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Sandia National Laboratories
Albuquerque, New Mexico 87185

February 15, 1986

Mr. Walton Kelly
U.S. Nuclear Regulatory Commission
Mail Stop 623-SS
Washington, DC 20555

Dear Mr. Kelly:

Enclosed is the monthly report for FIN A-1756, Geochemical Sensitivity Analysis for January 1986.

Please feel free to contact me if you have any questions or comments.

Sincerely,

R. M. Cranwell

R. M. Cranwell
Supervisor
Waste Management Systems
Division 6431

RMC:6431:jm

Enclosure

8603250337 860215
PDR WMRES EXISANL
A-1756 PDR

WM Record File WM-RES A1756 SNL

WM Project 10, 11, 16
Docket No.
PDR ✓
LPDR ✓ (B, N, S)

Distribution:
Kelly | Joan-Ticket
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(Return to WM, 623-SS) Sac

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Office of the Director, NMSS
Attn: Program Support Staff
Robert Browning, Director
Division of Waste Management
Malcolm R. Knapp
Division of Waste Management
Kenneth Jackson
Division of Waste Management
Office of Research, NRC
Document Control Center,
Division of Waste Management
G. Jacobs
Oak Ridge National Laboratory
6400 R. C. Cochrell
6430 N. R. Ortiz
6431 R. M. Cranwell
6431 M. D. Siegel
1500 W. Herrmann
1510 J. W. Nunziato
1512 J. C. Cummings
1512 K. L. Erickson

PROGRAM:	Geochemical Sensitivity Analysis	FIN#:	A-1756
CONTRACTOR:	Sandia National Laboratories	BUDGET PERIOD:	10/01/85 - 9/30/86
DRA PROGRAM MANAGER:	W. R. Kelly	BUDGET AMOUNT:	265K
CONTRACT PROGRAM MANAGER:	R. M. Cranwell	FTS PHONE:	844-8368
PRINCIPAL INVESTIGATOR:	M. D. Siegel	FTS PHONE:	846-5448

PROJECT OBJECTIVES

The objective of this project is to provide technical assistance to the NRC in determining the sensitivity of far-field performance assessment calculations to uncertainties in geochemical and hydrological input data and in the representation of geochemical processes in transport models. In Task I, the error in model calculations of integrated radionuclide discharge due to speciation, kinetic and sorption effects will be evaluated. In Task II, the potential importance of organic molecules and colloids will be examined. SNLA will assist the NRC in determining how geochemical processes should be represented in transport models under Task III. Short-term technical assistance will be carried out under Task IV.

ACTIVITIES DURING JANUARY 1986

Task I. Uncertainty in Integrated Radionuclide Discharge

Subtask 1A. Speciation Effects (M. Siegel, S. Phillips, R. Guzowski)

• Conceptual Models for Sites

The conceptual model for a basalt repository site was revised to represent the accessible environment at 5 km and to include data from Kowallis and others (1982), Loo and others (1984) and Long (1983).

Three alternate hypothetical flow paths to the path described in the Environmental Assessment for the Deaf Smith County Site were formulated. All of these alternate paths have a shorter flow path to an aquifer than the EA and do not require flow through a few hundred feet of shale as does the EA flow path.

Option 1 has flow downward to the first "significant" siltstone in the Glorieta Fim. The selection of siltstone as a potential flow path is based on generic conductivity data.

Option 2 has downward flow to a sandstone layer in the Glorieta. Data for the sandstone also is generic.

Option 3 has downward flow to the dolomite layer in the lower part of the same unit as the host salt. Whereas the conductivity of the dolomite indicates that this is at best a slightly transmissive unit, this path does not require flow across several salt units (only out of the host salt).

Thicknesses, composite conductivities, and composite porosities were determined for each option. The data for the EA path was adjusted for an accessible environment at 5 km instead of 10 km. (figures attached).

The 4 flow paths for hypothetical bedded salt repository are shown in Figure 1.

- Speciation/Solubility Calculations

M. Siegel and S. Phillips met with V. Parker and D. Smith-Magowan of the Chemical Thermodynamics Division, National Bureau of Standards on January 30, 1986. The topic of discussion was the use of the NBS computer Analysis of Thermochemical Data (CATCH) series of programs. The NBS approach to compilation of thermochemical data is described in NBSIR 76-1147, NBSIR 81-2341 and NBSIR 77-1300. These documents have been sent to the NRC Project Manager under a separate cover. At the meeting it was concluded that incorporation of the CATCH system in the LBL/SNLA Aqueous Solution Data base would not be feasible with the current resources available. The most beneficial use of the CATCH would be to ensure internal consistency in the ASD when new data were added. CATCH tables are available only for a few elements at this time (Th, Cs, Li and Rb). Catalogs for U, Na, K and B are incomplete and currently there are no resources to finish them. Based on these facts, it was felt that the NBS staff should seek funds to provide assistance to the ASD when new data for the above elements were added or replaced data previously compiled by the NBS.

Subtask 1B. Equilibrium Sorption Effects
(D. Kent, J. O. Leckie, M. Siegel)

Additional chapters on the application of the Stanford Generalized Model for Adsorption (SGMA) were written during January. These sections are currently under review at Stanford University and should be sent to SNLA in February. The subcontract with Stanford is currently under review due to failure by Stanford staff to meet scheduled milestones.

Subtasks 1C and 1D. Kinetic and Dynamic Effects
(K. Erickson and M. Siegel)

A draft of a paper to be published in the Waste Management '86 proceedings was partially completed during January.

