

# Status/Summary Report for Fiscal Year 1996 Activities Within the Performance Assessment Overview Study on the Consequences of Cementitious Materials

## INTRODUCTION

At the request of the Repository Design Organization in the DOE's Yucca Mountain Site Characterization Office, the Management and Operating Contractor's Performance Assessment (PA) staff planned an overview study to address potential postclosure performance issues concerning use of large quantities of committed cementitious materials within the potential waste-emplacement drifts (e.g., precast concrete lining segments). This strategy (Attachment I) includes five activities (1) PA analyses of the consequences from the performance impacts caused by geochemical effects of these materials reacting over geologic time; (2) incorporation of constraints derived from input from the Scientific Programs Organization (SPO) on the potential geochemical effects inside the drift (e.g., pH, mineral dissolution/precipitation); (3) incorporation of SPO derived constraints on the potential geochemical effects in the geosphere (e.g., cement fluid-driven rock alteration); (4) incorporation of Scientific Programs Organization (SPO) derived constraints on the impacts to performance parameters from the identified potential geochemical effects inside the drift (e.g., increased solubility-limits, generation of colloids); and (5) incorporation of Scientific Programs Organization (SPO) derived constraints on the impacts to performance parameters from the identified potential geochemical effects in the geosphere (e.g., reduced radionuclide sorption, porosity/permeability changes).

The timing of this overview study was initially designed to provide PA input prior to a Repository Design Review that was scheduled for March, 1997. Based on this original schedule, the Performance Assessment Report was to be completed in the first half of January 1997. Such a time frame would allow for only an *overview* study of both the technical issues and the consequences to potential repository post-closure performance. In the strategy, this outlined work was intended to augment previously planned FY1997 work in PA and the SPO and would consist mainly of summary reports of existing data and modeling studies of the processes involved. In order to get an efficient start to these additional studies, work was begun in a number of these areas in the last 5 weeks of FY1996. This status/summary report provides documentation of what was accomplished over this period. (Note: Since the inception of this strategy, changes in the manner with which this work is to be incorporated into the Project planned activities and changes in the timing of the planned Design Review Meeting—currently June 1997—have superseded the FY1997 portion of the strategy.)

## SUMMARY OF PRELIMINARY PERFORMANCE ASSESSMENT RECOMMENDATIONS

Preliminary consequence sensitivity analyses using current Total System Performance Assessment models have been conducted. These sensitivity analyses included the evaluation of enhanced solubility of radionuclides (Np, Am, and Pu) and reduction of sorption in the unsaturated zone (cases for no retardation for 10 m, 100 m, and the entire unsaturated zone-UZ) due to alkaline fluids that may result from the use of cementitious materials. These analyses

indicate that for migration of alkaline pH fluids, order-of-magnitude increases in peak dose and substantial shifts to earlier times may result due to:

- 1) negation of sorption throughout the entire UZ
- 2) increased concentrations of Np and Pu
- 3) combination of no retardation for 10 or 100 m into the geosphere and #2 (this is the case that would most represent an alkaline plume migrating through the rock matrix).

Recommendations are preliminary at this time. However, it is clear that if concrete is desirable to use as lining for ground support, then minimizing the potential postclosure impacts to the waste isolation capabilities of the site will most likely be achieved by (a) using precast concrete, (b) designing a mix with lower Ca/Si ratio, (c) using techniques such as particle size engineering, steam-curing, or pressure-curing to reduce the concrete permeability and water content needed for higher silica cements, (d) using tuff aggregate, and (e) investigating alternative cements, such as  $C_2S$ , that may have a lower pH than standard Portland cements.

Because the consequence analyses indicate that these impacts would lead to much higher doses at earlier time frames, additional work should be performed to (a) constrain the levels of pH perturbation actually expected from the selected concrete, (b) refine the solubility-limited concentration distributions/functions for Np and Pu for appropriate stable phases in relevant fluid compositions, (c) constrain the expected extent of impact of alkaline pH to sorption coefficients of Np and Pu, and (d) refine models of the expected extent of alkaline plume migration through unsaturated zone lithologies.

The remainder of this report consists of detailed summaries of the progress reported within each of the five activities laid out in the Performance Assessment plan that was drafted in August of 1996. In addition to these activities summaries, this status report has six attachments containing the details of the efforts in these areas. These six attachments are: 1) the *Performance Assessment Plan to Address Potential Post-Closure Performance Impacts from Cementitious Materials used in Potential Repository Drifts*; 2) a PA report titled *RIP Simulations to Investigate the Possible Consequences of Cement Placement within the Potential Yucca Mountain Repository*; 3) a meeting report titled *Performance Assessment Consequences of Cementitious Materials Scoping Study: Cement Expert Consultation Meeting Report*, which contains detailed meeting notes and associated meeting presentation materials; 4) Professor Della Roy's Expert Report titled *Potential Geochemical Effects of Evolving Cementitious Materials*; 5) Professor Hamlin Jennings' Expert Report titled *Report on Potential Geological Effects of Evolving Cementitious Materials Used in the Yucca Mountain Waste Disposal Project*; and 6) Dr. Maria Onofrei's Expert Report titled *Independent Analysis of Issues Related to Repository Performance*. These attachments are intended as support materials that can be accessed for additional details of the activities summarized below.

