	0.001450059
		8.12	0.001462951
		8.20	0.001540189
		8.30	0.001547833
		8.38	0.001624157
		8.47	0.001642183
		8.55	0.001736306
		8.65	0.00175399
		8.73	0.001802705
		8.82	0.001893405
		8.92	0.001906297
		9.00	0.001871843
		9.08	0.002038753
		9.18	0.002102757
		9.27	0.002190148
		9.35	0.002278909
		9.43	0.002256319
		9.53	0.002359569
		9.62	0.002283815
		9.70	0.00248575
		9.80	0.002457228
		9.88	0.002536862
		9.97	0.00263783
		10.07	0.002720658
		10.15	0.002765951
		10.23	0.002872281
		10.32	0.002894756
		10.42	0.002969826
		10.50	0.003075928
		10.58	0.003139019
		10.68	0.003187848
		10.77	0.003254247
		10.85	0.003306043

		10.93	0.003395945
		11.03	0.003476377
		11.12	0.00355601
		11.20	0.003683333
		11.30	0.003717673
		11.38	0.003757262
		11.47	0.00382811
		11.57	0.003918696
		11.65	0.004007229
		11.73	0.00411025
		11.82	0.004184978
		11.92	0.004219775
		12.00	0.004332722
		12.08	0.004362841
		12.18	0.004469513
		12.27	0.004573562
		12.35	0.004650571
		12.43	0.004737164
		12.53	0.004844635
		12.62	0.004852393
		12.70	0.004968306
		12.80	0.00497538
		12.88	0.005116963
		12.97	0.005205952
		13.07	0.005300531
		13.15	0.005363964
		13.23	0.005507258
		13.32	0.005513875
		13.42	0.005620434
		13.50	0.005710335
		13.58	0.005796243
		13.68	0.005872454
		13.77	0.006003998
		13.85	0.006087396
		13.93	0.006136796
		14.03	0.006231261
		14.12	0.006307358
		14.20	0.006433197
		14.30	0.00652789
		14.38	0.006639354
		14.47	0.006662058
		14.57	0.006778313

		14.65	0.006881335
		14.73	0.006946593
		14.82	0.007078593
		14.92	0.007153549
		15.00	0.007237974
		15.08	0.007338029
		15.18	0.007427018
		15.27	0.007500376
		15.35	0.007593358
		15.45	0.007720566
		15.53	0.007781261
		15.62	0.007943951
		15.70	0.007927636
		15.80	0.008091238
		15.88	0.008138243
		15.97	0.008239667
		16.07	0.008348735
		16.15	0.008547819
		16.23	0.008521807
		16.32	0.008583414
		16.42	0.008775767
		16.50	0.008842965
		16.58	0.009002117
		16.68	0.009032009
		16.77	0.009110615
		16.85	0.009236683
		16.95	0.009299203
		17.03	0.009355905
		17.12	0.009398573
		17.20	0.00955419
		17.30	0.009686532
		17.38	0.009798566
		17.47	0.009869529
		17.57	0.009933532
		17.65	0.01007021
		17.73	0.010146078
		17.82	0.010257086
		17.92	0.010359993
		18.00	0.01046233
		18.08	0.010589424
		18.18	0.010669971
		18.27	0.010765919

		18.35	0.010843955
		18.45	0.010946634
		18.53	0.011054333
		18.62	0.011196829
		18.70	0.011321642
		18.80	0.011482163
		18.88	0.011537154
		18.97	0.011690374
		19.07	0.011711252
		19.15	0.011872116
		19.23	0.011919121
		19.33	0.01208626
		19.42	0.012156082
		19.50	0.012270854
		19.58	0.012368399
		19.68	0.012564517
		19.77	0.012615172
		19.85	0.012714314
		19.95	0.012831141
		20.03	0.013006722
		20.12	0.013073121
		20.22	0.013099362
		20.30	0.013151614
		20.38	0.013327994
		20.47	0.013351382
		20.57	0.013660561
		20.65	0.013727759

Sample 3	Thickness = 0.7 cm		
	Co =	cps	22275
Time(min)	c.p.m	Time(hrs)	C/Co
10	12.48	0.20	0.000329
20	13.28	0.30	0.00031
30	13.55	0.40	0.000308
40	12.58	0.50	0.000307
50	13.68	0.60	0.000296
60	12.9	0.70	0.000298
70	12.31	0.80	0.000279
80	12.34	0.90	0.000303
90	13.66	1.00	0.000324
100	11.27	1.10	0.000308
110	11.05	1.20	0.000284
120	13.27	1.40	0.000303
130	13.074	1.50	0.00025
140	12.57	1.60	0.000273
150	12.93	1.70	0.000296
160	12.65	1.80	0.000246
200	13.14	2.43	0.000279
210	12.87	2.60	0.000225
220	11.64	2.77	0.000282
230	12.7	3.10	0.000283
240	11.66	3.27	0.000274
250	12.63	3.60	0.000282
260	12.95	3.77	0.000265
270	13.61	3.93	0.000251
280	13.25	4.10	0.000272
290	12.5	4.27	0.00024
300	12.64	4.43	0.000223
310	13	4.60	0.00031
320	13.2	4.77	0.000295
330	12.23	4.93	0.000291
340	13.33	5.10	0.000265
350	12.51	5.27	0.000245
360	12.73	5.43	0.00029
370	12.02	5.77	0.000257
380	13.36	5.93	0.000258
390	12.54	6.10	0.000256
400	13.11	6.27	0.000251

410	12.78	6.43	0.000269
420	13.13	6.60	0.000237
430	12.27	6.77	0.00026
440	12.55	6.93	0.000274
450	12.28	7.10	0.000235
460	13.17	7.27	0.00027
470	12.2	7.43	0.00026
480	12.85	7.60	0.000288
490	11.63	7.77	0.000296
500	13.24	7.93	0.000264
510	11.71	8.10	0.000271
520	12.92	8.27	0.000308
530	13.19	8.43	0.000341
540	12.49	8.60	0.000296
550	13.06	8.77	0.000336
560	12.82	8.93	0.000349
		9.27	0.000302
		9.43	0.000354
		9.60	0.000325
		9.77	0.000343
		9.93	0.000365
		20.02	0.002619
		20.12	0.002611
		20.28	0.002444
		20.45	0.002727
		20.62	0.002775
		20.78	0.00283
		20.95	0.002859
		21.12	0.002802
		21.28	0.003068
		21.45	0.003148
		21.62	0.003153
		21.78	0.003142
		21.95	0.003344
		22.12	0.003323
		22.28	0.00341
		22.45	0.003493
		22.62	0.003588
		22.78	0.003685
		22.95	0.003729
		23.12	0.003788
		23.28	0.003984

		23.45	0.003967
		23.62	0.004108
		23.78	0.004151
		23.95	0.004235
		24.12	0.004198
		24.28	0.004274
		24.45	0.004261
		24.62	0.004565
		24.78	0.004581
		24.95	0.004724
		25.12	0.004811
		25.28	0.004813
		25.45	0.005002
		25.62	0.004674
		25.78	0.005196
		25.95	0.005076
		26.12	0.005438
		26.28	0.005463
		26.45	0.005535
		26.62	0.005667
		26.78	0.005807
		26.95	0.005885
		27.12	0.005957
		27.28	0.005947
		27.45	0.0062
		27.62	0.006284
		27.78	0.006259
		27.95	0.006268
		28.12	0.006473
		28.28	0.006444
		28.45	0.006669
		28.62	0.007017
		28.78	0.007052
		28.95	0.006879
		29.12	0.00735
		29.28	0.007568
		29.45	0.007645
		29.62	0.007482
		29.78	0.007884
		29.95	0.00775
		30.12	0.007701
		30.28	0.007831