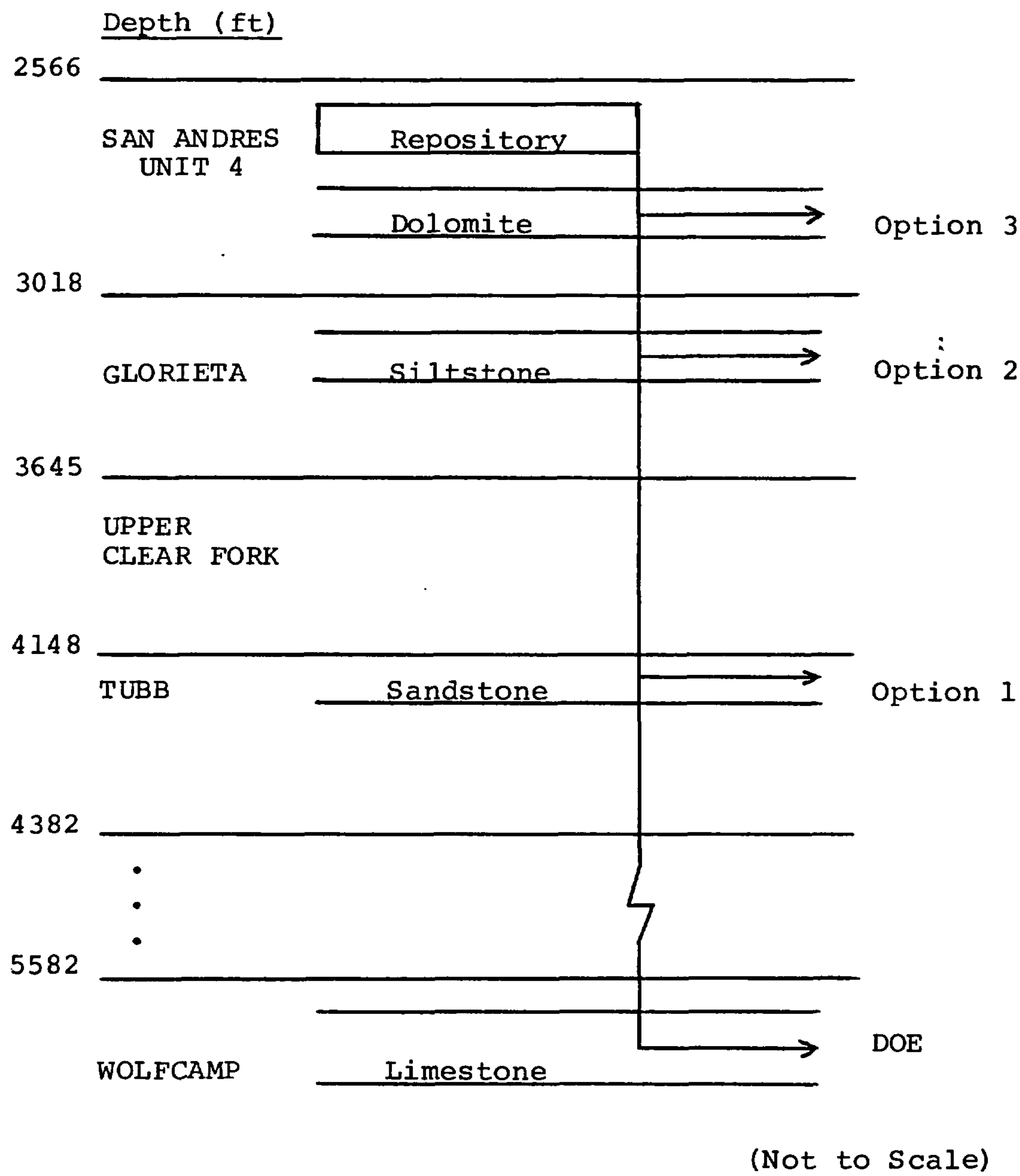

Figure 1. Possible Flow Paths, Deaf Smith Site

Calculations in support of the paper were also carried out. The final paper will be completed in early March. The results will be presented by K. Erickson at WM '86 on Thursday, March 6 at Session XXXII.

References

Kowallis, B. J., Roeloffs, E. A., and Wang, H. F., 1982, Microcrack studies of basalts from the Iceland Research Drilling Project: Jour. Geophys. Res., v. 87, no. B8, p. 6650- 6656

Long, P. E., 1983, Repository horizon identification report, Draft. volume 1: RHO, Rept. SD-BWI-TY-001, var. paginated.

Loo, W. W. Arnett, R. C., Leonhart, L. S., Luttrell, S. P., Wang, I. S. and McSpadden, W. R., 1984, Effective porosities of basalt: A technical basis for values and probability distributions used in preliminary performance assessments: RHO, Rept. SD-BWI-TY-54, 67p.

Task IV. Short Term Technical Assistance

M. Siegel delivered the keynote speech on geochemistry of the thermally undisturbed zone of a high-level waste repository at the NRC Workshop on Validation of Mathematical Models for Waste Repository Performance Assessment. Copies of the vuegraphs used in the talk are appended as Attachment 1. A trip report is being sent to the NRC under a separate cover.

Trips

- NRC Model Validation Workshop

M. Siegel participated January 27-29, 1986, in the NRC Workshop on Validation of Mathematical Models being used or developed for assessing the performance of a HLW repository. The models discussed included the entire spectrum of models used for a HLW repository including geomechanics, groundwater flow, radionuclide transport, and geochemistry. The purpose of the workshop was to identify laboratory experiments, field studies and natural analogues studies that can be used to establish the validity of the phenomena included in these models and the accuracy of the mathematical description of the phenomena. The discussions in the three-day workshop were divided into the thermally undisturbed zone (far from the repository), the thermally disturbed zone (near the repository) and the engineered facility (repository plus waste package). The workshop included formal presentations, panel discussions, and open discussions for all participants.

- Unsaturated Media Workshop

R. Guzowski attended the Workshop on Flow and Transport in Unsaturated Fractured Media January 6-9, 1986, in Tucson, Arizona. The workshop is the third co-sponsored by the University of Arizona, SNLA, and the Nuclear Regulatory

Commission. Six panel discussions were held on the following topics: Physical/Chemical Properties of Unsaturated Media, Matrix vs. Fracture Flow, Natural Analogs, Couple Processes, Modeling Approaches and Calibration, and Vapor Phase Transport.

A trip report is appended as Attachment 2.

Allocation of Resources

Task I	66%
Task IV	34%

Attachment 1

Viewgraphs for Speech
on Geochemistry of the
Thermally-Undisturbed Zone

USNRC Workshop
Validation of Computer Models

January 27, 1986

USNRC WORKSHOP
VALIDATION OF COMPUTER MODELS

MALCOLM SIEGEL
WASTE MANAGEMENT SYSTEMS DIVISION
SANDIA NATIONAL LABORATORIES

JANUARY 21, 1986

86TD6906.21

"THOUGHT SHOULD BE GIVEN ALSO TO THE AMOUNT OF DETAIL THAT IS REQUIRED IN THE RESULTS FROM EACH PROJECT. OBVIOUSLY, FOR EXAMPLE, ONE WOULD LIKE TO KNOW THE THERMODYNAMIC PROPERTIES OF PLUTONIUM WITH GREAT ACCURACY, OR THE PRECISE VALUES OF K_D FOR DIFFERENT VALENCE STATES OF PLUTONIUM UNDER A VARIETY OF CONDITIONS: BUT IS SUCH ACCURACY REALLY NECESSARY FOR A DECISION AS TO WHETHER A GIVEN SITE IS OR IS NOT SUITABLE? ONE CAN HOPE THAT THE PLANNED RESEARCH WILL BE CONTINUED FAR INTO THE FUTURE, AFTER A REPOSITORY IS UNDER CONSTRUCTION OR IN OPERATION, BUT AT PRESENT THE PROJECTS SHOULD BE PUSHED AND THE DEGREE OF ACCURACY SHOULD BE TAILORED TO THE IMMEDIATE PROBLEMS OF LOCATING AN EXPLORATORY SHAFT AND A POSSIBLE REPOSITORY SITE."