## ACTIVITY SUMMARIES

In the remainder of Fiscal Year 1996, each of the five activities in the study were started, although it was not expected that any aspect of the above plan would be completed within that time. Listed below for each of the five activities are the allocated resources for FY1996 and the tasks that were laid out in the initial planning. Because much of the time of the people involved in this work was already committed to other projects at the end of the fiscal year, progress was not uniform for all of the tasks. The priority for FY1996 was on performing PA sensitivity studies analyzing the potential consequences caused by pH perturbations (Activity 1) and on evaluating the importance of cement composition to the generation of potential geochemical effects. These are the areas in which the majority of the progress was achieved in FY1996. In addition, another accomplishment in FY1996 was improved integration among the Performance Assessment department, the Scientific Program Office, and the Repository Design Group. This refined integration should provide for more efficient work in the future.

### Activity 1. *Performance Assessment Analysis of Impacts and Consequences*

Task A. To start, this activity would address, using the RIP code, the consequences of having decreased (possibly to zero) sorption coefficients for radionuclides along a portion of the geosphere pathway. These sensitivity analyses will be used to evaluate the consequence to peak doses of such decreased retardation along the first 10 m and the first 100 m of geosphere pathway (1.2.5).

This activity was coordinated by D. Sassani and J. McNeish with T. Dale performing the analyses. Using the Repository Integration Program (RIP) code, this activity began to address the consequences of alkaline plumes reacting with the engineered barrier system (including the waste form) and migrating through a portion of the geosphere pathway. These sensitivity analyses will be used to evaluate the consequence to peak doses from impacts to the source term and retardation along various portions of the geosphere pathway. The discussion presented directly below is a summary of the more detailed report provided as Attachment II.

The preliminary consequence analyses were accomplished by modification of the TSPA-1995 base case (set with the TSPA-1995 parameters as 83 MTU/acre, backfill, high infiltration rate, climatic variation, drips on the waste packages, and fluid pH of 7) to reflect the potential interaction of alkaline fluids from cementitious materials. The two scenarios that were analyzed are: (1) *modified geosphere transport only (mgto)*: this may be the case for migration of alkaline plumes in which enhanced complexing of dissolved radionuclides at high pH results in negatively charged species (performed by setting distribution coefficients ( $K_d$ ) for all radionuclides to zero, i.e., no retardation, for distances of 10 m and 100 m into the unsaturated zone (UZ), and for the entire unsaturated zone); and (2) *modified source-term and geosphere transport (mstagt)*: this combines the first scenario with pH-dependent waste-form dissolution rates and pH-dependent solubility-limited concentrations of Np, Pu, and Am evaluated at a fluid pH of 11.

The results of these simulations were compared to the TSPA-1995 base-case results for (1) a single realization, expected-value calculated dose (expected case) at the accessible environment at times of  $10^4$ ,  $10^5$ , and  $10^6$  years, and (2) the complimentary cumulative distribution function (CCDF) of 100 realizations of calculated dose at the accessible environment at times of  $10^4$  and  $10^5$  years.

For the  $10^4$  year time frame, the expected case results indicate essentially no change from the base case results for both modified scenarios (*mgto* and *mstagt*) where there is no retardation up to 100 m into the geosphere. For unretarded transport through the entire geosphere, only minor contribution to peak dose from  $^{237}\text{Np}$  (~1%) is calculated for *mgto*, but for *mstagt*  $^{237}\text{Np}$  becomes the primary contributor to peak dose at about 8700 years.

For the  $10^5$  year time frame, the expected-case calculations indicate that there is essentially no change from the base-case results for only 10 m of unretarded UZ transport and no modifications to the source term. However, for *mstagt*, the peak dose is increased by about a factor of 5 and dominated by  $^{237}\text{Np}$  release at greater than 60,000 years. For the 100 m unretarded geosphere pathway and the wholly unretarded UZ pathway, the peak dose results from  $^{237}\text{Np}$  for both *mgto* and *mstagt*. Dose contributions from  $^{229}\text{Th}$  and  $^{238}\text{U}$  are also elevated in these cases. For the wholly unretarded UZ pathway,  $^{237}\text{Np}$  contributes the highest doses after ~20,000 and ~10,000 years for *mgto* and *mstagt* cases, respectively. In the latter case, the peak dose is about 300 times the base case value, and  $^{239}\text{Pu}$  is the second highest dose contributor at ~60,000 to 100,000 years, comparable to that from  $^{229}\text{Th}$ .

