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Waste Isolation Safety Assessment Program Technical Progress Report for FY-1978

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July 1979

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**Pacific Northwest Laboratory
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WASTE ISOLATION SAFETY ASSESSMENT PROGRAM
TECHNICAL PROGRESS REPORT FOR FY-1978

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Richland, Washington 99352

EXECUTIVE SUMMARY

Associated with commercial nuclear power production in the United States is the generation of potentially hazardous radioactive wastes. The Department of Energy (DOE) is seeking to develop nuclear waste isolation systems in geologic formations that will preclude contact with the biosphere of waste radionuclides in concentrations which are sufficient to cause deleterious impact on humans or their environments. Comprehensive analyses of specific isolation systems are needed to assess the expectations of meeting that objective. The Waste Isolation Safety Assessment Program (WISAP) has been established at the Pacific Northwest Laboratory (operated by Battelle Memorial Institute) for developing the capability of making those analyses.

During FY-1978 the work within WISAP involved five tasks, including the development of release scenario methodology, the development of release consequence methodology, studies on leach rates from candidate waste forms, studies on sorption of radionuclides by geological media, and assessment of public perceptions of the nuclear waste problem.

Task 1, the task developing the release scenario methodology, refined the list of potentially disruptive phenomena based on an improved understanding of the basic mechanisms. Various safety analysis methods were examined to determine their applicability to the needs of Task 1. Consultants continued to investigate potentially disruptive phenomena and the way in which these phenomena may interact with the geology surrounding a repository. The development of a first generation computer program for assisting in the analysis of disruptive scenarios continued in FY-1978 with the completion of a one-dimensional deterministic program. This pilot program demonstrated the potential feasibility of a combined deterministic/stochastic approach to breach scenario analysis. A second-generation code is under development which should handle a large percentage of the identified natural phenomena and facilitate the development of release scenarios.

During FY-1978, the measurement of leach rates from candidate waste forms by Task 2 was continued. Leach tests were conducted on glass doped with

actinides and technetium. Spent irradiated reactor fuel pellets with average exposures of 28,000 MWD/MTU were obtained and IAEA leach tests were initiated. Data received from the glass leaching tests indicate that varying solution compositions affects radionuclide release rates. Leach rates obtained for curium, plutonium and neptunium in simulated bicarbonate groundwater are a factor of ten higher than corresponding leach rates obtained in WIPP salt brine. In WIPP brine neptunium displays the highest leach rate followed by plutonium and then curium. However, for other solutions, curium has nearly the same or slightly higher release rates. The leach rates tend to decline by an order of magnitude after 20-30 days.

A continuous flow leach test was started at Lawrence Livermore Laboratories (LLL) using the same glass and solutions being used at PNL. Preliminary results show that flow rate has little effect at low temperatures (25°C), but a pronounced effect at higher temperatures (75°C). Flow rates varying from 7 to 216 m/year increase the radionuclide release by a factor of 10. Plutonium appears to exhibit complex behavior by having lower release rates at 75°C than at 25°C for a given flow rate.

Brookhaven National Laboratory has set up facilities for leaching actual transuranic waste forms. Upon receipt of Rocky Flat's incinerator ash, they will start leach tests paralleling those at PNL.

Leaching work on actual spent reactor fuel started in 1978 at PNL. To study higher temperature behavior of both spent fuel and glass, two systems of autoclaves were designed: (1) a set of three autoclaves for use with cold and doped waste forms was designed, received and installed, and (2) a second set of three autoclaves, including a 5 gallon size, were designed for hot cell use. This work compliments spent fuel leach studies performed at PNL since FY-1976 under sponsorship by Rockwell Hanford Operations.

During FY-1978, Task 3 work continued with the conversion, implementation, modification, documentation, and demonstration of hydrologic transport, and dose models for use in release consequence analysis. The following work was performed on the hydrologic models, PATHS, VTT, and DAVIS FE: (1) conversion and implementation of the codes and all associated auxiliary codes for use on

the PNL computer system, (2) interfacing the hydrologic code output with the transport code input, (3) verification runs with the models, (4) application of the models for demonstration release consequence analyses, and (5) initiation of model documentation, including user's manuals for each model.

A reconnaissance level release consequence analysis was performed for the bedded salt formation of the Paradox Basin during the last quarter of FY-1978. This work successfully demonstrated application of the WISAP hydrologic and transport models using site-specific data. Geologic and geohydrologic data for the Paradox Basin were used to simulate movement of groundwater and radioactive contaminants from a hypothetical nuclear reactor spent fuel repository after an assumed accidental release caused by a major seismic event (fault). The pathlines, travel times and velocity of the groundwater from the repository to the discharge locale (river) were determined after the disruptive event by use of a two-dimensional finite difference hydrologic model. The concentration of radioactive contaminants in the groundwater were calculated along a series of flow tubes by use of a one-dimensional mass transport model which takes into account convection, dispersion, contaminant/groundwater/rock interactions, and radioactive decay.

During FY-1978 various experimental techniques were evaluated by Task 4 using a wide range of geologic materials and nuclide-spiked waters to prepare recommendations for standard sorption measurement procedures. K_d values for each method were determined and evaluations made on precision, ease of use, time and cost, and limitations.

Methods currently being used include static (batch K_d), axial filtration K_d , flow-through column (crushed media), and flow-through contact core (whole rock and fissures). Research on channel chromatography K_d techniques has been terminated because of limited applicability and complicated data reduction needs. The static and dynamic methods for radionuclide-geologic media interaction studies are complementary. The static method is most useful for screening investigations of radionuclide behavior in a variety of systems and for estimating the time needed to attain equilibrium. To verify results, static radionuclide adsorption distributions may be compared to retardation factors

obtained from dynamic systems under similar conditions. Crushed or uncrushed material may be used in either method, and equilibrium solution compositions obtained from static tests may be used in dynamic experiments. The most urgent current need is for a quantitative method to relate K_d values obtained on disaggregated crystalline rock to actual core material containing heterogeneous fissures and cracks.

Although no one method of K_d determination can be identified as being superior, some of the past variability noted when comparing results from various methods have been identified as being related to solids-liquid separation techniques, tracer concentration and groundwater spiking technique, container sorption correction, and subtle changes in pH, Eh and groundwater compositions. Work to date has also led to standardization of more detailed characterization of rocks, groundwaters and experimental conditions, such that variability in K_d results may be better explained. Although a standard sorption method is not at present available, a standard protocol for media characterization and K_d reporting has been identified.

Another area in which our understanding is incomplete concerns the oxidation-reduction conditions to be expected in deep geologic repositories. Representative oxidation-reduction conditions have not been established for many systems under consideration, but most researchers agree that oxygen partial pressures will be low in the groundwaters near deep geologic repositories. Therefore, experiments under anoxic conditions have begun.

K_d values were evaluated statistically as functions of rock, groundwater, and nuclide characteristics. This work will be a continuing effort as more data become available for analysis. Preliminary predictor equations for K_d 's as functions of geologic and chemical conditions have been developed under a subcontract with Adaptronics, Inc. Although the derived relationships do not prove causation, they do allow prediction of trends. Thus, from K_d data on a limited number of rock, mineral, and water types, estimates can be made of K_d 's for other rocks and water environments not directly studied. The significant results of Adaptronic's work warrant the conclusion that modeling K_d values empirically as a function of geological and chemical characteristics can yield

sufficiently accurate empirical models. The parameters measured to describe the geologic media were shown to be statistically significant, and the ability to establish their interactions has been demonstrated.

More reliance on mechanism studies will be needed for extrapolation to situations not studied and for delineating the basic assumptions involved in migration simulation. Underlying assumptions are always involved in modeling efforts. Indeed, they frequently emerge as the key factors in assessing simulation results, such as done in a licensing process, rather than the output answers themselves. Also, extrapolation to geologic regimes not measured will inevitably occur, since all mineral combinations with all solutions under all physico-chemical conditions cannot be evaluated experimentally. For these reasons, mechanistic studies of the sorption/desorption processes will become essential for providing scientific defensibility for the assessments used for site qualification and licensing. Some work is underway to investigate the basic factors and their interactions that control the sorption/desorption processes of actinides, long-lived fission products, and activation products by geologic media. With a knowledge of mechanisms, migration rate predictions can be performed from a more theoretical and fundamental basis for any proposed storage environment. The use of theoretical and fundamental data may reduce the costs expended to quantify the migration rates of nuclides at specific sites.

Significant results on mechanisms to date show that ferrous iron bearing rocks (such as basalt and many granites), some shales, and a few evaporites can reduce significant percentages of nuclides such as Tc, U, Np and Pu. The reduced species of these elements are characterized by very low mobility and by rather irreversible exchange properties.

During FY-1978, Battelle's Human Affairs Research Center (HARC) completed five topical reports documenting work performed for WISAP Task 5 during FY-1977 covering various aspects of public perceptions and legal issues of nuclear waste management.

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INTRODUCTION

The objectives of the Waste Isolation Safety Assessment Program (WISAP) are to: 1) develop the capabilities needed to assess the post-closure safety of geologic repositories, 2) obtain scientifically defensible generic and site-specific data necessary for safety assessments, 3) provide, as needed, studies to further support these data and analyses, 4) demonstrate the assessment capabilities by performing analyses of reference sites, 5) apply the assessment methodology to assist the National Waste Terminal Storage Program in site selection, and 6) perform repository site analyses responsive to the time schedule and to the level of sophistication required to meet the licensing needs of the National Waste Terminal Storage Program.

Post-closure safety assessments will be required at differing levels of detail as the repository site selection, qualification, and licensing processes develop. Thus, the safety assessment program needs to continue to evolve to match the technical detail and sophistication of the assessment input required by the various site qualification and licensing stages. A post-closure safety assessment program must advance the state-of-the-art for assessment capabilities while providing, in a timely manner, the credible assessments required to evaluate specific geologic isolation systems.

There are two basic components of repository post-closure safety assessments:

- identification and analyses of breach scenarios and the pattern of events and processes causing each breach;
- identification and analyses of the environmental consequences of radionuclide transport and interactions subsequent to a repository breach.

The current scope of the Waste Isolation Safety Assessment Program is limited to long-term, post-closure analyses. It excludes the consideration of processes that are induced by the presence of the wastes that may affect the repository integrity, and it excludes the consideration of nuclear waste isolation other than geologic isolation repositories. The near-field/short-term

aspects of geologic repositories are being considered by ONWI/DOE under separate programs. They will be integrated with the WISAP methodology for future site-specific repository safety analyses.

During FY-1978, the Waste Isolation Safety Assessment Program was divided into a management task and the following five technical tasks:

- Task 1 - Release Scenario Analysis
- Task 2 - Waste Form Release Rate Analysis
- Task 3 - Release Consequence Analysis
- Task 4 - Sorption/Desorption Analysis
- Task 5 - Societal Acceptance Analysis

These tasks are designed to be integrated to produce the needed post-closure, long-term/far-field assessment methodology and site analyses.

Task 1, Release Scenario Analysis, utilizes geoscientist teams and mathematical models to identify and predict the events and processes which could potentially affect the repository integrity. This includes the analysis of the interactions and sequences of phenomena which could result in a loss of containment by the repository. Based upon the particular nature of a release sequence of phenomena, the condition of the geology surrounding the repository at the time of the breach will be determined as initial conditions for the consequence analysis. Thus, the functions of Task 1 are to:

- specify possible release scenarios;
- identify the sequence of events and processes which could lead to such scenarios;
- describe the state of the surrounding geology as initial conditions for consequence analyses.

The purpose of this task is to analyze nuclear waste repository release scenarios. Task 1 considers geologic events and processes, man-caused events and processes, and the impact of these on the integrity of the repository. Events, such as earthquakes, faulting and human-intrusion, and processes, such as erosion, uplift and diapirism, could alone or in concert significantly alter the geology surrounding the repository, leading to a loss of repository integrity. The output from this task will establish the conditions of the geology

and hydrology surrounding the repository at the time of an identified breach. Thus, Task 1 will provide the major geologic boundary conditions for input into the consequence analysis models of Task 3.

Task 2, Waste Form Release Rate Analysis, is investigating leaching rates and processes of radionuclide release from nuclear waste forms, providing essential source terms for radionuclide movement. These rates are of major importance to breach consequences because slower leach rates add time delays prior to the hydrologic transport of the radionuclide inventory. Such delays can be important factors in containment, especially for radionuclides of rapid or intermediate decay rates. Leach rates are dependent upon the characteristics of the waste forms and the extent physico-chemical conditions within the repository at the time of breach. The functions of Task 2 are to:

- simulate actual repository physico-chemical conditions during the leach rate measurement;
- perform leaching measurements on the anticipated waste forms, geomedias, and groundwaters of specific sites for utilization by Task 3 analyses;
- provide actual leachate solutions for Task 4 measurements;
- investigate the fundamental physico-chemical phenomena governing waste form leaching under repository conditions for the development of a model for prediction of long-term waste form behavior;
- develop mathematical relationships of waste leaching for incorporation into the Task 3 radionuclide transport models.

The purpose of this task is to measure and understand radionuclide release rates for waste forms anticipated for geologic isolation. At the present time, these waste forms include spent fuel, high level waste (HLW) glass and, for transuranics (TRU), concrete, bitumen, urea-formaldehyde and polymers. The activities necessary for the acquisition of data include the preparation and characterization of waste form samples, the measurement of leach rates of selected radionuclides using leaching solutions and physical parameters which span the range anticipated for waste repositories, the development of a data base from leach measurements, mechanistic/modeling studies for use by Task 3, and the preparation of leachate from actual waste forms for use by Task 4.

Task 3, Release Consequence Analysis, is utilizing groundwater and radionuclide migration models to simulate the pathways and transit times of each radionuclide to the biosphere, assuming that radionuclide geosphere transport would be primarily by water. For radionuclides reaching the surface, radiological dose models are used to compute exposures to humans and their environment. Thus, the functions of Task 3 are to:

- provide simulations of water movement through the geosphere from the repository proximity;
- provide simulations of the transport of radionuclides through the geosphere, driven by the water flow;
- provide source terms for the radiological dose models;
- predict anticipated radiological dose levels for humans and their environment based on the geosphere simulations.

The purpose of this task is to provide the capability for analysis of radiological consequences of a repository breach. This includes analysis of the transport of radionuclides from the repository proximity to the biosphere and computation of the individual and population doses resultant from the biosphere entry.

It is assumed that the movement of radionuclides through the geosphere would be primarily by water transport. Thus, the geosphere transport aspect of this task has two components: 1) the identification, through simulation, of the potential water pathways and transit times, and 2) the juxtapositioning of the actual radionuclide movement onto this hydrologic regime, taking into consideration factors affecting chain decay and transport. Added onto the output of these geosphere models are radiological dose models, so that three model sets are involved in this task. Additionally, within each model grouping are models of differing levels of complexity, so that the degree of model sophistication can be attuned to the adequacy of the data base for each particular analysis, and to the purpose of the analysis (e.g., preliminary planning, site selection, licensing of specific site). Thus, Task 3 currently provides a flexible capability for consequence analysis.

Task 4, Sorption-Desorption Analysis, is investigating radionuclide sorption processes. If radionuclides are actually released into a transporting groundwater, these may be sorbed by the geomeia which they contact. Irreversible sorption would act to remove the radionuclide from the water. Reversible sorption would act in a manner similar to waste form leaching, by providing time delays to the migration of radionuclides. Geomeia of sufficient sorption capability could provide isolation of the waste from the biosphere by extending transit times to very long periods of time. As with leaching, sorption/desorption by geomeia is dependent upon the specific radionuclide involved and the physico-chemical characteristics of the geomeia and transporting solutions. The functions of Task 4 are to:

- determine the fundamental phenomena governing sorption/desorption of radionuclides by geomeia;
- provide measured values of sorption distributions for specific nuclides and media;
- develop predictive equations for sorption distribution extrapolations for non-measured situations.

Task 5, Societal Acceptance, concluded its activities within WISAP during FY-1978. This task was performed under auspices of the Battelle Human Affairs Research Center (HARC) in Seattle, Washington. During FY-1978, HARC completed several reports on studies of public perception and institution aspects of nuclear waste management performed during FY-1977.

In July 1978, a Management Task was created to provide overall management coordination to the five task efforts. The functions of this task are to:

- provide fiscal project control and management, and program planning;
- provide technical coordination across the tasks;
- provide a centralized communication link with DOE and the Office of Nuclear Waste Isolation (ONWI);
- provide communications and coordination with site Geological Project Managers (GPM) and Repository Project Managers (RPM);

- enhance interfaces of WISAP with other research and development efforts (e.g., near-field methodology, in-situ testing);
- implement the quality assurance (QA) program as specified by the WISAP QA Plan;
- provide integration of WISAP efforts with requirements for site selection and licensing.

The project management task provides the coordination of the diverse activities among the technical tasks. To meet this objective, this task monitors each of the other tasks and continuously analyses all ongoing WISAP activities with respect to their need. This task thus provides the integration of the overall WISAP effort with the requirements for site selection, qualification, and licensing.

The creation of the management task coincided with the transfer of control from the Office of Waste Isolation (OWI), operated by Union Carbide for the Department of Energy, to control by the Office of Nuclear Waste Isolation (ONWI), operated by the Battelle Memorial Institute. Simultaneously, WISAP was assessed by an in-depth, formal review by the WISAP Review Committee. The WISAP Review Committee Report by Kehnemuyi, et al. (1978), provided significant guidance for program planning for FY-1979 and subsequent years. The performance of the exercise of the consequence analysis methodology for the Paradox Basin reference bedded salt site, in response to a Review Committee request, marked the termination of the initial phase of WISAP. Specifically, WISAP concluded during FY-1978 its sole orientation towards methodology development and initiated the transition towards site applications.

TASK 1 - RELEASE SCENARIO ANALYSIS

INTRODUCTION

The purpose of the Release Scenario Task (Task 1) is to develop a methodology that analyzes how changes in a geologic system might result in a failure of the integrity of a geologic repository. This methodology, called Release Scenario Analysis Methodology (RSAM), has as its primary objectives:

- identification of phenomena that, alone or in concert, could perturb in a significant way the geologic system surrounding a repository
- determination of quantitative bounds for the types, magnitudes, and rates of such phenomena
- formulation of a methodology for analysis of the relationship of these phenomena to the containment capability of the repository
- analysis of these phenomena to provide a parameterization of the processes and their interactions
- formulation of a semi-empirical, quantitative methodology to estimate the occurrence probabilities of various repository failures and the changes in the geologic and hydrogeologic system induced under these failures.

The total set of variables that should be considered forms a highly coupled and, in most cases, a poorly understood system. Time is a key parameter in any RSAM analysis. The reference time period for RSAM is in the order of 10^6 years after final sealing of the repository.

A repository breach is defined as a non-zero nuclide flux from the repository proximity. To compute the movement and concentrations of this flux, the release time, decay rates, pathlengths, permeabilities, effective porosities, hydraulic gradients, thermal gradients, and density gradients of the geosystem must be estimated. The RSAM is designed to analyze how these parameters can change over time and to assess how the geologic and hydraulic systems can vary over the next 10^6 years, the probabilities of such variation, the minimum times required to initiate variations, and the rates at which these can proceed.

Estimating defensible occurrence probabilities for each single phenomenon and for various combinations of phenomena is an exceedingly difficult task because of the current limited understanding of the geophysical and geochemical system within which the repository is to be placed. Certainly, long-term prediction of system behavior is beyond the capabilities of current technology. However, we can hypothesize various scenarios, attempt to characterize the system's response to these disruptive event chains, and then provide bounding estimates of source data for analyses of the consequences of scenarios in terms of contaminant releases to the biosphere.

The primary mission of the Release Scenario Analysis Task is to facilitate understanding of how disruptive phenomena might change or perturb the geologic and hydrologic systems. In FY-1977, the first year of work on Task 1, many disruptive phenomena were identified and some were selected for further study. A group of experts in geology and related fields was assembled to help identify and study these phenomena. The identification, description, and evaluation of various safety analysis methods was begun at that time. The concept of a repository simulation computer model was also defined in FY-1977.

During FY-1978, the list of potentially disruptive phenomena was refined based on improved understanding of these phenomena; the phenomena are listed in Table 1.1. Safety analysis methods were examined to determine their applicability to the needs of Task 1. This analysis is described briefly in the Scenario Analysis Methodology section. During FY-1978, consultants continued to investigate potentially disruptive phenomena and the way in which these phenomena may interact with the geology around a repository. A brief discussion of the results of these studies is given in the Consultant Studies section.

The development of a computer program for assisting the analysis of disruptive scenarios continued in 1978, and a first generation, one-dimensional program was completed. This program demonstrated the potential feasibility of such an approach to failure scenario analysis, and is discussed in the Repository Simulation section.

TABLE 1.1. Potentially Disruptive Phenomena for Nuclear Waste Repositories

Natural Phenomena	Man-Induced Phenomena	Waste-Induced Phenomena
<ul style="list-style-type: none"> *Climatic fluctuations *Glaciation *Denudation and stream erosion Magmatic activity <ul style="list-style-type: none"> • Extrusive • Intrusive Epeirogenetic displacement <ul style="list-style-type: none"> • Igneous emplacement • Isostasy Orogenic diastrophism <ul style="list-style-type: none"> *• Near-field faulting • Far-field faulting • Diapirism • Diagenesis Static fracturing <ul style="list-style-type: none"> • Surficial fissuring *• Impact fracturing *• Hydraulic fracturing *Meteorites *Dissolutioning *Sedimentation *Flooding Undetected features <ul style="list-style-type: none"> • Faults • Breccia pipes • Lava tubes • Gas or brine pockets • Shear zones 	<ul style="list-style-type: none"> Improper design/operation: <ul style="list-style-type: none"> • Shaft seal failure • Improper waste emplacement Undetected past intrusion: <ul style="list-style-type: none"> • Undiscovered boreholes or mineshafts Inadvertent future intrusion: <ul style="list-style-type: none"> • Archeological exhumation • Weapons testing • Nonnuclear waste disposal • Resource mining (mineral, hydrocarbon, geothermal, salt) • Storage of hydrocarbons or compressed air Intentional intrusion: <ul style="list-style-type: none"> • War • Sabotage • Waste recovery Perturbation of groundwater system: <ul style="list-style-type: none"> • Irrigation *• Reservoirs *• Artificial recharge <ul style="list-style-type: none"> • Establishment of population center 	<ul style="list-style-type: none"> Thermal loading (stress) <ul style="list-style-type: none"> • Differential elastic response • Non-elastic response • Fluid pressure changes • Fluid migration • Canister migration Geochemical alterations Waste-rock interactions

* Indicates those phenomena being studied in a pilot program developed during FY-1978.

SCENARIO ANALYSIS METHODOLOGY

To analyze the potential modes for breach of a nuclear waste repository, an appropriate methodology for analysis must be chosen. Researchers selected several possible approaches for analysis and evaluated each of them on the basis of the criteria that follow. The analysis method should:

- be quantitative and scientifically based
- model the potential disruptive events and processes
- model the system over time through the failure event in sufficient detail to provide input to a subsequent consequence analysis
- be compatible with the currently foreseeable level-of-knowledge of system data and understanding of the operative events and processes.

Possible analytical approaches were reviewed for their applicability for the WISAP scenario analysis, using these criteria. The approaches reviewed were expert opinion, perspectives analysis, fault tree/event tree analysis, classical systems analysis, Markov chain simulation, and Monte Carlo simulation. These analysis methods were chosen for review because of their potential suitability for the requirements of the WISAP scenario analysis.

Expert opinion is an assessment technique that uses a body of recognized experts to perform the analysis based on the professional judgment. As such, there are elements of subjectivity associated with the expert opinion method. Nevertheless, we concluded that the WISAP scenario analysis can profit by incorporating expert opinion where scientifically quantifiable data are unavailable, and where geologic processes and events and their interactions are poorly understood.

Perspectives analysis is a qualitative method for comparing a poorly understood attribute of a given activity with a similar, but better understood, attribute of some other activity. Inherently, this approach is nonquantitative but it can be made semiquantitative by developing a set of indices against which a number of well understood activities that bracket the poorly understood activity may be compared. Our general conclusion regarding

perspectives analysis was that this method would be ill-suited for the total WISAP scenario breach analysis, but the method may have limited applications within the overall analysis.

Fault trees and event trees are mathematical logic modeling systems that analyze the failure modes or possible fates of a system. The strength of these approaches is the deductive or inductive reasoning on which they are based. When applied to WISAP, however, they have a limited ability for dealing with time-dependent processes and multi-state situations. We concluded that for WISAP repository breach scenario analyses, a combined fault tree/event tree approach would be useful in an early model-design function.

Classical systems analysis is the deterministic prediction of system behavior using governing equations derived from appropriate laws of nature. Suitable approximation to the exact equations can often lead to adequate analyses of very complicated systems. However, the equations governing most geologic processes and events are not known. Therefore, classical systems analysis was not judged to be suitable for overall analysis of repository breach.

Markov-chain analysis is a set of stepwise analytic procedures that can reduce a system of many random events into a single stochastic relationship. The Markov-chain method, in its simplest form, is not well-suited to analysis of continuous processes nor to interacting processes and events. More sophisticated Markov-chain approaches could be developed but, because of the complicated mathematical structure and the resulting difficulty in communicating the complex structure among disciplines, the technique was considered unsuitable for WISAP.

Monte Carlo simulation is an analysis method that replaces an analytical approach with a probabilistic approach for the solution of complicated problems. As such, it is particularly well-suited for use when analytical relationships are unavailable, which is the case for most geologic events and processes. For this reason, Monte Carlo simulation was chosen as the method to be used for development of the first generation simulation model.

The scope of the Monte Carlo simulation model requires the integration of additional analysis methods that will include the use of expert opinion in selecting the geologic events and processes to be considered. Fault trees/ event trees will probably play an important role in developing the logic describing the internal interactions of the various events and processes. Expert opinion will also be used throughout the analysis to analyze the simulation results and make recommendations for future model improvements and refinements.

We have briefly outlined the basic methodology that was selected to be used in a first generation computer simulation model. The methodology which was used in this first generation model is not fixed. As the quantification of geological processes and events is refined and the sensitivity of these processes to the overall WISAP consequence analysis is better outlined, the simulation model will evolve. While doing so, it may assume a character quite different from the initial concept and use some different and/or additional analysis methods.

CONSULTANT STUDIES

Task 1 of the Waste Isolation Safety Assessment Program (WISAP) is charged with developing a methodology that assesses the factors, both geologic and man-caused, which may result in the failure of a nuclear waste repository. As a first step in the methodology development, experts in various fields of geology and human activity were asked to provide information concerning natural or man-caused events that might lead to a repository breach. The information requested included geologic processes that could directly or indirectly cause a repository breach; rates and magnitudes for these processes; and estimates of the probability of occurrence of these processes. The following paragraphs provide a brief synopsis of each of the reports prepared by the WISAP consultants.

During FY-1978, Task 1 engaged the services of sixteen consultants to investigate the phenomena and issues identified during the previous year. Task 1 convened a workshop in June 1978 in Seattle during which the consultants

discussed their Task 1 efforts. This section of the report presents a brief description of the consultant research including their conclusions. More detailed reports on these studies are being prepared for publication.

Geomorphology and Surface Hydrology of the Pacific Northwest (D. Tubbs, University of Kansas)

The rates and probabilities of selected geomorphologic and hydrologic processes and events in the Pacific Northwest were investigated by Dr. Donald Tubbs. Three general topics were considered in this study: 1) determination of rates of denudation, 2) estimation of the probabilities of flooding, and 3) landslides. Denudation rates presented in his report vary from 0.25 m/100 yrs to 3.35 m/100 yrs depending on the geomorphologic conditions used in determining the rates. Several types of floods are discussed including floods caused by precipitation and snow melt, and floods caused by glacial effects. The author indicates that landslides may present an indirect hazard to a waste repository because landslides may be considered a source of seismic energy.

Preliminary Subsurface Hydrologic Considerations of the Columbia River Plateau (M. Veatch, Shannon and Wilson, Inc.)

The hydrologic conditions related to the Columbia River Plateau physiographic province, and specifically to the Pasco Basin were studied by Dr. Maurice Veatch. His report describes the general geologic and subsurface hydrologic conditions of the Plateau and then focuses to a specific description of the subsurface hydrologic conditions in the Pasco Basin. Four conceptual hydrostratigraphic systems are described in the discussion of subsurface hydrologic conditions of the Basin. The four systems are: 1) the unsaturated zone, 2) the unconfined aquifer, 3) the uppermost confined aquifer, and 4) the lower Yakima basalt hydrologic sequence. In conjunction with the description of the four hydrostratigraphic systems, a conceptual layered earth model is presented. It provides a basis for comparing the potential effects of geologic disruptive phenomena on a waste repository located in the geologic media of the Columbia Plateau.

Structural Geology of the Gulf Coast (R. Kehle, Turk, Kehle, and Associates)

A study on the tectonic framework and history of the interior region of the Gulf of Mexico was performed by Dr. Ralph Kehle. His report presents a short geologic history of the area followed by a description of late mesozoic and tertiary structural activity. Although structural activity is continuing, it is aseismic and thus presents little hazard to human endeavor. The boundary fault system is discussed resulting in a conclusion that this fault system is unlikely to be reactivated in the future because no driving mechanism for fault activity is apparent. A discussion of subsidence of the Gulf of Mexico region indicates that differential subsidence in this region has been evidenced throughout its history but that the potential for damaging earthquakes is judged to be remote. A theory for salt dome development in this region is presented along with a conclusion that the salt domes in this region display no potential for subsidence and are judged to be acceptable waste sites because no potential for subsidence-related seismic activity exists.

Meteorology (G. Kukla, Lamont-Doherty Geological Observatory)

Before presenting his final Task 1 report, Dr. George Kukla held a workshop in Reno, Nevada on 16/17 July 1978, during which past climates and climatic events in North America were discussed. This workshop provided Dr. Kukla with a larger framework of knowledge upon which to base his Task 1 research. Dr. Kukla studied the probability of expected climate stresses for the next one million years in North America. Earth climate history, including rates of change, and climate-relief interactions are described, and the probability estimates of future climates were obtained. Probability estimates of future climate related stress events in western North America were calculated. Events with the largest disruptive potential relate to changes in precipitation, evaporation and runoff; with event impact being dependent on site location. Probability estimates are given for the development of technology which could result in climate changes initiating a catastrophe.

Volcanology and Igneous Intrusion (B. Crowe, Los Alamos Scientific Laboratory)

The potential effects of volcanism and igneous intrusion on a nuclear waste repository was studied by Dr. Bruce Crowe. Three basic questions are

addressed by this report: 1) what is the range of consequences of disruption of a radioactive waste repository by volcanic activity? 2) can a repository site be selected to reduce the risk of disruption by future volcanic activity? and 3) can a geologically reasonable procedure be developed for calculating the probability of volcanic disruption of a waste disposal site? The main variables affecting an evaluation of the consequences of repository disruption by volcanic activity are the geometry of the magma-repository interaction and the nature of the volcanism. Careful repository site selection will reduce the risks of repository breach by volcanic processes. His report states that determining a rate of volcanic activity is beyond the current state-of-the-art in volcanology, but that a numerical evaluation of the areal extent of volcanic disruption for a designated region is possible. Simplified probability calculations are attempted for areas of past volcanic activity.

Geomorphology and Surface Hydrology of the Southwest (S. Mara, Stanford Research Institute, International)

The geomorphology of the Gulf Coast and Southwest was investigated by Ms. Sue Mara of the Stanford Research Institute. The rate, duration, and magnitude of changes caused by geomorphic processes and events in the Southwest and the Gulf Coast over the next million years are projected. A geomorphic description of the study areas is presented together with the Quarternary geomorphic history of the areas. Long-term estimates of continuous geomorphic processes (e.g., denudation, aggradation, entrenchment) are given, as are long-term estimates for the occurrence rates of certain catastrophic events (e.g., landslides, flooding, volcanic ashfall). Regarding the geomorphic processes, denudation was found to be an important mechanism of overall basin lowering, entrenchment will occur in the major river basins, and aggradation will occur in the Gulf Coast during the waning stages of glaciation. Conclusions concerning the catastrophic events for the study areas were that catastrophic floods are not expected to occur in the two study areas, landslides may occur in the Southwest but should be of small impact when compared to regional denudation, and ashfalls may lead to significant increases in erosion rates.

Structural Geology of the Pacific Northwest (H. Coombs, University of Washington)

Dr. Howard Coombs of the University of Washington was asked to provide information on the structural geology of the Columbia Plateau in regard to selecting a site for radioactive waste disposal. His report describes the folding and faulting that has taken place during the past several million years, thus providing background for the general stress conditions of the area and giving clues as to the mechanism of deformation. Some of Dr. Coombs's conclusions are: 1) the time interval of significant deformation of the Columbia Plateau was between 4 and 8 millions years ago; 2) basining of the Plateau occurred on a broad scale at the time the basalts poured out and may still be occurring on a very small scale; and 3) the maximum tectonic stress is essentially in a north-south direction in the area of the Yakima Ridges, with the greatest yielding to stress having occurred northwest of the Pasco Basin in the Manostash and Umtanum Ridges.

Groundwater Hydrology of the Southwest (S. Davis, University of Arizona)

The hydrologic effects of natural disruptive events on nuclear repositories located in the Southwest were studied by Dr. S. Davis. The most probable disruptive events which might affect groundwater flow patterns include faulting, dissolution of rocks, miscellaneous fracturing, and rapid changes of the groundwater regime. These events are placed into four geologic settings within this report, including: 1) interior salt domes of the Gulf Coast, 2) bedded salt, 3) argillaceous rocks, and 4) granitic rocks. Dr. Davis discusses the porosity and permeability of natural geologic materials and the changes in these two parameters that might occur as a result of a disruptive event.

Man-Caused Events (R. Gastil and B. Smernoff, Freedom House, Hudson Institute)

Drs. Raymond Gastil and Barry Smernoff provided some possible answers to the question of how future human activity might affect the safety of a nuclear waste repository. Social, biological, and historical data concerning human activity was gathered to provide background for predictions of future activity.

Based on the background data, Drs. Gastil and Smernoff propose a future characterized by spiraling economic and technological progress along with recurring periods of retrogression. The report notes that the most probable human intrusions into the repositories would be associated with natural resource development, construction of underground facilities, or non-nuclear waste disposal. Probabilities for repository breach by human intrusion are given with the qualifier that the probabilities should be adjusted for site specific evaluations.

Structural Geology of the Southwest, WIPP Area (J. Hills, University of Texas, El Paso)

This study by Dr. John Hills assesses the subsurface geological factors that might affect the stability of southeastern New Mexico and specifically the Waste Isolation Pilot Plant (WIPP) site in New Mexico. Assumptions include: 1) a time frame of the next one million years and 2) little movement of the North American Plate. The following conclusions are noted in this report.

1. Southeastern New Mexico east of the Pecos River is a tectonically stable area with no major fault movements for the past 250 million years. No major tectonic adjustments are expected in the next million years.
2. Minor adjustments during Triassic time (200-800 million years ago) and Early Tertiary time (70 million years ago) have resulted in deepening and eastward tilting of the Delaware basin and the solution of the upper part of the Salado salt. This effect has been most severe on the west edge of the basin near the Pecos River and in the southeast edge of the basin adjoining Winkler County, Texas.
3. Recent minor seismic activity is probably the result of secondary petroleum recovery operations. This activity may result in the relief of strain and contribute to the long term tectonic stability of the area.
4. The clearest danger to the WIPP site is that during a future glacial stage the Pecos River may migrate to the vicinity of the site. The river underflow might then dissolve salt from the Salado Formation resulting in faulting and brecciation of the remaining anhydrite and clastic beds of

the formation. A 300-foot thick salt bed is present in the Castile formation 1200 feet below the base of the Salado and at about a depth of 4000 feet below the surface at the WIPP site. This salt seems reasonably secure from the solution process.

Remote Seismology, (L. Wight, TERA Corporation)

The potential earthquake hazard to an underground waste repository was analyzed by Lawrence Wight of TERA Corporation. This report's objectives were to evaluate qualitatively the overall possible effects of earthquakes on the repository, and also to develop a preliminary methodology for specifying repository seismic design criteria. The approach to accomplishing these objectives was to build upon the convenient (and physically appropriate) classification of earthquake effects into vibratory and fault displacement hazards. The report's conclusions are that:

1. The risk associated with intense vibratory shaking of a well-designed repository is essentially negligible.
2. The specification of an appropriate seismic vibratory design criterion could best be accomplished with a Bayesian seismic hazard assessment using geologic slip rates as input.
3. The risk associated with fault displacement is very site-specific and dependent on the host geologic media and its permeability changes in response to fault displacement.
4. The hazard of faulting through a repository in its million-year design life is rather high, principally because of a high probability of primary or secondary faulting on undetected faults.
5. The faulting hazard can be minimized by deploying sophisticated site certification programs (high resolution microseismic surveillance seems to us to be most appropriate).

Glaciology (C. Bull, Ohio State University)

Glaciological parameters and their possible effects on a nuclear waste repository were studied by Dr. Colin Bull. This study was assisted by a workshop convened by Dr. Bull in Columbus, Ohio on 12/13 May 1978. Dr. Bull

concluded that the possibility of worldwide glaciation is small but that abundant evidence exists which shows that the quantity of ice on earth has varied over the last million years, with cycles of glaciation being apparent for the last 600,000 years. An assumption was that variations in ice cover will continue into the future accompanied by global sea-level changes. Glacial erosion rates were determined, as were limits on ice loading and subsequent subsidence of North American land masses. Dr. Bull concluded that permeabilities of earth materials below the ice sheet, at equivalent elevations relative to a fixed datum, should not be affected by the ice loading and subsidence. Other topics discussed in Dr. Bull's report are groundwater recharge under glacial conditions, isostatic rebound rates, and the correlation of continental glaciation episodes to harmonic analysis.

Meteorites (W. Hartman, Planetary Sciences Institute)

Long-term meteorite hazards to buried nuclear waste materials were studied by Dr. William Hartman. The main thrust of this study was to put into analytic form information on the frequency of meteorite impact events which are large enough to affect buried wastes. Dr. Hartman's report presented data on the relation between meteorite crater size and total impact energy. An equation was derived which yields the rate of accumulation of area covered by a crater larger than diameter D , and a graphical relation between D and the depth of disturbance was determined. Dr. Hartman's report notes that meteorite impacts are also a source of seismic disturbance and he gives a methodology for including this type of seismic disturbance into a seismic model. This report also presents a methodology for dealing with repositories of extended surface area.

Structural Geology of the Southwest Basin and Range Province (E. Lovejoy, University of Texas, El Paso)

Dr. Earl Lovejoy of the University of Texas at El Paso studied the Basin and Range Province of Nevada and Utah and developed a new model of tectonogenesis for the Basin and Range Province. Dr. Lovejoy's report first presents a discussion of the "classic" interpretations and theories of Basin and Range tectonics. He then summarizes his evidence for a temporal history of the Basin and Range and proposes a new tectonic model. Based upon this model,

Dr. Lovejoy presents predictions and probabilities for earthquake activity in the Basin and Range province for the next one million years. Major conclusions of this report are:

1. Important seismic activity in the next one million years will be restricted to the Intermountain Seismic Belt.
2. Minor seismic activity in the same period will be restricted to the Nevada Seismic Belt, Sierra Nevada front, and Reno-Yellowstone lineaments.
3. There will be seismic activity in the same period in the rest of the Basin and Range province except locally along high mountain frontal fault zones where isostatic unloading will produce slow, secular, mild seismic activity for many millions of years to come.

Coastal Geomorphology and Sea Level Fluctuations (M. Schwartz, Western Washington University)

Sea level characteristics and their possible changes over the next one million years were analyzed by Dr. Maurice Schwartz. As a continuation of earlier efforts to outline past, present, and, possibly, future sea levels, a Sea Level Prediction Symposium was convened by Dr. Schwartz at Western Washington University in Bellingham, Washington on 31 August 1977. This symposium supplied technical information which Dr. Schwartz incorporated during the course of his Task 1 research.

Dr. Schwartz's report indicates that the overall lowering of sea level that has occurred worldwide since the end of the Cretaceous period can be attributed to subsidence of the global ocean floor and midocean ridges, and the accompanying decrease in plate-tectonic activity during this time. If the trend of sea-level lowering continues for the next one million years, then a reduction in the world sea level of 3-6 meters is projected. Included in Dr. Schwartz's report were notes on the Sea Level Prediction Symposium, convened by the author at Western Washington University, at which sea erosion-deposition characteristics and sea-level change parameters were discussed.

REPOSITORY SIMULATION

Repository simulation is an evolving methodology designed to provide information about the release scenario question. It is basically a departure from classical risk assessment methodologies such as fault and event tree analyses or expert opinion sessions. However, it uses fault trees in the development of phenomena chains or scenarios and relies on expert opinions for:

- establishing system response rules
- providing input data distributions
- analyzing the output.

Repository simulation is a computer tool designed to assist the user in studying release scenarios. Furthermore, it permits the expansion of the data base as more individuals use it.

There are a number of factors which have to be considered in developing a computer-based methodology for analyzing repositories, including:

- The disruptive events or release scenarios have nonzero but, in general, exceedingly low occurrence probabilities.
- Estimates of occurrence probabilities are very difficult to defend.
- The time that a "breach" might occur must be specified so that the nuclide inventory in the repository can be determined.
- The geological and hydrological system at any given site may significantly change in the future without affecting the repository and its contents.
- The significant impact on the repository of a disruptive process might be manifested tens or hundreds of thousands of years after the process begins.
- Consequence analyses based on accidents or release scenarios occurring hundreds of thousands, or millions, of years in the future must consider the potential for system changes and not conduct the analysis based on the geological and hydrological conditions as they exist today.
- Predictions are not currently possible, but bounding of the magnitudes and rates of possible system perturbations may be achievable through sensitivity analyses.

- The synergism or phenomena coupling is so complex that computer techniques may be required to augment the decision process of the geoscience community.

Much has been said about the length of time radioactive wastes might be considered hazardous to man (Serne 1979, Barney and Anderson 1978). Estimates, based on various assumptions and relative comparisons, range from hundreds of years to millions of years. The time frame on which a safety assessment methodology must be applied greatly affects the type of methods, tools, and data required for a study. Repository simulation is being developed in Task 1 for the case where long time frame studies are deemed necessary for repository safety analysis. The Release Scenario Analysis Task has directed its efforts at analyzing the 10^6 to 10^7 years after closure of the repository.

Whatever approach is selected for final site analyses, the approach must fulfill certain basic requirements. It must be able to address the long time frame and yet rely only on available data. A coupled mechanistic systems analysis model incorporating such factors as tectonics, dynamic fracturing, and sophisticated fluid flow calculations would be ideal, but is not within current technological capabilities. The approach must be auditable and must identify inherent uncertainties in the analysis. It must permit analysis of disruptive event interactions and facilitate parametric sensitivity studies. The methodology should estimate breach frequencies and establish limits on such site characteristics as hydraulic potentials and conductivities, flow paths, and post-closure time of disruption. Finally, the methodology should assist in focusing the thinking of the user and provide bookkeeping of diverse sets of theories and data. Thus, the methodology must be flexible enough to incorporate numerous revisions as the state-of-the-art changes.

THE PILOT PROGRAM

During FY-1978, a preliminary version of the Repository Simulation code was completed and tested. The code, the Pilot Program, is only one-dimensional and is primarily designed to demonstrate the stochastic methodology and to be a resource for the team of consultants charged with the responsibility of

developing improved submodels that characterize the various phenomena identified in Table 1.1. None of the information generated in FY-1978 concerning geological or hydrological phenomena is included in the Pilot Program, rather, the pilot model is primarily based on FY-1977 information.

A fundamental step in the release scenario methodology is the development of a layered-earth model (LEM) for the repository site in question. It is currently not possible to develop a single model applicable to all geologic conditions, due to the limited quantitative knowledge of geologic phenomena and the extreme differences between geologic media. For the initial model development, conditions representative of the Columbia Plateau basalts were selected due to the familiarity of PNL researchers with the geology. An example LEM for a hypothetical layered-basalt site is shown in Figure 1.1. Necessary parameters for each layer in the model include, but are not limited to, thicknesses, relative elevations, hydraulic conductivities, hydraulic potentials, effective porosities, rock strengths, deformation moduli, existing fracture distributions, effective stresses, thermal properties, and lithologic characteristics.

Figure 1.2 portrays the conceptual logic flow in the Pilot Program computer code. Three qualifications are important:

- 1) At each time step (e.g., each 100 years) the characteristics of the layered earth model are updated based on the programmed response to the various ongoing phenomena. For example, if the surface is flooded, the vertical recharge and fluid potentials are adjusted accordingly. If the state of stress and rock properties are such that fracturing is induced, these system permeabilities are adjusted. A breach is flagged when the parameters of the system are such that the transport of nuclides from the repository proximity is initiated.
- 2) Initiating and coupling probability distributions for each individual phenomenon and associated distributions for process rate, magnitude, and delay time must be supplied by the user. Selections from these distributions are based on Monte Carlo routines.
- 3) At the conclusion of any given case history, the complete system is reinitialized and a new case history is developed.

GENERAL LITHOLOGY	LEM UNIT NUMBER	LEM LAYER THICKNESS (METERS)	LAYERED EARTH MODEL (LEM)	HORIZONTAL CONDUCTIVITY (MILLIDARCIES)	VERTICAL CONDUCTIVITY (MILLIDARCIES)	GROUNDWATER HEADS (METERS BELOW SURFACE)
LOSE SILT SAND AND GRAVEL	1	125		2000.0	200.0	40.0
CEMENTED SAND AND GRAVEL	2	200		1000.0	100.0	40.0
BASALT	3	300		0.13	0.13	52.0
SEDIMENTARY INTERBED	4	25		300.0	30.0	43.0
BASALT	5	250		0.013	0.013	55.0
SEDIMENTARY INTERBED	6	25		1330.0	133.0	43.0
BASALT	7	100		0.013	0.013	52.0
SEDIMENTARY INTERBED	8	25		1330.0	133.0	44.0
BASALT	9	m		0.013	0.013	61.0

FIGURE 1.1. LEM for Layered Basalt

FIGURE 1.2. Conceptual Logic Flow Diagram

Repository simulation progress to date includes: 1) development of a pilot repository simulation program, 2) preliminary use of the code for a hypothetical site at Hanford, and 3) initial conceptual development of submodels and preliminary data acquisition for a second-generation code.

Realistic but hypothetical data for a layered-basalt site were used for the pilot program. Table 1.2 summarizes the input to the Pilot Program and Figure 1.3 presents the somewhat innocuous output. Based on the simple nature of the pilot model and the limited data set, the only observed perturbation to the local geology and hydrology over the 10^6 year simulation period was a slow, unspectacular erosion modified by some surface flooding. Specifically, the erosional pattern first showed relatively rapid removal of material from the site when the elevation difference between the ocean and the site location was great. However, the erosion started to plateau at about 200,000 years. At about 300,000 years, the first flooding by the sea occurred, marking a change in the erosional pattern to a stable oscillatory-like pattern of erosion and sediment deposition. Superimposed on the total overall pattern were periods of extreme erosion caused by catastrophic flooding from glacial ice dam failures. Several of these floods are represented in Figure 1.3 by relatively sudden changes in the slope of the curve. No fracturing, faulting, or other breach-inducing phenomena were generated.