K. KRAUSKOPF
NNWSI REVIEW COMMITTEE
ON GEOCHEMISTRY

OUTLINE

- ESTABLISHING A FRAMEWORK
  1. GEOCHEMICAL ISSUES
  2. COMPONENTS OF MODELS
  3. DEGREES OF VALIDATION
  4. PERFORMANCE ASSESSMENT ISSUES
- PARALLEL APPROACHES ARE REQUIRED
  1. LONG-TERM PERSPECTIVE
     - MODEL BUILDING
     - VALIDATION
     - GATHERING OF FUNDAMENTAL DATA
  2. SHORT-TERM PERSPECTIVE
     - BOUNDING CALCULATIONS
     - SENSITIVITY ANALYSES
     - EMPIRICAL OBSERVATIONS
- GAPS BETWEEN GEOCHEMICAL MODELS, DATA COLLECTION AND PERFORMANCE ASSESSMENT MUST BE BRIDGED

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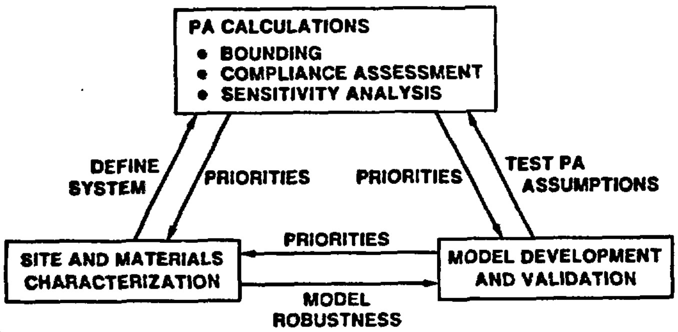
VALIDATION OF GEOCHEMICAL MODELS FOR HLW DISPOSAL

- **GEOCHEMICAL ISSUES**
  - EQUILIBRIUM VS KINETICS DESCRIPTION OF SYSTEM
  - ACTIVITIES OF SPECIES IN SOLUTION AND SOLIDS
- **MODEL VALIDATION ISSUES**
  - IDENTIFICATION OF IMPORTANT PHENOMENA TO MODEL
  - DEGREE OF ROBUSTNESS OF MODELS WITH RESPECT TO SITE-SPECIFIC CONDITIONS
  - REQUIRED DEGREE OF AGREEMENT BETWEEN OBSERVATIONS AND CALCULATIONS
- **PERFORMANCE ASSESSMENT ISSUES**
  - DEMONSTRATE COMPLIANCE WITH NRC AND EPA PERFORMANCE MEASURES
  - PROVIDE ADDITIONAL ASSURANCE FOR SAFETY OF PUBLIC

FRAMEWORK FOR HLW DISPOSAL



COMPONENTS OF MODELS/ SIMULATIONS

1. **REAL SYSTEM:** SOURCE OF OBSERVABLE DATA
2. **EXPERIMENTAL FRAMES:** SUBSET OF OBSERVATIONS
   - MODEL VALIDITY MUST BE ASSESSED RELATIVE TO A PARTICULAR EXPERIMENTAL FRAME
3. **BASE MODEL:** HYPOTHETICAL COMPLETE MODEL VALID IN ALL EXPERIMENTAL FRAMES
4. **LUMPED MODE:** SIMPLE MODEL FOR A PARTICULAR EXPERIMENTAL FRAME
5. **COMPUTER CODE:** CARRIES OUT SIMULATION
   - COMPLEXITY AND RESOURCES REQUIRED MUST BE CONSIDERED

LEVELS OF MODEL VALIDATION (ZEIGLER, 1976)

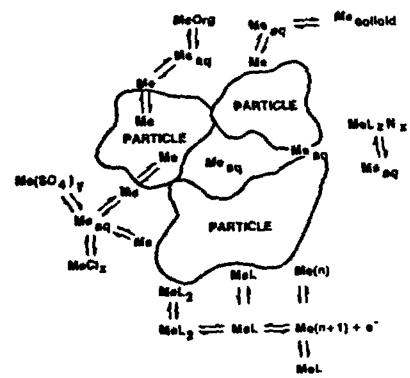
1. REPLICATIVELY VALID
   - MATCHES DATA ALREADY ACQUIRED
2. PREDICTIVELY VALID
   - MATCHES NEW DATA
3. STRUCTURALLY VALID
   - TRULY REFLECTS OPERATION OF REAL SYSTEM

WHAT LEVEL IS REQUIRED FOR HLW DISPOSAL?

EXPERIMENTAL FRAMES MAY LIMIT MODEL DEVELOPMENT AND VALIDATION

- ACTIVITY COEFFICIENTS FOR SALINE BRINES
- SURFACE COMPLEXATION CONSTANTS
- REACTION RATE DATA
- VALIDATED THERMOCHEMICAL DATA SET FOR ACTINIDES AND FISSION PRODUCTS
- THERMOCHEMICAL DATA FOR SOLID SOLUTIONS OF CLAYS AND ZEOLITES

REAL SYSTEM: REACTIONS BETWEEN SOLUTION SPECIES AND ROCK



SOLUTE-ROCK INTERACTIONS

- **BASE MODEL**

  MODEL MUST BE ROBUST WITH RESPECT TO WIDE RANGE OF SOLUTION AND SUBSTRATE COMPOSITIONS, IONIC STRENGTH, SOLUTE / SOLID RATIOS, AND OBSERVATION TIME FRAMES.

- **LUMPED MODELS FOR SORPTION**
  - TRIPLE-LAYER MODEL
  - STERN AND MODIFIED STERN MODELS
  - CONSTANT CAPACITANCE MODEL
  - ION-EXCHANGE
  - ISOTHERMS (LANGMUIR, FREUNDLICH AND OTHERS)
  - K_d

LUMPED MODELS FOR SORPTION (I)

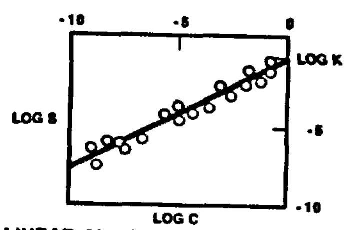
- **DISTRIBUTION RATIO OR COEFFICIENT**

$$R_d, K_d = \frac{\text{GM NUCLIDE/GM SOLID}}{\text{GM NUCLIDE/GM SOLUTION}} = \frac{S}{C}$$

- **ISOTHERMS**

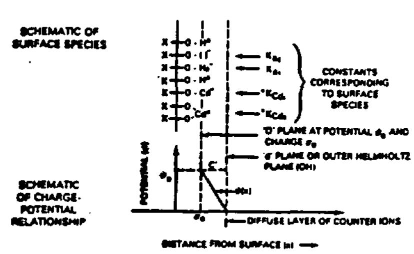
  FREUDLICH MODEL

  $S = KC^n$

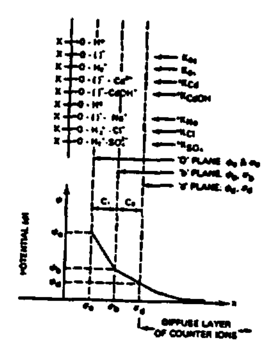


FOR $n = 1$, SORPTION IS LINEAR AND $R_d = K$

ELECTROSTATIC MODELS



CONSTANT CAPACITANCE



TRIPLE LAYER MODEL

EXPERIMENTAL DATA FOR SORPTION MODELS

K_d MEASUREMENTS

- MEASURE
  - pH (TRACER, PRE- AND POST CONTACT)
  - CHANGES IN GROUND-WATER CHEMISTRY DUE TO PRE-EQUILIBRATION)
  - RADIONUCLIDE CONCENTRATION (SOLUTION PRE- AND POST CONTACT, SOLID)
- VARY
  - LITHOLOGY/MINERALOGY OF ROCK SAMPLE
  - GROUND WATER COMPOSITION (NATURAL SAMPLES)
  - IONIC STRENGTH (SYNTHETICS)
  - TEMPERATURE
  - REDOX POTENTIAL
  - CONTACT TIME
  - BATCH, CIRCULATING, AND COLUMN TESTS