For the  $10^6$  year time frame, the expected-case results for *mgto* indicate that the longterm  $^{237}\text{Np}$  peak dose is (a) relatively unchanged for 10 m of unretarded transport, (b) about twice the base case for 100 m unretarded transport, and (c) about 4 times the base case for unretarded transport throughout the unsaturated zone. For this last case,  $^{227}\text{Ac}$  and  $^{231}\text{Pa}$  become contributors essentially equal to  $^{237}\text{Np}$  for the longterm doses. [In addition for this case, results indicate that  $^{135}\text{Cs}$  becomes the peak dose contributor after about 250,000 years. However, this is not much of a real concern because it is unlikely that  $\text{Cs}^+$  (an alkali metal) would be highly complexed by hydroxide or carbonate even at very alkaline pH values, and therefore probably would not experience such a change in retardation.] For *mstagt* over the  $10^6$  year time frame, the expected-case results show that the longterm  $^{237}\text{Np}$  peak dose is higher and shifted to earlier times for both 10 m and 100 m of unretarded geosphere pathway. For unretarded transport throughout the entire UZ, the results indicate that after about 150,000 years the major dose contributors would be  $^{239}\text{Pu}$  and  $^{242}\text{Pu}$  (the same comment on  $^{135}\text{Cs}$  made above applies to this case).

Except for the case of *mstagt* for the entire UZ (for which  $^{237}\text{Np}$  is the major peak dose contributor), there is relatively little change to the peak doses at 10,000 years, because these peak doses are dominated by  $^{129}\text{I}$  and  $^{99}\text{Tc}$ , which were unretarded in the base case. In addition, for *mgto* with unretarded transport through the unsaturated zone of only 10 m,  $^{237}\text{Np}$  peak doses are relatively unaffected at all time frames. In the corresponding *mstagt* case, the peak dose is increased by about a factor of 10 in the  $10^5$  year time frame, but are only about 5 times higher for the  $10^6$  year time frame. These modified peak doses are shifted to substantially earlier times. For  $10^5$  years and *mgto*, the impacts to  $^{237}\text{Np}$  peak doses are about

0.5 and 1.5 order-of-magnitude increases for 100 m unretarded and entire unsaturated zone unretarded transport, respectively. In the corresponding *mstagi* case, the changes are ~1.0 and 2.5 orders of magnitude, respectively. In the  $10^6$  year time frame, these modified scenarios represent about 0.5 and 1.5 order-of-magnitude increases relative to the base case, but occur within the first 200,000 years. For these modified cases, the largest increases occur for the scenario of modified source term and geosphere transport. Even higher increases to  $^{237}\text{Np}$  peak doses would be expected at higher pH values because functions for solubility-limited Np concentrations increase with increasing pH in the alkaline pH conditions.

For the 1,000,000 year time frame, the doses from  $^{239}\text{Pu}$  and  $^{242}\text{Pu}$  are increased by about five orders of magnitude for the *mgto* case with unretarded transport through the entire unsaturated zone. Even though these are relatively large increases for the doses from these radionuclides, they do not reach 10 millirem levels and do not become major contributors to peak dose within that time frame. However, for the corresponding *mstagi* case, the changes are ~7.5 and 7.0 orders of magnitude, respectively, and the Pu isotopes are the major contributors to peak dose after about 150,000 years. The peak dose from either Pu isotope is only about half that of  $^{237}\text{Np}$  for this case.

The CCDF results for 10,000 years indicate that only for the *mstagi* case where retardation is nonexistent for the entire UZ is there a detrimental change relative to the base case results. This change amounts to about a factor of 2 either in peak dose or probability of occurrence for doses greater than ~4 mrem. However, for 100,000 years the CCDF results indicate that shifts in peak dose an order of magnitude or greater are possible for the cases where no retardation occurs through the entire UZ, or where changes to the source term are combined with no retardation for at least 100 m through the unsaturated zone pathway.

**Activity 2. Constraints on the potential effects of evolving cementitious materials on in-drift (near-field) geochemistry as a function of time and space.**

**Task A.** Summary report on current thermochemical data available for modeling evolution of solid phases in the cement system (1.2.3).

No progress was reported for this task.

**Task B.** Meeting (in August) between PA and SPO staff to exchange information on modeling cement/water evolution, coordinate modeling effort, and plan modeling strategy (1.2.3 & 1.2.5).