However, the following statement cannot be over-emphasized: These test cases were run for edification and illustration only and have limited relevance to the real world. The pilot program is too embryonic at this stage and does not incorporate most of the information generated by the WISAP research team or the support group of sixteen consultants during FY-1978. The bulk of this information will be incorporated into an advanced version of the model scheduled for completion in FY-1979.

Conceptual Plans for the Second Generation Code

The pilot program was primarily designed for illustrative purposes, and was developed simultaneously but independently of the consultant efforts during FY-1978. The code, which is basically one-dimensional, incorporates only a

TABLE 1.2. Some Example Input Data for the Pilot Model (Layered Basalt)

Variable	Units	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7	Layer 8	Layer 9	Comments
Elevation	(m)	125	0	-200	-500	-525	-775	-800	-900	-925	
Thickness	(m)	125	200	300	25	250	25	100	25	2x10 ⁴	
Lithostatic stress	(bars/m)	14	50	104	140	170	201	214	228	2431	(0.22 bars/m)
Lateral stress	(bars/m)	14	50	100	120	130	140	150	200	2600	Devictoric plots (Coombs)
Fluid pressure	(bars)*	3	20	46	65	79	96	102	109	1209	(0.11 bars/m), head differences ARCHO ST-137
Vertical perm.	(md)	200	100	.13	30	.013	133	.013	133	.013	ARCHO ST-137 report 1m/day=1.33 Darcys
Horizontal perm.	(md)	2000	1000	.13	300	.013	1330	.013	1330	.013	ARCHO ST-137 report
Ice load	($\frac{\text{bars}}{\text{m of ice}}$)	.09	.09	.09	.09	.09	.09	.09	.09	.09	If in contact with water table
Water load	($\frac{\text{bars}}{\text{m of H}_2\text{O}}$)	.11	.11	.11	.11	.11	.11	.11	.11	.11	If in contact with water table
Normal fault	(md)	0	500	1x10 ²	200	1x10 ²	200	1x10 ²	200	1x10 ²	Incremental
Reverse fault	(md)	0	250	1x10 ¹	100	1x10 ¹	100	1x10 ¹	100	1x10 ¹	Incremental
Hydraulic fracture	(md)	0	500	1x10 ²	200	1x10 ²	200	1x10 ²	200	1x10 ²	Incremental

* HEAD 40 40 52 43 55 43 52 43 61.
(Water depth in meters below land surface.)

FIGURE 1.3. Example Output of Surface Erosion

limited number of natural phenomena, and neglects some potentially important ones, e.g., fracturing at the periphery of continental ice sheets, undetected fault rupture, and small-scale fracturing associated with earthquake swarms.

The output of the pilot program has little relevance to the real world, but handles a few of the identified natural phenomena to illustrate the methodology. The second generation program, however, should facilitate the development, if necessary, of release scenarios and bound the initial conditions, e.g., pathlengths, hydraulic conductivities, hydraulic potentials, and time necessary for the more sophisticated geosphere transport codes.

Development of a second-generation code is planned which will be two-dimensional, and which will incorporate an elemental incremental area grid. Some examples of potential additions to the code being developed for a repository located in layered basalt are listed below:

- sensitivity zones (maximum influence zones)
- revised coupling of climate and glaciation
- ice sheet margin fracturing and pressurized recharge
- surface water body recharge and perturbations to the hydraulic potentials
- magmatic activity
- far field faulting and mismatch of acoustic impedance of a borehole plug with surrounding rock
- earthquake swarms and induced permeability changes
- surficial fissuring caused by differential material loading or unloading
- rupture on undetected faults
- fracture "healing"
- anticlinal uplift
- undetected breccia pipes or lava tubes
- man-caused phenomena.

Near-field effects (the thermo-mechanical and geochemical response of the rock matrix and the interstitial fluids caused by thermal or mechanical loading and subsequent unloading) will not be studied, although provision for inclusion of these at some later date will be made. Consideration of these questions is being deferred pending a state-of-the-art assessment of the knowledge in this area by the Office of Nuclear Waste Isolation (ONWI).

TASK 2 - WASTE FORM RELEASE RATE ANALYSIS

INTRODUCTION

Elemental release rate data from radionuclide inventories that are keyed to geologic disposal are necessary for waste isolation safety assessments. Task 2, Waste Form Release Rate Analysis, is measuring radionuclide release rates for waste forms anticipated for geologic isolation. At the present time, these forms include spent fuel, transuranic waste, and waste glass. Although leach rate measurements for spent fuel have always been a part of this task, their emphasis has been increased because of the changes in the U.S. Government's policy regarding fuel reprocessing.

The methods of repository failure identified in Task 1 will be used to determine the most likely waste release scenarios. The most important release scenario is currently believed to be contact with groundwater. Thus, the initial investigations of this task are focusing on leach rates into aqueous solutions. Task 2 activities include:

- the preparation and characterization of samples of waste forms under consideration for geologic isolation
- the measurement of leach rates of significant long-lived radionuclides and principle fission products from those waste forms, simulation of leach solutions and conditions within the range of conditions expected for waste repositories
- the determination of the effects of important physical and chemical parameters on the leaching mechanisms
- the performance of waste form hydrothermal studies under isolation conditions in geologic media, including increasing the complexity of the experiments to study the effects of the container, backfill and geologic media on waste form release.

Accomplishments

During FY-1978, the International Atomic Energy Agency (IAEA) leaching tests on actinide-doped glass were continued. Spent irradiated reactor fuel

that had an average burnup of 28,000 MWD/MTU was obtained, and IAEA leach tests were started with this material. Improved autoradiographs of the glass material and metallography on the spent fuel were completed.

A system of three autoclaves was designed, purchased, and installed for operation for cold and doped waste material. A system of three additional autoclaves for hot cell use was designed, and bids were let. This system will allow independent flow capability for each autoclave. Gold foil tubes were ordered and received for conducting the autoclave cold and doped waste form tests. A pressure weld device was received for sealing these gold capsules.

A stainless steel leach test cabinet was designed and fabricated for hot-cell use. This cabinet can accommodate up to 140 leach tests.

Efforts to put a multichannel analyzer into operating condition for the hot-cell Ge(Li) detector were abandoned after numerous factory repairs, replacement parts, and many hours of debugging. A new multichannel analyzer was obtained at no cost and the system is now in operable condition.

Proposals were received from Lawrence Livermore Laboratory (LLL) for continuous flow leach testing and Brookhaven National Laboratory (BNL) for leach tests on transuranic wastes. These proposals were reviewed, amended, and finalized as subcontracts by January 1978. Subcontractor reports are included in this report.

Problem Areas

The major problem in FY-1978 was analyzing the leachate solutions from the doped glass and spent fuel tests. Efforts to get this work accomplished within Pacific Northwest Laboratory (PNL) failed. The Hanford Engineering Development Laboratory (HEDL) agreed to help out on this work but was hampered because of higher priorities placed on them by the Nuclear Waste Vitrification Program at PNL. Recent discussions appear to have succeeded in finding a method to increase the amount of samples handled by HEDL; however, a major effort will be required to eliminate the sample backlog. Currently, Tasks 2 and 4 are developing the capability to analyze samples as soon as possible.

PNL LEACHING TESTS

Leaching experiments have continued on actinide doped glasses and actual spent fuel using a modification of the IAEA procedure. The leach schedule is shown in Table 2.1, and the five leach solutions used are listed in Table 2.2. The detailed composition of the salt brine is given in Table 2.3. The composition of the actinide doped glass, which is specific for the glass doped with $^{239}\text{Pu} + ^{237}\text{Np}$, is shown in Table 2.4. Three other glasses of the same base composition were doped with ^{99}Tc , ^{244}Cm , and $^{233}\text{U} + ^{243}\text{Am}$. The dopants were incorporated into the glass (containing 33 wt% waste) in the amounts expected from reprocessed spent fuel having the following characteristics:

- Burnup: 33,000 MWD/MTU
- Reactor Type: Reference PWR, 3.3% enriched
- Age of Waste: 2 yr. old
- Reprocessing Loss: 0.5% Pu + U
- Specific Power: 26.4 MTU

The fission products were put into the glass on a nonradioactive basis to ensure that the doped glass chemically represents actual high-level waste glass. A detailed discussion on the preparation of this glass and the IAEA test is given in PNL-2642 (Burkholder et al. 1979).

Improved autoradiographs have been obtained for the doped glass and optical metallography has been completed on the spent fuel. The glass autoradiographs are shown in Figures 2.1 through 2.4, with corresponding optical micrographs. With minor exceptions, the actinide dopants are seen to be very homogeneously incorporated into the glass. Undissolved crystalline material can be seen as actinide depleted regions, especially for the spinel phase (Fe_3O_4) arising from oxidation/spalling from the steel crucible used to initially melt the glass.

The glass doped with Tc shows a higher porosity than the other preparations and a very high concentration within the pore regions, suggesting Tc was present as a volatile higher oxide during the glass melting. As has been found for Mo, this result suggests reducing conditions may be desirable for incorporating Tc in waste glasses. In any case, leaching behavior of Tc

TABLE 2.1. Leaching Schedule for Doped Waste Glasses

<u>Time</u>	<u>Cumulative Leach Solution Changed</u>	<u>Series Number</u>	<u>Leach Solutions Analyzed</u>
Days	1	1	1
	2	2	2
	3	3	3
	4	4	4
Weeks	2	5	5
	3	6	6
	4	7	7
	5	8	8
	6	9	--
	7	10	9
	8	11	--
	9	12	10
Months	3	13	11
	4	14	--
	5	15	12
	6	16	--
	7	17	13
	8	18	--
	9	19	14
	10	20	--
	11	21	15
	12	22	--

TABLE 2.2. Leach Solutions

<u>Solution</u>	<u>Composition</u>
WIPP site natural salt brine	80% saturated in deionized water
Synthetic calcium	1.666 g CaCl_2 /l
Synthetic sodium groundwater	1.76 g NaCl /l
Synthetic bicarbonate groundwater	2.52 g NaHCO_3 /l
Deionized water	

from this initial preparation will be undertaken with an expectation of rather different behavior than the homogeneously doped actinides.

TABLE 2.3. Chemical Composition of WIPP B Salt Brine

<u>Compound</u>	<u>Concentration (g/l)</u>
NaCl	287.00
Na ₂ SO ₄	6.20
Na ₂ B ₄ O ₇ · 10H ₂ O	0.0160
NaHCO ₃	0.0140
NaBr	0.5200
KCl	0.0290
KI	0.0130
MgCl ₂	0.0400
CaCl ₂ · 2H ₂ O	3.30
FeCl ₃	0.0060
SrCl ₂ · 2H ₂ O	0.0330
Rb ₂ SO ₄	0.0016
CsCl	<u>0.0013</u>
Total Dissolved	297.174

TABLE 2.4. Composition of NFS (76-68) Glass

<u>Glass Composition wt%</u>	
SiO_2	40.0
Na_2O	12.5
Fe_2O_3	9.6
B_2O_3	9.5
ZnO	5.0
$^{238}\text{UO}_2$	4.2
TiO_2	3.0
MoO_3	2.2
CaO	2.0
ZrO_2	1.7
Nd_2O_3	1.65
CeO_2	1.19
RuO_2	1.07
Cs_2O	1.03
BaO	0.56
PdO	0.53
La_2O_3	0.53
Pr_2O_3	0.53
$^{237}\text{NpO}_2$	0.46
P_2O_5	0.46
Cr_2O_3	0.40
SrO	0.37
Sm_2O_3	0.32
TeO_2	0.26
Y_2O_3	0.21
NiO	0.20
Rh_2O_3	0.17
Rb_2O	0.13
Eu_2O_3	0.070
Gd_2O_3	0.050
$^{239}\text{PuO}_2$	0.046
CdO	0.033
Ag_2O	0.031

Pu, Np

OPTICAL

1 mm

RADIOGRAPH

FIGURE 2.1. Pu, Np Doped Glass Autoradiograph

Am, U

OPTICAL

RADIOGRAPH

FIGURE 2.2. Am, U Doped Glass Autoradiograph

Cm

OPTICAL

RADIOGRAPH

FIGURE 2.3. Cm Doped Glass Autoradiograph

Tc

OPTICAL

1 mm

RADIOGRAPH

FIGURE 2.4. Tc Doped Glass Autoradiograph

The IAEA test procedure requires periodic replenishment of the leach solution. The leach rate is obtained from the activity A_n of the leach solution used during the leaching period t_n :

$$\frac{\text{Moles}}{\text{cm}^2 \cdot \text{day}} \text{ Leach rate} = \frac{A_n}{\lambda N_o S t_n} \quad (2.1)$$

where

- A_n = activity of solution
- λ = decay constant
- N_o = Avogadro's number
- t_n = leach time
- S = surface area of the sample.

Results presented here are part of an ongoing IAEA experimental leaching program studying the release of actinides from doped (76-68) glass. The composition of this glass is given in Table 2.4. Data are available up to the 46th day of leaching from glass beads doped with ^{244}Cm (1.87×10^{-4} g/g-glass) and ^{237}Np (4.1×10^{-3} g/g-glass) combined with ^{239}Pu (4.1×10^{-4} g/g-glass). Five leach solutions were used and are described in Table 2.2. The first four solutions were selected for study as a simulation of expected repository groundwaters. Deionized water serves as a reference. Experiments were performed at room temperature.

Figure 2.5 shows the $^{239}\text{Pu} + ^{237}\text{Np}$ doped glass beads (in their basket) used for the IAEA leach test. Solution analyses to date have yielded leach information on ^{244}Cm , ^{239}Pu , and ^{237}Np . Figures 2.6 through 2.9 show the cumulative fraction leached for ^{244}Cm and ^{239}Pu as a function of time and solution composition. Figures 2.10 through 2.13 show typical ^{239}Pu leach rates for these solutions.

FIGURE 2.5. One cm Diameter $^{239}\text{Pu} + ^{237}\text{Np}$ Doped Glass Beads in their Basket

FIGURE 2.6. Cumulative Fraction of ^{244}Cm Leached by Concentration Brine, Bicarbonate Groundwater, and Deionized Water, IAEA Tests

FIGURE 2.7. Cumulative Fraction of ^{244}Cm Leached by Chloride Groundwater and Sodium Groundwater, IAEA Tests

FIGURE 2.8. Cumulative Fraction of ^{239}Pu Leached by Concentrated NaCl Brine, Bicarbonate Groundwater, and Deionized Water, IAEA Tests

FIGURE 2.9. Cumulative Fraction of ^{239}Pu Leached by Calcium Chloride Groundwater and Sodium Chloride Groundwater, IAEA Tests

FIGURE 2.10. Leach Rate of ^{237}Np in Concentrated Brine, Bicarbonate Groundwater, and Deionized Water, IAEA Tests

FIGURE 2.11. Leach Rate of ^{237}Np in Calcium Chloride Groundwater and Sodium Chloride Groundwater, IAEA Tests

FIGURE 2.12. Leach Rate of ^{239}Pu in Concentrated Brine, Bicarbonate Groundwater, and Deionized Water, IAEA Tests

FIGURE 2.13. Leach Rate of ^{239}Pu in Calcium Chloride Groundwater and Sodium Chloride Groundwater, IAEA Test

The cumulative fraction is obtained from the sum of A_n :

$$\text{Cumulative Fraction} = \frac{1}{A_0 W} \sum A_n \quad (2.2)$$

where W is the weight of the sample in grams. The experiments are performed in triplicate, and data presented are an average of three parallel experiments.

Figures 2.6 through 2.13 give plotted cumulative fractions and leach rates for the five solutions and three actinides. By inspecting the cumulative fraction curves the actinides can be ranked according to the total amount released:

$$^{244}\text{Cm} < ^{239}\text{Pu} < ^{237}\text{Np} \quad (2.3)$$

This range covers about one order of magnitude. The same relationship between ^{244}Cm and ^{239}Pu was observed previously (Bradley 1978) in an actual HLW glass of different composition (72-68).

Variations caused by different leach solutions in the fraction released of a given actinide are somewhat less than an order of magnitude and are often quite small (see Figures 2.7 and 2.9). Table 2.5 shows relationships found in these data. The bicarbonate groundwater was found to be most corrosive, probably because of its higher pH. Concentrated brine is the least corrosive. In high temperature tests, Westsik and Turcotte (1978) found salt brine to be less corrosive than deionized water, which is in agreement with the present results at 25°C.

Since the experimental work has only provided data up to a few months of leaching and analytical results are not available yet for the glass structural elements (e.g., Si,B), any detailed interpretation is premature. It has been general practice to attempt curve fitting leach data based on assumed diffusion ($t^{1/2}$) and (t^1) models of various forms. We have examined one of the more sophisticated models proposed by Godbee et al. (1978) which incorporates both corrosion and diffusion related components according to the equation:

$$\Sigma F = \frac{D\rho A}{uw} \left[\frac{1}{2} \frac{u^2 t}{D} + \left(1 + \frac{1}{2} \frac{u^2}{D} t\right) \operatorname{erf} \sqrt{\frac{u^2 t}{4D}} + \sqrt{\frac{u^2}{D}} \exp\left(\frac{-u^2 t}{4D}\right) \right] \quad (2.4)$$

where

D = glass diffusion coefficient, cm²/day

u = corrosion rate of the glass, cm/day

ρ = density of the glass, g/cm³

A = sample surface area, cm²

w = sample weight, g

t = time, days

erf = error function

TABLE 2.5. Relative Magnitudes of Cumulative Fraction Compared for Various Leach Solutions.

Actinide	Relationship Between Cumulative Fractions Obtained from Various Solutions
²⁴⁴ Cm	#1 < #2, #3, #4, #5
²³⁷ Np	#1, #5 < #3 < #2, #4
²³⁹ Pu	#1 < #2, #3, #5, < #4

#1 WIPP brine

#2 CaCl₂ groundwater

#3 NaCl groundwater

#4 NaHCO₃ groundwater

#5 deionized water

There are two adjustable parameters, u and D. A computer implemented calculation procedure uses a least-squares minimizing routine to evaluate u and D. Figure 2.14 gives a representative plot of experimental and theoretical data points. Other elements and leaching solutions give comparable 'good' fits to theory, but considered as a group it is clear that the assumed (corrosion + diffusion) models cannot be applied to leaching of waste glasses. The apparent diffusivity values (D) and corrosion rate constants (u) evaluated using

FIGURE 2.14. Comparison of Experimental and Theoretical Values of Cumulative Fraction ^{239}Pu Leached Out of Glass/ Total Initial Amount of ^{239}Pu in Glass

diffusion) models cannot be applied to leaching of waste glasses. The apparent diffusivity values (D) and corrosion rate constants (u) evaluated using equation (4) are shown in Table 2.6. In order for the model to be acceptable, the corrosion rate constants should be independent of the actinide dopant and the apparent D values for Pu and Np (both +4 ions) should be comparable. Neither of these trends is observed. The corrosion rate constants for solutions 4 to 5 vary by seven orders of magnitude and D values by two orders of magnitude. D values for Cm vary by 6 orders of magnitude in comparing bicarbonate groundwater and deionized water whereas Pu and Np vary only by two orders of magnitude. These are clearly unreasonable trends.

TABLE 2.6. Diffusion Coefficients and Corrosion Rates of Glass

	Solution	Diffusion Coefficient D (cm ² /day)	Corrosion Rate u (cm/day)
²³⁹ Pu	#1	9.2 x 10 ⁻¹⁵	1.8 x 10 ⁻¹⁶
	#4	1.17 x 10 ⁻¹²	6 x 10 ⁻¹⁴
	#5	2.9 x 10 ⁻¹³	1 x 10 ⁻¹⁴
²³⁷ Np	#1	1.5 x 10 ⁻¹²	1 x 10 ⁻¹⁴
	#4	7 x 10 ⁻¹²	2 x 10 ⁻⁷
	#5	2.4 x 10 ⁻¹²	2 x 10 ⁻¹⁴
²⁴⁴ Cm	#1	7.8 x 10 ⁻¹⁵	3.5 x 10 ⁻¹⁵
	#4	1 x 10 ⁻¹²	7.4 x 10 ⁻⁸
	#5	8 x 10 ⁻¹⁹	2.2 x 10 ⁻⁷

#1 = WIPP brine

#4 = NaHCO₃ groundwater

#5 = deionized water

and complex sorption effects in the developing silica gel (as mobile alkali is selectively leached) are major rate controlling features in removal of actinide elements from waste solids.

The spent fuel leach tests using the IAEA procedure are underway in the facility shown in Figure 2.15. These tests are conducted on fragments of spent fuel having an average burnup of 28,000 MWD/MTU. Figure 2.16 is a photograph of a typical batch of fuel fragments. Although no data are currently available on the particle size distribution, four fuel fragments were mounted and polished at the HEDL radiometallurgy facility. Light optical examinations of the fuel fragments were made in the as-polished and etched conditions (Figure 2.17 and 2.18). The surface roughness of the fractured surfaces are comparable to the pellet exterior surfaces. The microroughness

FIGURE 2.15. PNL Hot Cell Facility Used for Spent Fuel Leach Experiments

FIGURE 2.16. Typical Size of Spent Fuel Fragments Used in PNL Leach Tests
(the scale is in inches)

of the surface, when viewed at 750X, would add approximately 25% to the calculated macro-surface area. The etched surface at 750X showed equiaxed grains which increased approximately 25% radially from edge to center of the pellet. A few cracks were observed on the polished surface, and the closed porosity was uniformly distributed. During FY-1978 not enough data were compiled to present meaningful release curves.

AUTOCLAVE WORK

Measurements of leaching at elevated temperature are important because the measurements provide data on leaching under conditions of natural or induced hydrothermal activity. In addition, for many matrix-related processes involving solids, higher temperatures simulate prolonged time periods. The kinetic data obtained under autoclave conditions will enable extrapolation to long-term, low temperature effects.

In FY-1978 a system of three autoclaves was designed, purchased and installed for operation. These autoclaves will be used for nonradioactive and doped waste form studies. The three autoclaves are made from Hastelloy C and have 850 cm³ working volume.

Hastelloy C was selected for all the wetted parts, including valves, because of its excellent general resistance to corrosion in brine solutions and minimal risk of stress-corrosion cracking. A few items, such as the high pressure tubing, are made from Inconel 600, which has about the same general corrosion resistance. The autoclaves are capable of operating at pressures up to 4250 psi and at temperatures up to 400°C. The autoclave is sealed with a metal gasket with the sealing pressure provided by bolts clamping the autoclave cap to the body. This arrangement is economical, very easy to use, durable, and provides an excellent pressure-tight seal. Heat is supplied by strip heaters, which are strapped to a sleeve. The sleeve fits closely over the autoclave body, so that air gap thermal resistance is minimized. Temperature is measured by an internal sheathed (Inconel 600) thermocouple. This thermocouple is also used for temperature control. The autoclave cap is penetrated by an inlet line from the high pressure pump and an outlet line. The

FIGURE 2.17. Polished Fuel Fragment Viewed at 750X

FIGURE 2.18. Etched Fuel Fragment Viewed at 750X

outlet line has a rupture disc assembly connected to it to provide protection against autoclave overpressure, a valved line to permit samples to be taken, a pressure regulating valve to permit water or solution to flow through the autoclave at a preset pressure, and a pressure transducer (a strain gauge bridge) to convert the pressure to an analog electrical signal. Figure 2.19 illustrates the autoclave design and Figure 2.20 is a photograph of the actual work area.

The instrumentation for recording the autoclave temperature and pressure and for controlling the temperature is mounted in a portable control panel adjacent to the autoclaves. Temperature control is provided by Leeds and Northrup Electromax III controllers. These controllers drive a silicon controlled rectifier (SCR) power package, which in turn drives the strip heaters. An Electromax III overtemperature controller provides protection against a runaway control system and resultant overheating. An outside thermocouple provides the temperature sensing for the overtemperature controller. Pressure and temperature for all three autoclaves are recorded on one chart recorder, a Leeds and Northrup Speedomax 250. In addition, a digital readout of the pressures is provided, separate from the recorder. Figure 2.20 shows the three autoclaves and instrumentation as installed.

Because of the presence of radioactivity in some experiments, special safety features are incorporated in the system. In the event of overpressure and consequent bursting of a rupture disk, the resultant steam is passed through two HEPA filters before being exhausted to the atmosphere. This prevents radioactive particles from entering the atmosphere. The resulting pressure drop also trips an alarm switch in the chart recorder, which in turn shuts down the heat supplied to the autoclave and trips an audible and visual alarm outside the entrance to the autoclave laboratory. This warns the operator that radioactivity may be present in the room.

The first autoclave tests will be run on beads of 76-68 glass, the same glass used in the IAEA tests. Individual beads, undoped or doped with Cm, Tc, U and Am, or Pu and Np are reacted with deionized water, 1.26 g/l NaHCO_3 , or the WIPP B salt brine. Each dopant-solution combination is tested at 150°C

FIGURE 2.19. Autoclave Design for PNL Leach Tests at Elevated Temperatures

and 250°C at 2000 psi for periods of 2, 4, 8, 16, and 32 days. The 2, 8, and 32 day times provide cross reference points with static leach tests, which are scheduled to start in FY-1979. These tests are being run at 25°C and 75°C.

Solutions from the undoped bead tests will be analyzed for a large number of elements by inductive coupled plasma spectrometry (ICP). Radioactive solutions from the doped beads will be analyzed for the leached dopant plus cesium, strontium, and silicon. Depending on the type and quantity of solid reaction products formed, the solution will be examined by X-ray fluorescence, X-ray diffraction, Auger spectroscopy, metallography, and/or scanning electron microscopy (SEM).

FIGURE 2.20. Autoclave and Instrumentation Work Area

Each sample will be contained with a sealed gold capsule. A typical capsule is formed from gold tubing 1.0 in. ID x 0.010 in. thick x 4.1 in. long. The vendor sealed one end of the tube using the gas tungsten arc welding process. The other end will be sealed by a cold-weld pinch-off device after the sample and solution are added. The gold capsule then has a nominal internal volume of 35 ml. This is of sufficient size to contain 15 ml of solution and the glass bead. The remaining volume is available for expansion of the fluid as the temperature increases. A maximum of six capsules can be placed in each 1-liter autoclave per run.

Another autoclave system was designed for use on fully radioactive waste forms in hot cell conditions. This system is a remotely operable autoclave station that has been designed for use in the 324 Building "C" cell. This station is intended for 5 yrs useful life in a 20,000 R field. The station consists of four autoclaves (500 cc, 850 cc, 1000 cc, and 5 gal), a blowdown tank, sampling and cleaning facilities, and necessary safety devices located in the hot cell. Outside the hot cell will be the control and recording instrumentation, solution tankage and pumps. Figure 2.21 shows a schematic of the remote autoclave station.

Details of the individual autoclaves follow:

- A 5-gal vessel will be made with Inconel 600 or will be Inconel 600 lined. All wetted parts will be covered. Minimum working dimensions are 8 in. diameter by 23 in. The vessel is equipped with sampling ports spaced along its side for solution sampling at various depths. The vessel head will employ a self energizing closure, requiring minimum torque application. The head has five penetrations for thermocouples or sampling tubes. Designed maximum operating conditions are 3500 psi at 400°C. The vessel may operate in either a static or refreshed mode. Heating is by replaceable strap-on strip cartridges. Figures 2.22 and 2.23 show autoclave details.
- A 1000 cc vessel is a standard 1-liter Inconel 600 vessel, 3 in. dia by 9 in. There are provisions for five cover penetrations and four body penetrations for sampling lines and thermocouples. The unit may be run

FIGURE 2.21. Remote Autoclave Station Schematic

FIGURE 2.22. Autoclave Schematic Details

sideways

- ① DRILL 0.260"
 ② WITH 6M94E2 ADAPTER AND PLUG

- A 4 TAPPED HOLES FOR LIFTING EYEBOLTS
 @ 90° SEPARATION AND ~3" RADIUS NOT
 A THRU HOLE
 B 4 HOLES AT 90° INTERVALS ON 3" RADIUS
 FROM CENTER
 1 HOLE AT CENTER
 ALL HOLES DRILLED THROUGH TO ACCERT A 1/8"
 SHEATHED THERMOCOUPLE; WITH A 1/8" COMPRESSION
 TYPE FITTING. SUPPLIED WITH FITTINGS AND PLUGS

FIGURE 2.23. Autoclave Piping Schematic

either static or refreshed. Heat is supplied by a slip-on canister heater. Maximum rated operating conditions are 3500 psi at 400°C.

- A 850 cc vessel is a Hastelloy C vessel 2 in. dia by 15 in. Operating limit is 4250 psi at 400°C. There are five cover penetrations for thermocouples and sample tube. The unit is heated by a slip-on cannister heater. Operation may be refreshed or static.
- A 500 cc vessel is rated for service at 5000 psi at 510°C. Constructed of Hastelloy C, the vessel has useful specimen dimensions of 2.12 in. dia by 9 in. long. There are two body and four cover penetrations for placement of either sample lines or thermocouples. Heating is by a slip-on canister heater. Operation may be static or refreshed. This autoclave was purchased by another PNL program.

The temperature in each autoclave is controlled by a Leeds and Northrup Electromax III controller with reset, rate, proportional band, and approach functions. The controller powers the autoclave heaters through an SCR. Overtemperature protection is provided by an independent Electromax III overtemperature controller. Temperature information is recorded on a multi-channel Leeds and Northrup series 250 recorder. Pressure is controlled by a back-pressure relief valve. Pressure information is obtained with calibrated gauges with gauge isolators to protect the bourdon tubes. Pressure safety is provided by frangible discs that relieve into a blowdown tank partially filled with water to condense steam blowdown. The tank is of sufficient capacity that all four autoclaves could simultaneously blowdown from maximum temperature and not raise the blowdown tank above 200 psi. Check valves protect other autoclaves from pressure surge should any vessel blowdown.

Piping

Figure 2.23 shows the piping schematic typical of each autoclave in the hot cell. Valving combinations are available that permit static or refreshed operation. It is also possible to valve the system to run cleaning solutions through various portions. This later ability is necessary because of the tendency of precipitation from chlorinated waters or waters that have been in contact with geologic media at high temperatures. We anticipate the need to pump acids through the tubing and autoclaves for periodic cleaning.

CONTINUOUS-FLOW LEACH TESTS

A subcontract was placed with Lawrence Livermore Laboratory (LLL) to develop a continuous flowing leach test that correctly simulates the case in which solutions with low flow rates pass waste forms that may occur in a repository. This contract was finalized in early FY-1978 to design, fabricate, and start a series of continuous-flow leach tests that use the same solutions and waste glass that were used at PNL. The leaching system developed at LLL for this study represents a modified and updated version of the apparatus used for leaching NTS nuclear melt glass (Coles et al. 1978). The important advantages of the single-pass leach system are:

- control of resorption effects because leached species do not remain in contact with the glass sample
- provisions for a large number of simultaneous experiments with limitations being principally the analytical capability for large numbers of samples
- ability to handle concentrated Cl^- leaching solutions.

Experimental Design

The experimental design for the single-pass leaching system was based on a statistical analysis of the experimental plan. After reviewing many design options, it was decided on the basis of cost, analytical capability and equipment maintenance requirements, to fabricate a twenty-eight channel statistically-designed factorial experiment with unequal replication. Flow rate, temperature, leachant composition, and time are the independent variables, and leaching rate is the dependent variable. Of the twenty-eight channels, twenty-four are leaching doped samples, three channels have undoped blanks and one doped sample does not have the $0.1\ \mu\text{m}$ filters in the sample holder that are present in all other doped samples. This design results in a two degrees of freedom (i.e., two replicated measurements) estimate of random variation for comparing the leaching rate for different flow rates and temperatures and a four degrees of freedom estimate of random variation for comparing the leaching rates between the three liquids. The design does not permit a separation of the random variation caused by the use of different pumps and different temperature

baths. A more thorough design would replicate the entire experiment, that is, all rates and temperatures at least once, but this design would yield an unmanageable number of samples for analysis.

The experimental design is depicted schematically in Figure 2.24. Figure 2.25 shows the actual continuous-flow experiment. The polyethylene solution reservoirs are connected to a manifold system that allows collection and release of entrapped gas from the flow lines. From the manifold, the fluid flow lines are connected to Cole-Parmer Manostat peristaltic metering pumps, which control flow rate by alteration of gear ratios. Flow lines extend from the pumps to temperature baths in which the sample chambers (Figure 2.26) are immersed. The low temperature baths are water-filled; the high temperature bath is filled with mineral oil. The plexiglas and metal sample chamber is LLL-designed. The side-filler plug enables the glass-bead samples to be introduced after assembly and pressure testing for leakage. The sample holder is equipped with 0.1 μm membrane filters upstream and downstream of the sample to contain the beads. All connecting lines consist of small-bore plastic tubing and Luer press-fit plastic connectors. Fluid exiting the top of the sample cells goes directly into plastic collection bottles.

Experimental and Analytical Procedure

The glass used in this study, ^{239}Pu and ^{237}Np doped waste glass, was prepared in the same glassmaking run at PNL that furnished doped glass for the PNL IAEA test.

The leachant solutions are distilled water, a 0.03 M bicarbonate (NaHCO_3) solution and a synthetic concentrated brine which corresponds in composition to a brine resulting from the dissolution of a salt core from the 831 m level of well AEC #8 at the Waste Isolation Pilot Plant (WIPP) in New Mexico. The compositions of these solutions are the same as those given in Tables 2.2 and 2.3.

The three flow rates for the single-pass leaching experiment were chosen to correspond to the fluid volumes that the beads are exposed to in the daily, weekly and monthly sample schedule of the PNL IAEA experiment; e.g., the flow rate corresponding to the daily IAEA sample is seven times the rate which corresponds to the IAEA weekly sample. The three flow rates, labeled fast,

FIGURE 2.24. Single-pass System for Leaching Simulated Reactor Waste Glass

FIGURE 2.25. Continuous Flow Experiment

FIGURE 2.26. Sample Holder for the Single-pass Leaching System; (a) Assembly, (b) Cross-section

medium and slow in Figure 2.23, are 0.208 m /min (300 ml/day), 0.030 ml/min (43 ml/day), and 0.007 ml/min (10 ml/day). The corresponding flow velocities are 216, 31, and 7 m/yr, respectively.

The sampling frequency in the single-pass system is designed to represent approximately equal intervals on a log time plot. They are 1, 2, 3, 6, 11, 20, 37, 68, 120, 230, 420 days. The leach test was started in April 1978 and the final sample day will be in June 1979. Of the eleven total sampling days, which represent 308 samples, nine occurred in FY-1978 and two remain in FY-1979. In FY-1978, the analytical capability has not kept pace with sample generation and a backlog exists of samples to be analyzed.

The two temperatures which the samples are subjected to are 25°C (low) and 75°C (high).

The analytical procedures for ^{239}Pu and ^{237}Np include:

- TTA extraction for Pu and Np separation
- ion exchange column purification
- a second TTA extraction for ^{237}Np purification
- fluoride and hydroxide precipitation
- plating of Pu and Np on platinum discs in a sulfate medium
- alpha counting.

In addition, analysis for silicon, cesium, strontium and other elements will be done by means of ion-coupled plasma emission spectroscopy. Liquid samples are routinely analyzed to determine conductivity, Eh and pH.

Preliminary Analytical Results

The analytical results for the first three samples (days 1, 2, and 3) for two temperatures and three flow rates (F, M, and S) are plotted in Figures 2.27 through 2.31. The IAEA results for the same sampling period are also presented for purposes of comparison. The leach rate (R) in $\text{g}/(\text{cm}^2\text{-day})$ is shown as a function of mean time (t_m) on a log-log plot. Each line has been traced through three data points.

At the low temperature, 25°C, the ^{237}Np leach rate is 3 or 4 times the corresponding ^{239}Pu rate, depending on the leach solution. At this temperature, there is no correlation between leach rate and flow rate, indicating no

FIGURE 2.27. ^{237}Np Leach Rate in Distilled Water

FIGURE 2.28. ^{237}Np Leach Rate in 0.03 M NaHCO_3

FIGURE 2.29. ^{239}Pu Leach Rate in Distilled Water

FIGURE 2.30. ^{239}Pu Leach Rate in 0.03 M NaHCO_3

FIGURE 2.31. ²³⁹Pu Leach Rate in WIPP Brine

influence of the flow rate on leaching. In general, the continuous-flow leach rates are in close agreement with those determined at PNL by the modified IAEA method, as shown by the PNL data in Figure 2.26 through 2.30. At 75°C, the leach rate is positively correlated with flow rate; i.e., R is greater at higher flow rates. The leach rate is also a function of leachant composition at high temperature. For ²³⁷Np, the 75°C leach rate is greater than the 25°C rate, whereas for ²³⁹Pu the 75°C leach rate is less than or equal to the 25°C.

Early in the experimental run, experiments were conducted to determine whether the membrane filters downstream from the glass beads have an effect on Pu analysis; i.e., do polymerized Pu complexes get caught in the filters? Preliminary results indicate that the membrane filters do not have any significant effects.

TRANSURANIC WASTE FORM RELEASE STUDIES

Transuranic (TRU) waste constitutes the largest quantity of waste to be isolated from the biosphere. Current repository planning includes co-storage of high-level wastes, TRU wastes and spent fuel.

The recent Interagency Review Group (IRG) report (1978) indicates that TRU wastes constitute a long-term hazard of equal importance to high-level wastes. As such, the release behavior of transuranic waste forms under storage conditions must be known. To study the release behavior of transuranic waste forms a subcontract was initiated with Brookhaven National Laboratory (BNL) in FY-1978.

The progress in FY-1978 relates primarily to the determination of waste form formulations and formulative techniques, modification of a hot cell to provide a TRU leaching facility, design and construction of the leaching apparatus, and the development of leachant analysis techniques. A more detailed explanation of this work follows.

While there is some question whether existing TRU wastes will be disposed in their current form, or first undergo some additional volume reduction process, it is evident that volume reduction will be required for future TRU wastes. Since the bulk of these wastes consist of contaminated combustible solids, including such items as protective cloth, rubber boots and gloves, paper, rags, filter aids, wood, and ion exchange resins, volume reduction is of considerable importance in order to reduce waste shipment volumes, conserve repository capacity, lower disposal costs, and meet repository criteria directed at restricting the amount of combustible material in disposal. A number of volume reduction options are available for combustible TRU wastes. Currently, the most viable option is some form of incineration. While incineration does result in a large volume reduction for combustible solid wastes, the ash that results is highly dispersible. As such, the immobilization of incinerator ash by solidification producing a solid monolithic waste form is desirable.

The experimental program conducted at Brookhaven National Laboratory (BNL) will determine the leaching properties of TRU-contaminated incinerator

ash waste forms using hydraulic cement, urea-formaldehyde, bitumen and vinyl ester-styrene as solidification agents. The data obtained will indicate the relative activity retention abilities of these waste forms and provide the basis for long-term release projections from full scale waste forms. The leach rates of the radionuclides ^{239}Pu , ^{235}U , ^{237}Np , ^{241}Am , ^{137}Cs , and ^{90}Sr will be monitored. Waste form leach rates for these radionuclides will be determined where practical, although experimental considerations may dictate the use of other isotopes of these elements.

IAEA, static, and continuous flow leach tests will be conducted. The leach test procedures and leach solutions will be the same as those being used at PNL.

Waste Form Formulations

Solidification agents should incorporate relatively as much incinerator ash as possible in the final waste form to increase packaging efficiency and reduce associated disposal costs. However, the waste form ash content should not be so high as to either impose substantial difficulties in the solidification process or to compromise waste form properties. The amount of ash that can be reasonably incorporated in the waste form is dependent on the composition of the ash and its interaction with the solidification agent. Simulated incinerator ash compositions have been formulated for various waste producing sites. These compositions vary considerably and have been shown to result in different compositional phase diagrams for acceptable solidification with Portland type I cement (Neilson and Colombo 1978). In addition, simulated waste compositions, while similar chemically to actual wastes, may not adequately simulate the physical form or chemical distribution of actual incinerator ash. As such, this program will use an actual incinerator ash resulting from the incineration of a mixed combustible waste representative of plutonium handling and processing facilities.

Waste forms will be formulated using incinerator ash waste produced by the rotary kiln incinerator at Rocky Flats. This incinerator is being used to burn a nonradioactive mixed combustible waste formulation that is representative of the low-level wastes produced at Rocky Flats. Currently, low-level

contaminated combustibles are not incinerated at Rocky Flats, but are compacted instead. A dual-chamber burner is used to burn more highly contaminated waste; however, this waste is not representative of the bulk of TRU-contaminated waste at Rocky Flats. The dual-chamber burner incinerator ash is typically ~2.6 wt.% Pu and contains ~25 wt.% carbon resulting from incomplete combustion. A portion of this waste will be obtained prior to acid leaching for plutonium recovery and will be mixed with the cold incinerator ash from the rotary kiln to provide a source of plutonium in the waste form. This procedure is preferable to simple addition of plutonium because the plutonium incorporated in the waste form will be in the chemical and physical state resulting from incineration. The relatively small quantity of hot ash used will not appreciably alter the average chemical composition of the incinerator ash incorporated into leach specimens. The hot ash will be assayed prior to use, but is expected to contain 94% of the plutonium as ^{239}Pu (0.5% ^{241}Pu). The americium-241 content of the ash is 0.3% of the total plutonium content. Both the cold and hot incinerator ash wastes are expected to be received from Rocky Flats in FY-1979.

Waste form formulations for solidification with Portland type I cement, urea-formaldehyde, bitumen and vinyl ester-styrene were investigated using the simulated Rocky Flats plutonium recycle incinerator ash composition shown in Table 2.7. Waste forms were produced containing a wide range of ash content with each solidification agent. These formulations were immersion tested in distilled water for three months to determine the approximate maximum ash content which resulted in waste forms that would be expected to maintain their integrity during each testing. In addition to formulation investigation, BNL work assisted in the development of waste form production procedures that are consistent with glove box operations. When the actual incinerator ash is received, the formulations determined from simulated ash will be verified as acceptable for the solidification of the actual waste.

Hydraulic Cement

Hydraulic cement, of which Portland type I is the most commonly available, requires the presence of water to produce hydrated silicate and aluminate compounds, resulting in a monolithic solid. The incinerator ash is contained

TABLE 2.7. Simulated Rocky Flats Plutonium Recycle
TRU Ash Composition

<u>Material</u>	<u>Weight Percentage</u>
Al_2O_3	3.69
BaO	0.59
B_2O_3	1.67
CaO	3.64
Cr_2O_3	2.36
CuO	0.64
Fe_2O_3	5.85
PbO	0.54
MgO	2.90
MnO_2	0.10
NiO	0.50
P_2O_5	0.59
KOH	0.50
PbO_2	2.61
SiO_2	45.00
NaOH	0.89
V_2O_5	0.64
SnO	0.15
TiO_2	2.17
C	25.00

in the waste form largely as an aggregate material. The additional water that is necessary to hydrate cement constituents is added directly to the ash prior to mixing with cement in order to reduce the possibility of contamination from ash dispersion. Sufficient water must be added to produce a minimum workability in the cement-waste mixture. However, while water additions above this minimal amount will increase workability, if the water addition is too large, free standing water will be present after solidification. Water may have to be added to compensate for water adsorption by the ash. Constituents in the ash may also have an effect on cement setting time. This is especially crucial if the ash contains set accelerators. Short set times may result in cement hardening in the mixing apparatus.

Studies have previously been performed at BNL to determine a compositional phase field over which satisfactory solidification of simulated Rocky Flats plutonium recycle TRU incinerator ash can be obtained using Portland type I cement (Neilson and Colombo 1978). These results are illustrated in Figure 2.32. The product contains three components (ash, cement, and water). When the ash content is fixed, the mixture composition is determined by variation of either one of the two remaining constituents. Formulation work thus focused on water content because of its importance relative to workability and free-standing water. While Portland type I cement requires a water/cement ratio of 0.30 by weight for minimum workability, this quantity of water was not sufficient when ash was incorporated in the mixture. Experiments indicated that the ash itself required a supplemental water addition quantified by a water/ash ratio of 0.30 by weight to satisfy its absorptive requirements. Much of the water absorbed on ash would not be available for cement hydration. Conversely, the addition of larger quantities of water, while improving mixture workability, eventually exceeds the amount that can be effectively bound in the mixture. This boundary is delineated by the maximum water curve in Figure 2.32.

Mixture set times were determined using ASTM method C 191-74, "Standard Method of Test for Time of Setting of Hydraulic Cement by Vicat Needles." Set time is a measure of the rate at which the cement mix hardens and is important because cement mixes should be placed prior to initial setting to prevent cement hardening in the mixing apparatus (and the maintenance problems which would result), and also because cement mixes disturbed after the initial set generally do not achieve maximum strength characteristics.

On the basis of cement mixing technology, the cement formulations that are used should have set times of thirty minutes or more to allow ample time for mixing and pouring. ASTM specification C 150-74 requires that the initial set for Portland cement be not less than forty-five minutes (Vicat test) to allow mixing and placing. For the incinerator ash solidification application considered here, somewhat shorter set times are acceptable since large mass placings are not envisioned. Set time, as determined by this method, increased when the simulated Rocky Flats ash content was increased over the range of 40 to 55 wt% ash.

FIGURE 2.32. Compositional Phase Field Over Which Satisfactory Solidification of Simulated Rocky Flats Plutonium Recycle TRU Incinerator Ash can be Obtained Using Portland Type I Cement

One-in. diameter by two-in. cylindrical specimens were produced containing 20, 30, 40, and 50 wt% ash. In these formulations, the remaining weight fraction was composed of Portland type I cement and water such that sufficient water was added to provide both a water/cement ratio and water/ash weight ratio of 0.30. These specimens were each immersed in 500ℓ of distilled water for a period of three months to determine if the specimens would maintain their integrity in leaching. Specimen integrity was maintained for all formulations. Figure 2.33 shows these specimens after leaching. Holes that appear

FIGURE 2.33. Leached Specimens of Rocky Flats Incinerator Ash, Portland Type I Cement

in the sides of these specimens were caused by air bubbles along the side of the container that were not removed during mixing. Since all formulations were able to maintain their physical integrity during leaching, Portland type I cement leach specimens used in this program will contain 50 wt% incinerator ash. This formulation includes, in addition to the ash, 26.9 wt% cement and 23.1 wt% water.

Urea-Formaldehyde

Urea-formaldehyde (UF) is an aqueous emulsion of urea and formaldehyde that is chemically combined to form linear polymeric chains. The resulting liquid is a viscous, milky colored, sticky material containing approximately 65 wt% solids and has a density of 1.3 g/cm^3 . It is completely miscible with water, but immiscible with nonpolar organic solvents. Upon prolonged exposure to air, or with the addition of an acid catalyst, cross-linking polymerization occurs and a solid is obtained. During this cross-linking process, solids added to the resin before the addition of the acid catalyst are entrapped in the polymer matrix forming a monolithic solid. Weak acid catalysts such as sodium bisulfate or phosphoric acid are usually employed to induce polymerization. The gel time of the resin is dependent upon the pH of the UF-waste mixture. Normally, sufficient catalyst is added to produce a mixture pH of 1.5 ± 0.5 , which typically results in a gel time of 5-30 minutes at 25°C . Gel time increases with mixture pH. Reasonably short set times are necessary to prevent settling out of higher density solids in the waste.

Initial formulational development using urea-formaldehyde to solidify the simulated Rocky Flats incinerator ash waste have not been entirely successful. The waste is highly alkaline and, as such, large quantities of catalyst are needed to provide the acidic mixture pH required to initiate polymerization. Work is continuing to determine how the polymerization can best be initiated. This work includes selection of the most suitable catalyst and consideration of waste pretreatment to provide a neutral waste pH.