ISOTHERMS

- VARY
  - RADIONUCLIDE CONCENTRATION
  - PARTICLE SIZE OF ROCK SAMPLE
  - SOLUTION VOLUME: SOLID MASS

EXPERIMENTAL DATA FOR ELECTROSTATIC SORPTION MODELS

MEASURE

- RADIONUCLIDE CONCENTRATION
  - SOLUTION
  - SOLID
  - CONTAINER LOSS
- SOLUTION VOLUME/SOLID MASS OF SUSPENSION
- SPECIFIC SURFACE AREA OF SOLID
- DENSITY OF SURFACE HYDROXYL GROUPS
- ALKALIMETRIC/ACIDIMETRIC TITRATION DATA (pH VS C_a, C_b)
  - DATA FROM SEVERAL TITRATIONS OVER >2 ORDERS MAGNITUDE IONIC STRENGTH (TL MODEL)
- SOLUTION COMPOSITION (COMPLETE DESCRIPTION)
  - MAJOR CATIONS AND ANIONS
  - MINOR AND TRACE CONSTITUENTS
  - pH
  - REDOX STATE

EXPERIMENTAL DATA FOR ELECTROSTATIC SORPTION MODELS (II)

VARY

- RADIONUCLIDE CONCENTRATION (TOTAL)
- SOLUTION/SOLID
- SOLUTION COMPOSITION
  - IONIC STRENGTH OF ELECTROLYTE (FOR TL MODEL VARIATION OF >2 ORDERS OF MAGNITUDE)
  - CONCENTRATION OF MAJOR LIGANDS AND COMPETING IONS
- SUBSTRATE COMPOSITION

OTHER REQUIREMENTS

- FORMATION CONSTANTS FOR ALL SIGNIFICANT AQUEOUS SPECIES AND SURFACE COMPLEXES
- COMPUTER CODE SUCH AS MINEQL+SGMA OR MINTEQ

COMPARISON OF SORPTION MODELS
CONDITIONAL VERSUS INTRINSIC CONSTANTS

MODEL	CONSTANTS	CONDITIONAL FOR
K_d	K_d	(Me), pH, I, M, L, ROCK TYPE, PARTICLE SIZE, (S) . .
ISOTHERM	K, n	pH, I, M, L, ROCK TYPE, PARTICLE SIZE, (S)
CONSTANT CAPACITANCE	K_+, K_-, C, EC	pH RANGE, I, M, L, ROCK TYPE, N_S, S_a, (S) RANGE
TRIPLE LAYER	K_+, K_-, K_a, K_c, C_1, C_2, EC	I, pH RANGE, ROCK TYPE, N_S, S_a, (S) RANGE

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LIMITATIONS OF ELECTROSTATIC MODELS

- DEGREE OF VALIDITY DEPENDS STRONGLY ON EXPERIMENTAL FRAME
  1. MODELS ARE PREDICTIVELY VALID IN PROPER EXPERIMENTAL FRAME
  2. MODELS ARE NOT STRUCTURALLY VALID. COMPARISON OF 5 MODELS (WESTALL AND HOHL, 1980) FOUND "ONE MODEL IS ABOUT AS GOOD AS ANOTHER FOR DESCRIPTION OF MATERIAL BALANCE DATA" IN APPROPRIATE EXPERIMENTAL FRAMES
- CURRENT MODELS DO NOT ADEQUATELY ADDRESS
  1. ACTIVITY COEFFICIENTS OF SURFACE SITES
  2. STRUCTURE OF SURFACE SPECIES
  3. BEHAVIOR OF ELECTRICAL DOUBLE LAYER IN BRINES
  4. EXISTENCE OF MULTIPLE SITES

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PERFORMANCE ASSESSMENT CALCULATION COSTS

• NWFT/DVM SINGLE VECTOR, SINGLE CHAIN (10)	$ 10
• SWIFT SINGLE VECTOR, SINGLE CHAIN (10), CONC.	$ 100
• CHEMTRN 15 SPECIES, NO DECAY 1-D, POROUS	"TAXES 7600"
• TRANQL NO DECAY, MONOMINERALIC, 1-D POROUS, 14 AQUEOUS COMPLEXES, 10 km, 10^4 YEARS	CURRENT ESTIMATE > $ 20K

X 100 VECTORS X 20-100 SCENARIOS X 5-9 SITES

TM6000.10

SHORT TERM OBJECTIVES

1. IDENTIFY CASES WHERE SPECIATION, COLLOIDAL TRANSPORT, ETC., MUST BE CONSIDERED IN COMPLIANCE ASSESSMENTS

2. FOR CASES IDENTIFIED IN (1), DETERMINE THE NATURE OF INFORMATION THAT IS NEEDED TO ACCURATELY ASSESS DEGREE OF COMPLIANCE OF REPOSITORIES WITH EPA STANDARD. (i.e., CHEMICAL REACTION RATES, DISTRIBUTION FUNCTIONS)

TJ8000 84

OBJECTIVES (II)

3. WITH INSIGHTS GAINED FROM (1) AND (2):

   (A) DETERMINE CRITERIA FOR DESIGNING LABORATORY OR SMALL-SCALE FIELD EXPERIMENTS WHICH WILL YIELD DEFINITIVE (i.e, NON-NULL) RESULTS

   (B) EVALUATE ADEQUACY OF PUBLISHED OR ON-GOING DOE RADIONUCLIDE TRANSPORT EXPERIMENTS

TJ8000 05

OBJECTIVES (III)

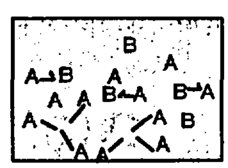
4. REPRESENT RADIONUCLIDE RETARDATION IN PERFORMANCE ASSESSMENT METHODOLOGY IN A MANNER WHICH WILL ALLOW US TO PLACE REASONABLE UPPER BOUNDS ON RADIONUCLIDE DISCHARGE. THIS METHOD SHOULD BE THEORETICALLY SOUND, COMPUTATIONALLY EFFICIENT AND ADEQUATE FOR EPA COMPLIANCE ASSESSMENTS.