Personnel from the PA Department (D. Sassani, J. Lee, W. Halsey) participated in a meeting with M&O SPO staff (A. Meike, D. Wilder, W. Clarke, C. Palmer, W. Glassley) and PMO personnel (B. Mukhopadhyay) on 08/12 and on 08/13 (D. Sassani, J. Lee, and A. Meike only) to cover planning of the PA overview studies and to exchange technical information. The meetings covered initial inputs concerning the potential geochemical effects of cementitious materials and what the SPO could provide to PA within the time frame outlined for the scoping study on potential impacts on the post-closure repository performance from the use of

precast concrete linings in emplacement drifts. The discussions focussed on the paucity of thermochemical data for solid phases relevant to the cementitious compositions. It was indicated that to better integrate the data from the Scientific Program into PA, active geochemical process-level modeling within PA was going to be a high priority in the FY1997. Process-level modeling performed within PA would be done using the EQ3/6 geochemical mass transfer code package for reaction path calculations, and the OS3D/GIMRT numerical software package and the AREST-CT package for simulating multicomponent reactive transport in porous media. The first two packages are in use within the SPO at LLNL and the latter has been improved for the PA Dept. by subcontracted personnel at PNL for enhanced near-field evaluations. In order for PA to be linked accurately to the SPO work, it was requested that a summary of the thermochemical datasets for cementitious system solid phases developed within the Project and International Studies program be made available to the PA Department within this overview study (Task A within this Activity). In addition, the need for experimental measurements was stressed by the SPO. The possible use of samples of ESF-invert concrete for the strategic experiments was discussed. Finally the PA plans for contracting outside experts were reviewed and a number of possible candidates with diverse expertise in the area of cementitious materials studies were discussed.

**Task C. Meeting with Outside Cement Experts (early September, or sooner) on cementitious materials to get initial constraints for expected geochemical effects and define content of Experts Report. Summarize meeting discussion/findings (1.2.3 & 1.2.5).**

This FY1996 work focussed on constraining the potential geochemical effects of cementitious materials, which will provide input to the other areas. One part of this work was to contract a few outside experts on cementitious materials to (a) participate in a PA-SPO-Repository-Design meeting to discuss potential geochemical effects and possible cementitious mixes that would assuage the potential post-closure performance impacts, and (b) produce a short report covering the potential evolution of cementitious materials in the Near-Field Environment (NFE) over geologic time periods, the potential compositional effects to the NFE of that evolving material, focussing on those effects prioritized by PA. D. Sassani and J. Lee contracted (through the lead M&O cotractor TRW) three outside cementitious materials experts and planned a one day meeting between project personnel from PA, RD, and SPO and the external experts. The meeting was held on September 5, and their reports were delivered the last week of September, 1996. Below is a synopsis of the meeting with the cementitious materials experts (for the detailed Meeting report see Attachment III), followed by a summary of the report findings (each Experts' report can be found in Attachments IV-VI).

In the meeting and within their reports a number of recommendations were made by the experts concerning the cement/concrete compositions and the curing techniques to consider in order to minimize potential compositional impacts from concrete. The most common of these are summarized here:

- a) use precast concrete because of mix and curing options,
- b) design the cement mix with lower Ca/Si ratio than Type II cement to be closer to the rock composition and lessen pH perturbations,

- c) use techniques such as particle size engineering, steam-curing, or pressure-curing to reduce the concrete permeability and the water content needed for higher silica cements,
- d) use tuff aggregate for chemical compatibility to the tuff, and
- e) investigating alternative cements, such as C<sub>2</sub>S, that may have a lower pH than standard Portland cements

***Cement Experts Meeting Summary:***

The Meeting between the outside experts on cementitious materials and the PA, SPO, and RD groups of the M&O took place on Thursday September 5, 1996 (Attachment III). The experts that were brought in for the meeting are Prof. Della Roy of The Pennsylvania State University, Dr. Maria Onofrei of the Atomic Energy Canada Ltd. (AECL), and Prof. Hamlin Jennings of Northwestern University, each of whom will write a short report with their ideas on the potential geochemical effects of concrete and possible cement options that minimize those effects. The PA Cement Study Meeting with the outside cement experts involved personnel from the Waste Package group, the Repository Design group, Scientific Programs, and the Performance Assessment Dept of the M&O, and from the Assistant Manager of Suitability and Licensing (AMSL) organization of YMSCO.

Presentations were made to introduce the outside experts to the Yucca Mountain site, the current Repository Design and Concrete formulations considered for ground support, the potential in-drift environment that materials would experience on the 10,000+ year time-frame, and the potential post-closure performance issues with cementitious materials. The afternoon was spent discussing the possible evolution of cementitious materials in the potential near-field environment and conceivable methods to assuage or eliminate the potential performance impacts. The experts were in agreement that precast concrete would allow a number of possible solutions to lessen the likelihood of pH perturbations to very alkaline conditions in the long-term. The options proposed included alkali activated cements, C<sub>2</sub>S-rich (lower calcium/higher silica) cements, and lower pH cements being developed at AECL. In addition, discussion of the evolved cementitious materials focussed on the potential for carbonation reactions over geologic time to mitigate any alkali generating phases in the solids. The experts all agreed that discussion of the evolution of the materials over such a time frame and at such extreme conditions would necessarily be speculative because of the lack of data concerning cementitious materials in such an environment.