Bitumen

Bitumen (asphalt) systems are not currently in use in the United States for radioactive waste solidification. The first bitumen systems employing an extruder-evaporator process have been ordered for commercial nuclear power plant waste solidification.

Bitumen is a mixture of high molecular weight hydrocarbons that are obtained as a residue in coal tar refining. This has two major components: asphaltene compounds, which give bitumen colloidal properties, and maltheane compounds, which impart viscous liquid properties. Bitumen is a thermoplastic material and, as such, can behave mechanically as either a viscous liquid or a solid, depending upon the temperature. Several types of bitumen are available, but direct distillation of oxidized products are most widely suggested for radioactive waste solidification. Within these two basic bitumen types, many grades exist with properties that vary on even across batches. This variation can, however, be minimized by specifying named products or grades of bitumen. The bitumen specified in this country typically has a density of 1.01 g/cm^3 at 25°C , a softening point of 90°C , and a flash point exceeding 290°C .

In most bitumen solidification systems, wet solid wastes are added to heated bitumen under a mixing action. Water from the waste evaporates and cooling the mixture results in a solidified mass. The waste solids are coated with bitumen and distributed throughout the waste form mass. As such, the process results in both volume reduction and solidification with wet solid wastes. Dry wastes, such as the incinerator ash considered in this program, can also be solidified with bitumen. As much as 50 wt% simulated Rocky Flats incinerator ash has been incorporated in bitumen mixtures in which the bitumen is heated above its softening point and the ash is slowly added while the bitumen is stirred. The bitumen-ash mixture becomes increasingly viscous as additional ash is added. It appears that 50 wt% ash is the approximate upper limit that can be incorporated using small laboratory mixing motors for stirring. Because of the stirring action required, it is difficult to fabricate individual samples in one-in. diameter containers. Leach specimens of this size can be obtained by casting heated bitumen-ash mixtures or coring from a larger mass.

Bitumen specimens containing 20, 30, 40 and 50 wt% simulated Rocky Flats incinerator ash were immersed in distilled water for three months to determine the effect of long-term leaching on specimen integrity. All formulations were found acceptable on this basis, and the 50 wt% ash formulation was chosen for future leaching experiments. These specimens are shown in Figure 2.34 after three months of leaching. The rough area around the edge of the specimen upper surface resulted from wetting effects with the specimen container during solidification. This material was not removed prior to leaching.

Vinyl Ester-Styrene

A proprietary vinyl ester-styrene thermosetting resin has been marketed by the Dow Chemical Company for the solidification of radioactive wastes. While this material was specifically developed for wastes containing appreciable quantities of water, it can be used for the solidification of dry wastes. After mixing with waste, polymerization at room temperature is initiated by a catalyst-promoter system. The polymerization reaction is exothermic, however, and produces a monolithic solid within 15-60 minutes. Related thermosetting polymer systems, such as styrene or polyester-styrene, can produce similar results.

Vinyl ester-styrene has been used to solidify simulated Rocky Flats incinerator ash containing as much as 75 wt% ash. Specimens containing 50 and 75 wt% ash have been immersed in distilled water for three months without any appreciable loss in integrity as shown in Figure 2.35. At this point, the 50 wt% ash formulation will probably be used for further leach testing because it appears this ash content represents a reasonable formulation for all solidification agents considered.

Leaching Facility

The transuranic leaching facility has been constructed inside the former Irradiation Cell in Building 830. The inside dimensions of this hot cell are 14 ft x 20 ft x 14 ft.

While the extensive shielding capability provided by the irradiation hot cell is not necessary for the transuranic leaching experiments proposed, the space was available and it does serve as an effective means of isolating the

FIGURE 2.34. Leached Specimens of Rocky Flats Incinerator Ash, Bitumen

FIGURE 2.35. Leached Specimens of Rocky Flats Incinerator Ash, Ester-Styrene

work from general laboratory facilities. Some modification of the cell interior was required to make this space suitable for a leaching facility. The cell was surveyed to determine the level of existing contamination, if any. No significant contamination was detected (none was expected since the cell was only used for irradiation experiments using sealed sources). The General Mills arm manipulator was removed, as were two canal elevator lift and transfer assemblies. Floor openings were covered with stainless steel plates. The interior of the cell was then completely repainted. A fire retardant wooden interior doorway was constructed to permit access restriction to the facility during the working day when the lead shielding door is open. While the cell has installed gamma radiation monitoring equipment and alarms, an alpha air monitoring unit* has been ordered. In addition, both photoelectric and ionization chamber smoke detectors will be installed. The cell has its own temperature controlled air recirculation system, which contains two levels of HEPA filtration.

A two-compartment stainless steel glove box with an air lock entry assembly for each compartment has been modified and installed in the leaching facility to provide capability for remote fabrication of transuranic contaminated leaching specimens. This glove box, which is shown in Figure 2.36, had been previously used at the laboratory for plutonium handling operations. The unit was thoroughly decontaminated prior to receipt in Building 830. Each of the two compartments is 33 in. x 24 in. x 33 in. They are separated by a stainless steel barrier containing an 11-1/2 in. diameter door. Each compartment has lighting, electrical supply outlets, and its own internal HEPA filter, in addition to a pair of glove ports. There is an airlock assembly for each glove box compartment. The air from the glovebox is exhausted through two levels of HEPA filtration.

A semi-automated facility has been designed for performing IAEA leach tests. The technique requires that the leaching solution be changed and completely replaced at frequent intervals (daily for the first week, once per week for the following eight weeks, and subsequently once per month). Since the leachant solutions are expected to contain quantities of plutonium removed

*Eberline Model Alpha-3

FIGURE 2.36. Leaching Facility Glovebox

from the leach specimens, we decided to build an apparatus that would require a minimum of direct manual handling of the specimens and solutions. The leaching experiment will be performed in the following manner: the leach specimen is placed into a one-liter capacity polymethylpentene screw cap container. Polymethylpentene was chosen because it is autoclavable and has a low potential for reacting and "plating out" with species that may be of interest on the container walls. The specimen is supported on a plexiglass stand, which makes essentially the entire surface area of the leach specimen accessible to the leachant. Any desired amount of leachant can be added to any individual leach container through a 1/4-in. O.D. valved inlet manifold. A separate inlet manifold is used for each leachant container. The manifold and 1/4-in. I.D. ball valves are type 304 stainless steel. The inlet manifold also has a recirculation return line to prevent clogging of the inlet manifold as well as to provide a mixing action in the leachant storage container.

Leachant is stored in steel drums with 27-gallon polyethylene liners. A small Flotec gear pump is used to provide the motive force for leachant transfer. After the appropriate period of leaching, the leachant in the leach container is stirred and sampled using a Eppendorf pipette. After sampling, the valve to the exhaust manifold is opened. Since the exhaust manifold is maintained at a negative pressure, opening the ball valve of a leach container removes the leachant under a suction action. A Teflon suction tube that is positioned in the leachant container allows removal of essentially all of the leachant. A typical leach cell is shown in Figure 2.37. The exhaust manifold is 3/8-in. O.D. type 304 stainless steel which drains the leachant to a 40-gal capacity glass-lined mild steel tank with a fluid level indicator. When full, this tank can be drained directly into a feed line to a 2000-gal capacity pair of buried waste holding tanks (outside of Building 830), which are periodically emptied by tank trucks. The leachant exhaust manifold leads to a plexiglass measuring cell apparatus before emptying into the waste holding tank. The measuring cell, which is shown in Figure 2.38, allows determination of leachant pH, conductivity, and (if desired) Eh and oxygen content.

FIGURE 2.37. Typical Leach Cell

FIGURE 2.38. Measuring Cell Which Determines Leachant pH, Conductivity, Eh and Oxygen Content

Leachant Analysis

Quantitative alpha spectrometry typically employs a solid state silicon surface barrier detector to count specimens electroplated onto stainless steel planchets. The resolution of such a detector is of the order of 50 KeV, which permits simultaneous analysis of alpha emitters with similar energies. However, the sample preparation required in this technique is very labor intensive.

The leaching experiments to be conducted at BNL will produce more samples for analysis than can be conveniently prepared in this manner. Therefore, other analytical techniques were investigated and liquid scintillation counting (LSC) was chosen as the primary analytical technique.

Liquid scintillation counting has been utilized for alpha counting since 1954 (Basson and Stayn 1954, Horrocks 1974). This method is attractive because of the ease of specimen preparation, the commercial availability of remote sample changers, and the 100% efficiency usually obtained in alpha counting. (Alpha particles are counted at 100% efficiency in LSC if the activity is dissolved in the scintillation solution. The efficiency is lowered if the activity plates out on the container walls, or is suspended on a solid matrix.) While energy resolution is not as good as that which can be obtained with other methods, different alpha emitters can be counted simultaneously if their respective alpha particle energies are sufficiently different. Peak resolution in LSC is a function of a number of factors but alpha particles of approximately 5 MeV generally can be resolved if peak energy differences are of the order of 0.5-0.7 MeV. As such, some alpha emitting radionuclides may possibly be analyzed simultaneously since appreciable primary particle energy differences exist: ^{239}Pu (5.147 MeV), ^{241}Am (5.482 MeV), ^{237}Np (4.787 MeV), and ^{235}U (4.354 MeV).

An automatic liquid scintillation counter* was purchased for this program. Figure 2.39 is a photograph of this counter and the sample changer. The counter employs a bidirectional automatic conveyor sample changer, which accepts up to 300 samples. The detector consists of two 2-in. diameter bi-alkali photomultiplier tubes that are situated 180° apart in a metal chamber with

* Searle Model 6892.

FIGURE 2.39. Automatic Liquid Scintillation Counter and Sample Changer

specular aluminum reflectors in a 2-in. thick lead shielding housing. There are two variable simultaneous sample analysis channels with two additional fixed level channels for external standard source (ESR) analysis. Analysis channel baseline and width, counting time, preset count terminators, and sample changing mode can be independently determined and incorporated into internally stored program instructions. Data output is through a Teletype Model 43 printer.

Initial work has employed Insta-Gel* as the liquid scintillation cocktail. This solution is able to form a stable counting media with relatively large quantities of aqueous sample. Work has begun to demonstrate that this cocktail can be used with the expected range of leachant solution compositions.

* Packard Instrument Company, Inc., Downers Grove, IL.

TASK 3 - RELEASE CONSEQUENCE ANALYSIS

INTRODUCTION

During FY-1978, task work continued with code modification, interfacing, verification, and documentation. Data system methodology was selected and the system was implemented. The second workshop was held for peer review of the WISAP release consequence analysis methodology, and two test cases were run to demonstrate the methodology. This section reviews the current status of the suite of codes which have been selected for calculating the consequences of repository release scenarios.

HYDROLOGIC MODELS

A number of existing models (both hydrologic and transport) were identified during FY-1977 as a result of an extensive compilation of models applicable to the WISAP release consequence analysis task. These models, which range through four levels of complexity, are listed in Table 3.1. From this set of models, the models listed in Table 3.2 were chosen for implementation and testing for the WISAP release consequence modeling program since they could most efficiently be adapted for use on the PNL computing system.

Work during FY-1978 has been involved with the conversion, implementation, modification, documentation, and demonstration of these models to obtain an efficient modeling system for release consequence analysis. The following work was performed on the three hydrologic models shown in Table 3.2:

- conversion and implementation of the codes and all associated auxiliary codes for use on the PNL computer system
- interfacing the hydrologic code output with the transport code input
- verification runs with the models
- application of the models for demonstration release consequence cases
- preparation of model documentation, including users' manuals, for each model.

TABLE 3.1. Hydrologic and Contaminant Transport Models Useful for Waste Isolation Safety Assessment

<u>Level of Modeling Complexity</u>	<u>Hydrologic</u>	<u>Contaminant Transport</u>	<u>Additions Needed to Meet Selection Criteria</u>
1. Simple	Analytic Solution of Steady State Flow Equation	GETOUT	None
2. Simple-Intermediate	PATHS	GETOUT	None
	PATHS	PATHS (EXTENDED)	Equilibrium Sorption and Chain Decay
	FLOP-1	FLOP 1 (EXTENDED)	Equilibrium Sorption and Chain Decay
	FLOP-2	FLOP 2 (EXTENDED)	Equilibrium Sorption and Chain Decay
	FRONT-N	FRONT-N (EXTENDED)	Equilibrium Sorption and Chain Decay
	RCPIGW	RCPIGW (EXTENDED)	Equilibrium Sorption and Chain Decay
3. Intermediate-Complex	HCIM	MMT	None
	TRIGAT	MMT	None
	(COOLET)	MMT	None
	VTT	MMT	None
	MULTIAQUIFER	MMT	None
	MOC	MMT	None
	BEWTA	MMT	None
	MTMVMC	MMT	None
	ISQUAD2	MMT	None
	NEWSAM	NEWSAM (EXTENDED)	Equilibrium Sorption and Chain Decay
	MOD	MOD (EXTENDED)	Equilibrium Sorption and Chain Decay
	HCTM	HCTM (EXTENDED)	Equilibrium Sorption and Chain Decay
4. Complex	DAVIS FE	MMT	None
	DWDM (Newer Version)	DWDM (Newer Version)	None
	VCHFLO	VCHFLO	Equilibrium Sorption and Chain Decay
	DAVIS FE	DAVIS FE (EXTENDED)	Equilibrium Sorption and Chain Decay

TABLE 3.2. Characteristics of WISAP Release Consequence Analysis Models Chosen for Implementation and Testing During FY-1978

HYDROLOGIC

PATHS	-	Two-dimensional, analytical/numerical methods, homogeneous geology, saturated flow
VTT	-	Two-dimensional multiaquifer, finite difference numerical method, heterogeneous geology, saturated flow
DAVIS FE	-	Three-dimensional, finite element numerical method, heterogeneous geology, saturated flow

CONTAMINANT TRANSPORT

GETOUT	-	One-dimensional, analytical method, chain decay, single speciation, equilibrium sorption, constant leach rate, dispersion
MMT	-	One-, two-, or three-dimensional, numerical method, chain decay, single speciation, equilibrium sorption, time variant leach rate, dispersion

WATER DOSE

ARRRG	-	Drinking water, immersion, external shoreline, and aquatic food doses
FOOD	-	Terrestrial food dose

AIR DOSE

KRONIC	-	Chronic external dose
SUBDOSA	-	Acute external dose
DACRIN	-	Chronic or acute inhalation dose

PATHS 2-D Analytic Hydrologic Model

PATHS is a 2-D dimensional analytic model that represents flow in a single confined aquifer of large lateral extent in the horizontal plane. The aquifer is assumed homogeneous and isotropic, and is assumed to be of constant effective porosity. The model considers a uniform lateral flow gradient with superimposed leakage from a vertical cylindrical pond or cavern that completely penetrates the aquifer. A potential energy head is applied at the cavern or structure. This head is completely dissipated at a specified finite distance, and thereby introduces a worst-case situation into the evaluation procedure. The model can consider as many as 35 completely penetrating wells at optional locations with steady or time-dependent flow rates. In addition, the effect of Kd-type ion exchange for a single contaminant without dispersion can be simulated.

PATHS provides a preliminary evaluation capability that is both easy to use and inexpensive for two-dimensional subsurface pollution problems. This capability is based on a model that was designed to best use the usually limited data available in the early evaluation stages of a subsurface pollution problem. At some points, idealization and worst-case approximations were used rather than more elaborate data often not initially available. Through the conservative assumptions used, the predictive results should represent the worst-case expectations. Such worst-case estimates can be very useful for an initial evaluation. This PATHS two-dimensional evaluation capability evolved during the previous decade and was selected by WISAP as the needed evaluation capability for Level 2 modeling.

This evaluation capability has grown out of efforts to solve a variety of related problems over the past decade. A project for the Research and Development Department of Atlantic Richfield Hanford Company (ARHCO) in the late sixties provided a simplified single-source leakage model. Later, while working with pollution problems of a commercial mining operation, ARHCO incorporated features for considering several injections of pumping wells in addition to the central source. Finally, the original central source expression was replaced by the more complete and useful doublet expression used now. The extension to mass transport was made when the model was used for an underground siting study

of nuclear power plants. This feature allows the user to consider nuclide holdup caused by sorption of a single component.

From this experience with numerous applications has come an assessment procedure that balances the level of predictive sophistication with the limited amount and quality of data that are available for an initial or preliminary evaluation. PATHS provides procedures that are easily used and gives the results needed in a moderate amount of time and at minimal cost.

PATHS was fully documented in detail by Nelson (1978). This document describes the preliminary evaluation capability prepared for WISAP, including examples complete with arrival distribution obtained using the capability. Part of the report is written for users who have little or no experience with computers and part informs the programmer how input parameters are passed through programs in the system. Appendix A contains an example of PATHS input requirements and output forms. Interactive computer programs such as PATHS are provided to make it easy for people without computer experience to use the evaluation capability. These programs aid the user by asking for the necessary input parameters and by guiding the user through selecting the options needed to obtain the required results.

The WISAP methodology was demonstrated utilizing data for a hypothetical repository located in the bedded salt of the Paradox Basin. This exercise was simply for demonstration of the WISAP release consequence modeling codes. No implication of the use of the Paradox salt for a repository was intended. The data available from Paradox Basin indicated a uniform, homogenous 1,000-ft thick aquifer of 100-ft/yr hydraulic conductivity with the initially estimated uniform lateral gradient of .002 ft/ft, and the initially estimated distance to the discharge site of 12,000 ft. The results of this run are illustrated in Figure 3.1. The results of the PATHS model-water travel times years agree very well with those generated by the more complex two-dimensional VTT multi-aquifer finite difference model, which predicted water travel times of 43,250 years.

PARADOX BASIN - WELL SCENARIO
 DEPARTURE TIME = 0.00 YEARS
 SCALE 1 INCH = 15000 FEET

FIGURE 3.1. PATHS Model Results for Paradox Path and Isochronal Lines

VTT 2-D Finite Difference Hydrologic Model

The VTT is a PNL hydrologic computer code (Kipp et al. 1976) that has been used successfully for studying a variety of groundwater supply and subsurface pollution problems (Schreiber et al. 1973; Cole and Foote 1975a,b; Cearlock et al 1975; Reisenauer 1977a,b; Grant and Associates 1977; Arnett et al 1977; Cearlock and Reisenauer 1971). The model is one of a variety of similar two-dimensional finite-difference and finite-element hydrologic models that characterize groundwater movement as typically horizontal through more permeable zones called aquifers. The groundwater equation solved by VTT and other 2-D horizontal numerical models is the Boussinesq equation:

$$n_e \frac{\partial h}{\partial t} = \frac{\partial}{\partial x} (K h_e \frac{\partial h}{\partial x}) + \frac{\partial}{\partial y} (K h_e \frac{\partial h}{\partial y}) + N \quad (3.1)$$

where

$h(x,y)$ = elevation of the free surface in an open well from some reference elevation R (units L)

$n_e(x,y)$ = vertical average of the effective porosity of the aquifer at point (x,y) (no units) or storage coefficient

x,y = cartesian coordinants

t = time

$K(x,y)$ = vertically averaged value of hydraulic conductivity at point (x,y) (units LT^{-2})

$h_e(x,y)$ = thickness of the saturated aquifer material at point (x,y) (units L)

$N(x,y)$ = source or sink value per unit area (units LT^{-1})

The Boussinesq formulation shown in Equation 3.1 allows the simulation of a single aquifer system. Many times in a real system one wishes to simulate a multiaquifer system with vertical leakage between the various aquifers. This kind of simulation can be performed with VTT for up to a three-aquifer system using the multiaquifer form of Equation 3.1 shown in Equation 3.2:

$$s^i \frac{\partial h^i}{\partial t} = \frac{\partial}{\partial x} (T^i \frac{\partial h^i}{\partial x}) + \frac{\partial}{\partial y} (T^i \frac{\partial h^i}{\partial y}) + N^i + \sum_{j=1}^{i-1} C_{ji} (h^j - h^i) + \sum_{j=i+1}^n C_{ji} (h^j - h^i) \quad (3.2)$$

where

- i = 1, 2 . . n (property for aquifer i)
- n = number of aquifers
- C_{mn} = interaquifer transfer coefficient between layer n and m
- s^i = porosity for an unconfined system or storage coefficient
- T^i = transmissivity for a confined sytem or hydraulic conductivity times aquifer saturated thickness for an unconfined system (vertical average)
- N^i = the flux or stress term for layer i.

The VTT model uses the finite-difference method to approximate the partial differential equations shown in Equation 3.2. Equal node spacing in the x and y direction is required but the model has the ability to do higher resolution modeling in any area of interest. The VTT model has the ability to solve the transient problem Equation 3.2 as well as the steady-state problem, which is the right side of Equation 3.2 set equal to zero. The transient model equations are solved by line-successive overrelaxation techniques and the steady-state model can be solved by either a Newton iteration technique for aquifer systems that contain unconfined systems (which are nonlinear) or by a Cholesky decomposition method for totally confined sytems that are linear. Specific data requirements for the VTT model include:

- Physical Parameters
 - vertically averaged hydraulic conductivity or transmissivity distribution for each aquifer

- storage coefficient distribution for each aquifer
- interaquifer transfer coefficient distribution for each aquifer
- Initial Conditions (potentiometric distribution for each aquifer)
- Boundary Conditions
 - geometrical description of the lateral extent of aquifer to be simulated
 - contour maps of aquifer base and aquifer tops
 - definition of the type of boundary along lateral boundaries: held potential boundary (Dirichlet), flow boundary (lateral inflow or outflow specified as a function of time), or no flow boundary.
- Aquifer Stress
 - description of aquifer stress distribution for each aquifer.

The VTT model assumes that the transport process has no effect on the hydrologic or water flow process and, thus, that the hydrologic model can be solved independently from the transport problem. As a result, the appropriate output from the VTT hydrologic model must be in a format that can be used for input to a transport model. VTT model auxiliary codes were created and/or modified as necessary to insure a smooth flow of information from the VTT hydrologic model to the various transport models (GETOUT, 1-D MMT, 2-D MMT). For one-dimensional models, like GETOUT and 1-D MMT, information on flow tube flow rates, velocities, lengths and size must be extracted from the VTT hydrologic model. The VTT auxiliary codes MXPLT were modified and EQFLOW was created to analyze VTT model output to provide this information for input to the transport codes. EQFLOW uses the VTT model data base along with the model predicted potentiometric distribution to determine starting locations for streamlines spaced such that the flow between any pair of adjacent streamlines is equal. These pairs of streamline starting coordinates are then analyzed by the MXPLT program to determine the average velocity and length of the various flow tubes. Figure 3.2 illustrates the output of EQFLOW for the Paradox release scenario analysis and Figure 3.3 illustrates the output from the MXPLT program.

FIGURE 3.2. Calcomp Plot Output from the MXPLT Auxiliary Program Illustrating the Six Streamlines and Five Flow Tubes Used in the Paradox Transport Analysis

FIGURE 3.3. VTT Model Predicted Potentiometric Surface for the Large Region (7500 ft nodes) Paradox Simulation. Small Region Potentials are Illustrated in Figure 3.2

When the 2-D MMT transport model is to be run then the appropriate matrices representing aquifer thickness, aquifer hydraulic conductivity and effective porosity and aquifer potential distributions must be supplied to the transport code so that the (V_x, V_y) velocity components at each model node can be calculated.

Finite Element Three-Dimensional Groundwater Model

The Three-Dimensional Finite-Element Groundwater Model (FE3DGW) is the fourth level of the hydrologic models. Some complex site specific geologic configurations consist of multiaquifer systems separated by semiconfining layers. In these systems the aquifers respond conjunctively to stress imposed on either aquifer. Such coupling of aquifers requires modeling all the layers simultaneously. The FE3DGW is the result of improvements in the Davis Finite-Element Model (Gupta et al. 1975; Gupta and Pinder 1978; Cole and Gupta 1978) and provides the means to conveniently simulate such sites by considering saturated groundwater flow (transient and steady state) in three dimensions through a heterogeneous anisotropic geologic media.

During FY-1977, the DAVIS Finite-Element Model was made operational on the PDP-11/45 computer. It was verified by data depicting the multilayered groundwater system beneath Long Island, New York, illustrated in Figure 3.4.

During FY-1978, the DAVIS Finite-Element Model was revised and updated with the new version called PNL-FE3DGW. For each time step, the new version (PNL-FE3DGW) simulates changes in potentials instead of total potentials. This reduces round-off errors considerably. Also during FY-1978, existing programs were converted and new supportive programs were developed to check input data and further validate the model with analytical solutions. A brief description of the new version (PNL-FE3DGW) is given in Appendix B.

TRANSPORT MODELS

GETOUT Transport Model

At the beginning of FY-1978, the Geosphere Transport Model, GETOUT (Lester et al. 1975), existed only on an INFONET computer system. It was coded in BASIC programming language. At that time, the decision was made to convert the code to FORTRAN programming language.

During FY-1978, work was conducted to convert GETOUT to FORTRAN on Digital Equipment Corporation's PDP-11/45 minicomputer and on a UNIVAC 1100/44 main-frame computer. The work of converting to the PDP-11/45 was directed toward programming the equations documented in BNWL-SA-5079, and the effort on the

FIGURE 3.4. Three-Dimensional Finite-Element Representation of Groundwater Reservoir Beneath Long Island, New York

UNIVAC 1100/44 was directed at programming a new set of equations not yet documented, and removing GETOUT from the INFONET system. Appendix C contains a brief description of the GETOUT code and conversion work.

Multicomponent Mass Transport (MMT) Model

At the beginning of FY-1978, the Multi-component Mass Transport (MMT) model did not account for all factors that affect migration of radionuclides. During FY-1978, MMT was modified for analyzing potential nuclear waste repositories, and it was used to perform analyses on two waste repository scenarios.

Previous work indicated that the radiological doses from daughters such as ^{226}Ra could be significant. Prior to the work performed in FY-1978, MMT did not account for decay of radionuclides to their daughters. Therefore, MMT had to be modified to account for this effect.

The previous method of handling multiple contaminants was to use one parcel set that had the masses of each contaminant associated with it. Each parcel moved with the water velocity, and sources and sinks were accounted for by altering the mass associated with each component.

For the purposes of long-term simulations, however, working with the nuclide velocity rather than the water velocity is advantageous. This requires that each contaminant have its own set of parcels, since each nuclide moves with a different velocity. Thus, to account for the decay of nuclides to their daughters, new parcels must be created. A one-dimensional version of MMT was developed to determine:

- the best means of accounting for radioactive chain decay
- the feasibility of performing long-term analyses of potential nuclear waste repositories with the discrete-parcel, random-walk (DPRW) technique.

The resulting version was used to perform analyses of the Paradox Basin and to analyze a scenario defined by Working Group 7 of the International Nuclear Fuel Cycle Evaluation (INFCE) committee.

The results of the one-dimensional MMT were compared with results of GETOUT for the same problem. Table 3.3 summarizes input information. Each model obtained essentially the same results for a two-member chain as shown in Table 3.4.

Two criteria are used to determine feasibility of a model. One is whether it predicts the correct results. The other criterion is the amount of computer time used for a simulation. The Paradox Basin and other test cases were completed in less than an hour of wall clock time on the PDP computer system for each decay chain.

The method adopted to account for decay chains includes using the analytical solutions of the simultaneous ordinary differential equations, and creating parcels as a function of the center of mass of the primary parent and the relative velocity between the parent and daughter. The equations solved analytically are:

$$\frac{dN_1}{dt} = -\lambda_1 N_1 \quad (3.3)$$

$$\frac{dN_2}{dt} = -\lambda_2 N_2 + \lambda_1 N_1 \quad (3.4)$$

$$\frac{dN_i}{dt} = -\lambda_i N_i + \lambda_{i-1} N_{i-1} \quad (3.5)$$

for the three initial conditions at $t = 0$:

$$N_1 = N_{10}, N_2 = N_{20}, N_i = N_{i0}$$

where:

N_i = activity concentration of species (Ci/L^3)

λ_i = decay constant (T^{-1})

t = time.

TABLE 3.3. Data Input Used for Comparison

Nuclide:	^3H
Retardation Coefficient:	1.0
Flow Velocity:	1 foot/day
Dispersion Coefficient:	1 foot ² /day
Initial Inventory:	7.23×10^8 Ci
Release Time:	333 years

TABLE 3.4. Comparison of Output Results, Ci ^3H

<u>Time (years)</u>	<u>GETOUT</u>	<u>MMT 1-D</u>
140	0.	0.
145	336.	307.
150	450.	463.
155	340.	349.
160	256.	263.
165	193.	198.
170	145.	149.

The results obtained from the one-dimensional MMT indicate that:

- the DPRW technique is feasible for performing long-term simulations (10^6 years)
- the method of creating parcels after each time step to account for decay chains is acceptable
- analyses of potential nuclear waste repositories can be performed with MMT.

Appendix D contains a description of the Discrete Parcel Random Walk (DPRW) method used in the MMT model development during FY-1978.

In FY-1978 the one-dimensional MMT was used on test cases for the Paradox Basin (Utah). The Paradox Basin study had very little data available. Because of the lack of data, it was primarily a test of the models, and no conclusions can be drawn in this case as to the suitability of the Paradox Basin for storage of nuclear waste.

In the Paradox Basin Study, five "flow tubes" were used to simulate the arrival of radiocontaminants at the "S" River (see Figure 3.2). These flow tubes were used to simulate the two-dimensional character of the radionuclide transport. Each flow tube originates from a different point in the waste repository and represents an equal water flow rate. The inventory used in this case was split evenly among the five flow tubes. Results of MMT calculations appear in the output:

- as a plot of concentration (ci/ml) for each nuclide in the groundwater versus time for each flow tube
- as a plot of maximum concentration (ci/ml) in the groundwater versus time for each exiting nuclide
- as a plot of maximum total curies versus time
- concentration in the groundwater versus distance plots for the actinides that had not reached the "S" River in two million years.

The transport model requires that a maximum simulation time be specified as part of the input. To properly represent the transport of the four actinide decay chains, the model should be run until all isotopes have either reached the river or have decayed to zero mass. For the scenario described above, the model would require 1312 million years of simulation time for the slowest moving isotopes to reach the river. Such a lengthy run would not be practical in terms of time or cost. Therefore, a more reasonable simulation time was selected. A simulation time of two million years was used and the results for the actinide chains were obtained in terms of concentration in the groundwater versus fraction of the distance traveled along the flow path to the river.

The primary error resulting from approximating 2-D transport with multiple 1-D flow tubes is that no lateral dispersion is considered. Each flow tube does not receive any contaminants from neighboring flow tubes because of this

error. However, the magnitude of the lateral dispersion coefficient is small, and the amount of error introduced is also small when compared with the uncertainty in all other parameters. Also, the error is introduced on the conservative side.

Both the Paradox Basin Study and other exercises shows the overall hydrologic modeling system is working well and capable of quick turnaround. The cases provided information for further refinement of production versions of the transport models and for input and output data processing routines. As a result of these studies, a waste-form leach rate model was developed for a more realistic leaching of radionuclides from the waste form into the ground water. This model was derived from experimental information that was obtained from Task 2 of WISAP. The model accounts for leaching of radionuclides as a function of temperature, surface area of the waste form, and time. Appendix E contains a detailed description of the leach rate model.

DOSE MODELS

During FY-1978 available models were reviewed for calculation of radiation doses to individuals and populations from the several potential pathways of exposure from nuclear waste stored in geologic formations. Models selected were compatible with previous waste management studies, accepted by the cognizant scientific community, easily adaptable to PNL use with the UNIVAC 1100/44 computer, and were capable of being interfaced with the output of the geologic transport models.

The exposure pathways involved, the models selected, and their status at the end of FY-1978 are discussed below.

Exposure Pathways

Radionuclides isolated with high-level wastes in geologic formations might be transported to the human environment. Once the radionuclides reach either surface water, such as rivers or lakes, or a well-water source, a variety of aquatic pathways can internally and externally expose man. These pathways are summarized in Table 3.5 and illustrated in Figure 3.5.

TABLE 3.5. Pathways of Exposure to Man(a)

Pathways	Exposure	
	Internal	External
Aquatic	Injection of Water	Water immersion
	Injection of aquatic foods	Water surface
	Injection of irrigated food crops	Exposure to shoreline
	Injection of products from animals fed irrigated foods	
Air	Inhalation	Air submersion
	Transpiration of tritium oxide	Exposure to deposited materials
	Ingestion of food crops	
	Ingestion of animal products	

(a) Brenchley et al. 1977

In addition to the aquatic pathways, there is the extremely small probability of exposure via air pathways. Mechanisms required for waste materials to become airborne include severe natural phenomena, such as earthquakes or volcanoes, whose physical damage could far outweigh any resulting radiological impact. In addition, the mining of the storage site at some future time after its location is forgotten could bring materials to the surface where they would be available for a variety of terrestrial exposure pathways, including resuspension by wind erosion. Airborne pathways are included in Table 3.5, but currently only limited use of them in the WISAP study is foreseen because of their extremely low probability.

Depending upon the nuclides involved, air resuspension of materials deposited from the air or with irrigation water might also slightly increase the total doses from other pathways listed in Table 3.5. The impact of such resuspended materials could be assessed by coupling the output of empirical resuspension formulas available in the literature (Anspaugh et al. 1975, Cohen 1977) to the input of airborne pathway codes. Materials deposited with irrigation water or washed out of the air by rain are generally less available for resuspension than are materials from dry deposition (Cohen 1977).

FIGURE 3.5. Aquatic Pathways of Exposure from Geologic Storage Site for SHLW.

Review of Dose Models and Codes

Extensive reviews of models and computer codes for calculating radiation doses to man have been published recently. Strenge et al. (1975) published a comprehensive review in 1976. They discussed about 20 codes, their applications and limitations, and the particular computer and language for which they were designed. A similar but more inclusive review by Hoffman et al. (1977a,b) included the identification of 83 computer codes.

The authors also recommended that, for long-lived nuclides, the man-rem concept be replaced with a calculation of the incremental increase in dose above background. However, for the time being, the man-rem concept must still be employed, although the ratio of doses from the release of radionuclides from the storage facility and from background radiation should also be evaluated.

Another consideration involved in selection of models and codes is a knowledge of the many inherent idiosyncrasies that facilitate or hinder the successful operation of each code. Also, since a set of codes is required to cover a wide range of pathways, a compilation of codes that are internally consistent in their basic assumptions about nuclide behavior in the environment, dosimetry, and requirements for input data format is desirable. The codes should also be consistent in output format so that the results of the several codes can be automatically compiled into summary tables of total doses. A summary of the computer codes selected and their capabilities are presented in Table 3.6. The individual codes were discussed briefly in Appendix B of the FY-1977 WISAP Technical Progress Report (Burkholder et al. 1979); they are described more extensively in Appendix F of this report.

TABLE 3.6. Dose Programs Selected for WISAP

Program	Item Calculated	Organ Doses Calculated	Status as of 9/30/78	References
ARRRG	Individual and population doses from ingested water	Dose and dose commitment to total body and selected internal organs	BASIC version for 1108 documented	Soldat et al. 1974
	Individual and population doses from aquatic foods (fish, crustacea, molluscs, plants)	Dose and dose commitment to total body and selected internal organs	FORTTRAN version for 1100/44 compiled and operational, but not yet documented.	
	Individual and population doses from sediment exposure (shoreline)	Dose to skin and total body ^(a)		
	Individual and population doses from swimming and boating	Dose to skin and total body ^(a)		
FOOD	Individual and population doses ^(b) from ingestion of farm products	Dose and dose commitment to total body and selected internal organs	BASIC version for 1108 documented	Baker et al. 1976 Baker 1977
			FORTTRAN version for 1100/44 compiled and operational, but not yet documented.	
KRONIC	Individual and population doses ^(b) from gaseous effluent plumes from chronic releases	Dose to skin, testes, and total body	FORTTRAN version for 1108 documented	Strenge and Watson 1973
			FORTTRAN version for 1100/44 compiled and operational. Redocumentation not required.	
SUBDOSA	Similar to KRONIC except for accidental releases	Dose to skin, testes, and total body	FORTTRAN version for 1108 documented	Strenge et al. 1975
			FORTTRAN version for 1100/44 compiled and operational. Redocumentation not required.	
DACRIN	Individual and population doses ^(b) from inhalation of radionuclides from either chronic or accidental releases	Dose and dose commitment to total body, lung, and other selected internal organs	FORTTRAN version for CYBER documented	Houston et al. 1975 and Strenge 1975
			FORTTRAN version for 1100/44 compiled and operational. Redocumentation not required.	
PABLM	Individual and population doses ^(b) from ingestion of farm products	Dose and accumulated dose to total body and selected internal organs	BASIC version for 1108 not documented (used for CWM/GEIS)	---
			FORTTRAN version for 1100/44 will be compiled in FY-79 with addition of "items" from ARRRG to form a consistent set.	

(a) For these external pathways the dose to any internal organ is taken to be equal to the dose to the total body.
(b) Population doses can be calculated by using population weighted-average input data.

TASK 4 - SORPTION-DESORPTION ANALYSIS

INTRODUCTION

The objective of Task 4 is to provide information about sorption-desorption of radionuclides by geologic media to the Waste Isolation Safety Assessment Program. Specific activities pursued during FY-1978 were:

1) evaluation of sorption-desorption measurement methods and development of standardized measurement procedures, 2) laboratory measurement of the sorption-desorption behavior of significant long-lived radionuclides using a wide range of geologic media and groundwaters, 3) statistical analysis and synthesis of these data to provide information on those variables which correlate best with the observed sorption-desorption and to allow interpolations to be performed within the environments studied, 4) performance of validation studies to assess the degree to which these short-term laboratory studies predict long-term in-situ behavior, 5) development of a more fundamental understanding of sorption-desorption processes to permit prediction of the fate of nuclides at a specific site from data available on other similar sites and from common measured parameters, and 6) generation of x-ray and gamma-emitting isotopes of actinide elements.

EVALUATION OF EXPERIMENTAL SORPTION-DESORPTION METHODOLOGY

There are several unresolved issues in the area of sorption-desorption data collection. Presently, investigators from various laboratories use numerous experimental techniques to determine sorption K_d values and/or migration rates for nuclides. Unfortunately, it appears that the resultant data are dependent upon the experimental technique employed and it is difficult to compare the results of different methods. Thus, study of the various experimental methods is imperative in order to determine sorption-migration data and, if possible, to form a consensus as to which method or methods should be proposed as a standard measurement technique.

Various laboratory methodologies are being evaluated using a wide range of geologic materials and nuclide-spiked groundwaters. K_d values for each method are being determined and evaluations are being made on precision, ease

of use, time and cost expenditures, and limitations. Disagreements and range of applicability for observed results will be investigated through further experimentation on the independent variables (geologic media, ground-water composition, pH, Eh).

The methods of determining K_d values can be grouped into two categories: the static or batch technique and the dynamic or column methods. In the static method, solution traced with radionuclides is shaken with samples of geomeedia for a period before sampling and analysis. The dynamic systems study a tracer solution as it flows through geologic media. The dynamic methods (low pressure flow, axial filtration, high pressure intact core) differ in the type of pressure required to force liquid through the geomeedia.

Since a large number of factors inherent in the geomeedia and solution can affect the K_d (Figure 4.1), a small change in procedures may give different results. Therefore, thorough characterization of solution and geomeedia should be done for all K_d determinations.

Information gathered in FY-1978 on method evaluations is presented below. Past work is summarized in PNL-2642 (Burkholder et al. 1979), PNL-SA-7245 (Serne et al. 1979), and PNL-SA-7289 (Relyea et al. 1978), while detailed data are reviewed in PNL-SA-6957 (Serne 1978) and PNL-SA-7352 (Serne 1979).

Static or Batch K_d Method

The batch method involves contacting an adsorbent (rock) with a liquid adsorbate (nuclide in groundwater) within a container. In most instances the system is continually agitated to facilitate mixing and contact. At specified times the solid and solution are separated and the resultant distribution of adsorbate is determined. The batch method is a very convenient and inexpensive method of studying adsorption and thus has been used more often than any dynamic method. Critical examination of the batch method, however, showed several complications and potential limitations. In FY-1978 WISAP explored several of the complications to determine their effects on the prediction of nuclide migration through geomeedia. Specifically the effects of solid-liquid phase separation techniques, container adsorption of tracer, method of tracer addition to groundwater and calculational scheme used to produce K_d values were assessed.

FIGURE 4.1. Factors That Determined the Concentration of Radionuclides in Solutions Leached Through the Waste

To evaluate the K_d for a nuclide by batch methods, the solid adsorbent must be separated from the liquid. Two methods are used for making this phase separation: centrifugation and filtration. The definition of what are soluble and what are suspended solids has not been rigidly established nor is it clear for purposes of nuclide migration what molecular size would be so large that migration would be most influenced by physical filtration as opposed to chemical sorption processes. Using some simplifying assumptions, one can ascertain the most likely maximum particle size in the centrate or filtrate and adjust techniques to give comparable results.

In the past year WISAP experimenters have often found centrifugation yields sporadic K_d results such as shown in Figure 4.2 (Barney and Anderson 1978). In general, the variation appears to be caused by uncentrifuged particles with adsorbed or innate radioactivity which appeared in the counted solution.

FIGURE 4.2. Large Volume Sorption Curves for Americium on Basalt

Filtration of centrates often removes the variability in measured activity and can reduce the observed solution activity. More studies need to be performed to evaluate the apparent discrepancy between the observed "larger than expected particulates" in centrate versus the maximum expected particulate size from Stokes falling velocity theory. One commonly mentioned deficiency in the use of Stokes falling velocity calculations is the assumption of spherical particles. Plate-like or odd-shaped particles are qualitatively known to settle slower than spheres. Thus if nuclides are adsorbed on plate-like particles, they could stay in suspension longer than predicted.

Although WISAP experimenters have presented no quantitative data, some have voiced concern that filtration membranes can adsorb nuclides from solution like other solid adsorbents as well as remove particulates. Thus, some of the apparent discrepancies between centrifugation and filtration may be caused by filter membrane adsorption phenomena. No known definitive studies address filter adsorption. However, based on personal observation, we feel that the new filter membranes constructed from polycarbonate rather than cellulose minimize adsorption effects.

Until definitive data are obtained, we recommend that phases be separated by centrifugation followed by filtration through 0.4 μm or smaller polycarbonate membranes. The K_d values calculated from experiments where only centrifugation was used have the potential of producing lower K_d values because of particulate contamination of solutions. This bias towards lower numbers provides conservative safety assessment concepts.

Blank experiments are commonly run with batch K_d experiments to account for any container adsorption. The blank is a container without the sediment or rock present, but with nuclide-spiked solution, which is treated in a similar fashion to actual samples. Oftentimes, especially for rare earth and actinide elements, a percentage of the activity originally present in the groundwater will be removed after contact. At least two removal mechanisms are operating: container adsorption and solid formation (e.g., precipitation, polymer, etc.). In past work the observed loss in solution activity was used to adjust the influent activity value used to calculate the K_d (Relyea et al. 1978). Several of the WISAP subcontractors (Erdal et al. 1978, Seitz et al.

1978) investigated this practice and found the container walls in blanks adsorbed more activity than the walls of sample containers. Apparently when a material with a larger capacity for sorption is present in the container, the sample competes with the wall. Also, abrasion of the container surface by crushed material possibly causes less tracer to be sorbed. Thus, by following the previously proposed blank correction procedure, resultant K_d values are biased low, i.e., conservatively. The present procedure is to count only the liquids, influent and effluent, and calculate the amount adsorbed on the solid by calculating the difference. A few subcontractors have proposed that the sample effluent and solid adsorbent be counted directly to calculate the K_d (Erdal et al. 1978a, Silva et al. 1978). This approach alleviates the need for container adsorption corrections but introduces logistical problems for solid counting. Two approaches are used to count the solids: one method removes all the solid from the container and places it in a suitable counting vial; the other method takes a known weight of a representative aliquot. The former procedure is often quite tedious for disaggregated materials, especially if the material is caked in the bottom of a centrifuge tube. The latter procedure is difficult when the adsorbent is heterogeneous disaggregated material. During centrifugation or filtration, the disaggregated media will sort by particle size; thus, obtaining a representative subsample may prove difficult. Alpha, beta, weak gamma, and x-ray radiation will suffer from sample self-absorption. Obtaining an accurate count of activity on the solid may be difficult or impossible. Currently, no clear cut resolution to the container adsorption problem has been made, although the Argonne National Laboratory (Seitz et al. 1978) introduced a novel approach of coring out crystalline rock and performing a "rock test tube" batch K_d experiment. From a practical standpoint, correcting for container adsorption as originally proposed (Relyea et al. 1978) should build in an element of conservatism.

The K_d obtained by the batch method for certain elements appears to be sensitive to how the radiotracer is added to the groundwater and/or geomeia (Erdal 1978a,b; MacLean et al. 1978). Some research indicates that for solubility-limited elements such as rare earths and actinides, the tracer should be added to the groundwater, equilibrated for several days, and

filtered just prior to contact with the geomedia. This approach should remove any oversaturation-precipitation events that would appear like adsorption if the tracer had been added directly to the rock-groundwater slurry in the batch container. Even when the general intent of this process is followed for the element Pu, a further complication has been identified. In experiments performed at the Los Alamos Scientific Laboratory (LASL), Pu-traced waters were prepared by two methods (Erdal 1979). In the first method, a batch of groundwater was spiked with a Pu tracer that was stabilized in an acid solution. Subsequent to tracer addition the groundwater pH was readjusted to its normal value with NaOH solution. The groundwater was then equilibrated, filtered, and placed in contact with the rock samples. A second batch of Pu-traced groundwater was also prepared. Pu tracer in 3M HCl was evaporated to dryness at room temperature in polypropylene tubes. An aliquot of groundwater was added to the tube and the tube shaken vigorously for a few minutes. The tube was then centrifuged for one hour at 12,000 rpm. Centrate solution was extracted. New groundwater was added and the procedure was repeated two more times with the third shaking period lasting overnight. All centrates were combined and aliquots added to batch Kd containers. The batch Kd results on tuff rock samples treated identically with traced groundwaters formed by the two methods are shown in Table 4.1. At present there are no explanations for the observed differences.

Variations in Kd can be caused by the choices made in calculation. Two basic equations may be applied to determine a Kd value from batch data. When only liquid samples are analyzed, Equation 4.1 should be used. When both the liquid "effluent" and solid are counted, Equation 4.2 should be used.

TABLE 4.1. Differences in Kd (ml/g) Caused by Tagging Procedure

Sample	Tracer Kd(Pu)	Dried Kd(Am)	Tracer pH Adjusted		Contact Time Days
			Kd(Pu)	Kd(Am)	
106-150 μ m Tuff JA-32	110	110	1,800	1,000	14
106-150 μ m Tuff JA-37	390	430	7,200	7,200	7
	180	430	12,000	7,500	28

$$K_d = \frac{rA_i - A_e}{A_e} \frac{V}{W} \quad (4.1)$$

$$K_d = \frac{A_d}{A_e} \frac{V}{W} \quad (4.2)$$

where

A_i = activity of tracer in influent or blank. The proper choice of A_i is not always obvious because of container adsorption and phase separation complications.

A_e = activity of tracer in effluent or liquid at time of measurement after phase separation.

r = correction factor for excess wash solution left behind if rock samples were pre-equilibrated with water devoid of tracer prior to the sorption experiment.