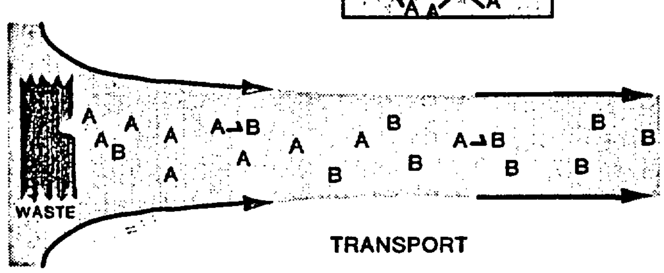
ASSUMPTIONS THAT MAY BE INHERENT IN USE OF CONSTANT RETARDATION FACTOR FOR A RADIONUCLIDE

- SINGLE AQUEOUS SPECIES FOR EACH RADIONUCLIDE
- CONSTANT KNOWN GROUND-WATER COMPOSITION
- CONSTANT KNOWN ROCK COMPOSITION
- LINEAR ISOTHERM ASSUMED
- ONLY AQUEOUS SPECIES TRANSPORT
- REVERSIBLE, EQUILIBRIUM CONDITIONS
- DEGREE OF SATURATION (UTILIZATION) IS KNOWN AND → 1

SCENARIOS

BATCH EXPERIMENTS
("AVERAGE" Rd)





SPECIATION/ KINETICS SCENARIO

SET SUM OF INTEGRATED DISCHARGES OF A AND B EQUAL TO W, THE EPA RELEASE LIMIT FOR THE RADIONUCLIDE

$t^* = 10{,}000$ YR.

$$Q\int_{t=t_o}^{t^*} (C_A + C_B)\,dt = f(R_A, R_B, k^*, \lambda, tg, t_o, C_{\dot{A}}, C_{\dot{B}})$$

WHERE

- t_o = INITIAL CONTAINMENT PERIOD
- tg = GROUND-WATER TRAVEL TIME
- Q = VOLUMETRIC WATER FLUX THROUGH FACILITY
- $C_{\dot{A}}$ = CONCENTRATION OF A IN FACILITY
- $C_{\dot{B}}$ = CONCENTRATION OF B IN FACILITY

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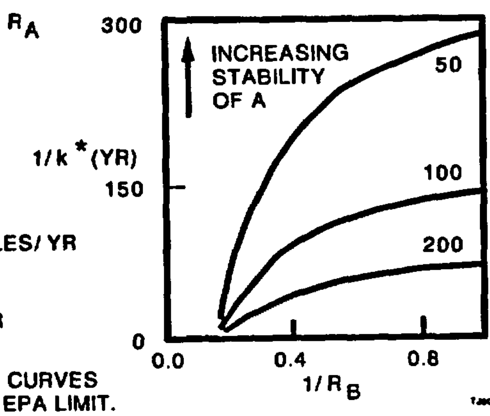
RESULTS: Np - 237

EFFECT OF R_A



W = 20 Ci

$Q C_{\dot{A}}$ = 3 MOLES/ YR

t_g = 1000 YR

t_o = 1000 YR

AREAS ABOVE CURVES COMPLY WITH EPA LIMIT.

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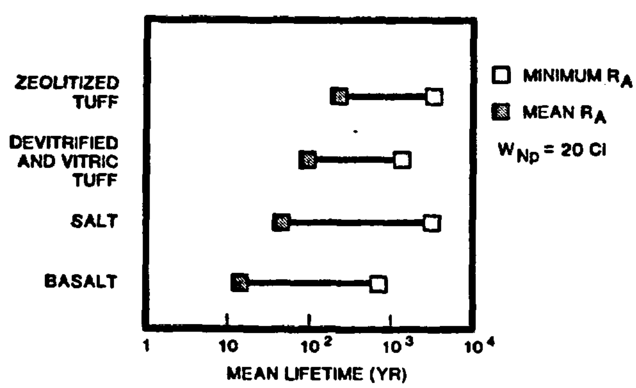
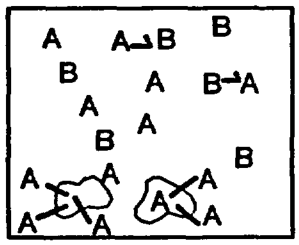
MINIMUM MEAN LIFETIME OF SORBING Np SPECIES NEEDED TO COMPLY WITH IO CFR 60



DETERMINATION OF MEAN LIFETIME

EXPERIMENTAL DESIGN

- DETERMINATION OF CRITERIA FOR DESIGN OF LABORATORY EXPERIMENTS TO ENSURE THAT IMPORTANT SPECIATION EFFECTS ARE NOT OVERLOOKED.



BATCH EXPERIMENT

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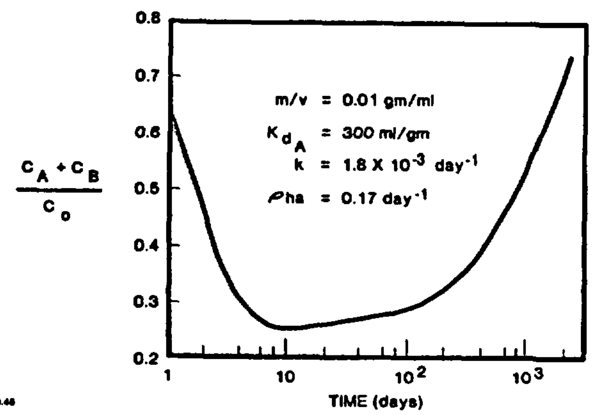
BATCH EXPERIMENT WITH SPECIATION REACTION



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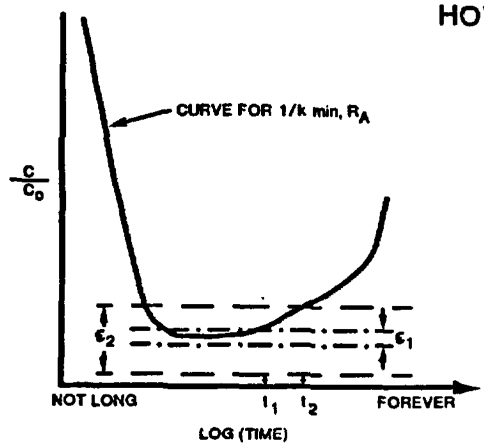
HOW LONG SHOULD EXPERIMENT RUN?



SHORT-TERM MODEL/ VALIDATION TASKS

- AVAILABLE MODELS AND DATA SHOULD BE PUSHED AS FAR AS POSSIBLE TO
  1. IDENTIFY WEAKNESSES IN THERMOCHEMICAL DATA BASES AND EQUILIBRIUM ASSUMPTION
  2. CALCULATE POTENTIAL GROUND-WATER EVOLUTION PATHWAYS TO BOUND POSSIBLE CONDITIONS
  3. EXAMINE ASSUMPTIONS OF BATCH K_d EXPERIMENTS
     - PRE-EQUILIBRATION OF ROCK AND WATER
     - SOLUBILITY LIMITS
     - MINERALOGICAL CONTROL ON K_d
     - SINGLE DOMINANT SPECIES
  4. BRACKET RANGE OF RETARDATION FACTORS FOR SPECIES THAT MAY BE PRESENT IN EXPERIMENTS AND AT SITES
- VALIDATION TASKS SHOULD BE DESIGNED IN SUPPORT OF ABOVE OBJECTIVES

CONCLUSIONS AND QUESTIONS

1. THOUGHT SHOULD BE GIVEN TO LEVEL OF ROBUSTNESS AND VALIDATION REQUIRED BY GEOCHEMICAL MODELS USED IN SUPPORT OF HLW DISPOSAL
   - ARE BOUNDING MODELS SUFFICIENT?
   - CAN 'MODELS' BASED ON K_d'S AND APPARENT CONCENTRATION LIMITS BE VALIDATED?
2. PARALLEL EFFORTS INVOLVING SIMPLE EMPIRICAL MODELS AND PHENOMENOLOGICAL MODELS SHOULD BE COORDINATED IN SUPPORT OF SAFETY ASSESSMENTS.
   - HOW CAN THIS BE EFFECTED?
3. GEOCHEMICAL MODEL DEVELOPMENT AND VALIDATION SHOULD FOCUS ON CRITICAL ASSUMPTIONS UNDERLYING USE OF SIMPLE GEOCHEMICAL MODELS IN PERFORMANCE ASSESSMENT.
   - SHOULD CONDITIONAL OR INTRINSIC CONSTANTS BE OBTAINED?
4. REALISTIC PARAMETER COMBINATIONS AND REPOSITORY BREACH SCENARIOS REQUIRING USE OF COMPLEX MODELS SHOULD BE IDENTIFIED.
   - HOW MUCH EFFORT SHOULD FOCUS ON UNEXPECTED CONDITIONS?