***Prof. D. Roy Report Summary:***

Prof. Roy presents a summary of relevant thermochemical data, evolution of cementitious materials in the potential drift environment, potential water composition effects, and alternative cement compositions including alkali-activated cements and other specialized cement formulations designed to be more chemically compatible with the tuffaceous host-rock (Attachment IV). The discussion of thermochemical data covers assessment of the reliability of the experimental results, as well as that of the estimated data from the Russian literature. In addition, the assessments of phase stability based on natural occurrences are discussed for which it is concluded that portland cements would probably be incompatible with the zeolites in some of the tuffaceous rocks.

Within the section covering evolution of concretes is discussed the results of experiments to characterize the physical/mechanical properties of grouts at temperatures up to 90°C. Some of the mixes used in the tests were formulated to be more compatible with Yucca Mountain tuffs. It is suggested that steam-curing of precast concretes be considered for the Yucca Mountain Project. Under the effect on water chemistry section it is recommended to use aggregates derived from the host rock to provide chemical compatibility and minimize perturbations by reduction of the cement component. Also discussed in that section is using a more siliceous cement to alleviate large chemical perturbations. A summary of experimental work on various concrete mixes, tuffaceous rocks, and J-13 water vapor at 150 to 300 °C is included. The section on alkali activated cements covers ancient cements used in Rome and modern cements referred to as "soil silicate concretes" and "soil cements". The latter are so called because they form phases analogous to zeolites within a synthetic highly alkaline environment. Some of these cements have higher strengths than portland cements can provide and many of the components undergo thermal activation which may make them well suited for the intended application. Finally, the results of heating experiments (dry and hydrothermal) on low-Ca concrete formulated with a low water to cement ratio indicated that in a dry environment that the concrete underwent little alteration up to 150 °C.

*Prof. H. Jennings Report Summary:*

Prof. Jennings presents in his report a summary of the background information presented to the experts at the September 5 meeting, a general overview of cements/concretes and the dependence of their physical properties on hydration, specific comments on the issues raised by PA regarding evolution of concrete and geochemical effects, recommendations for the types of cement/concrete and curing/manufacturing techniques, and finishes with a discussion of some recent work on cements for use with Hanford wastes (Attachment V). In the background summary and in other sections of the text, Prof. Jennings indicated that the complexity of the cement system and potential conditions makes it difficult to predict how the system would evolve, but recommends that the cement be formulated to minimize changes with time. Within the cement overview, the report documents the basics of cement reaction and provides relations between cement hydration and the volumes of the multiple phases that form, as well as that of the pore spaces. It is recommended in this section that reducing the water/cement ratio would provide a denser cement and minimize water.

Comments on specific concerns of PA include that the higher temperatures in potential repository drifts are likely to produce polymerized silicates and more crystalline phases such as tobermorite, zeolite, and hydrogarnet. Dehydration would possibly lead to essentially similar phases to the cement starting phases and carbonation could produce calcium carbonate. Alkalis may form zeolites, which together with calcite formation would be very positive towards reducing pH of fluids equilibrated with the cement/concrete. It is stated that this condition and high temperatures would cause increased corrosion of the steel fibers. In terms of recommendations on composition, Prof. Jennings suggests making the cement as simple as possible, reducing  $\text{Ca}(\text{OH})_2$  by adding silica (as fume, slag, or fly ash), which would also reduce the permeability of the concrete. In addition, using tuff as aggregate is suggested, because limestone would not react with alkalis to reduce them.

A discussion of C<sub>2</sub>S cements (lower Ca) indicates that their strength is not an issue and they may be chemically more compatible with the Yucca Mountain lithologies. Keeping the water/cement ratio low was also suggested so that unreacted material might act to reduce water flow back into the drift by incorporating it into hydrating phases. This was also favorable because of the stability of unreacted cement clinker and the higher strength of low water cements. Particle size distribution was also discussed as a means to achieve higher strength, enhance fluidity, and reduce water content. In addition, precast concrete allows consideration of pressure and temperature treatments during curing to enhance strength and durability, and permits consideration of a wider range of composition, possibly eliminating the need for organic admixtures. Finally, Prof. Jennings presents recent work on cements generated with highly alkaline starting solutions plus clay and fly ash. The evolution of pore fluids for these cements indicates that as reaction proceeds, pH continues to drop even after 30 days. Phases formed include zeolites, apatite, and minor calcite, quartz and monosulfate. After ~100 days the pH of these cements was more than an order of magnitude lower than the standard cement mix.

*Dr. M. Onofrei Report Summary:*

This report was not received until September 30, 1996 and could not be reviewed in time for this status report but can be seen in its entirety in Attachment VI.