		30.45	0.008305
		30.62	0.008374
		30.78	0.008328
		30.95	0.008513
		31.12	0.00871
		31.28	0.008851
		31.45	0.008705
		31.62	0.008999
		31.78	0.009188
		31.95	0.00921
		32.12	0.009315
		32.28	0.009479
		32.45	0.009505
		32.62	0.009621
		32.78	0.010024
		32.95	0.010124
		33.12	0.010039
		33.28	0.010437
		33.45	0.010063
		33.62	0.010504
		33.78	0.010639
		33.95	0.01068
		42.27	0.017018
		42.37	0.017133
		42.47	0.017251
		42.57	0.017195
		42.67	0.016963
		42.77	0.01752
		42.87	0.017434
		42.97	0.017469
		43.07	0.016918
		43.17	0.017829
		43.27	0.017598
		43.37	0.017744
		43.47	0.017829
		43.57	0.018149
		43.67	0.018266
		43.77	0.018377
		43.87	0.018134
		44.07	0.01855
		44.17	0.018661
		44.27	0.018733

		44.67	0.019036
		44.77	0.019104
		44.88	0.019303
		45.17	0.01945
		45.33	0.019548
		45.50	0.019705
		45.67	0.019759
		45.77	0.020019
		45.87	0.019645
		45.97	0.020293
		46.07	0.019899
		46.17	0.020305
		46.27	0.020252
		46.37	0.020736
		46.47	0.020119
		46.57	0.02071
		46.67	0.020748
		46.77	0.020709
		46.87	0.020662
		46.97	0.020404
		47.23	0.021516
		47.33	0.021307
		47.43	0.021269
		47.53	0.021625
		47.80	0.021579
		47.90	0.021763
		48.07	0.022451
		48.75	0.022382
		48.80	0.022775
		48.85	0.023507
		48.90	0.023676
		48.95	0.023593
		49.00	0.023352
		49.05	0.023008
		49.10	0.023573
		50.62	0.025059
		50.78	0.025634
		50.95	0.025578
		51.12	0.025471
		51.28	0.026179
		51.45	0.026315
		51.62	0.026258

		51.78	0.026108
		51.95	0.026733
		52.12	0.026619
		52.28	0.027143
		52.45	0.027207
		52.62	0.027187
		52.78	0.02708
		52.95	0.027484
		53.12	0.027507
		53.28	0.027676
		53.45	0.027351
		53.62	0.02783
		53.78	0.02796
		53.95	0.027908
		54.12	0.028551
		54.28	0.028616
		54.45	0.028594
		54.62	0.028204
		54.78	0.028959
		54.95	0.028958
		55.12	0.028877
		55.28	0.029557
		55.45	0.02975
		55.62	0.0299
		55.78	0.029995
		55.95	0.030255
		56.12	0.029909
		56.28	0.030399
		56.45	0.030509
		56.62	0.030856
		56.78	0.030439
		56.95	0.030845
		57.12	0.03138
		57.28	0.031443
		57.45	0.031969
		57.62	0.032072
		57.78	0.031791
		57.95	0.031917
		58.12	0.031879
		58.28	0.031601
		58.45	0.032037
		58.62	0.032215

		58.78	0.032104
		58.95	0.032045
		59.12	0.032524
		59.28	0.032562
		59.45	0.032315
		59.62	0.032973
		59.78	0.032806
		59.95	0.033391
		60.12	0.03358
		60.28	0.034748
		60.45	0.035244
		60.62	0.034747
		60.78	0.035281
		60.95	0.035582
		61.12	0.03542
		61.28	0.035741
		61.45	0.03583
		61.62	0.035774
		61.78	0.036091
		61.95	0.036115
		62.12	0.036653
		62.28	0.036163
		62.45	0.036144
		62.62	0.036874
		62.78	0.036992
		62.95	0.036545
		63.28	0.037301
		63.45	0.037197
		63.62	0.03747
		63.78	0.037475
		63.95	0.037124
		64.12	0.037727
		64.28	0.037207
		64.45	0.03799
		64.62	0.038074
		64.78	0.037997
		64.95	0.038305
		65.12	0.038356
		65.28	0.03862
		65.45	0.039043
		65.62	0.039056
		65.78	0.038896

		65.95	0.039589
		66.12	0.040655
		66.28	0.040769
		66.45	0.040912
		66.62	0.040905
		66.78	0.040713
		66.95	0.04138
		67.12	0.041355
		67.28	0.041258
		67.45	0.041457
		67.62	0.041695
		67.78	0.04131
		71.70	0.047255
		71.95	0.047118
		72.20	0.047621
		72.45	0.047775
		72.70	0.04791
		72.95	0.047955
		73.20	0.048488
		73.45	0.048501
		73.70	0.048507
		73.95	0.049181
		74.70	0.049624
		74.95	0.050061
		75.20	0.050228
		75.45	0.050382
		75.70	0.050716
		75.95	0.051217
		76.20	0.051114
		76.45	0.051589
		76.70	0.051538
		76.95	0.051949
		77.20	0.052397
		77.45	0.052135
		77.70	0.052989
		77.95	0.053297
		78.20	0.053599
		78.45	0.053701
		78.70	0.054279
		78.95	0.054636
		79.20	0.0546
		79.45	0.055095

		79.70	0.055236
		79.95	0.0553
		80.20	0.055101
		80.45	0.055801
		80.70	0.05634
		80.95	0.056376
		81.20	0.056661
		81.45	0.05679
		81.70	0.056925
		81.95	0.05695
		82.20	0.057515
		82.45	0.057592
		82.70	0.058279
		82.95	0.058109
		83.20	0.058427
		83.45	0.058889
		83.70	0.059101
		83.95	0.059493
		84.20	0.059987
		84.45	0.059795
		84.70	0.060128
		84.95	0.06027
		85.20	0.060597
		85.45	0.060912
		85.70	0.061265
		85.95	0.061496
		86.20	0.06177
		86.45	0.061933
		86.70	0.062498
		86.95	0.062596
		87.20	0.062851
		87.45	0.063043
		87.70	0.063165
		87.95	0.063589
		88.20	0.063968
		88.45	0.06373
		88.70	0.064289
		88.95	0.064372
		89.20	0.064642
		89.45	0.065098
		89.70	0.065409
		89.95	0.065528

		90.20	0.065612
		90.45	0.066343
		90.70	0.066318
		90.95	0.066677
		91.20	0.06705
		91.45	0.067133
		91.70	0.067621
		91.95	0.067364
		92.20	0.067801
		92.45	0.068283
		92.70	0.06809
		114.20	0.097329
		114.45	0.098915
		114.70	0.098761
		114.95	0.09921
		115.20	0.09966
		115.45	0.098311
		115.70	0.099974
		117.82	0.100925
		118.07	0.101085
		118.32	0.101124
		118.57	0.100803
		118.82	0.10088
		120.07	0.10174
		120.82	0.102119
		121.07	0.102299
		121.32	0.102459
		121.57	0.102356
		121.82	0.102587
		122.07	0.102376
		122.32	0.102729
		122.57	0.1026
		122.82	0.102665
		123.07	0.102793
		123.32	0.101894
		123.57	0.102279
		123.82	0.102793
		124.32	0.10305
		124.57	0.103178
		124.82	0.103756
		125.07	0.104334
		125.32	0.10382

		125.57	0.104912
		125.82	0.106003
		126.07	0.105361
		126.32	0.106517
		126.57	0.106902
		126.82	0.107352
		127.07	0.106388
		127.32	0.10825
		127.57	0.108507
		127.82	0.108636
		128.07	0.108507
		128.32	0.108828
		128.57	0.108957
		128.82	0.109791
		129.07	0.110112
		129.32	0.109599
		129.57	0.108828
		129.82	0.110112
		130.07	0.10992
		130.32	0.110241
		130.57	0.110498
		130.82	0.110947
		131.07	0.111075
		131.57	0.11191
		131.82	0.11236
		132.07	0.112167
		132.82	0.113194
		133.82	0.1139
		134.32	0.114735
		134.57	0.115056
		134.82	0.11634
		135.07	0.116597