Attachment 2

TRIP REPORT

UNSATURATED ROCK/CONTAMINANT TRANSPORT

WORKSHOP III

JANUARY 6-9, 1986, TUCSON, ARIZONA

ROBERT GUZOWSKI

FLOW

The fundamental process by which liquid migrates through a fractured porous medium is not known, and no consensus existed at the meeting as to the theoretical basis of flow. In general, the proposed flow mechanisms centered on film flow along the fracture walls and dewatering of the fractures by suction into the matrix accompanied by matrix flow. Plug flow was mentioned only in passing.

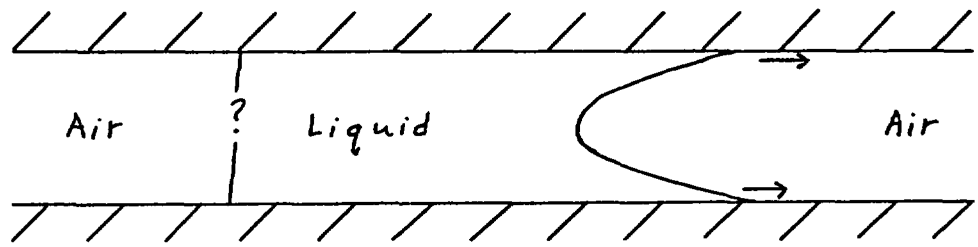
Plug Flow

In an overview of the types of liquid flow theoretically possible in the unsaturated zone, Davis stated that plug flow is dependent upon the surface energy of the liquid in the fracture. Surface energy is a function of the contact angle between the liquid and the fracture surface, the wet ability and capillarity of the fracture surface, and the air/water distribution in the fracture. If the surface energy is a high value, which means that the water will tend to spread over a surface, the liquid migrates along the walls of the fracture (Figure 1a). If the surface energy is low, the liquid will remain as a plug of water in the fracture (Figure 1b). To get movement of the liquid, the plug of water must be pushed by the air on the higher pressure side of the plug, and the required pressure is relatively large (Bonano).

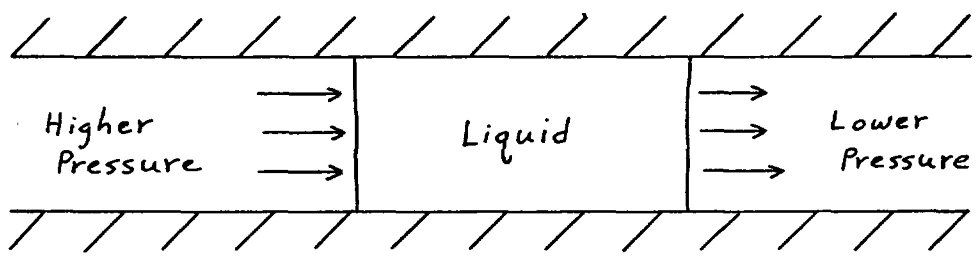
Matrix Flow

Matrix flow instead of fracture flow seems to have the most support from those attending the meeting. The main proponents of matrix flow were Wang and Montazer, and the following description was compiled from their presentations. (Note: Wang was one of several DOE speakers who could not get approval to have copies of his viewgraphs distributed to the attendees.)

Wang claims that if a fractured porous rock is fully saturated and allowed to drain, the only water remaining in the fractures (pendular water) will be at the points where the fracture walls are in contact (contact points). The amount of water (percent of total possible) remaining in the fractures will be the same as the proportion (as a percent) of the fracture walls in contact with each other. Montazer's idealized situation (Figure 2) does not require actual contact of the asperities on the fracture walls. Figure 3 shows that the contact points (asperities) on a fracture surface will each be surrounded by pendular water. This water will flow only if the pendular water zones of enough adjacent contact points overlap so as to provide a continuous flow path. This occurs at high levels of saturation. At other than nearly complete saturation, capillary forces are greater than gravity, so the



a. Movement of a plug: high surface energy



b. Movement of a plug: low surface energy

Figure 1. Mechanisms of Plug Flow

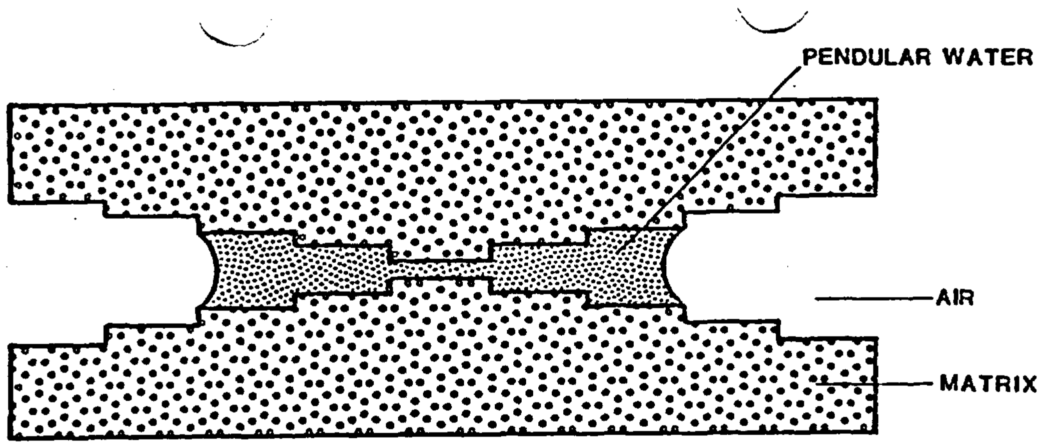
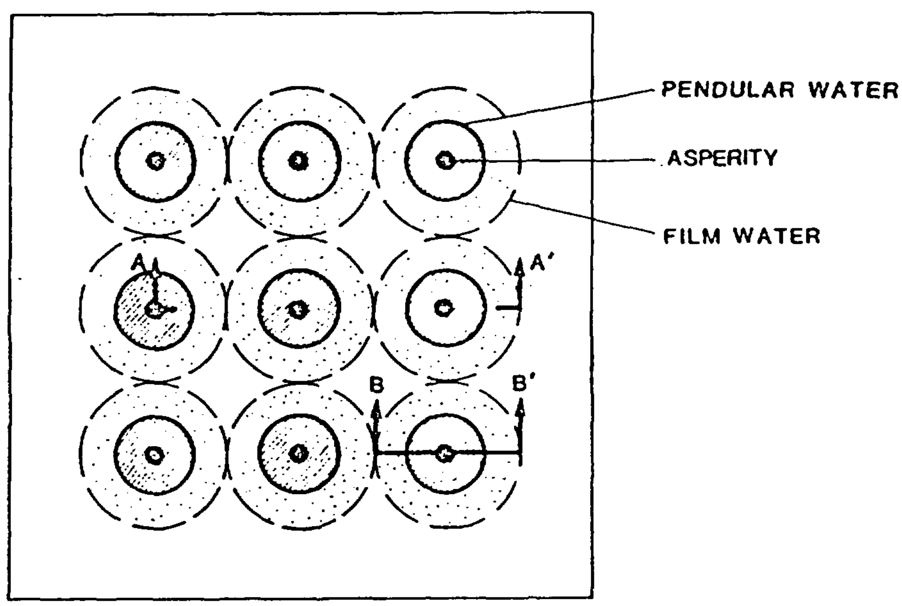