**Task D. Initiation of modeling studies (scenario development), definition of inputs, and preparation of materials for experiments (1.2.3 & 1.2.5).**

Within this task, the focus was on preparation of cementitious materials for the strategic experiments to test future reactive transport calculations. Through early integration with the RD group, PA provided the SPO with the preliminary conceptual design for concrete to be used within potential repository drifts. This preliminary mix is effectively the same as that used in the Exploratory Studies Facilities' (ESF) invert sections, although RD is evaluating other mix formulations and is being integrated with the input on concrete/cement mix design information that the outside experts are providing. This preliminary concrete mix design was presented at the September 5 meeting in detail and is essentially Type II Portland cement with limestone aggregate, added silica fume, and steel fibers for reinforcement (for more details, see Attachment III). Because of this preliminary mix design is based on that used for the ESF inverts, the SPO could use already cured samples of the inverts for the material to use in the strategic experiments. This saved much time that would have been spent mixing and curing concrete samples to appropriate conditions.

In addition, PA personnel have begun reviewing various methods used to evaluate reaction of cementitious materials with ground water and the effects on geochemistry that may be generated. Meetings and phone conferences between Las Vegas PA personnel (D. Sassani and J. Lee) and associates in Albuquerque, NM (P. Domske and C. Stockman) indicate that relevant experience in this system exists from work on the German program and from efforts on the WIPP. Preliminary efforts to coordinate and synthesize this expertise in terms of thermochemical treatment of the cement system were begun with the goal of integrating this expertise into that received from the SPO to avoid disconnects between PA models and process level model development by the SPO. Integration of these aspects together with

actively running the process-level models in PA should result in robust abstraction of the process-level models and a realistically bounding PA model for the consequences of cementitious materials.

Task E. Letter Report advising on status of all activities at the end of FY96 provided by September 30, 1996 (1.2.5).

This document is the product of this task.

**Activity 3. *Potential effects of cementitious materials on geosphere (far-field) geochemistry as a function of time and space.***

Task A. Begin summary of existing literature concerning reaction of cementitious fluids in the geosphere (including natural analogue, experimental, and modeling studies).

See discussion directly below Task B.

Task B. Formulate strategy for modeling studies of the system using reaction path and reactive transport code packages (e.g., EQ3/6, AREST-CT, OS3D/GIMRT).

The funds for these tasks were used (together with some from Activity 2) to provide sufficient means with which to get sample preparation underway for materials to be used in strategic experiments. Such experiments would provide the means to independently check the results of reactive transport calculations in order to assess confidence in any predictive calculations performed. These small number of strategic experiments are highly desirable in order to assess uncertainty in these reactive transport calculations because of the complex nature of the geochemical system. The experiments would be designed such that the reactive transport code could easily be set to mimic the conditions and simulate unambiguously the situation in the experiment. Calculated results would be compared to the observed effluent water compositions as a means to check the accuracy of the calculation and assess major sources of uncertainty within the model. Related work occurring within the SPO (W. Glassley, LLNL) provides some of the planning required for model calculations and indicates that the focus for the reactive transport modeling will be to (a) produce faster computer runs by scoping down the compositional system and the phases involved to only those that appear relevant from preliminary runs and reaction mass transfer calculations, (b) screening of relevant thermochemical data to ensure consistency, and (c) ensuring that experimental conditions can be accounted for fully within the reactive transport calculations.

**Activity 4. *Potential impacts of changes in-drift geochemistry on performance-assessment related parameters (e.g., solubility-limited concentrations, colloidal radionuclides, and stability, corrosion degradation).***

Task A. Begin review and summary of existing experimental and modeling studies for high pH conditions (i.e., >10) focussing initially on actinides (Np, Pu, Am, U). Include

an outline of other radionuclides that should also be evaluated. This summary report should assess the potential under these conditions for formation of more-stable phases for which data are lacking (1.2.3).

Only minimal planning activities occurred within this task. In addition to evaluating the literature data for high pH fluids in a Ca- and Si-rich system, a decision-making tree for geochemical factors to consider as a result of introducing cement was outlined. Such a tree would provide links between geochemical effects and impacts to performance parameters, e.g., increased pH would cause possible increased phase solubilities; increased dissolved silica concentrations would possibly generate a different solubility controlling solid phases. Combined with a summary of applicable data in the literature, such a decision tree might allow delineation of a few key experiments to identify and quantify the possible impact in the regions of greatest uncertainty.

***Activity 5. Potential impacts of changes in far-field geochemistry on geosphere performance assessment related parameters.***

**Task A.** Begin review and summary of existing experimental and modeling studies for high pH conditions (i.e., >10) focussing initially on those radionuclides that are highly sorbed for base-case (i.e., J-13-like) fluids and that could contribute largely to dose if not sorbed effectively (e.g., Pu). Include an outline of other radionuclides that should also be evaluated (1.2.3).

No progress was reported in this task..