Sample 4			
Thickness = 0.7 cm			
Co =	22237	cps	
Time(min)	c.p.s	Time(hrs)	C/Co
10	11.2	0.166667	0.0005037
20	11.2	0.333333	0.0005037
30	11.3	0.5	0.0005082
40	11.1	0.666667	0.0004992
50	11	0.833333	0.0004947
60	10.7	1	0.0004812
70	11.3	1.166667	0.0005082
80	11.4	1.333333	0.0005127
90	10.6	1.5	0.0004767
100	11	1.666667	0.0004947
110	11.4	1.833333	0.0005127
120	10.7	2	0.0004812
130	11.2	2.166667	0.0005037
140	11.6	2.333333	0.0005217
150	9.97	2.5	0.0004484
160	10.7	2.666667	0.0004812
170	11.6	2.833333	0.0005217
180	11.2	3	0.0005037
190	12.1	3.166667	0.0005441
200	10.9	3.333333	0.0004902
210	11.8	3.5	0.0005306
220	10.8	3.666667	0.0004857
230	11.4	3.833333	0.0005127
240	10.7	4	0.0004812
250	11.4	4.166667	0.0005127
260	11.5	4.333333	0.0005172
270	11.4	4.5	0.0005127
280	11.5	4.666667	0.0005172
290	10.7	4.833333	0.0004812
300	11.4	5	0.0005127
310	10.4	5.166667	0.0004677
320	12.1	5.333333	0.0005441
330	11.6	5.5	0.0005217
340	11.6	5.666667	0.0005217
350	11.6	5.833333	0.0005217
360	10.6	6	0.0004767
370	11.1	6.166667	0.0004992

380	12	6.333333	0.0005396
390	11.3	6.5	0.0005082
400	12	6.666667	0.0005396
410	12.4	6.833333	0.0005576
420	12.6	7	0.0005666
430	12.1	7.166667	0.0005441
440	11.1	7.333333	0.0004992
450	12.4	7.5	0.0005576
460	11.7	7.666667	0.0005262
470	11.6	7.833333	0.0005217
480	12.2	8	0.0005486
490	12.4	8.166667	0.0005576
500	13	8.333333	0.0005846
510	13.1	8.5	0.0005891
520	12	8.666667	0.0005396
530	12.2	8.833333	0.0005486
540	14.1	9	0.0006341
550	13	9.166667	0.0005846
560	13.9	9.333333	0.0006251
570	13.8	9.5	0.0006206
580	13.9	9.666667	0.0006251
590	14.6	9.833333	0.0006566
600	15.1	10	0.000679
610	14.7	10.16667	0.0006611
620	14.7	10.33333	0.0006611
630	15.3	10.5	0.000688
640	15.3	10.66667	0.000688
650	16.1	10.83333	0.000724
660	16.6	11	0.0007465
670	16.5	11.16667	0.000742
680	16.7	11.33333	0.000751
690	17	11.5	0.0007645
700	17.9	11.66667	0.000805
710	17.9	11.83333	0.000805
720	17.3	12	0.000778
730	18.4	12.16667	0.0008274
740	18.8	12.33333	0.0008454
750	18.4	12.5	0.0008274
760	20.3	12.66667	0.0009129
770	17.9	12.83333	0.000805
1260	62.3	21	0.0028016
1270	64.9	21.16667	0.0029186

1280	67.2	21.33333	0.003022
1290	65.2	21.5	0.0029321
1300	67.5	21.66667	0.0030355
1310	63.8	21.83333	0.0028691
1320	71.9	22	0.0032333
1330	74.5	22.16667	0.0033503
1340	75.2	22.33333	0.0033818
1350	77.7	22.5	0.0034942
1360	77.3	22.66667	0.0034762
1370	78.9	22.83333	0.0035481
1380	82.2	23	0.0036965
1390	83.9	23.16667	0.003773
1400	81.3	23.33333	0.0036561
1410	86.4	23.5	0.0038854
1420	89	23.66667	0.0040023
1430	90.4	23.83333	0.0040653
1440	90	24	0.0040473
1450	89.6	24.16667	0.0040293
1460	94.4	24.33333	0.0042452
1470	95.5	24.5	0.0042946
1480	96.4	24.66667	0.0043351
1490	99.7	24.83333	0.0044835
1500	99.3	25	0.0044655
1510	102.2	25.16667	0.0045959
1520	102.8	25.33333	0.0046229
1530	105.2	25.5	0.0047309
1540	107.8	25.66667	0.0048478
1550	109.6	25.83333	0.0049287
1560	107.9	26	0.0048523
1570	114.9	26.16667	0.0051671
1580	111.4	26.33333	0.0050097
1590	115.3	26.5	0.0051851
1600	113.9	26.66667	0.0051221
1610	120.8	26.83333	0.0054324
1620	119.9	27	0.0053919
1630	120.5	27.16667	0.0054189
1640	121.4	27.33333	0.0054594
1650	125.1	27.5	0.0056258
1660	127.6	27.66667	0.0057382
1670	130.3	27.83333	0.0058596
1680	130.2	28	0.0058551
1690	132.8	28.16667	0.005972

1700	135.5	28.33333	0.0060934
1710	138.2	28.5	0.0062149
1720	140.1	28.66667	0.0063003
1730	138.6	28.83333	0.0062329
1740	141.9	29	0.0063813
1750	144.8	29.16667	0.0065117
1760	149.7	29.33333	0.006732
1770	148.9	29.5	0.006696
1780	151.4	29.66667	0.0068085
1790	154.7	29.83333	0.0069569
1800	159	30	0.0071502
1810	154.9	30.16667	0.0069659
1820	159.8	30.33333	0.0071862
1830	161.3	30.5	0.0072537
1840	165	30.66667	0.0074201
1850	165.6	30.83333	0.007447
1860	168	31	0.007555
1870	172.1	31.16667	0.0077394
1880	172	31.33333	0.0077349
1890	175.4	31.5	0.0078878
1900	175.7	31.66667	0.0079012
1910	178	31.83333	0.0080047
1920	180.9	32	0.0081351
1930	181.4	32.16667	0.0081576
1940	185.7	32.33333	0.0083509
1950	189.7	32.5	0.0085308
1960	191.4	32.66667	0.0086073
1970	196	32.83333	0.0088141
1980	195.3	33	0.0087827
1990	199.1	33.16667	0.0089535
2040	211.6	34	0.0095157
2050	213	34.16667	0.0095786
2060	214.8	34.33333	0.0096596
2070	215.6	34.5	0.0096956
2080	218.9	34.66667	0.009844
2090	220.5	34.83333	0.0099159
2100	226.8	35	0.0101992
2110	228.1	35.16667	0.0102577
2120	228.4	35.33333	0.0102712
2130	234	35.5	0.010523
2140	234.1	35.66667	0.0105275
2150	237.8	35.83333	0.0106939

2160	240.1	36	0.0107973
2170	241.6	36.16667	0.0108648
2180	244.7	36.33333	0.0110042
2190	246.7	36.5	0.0110941
2200	249.6	36.66667	0.0112245
2210	245.1	36.83333	0.0110222
2220	255.5	37	0.0114899
2230	254.1	37.16667	0.0114269
2240	258.4	37.33333	0.0116203
2250	261.7	37.5	0.0117687
2260	265.2	37.66667	0.0119261
2270	265.1	37.83333	0.0119216
2280	269.7	38	0.0121284
2290	268.6	38.16667	0.012079
2300	273.1	38.33333	0.0122813
2310	277.3	38.5	0.0124702
2320	275.4	38.66667	0.0123848
2330	281.8	38.83333	0.0126726
2340	284.7	39	0.012803
2350	286	39.16667	0.0128614
2360	287.7	39.33333	0.0129379
2370	291.6	39.5	0.0131133
2380	292.1	39.66667	0.0131358
2390	299.5	39.83333	0.0134685
2400	300.9	40	0.0135315
2410	301.7	40.16667	0.0135675
2420	306.6	40.33333	0.0137878
2430	306.9	40.5	0.0138013
2440	312.8	40.66667	0.0140666
2450	305.1	40.83333	0.0137204
2460	304.4	41	0.0136889
2470	317.6	41.16667	0.0142825
2480	307.4	41.33333	0.0138238
2490	315.7	41.5	0.0141971
2500	301.9	41.66667	0.0135765
2510	322.9	41.83333	0.0145208
2520	312.9	42	0.0140711
2530	329.98	42.16667	0.0148392
2540	327.3	42.33333	0.0147187
2550	340.8	42.5	0.0153258
2560	340.5	42.66667	0.0153123
2570	344.8	42.83333	0.0155057