V = total volume of solution = (volume of A_i + residual wash solution).

W = total weight of solid adsorbate used or for Equation 4.2, total weight of solid counted.

A_d = activity of solid adsorbate.

For weakly penetrating radioactivity the effects of self absorption can complicate accurate measurement.

The researcher must judiciously decide what is the most proper calculational scheme and choose the most appropriate values of A_e , A_d and/or A_i . For many elements and rocks, phase separation techniques appear to have little effect. In general, systems that have shown variability or sensitivity to the above factors include rare earth and actinide elements and systems where crushed basalt is present. The rare earth and actinide complications probably occur because of colloidal formation of tracer caused by solubility restrictions or hydrolysis tendencies.

The glassy matrix of basalts is rather easily eroded in groundwaters and small particles (submicron-micron) with adsorbed radioactivity are quite common in suspension in batch K_d solutions in contact with crushed basalt

samples. The severity of physical shaking of static systems also appears to affect the formation of colloids and K_d caused by the physical grinding of the geomedial.

The time dependence of K_d is conveniently studied by static methods. For many geomedial-groundwater-nuclide systems adsorption reactions appear to reach equilibrium rapidly (Meyer 1978, Shiao et al. 1978) within a few hours. For other systems (crushed basalt, granite, argillite) the macro constituents of contacting groundwaters were still changing after four months contact. K_d values also varied with time. In general the K_d value increased with time from weathering processes, which is understandable. The alteration products formed from weathering of primary minerals, in general, exhibit larger surface areas and exchange capacities. In a few instances, the K_d value for an element appears to decrease. One apparent reason for this is colloid formation that is possibly encouraged by physical grinding effects during shaking. Whether colloid formation will be important in the real world has not been ascertained. Months or years may be required to attain sorption equilibrium in some systems as secondary minerals are formed (Barney and Anderson 1978). Studies should be made to identify slow reactions that could reduce sorption measured in short term laboratory experiments. Some of these studies are described in the section on validation studies.

Batch experiments yield more precise results when the experimental conditions are chosen such that the change in tracer solution concentration upon contact with the geologic material is neither very small nor extremely large. If the sorption (K_d) is very small, the effluent is nearly the same as the influent, and counting statistics significantly affect calculations. If the sorption (K_d) is very great, the effluent will have very little activity left, and counting difficulties will result. By varying the solution to geologic media ratio over a practical range (2 to 100) and by attempting to keep the effluent/influent ratio between 0.2 and 0.8, researchers have discovered that batch K_d experiments are best used to measure K_d values between 1.25 and 400 ml/g.

Despite these complications, static or batch adsorption experiments remain the most frequently used technique to obtain K_d data to predict nuclide migration. Identified complications are being studied so that recommended procedures for future work can be delineated.

Axial Filtration K_d Method

The axial filtration K_d method, illustrated in Figure 4.3 (Meyer 1978), uses a cylindrical filter that rotates about its axis and is enclosed in a coaxially mounted cylindrical pressure vessel. Solution is introduced into the outer chamber and then flows through the filter into the cylindrical space within the filter and finally out through a tube mounted on the axis of rotation. At sufficiently high rpm (typically several thousand) the adsorbent is uniformly suspended in the pressure chamber and thus the device acts as a single plate stirred-tank reactor. The tracer (adsorbate) is introduced into

FIGURE 4.3. Axial Filter

the slurry and the breakthrough monitored versus volume of effluent. Provided the breakthrough curve follows ideal chromatographic theory the K_d is easily calculated (Meyer 1978).

Limitations that have been identified include proper selection of the filtering surface, restriction to disaggregated geomedia and difficulty in quantifying a K_d from a nonideal breakthrough curve. Although studies have not been performed to date on a wide range of geomedia and tracers, the method has proven useful for adsorption on silt to clay size disaggregated clay minerals in contact with salt brines traced with Sr, Cs, Co, Cd and Zn.

The principal advantages of axial filtration methods are the ease and rapidity with which a series of determinations may be made to ascertain reversibility and kinetic effects. The method, being a dynamic (flow) technique can also identify the different migration potentials possible for different element species that might be present together.

More experiments need to be performed to identify the applicability of axial filtration techniques, especially for the more troublesome (from an experimental standpoint) rare earths and actinide elements. To date, the technique has been used only casually because of high capital equipment investment requirements. Results (summarized in this report) show good comparison for Sr and Cs adsorption experiments by any of the methods (batch, column or axial filtration).

Channel Chromatography K_d Method

Channel chromatography offers a third technique for measuring K_d s. Channel chromatography is described in detail by Francis et al. (1978a,b). Crushed geomedia are placed in shallow (2 mm) channels; in this instance, 10 mm wide and 20 cm long on a typical chromatography plate (9 channels/plate). Strips of blotter paper that are wrapped in polyethylene to minimize evaporation are used to deliver the solution. Capillary action is used to draw the solution up the media within the channel. The movement of a tracer versus the water front is used to estimate the migration potential of an element. Multiple wetting and drying cycles may be used.

The channel chromatographic method has proven to be a convenient and rapid method for qualitatively monitoring the migration potential of substances with low or moderate sorption qualities. The method also is one of the only two known methods of studying sorption-migration at unsaturated conditions.

Limitations discovered during WISAP studies include the necessity of a complex data reduction scheme to obtain quantitative Kd values (Francis et al. 1978b). The complexity of unsaturated flow up the channel necessitates several replications to lower variance and the measurement of several parameters such as dispersivity and water contents versus time and space. The method also is limited to tracers that exhibit low to medium Kds (<20 ml/g). Because of these complications and limitations, further work on this method has been postponed. In principle, the method should be usable on thin rock slabs, but no practical demonstration has been performed nor are any presently planned. Through the use of sophisticated data reduction techniques, Kds calculated from channel chromatography were shown to be comparable to Kds obtained by batch methods for the system (crushed shale, 0.1 N Ca solution and the tracers Ni and Sr) as shown in Table 4.2.

Flow-Through Column Kd Methods

The classical dynamic method for determining Kd values is the low pressure column method on disaggregated materials. The method has been used for many years to validate Kds determined by batch methods for sand soils. For

TABLE 4.2. Comparison of Kd Values (ml/g) Obtained by the Chromatographic Technique and Batch Equilibrium Measurements^(a)

	Chromatographic Kd	Batch Equilibrium Kd
⁶³ Ni	5.3 - 9.6	6.5
⁸⁵ Sr	2.4 - 3.6	2.4

(a) For both cases, calcium concentrations in the solution phase were 0.1 meq/cm³.

WISAP needs, the procedure is being modified to allow experimentation on intact or fissured core materials. By increasing the hydrostatic head with pressurized pumps, flow through intact cores of slightly to moderately permeable rocks can be attained.

Dynamic flow-through column experiments allow observation of nuclide migration rates and calculation of nuclide Kds for porous materials without significant sample alteration. Reversibility and multiple oxidation-state or species can be observed; physical transport of colloids and fine particulates can be studied; realistic solution to solid ratios for both porous and fracture flow may be studied; and unsaturated as well as saturated flow can be studied. Disadvantages include the length of time necessary to perform the experiment (especially for strongly sorbed nuclides), inability to create practical flow rates in "tight" rock materials, experimental artifacts such as channeling and wall effects caused by use of small column sizes, greater difficulty in control of Eh and pH, and lack of a data reduction scheme for nonideal (chromatographic) curves.

Because of the amount of equipment and time required to complete an experiment, fewer dynamic experiments can be conducted simultaneously compared to the static method. Normal flow rates for columns of permeable rock or soil (10^{-3} to 10^{-1} cm/sec) may require weeks or months for the nuclide to break through in the effluent. Flow rates in geologic media (10^{-7} to 10^{-3} cm/sec) are expected to be several orders of magnitude slower (Erdal et al. 1978). To produce short-term results, the higher flow rates are used and frequently kinetic effects are thought to dominate results (Seitz et al. 1978). The effective porosity of the media and the radionuclide residence time in the media decrease with increasing flow rates. This effect might lessen the radionuclide retardation.

In FY-1978 dynamic Kd experiments using crushed montmorillonite percolated by either calcium chloride or sodium chloride were shown to yield comparable values with results obtained by batch and axial filtration techniques. One example of the comparison is shown in Figure 4.4 (Meyer et al. 1978).

One difficulty in performing column experiments on fine grained sediments (such as clays) is their low permeability. To enhance water flow through

FIGURE 4.4. Distribution of Sr(II) Between Montmorillonite and Sodium Chloride - 0.1 M Sodium Acetate Solutions [Low Loading Sr(II)]

laboratory columns of disaggregated rocks and sediments, a "dilution" technique that employed relatively inert material with greater permeability was used (Meyer et al. 1978). Glass beads, purified SiO_2 (clean beach sand), asbestos, and Celite (a diatomaceous filter aid) were mixed with clays to enhance the water flow characteristics of packed columns. Meyer et al. (1978) recommend a mixture of 20% clay and 80% Celite for small columns (0.5 cm dia x 2 cm long) run with gravity flow. Flow rates of 0.2 cm/min were typical. For many aquifer simulations this flow rate is exceedingly high and caution should

be taken that kinetic effects are either accounted for or are insignificant. If kinetic effects are not important such flow rates allow experimentation to be performed rapidly and conveniently.

Gravity flow column experiments sometimes exhibit a variable flow rate history versus time (Seitz et al. 1978). Usually the observed flow rate will decrease with time possibly caused by column plugging by fine grained materials. Oftentimes the flow rate drops to zero. In any case, data reduction of breakthrough curves from a column under variable flow conditions is more difficult than under constant flow conditions. To alleviate the variable flow complications a low-pressure pump is often used to control the fluid flow. This increases the equipment needs but allows data reduction. Pumping upflow appears to lessen problems associated with performing column experiments. The effect of upflow execution on column hydrodynamics needs further study before this technique should be universally adopted.

Typically column experiments are performed to validate the migration potentials obtained from simpler static adsorption tests. The observed results of laboratory column experiments are affected by both the chemical interactions and hydrodynamic characteristics of the media placed within the column. Thus, to validate the chemical aspects, the hydrodynamic aspects must be understood and measured. A classical method of elucidating hydrodynamic properties such as apparent porosity and dispersion, is to use tritium as a water tracer. HTO water has commonly been assumed and often verified to be a non-reactive moiety and thus a good tracer of the bulk water (Ames and Rai 1978). In some cases, though, tritium migration does not appear to mimic the bulk water (Francis et al. 1978).

An example of nuclide migration column studies on 40 to 70 mesh (420 to 210 μm) glauconite, a hydrous silicate, can be found in Seitz et al. (1978). A tritium breakthrough curve gives an apparent porosity value very similar to the value calculated from the saturated water content. Pulse injections of ^{85}Sr traced calcium sulfate waters were observed to elute from the columns in a single peak that moved with a velocity of about 0.04 times the water velocity (retardation factor = 25). Figure 4.5 shows the change in breakthrough curve with variable flow rate. The spread in the curve was explained as being

FIGURE 4.5. Elution of Strontium from a Column of Glaucinite. Peak Width Increases with Flow Rate (Top to Bottom), Indicating Nonequilibrium Behavior

caused by reaction kinetics. A second explanation could be velocity-dependent hydrodynamic dispersion (Ahlstrom 1974). Neither explanation explains the slight decrease in volume for peak breakthrough versus increasing velocity. The flow rate 0.1 ml/min equals a velocity of 1.2 km/yr, which would be considered as near the upper boundary for normal aquifers. In general, the results with the glauconite disaggregated columns obeys idealistic ion-exchange chromatographic theory.

Similar experiments using intact but porous limestone core were performed (Seitz et al. 1978). Tritium breakthrough curves give a calculated porosity of 19% whereas water capacity at saturation gives a value of 49%. The large difference is disconcerting and must reflect, in part, a significant percentage of unconnected pores typically called "dead-end" pores. Similar discrepancies in observed porosities versus calculated porosities for shale and chalk intact cores were also observed. Further work is needed to ascertain the application of laboratory intact cores to simulation of in-situ flow in "semi" porous media.

The resultant Sr elution curves from the intact limestone cores are broad and skewed, indicating possible complications caused by kinetics and irreversibility (see Figures 4.6 and 4.7) (Seitz et al. 1978). In other batch experiments on crushed limestone with the same synthetic groundwater that was used to prepare the breakthrough curve shown in Figure 4.7, a calculated retardation factor of 67 was found. The retardation factor calculated from Figure 4.7 is seven, or about one order of magnitude lower. This lack of agreement merits further study and must be explained or discredited before laboratory batch K_d values on crushed material may be used with confidence to predict migration through intact but porous rock.

High pressure intact core methods are under study (Ramspott et al. 1977, Tewhey 1979). For most deep geologic scenarios, this technique would apparently better simulate actual expected conditions than the static or packed columns methodologies discussed.

A design chosen by LLL (Ramspott et al. 1977) for intact core work is shown in Figure 4.8. The apparatus is designed for longitudinal driving pressures up to 3.4 MPa (500 psi) and radial confining pressures up to 40.8 MPa

FIGURE 4.6. Elution Curve for ^{85}Sr Forced Through an Oolitic Limestone Column with REW Solution. Solution flow rate was 0.1 ml/min.

FIGURE 4.7. Elution Curve for ^{85}Sr Forced Through an Oolitic Limestone Column with Recipe Solution. Solution flow rate was 0.043 ml/min.

(6000 psi). The rock samples are 13 or 26 mm diameter, and 26 mm in length; they are covered along the sides by cast plastic jackets that also seal the samples to the end fittings and prevent leakage of the confining pressure

FIGURE 4.8. High Pressure Sorption Apparatus

fluid. Brass and stainless steel have been specified for the prototype sample holder since both metals have mechanical properties that are quite adequate for the initial tests and they are more quickly and cheaply fabricated than high-pressure steel. The injection valve and supply line are made of teflon to minimize sorption effects.

The brass high-pressure sample chamber is rated for confining pressures up to 40.8 MPa (6000 psi), which correspond to a depth of 1.7 km (5700 ft) in media with a density of 2.4 mg/m^3 and should, therefore, be large enough for a simulation of reasonable waste repository depths.

The adapters that hold the ends of the cylindrical sample have been designed in both 13 mm and 26 mm sizes, with the 13 mm size being used for initial pressure and jacket fabrication tests. The small size minimizes

sample support problems, but the larger size tends to average out sample inhomogeneities. Preliminary findings show that construction of an apparatus that will accept intact cores with dimensions 12 to 25 mm length will cost about \$10K and the time necessary to collect migration data may be extremely long.

In FY-1978 initial runs were made with a tuff core with distilled water to debug the apparatus (Tewhey 1979, Tewhey et al. 1979). Subsequent runs with groundwaters traced with ^{85}Sr and $^{95\text{m}}\text{Tc}$ have shown under air-equilibrated conditions that Tc migration is not retarded and Sr retardation yields a Kd of about 5. Both isotopes exhibit ideal chromatographic breakthrough curves when input as a spike impulse. The Tc results compare with batch Kd values, but Sr retardation in the core is nearly a factor of 8 lower than would be predicted from batch results on crushed rock. More experiments are underway to investigate this discrepancy.

Theoretical studies (Apps et al. 1978) show that for intact crystalline rock, extremely large pressures would be necessary to force water through the grain boundaries. For crystalline rocks, fracture flow appears to be the most feasible mechanism for nuclide transport. Proper experimental methodology to use in studies of fracture or crack flow will need to be assessed.

Dynamic experiments on machined (artificial) fissures have been performed in the laboratory (Seitz et al. 1978). The polished sides of two rock slabs (2.5 cm wide x 5 cm long) were separated by 0.027-cm wax gaskets. Preliminary static experiments were performed to ascertain the time needed to reach equilibrium and to obtain surface adsorption and desorption coefficients for the nuclide Am.

Fissure infiltration experiments at three velocities were then performed with a pulse input of Am-traced rock-equilibrated water (REW) followed by elution with "cold" REW. Observed results were compared with a computer model, which includes first-order kinetic terms (Strickert et al. 1978). Example comparisons are shown in Figures 4.9 and 4.10. The general shape of the observed Am distribution on the fissure surface is predicted by the computer model but in each instance the observed distribution exhibits a larger tail protruding down the fissure. Autoradiographs of the fissures showed that the

A. AMERICIUM DISTRIBUTION ON SURFACE OF FISSURE.

B. MODEL PREDICTION OF AMERICIUM ON SURFACE OF FISSURE.

FIGURE 4.9. Experimental and Predicted Distributions of Americium on the Fissure Surfaces after Elution with 20 Fissure Volumes of Solution at a Flow Rate of 1.13 cm h^{-1}

A. AMERICIUM DISTRIBUTION ON SURFACE OF FISSURE.

B. MODEL PREDICTION OF AMERICIUM ON SURFACE OF FISSURE.

FIGURE 4.10. Experimental and Predicted Distributions of Americium on the Fissure Surfaces after Elution with 20 Fissure Volumes of Solution at a Flow Rate of 4.77 cm h^{-1}

adsorption was not uniform across the cross-section. This was probably caused by nonuniform flow (wall effects) and grain edge and mineral-filled vein boundaries, but these effects were secondary. The conclusion drawn from the fissure experiments is that migration of nuclides in rock fissures is tractable and can be approximated by data from static experiments obtained on similar geometries, as long as kinetics are analyzed. The results show measurement of kinetic parameters are as important to understanding migration behavior as are measurements of the equilibrium adsorption values. The validity of this conclusion is difficult to ascertain without comparing results to model predictions assuming local equilibrium (i.e., ignoring kinetics) or to model results which are devoid of numerical dispersion. In the latter case, the match to the observed fissure Am data would not improve, but the percentage of increased error might be insignificant, suggesting kinetic effects are also of only secondary importance.

Effects of Geologic Media, Groundwater and Nuclide Parameters on Kd

In FY-1978, studies for selected radionuclides on the dependence of Kd on variations in geomeedia parameters (particle size), groundwater parameters (pH, temperature, salt content), nuclide parameters (concentration, exchange site loading), reversibility, and contact time were performed.

A summary of the results is given here and specific details may be found in the subcontractor reports published in PNL-SA-7352 (Serne 1979). Some work on the Kd dependence on these variables was also performed in FY-1977. A summary of FY-1977 results may be found in PNL-2642 (Burkholder et al. 1979), and technical details may be found in PNL-SA-6957 (Serne 1978).

Particle Size Effects

The Kd value is generally assumed to depend on the exposed surface area when reported on a mass basis (ml/g). In other words, as the geomeedia are crushed to smaller and smaller particle sizes, the Kd value on a weight basis should increase. This effect has implications for simulation of real world situations from laboratory data on crushed rocks. If crushed samples are used to perform laboratory experiments, the Kd values obtained must be modified by an appropriate scaling factor to simulate intact rock. To date, investigations

on the appropriate scaling factors have been sparse. Two parameters have been identified as potential candidates: surface area and cation exchange capacity. The former parameter suffers from measurement complications. Two common methods, BET (Branauer, Emmet, and Teller 1938) and ethylene glycol sorption (Bower and Goertzen 1959, Rai and Franklin 1978), have been used. There does not appear to be any direct correlation between results using these two methods, but the ethylene glycol method does appear to correlate with cation exchange capacity, which is a parameter known to affect the sorption of many radionuclides (Apps et al. 1978). Thus, present recommendations are that surface areas be measured by the ethylene glycol method or an equivalent. Work should also be performed to perfect a surface area determination method which more accurately reflects the area contacted by water molecules; i.e., a water adsorption method would be an ideal surface area measurement technique. All surface area techniques that are presently used are limited in sensitivity (detection limit 0.1 to 1.0 m²/g), and thus, accurate values on small chunks of impermeable rock are very difficult to obtain.

For radionuclides that adsorb predominately by ion exchange types of reactions, the use of exchange capacity as a scaling factor is quite logical. The number of elements that can be classified as depending predominately on exchange adsorption has not been determined but preliminary results on rare earths and actinides at neutral pH suggest that ion exchange may not universally describe radionuclide adsorption. The dependence of K_d on exchange capacity is not a simple linear relationship. For example, in a 2:1 exchange reaction (e.g., Ca versus Na) the distribution coefficient of calcium on the sodium form of an exchanger varies with the square of the exchange capacity, but the distribution coefficient of sodium on the calcium form varies with the square root of capacity. In the adsorption of strontium on a calcium form of an exchanger, the dependence of K_d on exchange capacity is linear or first order.

Batch studies were performed at the Los Alamos Scientific Laboratory (LASL) on the dependence of K_d on rock particle size (Serne 1979; Erdal et al. 1978a,b). Four particle size fractions of argillite were studied: 75 μm, 106-150 μm, 350-500 μm and chunks 2-5 mm (2000-5000 μm). Both cation exchange

capacity and surface area measurements were made of the two middle-size fractions. Since the differences were minor a quantitative determination of K_d dependency on these parameters was not attempted. More characterization over a larger range of particle sizes is needed to develop a quantitative relationship. At least qualitatively, an increase in the surface area was accompanied by an increase in the sorption ratio. However, the changes were not very large and may have been due to other factors. Since the permeability of the argillite was low, the K_d values for the chunk samples were significantly lower than those obtained for crushed samples. Similar statements may be made about K_d determinations on granite versus particle size distribution. Table 4.3 gives a brief summary on the variation of K_d versus particle size for these two media.

Generally the average K_d data show a factor of 3 to 5 increase and, in a few instances, a factor of 10 increase in K_d as the particle size is decreased from sand-sized to silt-sized material. For the K_d data on argillite chunks, the Eu and Ce data show a large variation between two pieces, possibly reflecting mineral heterogeneities. The technetium adsorption versus particle size shows a large variation in the smallest size fraction.

In an experiment performed at the Oak Ridge National Laboratory (ORNL), the K_d for limestone and basalt rocks were measured for two particle size ranges, 45-63 μm and 300-850 μm (Meyer 1978). The surface area and exchange capacity of the smaller particle size range were not measured, thus no quantitative relationship has been established. The results in Table 4.4 show there is little difference in the K_d values for Sr but there are significant increases in $K_d(\text{Cs})$ when the samples are crushed and when the solution is a low ionic strength groundwater. Sorption of these two isotopes from salt brine is minimal for either particle-size rock samples.

Work to correlate adsorption on machined fracture surfaces versus natural rock fissures is underway by researchers at Whiteshell Nuclear Research Laboratory (Vandergraaf 1979) in Canada. Because the Canadian repository concept is based on hard rock, they expect that, if groundwater reaches the disposed wastes, the dissolved radionuclides will mainly encounter fracture surfaces

TABLE 4.3. Average Kd Value (ml/g) Versus Particle Size

	<u><75 μm</u>	<u>106-150 μm</u>	<u>250-350 μm</u>	<u>350-500 μm</u>	<u>500-800 μm</u>	<u>2000-5000 μm</u>
ARGILLITE						
Cs	2,415	1,540		2,410		5000-6000
Sr	236	83		80		52.5
Ba	9,810	866		1,000		520-560
Ce	136,500	43,100		47,900		21,500-155,000
Eu	105,300	43,100		49,200		19,500-113,000
GRANITE						
Cs		516	283		411	
Sr		19	13		11	
Ba		415	150		78	
Ce		1,340	366		186	
Eu		3,580	1,040		367	
Tc		160	-0.9		-0.7	
U		10.1	2.4		1.7	

TABLE 4.4. Average Kd(ml/g) of Sr and Cs Versus Particle Size

System	Kd(Sr)		Kd(Cs)	
	<u>350-850 μm</u>	<u>45-63 μm</u>	<u>300-850 μm</u>	<u>45-63 μm</u>
Limestone-gw	5.9	6.1	227	485
Limestone-brine	1.0	1.3	0.6	0.8
Basalt-gw	89	108	380	677
Basalt-brine	0.7	1.4	2.2	2.8

rather than large volumes of porous particulate sediments. Thus, the Canadians are measuring surface adsorption coefficients on machined rock surfaces rather than on crushed and sieved material, as the former should be more readily related to actual rock fracture surfaces. Standardization of surface

area sorption coefficients, K_a , is performed using pieces of machined rock with a geometrical surface area of 10 cm^2 in contact with 10 ml of solution for periods of 2 to 4 weeks. Initial experiments were performed with "cold" wash and with only occasional shaking for a simulated groundwater. More recent experiments include two "cold" pre-equilibrations with the synthetic groundwater and agitation of the system at 0.7 Hz. The relationship between smooth machined rock surfaces and actual rock fracture surfaces on samples with similar apparent geometric surface areas is measured by comparing the adsorption of various radionuclides on both samples. For an albite-quartz-biotite gneiss rock the Canadians obtained a ratio (real fissure surface/machine surface) of 5-9 depending upon the nuclide used. This comparison method is an alternative to BET or ethylene glycol methods to determine surface areas.

pH Effects

In FY-1978, little work was performed on artificially controlling the pH of rock-water slurries. As most groundwaters are found to exist in a narrow pH range typically between pH 6 to 8.5, most experimenters have not performed controlled pH experiments. The geomeedia in most instances has enough inherent buffering capacity to control the system pH. Thus, the pH of the rock-groundwater system was often difficult to control without addition of solution buffering agents. Long contact times and frequent additions of acid or base can drive the pH of a rock-water slurry to an unnatural value to allow experimentation at variable pH. This process undoubtedly forces changes in the adsorbing geomeedia by exhausting their natural buffering capacity. The effect on K_d of these forced changes are not fully quantifiable at present. For many of the nuclides, pH dependent hydrolysis occurs and affects the solution species distribution. This variation in solution speciation can lead to variations in nuclide sorption. Rare earths, actinides, and some transition metals are especially sensitive to solution pH. Thermodynamic predictions of aqueous species distributions of important radionuclides are summarized in Rai and Serne (1978). Such data may be used to predict the pH dependency of solution species.

In FY-1978 Meyer (1978) continued a few experiments on K_d dependence on pH. The adsorption data of the elements Am, Cd, and Co on montmorillonite clay show significant increases as the pH is increased from pH 5 to pH 6.5 as shown in Figures 4.11, 4.12, 4.13. Figure 4.11 shows for Am adsorption that ion exchange competition appears to affect adsorption at the low pH experiments (pH 4 and 5) but that at pH 6.5 Am adsorption is independent of solution composition. Both Figure 4.12 and 4.13 show that Cd and Co adsorption K_d values may be quite sensitive to the tracer concentration in solution. All three of these elements (Am, Cd, and Co) are somewhat sensitive to pH-dependent hydrolysis and thus the dependence of K_d on solution pH is not surprising.

Even for elements whose solution chemistry is not very sensitive to pH, such as Cs, a K_d dependence on pH may still be observed (Elprince 1978). Elprince found the pH dependent Cs adsorption on Savannah River Plant sediments to be caused by hydrous aluminum surfaces present in the sediments. Thus both the aqueous trace element itself and the adsorbing solid may exhibit pH dependence which can manifest itself as a variable K_d with changes in pH.

Studies performed at PNL (Relyea et al. 1979, Serne 1978) and statistically analyzed by Adaptronics (Mucciardi et al. 1978) also show that pH is an important factor in predicting the K_d for some elements.

Eh Effects

The effects on nuclide adsorption caused by variation in oxidation-reduction potential are discussed in the section on mechanism studies.

Temperature Effects

In FY-1978, experiments on K_d sensitivity to temperature were performed on argillite and granite, using batch K_d techniques at 22°C and 70°C (Erdal et al. 1978a,b). Average values (across several geomeedia particle sizes) are shown in Tables 4.5 and 4.6. For the argillite, K_d appears to increase with increasing temperature for Sr and Ba with no significant temperature effect for Cs. The values for Ce, Eu and Tc show a decrease in K_d as the temperature is raised to 70°C. For the granite, the K_d for Sr, Cs and Ba increases with

FIGURE 4.11. Adsorption of Am-241 on Na-Montmorillonite

FIGURE 4.12. Loading Effect on Distribution Coefficient of Cobalt

FIGURE 4.13. Distribution Coefficients for Cd(II)/Na(I) Exchange Versus Loading on Montmorillonite

TABLE 4.5. Recommended Sorption Ratios (ml/g) for Argillite

Element	22 ± 2°C		70 ± 1°C	
	Sorption	Desorption	Sorption	Desorption
Sr	135 ± 10	126 ± 14	322 ± 37	268 ± 36
Tc(VII)	47 ± 15		3.4 ± 0.8	17 ± 8
Cs	1,990 ± 120	3,610 ± 210	1,580 ± 90	2,680 ± 140
Ba	3,920 ± 710	5,240 ± 790	13,200 ± 3,000	31,300 ± 6,700
Ce(III)	41,900 ± 6,400	86,400 ± 14,000	10,800 ± 2,500	17,400 ± 3,900
Eu(III)	36,000 ± 5,100	89,200 ± 6,000	11,400 ± 2,300	42,700 ± 7,400

TABLE 4.6. Recommended Sorption Ratios (ml/g) for Granite

Element	22 °C		70 °C	
	Sorption	Desorption	Sorption	Desorption
Sr	16 ± 1	20 ± 1	38 ± 5	39 ± 5
Tc(VII)	30	100	10	100
Cs	320 ± 30	550 ± 40	795 ± 70	1,370 ± 240
Ba	164 ± 25	170 ± 30	718 ± 240	750 ± 230
Ce(III)	240 ± 60	1,410 ± 270	41 ± 5	1,050 ± 190
Eu(III)	550 ± 150	1,500 ± 250	71 ± 12	1,160 ± 140
U(VI)	4.4 ± 1.0	15 ± 2		
Pu	1,500 ± 330		3,800 ± 3,200	
Am	3,800 ± 1,100	1,000 ± 410	10,000 ± 7,500	1,200 ± 740

increasing temperature, the K_d for Tc, Ce and Eu decreases with increasing temperature. The apparent decrease in Ce and Eu adsorption may indicate an increase in solubility of these elements, which are typically only slightly soluble at neutral pH values. The variation in K_d , Am and Pu makes a definitive statement of temperature effects impossible at present. In all instances the K_d differences caused by temperature are an order of magnitude or less. Also note that desorption K_d 's are in general larger than adsorption K_d 's.

Ionic Strength or Groundwater Salt Content Effects

For those elements which exhibit cation-exchange adsorption the K_d would be expected to decrease as the groundwater salt content increased. Systematic studies of Cs, Sr, Ba, Eu, and Am versus NaCl or CaCl_2 salt concentration were performed at ORNL (Meyer 1978, Shiao et al. 1978) in FY-1978. Sorption predictions based on ion exchange theory are discussed in the section on mechanism studies. Figures 4.11, 4.14, 4.15, 4.16, and 4.17 show the variation in Cs, Sr, Ba, Eu, and Am adsorption on montmorillonite clay with solution NaCl concentration at pH 5 unless stated otherwise. Similar curves were obtained in CaCl_2 solutions. The observed variation in K_d with salt concentration for Cs, Sr, and Ba follows expected trends but the Eu and Am results deviate. The upswing in Eu adsorption in brines above 1-2 M is

FIGURE 4.14. Adsorption of Cs(I) on the Sodium Form of Montmorillonites From Several Sources (loading: 2×10^{-4} - 4×10^{-2} M Cs(I)/kg equilibration for 24 hr)

FIGURE 4.15. Adsorption of Sr(II) on the Sodium Form of Wyoming Montmorillonite (loading: 6×10^{-5} - 2×10^{-2} M Sr(II)/kg, pH 5, equilibrium for 45 hr)

FIGURE 4.16. Adsorption of Ba(II) on the Sodium Form of Wyoming Montmorillonite (loading: 8×10^{-5} - 1.6×10^{-2} M Ba(II)/kg, pH 5, equilibrium for 20 hr)

FIGURE 4.17. Adsorption of Eu(III) on the Sodium Form of Wyoming Montmorillonite (trace loading, pH 5, equilibration for 16 hr)

presently unexplainable. The Am results at pH 6.5 show that adsorption is independent of salt concentration. If other actinides and rare earth elements show this trend, adequate adsorption of these elements from salt brine may support burial in salt repositories. All results to date indicate that Sr and Cs adsorption from salt brines is much lower than from other types of groundwaters.

The batch Kd results presented by PNL (Relyea et al. 1978, Serne et al. 1978) and statistically analyzed by Adaptronics (Mucciardi 1978) also show the effects of groundwater salt content.

Nuclide Concentration and Exchange Site Loading Effects

The Kd value has been assumed to be independent of the concentration of the tracer present in the experiment or contaminated environment being modeled. Ion exchange theory predicts a region where Kd would be independent of tracer concentration or percentage of exchange sites filled by the tracer.

In FY-1978, experiments involving these factors were performed at ORNL (Meyer 1978) and Rockwell Hanford Operations (RH0) (Barney and Anderson 1978).

Loading curves for the elements Sr, Cs, Ba, Co, Cd, and Eu on montmorillonite from NaCl and CaCl₂ solutions have been determined. Figures 4.18, 4.19, and 4.20 show the effects of loading on the adsorption of Cs, Sr and Eu on montmorillonite for a NaCl brine. Significant decreases in Kd are not seen until the loading of tracer reaches well over 10% of the total exchange capacity. Thus for this mineral-ground-water system and for these elements Kd would be independent of tracer concentration until values reach threshold levels. Loading results for these elements onto calcium-saturated montmorillonite from CaCl₂ solutions showed significant decreases in Kd when loading reached a few tenths of a percent of the cation exchange capacity. Thus, in calcium dominated systems one must be more cognizant of the expected tracer concentrations and loading effects.

The effect of increasing the initial tracer concentration for the elements Cs, Sr, Np, Am and Pu in batch Kd experiments for the rocks basalt, granite, and argillite are shown in Table 4.7. The results show that the Kd for Cs is significantly lower when initial concentrations reach 1×10^{-5} M than when Cs is present at lower concentrations. The granite Kd apparently is sensitive to Cs concentrations greater than 10^{-8} M. The Sr data show that little concentration dependency exists. For both Sr and Cs, the natural background concentration should be larger than any waste concentration, and thus, the Kd will be controlled by the natural concentration.

For Np, Am, and Pu the general trend shows an increasing Kd with increasing original concentration. Since the concentrations used often exceed projected solubility limits for these elements at neutral pH values, the increasing Kd is likely caused by element precipitation. This effect must be evaluated in most reported work on actinides. To facilitate counting, experimenters have spiked unrealistically high concentrations of tracer into groundwater and possibly biased observed Kd values to higher than true values.

Reversibility

To date the retardation factors used in mathematical transport models have assumed reversibility (i.e., Kd for adsorption equals Kd desorption, and if time is considered, the rate of adsorption equals the rate of desorption).

Experimental studies performed in FY-1977 and FY-1978 have shown that for certain elements, the rate of desorption in short-term laboratory studies is slower than the rate of adsorption and when apparent steady-state conditions are met the resultant Kd for desorption is higher than the Kd for adsorption. There are two explanations for these phenomena. Neither explanation has been investigated enough to ascertain whether it causes the observed differences.

The first explanation considers the type of adsorption process. When adsorption is caused by ion exchange reactions with surface sites, the concept of reversibility is usually considered to occur because the exchange sites are assumed to be impartial to the type of ion which they will attract if competing ions have the same electrostatic charge. All competing ions of like charge can substitute for each other. Reversibility is observable for many

FIGURE 4.18. Effects of Loading on Distribution Coefficients of Cs(I) on the Sodium Form of Wyoming Montmorillonite (0.5 M NaCl + 0.01 M NaOAc, pH 5, equilibration for 74 hr)

FIGURE 4.19. Effect of Loading on Distribution Coefficients of Sr(II) on the Sodium Form of Wyoming Montmorillonite

FIGURE 4.20. Effect of Loading on Distribution Coefficients of Eu(III) on the Sodium Form of Wyoming Montmorillonite (pH 5, equilibration for 44 hr)

TABLE 4.7. Effect of Tracer Concentration on Kd

Isotope	Initial Concentration	Kd (ml/g) for		
		Basalt	Granite	Argillite
^{137}Cs	1.1×10^{-8}	613	1,433	6,250
	1.1×10^{-7}	592	907	7,591
	1.1×10^{-6}	429	232	4,446
	1.1×10^{-5}	281	107	3,345
^{85}Sr	1.1×10^{-7}	119	6.31	78.4
	1.1×10^{-6}	123	7.01	72.8
	1.1×10^{-6}	114	6.30	68.3
	1.5×10^{-6}	111	7.86	75.9
^{137}Np	9.2×10^{-7}	7.24	256	44.2
	7.8×10^{-6}	1.37	31.3	63.7
	9.0×10^{-5}	40.1	147	238
	7.0×10^{-4}	106	153	1,365
^{241}Am	1.5×10^{-10}	17.1	6,141	3,243
	1.6×10^{-9}	7,955	17,957	32,426
	1.1×10^{-8}	17.1	26,782	72,878
	1.5×10^{-7}	23,738	59,173	88,544
Pu	1×10^{-8}	3.39	644	1,233
	1×10^{-7}	1,919	8294	23,199
	1×10^{-6}	4.03	773	727
	1×10^{-6}	47.4	165,043	175,502

instances where ion exchange is the predominant sorption mechanism. For certain 2:1 lattice clays, ions can invade the interlayer sites and collapse the spacing between layers. The entrapped ions can be exchanged only at much slower rates than during the loading phase. Cesium sorption onto illite-type clays is a classic example (Ames and Rai 1978, Frink 1971). Other types of adsorption which may contribute to nuclide retention include precipitation of insoluble mineral phases, coprecipitation or entrapment in amorphous coatings, especially hydrous alumino, manganese, and iron oxides. Under certain conditions, these sorption reactions may appear irreversible. Changes in pH or oxidation-reduction conditions are often needed to create dissolution of these phases. If the water remains at constant pH and Eh conditions but changes soluble cation or anion composition, precipitated or entrapped nuclides may remain adsorbed because competition by ion exchange is of lesser importance. Since many rocks have a large pH and Eh buffering capacity, it is quite possible that pH and Eh could be held relatively constant despite changes in groundwater composition. Thus, for some types of adsorption, changes in competitive ion composition of the groundwater may not provoke desorption.

A second mechanism that manifests itself as partial irreversibility or slower rate of desorption is diffusion controlled sorption. During adsorption, especially on aggregated material or onto fracture surfaces, the concentration gradient will allow diffusion deeper into the bulk rock or rock fragment which removes nuclides slowly from the main flow conduits. When the concentration gradient reverses in the main water-bearing conduits because of exhaustion of the contamination plume, leaching will start. Within the bulk rock and dead-end pores, there will be a delay time before the concentration gradient reverses itself and diffusion begins in the opposite direction (back towards the main water-bearing conduits). In short-term laboratory experiments a slower rate and lesser amount of desorption would be observed. The importance of this diffusion controlled phenomenon over the long time frames considered in repository simulations has not been assessed.

Reversibility experiments were performed in FY-1978 at LASL (Erdal et al. 1978a,b), LBL (Silva et al. 1978), and PNL (Relyea et al. 1979). The work at the Lawrence Berkeley Laboratory (LBL) was performed on small rock tablets. The other work used crushed rock. The comparison of sorption versus desorption for the elements Cs, Ba, Sr, Tc, Ce and Eu contacting argillite showed significantly larger desorption K_d values for Ce and Eu. The same was true for these elements contacting granite. This observation may be a consequence of the following phenomena. The solution from which sorption takes place may contain different species of the same element. If interchange between such species is very slow and they exhibit different sorption characteristics, only a few species may sorb strongly while the others remain in solution. The nonsorbing species are then absent in the desorption experiment and a smaller amount of the element would be expected in solution. Other explanations include the diffusion into the solid and the slow alteration of the rock surfaces (weathering) to a form more prone to nuclide retention.

Cylindrical rock wafers (3.2 cm dia x 0.5 cm thick) of basalt, granite, and shale were used in adsorption-desorption experiments for the elements U, Np, Pu, Am, and Cm. Results for all but Am show some increase in K_d desorption when compared to K_d adsorption, but the scatter in data make a definite conclusion impossible.

The largest increase was found for shale, which apparently shows some sorption occurring deeper within the tablet. The diffusion effect mentioned above may be creating the differences in K_d .

Batch adsorption-desorption experiments on common minerals were performed at PNL (Relyea et al. 1979, Serne et al. 1978) for the elements I, Tc, Cs, Sr, Np and Am. Because of the larger uncertainty in the amount of activity adsorbed by a mineral caused by container adsorption and remaining activity in pore waters, the range of values obtained for a desorption K_d is usually larger than the range found for the corresponding adsorption K_d . This is especially true for elements with very low adsorption K_d values. When almost no activity is adsorbed on the mineral in the loading portion of the experiment, there is

very little activity to desorb. In the calculation of K_d this leads to subtracting one small number from another and dividing by a small number resulting in the potential for large differences. Even with the large variation in K_d desorption values, significant differences were detected. Almost half the desorption K_d values were significantly larger than their adsorption counterparts, and very few K_d values decreased.

Adsorption-desorption experiments on a machined smooth fissure in a gray hornblende schist for the element Am were performed at ANL (Seitz et al. 1978). The adsorption data indicate a rapid, exponential decrease of activity in solution with 99.9+% adsorbed in 70 hr. Desorption experiments performed with contact times between 10 seconds and 60 min yielded results which were so varied that no quantitative conclusions could be drawn about the rate of desorption. Qualitatively it appeared that desorption did occur with a rate equal to or less than the adsorption rate.

Using various groundwaters and 0.1M salt solutions as desorbing solutions, Barney (1978) investigated the reversibility of nuclide adsorption on basalt, granite and shale. Although long-term desorption was not studied and the competing salt solution technique is somewhat arbitrary, the following conclusions were made: 1) cesium adsorption onto granite shows irreversibility but Ce appears to be reversibly adsorbed on the shale and basalt, 2) ruthenium is irreversibly adsorbed on all three rocks, and 3) plutonium and americium adsorption on basalt is reversible, but is irreversible on granite and shale. More properly one could state a salt solution of competing cations readily removes sorbed nuclides in the instances where reversibility is claimed.

Contact Time Effects

Many experimenters evaluated adsorption as a function of time. At ORNL (Meyer 1978) Sr and Cs adsorption on montmorillonite was found to reach equilibrium within two hours. For the mineral attapulgite, Rb(I) adsorption reached equilibrium extremely rapidly (within 30 min), Cs(I) adsorption reached equilibrium with 10 hr, but Am(III) required 21 days. In each

instance the minerals were crushed to below 325 mesh ($<44\ \mu\text{m}$) and the contact performed at high solution to solids ratios in batch experiments.

At LASL (Erdal et al. 1978a,b) batch experiments were performed with K_d measurements performed at 1, 2, 3, 4 and 8 weeks. On the average, K_d values for most elements increased with time. Some elements show an increase over the eight weeks of over an order of magnitude such as the hydrolyzable ions Eu and Ce. For Sr sorption on granite, the observed K_d increased very little with time. At the elevated temperature of 70°C , Cs adsorption increased dramatically (almost 2 orders of magnitude) over the 8-week period. A possible explanation is alteration of the geomeadia's surface mineralogy.

Sorption of actinides onto rock tablets was followed for 32 days (Silva et al. 1978). For the elements Pu, Am, and Cm, adsorption was essentially complete after 10-15 days with only a few percent of activity left in solution. The decrease in solution activity was quite rapid with less than 10% of the initial activity left in solution after 5 days. A similar trend was found in blank (no rocks present) containers with less than 10% of the initial activity left in solution after 10 days. Thus sorption by itself may not be the cause. U and Np sorption was much smaller and, excepting Np adsorption on shale and U sorption on basalt, did not show any trends versus time. For the two exceptions, adsorption slowly increased over the observation period.

Long-term (>100 day) experiments on nuclide adsorption are underway at RHO (Barney and Anderson 1978). After 110 days, the sorption of Cs is still increasing on granite and has possibly leveled off for basalt and argillite (shale). For Sr, the adsorption onto granite is increasing and appears to be decreasing for basalt and shale. Np sorption onto basalt is increasing and may be very slowly increasing on granite and shale. Americium sorption on granite and shale became constant after 30 days but appears to be decreasing for basalt. Plutonium adsorption appears to be increasing for granite and shale and decreasing for basalt. The macro constituents (major cations and anions and selected trace metals) were also monitored over these times. Apparently slow groundwater-geomeadia reactions are occurring. The system continues to be dynamic and thus the variation in sorption is not surprising.

The apparent decrease in sorption with time for some of the nuclides contacting basalt has recently been found to be caused by colloidal particles (Barney and Anderson 1979). The unstable glassy matrix of the basalt appears to be spalling fine siliceous particles into solution. These particles are not easily removed by centrifugation yet are retained on filters. In general, time dependence of sorption shows increases in sorption over long times. The weathering of fresh rock to alteration products in general leads to higher sorption capacity minerals (clays, zeolites). Diffusion into the bulk matrix over long time periods also will increase sorption values measured at shorter times.

For the first safety assessments, observed values of K_d should be adequate. If these values, which most likely are lower than values to be expected over very long time periods, are large enough to reduce environmental effects to acceptable levels, more comprehensive studies at longer contact times may not be necessary. On the other hand, experimentalists should continue to consider time effects and watch out for events where sorption decreases over long times.

The effects of geomedia weathering on sorption will be discussed further in the sections on validation and mechanism studies. To date weathering effects on sorbing media appear to have positive effects on nuclide sorption.

As the solution to solids ratio used in batch K_d experiments are quite large compared to flow in porous media and possibly to flow in fractured media, quantitative calculations of contact time (kinetic effects) from laboratory experiments would be quite tenuous. In-situ or long-term dynamic laboratory experiments may yield useful kinetic information, but it will be impossible to perform actual experiments in which geologic time scales are directly observed. A key endeavor should be to assess whether any mechanisms can be identified that actually decrease sorption over very long time periods.

Controlled Sample Program

An interlaboratory comparison of batch K_d values of oolitic limestone (Bedford, Indiana) and basalt (Sentinel Gap, Washington) for Cs, Sr, and Pu was performed in order to find the precision of determining K_d by the batch

method, and to assess the ability of various independent experimenters to obtain comparable results (Ames 1978, Relyea and Serne 1979). The participating laboratories (Table 4.8) were provided with homogeneous samples of limestone and basalt and were given recipes for groundwater preparation.

The results reported in Table 4.8 indicate that in general for all the isotopes compared (Cs, Sr, Pu), there was considerably more disagreement in K_d values for limestone than for basalt. The observed K_d values of Cs for limestone ranged over three orders of magnitude. For basalt, however, the K_d (Cs) varied by a factor of two if one datum is ignored. The K_d values for Sr for limestone varied by an order of magnitude and for basalt by approximately a factor of two. A quick glance at the K_d values of Pu for both limestone and basalt shows that the values are generally high and that these vary by two to three orders of magnitude. The reasons for poor precision in K_d values (Table 4.8) determined by the batch method are not readily apparent. Since the data in Table 4.8 were obtained using the same geomeedia and solutions, the poor precision may be due to some of the uncontrolled variables (such as tracer concentrations, Eh, preparation of tracer solution, shaking method and speed, temperature, variation of pH of the equilibrium solution, phase separation technique). This study reemphasized the need for mechanistic studies, strict control and understanding of factors and procedures that affect K_d , and realization that K_d is an empirical parameter most useful for site-specific geomeedia and solutions.

A second attempt using more control of variables is contemplated for the future because the observed wide variation in reported K_d values does not instill confidence in overall safety assessment calculations.