## **Performance Assessment Plan to Address Potential Post-Closure Performance Impacts from Cementitious Materials used in Potential Repository Drifts**

Based on ease of construction and pre-closure tunnel stability considerations, precast concrete is the primary option for ground support in the emplacement drifts of the potential Yucca Mountain repository. Using precast concrete lining segments for tunnel excavation and construction provides an efficient means of developing the vast lengths of emplacement drifts in the potential repository. Lining of the emplacement drifts with precast steel-reinforced concrete may enhance the stability of the emplacement drifts, possibly throughout the pre-closure period. These linings may also help to assuage potential rock falls on the waste packages in the early post-closure stages. However, the potential geochemical effects of the long-term evolution of cementitious materials in the potential repository drift environment may result in both beneficial and detrimental impacts to post-closure waste isolation capabilities of the system.

Current Performance Assessment judgement based on a qualitative analysis of the issues indicates that using large amounts of cementitious materials has potential to impact adversely waste isolation capabilities of a potential repository. Because concrete linings for potential emplacement drifts are currently the top-rated ground support option, a more detailed analysis of the post-closure performance issues for cementitious materials has been requested. The five (5) activities below describe the approach to analyzing these issues including the information needs of the Performance Assessment Department to address in a more rigorous manner the potential impacts to post-closure performance.

**Time Frame:** Performance Assessment Report completed in the first half of January 1997. This time frame will allow for an *overview* study of both the technical issues and the consequences to potential repository post-closure performance as outlined below. This study will provide the basis for a recommendation by the Performance Assessment Group on the potential for impacts to waste isolation capabilities of the Yucca Mountain potential geologic disposal site from a cement-based ground support system for the potential repository drifts.

### ***I. Post-Closure Performance Impacts to be addressed:***

Given the time frame above, the focus of this work will be quantifying the range of geochemical effects of cementitious materials and the potential *detrimental* impacts to post-closure performance from usage of large quantities of concrete. The primary potential benefit to post-closure performance from cementitious materials (identified thus far) is passivation of waste package surfaces and will be included in the analysis to the extent possible. Focussing on delineating the consequences of potential detrimental impacts to post-closure performance will enable Performance Assessment to bound the risk involved with cementitious materials and to provide a recommendation on using an in-drift, concrete-based ground support system.

It is recognized that various cementitious materials exist that have different physical and chemical properties. There are cements specially designed with higher silica ( $\text{SiO}_2$ ) content to

react with, and eliminate, portlandite ( $\text{Ca}(\text{OH})_2$ ) by forming Ca-silicate phases that maintain pore fluids at pH values of about 11. In terms of impacts to post-closure performance from alkaline fluids, these cement varieties would be preferred over those with excess CaO or alkalis such that pH values of 12.5 to 13.5 are attainable. In some cases though, organic admixtures must be added to control setting and consistency of concrete mixes that are chemically engineered to buffer pH to about 11. This evaluation will *assume that no organic additives are used* within the concrete. Analysis of the potential impacts to post-closure performance resulting from organic materials would require an amount of effort much larger than that being considered here.

#### **Activity 1. Performance Assessment Analysis of Impacts and Consequences**

The assessment of changes to system performance that may result from the geochemical effects of cementitious materials will be addressed by answering the following three questions relating to various portions of the system:

Q1. Does the emplacement of large masses of concrete into potential repository drifts cause greater release of radionuclides from the waste package and engineered barrier system (EBS)? Specifically, how are solubility-limited concentrations of dissolved radionuclides changed by the imposed geochemical effects, and how much cement-derived colloid forms and transports radionuclides?

Q2. Does the emplacement of large masses of concrete into potential repository drifts cause enhanced transport of radionuclides through the geosphere? Specifically, how are radionuclide sorption coefficients changed by the imposed geochemical effects of alkaline plumes (including primarily the aqueous phase effects, but also incorporating the host-rock alteration effects as much as possible)?

Q3. If the answer to either of the above questions is yes, then does the emplacement of large masses of concrete into potential repository drifts result in degradation of the total system performance to an unacceptable extent? (e.g., as shown via potential consequences of changes in EBS and geosphere PA-related parameters on 10,000 year peak dose at the accessible environment)?

These questions will be addressed by comparison of expected changes in performance parameters (identified in the studies discussed below) to the ranges of those values used in current Total System Performance Analysis models, sensitivity studies of consequences focussing on the subsystem impacts such as changes to solubility-limited concentrations and geosphere transport properties, and analyses of consequence from combined impacts. Consequence analyses will be performed with the Repository Integration Program (RIP) and compared with current base-case analyses to assess the changes in performance related to these effects. Comparison of such results with current post-closure performance standards will allow assessment of the meaning of any changes from the base case.