2580	342.7	43	0.0154113
2590	348.6	43.16667	0.0156766
2600	345	43.33333	0.0155147
2610	354.4	43.5	0.0159374
2620	352.3	43.66667	0.015843
2630	356.1	43.83333	0.0160139
2640	362.9	44	0.0163196
2650	362.8	44.16667	0.0163152
2660	369.8	44.33333	0.0166299
2670	372.4	44.5	0.0167469
2680	370.2	44.66667	0.0166479
2690	372.6	44.83333	0.0167559
2700	378.3	45	0.0170122
2710	376.3	45.16667	0.0169222
2720	380.8	45.33333	0.0171246
2730	385.5	45.5	0.017336
2740	389.8	45.66667	0.0175293
2750	389.4	45.83333	0.0175114
2760	397.9	46	0.0178936
2770	398.6	46.16667	0.0179251
2780	398.3	46.33333	0.0179116
2790	398.7	46.5	0.0179296
2800	401.7	46.66667	0.0180645
2810	408.8	46.83333	0.0183838
2820	407.5	47	0.0183253
2830	412.6	47.16667	0.0185547
2840	419.2	47.33333	0.0188515
2850	419.5	47.5	0.018865
2860	420	47.66667	0.0188874
2870	429	47.83333	0.0192922
2880	422.4	48	0.0189954
2890	432.6	48.16667	0.0194541
2900	427.9	48.33333	0.0192427
2910	436.3	48.5	0.0196205
2920	435.2	48.66667	0.019571
2930	440.9	48.83333	0.0198273
2940	440.8	49	0.0198228
2950	447.6	49.16667	0.0201286
2960	444.8	49.33333	0.0200027
2970	453	49.5	0.0203715
2980	452.2	49.66667	0.0203355
2990	457	49.83333	0.0205513

3000	463	50	0.0208212
3010	460	50.16667	0.0206862
3020	468.2	50.33333	0.021055
3030	470	50.5	0.0211359
3040	469.8	50.66667	0.021127
3050	476.6	50.83333	0.0214327
3060	478.9	51	0.0215362
3070	474.3	51.16667	0.0213293
3080	483.7	51.33333	0.021752
3090	485.8	51.5	0.0218465
3100	486.9	51.66667	0.0218959
3160	503.1	52.66667	0.0226245
3170	508.3	52.83333	0.0228583
3180	512.8	53	0.0230607
3190	505.6	53.16667	0.0227369
3200	510.7	53.33333	0.0229662
3210	518.2	53.5	0.0233035
3220	517.6	53.66667	0.0232765
3230	514.7	53.83333	0.0231461
3240	523	54	0.0235194
3250	532.7	54.16667	0.0239556
3260	529.5	54.33333	0.0238117
3270	536.1	54.5	0.0241085
3280	540.6	54.66667	0.0243108
3290	543.5	54.83333	0.0244412
3300	547.6	55	0.0246256
3310	543.4	55.16667	0.0244367
3320	552.7	55.33333	0.024855
3330	550.7	55.5	0.024765
3340	552.7	55.66667	0.024855
3350	559.3	55.83333	0.0251518
3360	567.4	56	0.025516
3370	561.6	56.16667	0.0252552
3380	567.7	56.33333	0.0255295
3390	569.3	56.5	0.0256015
3400	574.4	56.66667	0.0258308
3410	582.3	56.83333	0.0261861
3420	580.9	57	0.0261231
3430	586.2	57.16667	0.0263615
3440	589.6	57.33333	0.0265144
3450	592.3	57.5	0.0266358
3460	589.5	57.66667	0.0265099

3470	599.2	57.83333	0.0269461
3480	600	58	0.0269821
3490	601.6	58.16667	0.027054
3500	600.4	58.33333	0.027
3510	598	58.5	0.0268921
3520	619.7	58.66667	0.027868
3530	612.8	58.83333	0.0275577
3540	619.3	59	0.02785
3550	623.1	59.16667	0.0280209
3560	622.3	59.33333	0.0279849
3570	627.1	59.5	0.0282007
3580	628.3	59.66667	0.0282547
3590	635.4	59.83333	0.028574
3600	634.7	60	0.0285425
3610	643.6	60.16667	0.0289428
3620	646.1	60.33333	0.0290552
3630	650	60.5	0.0292306
3640	652.5	60.66667	0.029343
3650	652.3	60.83333	0.029334
3660	655.7	61	0.0294869
3670	656.3	61.16667	0.0295139
3680	660.5	61.33333	0.0297027
3690	664.2	61.5	0.0298691
3710	662.3	61.83333	0.0297837
3720	667.3	62	0.0300085
3730	678.5	62.16667	0.0305122
3740	678.5	62.33333	0.0305122
3750	672.3	62.5	0.0302334
3760	683.4	62.66667	0.0307326
3770	685.5	62.83333	0.030827
3780	685.1	63	0.030809
3790	690.8	63.16667	0.0310653
3800	696.3	63.33333	0.0313127
3810	697.9	63.5	0.0313846
3820	699.9	63.66667	0.0314746
3830	706.7	63.83333	0.0317804
3840	702	64	0.031569
3850	704.2	64.16667	0.0316679
3860	709.1	64.33333	0.0318883
3870	713.9	64.5	0.0321042
3880	708	64.66667	0.0318388
3890	714.6	64.83333	0.0321356

3900	728.1	65	0.0327427
3910	727.8	65.16667	0.0327292
3920	726.7	65.33333	0.0326798
3930	738	65.5	0.0331879
3940	738.9	65.66667	0.0332284
3950	736.6	65.83333	0.033125
3960	739.1	66	0.0332374
3970	748.1	66.16667	0.0336421
3980	743.3	66.33333	0.0334263
3990	755.1	66.5	0.0339569
4000	755.1	66.66667	0.0339569
4010	757.8	66.83333	0.0340783
4020	757.9	67	0.0340828
4030	766.8	67.16667	0.0344831
4040	770	67.33333	0.034627
4050	775.7	67.5	0.0348833
4060	776.9	67.66667	0.0349373
4070	777.3	67.83333	0.0349553
4080	783.8	68	0.0352476
4090	785.9	68.16667	0.035342
4100	790.8	68.33333	0.0355624
4110	793.4	68.5	0.0356793
4120	794.4	68.66667	0.0357242
4130	806.1	68.83333	0.0362504
4140	805	69	0.0362009
4150	796.1	69.16667	0.0358007
4160	804.5	69.33333	0.0361784
4170	810.3	69.5	0.0364393
4180	820	69.66667	0.0368755
4190	811.2	69.83333	0.0364797
4200	823	70	0.0370104
4210	830	70.16667	0.0373252
4220	821	70.33333	0.0369204
4230	833	70.5	0.0374601
4240	824.7	70.66667	0.0370868
4300	852.5	71.66667	0.038337
4310	852	71.83333	0.0383145
4320	858.7	72	0.0386158
4330	863.8	72.16667	0.0388452
4340	873.9	72.33333	0.0392994
4350	865.5	72.5	0.0389216
4360	875.6	72.66667	0.0393758