A comparison of the K_d (Cs) was performed at LASL (Erdal et al. 1978a,b) for argillite and granite. Subsamples of the rocks were contacted with radiotracers simulated groundwaters made up from stock chemicals and pre-equilibrated with crushed rock. Two separate batches of groundwater were used and the experiments were performed several months apart. All other activities were identical. The comparison for argillite was good but for granite the second set of experiments averaged a factor of three larger. Besides the

TABLE 4.8. Interlaboratory Comparison of Kd (ml/g) Values for Limestone and Basalt for Cs, Sr, and Pu*

Participating Laboratories	Cs				Sr				Pu			
	Limestone		Basalt		Limestone		Basalt		Limestone		Basalt	
	pH	Kd	pH	Kd	pH	Kd	pH	Kd	pH	Kd**	pH	Kd**
PNL	7.9	880 $\pm$ 160	8.7	380 $\pm$ 70	7.9	14.9 $\pm$ 4.6	8.7	92 $\pm$ 3	7.9	1090 $\pm$ 120 ^a 690 $\pm$ 320 ^b	8.6	200 $\pm$ 170 ^a 15 $\pm$ 2 ^b
ANL	7.9	65 $\pm$ 2	7.8	401 $\pm$ 21	8.0	5.4 $\pm$ 0.3	8.1	68 $\pm$ 17	7.6	1027 $\pm$ 41 ^a 2134 $\pm$ 77 ^c	7.5	8.8 $\pm$ 3.4 ^a 67 $\pm$ 14 ^c
LASL	8.5	88 $\pm$ 1	8.4	265 $\pm$ 4	8.5	1.4 $\pm$ 0.2	8.4	81 $\pm$ 1	8.1	4745 $\pm$ 4931 ^a 3198 $\pm$ 512 ^c	8.0	1078 $\pm$ 716 ^a 843 $\pm$ 658 ^c
LLL	ND	60 $\pm$ 30	ND	290 $\pm$ 70	ND	2.7 $\pm$ 0.5	ND	45 $\pm$ 1	ND	770 $\pm$ 36 ^b	ND	580 $\pm$ 12 ^b
ORNL-I	8.2	227 $\pm$ 14	8.3	380 $\pm$ 5	8.3	5.9 $\pm$ 0.2	8.4	89 $\pm$ 5	8.2	198 $\pm$ 50 ^a	8.2	592 $\pm$ 134 ^a
ORNL-II	ND	663 $\pm$ 61	ND	453 $\pm$ 12	ND	9.3 $\pm$ 2.4	ND	93 $\pm$ 6	ND	63000 $\pm$ 19000	ND	312 $\pm$ 66 ^a
RHO	ND	6.8 $\pm$ 0.6	ND	255 $\pm$ 7	ND	13.4 $\pm$ 0.6	ND	73 $\pm$ 4	ND	2616 $\pm$ 1135 ^b		89 $\pm$ 17 ^b
AEC (Canada)	7.8	1.3 $\pm$ 0.4	7.4	31 $\pm$ 2	7.6	1.8 $\pm$ 0.5	7.4	41 $\pm$ 6	7.5	547 $\pm$ 356 ^b	7.5	1000 $\pm$ 590 ^b
LBL	ND	48.9 $\pm$ 5	ND	296 $\pm$ 10	ND	2.4 $\pm$ 0.1	ND	55 $\pm$ 2	ND	1009 $\pm$ 162 ^d	ND	221 $\pm$ 147 ^d

* The limestone and basalt samples were crushed to a 297 to 840 μ m size. All Kds are for a 7-day equilibration period except ORNL-II, which are for a 29-day equilibration period. The ND in the data means "not determined."

** Equilibration solution treatment:

a = centrifuged at approximately 400 g and filtered through 0.2 to 0.45 μ m filter

b = centrifuged at approximately 4000 g

c = absorbed activity was determined directly from the geomeia sample instead of calculating from the change in concentration of the radionuclide in solution

d = based on original influent which was not corrected for the loss of activity from the solution not containing geomeia.

different batch of water and the fact the crushed granite had been stored for several months the experiments were identical. No explanation for the observed differences can be conclusively stated.

Shiao et al. (1978) compared the K_d values for Cs and Sr sorption on montmorillonite clays from NaCl and CaCl_2 brines with data presented by Wahlberg et al. 1965, Wahlberg and Rishman 1962, Wahlbert and Dewar 1965. The source of the clay samples, purification procedures and particle size distributions used in the reports differed. The $K_d(\text{Sr})$ reported by Wahlberg were 50% larger than those reported by Shiao. For cesium sorption from CaCl_2 solutions, Wahlberg's data are a factor of 10 to 25 lower than Shiao's data. For strontium sorption from CaCl_2 solutions Wahlberg's K_d values are about 40% greater than Shiao's values. A few other $K_d(\text{Cs})$ and $K_d(\text{Sr})$ values found in the literature agree with the range of values reported by Shiao. In FY-1977, Meyer et al. (1978) found that the maximum difference for $K_d(\text{Cs})$ adsorption from NaCl brines onto various samples of montmorillonite was a factor of 3.

Comparison between labs with literature values on similar rocks or minerals often show variations of a factor of 2 to an order of magnitude. For good comparisons, differences of 50% are quite common. Thus, at present, little work should be performed on generic samples to refine replicate comparisons to below 50%. The K_d precision will probably not be better than 50% under ideal conditions until adsorption mechanisms are understood. This level of uncertainty should be incorporated into model simulations while comparing various scenarios.

DATA ACQUISITION

To evaluate the influence of exchange and surface adsorption (Figure 4.1) on the concentration of radionuclides in solution, empirical sorption distributions (K_d , retardation factors, etc.) of long-lived radionuclides for a large number of geomeedia types are being determined by various subcontractors. The empirical adsorption-desorption determinations are carried out by reacting a known concentration of a radionuclide with well-characterized geomeedia. The

radionuclide concentration that remains in solution after the reaction is used to measure the adsorption distribution. These sorption distributions may also reflect the influence of mineral precipitation; however, this may be reduced by selecting lower tracer concentrations of the radionuclides. These data may not lend themselves to identification of adsorption mechanisms, but will provide empirical data required to assess migration from repositories and equations that can be used to assess the effects of different factors (such as pH, Eh, geomeia type) on adsorption. The equations relating the adsorption distributions to different solution and geomeia properties are being developed by fitting a polynomial to the multidimensional curve that actually describes the sorption distribution.

During FY-1978 the rocks, minerals, groundwaters, and nuclides shown in Table 4.9 were studied. To date, all experiments have been termed generic because the rock samples were not core samples from the exact depths identified as probable repository sites. A few at-depth samples and several surface outcrop samples from pertinent sites have been used in completed experiments. These pertinent rocks are identified in Table 4.10. Completed geochemical characterization of many of these rocks was performed and presented (Erdal 1978a,b; Silva et al. 1978; Ames 1978; Wolfsberg et al. 1978). Two recent PNL-generated literature searches identified reported values (Ames and Rai 1978; Ames, Rai, and Serne 1976). These values will also be extracted and properly formatted on a computer information retrieval system. Once this data bank is acquired, safety assessment modelers will have defensible and readily accessible data (from a geochemical standpoint) to attempt preliminary fate calculations. Site-specific data will be generated as soon as acceptable samples are furnished to WISAP.

Prioritized Sample Requirements for Site Assessment

To produce Kd data or retardation factors needed as input for the computer simulation of waste isolation, rock and groundwater samples and information are needed. Sample requirements are listed as an aid to any geologic site manager or interested party who might like to provide samples to WISAP experimentalists to use in this ongoing program. Those individuals or

TABLE 4.9. Rock-Groundwater-Nuclide Combinations for Which Data Were Generated in FY-1978

Rock	Groundwater	Nuclide
Glauconite	(a) 0.01m CaSO ₄ , .0001m SrCO ₃ (b) 0.01m CaSO ₄ , 1 x 10 ⁻⁷ m Sm	(a) Sr (b) Sm
Gray Horne Blende Schist	(a) REW	(a) Am, Pu
Oolitic Limestone	(a) REW 10 ppm Ca, 5 ppm HCO ₃ (b) .01m CaSO ₄ (c) 50 ppm Ca, 150 ppm HCO ₃ (d) REW	(a) Sr (b) Sr (c) Sr (d) Cs
Climax Stock "Granite"	(a) REW	(a) Am, Pu
Montmorillonite	(a) NaCl brines (0.01-4m) (b) CaCl ₂ brines (0.01-2m)	(a) Sr, Cs, Ba, Eu (b) Sr, Cs, Ba, Eu
Montmorillonite, Kaolinite, Attapulgite	(a) NaCl brine (.25-4m) pH 5	Am, Cm, Cf, Es, La, Sm, Yb, Cs*, Rb*, Sr
(a) Umtanum Basalt (b) Eleana Shale (c) Climax Stock Quartz Monzonite	(a) REW (b) REW (c) REW	(ALL) Am, U, Np, Pu, Cm
(a) Umtanum Basalt (b) Climax Stock Quartz Monzonite (c) Eleana Argillite "Shale"	(a) Na ₂ CO ₃ (b) Na-Ca-HCO ₃ -SO ₄ (c) Ca-Mg-HCO ₃	(ALL) Sr, Cs, Tc, Np, Am, Pu, Ru
Eleana Argillite	(a) REW	Sr, Cs, Tc, Cs, Ba, Ce, Eu
Climax Stock "Granite"	(a) REW	Sr, Cs, Tc, Ba, Ce, Eu, U, Pu, Am
Conasauga Shale	0.1N Ca(NO ₃) ₂	Sr, Ni
Climax Stock Granite	(a) Ca (8.6 ppm); Na (67 ppm); HCO ₃ (48 ppm); SO ₄ (2.7 ppm)	Sr, Tc, Cs, Pu
Green Argillaceous Shale	(a) Ca (50 ppm); Mg (3.6 ppm); HCO ₃ (153 ppm); SO ₄ (14 ppm)	Sr, Tc, Cs
Consauga Shale	(a) Ca (50 ppm); Mg (3.6 ppm); HCO ₃ (153 ppm); SO ₄ (14 ppm)	Sr, Tc, Cs
Thirsty Canyon Tuff	(a) Na (30 ppm); K (9 ppm); HCO ₃ (58 ppm); SO ₄ (23 ppm); Cl (16 ppm)	Sr, Tc, Cs, Pu
Westerly Granite	(a) Ca (8.6 ppm); Na (6.7 ppm); HCO ₃ (48 ppm); SO ₄ (2.7 ppm)	Sr, Tc, Cs, Pu

TABLE 4.10. Samples From Pertinent Sites Available in FY-1978

<u>Site</u>	<u>Rock</u>	<u>Sample Type</u>
WIPP	Culebra dolomite	outcrop
	Magenta dolomite	outcrop
	Cowden anhydrite	core
NTS	Eleana shale (argillite)	core
	Climax Stock granite (quartz monzonite porphyry)	core and mine shaft
	Tuff	core
Hanford	Sentinel Gap basalt outcrop	outcrop
	Umtanum basalt	outcrop and core
Canadian granite pluton	Lac du Bonnet granite (Ontario)	outcrop
Bedded salt	None available	
Southeast U.S. dome salt	None available	

institutions with useful rock samples should contact Mr. R. Jeff Serne at PNL if they have samples to donate in exchange for Kd measurements.

Most Desirable

50-100 lb of core material are required for each significant rock or sediment strata that lies along the probable pathways between the repository and the biosphere. The core material must not be contaminated with drilling muds or fluids. The material should be wrapped in a manner that discourages sample contact with extraneous surface waters and air. The material should be isolated such that different strata do not become mixed or severely broken up in transit.

50 gal of actual groundwater is needed from each existing or potential aquifer that might impact the repository. Groundwater samples must be placed in a polyethylene-lined metal drum with an airtight polyethylene-lined lid. The drum should be closed and hermetically sealed immediately after sampling.

Measurement of time-sensitive parameters such as dissolved O_2 , Eh, pH, HCO_3 , and CO_2 should be made on a subsample during sampling following USGS guidelines (Brown et al. 1970). Three one-liter subsamples of groundwater should be taken immediately and preserved according to USGS guidelines for trace metals and nutrients.

Very Acceptable

Core material requirements should be observed as outlined above.

If actual water is not available, a chemical recipe for the groundwater that should include the parameters in Table 4.11 may be substituted.

Acceptable

Representative outcrop material should include some pieces at least 5 in. x 5 in. of each significant rock or sediment (if consolidated) that lie along the probable pathways between the repository and the biosphere. Guidance on applicability of outcrop material (i.e., effects of weathering) should be provided by the site manager and/or ONWI. Either actual site groundwater or a recipe is adequate.

Marginally Acceptable

An available substitute rock or sediment that appears geologically and chemically to be similar to the actual site strata is marginally acceptable. 50-100 lb of material in any configuration (core, chunks, crushed) is needed. Guidance on applicability is needed from the site manager or ONWI. Either actual site groundwater or a recipe is adequate.

Prioritized Sample Requirements for Development of Generic Methodology

All options listed above for site assessments are applicable to generic studies. Sample requirements could be reduced to 10 lb of rock material and 5 gal of groundwater.

Slightly contaminated samples such as drilling mud and drilling fluid could be used. Weathered outcrops of pertinent materials could be used.

If absolutely no physical samples can be furnished WISAP, geologic information such as mineralogy, stratigraphy and other descriptive geologic data on potential sites would be a valuable aid to WISAP.

TABLE 4.11. Necessary Information to Prepare Realistic Simulated Groundwater

Required
Major Cation Content (Na^+ , K^+ , Mg^{2+} , Ca^{2+})
Major Anion Content (Cl^- , HCO_3^- , CO_3^{2-} , NO_3^- , SO_4^{2-})
Eh and/or dissolved oxygen content
pH
Very Useful But Not Mandatory
Soluble organic content
Minor constituents (Sr^{2+} , Cs^+ , Fe , Mn , I^- , Ba^{2+} , Rb^+ , Br^- , PO_4^{3-} , B , S^{2-} , F^- , U , Ra^{2+} , humic acids, fulvic acids)
Silica content
Temperature

For generic methodology development, WISAP researchers have enough information about groundwaters to choose scientifically sound examples. Thus if details are not provided there should be little impact.

Since the types of rock that could be studied are much greater than the types of waters, and the geochemical community's understanding of the rocks' effect on adsorption is much less well understood than for water, the lack of samples and guidance on selection of pertinent rock samples will adversely affect the WISAP Task 4 program.

SYNTHESIS OF DATA BANK

The ultimate objective of Task 4 is to develop a quantitative prediction tool that is capable of estimating the migration rate or K_d of a nuclide for any given geologic material and water type. The amount of data generated by the experimental work of Task 4, supplemented by literature values, will be quite large. With proper experimental design and media-water characterization, statistical methods can be used to relate the dependent variable (migration rate or K_d) to independent variables (e.g., rock type and solution type).

Although the derived relationships do not prove causation, they do allow prediction of trends. Thus, from K_d data on a limited number of rock, mineral, and water types, estimates can be made of K_d values for other rocks and water environments not studied directly.

Other products of this subtask will be: 1) the formulation of geochemical criteria capable of ranking the ability of media to isolate nuclear wastes, and 2) the identification of the more important variables that should be studied in greater detail in the mechanism studies. Presently the geochemical criteria are difficult to define fully or to quantify; thus, an iterative process is envisioned. A list of provisional criteria will be prepared when sufficient data are available. As better data and a more thorough understanding become available, the criteria will be progressively updated. Such an iterative process may also identify areas where additional study is necessary. Adaptronics, Inc., will perform correlation studies to identify significant relationships affecting K_d values.

Computerization

PNL personnel are responsible for installing all generated data onto a computerized information retrieval system and for coordinating all subcontractors' work into a set format amenable to the needs of Adaptronics. In FY-1978 all K_d data generated by subcontractors during FY-1977 and FY-1978 were transcribed on standard coding forms (Table 4-12), which will facilitate data inclusion in a computer-based information retrieval system similar to the CIRMIS system (Friedrichs 1977) for hydrogeologic data. The standard coding form and an example are shown below.

The data bank will be set up such that the operator is prompted through the procedure, so that it will be usable by people with differing technical capabilities. We want the data information retrieval system to be usable by modelers without requiring a lot of technical interpretation. If a modeler needs K_d values for a particular scenario the information retrieval system will inquire about the type of scenario, and after the operator inputs on the keyboard, the computer will select possible choices and display them along with any other basic details requested.

Once the Kd predictor equations from adaptive learning network synthesis (described below) or any other statistical manipulations desired are completed, the computer could also display the multinomial function describing Kd nuclides in terms of all pertinent rock, water, nuclide, and scenario characteristics included in the analysis.

Statistical Evaluation

Adaptronics is performing Adaptive Learning Network (ALN), pattern recognition, regression, and correlation studies on the Kd data base supplied by PNL. Output from Adaptronics includes Kd predictor equations expressed as a function of geologic media, groundwater, and radionuclide properties. A short summary of Adaptive Learning Networks is provided.

In principle, models that predict Kd values can be derived either analytically or empirically. An analytical model is one obtained by "reasoning from first principles." That is, the investigator attempts to interrelate all pertinent physical laws thought to influence Kd. The problem with the analytical approach to modeling is that many physical processes are so complex as to defy reasoning from first principles. Constructing a mathematical model necessarily requires a number of approximations about the relationship of one variable to another. If the guesses are wrong, the model proves to be inaccurate. Furthermore, the model may become quite cumbersome because of, for example, a large number of coupled equations, and thus the computer processing time increases to unacceptable amounts.

Empirical predictive methods involve finding a predictive equation that best fits the observed experimental data. But, with conventional empirical modeling methods, one still has to know important interrelationships to write the general terms of the equation. And the resultant models, like analytical ones, are inflexible. If unanticipated changes occur in the process, the models become obsolete.

A different approach, introduced over 15 years ago by Adaptronics, incorporates "self-learning" principles. To construct a self-learning model, the analyst first decides what variables may be important, but the effects of the variables upon each other do not have to be considered. What is needed

instead is a collection of data that is reasonably representative of the variety of situations that can occur in the system being modeled.

The next step is to construct a mathematical network (ALN), which is a nonlinear hypersurface linking inputs to output. A generalized equation is constructed automatically to link an output value to each possible pair of input variables. Special-purpose algorithms are used to find the coefficients (the weights assigned to the variables) within the equation. Those equations and variables that consistently produce the smallest prediction errors are determined. Additional equations are then constructed that examine interactions among four, eight, or more variables instead of only two. These additional equations result in added layers in the network and are retained if they can improve the prediction accuracy.

A model in the form of a network that has had its coefficients determined and has been reduced to the essential variables is called "adaptively trained." The synthesis of this model has proceeded directly from examination of an experimental data base without human intervention; hence the term "self-learning." To make certain that the model has discovered for itself the pertinent physical laws, additional experimental data not used in the training or synthesis phase are introduced to test the ability of the model to generalize on its prior experience in dealing with new situations.

In FY-1978 the PNL data shown in Table 4.12 were used to generate predictor equations. Seven radionuclides were studied, each in experiments comprised of combinations of 16 geomeedia and 4 solutions. The Kd was measured 3 times over an interval of 30 days. Each nuclide-mineral-solution experiment was repeated three times. The experimental data base was then transmitted to Adaptronics.

A total of 12 "independent" variables was measured in addition to the dependent Kd variable as shown in Table 4.12. The 16 "minerals" can be classified into 4 structural groups. Most of the analyses in the Adaptronics report (Mucciardi et al. 1978) are discussed as a function of this grouping. A detailed listing of the outputs of each of the ALN predictive Kd models is given in Adaptronics final report (Mucciardi et al. 1978).

TABLE 4.12. Description of Battelle Experimental Data Base

3 Experiments x 7 Isotopes x 4 Solutions x 16 Geomedia

Isotopes		Solutions	
Tc	Technetium	5130 meq/l NaCl	Salt brine
Sr	Strontium	30 meq/l CaCl_2	Calcium dominated
Cs	Cesium	30 meq/l NaCl	Dilute brine
Np	Neptunium	30 meq/l NaHCO_3	Bicarbonate dominated
Am	Americium		
I	Iodine		
Pu	Plutonium		
Geomedia		Variables	
Illite		Q	Charge
Kaolinite		R	Ionic radius
Montmorillonite		Q/R	Ionic potential
Vermiculite		Val	Valence
Biotite		CEC	Cation exchange capacity
Quartz		SA	Surface area
Albite		Na	Sodium
Anorthite		Ca	Calcium
Microline		Cl	Chloride
Hornblende		HCO_3	Bicarbonate
Enstatite		pH	Acid-base balance
Augite		Eh	Oxidation-reduction potential
Argillaceous shale		Kd	(Dependent variable)
Westerly granite			
Oolitic limestone			
Sentinel gap basalt			

A summary of analyses performed by Adaptronics is outlined below:

- univariate statistical analysis, correlation of adsorption and desorption Kd values per radionuclide per mineral
- model synthesis, one for each nuclide
- comparison of model Kd prediction to actual Kd values
- rank-ordering of the importance of geologic medium and groundwater variables for modeling adsorption and desorption Kd values per radionuclide.

An example of the Adaptronics is given in Table 4.13. Details are presented in Adaptronics FY-1978 annual report (Mucciardi 1978).

TABLE 4.13. Comparison of Actual and Predicted Sr Adsorption Kd Values for Data not Used in Model Synthesis

<u>Observation Number</u>	<u>Kd (ml/g)</u>	
	<u>Actual</u>	<u>Predicted</u>
1029	2.0	1.7
1030	3.2	2.8
1031	43.7	44.4
1032	293.0	246.7
1033	2.7	1.6
1034	2.6	2.7
1035	51.0	43.7
1036	123.0	192.5
1037	5.6	6.3
1038	3.9	3.8
1039	69.1	61.0
1040	635.0	653.7

(a) Correlation coefficient between actual and predicted Kd values = 0.991.

As found in Adaptronic's previous project (Mucciardi 1977), the results of these analyses warrant the conclusion that modeling Kd empirically as a function of geological media is feasible. The parameters measured to describe the geological media were shown to be significant in the modeling process, and

the ability to establish their interactions has been demonstrated. It has also been shown that the perturbations in these interactions resulting in changes in K_d can be used to establish quantitative relationships.

The specific major conclusions are:

- Very accurate empirical models are obtainable for predicting K_d , especially when treating each mineral group separately.
- Nonlinear interactions exist between the geomechanics and solution parameters. The exact relationship depends on the isotope considered.
- The "rocks" (shale, granite, limestone, basalt) appear to behave similarly with respect to the three isotopes tested (Tc, Sr, Cs).
- The minerals appear to behave similarly within each group (i.e., structural subclass).
- The results suggest that the number of geomechanics could be decreased in future experiments.

Recommendations based on FY-1978 progress include:

- The number of geomechanics considered could be reduced.
- More variables should be recorded per experiment, especially geomechanics characterization.
- The brine solution should be treated separately from the other three solutions (dilute brine, calcium, and bicarbonate dominated solutions) because of the large differences in ionic strength. Alternatively more solutions of intermediary ionic strength should be used so that better interpolations between values could be performed.

VALIDATION STUDIES

The need for empirical data to estimate the long-term fate of nuclides in geologic environments is urgent. Present data collection methods rely on laboratory analyses characterized by short times and small sample sizes. The applicability of scaling these results to the million-year time frame and path lengths of kilometers has not been conclusively shown. In many instances the scale-up is tacitly assumed to be valid without proof.

A major effort of the validation subtask is an evaluation of the scale-up from short-term laboratory results. The short-term results are being extrapolated and compared with theoretical concepts such as weathering, ore deposition geochemistry, mineral stability, and thermodynamic Eh, pH diagrams.

Thermodynamic Data Tabulation

Thermodynamic data (Gibbs free energy, solubility products, complex stability constants) have been extracted from the literature. At PNL (Ames and Rai 1978, Rai and Serne 1978) the data were used to prepare solution activity diagrams versus pH and Eh for the elements Am, Sb, Ce, Cs, Co, Cm, Eu, I, Np, Pu, Pm, Ra, Ru, Sr, Tc, ^3H , U, and Zr. Using the thermodynamic data, predictions were made of the nature of the solid phases and solution species expected in various geologic environments for the listed elements. The solution species and solid-phase diagrams allowed speculation on the degree of adsorption expected for each element. Speculations were compared with literature observations. Finally, the relative importance of various groundwater properties such as pH, Eh, and ligand concentrations on the fate of these elements was synthesized from the collected information. A summary of predominant solution species expected in both oxidizing and reducing environments is given in Table 4.14. Table 4.15 lists factors that are expected or have been reported to influence the adsorption of the listed elements.

In a separate effort LBL (Silva et al. 1978; Apps et al. 1978) has critically assessed the PNL data (Rai and Serne 1978) and data generated in an independent literature review for the elements Np, Pu, Am, and Cm. Free-energy data and reaction constant data need to be critically reviewed to produce self-consistent data reduced to standard state conditions. These exercises allow selection of best values for incorporation into mass transfer computer codes. These exercises also build a library of original sources, so that original data might be used in subsequent data interpretations and as a basis for further experimental studies to measure actinide solubilities and speciation in groundwater systems.

TABLE 4.14. Predominant Solution Species of Elements^(a)

Elements	Predominant Solution Species of Elements		
	Little Affect by Oxidation-Reduction	In An Oxidizing Environment	In A Reducing Environment
Am	$\text{Am}^{3+}, \text{AmSO}_4^+, \text{Am}(\text{OH})_2^+$		
Sb		$\text{HSbO}_2^0, \text{Sb}(\text{OH})_3^0,$ $\text{SbOF}_6^-, \text{Sb}(\text{OH})_4^-$	SbO^+
Ce	$\text{Ce}^{3+}, \text{CeSO}_4^+$		
Cs	Cs^+		
Co	$\text{Co}^{2+}, \text{Co}(\text{OH})_2^+$		
Cm	$\text{Cm}^{3+}, \text{CmOH}^{2+}, \text{Cm}(\text{OH})_2^+$		
Eu	$\text{Eu}^{3+}, \text{EuSO}_4^+, \text{Eu}_2\text{P}_2\text{O}_7^{2+}$		
I		$\text{I}^-, \text{IO}_3^-$	I^-
Np		$\text{NpO}_2^+, \text{NpO}_2\text{HPO}_4^-,$ NpO_2HCO_3	$\text{NpOH}^{3+}, \text{Np}^{4+}$
Pu		$\text{PuO}_2^{2+},$ $\text{PuO}_2(\text{CO}_3)(\text{OH})_2^{2-}, \text{PuO}_2^+$	$\text{PuOH}^{2+}, \text{Pu}^{3+}$
Pm	Pm^{3+}		
Ra	Ra^{2+}		
Ru		$\text{Ru}(\text{OH})_2^{2+}, \text{RuO}_4^-,$ RuO_4^{2-}	RuO_4^-
Sr	Sr^{2+}		
Tc		TcO_4^-	Tc^{2+}
Th	$\text{ThF}^{3+}, \text{Th}(\text{OH})_3^+$		
^3H	$\text{H}^+, ^3\text{H}-\text{O}-\text{H}$		
U		$\text{UO}_2^{2-}, \text{UO}_2\text{F}^+,$ $\text{UO}_2(\text{OH}_2)^0,$ $\text{UO}_2(\text{CO}_3)_3^{4-}$	$\text{UO}_2^{2+}, \text{UOH}^{3+}, \text{UO}_2^+,$ $\text{UO}_2(\text{CO})_3^{4-}$
Zr	$\text{Zr}(\text{OH})_4^0, \text{Zr}(\text{OH})_5^-,$ ZrF_3^+		

(a) In a pH 4 to 9, $p\text{O}_2$ 0.68 to 80, $p\text{CO}_2$ 1.52 to 3.52, $p\text{Cl}^- = p\text{NO}_3^- =$
 $p\text{SO}_4^{2-} = 3.0$, $p\text{F}^- = 4.5$ and $p\text{H}_2\text{PO}_4^- = 5.0$ environment without organic
ligands.

TABLE 4.15. Factors Reported to Affect Adsorption of Radioelements Over the pH Range of 4 to 9

Element	pH	Eh	Factors						Probable Adsorption Mechanisms ⁽²⁾
			Soil CEC ⁽¹⁾	Competing Ions	Selectively Adsorbed on	Inorganic Ligands	Complex Ions Organic Constituents	Colloid Formation	
Am			X	X		X			IE
Sb		X			Iron Oxides	X	X	X	PPT
Ce	X					X	X	X	TE, PPT
Cs			X		Zeolites, Micas				IE
Co	X				Illite, Iron Oxide	X	X	X	IE, PPT
Cm						X		X	PPT
Eu	X			X		X			IE, PPT
I					OM		X		OM
Np						X		X	UNK
Pu	X	X	X			X	X	X	IE, PPT
Pm	X			X			X		IE, PPT
Ra			X	X	Zeolites, Barite				IE
Ru	X				OM	X	X		PPT
Sr	X		X	X	Calcite, Zeolites	X	X		IE
Tc							X		UNK
³ H					H ₂ O				NONE
U	X	X	X		OM	X	X		PPT, IE
Zr	X					X	X	X	PPT

(1) CEC = Cation Exchange Capacity

(2) IE = Ion exchange, OM = Organic matter adsorption, PPM = Precipitation, UNK = Unknown

During the latter part of FY-1977 an initial compilation was made, but further revisions were required during FY-1978 to complete the compilation in an acceptable form. The compilation, drawn from 120 references, was released in the 1977 annual report of LBL (Apps et al. 1978). As part of a consulting agreement with Professor D. Langmuir, Pennsylvania State University, a critical review of thorium data was also prepared. During 1977, Professor Langmuir also reviewed and prepared a critical review of Gibbs free energy data for uranium (Langmuir 1978).

A summary of the acquired Gibbs free energy data for different actinides is given in Table 4.16. The table lists aqueous species by oxidation state, and solid phases. The most notable deficiency in the information pertaining to solid phases occurs for the transuranic element Cm. Information on aqueous species of americium and curium is also insufficient. Further experimental studies in these two areas are particularly recommended. Most of the reaction constant data have been measured at ionic strengths greater than 0.1M. Such data are particularly difficult to reduce to standard state conditions, because no satisfactory method exists for computing activity coefficients of species and complexes in such high ionic strength solutions. LBL has reviewed the techniques and theory developed by Pitzer (Pitzer et al. 1961), and discussed means of using available data for this approach, but the data are inadequate. LBL tested the Davies equation (Davies 1962) for calculating activity coefficients, but found this to be so crude for the systems under study, that no correction at all would probably be just as accurate. To date, LBL concludes that from the programatic point of view, the use of raw data may be appropriate for modeling purposes, at least initially.

The thermodynamic data, activity diagrams versus pH, and Eh computer programs (discussed below) allow speculation on the fate of elements in the geohydrologic system over long time periods when equilibrium concepts might best apply.

Chemical Computer Modeling

The mass of thermodynamic data collected is being critically assessed, corrected to standard state, and installed into existing thermodynamic equilibrium computer codes by Lawrence Berkeley and Livermore Labs. Several codes

TABLE 4.16. Summary of the Gibbs Free-Energy Data for Aqueous Species and Solid Phases of the Actinides

		Th*	U*	Np	Pu	Am	Cm
Aqueous	III	0	1	5	9	14	14
Species	IV	27	20	13	14	1	1
Oxidation	V	0	1	7	2	0	0
State	<u>VI</u>	<u>0</u>	<u>20</u>	<u>10</u>	<u>12</u>	<u>0</u>	<u>0</u>
	TOTAL	<u>27</u>	<u>42</u>	<u>35</u>	<u>37</u>	<u>15</u>	<u>6</u>
Solids		7	24	4	6	2	0

* Compiled by Langmuir (1978)

are being pursued at present to allow crosschecks and explore differing calculational schemes. Once the models are operational with the added data on important nuclides, test cases will be used to assess which model(s) has the most versatility and cost effectiveness. The best model(s) will be used to evaluate thermodynamic equilibrium conditions for a variety of hypothesized scenarios and to compare with experimental system studies performed in other subtasks. The use of these computer models will allow rapid and cost-efficient scoping and validation studies to be performed on sorption-desorption aspects of the overall safety assesement.

In general, equilibrium step codes attempt to solve the following problem. Given a reacting system consisting of solid, liquid, and gas phases of known gross composition with specified temperature, pressure, and boundary conditions, the codes attempt to determine what chemical and physical changes will occur in the system as a function of reaction progress. In particular, the step codes attempt to calculate the change in concentrations and thermodynamic activities of individual aqueous chemical species, and to identify and quantify solid and gas phases produced or destroyed as reactions progress toward a final state.

Geochemical codes are based on the concept of thermodynamic equilibrium, and thermodynamics do not provide information on reaction rates. In many chemical reactions, thermodynamic considerations tend to be overshadowed by

kinetic factors. However, the geochemical processes associated with the sub-surface disposal of waste tend to be infinitesimally slow, e.g., the movement of groundwater, suggesting that the geochemical reactions occurring in such an environment may approach equilibrium. Thus, an equilibrium code should be particularly applicable to these regimes.

Many gaps exist in the thermochemical data base that serves as input to geochemical code calculations. This is particularly true for species that are of interest to waste isolation problems. An attempt will be made to use geochemical analogies and estimation techniques to obtain reasonable solutions to waste isolation problems in cases where the data base is deficient. FY-1978 progress at LLL is summarized below and explained in more detail in the technical report (Tewhey 1979). The current focus of the development effort is a code that is being produced by Dr. Howard Levine of JAYCOR Corp. of La Jolla, California, under contract to LLL.

The Levine code represents a method for calculating the composition of geochemical species in complex aqueous systems at thermodynamic equilibrium. The code is considered to be state-of-the-art in that it is 1) faster than LLL's existing equilibrium codes, 2) requires only a small memory capability, 3) is particularly effective for multi-phase systems, and 4) is general enough to handle systems containing solids, liquids, and gases. The code is suitable for predicting the geochemical species that result from the processes of cooling, evaporation, precipitation, and mixing of dissimilar solutions.

The Levine code operates on a basis of finding the minimum free energy of a system by solving the nonlinear equilibrium constant equations for the reactions of that system. It differs from other codes in that it considers only one reaction at a time (univariant descent), instead of considering all reactions simultaneously (multivariant or steepest descent). Because the code considers only one reaction at a time, it 1) reduces storage needs, 2) simplifies arithmetic so that full machine accuracy is available, and 3) solves problems of heterogeneous equilibria faster. Thus, problems of rounding error from matrix inversion and unstable numerical solutions are

eliminated. The code will also converge for problems that other existing codes cannot handle, such as decomposition of carbonates and systems with multiple oxidation states.

The types of nuclear waste problems that the Levine code will be able to run are:

- The nature of the geochemical interaction among the waste form, container material, and the coexisting aqueous phase.
- The geochemical interaction between dissolved species and the enclosing geologic media (groundwater equilibration studies).
- The calculation of the type of material that would immobilize a particular dissolved species by means of precipitation and/or adsorption (geochemical barrier studies).

At the end of FY-1978, the Levine Code was 90% complete and is expected to be ready early in FY-1979.

Work performed at LBL in FY-1978 pertinent to computer simulation of mass transfer is documented (Silva, Benson, and Apps 1978; Apps 1978; Benson et al. 1978; Carnahan 1978). A summary of progress and conclusions follows. Two computer codes, FASTPATH and EQ3/EQ6, have been chosen by LBL to perform computer simulations for nuclear waste management.

FASTPATH is easy to use and possesses the advantage of permitting graphical presentation of the results of a simulation. It is also easy to incorporate additional basic components, minerals, and aqueous species, without major modifications to the code. However, it is limited to a maximum of 25 basic components for any run. This limitation is, however, an inconvenience for only the most elaborate simulations of groundwater chemistry. FASTPATH can simulate open or closed systems with equal facility.

FASTPATH simulations are restricted to temperatures prescribed in the original thermodynamic data base developed by Helgeson (i.e., 0°, 25°, 60°, 100°, 150°, 200°, 250°, and 300°C). This can be a disadvantage where simulations at intermediate temperatures are required. No provision exist in FASTPATH for starting a run from an initially supersaturated solution.

FASTPATH also contains a number of other inconveniences of a minor nature. For example, the graphical output is difficult to reproduce legibly.

EQ3/EQ6 was kindly made available by T. Wolery (Wolery 1978) early in FY-1978. Because it possessed certain advantages over the FASTPATH code, it was adapted to the LBL CDC 7600 computer and tested for use in WISAP and the RHO-funded LBL study of high level waste-basalt interaction. EQ3/EQ6 possesses the advantage of being able to simulate chemical reactions at any selected temperature between 0 and 300°C. It can also adjust an initially supersaturated solution to saturation by precipitation of those phases from solution that minimize the Gibbs free energy of the system. EQ3/EQ6 can also be used to simulate the behavior of systems subject to progressively changing temperatures. However, in its original form, it did not possess a graphical output, nor could it incorporate new basic components, minerals, or species without difficulty. Until further work had been done during FY-1978, it was not able to simulate open system conditions.

Both codes use similar type thermodynamic data bases consisting of reaction constants for translation equations relating the solid phase or aqueous species with the basic components, although each code contains basic components, minerals, and aqueous species data not possessed by the other. Provision for the calculation of oxidation state differs in each code; the FASTPATH code calculates free electron activity, whereas EQ3/EQ6 computes oxygen fugacity.

The decision was made that both codes would benefit from new data base and graphical output packages. During the last month of FY-1978, work was started on these modifications, but neither were completed by year end.

An application exercise on a Columbia River Basin basalt-groundwater system was described in detail (Apps 1978, Benson et al. 1978, Carnahan 1978). Computer simulations were run assuming the presence and absence of carbon dioxide at various temperatures between 25° and 300°C.

Several differences between the simulated reaction systems, with and without the presence of carbon dioxide, were apparent. The system containing carbon dioxide produced not only the carbonate minerals calcite and siderite,

but also four non-carbonate minerals (talc and the clay minerals kaolinite, calcium montmorillonite, and sodium montmorillonite) that do not appear in the reaction system lacking carbon dioxide. Magnesium chlorite appeared in both systems at low values of reaction progress, but was consumed reversibly in the system containing carbon dioxide, where talc becomes the more stable magnesium-containing phase at higher values of reaction progress. Also, tremolite and prehnite were precipitated in the carbonate-free reaction system, but did not reach saturation in the system containing carbonate. Four other product mineral phases common to both reaction systems were fayalite, laumontite, adularia, and low albite. Differences in concentrations of noncarbonate aqueous species and noncarbonate product mineral phases were attributable principally to the pH-buffering effect of the bicarbonate-carbonic acid equilibrium. In the carbonate-free system, the pH gradually increased from its initial value of seven and eventually stabilized at a value slightly higher than eleven. On the other hand, in the system containing carbon dioxide, the pH stabilized at about eight. The effects of pH buffering are reflected also by differences between the two reaction systems with respect to distributions of chemical elements among possible aqueous species.

A comparison was made between the results of reaction path simulation in the presence of carbon dioxide and distribution-of-species computations with real groundwaters for this basalt-groundwater scenario.

The presence of such minerals as muscovite, chalcedony, nontronite, kaolinite, celadonite, and microcline in the computer hypothetical solid-phase assemblages that removed supersaturation from the groundwater samples is in general agreement with direct observations of similar phases within vesicles and fractures of basalt samples from beneath the Hanford site. Although there is general agreement on the types of minerals formed during reaction progress (basalt weathering), the specific minerals and distribution at the reaction progress closest to that predicted by the observed distribution of cations and anions in real groundwater do not agree. Mineralogic studies (Benson et al. 1978) clearly indicate that the secondary alteration of the basalts is proceeding in an open system, and that the secondary minerals, once precipitated,

are not redissolved when the stability field of another mineral is entered. A more effective simulation of reaction progress would, therefore, be one in which the precipitated phases are not redissolved when they are no longer stable with respect to the aqueous phase. Open system simulations are useful because of their ability to model mass transfer during the passage of a volume of groundwater through a reactive medium, a situation in which product phases cannot react reversibly with the aqueous phase from which they were formed.

Another reason observed clays and zeolites were not reproduced by the mass transfer simulations is because the necessary thermochemical data for these minerals are not currently available, and thus are not included in the data bases of the mass transfer codes. Instead, the code follows the evolution of the of the basalt-carbon dioxide-water system by selection of those minerals that are included in the data base. Acquisition of thermochemical data for the observed mineral phases would allow more realistic modeling of their deposition history and groundwater evolution than is now possible. The code can simulate only those chemical reactions that are included in its data base. Thermochemical data for many clays, zeolites, some actinides, and some fission products are non-existent. Thus, experimental studies of interactions in waste-rock-water systems producing previously uncharacterized solid phases cannot be simulated by existing equilibrium codes without measurement of the thermochemical properties of the product phases.

Despite these shortcomings in the data base and uncertainties in some thermodynamic values, it is the opinion of John Apps, LBL, that the use of equilibrium thermodynamic computer codes for nuclear waste management needs is warranted. The reasons for this opinion are: 1) an accuracy of $\pm 1/2$ log unit in the reaction constant is really all that is needed to understand the distribution of complexes in solution and the stability of solid phases in the natural environment; ionic strength corrections would make only an incremental improvement at this state; and 2) errors of far larger magnitude can be made because investigators having misinterpreted their experimental results or by using the data in regions where other, as yet, unidentified complexes may be present. In the preliminary scoping work, one has to know only what goes on, what is important, and what is missing. Accuracy is essential only when it is required to resolve these questions.

Apps recommends that the following actions be undertaken to increase the usefulness of thermodynamic computer simulations:

- 1) The paucity of thermodynamic data of solid phases of transuranic actinides prevents researchers from calculating expected equilibrium concentrations of actinides in the natural environment. Experimental studies should be started.
- 2) Most actinide data have been obtained for ambient temperature conditions, usually around 25°C, but in some cases ranging from 0-50°C. Except in rare cases, this range is too limited, and the data too scattered to make any empirical extrapolation to higher temperatures. Furthermore, theoretical methods of extrapolation are generally impossible to apply for all but the simplest complexes (e.g. hydroxyl complexes). The use of correspondence plots or comparison with better known data of the lanthanides might be used, but some research efforts on solubility products and complex dissociation constant as a function of temperature would be worthwhile.
- 3) Thermodynamic data for natural phases of interest to the problem of groundwater transport of radionuclides are frequently unavailable. Because groundwater systems tend to be open thermodynamically, normally with several degrees of freedom, the number of secondary minerals in equilibrium with the groundwater of significance is, by Gibbs Phase Rule, relatively small. The number is further reduced because most secondary minerals are solid solutions (e.g., clays, zeolites). Thus the problem reduces to characterization of the thermodynamic properties of relatively few phases such as the clays, some zeolites, and possibly the chlorites. Estimates using equilibrium solution composition can be made, but questions normally remain as to whether true equilibrium conditions were observed. However, refined calorimetric measurements of selected clays and zeolites should be made to make real progress in this area.

Pertinent Sites

The literature on migration of trace constituents, especially radionuclide forming elements at existing natural (precious metal ore deposits,

Oklo) and man-made (DOE and international nuclear shallow land burial sites, Nevada Test Site, industrial land fills and tracer well tests) needs to be critically reviewed in terms of its relevance to time extrapolation from laboratory results to deep geologic nuclear waste disposal.

LASL, in a separate ONWI funded study of natural reactors, has yearly summarized progress on the processes that produced the Oklo natural reactor and that led to retention of many of the fission products (Cowan and Norris 1978, Apt 1977, Brookins 1977, Cowan 1977).

Detailed summaries of work carried out in France, the U.S., and elsewhere through 1977 are contained in two IAEA publications (IAEA 1975, 1977).

Within the Oklo deposit (an unmetamorphosed sequence of sedimentary and detrital volcanic rocks of middle precambrian age), the most common ore is a black, highly silicified sandstone with UO_2 content in the range 0.4-0.6%, rarely exceeding 1%. The uranium generally occurs in a reduced form as pitchblende, where it is associated with organic materials and abundant sulfides (pyrite and galena). The second type of ore is a black unsilicified sandstone with little or no organic material. The uranium content is in the range 5-25%. It is in this rich ore that the reactor zones formed. Within these zones the uranium occurs as crystalline uraninite, and the surrounding matrix has been almost completely desilicified. Usually these pockets of rich ore occur in strongly tectonized zones in regions of microfractures that appear to correspond to major planes of shear.

The reactor began to operate 2×10^9 years ago and the duration of the period of criticality was several hundred thousand years, possibly as long as 8×10^5 years. During this period, approximately 6 tons of uranium were fissioned, out of the 800 tons of uranium involved in the reactor zones, and nearly 3 tons of ^{239}Pu were made by neutron capture in ^{238}U . The operating temperature of the reactor zones increased to about 200°C above ambient. Weber (Weber, Geffroy, LeMercier 1975) and Gauthier-Lafaye (Gauthier-Lafaye in press) have shown that the depth of the deposit during the period of operation was in the range 3000-5000 m. Hot spots may have existed at higher temperatures of the order 450-650°C (Vidale 1977; Openshaw, Pagel, Poty in press).

Brookins (1977) concludes that the ambient temperature probably did not exceed 150°C beyond a 4 m radius of the reactor border.

To help understand element migration, Brookins (1977) correlated information from Eh-pH diagrams with the empirical retention data reported by Bryant et al. (see Table 4.17). The basis for the prediction of migration through the use of Eh-pH diagrams is the determination of the likelihood that an element will form either a stable solid phase or an aqueous species that might be easily transported. Brookins predicted the migration behavior of 20 elements under conditions where uraninite is stable. The predictions are in reasonable agreement with the empirical data for Y, Nb, Ru, Pd, Ag, Te, rare earth elements, Bi, U, Np, and Pu, which did not move significantly, and for Mo and Cd, which did migrate. Pb was predicted to be immobile, whereas significant migration was observed.

Cowan (1977) reviewed the various steps involved in the migration of reactor products at Oklo and concluded that, for most of the product elements, volume diffusion from extremely insoluble crystalline grains of uraninite was the most probable rate-limiting step. This suggests that the uraninite grains have retained their original structures and uranium composition. In such a case the reactor products, to the extent that they are initially deposited in the grains, can be dissolved away only after diffusion to the surface of the grain.

Recently new samples from outside the natural reactors have become available which may allow reconstruction of the paleohydrology of the Oklo environment. This will allow more quantification of nuclide mobility differences between elements. Although the results to date (Table 4.17) are only qualitative, the high percentage of comparability is encouraging and lends credence to the thermodynamic methods used to extrapolate long time frame nuclide migration.

Other successful uses of thermodynamic Eh-pH diagrams to predict or explain existing uranium ore bodies are briefly described in abstracts of a United States Geological Survey Uranium-Thorium Symposium (Campbell 1977).

TABLE 4.17. Comparison of Predicted vs. Observed Element Migration at Oklo

<u>Element</u>	<u>Migration Predicted</u>	<u>Migration Observed</u>	<u>Agreement</u>
Tc	No	Yes	No
Ru	No	No	Yes
Pd	No	No	Yes
Ag	No	No	Yes
Sb	No	Not Measured	--
In	No	Not Measured	--
Te	No	No	Yes
Mo	Yes	Yes	Yes
Cd	Yes	Yes	Yes
Zr	No	No	Yes
Rh	No	No	Yes
Sn	No	Not Measured	--
Nb	No	No	Yes
Pu	No	No	Yes
Am	No	Not Measured	--
Np	No	Not Measured	--
Th	No	Not Measured	--
U	No	No	Yes
Rb	Yes	Yes	Yes
Cs	Yes	Yes	Yes
Sr	Yes	Yes	Yes
I	Yes	Yes	Yes
Br	Yes	Not Measured	--
Y	No	No	Yes
Rare Earths	No	No	Yes
Pb	No	Yes	No
Xe,Kr	Yes	Yes	Yes
Bi	No	No	Yes

Literature on the Nevada Test Site (NTS) and shallow land burial sites germane to nuclide migration has been identified during an Environmental Protection Agency (EPA) funded literature review of Kd values (Ames and Rai 1978), but no critical synthesis was performed in FY-1978.