Figure 2. Schematic Figure of Fracture-bound Water in an Unsaturated, Fractured Porous Rock



View of idealized fracture plane.

Figure 3. Distribution of Pendular Water on a Fracture Plane

water is drawn into the matrix from the fractures. As a result, fractures as a component of flow can be virtually ignored.

As support for the proposal that matrix flow occurs almost to the exclusion of fracture flow, Wang cited an Australian study using colored dyes injected through large soil samples that contained root and worm holes. In this study, flow through the unsaturated soil was exclusively through the matrix, while flow in saturated soil was exclusively through the root and worm holes. This exampled was criticized by other participants as not being directly analogous to fractured tuff because of the much smaller matrix-pore and fracture apertures in tuff.

A comment by Montazer with regard to Wang's presentation contradicts to some extent his earlier statements in favor of matrix flow. He said that water moving down a fracture saturates a thin zone of matrix (a couple of molecules thick) along the fracture, and this saturated zone prevents the short-term movement of fluid into the matrix.

Fracture Flow

A University of Arizona experiment in unsaturated, fractured partially to nonwelded tuff near Superior, Arizona, suggests that fracture flow can occur under unsaturated conditions. The purpose is to measure flow through a fracture network. In one of the inclined drill holes, no flow was recorded in a zone where no fractures are present. Flow does occur in the fractured rock, although the amount of flow was independent of fracture density.

Film Flow

No presentations were made specifically about film flow, although Pruess, in his presentation, stated that for large-scale motion of liquid, film flow occurs in a small amount and at a rapid rate. Film flow is an integral part of Green's mechanism for the formation of aerosols.

In a response to a comment by Montazer that film flow should be dropped from consideration in dealing with flow through fractured, unsaturated rocks, Pruess cited evidence in fractured, unsaturated geothermal systems that indicated film flow was occurring. Montazer denied that this evidence supported a film-flow interpretation.

FACTORS AFFECTING FLOW AND TRANSPORT

Davis summarized the microscopic features and processes that affect the macroscopic properties as:

1. Surface energy -- described above.

2. Surface chemistry -- adsorption and ion exchange.

3. Surface charge -- the formation of an electric double layer by having ions in solution attach to an oppositely charged surface. Flow does not occur in the double layer, so flow and transport are retarded. An increase in the valence of the ions or the number of solutes can cause the double layer to collapse.

4. Colloidal filtration -- in the near field where cooling water can form colloids, both the colloids and the surfaces have double layers. Where constrictions occur between grains or along fractures, colloids can accumulate, thereby reducing flow.

5. Water shock -- particles attached to a surface by London-Van der Waals forces can be stripped from the surface by fresh water. Bridging can occur at restrictions reducing flow by as much as three orders of magnitude.

The factors that affect sorption at mineral surfaces were described by Theis as:

1. The electrostatic charge at the surface resulting either from ionization/ionic reaction or mineral lattice substitution.

2. The density of surface reactive sites and degree of lattice substitution.

3. The form of dissolved solutes.

4. Competition among solutes for the available sites.

5. Solute type, concentration, ionic strength, temperature, diffusion rate, and surface reactivity.

In addition, sorption/desorption is time dependent. Whereas sorption is a rapid process, desorption requires much longer times, and the longer the ions are in contact with the surface prior to desorption, the longer the desorption takes. This additional time may be the result of substitution and polymerization, rather than diffusion.

Another factor that seems to have a marked effect on matrix flow, and therefore transport, is the presence of fractures. Reda reported on a study in which a core of tuff was completely dried and evacuated. Water was then introduced at both ends of the core, and a gamma-beam densitometer was used to follow the progress of the water fronts. Because the tuff in the core was of uniform composition, the fronts should have met at the midpoint of the core. A minute fracture cutting the core near one end reduced the flow rate from that end by approximately one-half.

SOURCES OF ERRORS

Although not limited to sources of error in dealing with isothermal, homogeneous aqueous solutions in porous media, several sources of error were mentioned by Nielson. A major source is the use of Darcy's law to calculate flow. Because flow is dependent on such factors as temperature, salt content, and ionic species present, these factors need to be included in these calculations. Reda contradicted this in part by stating that water chemistry had no effect on the hydraulic conductivity of the tuff used in his core experiments.

Another source of error is the measurement of the moisture content. A two percent error in measuring the moisture content in a sample will produce an order of magnitude error in the log of the conductivity.

A simplification of the relationship between solute concentration and distance from the pore wall is another source of error. Figures 4a and 4b indicate how the plot of the relationship is modified to a more easily handled relationship. An apparent zone with no solute is introduced through which the solute would have to diffuse in order to reach the pore wall. This zone does not exist in reality.

VAPOR-PHASE TRANSPORT

(Based on presentations by Pruess, Smith, and Green)

A canister of nuclear waste is surrounded by a zone through which heat is transferred by conduction (Figure 5). This zone is surrounded by a zone in which water is vaporized, the vapor migrates to the fracture because of the lower pressure in the fracture, and the vapor is driven away from the canister by the heat. The heat of vaporization is carried to a cooler area and released to the surrounding rock and liquid when the vapor condenses. Capillarity pulls the liquid back into the matrix and primarily toward the canister. Capillarity away from the canister results in the outflow of vapor exceeding the inflow