4370	863.5	72.83333	0.0388317
4380	874.7	73	0.0393353
4390	885.7	73.16667	0.03983
4400	876.9	73.33333	0.0394343
4410	882.8	73.5	0.0396996
4420	890.4	73.66667	0.0400414
4430	898.7	73.83333	0.0404146
4440	897.8	74	0.0403742
4450	906.9	74.16667	0.0407834
4460	892.8	74.33333	0.0401493
4470	912.7	74.5	0.0410442
4480	913.2	74.66667	0.0410667
4490	916.4	74.83333	0.0412106
4500	915.3	75	0.0411611
4510	926.6	75.16667	0.0416693
4520	914	75.33333	0.0411027
4530	924.1	75.5	0.0415569
4540	930.5	75.66667	0.0418447
4550	920.4	75.83333	0.0413905
4560	933.8	76	0.0419931
4570	941.2	76.16667	0.0423259
4580	940.5	76.33333	0.0422944
4590	948.2	76.5	0.0426406
4600	943.7	76.66667	0.0424383
4610	946.5	76.83333	0.0425642
4620	962.2	77	0.0432702
4630	958	77.16667	0.0430814
4640	962.4	77.33333	0.0432792
4650	972.2	77.5	0.0437199
4660	973.3	77.66667	0.0437694
4670	974.8	77.83333	0.0438368
4680	979.5	78	0.0440482
4690	986	78.16667	0.0443405
4700	976.1	78.33333	0.0438953
4710	991.9	78.5	0.0446058
4720	994.3	78.66667	0.0447138
4730	1002	78.83333	0.04506
4740	997.9	79	0.0448757
4750	1006	79.16667	0.0452399
4760	1011	79.33333	0.0454648
4770	1014	79.5	0.0455997
4780	1019	79.66667	0.0458245

4790	1012.1	79.83333	0.0455142
4800	1018	80	0.0457796
4810	1013	80.16667	0.0455547
4820	1017	80.33333	0.0457346
4830	1036	80.5	0.046589
4840	1034	80.66667	0.0464991
4850	1037	80.83333	0.046634
4860	1040	81	0.0467689
4870	1041	81.16667	0.0468139
4880	1044	81.33333	0.0469488
4890	1042	81.5	0.0468588
4900	1052	81.66667	0.0473085
4910	1055	81.83333	0.0474435
4920	1049	82	0.0471736
4930	1056	82.16667	0.0474884
4940	1066	82.33333	0.0479381
4950	1057	82.5	0.0475334
4960	1044	82.66667	0.0469488
4970	1055	82.83333	0.0474435
4980	1059	83	0.0476233
4990	1058	83.16667	0.0475784
5000	1067	83.33333	0.0479831
5010	1066	83.5	0.0479381
5020	1063	83.66667	0.0478032
5030	1075	83.83333	0.0483429
5040	1077	84	0.0484328
5050	1080	84.16667	0.0485677
5060	1085	84.33333	0.0487926
5070	1077	84.5	0.0484328
5080	1090	84.66667	0.0490174
5090	1095	84.83333	0.0492423
5100	1095	85	0.0492423
5110	1097	85.16667	0.0493322
5120	1106	85.33333	0.0497369
5130	1101	85.5	0.0495121
5140	1110	85.66667	0.0499168
5150	1115	85.83333	0.0501417
5160	1117	86	0.0502316
5170	1117	86.16667	0.0502316
5180	1121	86.33333	0.0504115
5190	1120	86.5	0.0503665
5200	1129	86.66667	0.0507712

5210	1124	86.83333	0.0505464
5220	1140	87	0.0512659
5230	1138	87.16667	0.051176
5240	1142	87.33333	0.0513558
5250	1138	87.5	0.051176
5260	1152	87.66667	0.0518055
5270	1154	87.83333	0.0518955
5280	1153	88	0.0518505
5290	1161	88.16667	0.0522103
5300	1162	88.33333	0.0522553
5310	1160	88.5	0.0521653
5320	1166	88.66667	0.0524351
5330	1168	88.83333	0.0525251
5340	1181	89	0.0531097
5350	1171	89.16667	0.05266
5360	1182	89.33333	0.0531547
5370	1173	89.5	0.0527499
5380	1191	89.66667	0.0535594
5390	1189	89.83333	0.0534694
5400	1190	90	0.0535144
5410	1197	90.16667	0.0538292
5420	1205	90.33333	0.054189
5430	1211	90.5	0.0544588
5440	1187	90.66667	0.0533795
5450	1204	90.83333	0.054144
5460	1220	91	0.0548635
5470	1210	91.16667	0.0544138
5480	1224	91.33333	0.0550434
5490	1220	91.5	0.0548635
5500	1218	91.66667	0.0547736
5510	1230	91.83333	0.0553132
5520	1223	92	0.0549984
5530	1234	92.16667	0.0554931
5540	1231	92.33333	0.0553582
5550	1241	92.5	0.0558079
5560	1243	92.66667	0.0558978
5570	1238	92.83333	0.055673
5580	1239	93	0.0557179

Sample 5			
Thickness = 0.7 cm			
	Co =	22275	cps
Time(min)	c.p.m	Time(hrs)	C/Co
10	12.48	0.16667	0.0005603
20	13.28	0.33333	0.0005962
30	13.55	0.5	0.0006083
40	12.58	0.66667	0.0005648
50	13.68	0.83333	0.0006141
60	12.9	1	0.0005791
70	12.31	1.16667	0.0005526
80	12.34	1.33333	0.000554
90	13.66	1.5	0.0006132
100	11.27	1.66667	0.0005059
110	11.05	1.83333	0.0004961
120	13.27	2	0.0005957
130	13.074	2.16667	0.0005869
140	12.57	2.33333	0.0005643
150	12.93	2.5	0.0005805
160	12.65	2.66667	0.0005679
200	13.14	3.33333	0.0005899
210	12.87	3.5	0.0005778
220	11.64	3.66667	0.0005226
230	12.7	3.83333	0.0005701
240	11.66	4	0.0005235
250	12.63	4.16667	0.000567
260	12.95	4.33333	0.0005814
270	13.61	4.5	0.000611
280	13.25	4.66667	0.0005948
290	12.5	4.83333	0.0005612
300	12.64	5	0.0005675
310	13	5.16667	0.0005836
320	13.2	5.33333	0.0005926
330	12.23	5.5	0.000549
340	13.33	5.66667	0.0005984
350	12.51	5.83333	0.0005616
360	12.73	6	0.0005715
370	12.02	6.16667	0.0005396
380	13.36	6.33333	0.0005998

390	12.54	6.5	0.000563
400	13.11	6.66667	0.0005886
410	12.78	6.83333	0.0005737
420	13.13	7	0.0005895
430	12.27	7.16667	0.0005508
440	12.55	7.33333	0.0005634
450	12.28	7.5	0.0005513
460	13.17	7.66667	0.0005912
470	12.2	7.83333	0.0005477
480	12.85	8	0.0005769
490	11.63	8.16667	0.0005221
500	13.24	8.33333	0.0005944
510	11.71	8.5	0.0005257
520	12.92	8.66667	0.00058
530	13.19	8.83333	0.0005921
540	12.49	9	0.0005607
550	13.06	9.16667	0.0005863
560	12.82	9.33333	0.0005755
570	13.3	9.5	0.0005971
580	13.31	9.66667	0.0005975
590	11.4	9.83333	0.0005118
600	11.36	10	0.00051
610	13.29	10.1667	0.0005966
620	12.47	10.3333	0.0005598
630	13.41	10.5	0.000602
640	12.71	10.6667	0.0005706
650	13.43	10.8333	0.0006029
660	13.19	11	0.0005921
670	13.51	11.1667	0.0006065
680	11.87	11.3333	0.0005329
690	12.79	11.5	0.0005742
700	12.85	11.6667	0.0005769
710	12.63	11.8333	0.000567
720	13.25	12	0.0005948
730	13.58	12.1667	0.0006097
750	13.73	12.5	0.0006164
760	12.99	12.6667	0.0005832
770	12.59	12.8333	0.0005652
780	13.2	13	0.0005926
790	13.22	13.1667	0.0005935
800	13.13	13.3333	0.0005895
810	13.1	13.5	0.0005881