Tracer Well and In-Situ Testing

Lawrence Livermore Laboratory is evaluating the feasibility of performing field-scale migration validation experiments using traditional tracer well pump tests. The costs, logistics and details for in-situ nuclide migration studies will also be analyzed. Following is a summary of FY-1978 progress. Details may be found in the final technical report (Tewhey 1979).

A major concern in formulating a field tracer experiment, using isotopes whose movement will be retarded relative to that of groundwater, is to estimate their average rates of movement. If they move too slowly, their transit times between measuring points may be great enough to render an experiment impractical. The average rate of movement of an isotope can be estimated using the following relationship:

$$V_i = \frac{V_w}{1 + Kd \frac{\rho_b}{\theta}} \quad (4.2)$$

where

V_w = the average ground-water flow speed

Kd = the equilibrium distribution coefficient for the isotope expressed in ml/g

ρ_b = the bulk density of the saturated medium

θ = the effective porosity of the medium.

Estimates of V_w , under the usual operating conditions, ρ_b , and θ can be obtained for the aquifer at the Amargosa tracer site near NTS. V_w between the injection well and the observation wells is about 140 ft/day, ρ_b

is about 2.5 g/cc, and θ is likely in the range of 1.5 to as much as 6%. Assuming Kd values of 0.1, 1.0, and 10.0 ml/g, and θ values of 1.5 and 6.0%, V_i was calculated along with corresponding travel times between the injection well and nearest observation well. These values appear in Table 4.18. It seems that rather protracted experimental run times for isotopes with Kd values in excess of 1.0 would be required.

Batch Kd determinations with samples of the Bonanza King dolomite, the formation which comprises the principal aquifer system at the tracer site, resulted in the following values:

$$\begin{aligned} Kd(\text{Sr}) &= 1.0 \pm 6\% \\ Kd(\text{Cs}) &= 33 \pm 12\% \\ Kd(\text{Pu}) &= 618 \pm 0.7\% \end{aligned}$$

The laboratory Kd results suggest that strontium is the only tracer studied that would be feasible for test use.

Scoping studies for in-situ tracer studies have also been performed on fractures (up to 3 mm wide) and shear zones (zones of multiple fractures and broken rock up to 2 ft thick) at the 1400 ft level in the Climax Stock granite at NTS. Core logging data obtained during exploratory drilling for the spent fuel test indicated that fractures are continuous over several meters and shear zones are continuous over tens, and occasionally a hundred or more meters. X-ray diffraction and batch Kd studies were performed on shear zone material as a first step in scoping tracer studies.

The object of tracer tests in the Climax Stock would be to measure the lag or retardation of slugs of various isotopes relative to tritium or technetium. The retardation factor, V_w/V_i , determined in the Climax fractures could then be compared to retardation factors calculated according to

$$K_f = \frac{V_w}{V_i} = 1 + \frac{2Ka}{b}, \quad (4.3)$$

TABLE 4.18. Flow Velocities and Travel Times Between Injection Well and Observation Well at the Amargosa Site

θ %	Kd (ml/g)		
	0.1	1.0	10.0
1.5	8 ft/day	0.83 ft/day	0.08 ft/day
	17 days	169 days	1750 days
6.0	28 ft/day	3.3 ft/day	0.33 ft/day
	5 days	42 days	424 days

using laboratory measured values of K_a , defined as

$$K_a = \frac{K_d}{A}, \quad (4.4)$$

where A = total surface area of particles (per gram) used in laboratory measurement, and values of b , the average width of fractures through which flow took place. Difficulties in this scheme include determination of which fractures were involved in the circulating water flow system and measurement of their widths. If this scheme is followed, some means must be devised to measure fracture widths in horizontal boreholes.

A proposal to perform in situ tracer studies in the Climax Stock will be made in FY-1979. Additional field studies at sites of past underground nuclear explosions might produce data of interest for the verification of nuclide migration results. Two sites, a salt site code-named GNOME located 48 km southeast of Carlsbad, New Mexico and a granite site code-named SHOAL located 48 km southeast of Fallon, Nevada, should be considered as candidate sites for future field studies (Ramspott et al. 1977).

One ongoing field program (Hoffman et al. 1977) at NTS is pumping water from wells within and surrounding an underground test shot (Cambric). The media around the blast site is alluvium. Analyses to date show most all the radionuclides are still retained in vitrified or fused debris within the bomb cavity. Water is now being pumped from a satellite well 91 m away from the cavity in an attempt to draw tritiated water from the cavity and to determine whether any other radionuclides accompany it.

No WISAP effort has specifically delineated the approach needed to perform a cost-effective and relevant in-situ chemical migration study. A recent workshop funded by the Office of Nuclear Waste Isolation concluded that specific in-situ tests for chemical migration experiments in hard rock environments would be premature. Instead, more theoretical, laboratory and large-scale bench experiments should be initiated (Gates 1978).

SORPTION-DESORPTION MECHANISM STUDIES

As discussed in the section summarizing the evaluation of experimental methodology, the migration rates of nuclides determined by various methods show significant variation. When this experimental design dependency is understood, there will still not be a general understanding of the mechanisms controlling the migration rates of nuclides. Current sorption data determination is empirical, and geologic material and solution-specific. Results of this nature do not rigorously lend themselves to extrapolation to other situations or to an understanding of controlling mechanisms. The emphasis of the mechanism studies will be to investigate those factors and interactions that control the sorption-desorption of actinides, long-lived fission products, and activation products by geologic media. With knowledge of mechanisms, migration rate predictions can be performed from more theoretical and fundamental data for any proposed storage environment. The use of theoretical and fundamental data may reduce the costs of quantifying the migration rates of nuclides at specific sites.

Multivalent Element Studies

The adsorption and migration of multivalent elements in the geologic media are highly dependent upon the distribution of their oxidation states in the groundwater. To study the adsorption behavior by geologic media of different oxidation states of multivalent elements, the oxidation/reduction potential (Eh) must be controlled. A potentiostat was used to control potentials of the mineral suspensions at a given Eh and to maintain plutonium as Pu(VI) in suspensions in 0.01 N CaCl₂ in preliminary studies (Rai et al. 1978). Pu(VI) was added to a suspension that was previously equilibrated at

-0.9 V (vs. SCE), a potential at which Pu(VI) is stable. The oxidation state of the Pu was monitored during the course of the experiment. The solutions, monitored for 120 hr, indicated that the oxidation state distribution did not change and essentially all of the plutonium was still present as Pu(VI). The preliminary data suggest that the potentiostat control might be very effective in rigidly controlling Eh and that it can be used to maintain a given oxidation state of an element in solution during its adsorption by geologic media. Subsequent studies showed that the geologic media was interacting with the working electrode and that the solution potential was actually being controlled at the measured potential only in the immediate vicinity of the electrode. The Eh of the bulk solution differed from that close to the electrode.

In another experiment the valence states of soluble plutonium in contact with $\text{Pu}(\text{OH})_4$ and PuO_2 solids in air-equilibrated simulated groundwaters were determined. Predictions based upon thermodynamic data indicate the plutonyl(V) is the dominant species in oxidizing environments (Rai et al. 1978). However, no available data on environmental samples confirm the presence of plutonyl(V). In fact some of the available data indirectly contradict the theoretical predictions. The discrepancy between the predicted (Rai et al. 1978) and observed oxidation states (Bondietti and Reynolds 1976; Dahlman, Bondietti, and Eyman 1976) can probably be attributed to lack of Pu(V) identification methods and the somewhat nonspecific nature of the Pu(VI) determination methods.

In Rai's study (et al. 1978) several observations were made that support the predominance of Pu(V) over other valence states. The supporting evidence includes 1) the observed solubility dependence of PuO_2 and $\text{Pu}(\text{OH})_4$ on pH that is similar to a species with a net charge of ± 1 (PuO_2), 2) results of solvent extraction techniques that separate Pu(III), Pu(IV) from Pu(V) and Pu(VI) and 3) direct spectrophotometric studies.

A further study (Rai and Serne 1978) was performed to provide information on the presence of Pu polymer in environmental water samples. The uncertainty regarding the presence of Pu(IV) polymer in environmental studies is a

source of error in evaluating adsorption and in estimating Pu migration rates. Data presented on $\text{Pu}(\text{OH})_4$ solubility and literature citations on the occurrence of Pu polymer suggest that Pu(IV) polymer is similar to Pu(IV) hydroxide in its solubility and that the presence of the polymer may be predicted from pH and total Pu in solution.

Solubility experiments (Rai, Serne, and Moore 1978) begun in FY-1977 on $^{239}\text{PuO}_2$ and $^{239}\text{Pu}(\text{IV})$ hydroxide were continued throughout FY-1978. The experiments will be terminated in FY-1979 and solubility versus time, pH, and final soluble Pu valence state distributions will be performed. Identical experiments using ^{238}Pu , ^{240}Pu and ^{242}Pu will be started to assess the effects of variations in specific activity on solubility.

Effect of Redox Potentials on Sorption

Bondietti and Francis at ORNL (Francis et al. 1978) are performing systematic studies on the effect of redox potential on sorption. Redox measurements of igneous rock suspensions in anoxic stirred cells predicted that if thermodynamic aqueous stability diagrams were correct, the species TcO_4^- and NpO_2^+ would not be the stable forms of these elements under anoxic conditions probable in deep repositories. Experiments where TcO_4^- and NpO_2^+ in solution were added to these anoxic rock suspensions showed that these species in fact were reduced in part to less soluble states. The rocks used included Sentinel Gap basalt, Westerly granite, Climax Stock granite, Conasauga shale and a green argillaceous shale. Under anoxic conditions the granites and basalt readily removed TcO_4^- from solution by a reduction process. Neither shale exhibited this reduction-sorption capability but some (10%) TcO_4^- was removed by weathered Conasauga shale suggesting anion sorption by positively charged sesquioxides. Thermodynamic results suggested that Np(V) would be even more unstable in solution than TcO_4^- as the redox potential is decreased. Rock sorption studies of Np(V) showed that all of the above rocks rapidly removed >90% of the Np(V) in solution. Also more detailed work was performed to evaluate Np reduction. Basalt and granites were found capable of reducing the Np(V) in solution, the Conasauga shale results were inconclusive, and the green argillaceous shale apparently did not reduce the Np. Column verification of the TcO_4^- rapid reduction by basalt was attempted. Only at a

residence time of five days was there any indication of reduction. Thus, loss of TcO_4^- is much slower in columns than in the stirred cell.

Several experimental artifacts (grinding and O_2 leakage effects) are discussed in the ORNL report. A few preliminary statements on Pu(V) reduction to Pu(IV) and U(VI) reduction to U(IV) are given. We conclude that current risk assessments which consider the oxidized forms (TcO_4^- and NpO_2^+) only may be overestimating the potential hazard to the public.

Measurement of Eh

Much concern and some controversy exist over the measurement of Eh in the geologic systems under investigation in the laboratory. The discussion was started at the FY-1977 Workshop (Serne 1978), and new pertinent material (Francis et al. 1978, Benson 1978) is summarized below. Although researchers agree that oxidation-reduction processes can greatly affect adsorption, they disagree on whether the parameter can be accurately measured.

Eh is a measure of aqueous electron activity. In most geologic environments, reactions controlling Eh involve the elements iron, sulfur, carbon, nitrogen, and oxygen. Since measurement of absolute potentials is impossible, the electrometric measurement of Eh is based on the potential difference between a reference electrode of constant voltage and an indicator electrode whose voltage is a function of the electron activity.

The ultimate reference for Eh and pH measurements is the hydrogen electrode. The indicator electrode is usually made of platinum or, less frequently, gold. Although Eh and pH measurements are based ultimately on the potential of the hydrogen electrode, it is not practical for use in routine Eh-pH determinations. The most widely used secondary reference electrode for Eh and pH measurement are the mercury-mercurous chloride electrode and the silver-silver chloride electrode.

Thermodynamic, kinetic, and sampling limitations are also associated with Eh measurement.

Thermodynamic Limitations

When Eh measurements are made, the platinum electrode is assumed to be an inert sensor providing sites for electron exchange. If the metal actually

reacts with substances dissolved in the water, then potentials will be displayed that relate to the electrode and not the environment.

At high Eh values (oxidizing conditions) the platinum electrode exhibits a pH-dependent response described by the equation summarizing the function of a Pt-O, or possibly $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$, coated electrode.

Under this condition, the platinum electrode will not respond to changes in the partial pressure of oxygen (see Kinetic Limitations). The Eh value will, therefore, not give any indication of the oxidation-reduction status of the system unless other electroactive couples are present in sufficient concentration ($>10^{-5}\text{M}$) to dominate the electrode potential (Peshchevitsky et al. 1967). Iron may occasionally act in this way (Hem 1961).

In readings of stagnant or reducing waters where oxygen has been replaced by other electron acceptors, the platinum electrode no longer responds primarily to pH. Either the formation of the oxide coating is precluded by the low Eh values experienced as a result of oxidative degradation or the electrode is responding to other redox systems - either as mixed potentials (see Kinetic Limitations), reaction potentials, or redox potentials.

At lower Eh values, platinum sulfide becomes the stable phase and this might represent a lower limit to the usefulness of the platinum electrode (this limit is greater than the water dissociation limit).

In the intermediate region where thermodynamic analysis predicts that free platinum is stable, the surface of the electrode is likely to be coated with oxide, since the rate of release of oxygen by platinum is very slow compared to the reading times normally used in field work. The behavior of the electrode in this region needs further study, although it has been shown that under restricted circumstances the electrode may respond to redox reactions in manganese, iron, nitrogen, and sulfur systems.

Kinetic Limitations

Since many redox processes are very slow in reaching equilibrium and do not readily couple with one another, several different apparent oxidation-reduction levels in the same locale are possible. A conceptually meaningful

Eh cannot be defined for non-equilibrium systems. Descriptions of an operationally measurable couple (Fe^{2+} - Fe^{3+}) and a contrasting unmeasurable couple (O_2 - H_2O) can be shown by schematic representation of polarization curves (Benson 1978).

Poising (Eh Buffering)

Eh readings free of drift are only possible in well-poised systems. The redox capacity (actually oxidation capacity) is defined as the quantity of strong reductant in moles that must be added to a liter of sample solution to lower the Eh by one volt. In well-poised systems, the redox capacity is large, and Eh measurements are relatively simple and reproducible. In the case of the ferrous-ferric couple, the system is poorly poised when $\text{Fe}^{3+}/\text{Fe}^{2+}$ is less than 10^{-5} or greater than 10^5 or when both Fe^{2+} and Fe^{3+} are less than 10^{-6}M (.06ppm).

Despite practical considerations and literature references questioning the utility of Eh measurements by platinum group metals, Bondiotti reports on some actual experiments on rock-simulated groundwater solutions (Francis et al. 1978). Electrode potentials of the freshly ground rock suspensions were measured using Pt and Au plated electrodes referenced to a saturated calomel electrode in a cell that was continuously purged with research-grade N_2 . Before entry into the cell, the N_2 was scrubbed through two oxygen absorbing solutions. Multiple electrode measurements in poorly-poised systems do not always yield uniform results even though all electrodes agree in standard solutions. The differences in measurements of electrode redox potentials in poorly poised systems is apparently confounded by variable electrode response rates. In work with the ground basalt and granites, Bondiotti observed that the larger the Pt surface area, the lower the stable electrode potential. For example, Pt wire electrodes made in the laboratory have not performed as well (in terms of potentials achieved) as button-type commercial electrodes. However, electroplating Au over the Pt wire has resulted in the wire-type electrodes responding at least equally as well as the large surface area electrodes.

A promising method for evaluating Eh electrodes under poorly poised conditions is the in-situ reduction of an indicator dye. Bondiotti used indigo carmine because its midpoint potential (50% reduced) is below the electrode potentials observed for the igneous rocks examined, but above the hematite-magnetite boundary line. Since the midpoint potential is the point of maximum redox buffering, electrode potentials should be relatively constant in this region during the reduction of indigo carmine.

The above concept was illustrated by measuring Eh in a weakly-poised system. Using indigo carmine at 10^{-5} M and a mixture of Fe filings at 0.05 M of Fe^{2+} and Fe^{3+} in 0.1 M HClO₄ in a stirred cell containing a carbon-reduced electrode, the midpoint potential of the Fe²⁺/Fe³⁺ couple was determined. The electrode indicated stable potentials for 100 minutes, in good agreement with the theoretical value determined by the Nernst equation. However, by lowering the indigo carmine to 10^{-6} M, the agreement between electrodes was radically affected (a difference between the Pt and Au electrodes of 50 mv).

The major point to bear in mind is that as the system becomes less poised a greater variability occurs in the stable redox potential measured among the indicator electrodes. To measure Eh in unpoised systems, several electrodes should be used that have been checked versus the indicator buffers to assure proper operation.

Bondiotti concluded that Pt electrode response in rock-groundwater slurries at least qualitatively follow expected trends, and thus the measurement of Eh is useful.

Because oxidation-reduction mechanisms are quite important, some attempt must be made to measure Eh or a parameter that affects it. We recommend that each experimentalist continue to make measurements of Eh and other important parameters such as dissolved oxygen, Fe^{2+} - Fe^{3+} solution distribution and SO_4^{2-} - S^{2-} solution distribution especially in systematic mechanism studies. An attempt should be made in all sorption experiments to relate results to the oxidation-reduction potential of the system.

Weathering Experiments

Contaminated groundwater from a waste repository will contact weathered rock surfaces, in addition to fresh rock surfaces as it travels underground. These weathered rock surfaces will be composed of layers of alteration products from the parent rock such as clay minerals, oxides, and hydroxides. The alteration products will, of course, have different sorption characteristics than the parent rock. To determine the effect of weathering on radionuclide sorption, samples of crushed basalt, granite, and argillite were artificially weathered by leaching with hot, distilled water in a soxhlet extractor for six months. Weathering experiments were conducted both in air and in an oxygen-free nitrogen atmosphere (to simulate repository conditions) (Barney and Anderson 1978). Measurements of K_d were made on the weathered rock and compared to K_d values for fresh rock.

Weathered basalt sorbs each radionuclide much stronger than fresh basalt. Values of K_d for ^{137}Cs , ^{85}Sr , and ^{237}Np increase by about a factor of five and the increase for ^{241}Am and Pu is even greater. Sorption properties of weathered and fresh granite are identical, within the range of error of the experiments. Weathered argillite sorbs ^{137}Cs , ^{241}Am , and Pu more strongly than fresh argillite; however, the opposite is true for ^{85}Sr and ^{237}Np . Values of K_d calculated for ^{137}Cs , ^{85}Sr , ^{237}Np , ^{241}Am , and Pu for both weathered and fresh rock are compared in Table 4.19. Measurements of K_d values for the rocks weathered in the oxygen-free atmosphere have not yet been completed.

TABLE 4.19. Comparison of Radionuclide Sorption on Weathered and Fresh Rock Surfaces (K_d Values in ml/g)

Radionuclide	Basalt		Granite		Argillite	
	Weathered	Unweathered	Weathered	Unweathered	Weathered	Unweathered
^{137}Cs	1500 $\pm$ 300	350 $\pm$ 35	1100 $\pm$ 300	1100 $\pm$ 200	13000 $\pm$ 2000	2400 $\pm$ 400
^{85}Sr	520 $\pm$ 120	108 $\pm$ 20	6.4 $\pm$ 0.8	6.2 $\pm$ 0.5	78 $\pm$ 6	103 $\pm$ 5
^{237}Np	49 $\pm$ 16	10.4 $\pm$ 0.8	39 $\pm$ 3	45 $\pm$ 2	56 $\pm$ 17	79 $\pm$ 10
^{241}Am	18000 $\pm$ 17000	6.2 $\pm$ 2.3	21000 $\pm$ 5000	27000 $\pm$ 12000	64000 $\pm$ 44000	22000 $\pm$ 14000
^{239}Pu	2000 $\pm$ 200	18 $\pm$ 2	12000 $\pm$ 7000	12000 $\pm$ 10000	28000 $\pm$ 18000	15000 $\pm$ 5000

Scanning electron photomicrographs of the rocks before and after weathering show that the surface structure of the basalt is altered significantly by weathering. The relatively smooth surface of fractured, fresh basalt is contrasted with the rough, detailed surface of the weathered basalt. It appears that the glassy matrix of the basalt has been leached away, leaving the more persistent crystalline phases behind. The dendritic structure has been identified as ilmenite. No obvious changes were found in the microstructure of granite or argillite after weathering. However, the layered structure of the argillite did expand during weathering, as is indicated by a threefold increase in internal surface area.

Sorption Site Identification by Autoradiography

At LASL (Thompson and Wolfberg 1978) sorption site identification by autoradiography has been performed using tuffaceous clay, argillite (shale), Jackass Flat tuff and Unkar Shale granite from the Nevada Test Site. A 50 μ l drop of the solution containing the radioactive tracer of interest was spotted on the rock thin section, which was then stored in a closed container saturated with water vapor. The solutions were prepared with water from the original geologic site of the rock type (alluvium, granite, tuff) or with water synthesized to be similar to that found at the geologic site (argillite). After the thin section was contacted with the groundwater and spiked with ^{233}U or ^{241}Am for an appropriate time, it was rinsed with distilled water and air dried. The thin section was then coated with a thin layer of collodion by momentary immersion. This coating protected the sorbed material from contact with water during subsequent operations. By the same technique, a thin coating of gelatin was added over the collodion. The gelatin coating provided an adherent substrate for the stripable emulsion. A detailed analysis of the mineral phases responsible for sorption by the thin sections is in progress; however, the following qualitative observations may be made:

Uranium

In each of the rock types, uranium appeared to sorb preferentially on certain of the minerals. Clay material appeared to sorb strongly, while there was little sorption on quartz. The amount of sorption seemed to be constant and predictable from one experiment to the next.

Americium

In general, americium transferred activity from the solution to the rock substrate more readily than did uranium (VI). However, the distribution of sorption sites was noticeably less specific for americium than for uranium. Apparently at the air-solution-solid interface some process (perhaps formation of insoluble oxy-compounds or polymers) was taking place, resulting in deposition of the americium, irrespective of the type of underlying mineral. This phenomenon may be related to the observation of Fried et al. (1977) that americium (and plutonium) forms insoluble deposits when allowed to dry.

These preliminary studies lead to the following conclusions. The extent of sorption is not quantitatively measured in autoradiography; hence, it does not compete with column or batch methods used to determine distribution coefficients. It does, however, provide some insight into the sorption process because the state of aggregation of the sorbed particles is indicated. The technique of microautoradiography has proven to be applicable for sorption studies of two radionuclides on five different rock materials. No reason seems apparent why other alpha-emitting or spontaneous-fissioning transuranic elements might not be used in similar studies. If the problems associated with longer ranges and lower track visibility of beta particles could be solved, this technique might be applied to a much wider group of radionuclides, especially to the fission products. Even if the method is limited to alpha-emitting nuclides, however, it does appear to be a useful adjunct to existing ways of studying sorption phenomena.

In similar experiments at LBL (Silva, Benson, and Apps 1978) on rock wafers used in batch sorption-desorption experiments, autoradiography coupled with petrographic and microprobe data yielded the following information.

From measurements made with alpha sources of known strengths, researchers determined that from 10^4 to 10^5 alpha tracks per square millimeter are required to produce an autoradiograph that can be readily studied under low magnification, e.g., 5x. Less exposure required tedious and time consuming track counting under high power magnification, e.g., 100x. Using these criteria, the exposure times were estimated at 1-3 days for the Am and Cm

wafers, 2-3 weeks for the Pu and about 3 months for the U and Np. The autoradiographs of the Am and Cm wafers have been prepared and are under study. The Pu, Np, and U wafers are still in process.

Americium and Curium Results

The autoradiographs of the shale samples did not show any distinguishing features. This was to be expected since the wafers were so uniformly fine-grained. The basalt and granite autoradiographs, however, possessed sites that exhibited differential adsorption.

In the quartz monzonite sample, Am is preferentially sorbed on altered plagioclase feldspars containing sericite and clinozoisite, biotites partially altered to chlorite, and chlorite-filled fractures in quartz. In the basalt sample, Am is preferentially sorbed on fractures coated with clinoptilolite and smectite.

The sorption of Cm on basalt parallels the Am pattern, showing preferential uptake on smectite-bearing fracture and smectite-altered fracture walls. Close inspection of the basalt surfaces indicated that certain topographical irregularities (open pits and fractures) also contained anomalous Am and Cm.

Two mechanisms can be suggested for the observed selectivity of the mica-like minerals: 1) the combined potential and kinetic energy changes on adsorption may be greater for mica-like minerals than for quartz, glass, and unaltered feldspar, or 2) the selectivity is due to the greater ion exchange capacities of the mica-like minerals. In the latter case, the selectivity would be related to the three-dimensional structure of the minerals, and the autoradiography would be recording alpha emissions from within the mica-like structures.

Nuclide Adsorption Compared With Ideal Ion Exchange Theory

An attempt is being made at ORNL (Meyer 1978, Shiao et al. 1978) to reduce the number of measurements necessary to define nuclide migration behavior by comparing results versus ion-exchange theory. If sorption of certain nuclides or all nuclides in certain rock-groundwater systems compares favorably with ion exchange predictions, a minimum amount of data collection would be sufficient.

Present efforts have concentrated on sorption on a few minerals over a wide range of salinity for selected nuclides. Since the first two repositories are currently predicted to occur in salt deposits, the solutions chosen were NaCl and CaCl₂ brines of variable ionic strength.

Because of the high ion-exchange capacity of clays, they are likely to dominate behavior, even when present in relatively small fractions. ORNL has consequently emphasized them so far, in particularly montmorillonite. In later stages of the program, tests will be made of predictions for synthetic mixtures of minerals, and of natural rocks.

ORNL has given considerable attention to purification of samples and to investigation of possible modifications of minerals by purification procedures. The ionic form of the minerals' cation exchange capacity is controlled, and the effects on distribution coefficients of partial conversion of the ion-exchange capacity to finite loadings of the ion under study are determined. This process guards against possible distortion of results by minor impurities of very high distribution coefficients and evaluates the effect of nuclide loading above tracer levels. The latter condition is being studied because natural ions of the nuclide or chemically similar elements may be present in the groundwater in macro amounts.

Further, very high K_d values may be a property of minerals present in very small amounts within the bulk rock. These minerals' exchange capacity may become saturated over long periods of time even by tracer concentrations of nuclides. A large fraction of ORNL's attention in the early stages of this program has been focussed on adsorption of alkali metals and alkaline earths, because with these the solution chemistry is usually simplest with respect to complexing, hydrolysis, and valence state. Establishing the predictability of behavior by ion-exchange equations is therefore the least ambiguous with these ions.

Both experimental and mathematical studies were performed to compare the observed sorption behavior to predicted behavior for pure mineral systems and hypothetical mineral binary mixtures. Details are presented in the ORNL technical reports (Meyer 1978, Shiao 1978). A brief summary of results is presented here. For a given sample of clay, adsorption of alkali and alkaline

earth ions appears to correlate fairly well to equations for ion-exchange reactions. In many cases, K_d for trace levels were about the same as for finite loading. Significant exceptions were encountered only for alkali metal ions at low loading on the Ca(II) form of montmorillonite and to a lesser extent for Cs(I) at lower loading on the sodium form. A possible explanation for loading curves of this type are the presence of impurities or possible modifications of the clay that cause differences in the adsorption behavior as the loading is increased.

Important alkali and alkaline earth elements for nuclear waste disposal include Rb, Cs, Sr, and Ra. The rare earths, typified by work on Eu, adsorb at pH 5 in a similar fashion as described by ion exchange theory up to brine concentrations of 0.2 to 0.5 M. A minimum or a leveling of $\log K_d$ of rare earth and actinide (III) ions versus the logarithm of sodium or calcium concentration at moderate salt concentrations was noted contrary to ion exchange theory (see Figures 23 and 26, Meyer 1978). This minimum adsorbability is similar to the adsorption minima frequently observed with organic cation-exchange resins (Dowex 50 type) at high ionic strength (Nelson, Murase, and Kraus 1964).

Reasons for the significant effects on K_d at low loading are not clear to ORNL researchers, but the fact that Wahlberg, et al. (1965) and Wahlberg and Fishman (1962) reported similar behavior for Cs(I) on both the sodium and calcium form of montmorillonite, leads them to believe that their observations are real. Measurements of sorption on other clays so far have been mostly of Sr adsorption from sodium chloride brine. The clays attapulgite, illite, and kaolinite in general yield ideal shapes and thus compare favorably to ion exchange theory.

Although results involved clay from only one source, substantial differences are evident (a factor of four, see Figure 4.13) between samples of different origins. Purification of montmorillonite did not seem to have a marked effect on adsorptive properties, so long as the ionic form of the clay was controlled. In this connection, when the sample was processed to a controlled ionic form before measurement, alkaline earth carbonates, if present, were probably removed, because the operation usually involves equilibration at

pH 5. Oxidation to remove organic matter and treatment with complexing agents to remove iron oxides apparently had little effect on subsequent nuclide adsorption.

With respect to differences in K_d between samples of montmorillonite, ORNL researchers are not yet confident enough in their measurements of ion-exchange capacity to say to what extent the K_d variations may be correlated with differences in capacity.

Comparison of results reported here with some values in the literature are summarized in Table 4.20. The values quoted are not always precise, because many were read from graphs, were obtained by interpolation or extrapolation (most literature results are for low salinities), or were computed from numbers representing somewhat ambiguously defined quantities. The concentration of the "Exchange Ion" is that in the literature reference. The loading of the "Adsorbed Ion" is trace or very low.

TABLE 4.20. Comparison of ORNL and Literature K_d Data

Absorbed Ion	Exchanging Ion, Moles/l		K_d This Report	K_d Literature	K/Γ This Report	K/Γ Literature	Literature Reference
	Na(I)	Ca(II)					
Ca(I)	0.2		60-180	250-550			Wahlberg and Fishman 1962
	6		3-6	5			Tamura 1964
	0.001				15-30	35	Gast 1972
	0.04					40	Lewis and Thomas 1963
		0.1	5000	300-1000			Wahlberg and Fishman 1962
Sr(II)	0.1		100	70			Spitsyn and Gromov 1958
	0.2		25	32			Wahlberg et al. 1965
	0.1-0.6		(1)				Tamura 1964
		0.025	30	30			Spitsyn and Gromov 1958
		0.1	7	2.5			Wahlberg et al. 1965
		0.15			1	1.3	Heald 1960
Ba(II)	0.04				3	1	Lewis and Thomas 1963

(1) K_{dSr} in Tamura (1964) about half of values in Figure 4.4, this report.

In view of the differences ORNL has observed with clay samples of different origin (see Figure 4.13), agreement with literature values in most cases is fairly good. As one might expect, the largest discrepancies between ORNL's and literature values are for those cases in which there were pronounced effects on K_d at low loading, i.e., the alkali metal ions on the calcium form, and to a lesser extent, Cs(I) on the sodium form. Some disagreements were even greater than those in the table; for example, values of $K_{d_{Cs}}$ on the calcium form have been reported to be a factor of a hundred less than ORNL's under supposedly comparable conditions (Sawhney 1964). Accuracy in such situations is not readily attained; alkali metal impurities in even reagent-grade calcium salts make attainment of controlled low-sodium levels difficult.

A mathematical program was written to compute distribution coefficients of ions adsorbed on mixtures as a function of macro ion concentration and/or exchange loading. Computer simulations have shown that to detect the presence of an impurity or second adsorbate with different exchange capacity, the variation in K_d versus loading should be monitored. For example, Figure 4.21 shows that in a mixture of adsorbates a large decrease in K_d is observed at fractional loading of 0.2 to 0.4, whereas for a pure adsorbate, significant decreases in K_d are not observed until loading approaches 1.0.

Practical implications of ORNL's results have been described in ORNL reports (Meyer 1978, Shiao et al. 1978). The low adsorption of alkali and alkaline-earth ions at high salinity implies that clay fractions of natural formations will not significantly retard the migration of the corresponding radioisotopes if the contacting aqueous phase is of high salinity. However, this implication is highly provisional until information on other classes of minerals is accumulated. Metal oxides may be strong adsorbents in some cases. Experience with silica in the use of diatomaceous earth supports for montmorillonite columns indicates that, for the ions and conditions studied, its adsorption was low. However, this behavior was expected at the pH range in question, and it should have high cation-exchange capacity in contact with more basic solutions. Hydrous oxides common in nature, particularly those of iron and aluminum, may be active at lower pH values than silica. ORNL began

FIGURE 4.21. Log K_d Versus Loading for 1-1 Exchange

measurements with aluminum oxide during FY-1978. Its behavior has exhibited some puzzling aspects, and ORNL has elected to defer discussion of these results until a better understanding is attained.

Observed Nuclide Migration Versus Kinetic Model Predictions

Argonne National Laboratory (Seitz et al. 1978a, Seitz et al. 1978b) has approached the study of nuclide migration principally through the use of infiltration experiments in which solutions are percolated or forced through rock pores and fissures. To generalize the results of these experiments, data from the experiments are being related to models of nuclide migration.

Results of two studies (Seitz et al. 1978a) using 1) a disaggregated glauconite sand and 2) machined fissures in gray hornblende-schist were nicely predicted by a model (Strickert et al. 1978) that includes the kinetics of the reacting nuclide. Curves of Sr migration through glauconite sand (Figure 4.5) can be reasonably explained by kinetic effects. The broadened curve shape with increased flow results from less reaction of the liquid and solid at the higher flow rates. The broadening was successfully predicted using the referenced first-order kinetic model. The original work on glauconite sand by Inoue and Kaufman (1963) assumed local equilibrium occurred as long as flow rates were kept below 3.8 cm/min (equivalent to 1.6 ml/min in the ANL experiments). The apparent discrepancy (ANL researchers feel their data show non-equilibrium effects at velocities greater than 0.1 ml/min) may be a function of two events. The ANL model does not account for variable hydrodynamic dispersion as the groundwater velocity increases and Inoue and Kaufmans' original work has less stringent requirements in observed versus predicted curve shapes to assign local equilibrium.

The purpose of experiments on fissures of schist was to determine whether migration behavior was tractable with kinetic and partitioning values measured in static sorption experiments. If, at a particular ratio of surface area to volume, the rate of adsorption, rate of desorption, and equilibrium concentrations of a nuclide partitioned between rock and solution are known, rate of migration of a nuclide through that particular media can be predicted from the ANL dispersion code (Strickert 1978). These predictions are, in turn, checked by actual migration behavior observed from infiltration experiments with the fissures. A sampling of results of model predictions versus observed nuclide migration are presented in Figures 4.9 and 4.10. Details and other results are found in the technical report (Seitz et al 1978a).

Some complications in americium migration that were not repeated in the experimental analyses or by the dispersion code for model predictions are visible from features on autoradiographs. The fissure surfaces did not absorb activity homogeneously as evidenced by the structures in the radiographs that highlight features (e.g., mineral filled veins, grain edge boundaries) in the fissure walls. In addition, as evidenced by the radiographs, flow through the fissure may not have been uniform across the fissure opening. Flow may have been faster in the centers of the fissures than along the edges. Another complication not handled by the dispersion code is that the kinetics of the americium reaction with the schist were not first order, as assumed by the code, which may account for differences between the theoretical and measured migration behavior.

In spite of these complications, the migration behavior modeled using absorption parameters (partitioning and kinetic data) measured in static experiments do approximate the migration obtained experimentally. These results demonstrate that migration of nuclides in rock fissures is tractable and can be approximated by data from static experiments. The ability to predict successfully nuclide migration followed from the use of kinetic and partitioning data obtained from rocks and nuclides with specified geometries (i.e., transforming the kinetics obtained from a batch test to the kinetics appropriate to a fissure was not necessary). A similar predictive capability was obtained from kinetic data measured for strontium in glauconite. This success should encourage the measurement of migration characteristics using geometries such as rock or mineral columns or rock fissures that are most similar to geometries where the data will be applied. Another criterion of future work will be to predict under what conditions reaction rates are fast enough that they may be neglected in migration models without a loss of accuracy.

Actual Leachate Versus Synthetic Leachate

An uncertainty in past sorption work that needs to be addressed is the chemical and physical relationship of the nuclide in synthetic solutions or groundwaters to the same nuclide in actual leachates. Presumably, any element leached from solid waste could hydrate, change valence state, or form complex

alumino-silicate species in solutions that could affect its retention by geologic materials. These same mechanisms can occur in synthetic solutions, but the relative magnitudes and potential differences must be studied. Actual leachates generated from glass wastes will be compared with past work on fabricated leachates. Some work has actually started at ANL (Seitz et al. 1978a).

The apparatus shown in Figure 4.22 has been used for leachate work. Elevated temperatures are used to promote leaching and to simulate the temperatures that will exist initially around a waste form if cesium and strontium are not removed from the waste. A sample of simulated high-level waste glass containing uranium was used as a source of radionuclides. A slice of this glass was irradiated in the ANL CP-5 research reactor to activate some nuclides. For geologic storage, elements of interest in the glass and their short-lived isotopes were zirconium, iodine, cesium, uranium, and neptunium. Other elements, such as a light alkali (sodium) and rare earths, were also present as short-lived radionuclides in the glass.

In ongoing experiments, trace elements leached from the waste form are carried in the fluid stream to an oolitic limestone column where their migration characteristics are monitored. This apparatus indicates the leachability of waste forms in groundwater solutions at temperatures and under oxygen and carbon dioxide partial pressures that may exist in geologic repositories.

Two experiments were performed near the end of FY-1978 and final analyses and conclusions will be performed in FY-1979.

Transport of Nuclides on Particulates

Following a postulated incursion of water into a repository, slow leaching may occur on the solid wastes, particularly if any crack development has occurred from thermal or rock mechanical stresses, devitrification, or anisotropic expansion effects. The slow movement of trace concentrations of waste products may then proceed in the form of tiny granules of solid waste or in soluble form. Work underway at the Georgia Institute of Technology has been directed to the study of two related phenomena: 1) the movement of sub-micron particles of types expected near disposal sites through aquifers of

FIGURE 4.22. Apparatus for Leach/Migration Experiments in Which Nuclides Leached from a Solidified Waste Form at Elevated Temperature Migrate in Rock Columns.

appropriate characteristics, and, 2) the sorption processes associated with the uptake of waste ions in trace concentrations on submicron particles, and the measurement of subsequent partition coefficients leading to competitive transfer from the particles to surrounding bed media.

This work did not get formally under way until near the end of this fiscal year. To date, tests on fine particle migration are made in columns containing beds of sand through which particle-bearing solutions are allowed to flow. Traced particles in 1-2 ml of water are injected by hypodermic syringe through a spectrum at the column inlet. The progress of the particles through the column is monitored in two ways: by external scanning detectors described below, and by counting successive portions of the column effluent.

One of the most important parts of this project is the preparation and characterization of suspensions of fine particles that will serve as carriers for radiotracers in the column experiments. To date, stable suspensions ($<1\text{ }\mu\text{m}$ diameter) have resulted from the prolonged ball milling of kaolin. The kaolin content of the suspension is 30 mg/ml. Approximately 25 l of suspension have been generated in this way and have remained opaque for about two months.

In the first experiment, a column was used that was packed with sand with a geometric mean size of $244\text{ }\mu\text{m}$ with 37% porosity, 0.03 cm/sec hydraulic conductivity and a calculated average effective pore size of approximately $50\text{ }\mu\text{m}$. The injected particles were not especially affected by the bed, however. They behaved quite similarly in their elution profiles to an injection of an ionic tracer $^{24}\text{Na}_2\text{CO}_3$, as shown in Figure 4.23. Although a smaller fraction of the kaolin than of the Na_2CO_3 was recovered, the particles were not significantly delayed when compared to the ionic front.

Thus, the use smaller grains in the bed seemed desirable to decrease the average pore size. Particles would then spend more of their time near grain surfaces, with correspondingly greater probability of attraction. A second column was used that was packed with sand $88\text{--}178\text{ }\mu\text{m}$ diameter with 40% porosity, 0.008 cm/sec hydraulic conductivity and a calculated average pore size of $23\text{ }\mu\text{m}$.

The increased ability of the small column to restrain fine particles is shown in Figure 4.24, which compares the elution profiles for kaolin in the large and small columns. The figure is normalized to eliminate the effect of the volume difference of the columns. Although similar total fractions of the tracer are recovered in the two cases, the small column clearly makes the retardation of fine particle migration a visible effect. However, the behavior of cations (as observed in a $^{24}\text{Na}_2\text{CO}_3$ test) is not much different from that of particulates, as was observed in the large column (see Figure 4.25).

ISOTOPE GENERATION

To examine the migration of actinide and some fission elements in rock and soil strata, complicated and expensive wet chemical extraction procedures are usually needed to detect the alpha and beta-emitting isotopes. Gamma-emitting and x-ray isotopes of several of these elements may be generated by

FIGURE 4.23. Elution of Ionic and Particulate Tracers in the Large Column

cyclotron activation. The efforts needed to analyze gamma-emitters are much simpler, and the use of special isotopes has greatly facilitated the Task 4 experimental program. In addition, use of these isotopes allows the behavior of more than one element to be observed in a single experiment, thus not only saving time but also eliminating uncertainties in trying to duplicate exact conditions from one experiment to another. Therefore, Argonne National Laboratory is producing ^{237}Pu , ^{235}Np and $^{95\text{m}}\text{Tc}$ at several intervals each year to assure a continual supply for experimentalists. The isotope production schedule for FY-1978 is given in Table 4.23. Target preparation for Pu and Np involve roll-bonding 1/2 in. x 6 in. ^{235}U foils 6 mil for Pu and 12 mil for Np to massive copper heat transfer backing plates. For the $^{235}\text{U}(\alpha,\text{Zn})$

FIGURE 4.24. Elution of Particulate Tracers in the Large and Small Columns

^{237}Pu reaction a 12.5 mil aluminum attenuating foil is used to optimize the ^{237}Pu production over the competing (α, n) and $(\alpha, 3n)$ reactions yielding ^{236}Pu and ^{238}Pu . A deuterium bombardment is used for the $^{235}\text{U}(d, Zn) ^{235}\text{Np}$ reaction. Both types of targets are dissolved in HBr, converted to nitrate, and separated achieved by anion exchange in nitric acid.

Technetium-95m was made in the ANL cyclotron by an alpha bombardment of five niobium metal foils stacked together. After a cooling period to allow for the decay of the 4.3-day ^{96}Tc , the niobium foil was dissolved in a solution containing 15 M HNO_3 and 28 M HF . The niobium fluoroide complex was destroyed with boric acid and the Nb_2O_5 precipitate was removed by centrifugation. The solution was made basic and the $^{95\text{m}}\text{TcO}_4^-$ was sorbed on an anion exchange column. The technetium was eluted with 2 M perchloric acid

FIGURE 25. Elution of Ionic and Particulate Tracers in the Small Column

and coprecipitated with copper as a sulfide. The precipitate was redissolved in ammonium hydroxide and hydrogen peroxide and the copper was removed by passing the solution through a cation exchange column. The final technetium solution consisted of $^{95m}\text{TcO}_4^-$ in a dilute ammonium hydroxide solution.

Purity of the final product has been carefully checked for interfering gamma emitters by high resolution gamma and x-ray spectroscopy. Each batch has also been analyzed by alpha spectroscopy for extraneous alpha emitters as well as to monitor yields of ^{236}Pu and ^{238}Pu . Radiometric assay is done by low energy photon spectroscopy against a ^{243}Cm standard. Aliquots of this calibrated solution, in HNO_3 , are pipetted into glass vials, evaporated and sealed. Shipping is by truck per Department of Transportation (DOT) regulations.

TABLE 4.21. Isotope Production Schedule

Tracer	Date(a)	Assigned Time(b)	Actual Time(c)	Current(d)	Dose(e)	Yield(f)	Date of Yield Calculation	Shipped(g)
^{237}Pu	10/19-11/28/77	116 hrs	82.5 hrs	35.4 μA	2920 μAhrs	300 μCi	12/16/77	1/4/78
^{237}Pu	4/12-5/25/78	92.5 hrs	73.3 hrs	38.6 μA	2830 μAhrs	260 μCi	5/29/78	6/21/78
^{95m}Tc	7/5-7/13/78	35 hrs	28.5 hrs	31.9 μA	910 μAhrs	2 mCi	7/31/78	9/26/78
^{237}Pu	7/24-8/2/78	96 hrs	90.4 hrs	45.2 μA	4085 μAhrs	309 μCi	9/14/78	9/21/78

a = calendar period over which the target was irradiated

b = length of time the target was on the machine and time charged to WISAP account

c = length of time the target actually was irradiated

d = average beam current seen by target (dose/actual) the instantaneous current is a function of machine performance at the moment

e = accumulative exposure of the target as actually measured

f = amount of tracer recovered from target after chemical separation

g = date tracer left ANL.

NOTE: A check of some of the numbers and dates in this table will indicate the nature of the problems experienced so far at ANL. A comparison of irradiation dates and assigned hours shows scheduling difficulties, interruptions for short high priority target irradiations. It also indicates mechanical difficulties with the cyclotron (down time). A check of actual versus assigned hours shows the difficulty of one shift (8-hr) operation of the cyclotron. A substantial portion of the assigned time is lost getting the machine up and down again. Both of these problems have been minimized by scheduling two shift (16-hr) days for these long runs. This results in a tighter time window with less conflict to other users, more efficient use of assigned time and less loss of tracer due to decay during irradiation but a higher cost to WISAP.

The length of time between yield calibration and shipping dates reflects the logistical problems encountered in shipping Pu. Existing impediments are being removed and the shipment of these activities from ANL to the subcontractors is continually improving. Finally the delay between end of irradiation and calibration is time spent in chemical separation. The time expended in chemical processing should be continually reduced with increasing experiences. The goal is a one-week separation time.

TASK 5 - SOCIETAL ACCEPTANCE ANALYSIS

INTRODUCTION

FY-1978 was the second and final year of work by Battelle's Human Affairs Research Center (HARC) in the social sciences for WISAP. HARC's FY-1978 work was in large part limited to completion of projects begun in the latter part of the preceding year.

FY-1978 was also marked by two contract transitions. First was the beginning of direct contract relationship between DOE and HARC. Second, and perhaps more importantly, was the transition from OWI to ONWI, and HARC's negotiation of separate contracts with ONWI. For FY-1979, for example, HARC will work directly for ONWI and will not be part of WISAP. Despite these contractual and administrative transitions, a coherent body of social science work in commercial nuclear waste management continues at HARC for the NWTs program.