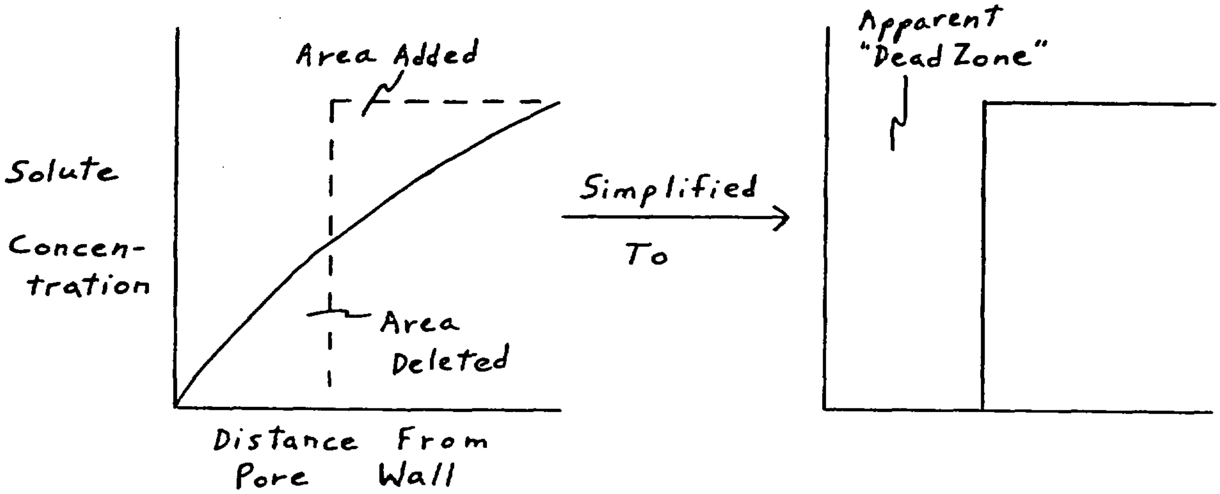


Figure 4. Simplification of Solute Concentration Relative to Distance from Pore Wall

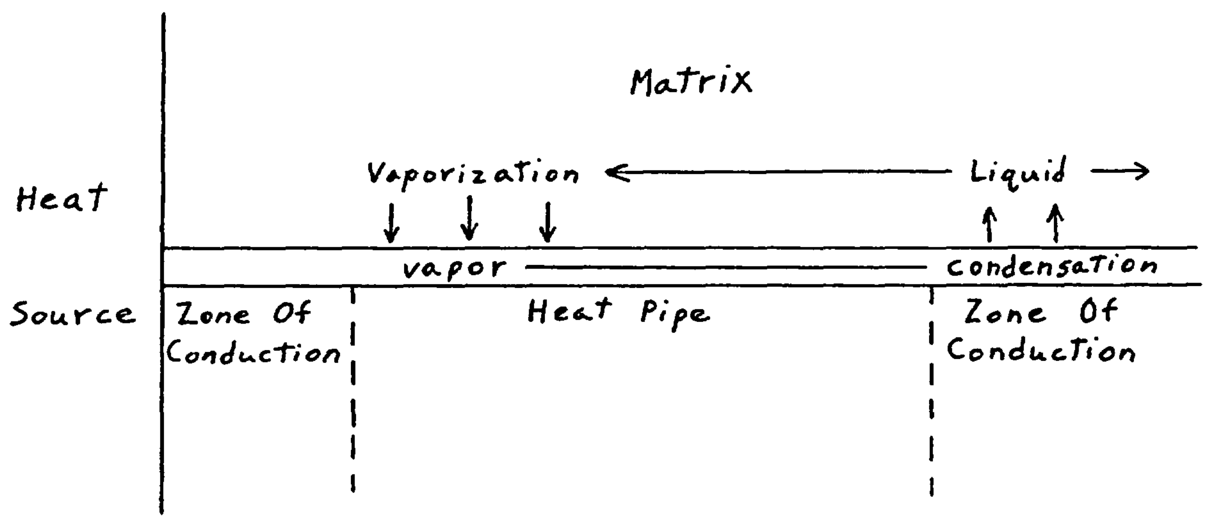


Figure 5. Schematic Figure of Vapor and Liquid Movement Near a Canister

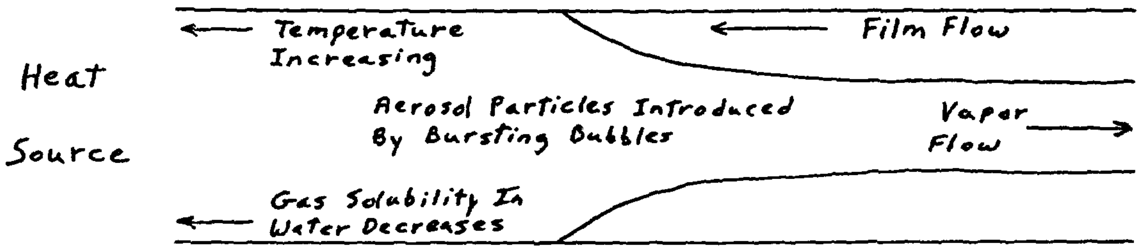


Figure 6. Schematic Diagram of Aerosol Formation

of water. The temperature of the canister will remain constant until the inflow of water ceases. At this time, the temperature of the canister will increase considerably.

Film flow along the fractures may result in the formation of aerosols. This process requires film flow, and involves only H-3, C-14, Kr-85, and I-129. As the film flow approaches the canister (Figure 6), bubbles form because of the heat. Bursting bubbles can introduce aerosol particles into the air space, where the vapor and particles are forced away from the canister by the heat. In addition, gamma rays generated by the waste can strip electrons from atoms and molecules. The movement of these electrons causes an electric current to form and a negative charge to form on the surface of the water film. As a result, particles with negative charges will be repelled by the water film, thereby being transported greater distances than expected. Gaseous radionuclides from a failed canister involved in this process could be transported to the saturated zone surrounding a canister for transportation downward toward the water table.

This process requires a minimum aperture of 100 µm and a film flow >10 cm/sec.

SPEAKERS CITED IN THIS TRIP REPORT

Evaristo J. Bonano
Division 6431
Sandia National Laboratories
Albuquerque, NM 87185

Jim Davis
Department of Chemical Engineering
University of Washington
Seattle, WA 98195

Ronald T. Green
Fishbeck, Thompson, Carr and Huber
1500 East Beltline
Grand Rapids, MI 49506

Parviz Montazer
USGS-WRD, Mail Stop 416
Federal Center
Denver, CO 80225

Don Nielson
Water Science & Irrigation
University of California
Davis, CA 95616

Karsten Pruess
Lawrence Berkeley Laboratories
University of California
Berkeley, CA 94720

Daniel C. Reda
Division 1512
Sandia National Laboratories
Albuquerque, NM 87185

Doug Smith
Department of Chem & Nuc Engineering
University of New Mexico
Albuquerque, NM 87131

Thomas Theis
Department of Civil & Environmental Engineering
Clarkson University
Potsdam, NY 13676

J. S. Y. Wang
Earth Science Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720

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THIS IS AN ESTIMATE ONLY AND MAY NOT MATCH THE INVOICES SENT TO NRC BY SANDIA'S ACCOUNTING DEPARTMENT.

		Current Month	Year-to-Date
I.	Direct Manpower (man-months of charged effort)	1.4	3.7
II.	Direct Loaded Labor Costs	16.0	41.0
	Materials and Services	1.0	1.0
	ADP Support (computer)	0.0	1.0
	Subcontracts	12.0	7.0
	Travel	1.0	2.0
	Other	0.0	0.0
	TOTAL COSTS	30.0	52.0

Other = rounding approximation by computer

III. Funding Status

Prior FY Carryover	FY86 Projected Funding Level	FY86 Funds Received to Date	FY86 Funding Balance Needed
None	265K	115K	150K