820	12.9	13.6667	0.0005791
830	13.61	13.8333	0.000611
840	13.15	14	0.0005903
850	12.6	14.1667	0.0005657
860	12.43	14.3333	0.000558
870	13.01	14.5	0.0005841
880	12.97	14.6667	0.0005823
890	13.24	14.8333	0.0005944
900	12.98	15	0.0005827
910	12.89	15.1667	0.0005787
920	13.37	15.3333	0.0006002
930	13.37	15.5	0.0006002
940	13	15.6667	0.0005836
950	11.67	15.8333	0.0005239
960	12.8	16	0.0005746
970	13.12	16.1667	0.000589
980	12.52	16.3333	0.0005621
990	12.69	16.5	0.0005697
1000	13.097	16.6667	0.000588
1010	11.39	16.8333	0.0005113
1020	12.54	17	0.000563
1030	12.51	17.1667	0.0005616
1040	13.3	17.3333	0.0005971
1050	12.68	17.5	0.0005692
1060	12.24	17.6667	0.0005495
1070	12.43	17.8333	0.000558
1080	12.91	18	0.0005796
1090	12.99	18.1667	0.0005832
1100	12.89	18.3333	0.0005787
1110	13.01	18.5	0.0005841
1120	13.52	18.6667	0.000607
1130	12.92	18.8333	0.00058
1140	13	19	0.0005836
1150	13.06	19.1667	0.0005863
1160	11.53	19.3333	0.0005176
1170	12.42	19.5	0.0005576
1180	13.09	19.6667	0.0005877
1190	12.79	19.8333	0.0005742
1200	12.62	20	0.0005666
1210	12.96	20.1667	0.0005818
1220	12.44	20.3333	0.0005585
1230	13.17	20.5	0.0005912

1240	12.87	20.6667	0.0005778
1250	13.33	20.8333	0.0005984
1260	12.62	21	0.0005666
1270	12.58	21.1667	0.0005648
1280	12.67	21.3333	0.0005688
1330	13.13	22.1667	0.0005895
1340	12.84	22.3333	0.0005764
1350	12.9	22.5	0.0005791
1360	13.08	22.6667	0.0005872
1370	11.89	22.8333	0.0005338
1380	13.57	23	0.0006092
1390	13.02	23.1667	0.0005845
1400	12.19	23.3333	0.0005473
1410	12.73	23.5	0.0005715
1420	12.7	23.6667	0.0005701
1430	14.43	23.8333	0.0006478
1440	13.89	24	0.0006236
1450	13.34	24.1667	0.0005989
1460	11.4	24.3333	0.0005118
1470	13.46	24.5	0.0006043
1480	12.96	24.6667	0.0005818
1490	12.39	24.8333	0.0005562
1500	13.76	25	0.0006177
1510	13.62	25.1667	0.0006114
1520	13.61	25.3333	0.000611
1530	12.74	25.5	0.0005719
1540	12.68	25.6667	0.0005692
1550	13.29	25.8333	0.0005966
1560	11.77	26	0.0005284
1570	13.62	26.1667	0.0006114
1580	13.58	26.3333	0.0006097
1590	12.54	26.5	0.000563
1600	13.52	26.6667	0.000607
1610	13.69	26.8333	0.0006146
1620	13.88	27	0.0006231
1630	13.05	27.1667	0.0005859
1640	13.55	27.3333	0.0006083
1650	13.29	27.5	0.0005966
1660	13.76	27.6667	0.0006177
1670	13.76	27.8333	0.0006177
1680	13.19	28	0.0005921
1690	13.51	28.1667	0.0006065

1700	13.39	28.3333	0.0006011
1710	13.28	28.5	0.0005962
1720	13.75	28.6667	0.0006173
1730	13.48	28.8333	0.0006052
1740	13.58	29	0.0006097
1750	13.93	29.1667	0.0006254
1760	12.97	29.3333	0.0005823
1770	13.79	29.5	0.0006191
1780	13.75	29.6667	0.0006173
1790	13.77	29.8333	0.0006182
1800	13.35	30	0.0005993
1810	13.91	30.1667	0.0006245
1820	13.79	30.3333	0.0006191
1830	13.67	30.5	0.0006137
1840	13.4	30.6667	0.0006016
1850	13.72	30.8333	0.0006159
1860	13.6	31	0.0006105
1880	13.97	31.3333	0.0006272
1890	14.3	31.5	0.000642
1900	13.92	31.6667	0.0006249
1910	14.14	31.8333	0.0006348
1920	14.13	32	0.0006343
1930	13.98	32.1667	0.0006276
1940	14.17	32.3333	0.0006361
1950	14.65	32.5	0.0006577
1960	14.49	32.6667	0.0006505
1970	14.36	32.8333	0.0006447
1980	14.06	33	0.0006312
1990	14.98	33.1667	0.0006725
2000	14.38	33.3333	0.0006456
2010	14.89	33.5	0.0006685
2020	13.83	33.6667	0.0006209
2030	14.6	33.8333	0.0006554
2040	14.1	34	0.000633
2050	15.04	34.1667	0.0006752
2060	14.71	34.3333	0.0006604
2070	14.82	34.5	0.0006653
2080	15.06	34.6667	0.0006761
2090	14.98	34.8333	0.0006725
2100	11.4	35	0.0005118
2110	14.91	35.1667	0.0006694
2120	15.51	35.3333	0.0006963

2130	14.44	35.5	0.0006483
2140	15.1	35.6667	0.0006779
2150	14.86	35.8333	0.0006671
2160	14.54	36	0.0006527
2170	15.65	36.1667	0.0007026
2180	15.14	36.3333	0.0006797
2190	15.21	36.5	0.0006828
2200	15.41	36.6667	0.0006918
2210	15.38	36.8333	0.0006905
2220	15.44	37	0.0006932
2230	14.67	37.1667	0.0006586
2240	16.08	37.3333	0.0007219
2250	15.88	37.5	0.0007129
2260	15.31	37.6667	0.0006873
2270	15.96	37.8333	0.0007165
2280	14.67	38	0.0006586
2290	15.43	38.1667	0.0006927
2300	16.63	38.3333	0.0007466
2310	15.9	38.5	0.0007138
2320	16.98	38.6667	0.0007623
2330	15.9	38.8333	0.0007138
2340	16.42	39	0.0007371
2350	15.4	39.1667	0.0006914
2360	16.57	39.3333	0.0007439
2370	16.59	39.5	0.0007448
2380	16.93	39.6667	0.00076
2390	15.78	39.8333	0.0007084
2400	16.76	40	0.0007524
2410	16.27	40.1667	0.0007304
2440	17.2	40.6667	0.0007722
2450	17.36	40.8333	0.0007793
2460	16.94	41	0.0007605
2470	16.69	41.1667	0.0007493
2480	16.8	41.3333	0.0007542
2490	16.99	41.5	0.0007627
2500	16.85	41.6667	0.0007565
2510	16.98	41.8333	0.0007623
2520	17.05	42	0.0007654
2530	17.45	42.1667	0.0007834
2540	17.4	42.3333	0.0007811
2550	17.6	42.5	0.0007901
2560	17.05	42.6667	0.0007654

2570	17.48	42.8333	0.0007847
2580	17.37	43	0.0007798
2590	17.83	43.1667	0.0008004
2600	18.29	43.3333	0.0008211
2610	18.45	43.5	0.0008283
2620	18.07	43.6667	0.0008112
2630	17.69	43.8333	0.0007942
2640	18.25	44	0.0008193
2650	18.15	44.1667	0.0008148
2660	18.26	44.3333	0.0008198
2670	18.8	44.5	0.000844
2680	18.38	44.6667	0.0008251
2690	19.23	44.8333	0.0008633
2700	18.24	45	0.0008189
2710	18.93	45.1667	0.0008498
2720	19.16	45.3333	0.0008602
2730	19.2	45.5	0.000862
2740	19.06	45.6667	0.0008557
2750	20.24	45.8333	0.0009086
2760	18.49	46	0.0008301
2770	19.46	46.1667	0.0008736
2780	20.03	46.3333	0.0008992
2790	19.57	46.5	0.0008786
2800	19.82	46.6667	0.0008898
2810	19.79	46.8333	0.0008884
2820	18.84	47	0.0008458
2830	20.59	47.1667	0.0009244
2840	17.72	47.3333	0.0007955
2850	20.26	47.5	0.0009095
2860	19.91	47.6667	0.0008938
2870	20.25	47.8333	0.0009091
2880	21.29	48	0.0009558
2890	21.22	48.1667	0.0009526
2900	21.53	48.3333	0.0009666
2910	20.61	48.5	0.0009253
2920	20.19	48.6667	0.0009064
2930	21.42	48.8333	0.0009616
2940	21.05	49	0.000945
2950	20.53	49.1667	0.0009217
2960	21.72	49.3333	0.0009751
2970	22.14	49.5	0.0009939
2980	20.04	49.6667	0.0008997