SUMMARY OF HARC WORK

HARC's FY-1978 work had three major components. First was a role in overseeing social science work undertaken for OWI/ONWI by other contractors. HARC had initially provided advice as to the subject matter, scope, and potential contractors for such work during FY-1977. HARC's role in FY-1978 was to monitor and comment upon the completion of these projects. The projects were:

- Bishop, A. B., et al. Public Consultation in Public Policy Information: State-of-the-Art Report.
- Bowes, J. E., et al. Communication of Technical Information to Lay Audiences.
- Burt, R. S., et al. Resolving Community Conflict in the Nuclear Power Issue: A Report and Annotated Bibliography.
- Garvey, G., and R. Brenner. Political and Socioeconomic Impacting of the Nuclear Waste Terminal Storage Program. Princeton University.
- Garvey, G. Planning for Nuclear Waste Disposal: Mitigating Socioeconomic Impacts. Princeton University.

- Brenner, R. D. The Social, Economic and Political Impacts of National Waste Terminal Storage Repositories. Princeton University.

The papers on Conflict Resolution and Public Participation were completed in the second quarter of FY-1978. The Communication paper was completed in the third quarter of FY-1978. A draft of the report from Princeton was completed at the end of the fourth quarter of FY-1978, and should be in final form early in calendar year 1979. The Princeton work is likely to be three separate papers, rather than a single one.

HARC completed five technical reports of its own during FY-1978 and submitted them to WISAP, OWI and ONWI. They will be issued in final form in FY-1979. These reports are:

- Cluett, C., et al. A Demographic Model for Assessing the Socioeconomic Impacts of Large-Scale Industrial Development Projects.
- Greene, M. R., and T. P. Hunter. The Management of Social and Economic Impacts Anticipated with a Nuclear Waste Repository: A Preliminary Discussion.
- Cole, R. J., et al. Compensation for the Adverse Effects of Nuclear Waste Facilities.
- Smith, R. F. State and Local Regulation Relevant to Nuclear Waste Isolation Facilities.
- Hunter, T. P. Nuclear Waste Repository Land Use Control Considerations in Selected States.

SUMMARIES OF HARC TECHNICAL REPORTS

Cluett, C. C., M. T. Mertaugh and M. Micklin. A Demographic Model for Assessing the Socioeconomic Impacts of Large Scale Industrial Development Projects. This model projects generic social and economic impacts for largescale industrial development projects, specifically including nuclear waste repositories. It uses baseline demographic data and labor force characteristics of

an industrial development to project population change as a result of that project. This change is then used as a basis for derivation of increased demands for various social services, normally both publicly and privately provided. Because of very wide ranges of regional and local variations, the model does not attempt objections of changes in economic activity, particularly local fiscal impacts. The model is then applied to two variations of an industrial development project at three surrogate sites: southeast, midwest and southwest.

Greene, M. R. and T. P. Hunter. The Management of Social and Economic Impacts Anticipated with the Nuclear Waste Repository: Preliminary Discussion. This paper provides very brief review of socioeconomic impacts likely to result from development of nuclear waste repositories and the need to manage (or mitigate) such impacts. It focuses on the means available to local and site officials for this management. Primarily, attention is directed towards the existing array of federal assistance programs that might be brought to bear.

Cole, R. J., D. V. Friedman, F. A. Morris and S. Smolkin. Compensation for the Adverse Effects of Nuclear Waste Facilities. This paper is a generic analysis of compensation as a method for dealing with adverse effects of waste facility development. It sets out a framework for considering, at a more specific level, whether or not to use compensation, and if so, how to do it. The framework includes: 1) examination of effects likely to induce consideration of compensation, 2) analysis of compensation from several viewpoints (legal authority, implementation, fairness, political feasibility, economic efficiency, and finally project strategy), 3) evaluation of the consideration of these varying viewpoints, 4) design of a compensation scheme, and 5) monitoring its implementation. The paper is an analysis of how to approach decision to compensate, and the implementation of that decision rather than an argument for compensation in the specific case of nuclear waste facilities.

Smith, R. F. State and Local Regulation Relevant to Nuclear Waste Isolation Facilities. This report is a guide detailing how state governments commonly regulate activities likely to occur during the siting and construction of a nuclear waste repository. It considers the stages of repository development and the related regulatory activities that would occur if such a facility

were privately developed. Implicit in this approach is the concept that state regulatory interests applicable to private facilities would also apply to federal ones, such as nuclear waste repositories, even though the federal government would have great power over the exercise of any state legal authority for such a facility. State regulatory interests will, despite very great federal preemptive powers, need to be taken into account. There is particular concern with the variety of regulatory concerns and powers within any state government; and especially the independent powers of various state officials and agencies. The paper does not provide detail on the existing relationships among agencies and officials within the states, apart from their formal statutory ones.

Hunter, T. P. Nuclear Waste Repository Land Uses Control Considerations in Selected States. This paper briefly analyzes land use control issues raised by potential waste repository development in a number of states (Louisiana, Mississippi, Texas, Ohio, New York, and Utah). Analysis is directed toward problems in land acquisition, land use controls, and particularly towards possible difficulties between surface and subsurface rights of land under both federal and state laws.

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APPENDIX A

PATHS MODEL INPUT AND OUTPUT

APPENDIX A

PATHS MODEL INPUT AND OUTPUT

The PATHS model input requirements and various output forms can best be illustrated by example. Table A.1 contains a completed PATHS input form for a transient case with two time-varying injection wells, and Figures A.1 and A.2 illustrate the two kinds of options available for time-varying wells. Model output can take various forms. Figures A.3a and A.3b illustrate the pathlines and isochronal lines for fluid leaving the source at 0 and 50 years, and 75 and 100 years, respectively. The lines represent the position of the fluid (or contaminant fronts) at that number of years after departure from the source. Other output forms necessary for understanding are the contaminant location/arrival time distribution (Figure A.4), the contaminant location/outflow quantity distribution at the river (Figure A.5), the contaminant concentration entering the river at various locations and times (Figure A.6), and the groundwater contaminant outflow rate into the river versus time (Figure A.7). These various output forms are needed to give a complete understanding of the effects of a groundwater contaminated source.

TABLE A.1. Input Parameter Worksheet for an Example Transient Case

CASE: Example Transient Case (Two Wells)

1. 100 ft. = D_0 is the stratum thickness.
2. 8500 ft. = R is the distance to the boundary. Units must be the same as D_0 .
3. 8500 ft. = X_{MAX}/T_{MAX} are the stopping distance or time for pathlines.
4. 250 ft. = r_0 is the cavern or pond radius. Units must be the same as D_0 .
5. 10 ft. = H_0 is the head in the cavern. Units must be the same as D_0 .
6. 1825 ft./yr. = K_0 is the stratum hydraulic conductivity. Length units must be the same as D_0 .
Whatever time units are in K_0 sets the units of the travel time.
7. 0.2 = P is the effective porosity.
8. T = S or T . A steady (S) or transient (T) case.
9. 0.001 = U_0 is the initial uniform gradient value. See Figure 1.
10. 0.001 = U_M is the lateral gradient value. See Figure 1.
11. 1 = T_M in time units of K_0 .
12. 1, 1, 1 = A, B, C are three time-related integers.
13. S = S or E or C . Use the serpin (S), exponential (E), or cyclic (C) head variation in the cavern.
14. 4 ft. = H_I is the initial head.
15. 8 ft. = H_M is the maximum head.
16. 50 yr. = T_N in time units of K_0 .
17. 0, 1, 1 = D, E, F . See Figure 1.
18. 2 = J is total number of wells.
19. 0° = θ_0 is the angle (deg) around the cavern wall to the starting point for the first pathline.
20. 160° = θ_M is the maximum angle (deg) to the last pathline starting point along the cavern wall.
21. 9 = N_θ is the number of pathlines to be generated from θ_0 to and including θ_M .
22. 1 = K_θ is the number of pathlines wanted between θ_M and 179.99° .
23. 0 yr. = t_0 is the departure time of the first fluid particles leaving the cavern.
24. 100 yr. = t_f is the departure time of the final fluid particles.
25. 5 = N_T is the number of equally spaced departure times beginning with t_0 and ending with t_f .
26. _____ = K_d is the equilibrium exchange distribution coefficient.
27. _____ = B_d is the bulk density of the porous material.
28. 30 in. = _____ inch wide plots are desired. Request either a 30" or 11" wide by 30" plot.
29. 3 in. = X_{CENTER} } The location (x & y in inches) on the plot where
30. 2 in. = Y_{CENTER} } the cavern center is to be located.
31. 1000 ft./in. = $SCALE$ is the scale for the plot. Length in units of D_0 per inch.

TABLE A.1. (contd)

SERPEN OPTION

- 18.05 1 = j is the well number.
- 18.10 3000 ft. = $XWELL_j = x_j'$ is the x-coordinate location of the center of the well. (Units consistent with D_0 .)
- 18.15 1000 ft. = $YWELL_j = y_j'$ is the y-coordinate location of the center of the well.
- 18.20 250 ft. = $ROWELL_j$ is the stopping radius around the well.
- 18.25 S = S or C. serpin (S) or cyclic (C) option. See Figure 1.
- 18.30 $4(10^3) ft^3/yr$ = QI_j is initial inflow (+) or outflow (-) rate in length cubed per time units the same as D_0 and K_0 .
- 18.35 $6(10^5) ft^3/yr$ = QM_j is a later inflow (+) or outflow (-) rate of this well option.
- 18.40 25 yr. = TN_j is the time parameter in the serpin option. See Figure 1.
- 18.45 1, 1, 1 = DW_j, EW_j, FW_j . serpin well option parameters.

CYCLIC OPTION

- 18.50 2 = j is the well number.
- 18.55 5500 ft. = $XWELL_j = x_j'$ is the x-coordinate location of the center of the well. (Units consistent with D_0 .)
- 18.60 3000 ft. = $YWELL_j = y_j'$ is the y-coordinate location of the center of the well.
- 18.65 300 ft. = $ROWELL_j$ is the stopping radius around the well.
- 18.70 C = S or C; serpin (S) or cyclic (C). See Figure 2.
- 18.75 0.0 = QQ_j is the mean inflow (+) or outflow (-) rate in length cubed per time units the same as D_0 and K_0 .
- 18.80 $5(10^5) ft^3/yr$ = QA_j is the amplitude of the cyclic inflow (+) or outflow (-) rate.
- 18.85 50 yr. = $TOWELL_j$ is the initial or beginning time for the cyclic well option.
- 18.90 450 yr. = $TMWELL_j$ is the later cyclic time parameter.

PATHLINE - IRREGULAR STARTING COORDINATES

(If 00 in Item 19 equals 0M in Item 20 then N0 pathlines will be generated from the individual coordinates provided below.)

21. _____ = N0 is the number of input data sets to be entered for starting pathlines ($1 \leq i \leq N0$).

Pathline i	Starting Coordinates		Starting Pathline Length*	Initial Time*
	X	Y		

*Values need not be supplied

$$\text{Serpín Equation } W(t') = W_0 + \frac{2(W_m - W_0) \left(\frac{t'}{t'_n} + A \right)}{B \left(\frac{t'}{t'_n} + A \right)^2 + C} \quad (14)$$

Parameters in serpín Equation (14) $W(t')$	Term defined on input worksheet for:		
	Uniform gradient, $U(t')$	Cavern or pond head, $H(t')$	Well flow rate $Q_j(t')$
W_0	UO	HI	QI _j
W_m	UM	HM	QM _j
t'_n	TM	TN	TN _j
A	A	D	DW _j
B	B	E	EW _j
C	C	F	FW _j

FIGURE A.1. Serpín Time-Dependent Forms for PATHS

Cyclic Equation

$$\begin{aligned} W(t') &= W & \text{if } W > 0 \\ W(t') &= 0 & \text{if } W \leq 0 \end{aligned} \quad (15)$$

where:

$$W = w_{mc} + w_{oc} \sin \left[\left(\frac{t' - t_{oc}}{t_{mc} - t_{oc}} \right) 2\pi \right] \quad (16)$$

Parameters in cyclic Equation (16) W	Term defined on input worksheet for:	
	Cavern or pond head, $H(t')$	Well flow rate, $Q_j(t')$
w_{mc}	HMC	QQ_j
w_{oc}	HAC	QA_j
t_{oc}	TOC	TO_j
t_{mc}	TMC	TM_j

FIGURE A.2. Cyclic Time-Dependent Forms for PATHS

FIGURE A.3a. Example Transient Flow Results for Fluid Particles Departing Pond at 0 and 50 Years

FIGURE A.3b. Example Transient Flow Results for Fluid Particles Departing Pond at 75 and 100 Years

FIGURE A.4. The Contaminant Location/Arrival-Time Distribution for the Transient Example Case

FIGURE A.5. Contaminant Location/Outflow-Quantity Distribution at the River for the Example Transient Case

FIGURE A.6. The Concentration of Contamination Entering the River at Various Locations and Times for the Example Transient Case

FIGURE A.7. The Outflow Rate of Groundwater Contamination for the Example Transient Case

APPENDIX B

FINITE ELEMENT HYDROLOGIC MODEL DEVELOPMENT

APPENDIX B

FINITE ELEMENT HYDROLOGIC MODEL DEVELOPMENT

SUPPORTIVE PROGRAMS

Simulation results are functions of the input parameters and should be verified thoroughly before the simulation runs. This is especially necessary for the complicated input data streams required for a complex 3-D model. Supportive programs were developed to provide both a check of the input parameters and to analyze model predictions, and thus to provide a better interface between the modeler and the geologists, engineers, and decision makers. The supportive programs all access the main input data file used by FE3DGW, as well as FE3DGW output files, to insure that the actual model input and output streams are analyzed.

PLOTEL

The PLOTEL program ensures that coordinates of each node are properly checked, the given region is separated into discrete elements, and the vertical stratification details at each node are performed. Past experience shows that in spite of manual checks, errors persist. The PLOTEL code aids in shortening the time to achieve correct geometry of nodes and finite elements.

Three-dimensional elements are generated using actual interpreted or synthetic well logs (the geologic section at a given node). A visual check or errors is provided by a plot of these well logs, shown in Figure B.1. Geologic sections, defined in the input data file, are drawn for each node location. A vertical dashed line identifies the elevation below mean sea level and a horizontal tick mark locates the interface of two hydrologic units. Each hydraulic unit is identified by an integer number. This provides the modeler or hydrogeologist a means of reviewing the well logs for errors before simulation.

GRINDIN and GRITIT

For a complex layered system, plotting of the well logs alone may not be adequate. Supplemental programs (GRIDIT and GRIDIN) retrieve the thicknesses,

FIGURE B.1. Illustrative Sample Plot From "PLOTTEL" Showing Node Locations, Finite Element Deliniations and Geologic Sections at Each Node

top elevations, or bottom elevations of each hydrogeologic unit for three-dimensional display, shown in Figure B.2, or for contour plotting, shown in Figure B.3. These plots reveal major discontinuities and keypunch errors.

PLOTBC

The locations and values of head potential or Dirichlet boundary conditions are plotted by the PLOTBC program.

PLFLUX

The surface infiltration rates specified for each subregion (element) are plotted by the PLFLUX program.

GRIDH

Potential maps of each hydrogeologic unit, either input initial conditions or model predictions, are displayed using the GRIDH program.

VERIFICATION OF FE3DGW WITH ANALYTICAL SOLUTIONS

For three-dimensional flow, no analytical solution is available. Therefore, the validation of the three-dimensional model was carried out with the following two-dimensional and quasi-three-dimensional solutions: the Theis nonequilibrium equation, two-dimensional-PATHS analytical solution, and analytical leaky aquifer solutions.

Verification With the Theis Nonequilibrium Equation

Unsteady radial flow to a well pumping at a constant rate in an infinite, homogeneous, isotropic aquifer is defined by the two-dimensional Theis nonequilibrium equation (Theis 1938). Since three-dimensional models can handle two-dimensional cases by prescribing identical boundary conditions at top and bottom layers, the Theis equation was used for sensitivity evaluations of both time increments and nodal density.

Because of the symmetry of radial flow to a single pumping level, a pie-shaped wedge was modeled with finite elements. Nodal distances and time steps were defined exponentially as functions of well location and initial time. Figure B.4 shows the comparison of analytical and finite element results.

FIGURE B.2. Three-Dimensional Representation of Glacial Aquifer Thickness Developed by Retrieving Data Using "GRIDIT" and "GRIDIN" from Input File of the Three-Dimensional Groundwater Model of Long Island, New York

FIGURE B.3. Contour Map Showing the Thickness of Magothy Aquifer Developed from Data Retrieved by "GRIDIT" and "GRIDIN" from Input File of the Three-Dimensional Groundwater Model of Long Island, New York

FIGURE B.4. Comparison Between the Theis Nonequilibrium Analytical Solution and FE3DGW Code

Verification with the Two-Dimensional PATHS Analytical Solution

For a given flow through a cylindrical reservoir cavern with a specified head above uniform lateral flow, and a large radial distance to the remote outer boundary, the steady-state potentials are defined by PATHS (Nelson 1978). A rectangular aquifer (30,000 ft x 24,000 ft) with a cavern of 2,000 ft radius located 21,000 ft from the lower left-hand corner of the region was simulated using 6,000, 3,000, and 1,500 ft square elements (Figure B.5) coupled with radial-linear elements. The results, even with the coarser grid of 6,000 ft (Figure B.6), compared well with the analytical solution.

Verification With Analytical Leaky Aquifer Solutions

Hantush (1960) provides an analytical solution of the drawdown distribution in the vicinity of a steady pumping well draining an elastic artesian aquifer confined by semipervious elastic strata. The discharge of the well is supplied by reduction of storage in the aquifer and by leakage from semipervious layers. The hydraulic conductivities in the semiconfining layers are

FIGURE B.5. Combined Square (a) 6,000 ft, (b) 3,000 ft and (c) 1,500 ft and Constant Radial Pattern Finite Element Grid Used for Sensitivity Analysis

FIGURE B.6. Comparison of Analytical Solution ("PATHS") and
 3-D Finite Element Solution for Grid Pattern
 Shown in Figure B.5

assumed very small in magnitude compared with those of the main aquifer, so that flow is vertical through semiconfining beds and horizontal in the main aquifer.

The analytical results and finite element model simulation with the pie-shaped wedge for the three-layered system are shown in Figure B.7.

FIGURE B.7. Analytical (Circles) and Finite Element (Line) Dimensionless Drawdown versus Dimensionless Time for a Three Layered Leaky Aquifer at 1 meter radius: K = hydraulic conductivity (L/T); t = time (T); S = specific storage (1/L); r = radius (L); G^S = thickness (L); Q = pumping

EXTENSION OF MODEL FOR COUPLED SOLUTION OF PRESSURE, TEMPERATURE, AND SOLUTE

During FY-1978, the PNL-FE3DGW model was extended for coupled solution of pressure, temperature, and solute. This extension was undertaken, since several of the prospective sites are in salt. More realistic (less conservative) modeling of brine-freshwater aquifers characteristic of the groundwater systems near bedded and dome salt sites require that the salt transport problem be solved simultaneously with the normal groundwater flow problem since changes in density caused by salt transport affect both the driving gradients and the hydraulic conductivity of the system. Upward movement of concentrated brines is retarded by gravity. Since this downward gradient can be partially balanced by the temperature anomalies caused by the presence of heat-generating wastes in the repository, temperature equations describing heat flow must also be solved simultaneously with the equations for groundwater flow and salt transport. Equations B.1, B.2, and B.3 represent the set of coupled partial differential equations being solved by the extended version of PNL-FE3DGW. The basic model structure will be the same as the current water-flow-only version of PNL-FE3DGW. The finite element formulation of Equation B.3 through B.5 has been completed. The input requirements have been identified and the data input programs have been completed.

Groundwater Flow Equations with Heat and Solute

Suppose x, y, z to be a Cartesian coordinate system and let $Z(x, y, z)$ be the height of a point above a horizontal reference plane. Then the basic equation describing single-phase flow in a porous medium results from a combination of the continuity equation:

$$\nabla \cdot \rho \mathbf{u} + q' = \frac{\partial}{\partial t} (\phi \rho) \quad (\text{B.1})$$

and Darcy's law in three dimensions:

$$\mathbf{u} = - \frac{k}{\mu} (\nabla p - \rho g \nabla Z) \quad (\text{B.2})$$

The result is the basic flow equation:

$$\nabla \cdot \frac{k}{\mu} (\nabla p - \rho g \nabla Z) - q' = \frac{\partial}{\partial t} (\phi \rho) \quad (B.3)$$

A material balance for the solute results in the solute or concentration equation:

$$\nabla \cdot \left[C \frac{k}{\mu} (\nabla p - \rho g \nabla Z) \right] + \nabla \cdot (E) \cdot \nabla C - q' C = \frac{\partial}{\partial t} (\phi \rho C) \quad (B.4)$$

The energy balance defined as: enthalpy in - enthalpy out = change in internal energy, is described by the energy equation:

$$\begin{aligned} \nabla \rho \frac{k}{\mu} H (\nabla p - \rho g \nabla Z) + \nabla \cdot K \cdot \nabla T - p_L - q' H \\ = \frac{\partial}{\partial t} [\phi \rho U + (1-\phi) (\rho C_p)_R T] \end{aligned} \quad (B.5)$$

Nomenclature:

- t = Time
- T = Temperature
- u = Superficial (Darcy) fluid velocity in the porous rock
- U = Internal energy
- C = Concentration, mass fraction
- C_p = Specific heat
- q' = Mass rate per unit volume
- H = Enthalpy
- q_L = Rate of heat loss from grid block
- x = Cartesian space coordinate
- Z = Elevation above a reference plane
- k = Permeability
- K = Thermal conductivity
- P = Pressure
- φ = Porosity

ρ = Density
 μ = Viscosity
 E = Dispersion coefficient
 g = Acceleration due to gravity.

The system of Equations B.6, B.7 and B.8 along with the fluid property dependence on pressure, temperature, and concentration describe the groundwater flow from injection of wastes into an aquifer.

In addition to extending PNL-FE3DGW to handle temperature and solute transport we have obtained a copy of the DWDM (extended) code and have started the conversion process to make this level 4 model, which is being used by NRC, operational on PNL computer systems.

RELEASE CONSEQUENCE ANALYSIS FOR A HYPOTHETICAL GEOLOGIC NUCLEAR WASTE REPOSITORY

The model PNL-FE3DGW was used to analyze groundwater flow patterns for a hypothetical groundwater system surrounding a generic salt repository. The generic site is located in a large undeformed sedimentary basin approximately 5 km from the regional groundwater discharge site (a river flowing at $500 \text{ m}^3/\text{sec}$). Figure B.8 illustrates the flow system (assumed uniform in the y direction). The top of the salt lies 250 m below the surface and extends great distances downward. The hydrologic structure above the salt includes: a) 50-m caprock, b) a 160-m low production aquifer of interbedded limestone-dolomite-sandstone, c) 30-m aquitard, and d) a 10-m thick relatively high production aquifer. Figure B.9 illustrates the X-Z cross-section modeled. For purposes of a release scenario, a violent sequence of multiple fracturing of infinite extent parallel to the river to a depth of 450 m into the salt was assumed to have occurred in the area of the repository, fracturing the caprock and salt in a 2400-m wide area through the repository. The fractured caprock and salt was assigned the same permeability and porosity as the sandstone-dolomite-limestone aquifer (see Table B.1). Since the 3-D model was used, this X-Z system was modeled with one row of 3-D elements in the X direction as shown in Figure B.10.

FIGURE B.8. Cross Section View of Regional Discharge to a River
(Vertical Scale Exaggerated)

FIGURE B.9. Cross Section of the Five Geologic Layers Used to Define the Model Region

FIGURE B.10. Three-Dimensional View of the Model Region

TABLE B.1. Finite Element Model Hydrogeologic Input Parameters

<u>Layer</u>	<u>Rock Type</u>	<u>Thickness (m)</u>	<u>Hydraulic Conductivity (m/day)</u>	<u>Porosity (%)</u>
1	Unconsolidated Sand, gravel and silt	10	5.9	20
2	Calcareous shale, partly sandy	30	.01	13
3	Sandstone, dolomite, cherty limestone	160	.06	20
4	Interbedded shale and dolomite (salt caprock)	50	.006	20
4a	Fractured interbedded shale and dolomite (salt caprock)	50	.06	20
5	Salt	Infinite	.00006	.5
5a	Fractured salt	450 m	.06	20

The regional water table was assumed to have a uniform gradient of one meter in one kilometer, and the river elevation was assumed to be 190 m above sea level. The repository was upgradient from the river and the water table elevation at the repository was about 195 m above sea level. To maintain this gradient, the appropriate flux was calculated for each of the top four layers and input in the model at the most upstream nodes (left end).

The river was assumed to be the regional discharge site for all the water-bearing layers. In order to simulate this in the model, the river was made to intersect the upper layer at nodes 23, 1023, 46, and 1046, and all nodes below this are considered no flow boundaries (Figure B.10). This would force the water in the lower layers to move up to the river as depicted in Figure B.8.

The output from the hydrologic model is the groundwater potential (elevations) distribution throughout the X-Z plane over the X-Z region that was

modeled. A contour plot of these potentials with superimposed water flow paths is shown in the X-Z cross section plot of Figure B.11. As a result of fracturing the salt formation and the overlying shale in the area of the repository, some of the water is able to flow down through the repository and eventually make its way up to the river.

An auxiliary program for the finite element model has the capability to calculate travel time, travel distance, and velocity of the water along any streamline within the region. These values are calculated according to the hydraulic conductivities, porosities, and gradients of the various layers along the flow path. The average flow values were calculated using a weighted average according to flow for multiple flow tubes and streamlines spaced along the repository. The average values determined for water leaving the repository were:

- average distance - 6,100 m
- average travel time - 100,000 yr
- average velocity - .06 m/yr
- average width of the repository flow tube - 60 m
- average flow through the repository - 190 m³/yr.

The 3-D groundwater flow is solved by finite-element techniques and is defined by the following equation:

$$\frac{\partial}{\partial x} (K_x \frac{\partial h}{\partial x}) + \frac{\partial}{\partial y} (K_y \frac{\partial h}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial h}{\partial z}) = -Q + S_s \frac{\partial h}{\partial t} \quad (B.6)$$

where

$$S_s = g (\alpha_p + \theta \beta_p)$$

g = gravity field strength, L T⁻²

h = head above common datum, L

$$h = z + \frac{1}{g} \int_0^p \frac{dp}{P_x(P)}$$

FIGURE B.11. Contour Plot of the Model Predicted Vertical Groundwater Potentials with Superimposed Streamlines

K_x, K_y, K_z = represents hydraulic conductivity of the saturated flow in the x, y, and z directions, $L T^{-1}$

p = fluid pressure, $M L^{-1} T^{-2}$

Q = strength of sink function defined by T^{-1}

$$Q = \sum_{i=1}^n Q_w(x_i, y_i, z_i, t) \delta(x-x_i)(y-y_i)(z-z_i)$$

Q_w = the well discharge from the aquifer $L^3 T^{-1}$

δ = Dirac delta function

t = time, T

S_s = specific storage L^{-1}

z = elevation above given datum, L

θ = porosity of medium, dimensionless

α = compressibility of medium, $LT^2 M^{-1}$
 β = compressibility of liquid, $LT^2 M^{-1}$
 ρ = density of fluid, $M L^{-3}$.

This equation provides the following capabilities:

- The given region of the problem can be divided into irregular subdivisions as dictated by the physical geometry of the problem. Individual sub-domains (elements) can vary in size. The advantages of irregular subdivisions and higher-order approximations are certainly important because complex "space domains" are often encountered in natural geologic systems.
- The model uses mixed order three-dimensional quadrilateral elements, thereby providing means of defining complex basins using a minimum number of nodes.
- Inhomogeneity and anisotropy are quite easily accommodated, thus allowing representation of fault zones and confining layers.
- Potential boundary conditions (given water elevation of lakes, ponds, sea-shores, or other Dirichlet boundaries), varying surface infiltration, and pumping stress at given locations or in given subregions can be handled easily.

APPENDIX C

GETOUT CONVERSION STATUS

APPENDIX C

GETOUT CONVERSION STATUS

BASIC FORMULATION

In the WISAP suite of models, GETOUT is the level-one transport model. It is used in situations where a minimum of data is available, or when a rough estimate of radiological hazards is required. GETOUT is a one-dimensional analytical solution to the general transport equation for up to three-member radionuclide decay chains.

$$K_1 \frac{\partial N_1}{\partial t} = D \frac{\partial^2 N_1}{\partial z^2} - V \frac{\partial N_1}{\partial z} - K_1 \lambda_1 N_1 \quad (C.1)$$

$$K_2 \frac{\partial N_2}{\partial t} = D \frac{\partial^2 N_2}{\partial z^2} - V \frac{\partial N_2}{\partial z} - K_2 \lambda_2 N_2 + K_1 \lambda_1 N_1 \quad (C.2)$$

$$K_3 \frac{\partial N_3}{\partial t} = D \frac{\partial^2 N_3}{\partial z^2} - V \frac{\partial N_3}{\partial z} - K_3 \lambda_3 N_3 + K_2 \lambda_2 N_2 \quad (C.3)$$

where

N = mass rate per unit time (M/T)

K = retardation coefficient ($= 1 + \beta K_d$)

D = longitudinal dispersion coefficient (L^2/T)

V = groundwater flow velocity (L/T)

λ = radionuclide decay constant (T^{-1})

β = soil to solution ratio (M/L^3) ($= B_D/\eta$)

K_d = distribution coefficient (L^3/m)

B_D = bulk density (M/L^3)

η = porosity

x = distance coordinate

t = time.

GETOUT accounts for:

- dispersion
- simple first-order decay
- three-member radionuclide decay chains
- convection
- retardation described by a linear sorption isotherm that assumes:
 - one-dimensional incompressible flow
 - longitudinal dispersion described by Fick's first law
 - transport of the components of interest are not affected by other constituents in solution
 - an isothermal system
 - insignificant molecular diffusion
 - homogeneous porous media
 - constant velocity and dispersion
 - a linear sorption isotherm description of all retardation phenomena
 - system is always at equilibrium
 - instantaneous sorption, i.e.:

$$\frac{dA}{dt} = K_d \frac{dC}{dt} \text{ where } A \text{ is the soil concentration and } C \text{ is the solution concentration and } K_d \text{ is the distribution coefficient}$$

Since GETOUT is an analytical solution, computer run times are very short, and as the assumptions in it show, GETOUT is limited to cases with idealized boundary conditions, aquifer conditions, and chemical interactions.

Equations C.1 through C.3 are solved for the initial and boundary conditions found in Table C.1. The shapes of the input boundary conditions that GETOUT can use are found in Figure C.1. They are impulse and decaying steps. The decaying band solution is achieved by superposition of two decaying step solutions. (The equations used for conversion to the UNIVAC 1100/44 are direct solutions for decaying band input boundary conditions.)

TABLE C.1. Boundary Conditions for Solution of Equations

Release Type	Initial t=0, all z	INLET		Outlet t>0, z=ω
		t>0, z=0	t=T, z=0	
Impulse	$N_1 = 0$	$N_1 = N_1^0 \delta(t)$		$N_1 = \text{finite}$
	$N_2 = 0$	$N_2 = N_2^0 \delta(t)$		$N_2 = \text{finite}$
	$N_i = 0$	$N_i = N_i^0 \delta(t)$		$N_i = \text{finite}$
Decaying Step	$N_1 = 0$	$N_1 = \frac{N_1^0}{T} e^{-\lambda_1 t}$	$N_1 = 0$	
	$N_2 = 0$	$N_2 = \frac{N_2^0}{T} e^{-\lambda_2 t} + \frac{\lambda_1}{\lambda_2 - \lambda_1} \frac{N_1^0}{T} (e^{-\lambda_1 t} + e^{-\lambda_2 t})$	$N_2 = 0$	$N_2 = \text{finite}$
	$N_i = 0$	$N_i = \lambda_1 \lambda_2 \cdots \lambda_{i-1} \frac{N_i^0}{T} \sum_{j=1}^i \frac{e^{-\lambda_j t}}{R_{\neq j} (\lambda_k - \lambda_j)}$ $+ \lambda_2 \lambda_3 \cdots \lambda_{i-1} \frac{N_2^0}{T} \sum_{j=2}^i \frac{e^{-\lambda_j t}}{R_{\neq j} (\lambda_k - \lambda_j)}$ $+ \frac{N_1^0}{T} e^{-\lambda_i t}$	$N_i = 0$	$N_i = \text{finite}$

FIGURE C.1. Example Input Functions for the GETOUT Transport Model

CONVERSION TO UNIVAC 1100/44 COMPUTER

Initial efforts in FY-1978 were expended to convert the equations found in BNWL-SA-5079 (Lester et al. 1974). The results obtained in BNWL-1927 (Burkholder et al. 1975) were compared with the results of the new ASCII FORTRAN code. The results did not agree. Then the BASIC version was tested with the same case and was found to agree with the new FORTRAN program. This was because a few terms had been set to zero. However, no justification was ever found for setting them to zero. Therefore, no previous result could be used to compare the accuracy of the FORTRAN code.

In mid FY-1978, changes were suggested in the equations. These changes were made because it was not clear whether the superposition of two decaying step release input solutions could be obtained from the result of the decaying band input. The new equations were derived directly from boundary conditions for a decaying band.

After incorporating these changes and testing, the equations were found to be incorrect. The program was modified to correct the errors. However, problems still exist in the digital implementation of the equations. Table C.2 shows the cases for which this version of GETOUT works.

TABLE C.2. Matrix of Workable Cases for GETOUT,
UNIVAC 1100/44

<u>Number of Chain Members</u>	<u>RELEASE FUNCTIONS</u>			
	<u>Pulse</u>		<u>Band</u>	
	<u>With Dispersion</u>	<u>Without Dispersion</u>	<u>With Dispersion</u>	<u>Without Dispersion</u>
1	X	X	X	X
2	X	X	X	*
3	X	X	*	*

X indicates GETOUT works for this case.

* indicates GETOUT does not work for this case.

CONVERSION TO DEC PDP-11/45 COMPUTER

This effort attempted to convert GETOUT to FORTRAN using the equations found in BNWL-SA-5079 (Lester et al. 1974). This task was completed. However, problems still exist in the digital implementation of these equations.

To determine whether the model worked correctly, results obtained by this version were compared with results found in BNWL-1927. The results obtained by the new version did not agree with results published in BNWL-1927 for three-member chains. This is because many exponential terms need to be evaluated in the analytical solutions; these terms are in the range of 50,000. On the PDP-11/45, the largest exponent that can be evaluated is approximately 90.

The approach taken by Burkholder et al. (1975) was to eliminate any terms that overflow. This approach appears to be acceptable for single nuclides and two-member decay chains. However, in the case of three-member decay chains, this results in eliminating about 80 percent of the terms in the equation.

Another possibility that may account for the disparity between results is superposition of decaying release solutions to obtain a solution for a decaying band input function. In some instances very large numbers must be subtracted to obtain small numbers. The result is usually random noise.

Because of the problems encountered in conversion, there appears to be justification for using the new equations developed by Burkholder, since no superposition is required. These new equations eliminate some of the numerical problems of subtracting large numbers in the process of superposition.

Digital implementation of the analytical solutions that are obtained for the transport equation with decay chains is not straightforward. One problem is obtaining an accurate approximation of the complimentary error function.

APPENDIX D

MULTICOMPONENT MASS TRANSPORT (MMT) MODEL DEVELOPMENT

APPENDIX D

MULTICOMPONENT MASS TRANSPORT MODEL DEVELOPMENT

The Multi-component Mass Transport (MMT) model solves the general transport equation for porous media by direct simulation of the phenomena that affect migration of radionuclides. The MMT is the second- and third-level model in the WISAP scheme.

The direct simulation approach, or DPRW method (Discrete Parcel Random Walk), uses an ensemble of parcels to model the convection and dispersion phenomena in mass transport. A parcel represents a discrete amount of mass of a contaminant, and many parcels (10^3 - 10^4) are used to represent the total amount of contaminant present in the region of interest.

The velocity field that is used for a simulation is divided into sets of discrete nodes that is similar to a finite difference grid. The concentrations are also separated in the same manner and are calculated by summing the masses of all parcels of a given species within one node. Also, aquifer thickness (in one- or two-dimensional simulations), porosity, and distribution coefficients (K_d) are assigned nodes on the same finite difference grid.

Direct simulation of convection of a parcel is carried out first by determining the groundwater velocity at the parcel location. Then that velocity is multiplied by the time step to obtain the distance the parcel will travel during a time step because of bulk fluid movement:

$$\Delta x = V\Delta t$$

where:

Δx = distance a parcel travels during Δt because of convection

V = velocity at the initial parcel location

Δt = time step.

A dispersive component is then calculated.

A dispersive transport component is calculated for each parcel by assuming that the ensemble of parcels is subject to Brownian-like random motion resulting from the tortuous path that the host fluid takes through a complex medium such as soil. Equation D.1 shows root mean square (rms) distance moved by the ensemble of parcels with respect to the advective flow of the system for a given time step, Δt , in a homogeneous one-dimensional system:

$$d_{rms} = \sqrt{2D\Delta t} \quad (D.1)$$

The direction of motion of each parcel is assumed to be random. The current version of the model allows two options for determining the dispersion coefficient D . It can be input directly and used as a constant, or it can be calculated by:

$$D = a|\bar{v}|$$

where "a" is a characteristic length parameter that is read in. "D" and "a" are the same variables used in the dispersion discussion with the subscripts omitted.

In three-dimensional porous media systems, the rate of dispersion has generally been observed to be higher in the direction of flow than in the direction lateral to the flow (Bear 1972, Dejong 1958). The rms step size coincident with the flow is expressed as:

$$d_{L,rms} = \sqrt{2D_L\Delta t} \quad (D.2)$$

and in both transverse directions as:

$$d_{T,rms} = \sqrt{2D_T\Delta t} \quad (D.3)$$

If an ensemble of particles initially concentrated at a point is allowed to disperse in this type of environment for a time, t , an ellipsoid-shaped cloud, such as that illustrated in Figure D.1, will be formed. The major semi-axis

FIGURE D.1. Sample Parcel Trajectory During Time Step n

of the ellipsoid will be coincident with the direction of flow and the rms value of the parcel displacements in this direction are given in Equation D.2.

The other two semi-axes of the ellipsoid are perpendicular to the flow. The rms parcel displacement in the transverse directions is specified by Equation D.3. This spreading process is numerically simulated in the DPRW algorithm as follows.

A second set of right-hand coordinate axes (X' , Y' , Z') is defined having its origin at (x_p^*, y_p^*, z_p^*) with the positive X' -axis oriented in the direction of the velocity vector, v . The transformation to the new coordinate system can be made by rotating the base coordinate system (X, Y, Z) through a horizontal angle and vertical angle, and then translating the origin.

A dispersive step length for a parcel is generated by selecting a value from a distribution of step lengths having the proper rms value (Equations D.2 and D.3) and a zero arithmetic mean. The exact shape of the chosen distribution is not critical; however, some types of distributions are much more convenient and economical to generate than others. Regardless of the shape of the distribution, if it has a zero mean and the proper rms value after a few time steps, the shape of a diffusing cloud of parcels will be statistically equivalent. This is a result of the central limit theorem, which states that the distribution of the sums of a series of sets of random samples from any arbitrary probability distribution will always approach a normal distribution (Hantush 1960).

For convenience, the MMT-DPRW code uses a uniform probability distribution from which to select dispersive step sizes. The generation of a dispersive step in the x' -direction can then be expressed by:

$$x'_p = [R] \begin{matrix} +\zeta_L \\ -\zeta_L \end{matrix} \quad (D.4)$$

where

$[R] \begin{matrix} +\zeta_L \\ -\zeta_L \end{matrix}$ indicates a random number from a population that is uniformly distributed in the range $-\zeta_L$ to $+\zeta_L$, with ζ_L selected so that the constraint $x'_{rms} = d_{L,rms}$ is satisfied.

To determine ζ_L , the rms value of parcel step sizes in this range must be calculated. The mean of the square of the step size is given by:

$$x'_{rms} = \sqrt{\int_{-\zeta_L}^{+\zeta_L} P(x) x^2 dx} \quad (D.5)$$

where $P(x)$ is a probability distribution function. For a uniform distribution in the interval $(-\zeta_L, +\zeta_L)$:

$$P(x) = \frac{1}{2\zeta_L} \quad (D.6)$$

Evaluating the integral in Equation D.5 and taking the square root yields:

$$x'_{rms} = \frac{L}{\sqrt{3}}$$

Equating this expression to the required dispersive step length, $d_{L,rms}$, given in Equation D.1, yields:

$$L = \sqrt{6D_L\Delta t} \quad (D.7)$$

which allows Equation D.4 to be rewritten as:

$$x'_p = \begin{bmatrix} R \end{bmatrix} \begin{matrix} +\sqrt{6D_L\Delta t} \\ -\sqrt{6D_L\Delta t} \end{matrix} \quad (D.8)$$

The random number generator routines available on most computer systems commonly return values uniformly distributed in the range 0,1. Adapting Equation D.8 to use this type of random number generator gives:

$$x'_p = \sqrt{24D_L\Delta t} \begin{pmatrix} .5 - [R]_0^1 \end{pmatrix} \quad (D.9)$$

Similarly, it can be shown that in the lateral directions:

$$y'_p = \sqrt{24D_T\Delta t} \begin{pmatrix} .5 - [R]_0^1 \end{pmatrix} \quad (D.10)$$

$$z'_p = \sqrt{24D_T\Delta t} \begin{pmatrix} .5 - [R]_0^1 \end{pmatrix} \quad (D.11)$$

The only remaining computation in the dispersive portion of the code involves transforming the current parcel location from the (X', Y', Z') coordinate system to the base system (X, Y, Z):

$$x_p^{k, n+1} = x_p^* + x_p' \cos \theta \cos \phi - y_p' \sin \theta - z_p' \sin \theta \cos \phi \quad (D.12)$$

$$y_p^{k, n+1} = y_p^* + x_p' \cos \theta \sin \phi - y_p' \cos \theta - z_p' \sin \theta \sin \phi \quad (D.13)$$

$$z_p^{k, n+1} = z_p^* + x_p' \sin \theta + z_p' \cos \theta \quad (D.14)$$

APPENDIX E

DESCRIPTION OF LEACH RATE MODEL

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DESCRIPTION OF LEACH RATE MODEL

A leach rate model was developed to determine the length of time and the rate at which the contaminants would be carried, via the aquifer water, through the fractured salt and repository and into the upper aquifer system. The leach rate model was formulated using preliminary data on waste leach rates and the observed effects of flow rate and temperature on leach rate. The data from leaching experiments on crushed spent fuel (3 cm^2 of surface area/gram of fuel with a density of 10.2 g/cm^3) and high-level waste glass indicate that the specific leach rates (g-leached/cm^2 of surface area/day) vary from nuclide to nuclide as shown in Table E.1. The data also indicate that for rates greater than one flush per year the specific leach rate is a function of the flushing rate. At less than one flush per year, the rates are essentially constant.

The data currently available on temperature effects indicate that specific leach rate versus temperature follows an Arrhenius-type relationship. Data currently available at $T = 25^\circ\text{C}$ and $T = 250^\circ\text{C}$ allow us to determine the constants in this relationship. Leach rate data comparisons between solid and crushed high-level wastes indicate that although leach rate depends on actual surface area, the rate is not directly proportional to the surface area because the internal surface area within the mass of crushed waste leaches more slowly than the outer surface area. This is because of the interference between the boundary layer concentration gradients between adjacent waste particles.

For this initial leach rate model the highest specific leach rate was used for all nuclides. This entire fuel rod or glass waste, including all drummed wastes, was assumed to leach at this rate. The fuel or glass was assumed to be crushed, and the crushed fuel or glass particles were modeled as spheres. Leach rate at any time t was calculated as follows:

$$LR \text{ (g/day)} = SLR(T) \times SA(t) \times WSP \quad (E.1)$$

where

t = time (days)

$SLR(T)$ = specific leach rate (g/cm^2 of surface area/day) and is dependent on the temperature T

WSP = mass of one of the spherical fuel or glass particles (g)

T = temperature of the fuel or glass at any time t in $^{\circ}\text{C}$

$SA(t)$ = surface area-to-mass ratio for a spherical waste particle (cm^2/g).

TABLE E.1. Preliminary Specific Leach Rate Values(a)

Isotope	Crushed Spent Fuel at 25°C, 3 cm ² /g, Weekly Flushing	Crushed Spent Fuel at 250°C, 3 cm ² /g, <One Flush/Year	Crushed Spent Fuel at 25°C, 3 cm ² /g, <One Flush/Year	Solid High- Level Particles Waste <One Flush/Year	Crushed High- Level Waste (42-60 mesh) <One Flush/Year
Cs	5×10^{-6}	5×10^{-6}	5×10^{-8}	4×10^{-7}	4×10^{-9}
Pu	5×10^{-6}	5×10^{-6}	5×10^{-8}		
Sb	2×10^{-6}				
Eu	1×10^{-6}				
Cu	1×10^{-6}				
Ce	3×10^{-7}				
U	8×10^{-8}				
I	1×10^{-6}				
Tc	5×10^{-6}				

a. Rates are in g-leached/ cm^2 of surface area/day.

The temperature of the fuel or glass is assumed to be proportional to the heat generation rate of the fuel or glass, and the heat generation rate is determined from a power function fit of the table of heat generation rate (HGR) for spent fuels. Equation E.2 shows the power function used,

$$HGR(t) = 7468 t^{-0.723}, \quad (E.2)$$

and Table E.2 compares published and fitted heat generation rates. The temperature is calculated by assuming that at $t = 10$ years, the crushed fuel in the breached canister and cladding will be at the design canister temperature, and at 1,000,000 years the fuel will be at a background or ambient temperature of 50°C. Temperature at any time is calculated by Equation E.3:

$$T(t) = 50 + \frac{(375 - 50)}{(1414 - 0.34)} \times (7468 t^{-0.723} - 0.34) \quad (E.3)$$

TABLE E.2. Comparison Between Fitted and Published Heat Generation Rate and Model Predicted Temperature

<u>Time, yr</u>	<u>Published HGR(a)</u>	<u>Fitted HGR(a)</u>	<u>Modeled Temperature, °C</u>
10	1,200	1,413	375
100	290	268	112
1,000	55	51	62
10,000	14	9.6	52
100,000	1.1	1.8	50.4
1,000,000	.39	.34	40.4

(a) W/MTHM

SLR(T) is assumed to follow an Arrhenius relationship which states that $\ln(\text{SLR}[T])$ is proportional to the inverse of the absolute temperature. Now, since we have measured values for the fuel leach rate at 25°C and 250°C, we can determine the constants C1 and C2 in this relationship:

$$\ln(\text{SLR}[T]) = \ln(\text{SLR}[T_a]) - (C2 \left[\frac{T_a + 273}{T + 273} \right] + C1) \quad (E.4)$$

where

T_a = ambient temperature, °C.