2990	21.1	49.8333	0.0009473
3000	22.59	50	0.0010141
3010	22.57	50.1667	0.0010132
3020	23	50.3333	0.0010325
3030	22.32	50.5	0.001002
3040	22.56	50.6667	0.0010128
3050	22.47	50.8333	0.0010088
3060	23.38	51	0.0010496
3070	23.66	51.1667	0.0010622
3080	23.28	51.3333	0.0010451
3090	24.23	51.5	0.0010878
3100	24.13	51.6667	0.0010833
3110	24.57	51.8333	0.0011103
3120	23.88	52	0.0010721
3130	22.74	52.1667	0.0010209
3140	23.76	52.3333	0.0010667
3150	24.94	52.5	0.0011196
3160	24.46	52.6667	0.0010981
3170	25.32	52.8333	0.0011367
3180	24.19	53	0.001086
3190	22.56	53.1667	0.0010128
3200	25.43	53.3333	0.0011416
3210	21.13	53.5	0.0009486
3220	25.84	53.6667	0.00116
3230	25.66	53.8333	0.001152
3240	25.39	54	0.0011398
3250	25.82	54.1667	0.0011591
3260	25.2	54.3333	0.0011313
3270	26.8	54.5	0.0012031
3280	27.11	54.6667	0.0012171
3290	27.29	54.8333	0.0012251
3300	25.87	55	0.0011614
3310	27.49	55.1667	0.0012341
3320	27.04	55.3333	0.0012139
3330	27.42	55.5	0.001231
3340	27.73	55.6667	0.0012449
3350	27.2	55.8333	0.0012211
3360	28.43	56	0.0012763
3370	28.03	56.1667	0.0012584
3380	27.27	56.3333	0.0012242
3390	29.07	56.5	0.0013051
3400	28.25	56.6667	0.0012682

3410	29.39	56.8333	0.0013194
3420	28.84	57	0.0012947
3430	28.84	57.1667	0.0012947
3440	30.27	57.3333	0.0013589
3450	29.54	57.5	0.0013262
3460	29.52	57.6667	0.0013253
3470	29.65	57.8333	0.0013311
3480	31.29	58	0.0014047
3490	30.8	58.1667	0.0013827
3500	31	58.3333	0.0013917
3510	30.4	58.5	0.0013648
3550	31.6	59.1667	0.0014186
3560	32.5	59.3333	0.001459
3570	32.3	59.5	0.0014501
3580	33.1	59.6667	0.001486
3590	32.4	59.8333	0.0014545
3600	32.6	60	0.0014635
3610	31.9	60.1667	0.0014321
3620	33	60.3333	0.0014815
3630	33.9	60.5	0.0015219
3640	34.1	60.6667	0.0015309
3650	34.9	60.8333	0.0015668
3660	34.7	61	0.0015578
3670	34.5	61.1667	0.0015488
3680	35.1	61.3333	0.0015758
3690	35.1	61.5	0.0015758
3700	35.3	61.6667	0.0015847
3710	34.6	61.8333	0.0015533
3720	37.1	62	0.0016655
3730	36.4	62.1667	0.0016341
3740	37.4	62.3333	0.001679
3750	33.8	62.5	0.0015174
3760	35.4	62.6667	0.0015892
3770	36.8	62.8333	0.0016521
3780	37	63	0.0016611
3790	37.2	63.1667	0.00167
3800	34	63.3333	0.0015264
3810	38.6	63.5	0.0017329
3820	36.5	63.6667	0.0016386
3830	38.9	63.8333	0.0017464
3840	38.9	64	0.0017464
3850	38.9	64.1667	0.0017464

3860	33.7	64.3333	0.0015129
3870	40.6	64.5	0.0018227
3880	40.9	64.6667	0.0018361
3890	40.9	64.8333	0.0018361
3900	39.3	65	0.0017643
3910	41.8	65.1667	0.0018765
3920	41.8	65.3333	0.0018765
3930	40.8	65.5	0.0018316
3940	40.7	65.6667	0.0018272
3950	41.6	65.8333	0.0018676
3960	43.6	66	0.0019574
3970	43.4	66.1667	0.0019484
3980	42.7	66.3333	0.0019169
3990	41.1	66.5	0.0018451
4000	43.7	66.6667	0.0019618
4010	42.5	66.8333	0.001908
4020	44.9	67	0.0020157
4030	44.7	67.1667	0.0020067
4040	45.2	67.3333	0.0020292
4050	42.7	67.5	0.0019169
4060	46.3	67.6667	0.0020786
4070	45.8	67.8333	0.0020561
4080	46.5	68	0.0020875
4110	48.9	68.5	0.0021953
4120	49	68.6667	0.0021998
4130	45.7	68.8333	0.0020516
4140	48.7	69	0.0021863
4150	47.8	69.1667	0.0021459
4160	50.1	69.3333	0.0022492
4170	49.8	69.5	0.0022357
4180	50.7	69.6667	0.0022761
4190	50.6	69.8333	0.0022716
4200	51.7	70	0.002321
4210	52.2	70.1667	0.0023434
4220	50.8	70.3333	0.0022806
4230	52.52	70.5	0.0023578
4280	54.7	71.3333	0.0024557
4290	56.1	71.5	0.0025185
4300	53.4	71.6667	0.0023973
4310	56.9	71.8333	0.0025544
4320	57.4	72	0.0025769
4330	57.1	72.1667	0.0025634

4340	52.2	72.3333	0.0023434
4350	57.1	72.5	0.0025634
4360	58.3	72.6667	0.0026173
4370	59.3	72.8333	0.0026622
4380	60.4	73	0.0027116
4390	60.3	73.1667	0.0027071
4400	60	73.3333	0.0026936
4410	60.4	73.5	0.0027116
4420	60.7	73.6667	0.002725
4430	58.9	73.8333	0.0026442
4440	60	74	0.0026936
4450	62.2	74.1667	0.0027924
4460	63	74.3333	0.0028283
4470	63.2	74.5	0.0028373
4480	63.1	74.6667	0.0028328
4490	64.9	74.8333	0.0029136
4500	66	75	0.002963
4510	65.5	75.1667	0.0029405
4520	65.5	75.3333	0.0029405
4530	66.7	75.5	0.0029944
4540	65.6	75.6667	0.002945
4550	68.3	75.8333	0.0030662
4560	68.7	76	0.0030842
4570	68.95	76.1667	0.0030954
4580	69.41	76.3333	0.003116
4590	69.5	76.5	0.0031201
4600	69.8	76.6667	0.0031336
4610	71.1	76.8333	0.0031919
4620	72.1	77	0.0032368
4630	72.5	77.1667	0.0032548
4640	73.4	77.3333	0.0032952
4650	72.3	77.5	0.0032458
4660	68.6	77.6667	0.0030797
4670	74.2	77.8333	0.0033311
4700	75.2	78.3333	0.003376
4710	76.7	78.5	0.0034433
4720	77.7	78.6667	0.0034882
4730	76.4	78.8333	0.0034299
4740	75.4	79	0.003385
4750	78.2	79.1667	0.0035107
4760	79.3	79.3333	0.00356
4770	78.9	79.5	0.0035421

4780	79.1	79.6667	0.0035511
4790	79.8	79.8333	0.0035825
4800	81.8	80	0.0036723
4810	82.2	80.1667	0.0036902
4820	83.2	80.3333	0.0037351
4830	81.3	80.5	0.0036498
4840	84	80.6667	0.003771
4850	83.2	80.8333	0.0037351
4860	87	81	0.0039057
4870	85.9	81.1667	0.0038563
4880	86.6	81.3333	0.0038878
4890	83.8	81.5	0.0037621
4900	89.2	81.6667	0.0040045
4910	87.7	81.8333	0.0039371
4920	86.8	82	0.0038967
4930	87.6	82.1667	0.0039327
4940	90.3	82.3333	0.0040539
4950	92.5	82.5	0.0041526
4960	92.3	82.6667	0.0041437
4970	93.1	82.8333	0.0041796
4980	91.6	83	0.0041122
4990	95.3	83.1667	0.0042783
5000	92.8	83.3333	0.0041661
5010	94.8	83.5	0.0042559
5020	96.1	83.6667	0.0043143
5030	96.9	83.8333	0.0043502
5040	96.4	84	0.0043277
5050	99.4	84.1667	0.0044624
5060	99.7	84.3333	0.0044759
5070	99.7	84.5	0.0044759
5080	99.2	84.6667	0.0044534
5090	101.2	84.8333	0.0045432
5100	101.3	85	0.0045477
5110	100.8	85.1667	0.0045253
5120	101.4	85.3333	0.0045522
5130	101.5	85.5	0.0045567
5140	105.1	85.6667	0.0047183
5150	104.9	85.8333	0.0047093
5160	104.2	86	0.0046779
5170	108.1	86.1667	0.004853
5180	109	86.3333	0.0048934
5190	106	86.5	0.0047587

5200	107.3	86.6667	0.0048171
5210	108.3	86.8333	0.004862
5220	112.1	87	0.0050325
5230	110.4	87.1667	0.0049562
5240	113.3	87.3333	0.0050864
5250	109.2	87.5	0.0049024
5260	112.6	87.6667	0.005055
5270	116.4	87.8333	0.0052256
5280	112.8	88	0.005064
5290	114.6	88.1667	0.0051448
5300	118.3	88.3333	0.0053109
5310	115.4	88.5	0.0051807
5320	117.7	88.6667	0.005284
5330	119.2	88.8333	0.0053513
5340	118.9	89	0.0053378
5350	120.1	89.1667	0.0053917
5360	118.9	89.3333	0.0053378
5370	120.1	89.5	0.0053917
5380	119.7	89.6667	0.0053737
5390	123.8	89.8333	0.0055578
5400	124.2	90	0.0055758
5410	126.1	90.1667	0.0056611
5420	125.2	90.3333	0.0056207
5430	124.4	90.5	0.0055847
5440	128.2	90.6667	0.0057553
5450	128.4	90.8333	0.0057643
5460	128.6	91	0.0057733
5470	130.5	91.1667	0.0058586
5480	128.6	91.3333	0.0057733
5490	132.4	91.5	0.0059439
5500	131.1	91.6667	0.0058855
5510	132	91.8333	0.0059259
5520	133.4	92	0.0059888

Sample 8 Thickness = 0.3 cm			
	Co =	cps	22275
Time(min)	c.p.m	Time(hrs)	C/Co
10	12.48	0.17	0.00027
20	13.28	0.33	0.00028
30	13.55	0.50	0.00026
40	12.58	0.67	0.00027
50	13.68	0.83	0.00022
60	12.9	1.00	0.00028
70	12.31	1.17	0.00032
80	12.34	1.33	0.00039
90	13.66	1.50	0.00046
100	11.27	1.67	0.0006
110	11.05	1.83	0.00073
120	13.27	2.00	0.00087
130	13.074	2.17	0.00118
140	12.57	2.33	0.00149
150	12.93	2.50	0.00187
160	12.65	2.67	0.00232
200	13.14	2.83	0.00267
210	12.87	3.00	0.00306
220	11.64	3.17	0.00369
230	12.7	3.33	0.00411
240	11.66	3.50	0.0046
250	12.63	3.67	0.00529
260	12.95	3.83	0.00583
270	13.61	4.00	0.0064
280	13.25	4.17	0.00715
290	12.5	4.33	0.00771
300	12.64	4.50	0.0083
310	13	4.67	0.00913
320	13.2	4.83	0.00979
330	12.23	5.00	0.0104
340	13.33	5.17	0.0111
350	12.51	5.33	0.01163
360	12.73	5.50	0.01258
370	12.02	5.67	0.0133
380	13.36	5.83	0.01424
390	12.54	6.00	0.01506
400	13.11	6.17	0.01569

410	12.78	6.33	0.01637
420	13.13	6.50	0.01714
430	12.27	6.67	0.01802
440	12.55	6.83	0.01868
450	12.28	7.00	0.01955
460	13.17	7.17	0.0202
470	12.2	7.33	0.02111
480	12.85	7.50	0.02193
490	11.63	7.67	0.02244
500	13.24	7.83	0.02315
510	11.71	8.00	0.02404
520	12.92	8.17	0.02517
530	13.19	8.33	0.02594
540	12.49	8.50	0.02671
550	13.06	8.67	0.02721
560	12.82	8.83	0.02794
570	13.3	9.00	0.02912
580	13.31	9.17	0.02986
590	11.4	9.33	0.03049
600	11.36	9.50	0.03168
610	13.29	9.67	0.03213
620	12.47	9.83	0.03264
630	13.41	10.00	0.03401
640	12.71	10.17	0.03372
650	13.43	10.33	0.03549
660	13.19	10.50	0.03607
670	13.51	10.67	0.03715
680	11.87	10.83	0.03746
690	12.79	11.00	0.03705
700	12.85	11.17	0.03887
710	12.63	11.33	0.03992
720	13.25	11.50	0.04107
730	13.58	11.67	0.04085
750	13.73	11.83	0.04205
760	12.99	12.00	0.0433
770	12.59	12.17	0.04373
780	13.2	12.33	0.04465
790	13.22	12.50	0.04416
800	13.13	12.67	0.04615
810	13.1	12.83	0.04724
820	12.9	13.00	0.04809
830	13.61	13.17	0.04862

840	13.15	13.33	0.04904
850	12.6	13.50	0.0497
860	12.43	13.67	0.04968
870	13.01	13.83	0.05021
880	12.97	14.00	0.0524
890	13.24	14.17	0.05281
900	12.98	14.33	0.05453
910	12.89	14.50	0.05496
920	13.37	14.67	0.05568
930	13.37	14.83	0.05603
940	13	15.00	0.05649
950	11.67	15.17	0.05418
960	12.8	15.33	0.05767
970	13.12	15.50	0.05741
980	12.52	15.67	0.06012
990	12.69	15.83	0.05964
1000	13.097	16.00	0.06018
1010	11.39	16.17	0.0604
1020	12.54	16.33	0.06238
1030	12.51	16.50	0.06347
1040	13.3	16.67	0.06418

VITA

Terry Lee Sams was born in Waynesville, North Carolina on January 27, 1954. He graduated from Pisgah High School in Canton, North Carolina in June 1972. He then served three years in the United States Army, 82nd Airborne Division at Fort Bragg, North Carolina. After completing his tour of duty, he enrolled in Asheville-Buncombe Technical College where he received an Associate of Applied Science Degree in Chemical Engineering in June 1978 with highest honors.

He then accepted a job at Union Carbide Corporation, Nuclear Division¹⁴, in June 1978 as an engineering technician. He enrolled at the University of Tennessee as a part-time student at night beginning in January 1979 and pursued an undergraduate degree in Chemical Engineering. He continued working full-time and eventually received a Bachelor of Science Degree in Chemical Engineering in June 1985. He was subsequently hired as a development engineer at Martin Marietta Energy Systems.

In January 1986, Terry enrolled in the University of Tennessee night school to pursue a graduate degree. He completed the requirements for a Master of Science Degree in Chemical Engineering in May 1993. He is currently an employee of Martin Marietta Energy Systems in the Environmental Restoration Division.

¹⁴DOE Contract was renegotiated in April 1984 and awarded to Martin Marietta Energy Systems, Inc.