Since we are dealing with crushed spent fuel ($3 \text{ cm}^2/\text{g}$ and density 10.2 g/cm^3) or broken glass, and our flushing rate is less than one flush/year, we have that $\text{SLR}(T_a) = \text{SLR}(25^\circ\text{C}) = 5 \times 10^{-8}$ and $\text{SLR}(250^\circ\text{C}) = 5 \times 10^{-6}$, then $C_1 = -10.72$ and $C_2 = 10.72$ and our resulting equation for $\text{SLR}(T)$ is given by Equation E.5:

$$\text{SLR}(T) = \text{SLR}_0 \times \exp(-[10.72 \left[\frac{T_a + 273}{T + 273} \right] - 10.72]) \quad (\text{E.5})$$

where

$$\begin{aligned} \text{SLR}_0 &= 5 \times 10^{-8} \\ T_a &= 25^\circ\text{C} \end{aligned}$$

The specific surface area of the fuel or glass (SA) assuming a spherical model is given by Equation E.6:

$$\text{SA}(t) = \frac{3}{R(t) \times D} \quad (\text{E.6})$$

where

$$\begin{aligned} R(t) &= \text{radius of a spherical particle} \\ D &= \text{density of fuel or glass.} \end{aligned}$$

The weight of a spherical particle of fuel or glass at any time t is given by Equation E.7:

$$\text{WSP} = \frac{4}{3} \pi R(t)^3 \times D \quad (\text{E.7})$$

The leach rate model uses the above equations to calculate the fraction of the waste remaining in the repository at any time t by a simple rectangular integration scheme that determines the current radius of the fuel or glass particles. At the time t_0 when the leaching begins, the fuel or glass is assumed to be composed of equal-sized spherical particles. The values for T , SA , SLR , and WSP are calculated for time t_0 to determine the current rate, LR , at which fuel or glass is being leached from the surface of each spherical

particle. This rate is assumed to hold for some time Δt , thus dissolving some weight of fuel or glass from the particle, $WD = LR \times \Delta t$. From this leached weight the decrease in radius, DR , of the fuel particle is then calculated from Equation E.8:

$$DR(t) = R(t) - \sqrt[3]{R(t)^3 - \left[\frac{WD(T)}{D \times 4/3 \times \pi} \right]} \quad (E.8)$$

$R(t_0 + \Delta t)$ is now $R(t_0) - DR(t_0)$ and the process is repeated until $R(t)/R(t_0)$ is < 0.1 , at which time all the fuel is assumed to be dissolved.

Figure E.1 and E.2 illustrate the leach functions used in this study. Table E.3 shows the density, ambient temperature leach rate, initial surface area per gram, and particle radius used by the leach model to generate the leach functions for reactor Strategy 1 (spent fuel) and Strategy 2 (HLW glass).

One problem in performing these tasks was the inefficient means of obtaining data such as half-lives, distribution coefficients (K_d), source inventory, and waste form leach rates. Because of this problem, design of a computer data base that contains this information was started. This data base will allow a much simpler, faster means of obtaining radionuclide specific data for future studies.

TABLE E.3. Parameters Used by the Leach Model to Generate the Leach Rate Functions Shown in Figures E.1 and E.2 for Reactor Strategies 1 and 2, Respectively

	Density, g/cm	Specific Leach Rate, g/cm /day at 25°C	Initial Surface Area per gram, cm /g	Initial Spherical Particle Radius, cm
Reactor Strategy 1	10.2	5.E-8	3.0	0.098
Reactor Strategy 2	3.3	4.E-7	0.424	2.14

FIGURE E.1. Release Rate Curve for Reactor Strategy 1

The data base will contain data from:

- batch, static, shaking, or jar tests
- low pressure column tests
- axial filtration
- intact core tests.

These data will include:

- K_d values
- E_h values
- pH values
- nuclide atomic weights, half-lives, and maximum permissible concentrations
- geologic materials
- other groundwater properties.

FIGURE E.2. Release Rate Curve for Reactor Strategy 2

From these data it will be necessary to determine:

- the geologic media for which K_d values exist in the data base
- the geochemical conditions that exist for these K_d values
- the geologic media and geochemical conditions for which K_d has been measured for a particular nuclide
- the isotopes remaining after a given length of time for a given radionuclide inventory table.

This data base will allow for systematic prediction of distribution coefficients for geochemical conditions for which no K_d are available. The present method relies heavily on experienced intuition. A similar data base will exist for waste-form leaching studies.

Both the Paradox Basin study and other exercises conducted during FY-1978 resulted in refinement of the transport model and the data input methods. The studies provided impetus for systematizing waste form transport parameter prediction and release rates. Further model and modeling system refinement will occur as more is learned about the mechanisms that affect waste-media interactions, leaching of radionuclides from waste forms, and dispersion phenomena.

APPENDIX F

DOSE MODELS AND CODES SELECTED

APPENDIX F

DOSE MODELS AND CODES SELECTED

ARRRG

The computer program ARRRG can be used to compute radiation doses and dose commitments from aquatic pathways. The mathematical models for ARRRG were derived from the comprehensive models developed for the Year 2000 Study, sponsored by the AEC (Soldat 1971, Soldat and Herr 1971). For ARRRG, a few simplifying assumptions that are based on experience in the Columbia River at Hanford were made for the calculation of accumulation of radionuclides in shoreline deposits. This reduces the running time of the resultant codes compared to the HERMES version. The shoreline model is discussed by Brenchley et al. (1977). The remainder of the water pathway code remains essentially the same as the original HERMES code. The ARRRG code was written in Computer Sciences Corporation BASIC interactive language to facilitate rapid turn-around time with the then existing UNIVAC 1108 computer at Hanford.

The fundamental equation for calculating radiation dose rate from the aquatic pathways listed in Table F.1 is:

$$R_{ipr} = C_{ip} U_p D_{ipr} \quad (F.1)$$

where

R_{ipr} = the dose rate to organ r from nuclide i via pathway p

C_{ip} = the concentration of nuclide i in the medium of pathway p

U_p = the usage: the exposure or intake rate associated with pathway p

D_{ipr} = the dose rate factor: a number specific to a given nuclide i, pathway p, and organ r which can be used to calculate radiation dose rate from exposure to a given radionuclide concentration or a radionuclide intake.

Equation F.1 can also be used to calculate a dose commitment, rather than a dose rate by using a dose commitment factor in place of a dose rate factor. A dose commitment factor is defined as the dose delivered to an organ over 50 years per unit intake of a nuclide during the first year, including the dose delivered the year of intake.

Equations tailored to each specific exposure pathway are derived from this equation. The principal difference between pathways is the manner in which the radionuclide concentrations are calculated. The three terms on the right of the equation are discussed in the following subsections.

Concentration of Nuclides in Environmental Media, C_{ip}

Concentrations of nuclides in water, in aquatic foods, and on shoreline sediment are calculated from the radionuclide release rates, the effluent flow rate, the mixing and dilution in the receiving waters, and bioaccumulation factors for aquatic foods.

Concentration of nuclides in irrigated farm produce are calculated from radionuclide concentrations in the irrigation water, the irrigation rate, length of time water is contaminated (which determines long-term soil buildup), and decay time between nuclide release and produce consumption.

Usage, U_p

Usage refers to duration of exposure to external sources of radiation and to intake rates of ingested water and food. The usage depends on the specific situation. In the absence of site-specific data, average usages and exposure times can be used to calculate individual adult doses (Soldat et al. 1974, USNRC 1977). For calculating population dose the usages of the average adult are multiplied by the size of the population.

Dose Factors, D_{ipr}

Equations for calculating internal dose rate factors as defined in Equation F.1 have been published (Soldat 1971). They were derived originally from those given by the International Commission on Radiological Protection (ICRP 1959) for body burden and maximum permissible concentration. For this study, effective decay energies for the radionuclides are calculated from the

ICRP model, which assumes that all of the radionuclide is at the center of a spherical organ with an appropriate effective radius.

For calculating external dose rate factors from air submersion or water immersion, the penetrating power of the radiation emitted determines whether it contributes to skin dose only, or to both skin and total body dose. Beta and gamma radiation are considered to contribute to total body dose (and dose to internal organs). The dose rate factors for air submersion and water immersion are derived by assuming that the contaminated medium is an infinite volume compared to the range of the emitted radiations. Under this assumption the energy emitted per gram of medium equals the energy absorbed per gram of medium. Corrections must be applied for differences in energy absorption between tissue and air or water, physical geometry of the specific exposure situation and the conversion from MeV per disintegration per gram to rem. The resulting dose rate factors have units of mrem/hr per pCi/m³ of air or mrem/hr per pCi/l of water.

Material deposited from irrigation water onto the ground represents a fairly large, nearly uniform, thin sheet of contamination. The factors for converting surface contamination in pCi/m² to gamma dose at 1 m above a uniformly contaminated plane are described by Soldat; Soldat and Harr; and Soldat, Robinson, and Baker (1971, 1971, and 1974, respectively). Dose rate factors for exposure to soil (or river sediment) have units of mrem/hr per pCi/m² of surface. The mathematical model for the computer program ARRRG is described below.

Drinking Water

The dose rate from ingestion of water is calculated by

$$R_{pr} = 1119 \sum_{i=1}^n \frac{Q_i N_i}{F} M_p U_p D_{ipr} \exp(-\lambda_i t_p) \quad (F.2)$$

where

R_{pr} = dose rate to organ r from all of the nuclides i via pathway p
(mrem/yr)

Q_i = release rate of nuclide i (Ci/yr)

N_i = reconcentration factor

F = flow rate of the liquid effluent (ft^3/sec)

M_p = the mixing ratio at the point of exposure (or the point of withdrawal of drinking water or the point of harvest of aquatic food)

λ_i = the radiological decay constant of nuclide i (hr^{-1})

t_p = the transmit time required for nuclides to reach the point of exposure for internal dose, t_p is the total time elapsed between release of the nuclides and ingestion of food and water (hr)

1119 = a constant which converts $(\text{Ci}/\text{yr})/(\text{ft}^3/\text{sec})$ to pCi/l .

The term $Q_i N_i / F$ in Equation F.2 defines the concentration of nuclide i in the effluent at the point of discharge. The expression $(Q_i N_i / F) M_p \exp(-\lambda_i t_p)$ yields the concentration at the time that the water is consumed. This latter concentration is the term C_{ip} in Equation F.1.

Aquatic Foods

Concentrations of radionuclides in aquatic foods are directly related to the concentrations of the nuclides in water. Equilibrium ratios between the two concentrations, called bioaccumulation factors, were reported by Thompson et al. and Freke (1972 and 1965) and are listed in Table F.1. The equation to calculate internal dose rate from consumption of aquatic food is:

$$R_{pr} = 1119 \sum_{i=1}^n \frac{Q_i N_i}{F} M_p B_{ip} U_p D_{ipr} \exp(-\lambda_i t_p) \quad (\text{F.3})$$

where B_{ip} is the bioaccumulation factor for nuclide i via pathway p (pCi/kg per pCi/l).

Shoreline Deposits

A simplified scheme for obtaining an order of magnitude estimate of the concentration of shoreline sediments was developed for the program ARRRG. The concentration of nuclide i in the sediment can be estimated from:

$$S_i = \frac{KA_i}{\lambda_i} [1 - \exp(-\lambda_i t_s)] \quad (F.4)$$

where

S_i = the concentration of nuclide i in sediment (pCi/kg)

K = the assumed constant in units of l/kg-day

A_i = the concentration of the nuclide i in the water adjacent to sediment (pCi/l)

t_s = the total time the sediment is exposed to the contaminated water, nominally taken to be the operating lifetime of the facility (hr).

In the original evaluation of the equation, λ_i was chosen to be the radiological decay constant, although the true value should include an unknown "environmental" removal constant. If the presence of a radionuclide in water and sediment is controlled primarily by radioactive equilibrium with its parent nuclide, then the water concentration and half-life of the parent should be used in the equation.

The relationship was tested and the value of K derived from radionuclide concentrations measured in water and sediment samples collected over a period of several years in the Columbia River between Richland, Washington and the river mouth (Nelson 1965, Toombs and Cutter 1968). Since the primary use of the equation is to facilitate estimates of the exposure rate from gamma emitters 1 m above the sediment, an effective surface contamination was devised. This surface contamination level was taken to be all of the nuclides contained within the top 2.5 cm (1 in.) of sediment.* The dose contribution from the radionuclides below 2.5 cm in depth was ignored. The resulting equation is:

$$S'_i = 100 T_i A_i W [1 - \exp(-\lambda_i t_s)] \quad (F.5)$$

* Calculated by multiplying the concentration (pCi/kg) by a mass thickness (40 kg/m²)

TABLE F.1. Bioaccumulation Factors (pCi/Kg per pCi/l)

Element	Salt Water Factors				Fresh Water Factors			
	Fish	Crus.	Moll.	Algae	Fish	Crus.	Moll.	Algae
H	1	1	1	1	0.9	0.9	0.9	0.9
Be	1,000	10,000	10,000	10,000	2	10	10	20
C	1	1	1	1	4,600	9,100	9,100	4,600
N(a)	0	0	0	0	0	0	0	0
F	4	4	4	1	10	100	100	2
Na	1	1	1	1	100	200	200	500
P	10,000	10,000	10,000	100,000	100,000	20,000	20,000	500,000
Ar	1	1	1	1	1	1	1	1
Ca	10	10	10	1	40	330	330	130
Sc	100	300	300	1,000	2	1,000	1,000	10,000
Cr	100	1,000	1,000	1,000	20	2,000	2,000	4,000
Mn	3,000	10,000	50,000	10,000	400	90,000	90,000	10,000
Fe	1,000	4,000	20,000	6,000	100	3,200	3,200	1,000
Co	100	10,000	300	100	50	200	200	200
Ni	500	100	100	100	100	100	100	50
Cu	1,000	5,000	5,000	1,000	50	400	400	2,000
Zn	5,000	5,000	50,000	1,000	2,000	10,000	10,000	20,000
Se	10	10	10	100	170	170	170	1,000
Br	3	10	10	100	420	330	330	50
Kr	1	1	1	1	1	1	1	1
Rb	30	50	10	10	2,000	1,000	1,000	1,000
Sr	1	1	1	20	30	100	100	500
Y	30	100	100	300	25	1,000	1,000	5,000
Zr	30	100	100	1,000	3	6	6	1,000
Nb	100	200	200	100	30,000	100	100	800
Mo	10	100	100	100	10	10	10	1,000
Tc	10	100	100	1,000	15	5	5	40
Ru	3	100	100	1,000	10	300	300	2,000
Rh	10	100	100	100	10	300	300	200
Pd	10	100	100	100	10	300	300	200
Ag	1,000	5,000	5,000	1,000	2	770	770	200
Cd	100	3,000	10,000	10,000	200	2,000	2,000	1,000
Sn	3	3	3	10	3,000	1,000	1,000	100
Sb	1,000	1,000	1,000	10,000	1	10	10	1,500
Te	10	10	100	1,000	400	75	75	100
I	20	100	100	10,000	15	5	5	40
Xe	1	1	1	1	1	1	1	1
Cs	30	50	10	10	2,000	100	100	500
Ba	3	3	3	100	4	200	200	500
La	30	100	100	300	25	1,000	1,000	5,000
Ce	30	100	100	300	1	1,000	1,000	4,000
Pr	100	1,000	1,000	1,000	25	1,000	1,000	5,000
Nd	100	1,000	1,000	1,000	25	1,000	1,000	5,000
Pm	100	1,000	1,000	1,000	25	1,000	1,000	5,000
Sm	100	1,000	1,000	1,000	25	1,000	1,000	5,000
Eu	100	1,000	1,000	1,000	25	1,000	1,000	5,000
Tb	100	1,000	1,000	1,000	25	1,000	1,000	5,000
Ho	100	1,000	1,000	1,000	25	1,000	1,000	5,000
W	10	10	10	100	1,200	10	10	1,200
Pb	300	1,000	1,000	5,000	100	100	100	200
Bi	15	1,000	1,000	10,000	15	10	10	1,500
Bo	300	5,000	5,000	2,000	500	20,000	20,000	2,000
Rn	1	1	1	1	57	1	1	1
Ra	50	100	100	100	50	250	250	2,500
Ac	25	1,000	1,000	5,000	25	1,000	1,000	5,000
Th	10,000	2,000	2,000	3,000	30	500	500	1,500
Pa	10	10	10	6	11	110	110	1,100
U	10	10	10	67	2	60	60	
Np	10	10	10	6	10	400	400	300
Pu	3	200	200	1,000	3	100	100	350
Am	25	1,000	1,000	5,000	25	1,000	1,000	5,000
Cm	25	1,000	1,000	5,000	25	1,000	1,000	5,000
Cf	25	1,000	1,000	5,000	25	1,000	1,000	5,000

(a) The values for nitrogen (0) were selected because N-13 has a half life of only 9.6 min.

where

S_i = "effective" surface contamination (pCi/m^2)

T_i = radiological half-life of nuclide i (days)

W = shore width factor (unitless).

Shore width factors were derived from data given in the Handbook of Radiological Protection, Part I (Dunster 1971), and are summarized in Table F.2.

TABLE F.2. Shore Width Factors Used in Equations F.5 and F.6

<u>Exposure Situation</u>	<u>Shore Width Factor, W</u>
Discharge canal bank	0.1
River shoreline	0.2
Lake shore	1.3
Nominal ocean site	0.5
Tidal basin	1.0
Organisms on surface or in burrow(a)	2.0

(a) Since the radionuclide concentration normally decreases with depth in the mud, the dose to a buried organism is probably no higher than that to one lying on the mud surface.

During FY-1978, the ARRRG code was rewritten into FORTRAN for the newer UNIVAC 1100/44 computer now operating at Hanford (the FORTRAN version will be documented in FY-1979). A change was made in the way in which the internal radiation dose calculations were performed: the BASIC version of ARRRG included tables of dose conversion factors that could be multiplied by the annual intakes calculated by ARRRG to yield either first-year dose or 50-year dose commitment. The FORTRAN version includes, instead, the basic equations by which the dose conversion factors were originally calculated and data libraries of the parameters required to solve these equations. Thus, the newer version calculates each dose (or dose commitment) directly for each nuclide pathway combination. This newer method of dose calculation is patterned after that used previously in the DACRIN code (Houston, Streng, and

Watson 1975). Although the computer running time is increased slightly, the resulting code is more flexible, because the time periods over which the radionuclide intake occurs and over which the dose is calculated can both be varied within reasonable limits.

The external doses from water and shoreline are still calculated using dose factors that convert concentrations in environmental media to dose rates to skin and total body.

The set of data libraries now used by ARRRG (and FOOD) is summarized in Table F.3.

TABLE F.3. Data Libraries Used by the ARRRG and FOOD Codes

<u>Library</u>	<u>Contents</u>
RMDLIB	Radionuclide Master Data: decay schemes, radiological half-lives
ORGLIB	Organ Data: organ mass, nuclide specific data on biological half-life, effective decay energy, uptake and retention
FTRANSLIB	Food Transfer Factors: uptake of individual nuclides by plants from soils, translocation of nuclides within plants following aerial deposition onto plants
GRDLIB	External Dose Conversion Factors: ground, shoreline, and swimming
BIOAC1	Bioaccumulation Factors: concentration ratio for nuclides in aquatic biota, water plant removal efficiencies for nuclides in drinking water sources

The combination of Equation F.2 and F.5 yields the following equation for calculating the radiation dose rate from exposure to shoreline sediments:

$$\begin{aligned}
 R_{pr} &= \sum_{i=1}^n S_i' U_p D_{ipr} = 100 \sum_{i=1}^n T_i A_i W U_p D_{ipr} 1 - \exp(-\lambda_i t_s) \\
 &= 111,900 \sum_{i=1}^n T_i \frac{Q_i N_i}{F} M_p \exp(-\lambda_i t_p) W U_p D_{ipr} 1 - \exp(-\lambda_i t_s)
 \end{aligned}$$

Swimming and Boating

The equation for external dose rate to the skin and total body from swimming (water immersion) or boating (water surface) is:

$$R_{pr} = 1119 \sum_{i=1}^n \frac{Q_i N_i}{F} M_p U_p D_{ipr} \exp(-\lambda_i t_p) \quad (F.7)$$

where K_p is a geometry correction factor equal to 1 for swimming and 2 for boating.

FOOD

The computer program FOOD (Baker, Hoenes, and Soldat 1976, Baker 1977) can be used to calculate radiation doses and dose commitments from external exposure to contaminated soil and from ingestion of farm products. Radionuclide contamination of foods may be either via deposition with water used for sprinkler irrigation or deposition of airborne radionuclides. In the absence of specific data, sprinkler rather than surface irrigation was assumed for this study, because the aerial spray produced by the sprinkler leads to foliar deposition, which results in higher radionuclide concentrations in the plants (and animals consuming them) than would irrigation via furrows or drip. Concentrations of radionuclides in the air or water are required as input. The output of ARRRG can be used to generate the water concentrations or the output of DACRIN can be modified to yield air concentrations. Contaminating events can be either acute or chronic. In the latter case, FOOD accounts for the long-term buildup and decay of radionuclides in the soil. In addition, radiation nuclide decay between food harvest and consumption is also evaluated. The material model presented for estimating the transfer of radionuclides (except for ^3H and ^{14}C) from irrigation water or from air to plants through both leaves and soil to food products was also derived from HERMES.

Two simplifying assumptions were made to reduce FOOD to a reasonable running time and data file storage space. The first was the restriction of the soil uptake parameters to one value per radioelement, rather than varying

the value for different types of crops. The second was limiting the translocation factors, which account for transfer of externally deposited radionuclides from plant surfaces to the portion eaten to a single value for all radioelements and food crops. The value chosen, 0.1, was the upper limit of the meager data available in the literature. The one exception was for green leafy vegetables where this translocation factor was taken to be 1. No credit was taken for radionuclide losses during food preparation from washing, peeling, or cooking. These losses were accounted for in the original HERMES codes. The maximum such loss documented in the literature is 50% for radioiodine from leafy vegetables.

FOOD performs calculations for 14 farm products:

- leafy vegetables
- other above-ground vegetables
- potatoes
- root crops
- berries
- melons
- orchard fruit
- wheat
- other grain
- eggs
- milk
- beef
- pork
- poultry

This list can be abbreviated by combining varieties of vegetables or meat into fewer categories.

Deposition by Irrigation Water

The deposition rate d_i from irrigation water is defined by the relation:

$$D_i = C_{iw} I \text{ (water deposition)} \quad (F.8)$$

where

d_i = deposition rate or flux ($\text{pCi m}^{-2} \text{ d}^{-1}$) of radionuclide i

C_{iw} = concentration of radionuclide i in water used for irrigation (pCi/l)

I = irrigation rate ($\text{lm}^{-2} \text{ d}^{-1}$); amount of water sprinkled on unit area of field in 1 day.

Deposition Directly From Air

The deposition rate onto the foilage from airborne radionuclides is:

$$D_i = 86,400 \bar{X}_i V_{di} \text{ (air deposition)} \quad (F.9)$$

where

86,400 = dimensional conversion factor (sec/d)

$\bar{X}_i$ = annual average air concentration (pCi/m^3) of radionuclide i

V_{di} = deposition "velocity" of radionuclide i (m/sec).

Concentration in Vegetation

In vegetation the radioactive material concentration resulting from deposition onto the plant foilage and uptake from the soil of prior depositions is given by:

$$C_{iv} = d_i \frac{r T_v [1 - \exp(-\lambda_{Ei} t_e)]}{Y_v E_i} + \frac{B_{iv} [1 - \exp(-\lambda_i t_b)]}{P_i} \exp(-\lambda_i t_h) \quad (F.10)$$

where

C_{iv} = concentration of radionuclide i in edible portion of plant v
(pCi/kg)

r = fraction of deposition retained on plant (dimensionless), taken to be 0.25

T_v = factor for the translocation of externally deposited radionuclide to edible parts of plants (dimensionless). For simplicity it is taken to be independent of radionuclide and set to 1 for leafy vegetables and fresh forage, and 0.1 for all other produce, including grain. Hoffman et al (1977b) lists values of this parameter which vary with nuclide.

λ_i = radiological decay constant for radionuclide i (d^{-1})

λ_{Ei} = effective removal constant of radionuclide i from plant (d^{-1})
 $\lambda_{Ei} = \lambda_i + \lambda_w$

λ_w = weathering removal constant = $0.693/14$ (d^{-1})

t_e = time of above ground exposure of crop to contamination during growing season (d)

Y_v = plant yield [kg(wet weight)/ m^2]

B_{iv} = concentration factor for plant uptake of nuclide i from solid
pCi/kg (wet weight) per pCi/kg (dry soil)

t_b = time for buildup of radionuclide in soil, (d). In this analysis t_b was 1.10×10^4 days, i.e., the 30-yr operating life time of the nuclear facility.

P = soil "surface density" [kg(dry soil)/ m^2]. Assuming a uniform mixing of all radionuclides in a plowlayer of 15-cm depth, P has a value of 224 kg/ m^2 .

t_h = holdup time (d) (time between harvest and consumption of the food).

The first term inside the brackets of Equation F.10 relates to the concentration derived from direct foliar deposition during the growing season,

whereas the second term relates to uptake from soil and reflects the deposition through the time from start of deposition until harvest of the plant.

For a cow grazing on fresh forage, t_e in Equation F.10 is set equal to 30 days, the typical time for a cow to return to a particular portion of a grazing site.

Concentration in Animal Products

The radionuclide concentration in an animal product such as meat, milk, or eggs is dependent on the amount of contaminated feed or forage eaten by the animal and its intake of contaminated water. The following equation describes this calculation (Baker et al. 1976):

$$C_{ia} = S_{ia} [C_{iF}Q_F + C_{iaw} Q_{aw}] \quad (F.11)$$

where

C_{ia} = the concentration in animal product (pCi/l) or (pCi/kg)

S_{ia} = the transfer coefficient of radionuclide i from daily intake of animal to edible portion of animal product [pCi/l (milk) per pCi/d or pCi/kg (animal product) per pCi/d]

C_{iF} = the concentration of nuclide i in feed or forage (pCi/kg) calculated from Equation F.2 above

Q_F = the consumption rate of contaminated feed or forage by animal (kg/d)

C_{iaw} = the concentration of nuclide i in water consumed by animals (pCi/l); assumed to be equal to C_{iw}

Q_{aw} = the consumption rate of contaminated water by animal (l/d).

The second set of terms in the brackets in Equation F.4 is omitted if the animal does not drink contaminated water. Animal consumption rates normally assumed are given in Table F.4.

TABLE F.4. Consumption Rates of Feed and Water by Farm Animals

	<u>Feed or Forage</u> (kg/day)		<u>Water</u> (l/day)
	Q_F		Q_{aw}
Milk Cow	55	(fresh forage)	60
Beef Cattle	68	(dry feed)	50
Pig	4.2	(dry feed)	10
Poultry (chickens)	0.12	(dry feed)	0.3

(a) Equivalent fresh weight used to ensure proper calculation of radionuclide intake by animal.

Plant concentration factors and animal product transfer coefficients for the elements considered in the study are given in Table F.5. Plant concentration factors were reported by Thompson et al. (1972) and supplemented radionuclide data as explained by Soldat and Harr (1971). The literature yielded coefficients of transfer from feed to animal products for a limited number of radionuclides. For those radionuclides lacking data, comparisons were made with the behavior of chemically similar elements in man (ICRP 1959) and animals. In some instances, those identified with an asterisk in Table F.5, the value was set to 9.9×10^{-4} . The most complete listing of transfer coefficients to be found is for milk (Ng et al. 1968). The milk transfer coefficients given in this reference were intended to be maximum or "worst case" values. The authors imply, by reference to ^{131}I , that average values would be about one-half of their listed values. As a result, the milk transfer values in Table F.5 for elements lacking specific radionuclide data are one-half of those reported by Ng et al. (1968).

Some experimental data are available on the transfer of several radionuclides for chicken, eggs and meat (Mraz et al. 1964, Annenkov et al. 1974). Some of these literature sources were referenced in HERMES (Hoffman et al. 1977b). Unfortunately, very little data are currently available on the transfer of radionuclides to beef and pork. Uncontrolled studies have been

**TABLE F.5. Plant Concentration Factors and Animals
Product Transfer Coefficients**

Element	Plant/Soil (Dimensionless) B_{iv}	Egg/Feed (day/kg)	Milk/Grass (day/L)	Beef/Feed (day/kg)	Pork/Feed (day/kg)	Poultry/Feed (day/kg)
				S_{ia}		
Bc	4.7E-01	2.0E-02	2.0E-02	0.0E-04	1.0E-02	4.0E-01
N	7.0E-06	9.9E-04 (a)	1.1E-02	9.9E-04	9.9E-04	9.9E-04
F	2.0E-02	9.9E-04	7.0E-03	2.0E-02	9.9E-02	9.9E-04
Na	5.0E-02	2.0E-01	4.0E-02	5.0E-02	1.0E-01	1.0E-02
P	5.0E+01	1.0E+01	1.2E-02	5.0E-02	5.4E-01	1.9E-01
Ca	4.9E-02	1.0E+00	0.0E-03	3.3E-03	3.3E-03	3.3E-03
Sc	1.1E-03	9.9E-04	2.5E-06	6.0E-03	1.0E-02	4.0E-03
Cr	2.5E-04	9.9E-04	1.1E-03	9.9E-04	9.9E-04	9.9E-04
Mn	3.0E-02	1.0E-01	1.0E-04	5.0E-03	2.0E-02	1.1E-01
Fe	4.0E-04	1.0E-01	6.0E-04	2.0E-02	5.0E-03	1.0E-03
Co	9.4E-03	1.0E-01	5.0E-04	1.0E-03	5.0E-03	1.0E-03
Ni	1.0E-02	1.0E-01	3.4E-03	1.0E-03	5.0E-03	1.0E-03
Cu	1.3E-01	2.0E-01	7.0E-03	1.0E-02	1.5E-02	2.0E-03
Zn	4.0E-01	4.0E-03	6.0E-03	5.0E-02	1.4E-01	2.0E-03
Se	1.3E+00	2.1E+00	2.3E-02	1.0E+00	4.5E-01	3.7E-01
Br	7.6E-01	1.6E+00	2.5E-02	2.0E-02	9.0E-02	4.0E-03
Rb	1.3E-01	3.0E-00	1.0E-02	1.5E-01	2.0E-01	2.0E+00
Sr	2.0E-01	4.0E-01	1.5E-03	3.0E-04	7.3E-03	9.0E-04
Y	2.5E-03	5.0E-04	5.0E-06	5.0E-03	5.0E-03	5.0E-04
Zr	1.7E-04	1.2E-03	2.5E-06	5.0E-04	1.0E-03	1.0E-04
Nb	9.4E-03	1.2E-03	1.2E-03	5.0E-04	1.0E-03	1.0E-04
Mo	1.3E-01	4.0E-01	4.0E-03	1.0E-02	2.0E-02	2.0E-03
Tc	2.5E-01	9.9E-04	1.2E-02	9.9E-04	9.9E-04	9.9E-04
Ru	1.0E-02	4.0E-03	5.0E-07	1.0E-03	5.0E-03	3.0E-04
Rh	1.3E+01	4.0E-03	5.0E-03	1.0E-03	5.0E-03	3.0E-04
Pd	5.0E+00	4.0E-03	5.0E-03	1.0E-03	5.0E-03	3.0E-04
Ag	1.5E-01	9.9E-04	2.5E-02	9.9E-04	9.9E-04	9.9E-04
Cd	3.0E-01	9.9E-04	6.2E-05	1.6E-02	1.6E-02	1.6E-02
Sn	2.5E-03	9.9E-04	1.3E-03	9.9E-04	9.9E-04	9.9E-04
Sb	1.1E-02	7.0E-02	7.5E-04	3.0E-03	7.0E-03	6.0E-03
Te	1.3E+00	4.0E-01	5.0E-04	5.0E-02	1.0E-02	1.0E-02
I	2.0E-02	1.6E+00	1.0E-02	2.0E-02	9.0E-02	4.0E-03
Cs	2.0E-03	6.0E-01	5.0E-03	3.0E-02	2.6E-01	4.5E+00
Ba	5.0E-03	4.0E-01	4.0E-04	5.0E-04	1.0E-02	5.0E-04
La	2.5E-03	2.0E-03	2.5E-06	5.0E-03	5.0E-03	4.0E-03
Ce	5.0E-04	3.0E-03	1.0E-05	1.0E-03	5.0E-03	6.0E-04
Pr	2.5E-03	4.0E-03	2.5E-06	5.0E-03	5.0E-03	1.0E-03
Nd	2.4E-03	2.0E-04	2.5E-06	5.0E-03	5.0E-03	4.0E-03
Pm	2.5E-03	7.0E-03	2.5E-06	5.0E-03	5.0E-03	1.0E-04
Sm	2.5E-03	7.0E-03	2.5E-06	5.0E-03	5.0E-03	4.0E-03
Eu	2.5E-03	7.0E-03	2.5E-06	5.0E-03	5.0E-03	4.0E-03
Tb	2.6E-03	7.0E-03	2.5E-06	5.0E-03	5.0E-03	4.0E-03
Ho	2.6E-03	7.0E-03	2.5E-06	5.0E-03	5.0E-03	4.0E-03
W	1.8E-02	9.9E-04	2.5E-04	9.9E-04	9.9E-04	9.9E-04
Pb	6.8E-02	9.9E-04	1.0E-05	9.9E-04	9.9E-04	9.9E-04
Bi	1.5E-01	9.9E-04	2.5E-04	9.9E-04	9.9E-04	9.9E-04
Po	9.0E-03	9.9E-04	1.2E-04	9.9E-04	9.9E-04	9.9E-04
Ra	1.4E-03	2.0E-05	2.0E-04	9.9E-04	9.9E-04	9.9E-04
Ac	2.5E-03	2.0E-03	2.5E-06	5.0E-03	1.0E-02	4.0E-03
Th	4.2E-03	2.0E-03	2.5E-06	5.0E-03	1.0E-02	4.0E-03
Pa	2.5E-03	2.0E-03	2.5E-06	5.0E-03	1.0E-02	4.0E-03
U	2.5E-03	3.4E-01	6.0E-04	5.0E-03	6.0E-04	1.2E-03
Np	2.5E-03	2.0E-03	2.5E-06	5.0E-03	1.0E-02	4.0E-03
Pu	2.5E-04	2.0E-03	2.5E-08	5.0E-03	1.0E-02	4.0E-03
Am	2.5E-04	2.0E-03	2.5E-06	5.0E-03	1.0E-02	4.0E-03
Cm	2.5E-03	2.0E-03	2.5E-06	5.0E-03	1.0E-02	4.0E-03
Cf	2.5E-03	2.0E-03	7.5E-07	5.0E-03	1.0E-02	4.0E-03

(a) Where value unknown, a default value of 9.9E-04 was used.

performed on the principal constituents by fallout ^{90}Sr , ^{131}I , and ^{137}Cr (Soldat and Harr 1971), and the EPA National Environmental Research Center at Las Vegas has an ongoing study of radionuclides in cattle and milk, which we hope will continue to generate usable data for our model.

Tritium and Carbon-14 Model

Table F.6 lists the parameters used in the computer program for tritium and ^{14}C . These values may be altered when based on site-specific data. The concentration of tritium or ^{14}C in environmental media (soil, plants, and animal products) is assumed to have the same specific activity (pCi of nuclide per kg of stable element) as the contaminating medium (air or water). The fractional content of hydrogen or carbon in a plant or animal product is then used to calculate the concentration of tritium or ^{14}C in the food product under consideration. Hydrogen content in both the water and nonwater (dry) portion of the food product is used to calculate the tritium concentration. The model assumes that plants obtain all their carbon from airborne carbon dioxide and that animals obtain all their carbon through ingestion of plants.

Because plants acquire most of their carbon from the air, the transfer of this nuclide to vegetation is difficult to model when ^{14}C is present only in the water used for irrigation. Since we have not yet determined the transfer of carbon from water to the air or soil, we have conservatively assumed that plants obtain all their carbon from irrigation water. Such an assumption could lead to plant concentrations that are high by about an order of magnitude or more. To date no operating nuclear facilities that specify releases of ^{14}C in their liquid effluents have been identified. However, this pathway could exist from migration of ^{14}C into groundwater from long-term storage of nuclear wastes.

The concentration of tritium in vegetation, C_{lv} is:

$$C_{lv} = 9 C_{lw} F_{hv} \quad (\text{F.12})$$

TABLE F.6. Fractions of Hydrogen and Carbon in Environmental Media, Vegetation, and Animal Products

Food or Fodder	Water f_w	Carbon (dry) f_c	Hydrogen (dry) f_h	Carbon ^(a) (wet) F_{cv}, F_{ca}	Hydrogen ^(b) (wet) F_{hv}, F_{ha}
Fresh Fruits, Vegetables and Grass	0.80	0.45	0.062	0.090	0.10
Grain and Stored Animal Feed	0.12	0.45	0.062	0.40	0.068
Eggs	0.75	0.60	0.092	0.15	0.11
Milk	0.88	0.58	0.083	0.070	0.11
Beef	0.60	0.60	0.094	0.24	0.10
Pork	0.50	0.66	0.10	0.33	0.11
Poultry	0.70	0.67	0.087	0.20	0.10
Absolute Humidity			0.008 l/m ³		
Concentration of carbon in water			2.0 x 10 ⁻⁵ kg/l ^(c)		
Concentration of carbon in air			1.6 x 10 ⁻⁴ kg/m ³ ^(d)		

(a) F_{cv} or $F_{ca} = f_c (1 - f_w)$

(b) F_{hv} or $F_{ha} = f_w/9 + f_h (1 - f_w)$

(c) Assumes a typical bicarbonate concentration of 100 mg/l

(d) Assumes a typical atmospheric CO₂ concentration of 320 ppm_v

where

C_{lw} = concentration of tritium in the environmental water (pCi/l); for a water release C_{lw} represents concentration in irrigation water; for an airborne release C_{lw} represents concentration in airborne moisture. For an airborne release: $C_{lw} = \text{air concentration in pCi}(^3\text{H})/\text{m}^3 \text{ absolute humidity in l/m}^3$

F_{hv} = the fraction of hydrogen in total vegetation (see Table F.6).

The coefficient 9 converts tritium concentration in environmental water to concentration in hydrogen.

The concentration of tritium in the animal product is:

$$C_{1a} = \left[\frac{C_{1F} Q_F + C_{1aw} Q_{aw}}{F_{hF} Q_F + Q_{aw}/9} \right] F_{ha} \quad (F.13)$$

C_{1F} = concentration of tritium in feed or forage (pCi/kg) calculated by Equation F.11 above, where now $C_{1F} = C_{1v}$

F_{hF} = fraction of hydrogen in animal feed, where now $F_{hf} = F_{hv}$ (grain)

F_{ha} = fraction of hydrogen in animal product (see Table F.6)

C_{1aw} = concentration of tritium in animal drinking water (set to 0 unless there is a release of water).

Similarly, the concentration of ^{14}C in vegetation, C_{3v} , is:

$$C_{3v} = C_{3w} F_{cv}$$

where

C_{3w} = the ratio of the concentration of ^{14}C in the environmental medium to carbon concentration in that medium (pCi $^{14}\text{C}/\text{kg C}$)

F_{cv} = the fraction of carbon in total vegetation.

The concentration of ^{14}C in the animal product, C_{3a} , is:

$$C_{3a} = \left[\frac{C_{3F} Q_F + C_{3aw} Q_{aw}}{F_{cF} Q_F + F_{cw} Q_{aw}} \right] F_{ca} \quad (F.15)$$

For an air release $C_{3aw} = 0$ and since F_{cw} is very small compared to F_{cf} , Equation F.15 reduces to:

$$C_{3a} = C_{3F} \left(\frac{F_{ca}}{F_{cf}} \right) \quad (F.16)$$

Human diets are used to calculate the quantity of radionuclides ingested, and the resultant internal radiation doses are calculated (using the libraries shown in Table F.3) the same way as those for the ARRRG program.

During 1978, FOOD was rewritten into FORTRAN for the UNIVAC 1100/44 computer. It is operational but not yet documented. The FORTRAN revision of both ARRRG and FOOD have been used for sample calculations and the results checked favorably with results of the same problems run on the original BASIC versions.

PABLM

The accumulated dose to a person that lives in the vicinity of the contamination source, and is exposed continuously throughout his/her lifetime to contaminated food, water, sediment and soil is also of interest. Such dose calculations will be possible with the computer code PABLM, which will be converted to FORTRAN for use on the UNIVAC 1100/44 computer in FY-1979. This code is capable of accounting for changing environmental concentrations resulting from continued releases of radionuclides and/or decay of previously released nuclides. The BASIC (UNIVAC 1108) version was used for dose calculations in the Commercial Waste Management Generic Environmental Impact Statement (DOE 1559, in press).

KRONIC

Since atmospheric pathways are expected to be of secondary importance, the programs KRONIC, SUBDOSA, and DACRIN will only be discussed briefly. Detailed descriptions that can be used to implement the FORTRAN version of all three codes have been published previously (Streng and Watson 1973, Streng et al. 1975, Houston et al. 1975, and Streng 1975).

The computer program KRONIC (Streng and Watson 1973) can be used to calculate annual external radiation doses to skin from beta and gamma radiation and to testes and total body from gamma radiation emitted from chronic releases of radionuclides dispersed in air. The program starts with calculation of a standard Gaussian plume formula to define the shape (concentration versus 3-dimensional position) of the radioactive cloud. The

gamma dose at the body surface (skin) is then calculated by summing the contributions of the several parts of the cloud, taking into account the gamma energy dependent absorption and buildup effects. Such a model is referred to as a "finite" plume model. The next step in the calculation is the correction of the surface dose rate to dose at tissue depths of 1 cm (testes) or 5 cm (total body) for energy absorption in the analyzed tissues.

The program then uses the calculated air concentration at the receptor position (ground level) to calculate the beta dose to the body surface (skin). Since the range of beta particles in air is relatively short, the calculation scheme assumes the person is exposed to a hemispherical cloud of beta emitters of infinite radius (bounded by the ground surface). Such a model is referred to as a "semi-infinite" cloud model. Under this assumption, the energy emitted per cc or cm^3 of air is equivalent to the energy absorbed per cc of air. All that is required, then, is to convert MeV per disintegration to rem and to correct for the differences in energy absorption between air and tissues and the geometry of the exposure situation. The latter correction is a factor of 0.5 because the skin is exposed from only one side as opposed to the parcel of air displaced by the presence of the body. The total skin dose is then the sum of the gamma and beta contributions.

Population doses can be obtained by summing the products of the dose to an individual located at the center of a "sector" and the number of persons residing in that sector. Standard practice is to define the sectors as lying between 10 rings of varying radii out to 50 miles, and 16 sectors of fixed width. Doses to population at larger distances can also be calculated provided atmospheric dispersion and population data are available.

KRONIC was originally written in FORTRAN and the modifications created to make it operational on the UNIVAC 1100/44 computer do not need to be redocumented.

The data libraries used by KRONIC are listed in Table F.7 along with those used by SUBDOSA. The first three libraries listed in Table F.7 are used by KRONIC, the last three are used by SUBDOSA.

TABLE F.7. Data Libraries Used by KRONIC, SUBDOSA and DACRIN

<u>Library</u>	<u>Contents</u>
DRFLIB	Problem Specific Dose Rate Factors for KRONIC
RNDBET	Radionuclide Data: decay schemes, beta energies
GISLIBS	Radionuclide Data: decay schemes, gamma energies
BIVLIB	Problem Specific Dose Factors for SUBDOSA

SUBDOSA

The computer program SUBDOSA (Streng et al. 1975) is similar to KRONIC except that the atmospheric dispersion calculations are designed for acute releases rather than chronic releases. The program generates an integrated (air concentration time) exposure with units of Ci-sec/m³ rather than the annual average air concentration generated by KRONIC. The result is a dose per release period rather than an annual dose.

Like KRONIC, SUBDOSA was originally written in FORTRAN and no redocumentation is planned. The data libraries required for SUBDOSA are listed in Table F.7.

DACRIN

Two lung models have been recommended by the International Commission on Radiological Protection (ICRP). The initial lung model (ILM), recommended in ICRP Publication 2 (1959), treats the inhaled material as either soluble or insoluble. When the inhaled material is soluble, the uptake by other organs is assumed to be essentially instantaneous. The newer, more sophisticated lung model (TGLM) recommended by ICRP (1966, 1972) treats the inhaled material in a more complex way. The derived equations for estimating the dose to organs other than the lung are considerably more complex than those for the ILM. A computer program, DACRIN (Houston et al. 1974, Streng 1975) has been developed for calculating the dose to lung and other organs using the TGLM. The mathematical model for calculating the dose to an organ of interest via

inhalation using the TGLM is considerably more complex than that used by the ILM. In the TGLM, the respiratory tract is divided into three regions: nasopharyngeal (P), the tracheobronchial (TB), and the pulmonary (P) regions. The schematic representation of the respiratory tract used in the development of the mathematical model for the deposition and clearance of inhaled radionuclides is shown in Figure F.1. Deposition is assumed to vary with the aerodynamic properties of the aerosol distribution and is described by the three parameters D_3 , D_4 , and D_5 . These parameters represent the fraction of the inhaled material initially deposited in the NP, TB and P regions, respectively. Each of the three regions of deposition are further subdivided into two or more subcompartments, each representing the fraction of material initially in a compartment that is subject to a certain clearance process. This fraction is represented by f_j , where j indicates the clearance pathway. The example, the quantity of material in the TB region, cleared by process (c), is then represented by the product $f_c D_4 Q_I$. Values of the (f_j) and the clearance half times T_j for each clearance process for the three solubility classes of aerosols used in the computer code are shown in Table F.8. Values of the deposition fractions D_3 , D_4 , and D_5 as function of activity median aerodynamic diameter in the form of a graph has been published (ICRP 1972). The respiratory tract model was incorporated into the simple metabolic model by Voilleque (1970). Transport of the radionuclides from the respiratory tract, lymph, and G.I. tract to organs and tissues, where significant accumulations of the inhaled activity occur, is assumed to take place via the blood. The report of the Task Group describes this translocation of the activity from the respiratory tract and lymph to the blood. Of the material clearing from the respiratory tract through the GI tract, a constant fraction, f_1 is assumed to be taken up by the blood. Uptake by the n th organ or tissue is assumed to be a constant fraction of the amount entering the blood stream at any time. Once in the n th organ, the activity is assumed to clear the organ and the body at a constant rate.

Development of the equation to describe the lung clearance model was divided into two parts. The first part is concerned with describing the organ

FIGURE F.1. Schematic Diagram of the Task Group Lung Model

TABLE F.8. Values of the Clearance Parameters for the Task Group Lung Model

Compartment	j	Solubility Class					
		D		W		Y	
		T	f	T	f	T	f
NP	a	0.01	0.5	0.01	0.1	0.01	0.1
	b	0.01	0.5	0.4	0.9	0.4	0.99
TB	c	0.01	0.95	0.01	0.5	0.01	0.01
	d	0.2	0.05	0.2	0.5	0.2	0.99
P	e	0.5	0.8	50	0.15	500	0.05
	f	n.a.	n.a.	1	0.4	1	0.4
	g	n.a.	n.a.	50	0.4	500	0.4
	h	0.5	0.2	50	0.05	500	0.15
L	i	0.5	1	50	1	1000	0.9

(a) Metabolic pathways from lung.

(b) Removal half time in days from compartment via pathway j.

(c) Fraction moved from compartment via pathway j.

burdens and the organ doses in the time interval during which the inhalation of radionuclides is taking place. The second part, requiring a different set of equations, describes the organ burdens and the organ doses for the contiguous time interval following the cessation of radionuclide intake.

The data libraries used by DACRIN are listed in Table F.9. The existing documentation for DACRIN (Houston et al. 1974, Strenge 1975) is sufficient to permit operation of the current UNIVAC 1100/44 FORTRAN version.

TABLE F.9. Data Libraries Used by DACRIN

Library	Contents
ORGLIB	Organ Data: Organ mass, nuclide specific data on biological half-life, effective decay energy uptake and retention
THERMA	Radionuclide Data: decay schemes radioactive half-life

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