Primary 1.2.5 investigators: D. Sassani  
J. Lee  
T. Dale  
J. McNeish

These questions will be addressed by both sensitivity/consequence studies within the Performance Assessment Department (as discussed above) and focussed studies by the Scientific Programs investigators to fill the process-level information needs of Performance Assessment presented below. The answers to the above questions will allow a recommendation to be made by the Performance Assessment Department regarding the use of large quantities of cementitious materials in the construction of potential repository drifts based upon the potential for impact to Post-Closure Performance of the site. The uncertainty in the analyses will be used to provide a level of confidence in the recommendation that is made. It should be noted though that such a recommendation will be based on post-closure issues *only*. Any decision about using pre-cast concrete lining as ground support for potential repository drifts should integrate this recommendation with those from other relevant areas of consideration (e.g., constructability, ground support and preclosure operational safety, etc.).

## ***II. Process-level Information Needs:***

The information needed to address the above performance questions encompasses (A) *effects* to the in-drift geochemical environment and to the geosphere geochemistry, and (B) the *impacts* of these changes upon performance parameters such as dissolved radionuclide concentrations, colloiddally bound radionuclides, and transport of these species through the geosphere. Such data forms the basis for establishing the likely scenarios for the potential repository environment and evaluating the consequences of using large masses of cementitious materials. Presented below is an overview and prioritization of the post-closure performance issues that Performance Assessment has identified followed by a plan detailing the approach to filling the information needs via four (4) activities that would support the Performance Analysis activity discussed above.

From a preliminary analysis by the Performance Assessment Waste Isolation Evaluation (WIE) group, a number of potential geochemical effects of cementitious materials and their associated potential impacts (positive, negative, & indeterminate) to post-closure performance parameters have been identified. These potential effects and impacts are:

### ***Generation of Highly Alkaline Solutions (pH ~12-13)***

- ◆ Increase Radionuclide Solubility Limits (e.g., via  $\text{CO}_3^{2-}$  &  $\text{OH}^-$  Complexing)
- ◆ Reduce/Eliminate Sorption in Natural Barrier (Anionic Species)
- ◆ Change Hydrology via Increased Silica Solubility & Host-Rock Alteration
- ◆ Reduce Waste Package Corrosion (via Passivation Films)

***Higher Ca Concentration (Stabilize Calcite)***

- ◆ Reduce CO<sub>2</sub> Migration (fix <sup>14</sup>C)
- ◆ Change Near-Field Hydrologic Properties

***In-Drift Water Source—Elevation of Relative Humidity***

- ◆ Increase Waste Package Corrosion

***Production of Aluminosilicate Colloids***

- ◆ Increase Mobile Radionuclides
- ◆ Change Sorption Properties

***Provide Sorptive Substrate In-Drift***

- ◆ Increase Near-Field Sorption (Alkalies, etc.)

The qualitative analysis of these potential impacts to post-closure performance has lead Performance Assessment to prioritize them in the following manner:

**1. Major Issue is pH Perturbation Impacts to Solubility Limits and Sorption**

This issue, which is relevant to both the in-drift environment and in the geosphere transport of radionuclides, appears to have the capacity for causing the largest changes to post-closure performance. Possible mitigation of extreme high values may be possible by using a particular cement formulation, i.e., adjust the Ca/Si ratio to reduce/eliminate the Ca(OH)<sub>2</sub> so that the resulting solution pH is set to about 11 by calcium-silicate-hydrate (C-S-H) phases. One of the top priorities is to evaluate potential effects to dissolved actinide concentrations (Np, Pu, Am). (For uranium, Ca-U-Si phases (e.g., -uranophane) appear to form over time and thereby constrain dissolved uranium to low values within cement pore fluids.) Because many dissolved constituents may have anionic forms at high pH, a second top priority is to evaluate the potential effects of alkaline fluids on far-field sorption coefficients of alkaline fluids.

**2. Host-Rock Alteration Impact on Hydrology/Transport**

Silica (quartz, amorphous silica, etc.) solubility increases above a pH of 10. Silica minerals in the host rock will be unstable and react readily in this environment. Formation of alteration phases resulting from the pH perturbation, as well as increased cation concentrations (e.g., Ca abundance stabilizing Ca-silicates and calcite), will probably change porosity and permeability in the host rock. In addition, mineralogic changes would also have potential to affect the capability of the rock to sorb radionuclides. The extent to which these effects would occur and their potential performance consequences are uncertain. Because the alteration capacity is increased under the identified changes to chemical conditions, these effects should be addressed in at least a preliminary manner.

### 3. Colloids/Sorptive Material

Cement solids (i.e., CSH phases) and possible alteration minerals may provide both sorption and cation exchange sites for radionuclides, thus providing some level of retardation within the drifts. Colloids generated from cementitious materials may also sorb radionuclides and could enhance transport if they migrate. These issues are currently viewed as somewhat of a trade-off, except for consideration of transport of colloids within fracture pathways. Although such enhanced transport may be offset by sorption/cation exchange in Near-Field, an attempt should be made to place bounds on the abundances of cementitious colloids and their capacity to sorb radionuclides.

### 4. Near-Field Water Source

Water held in the pores and from thermally-driven dehydration of C-S-H phases within the cement would be evolved in the near-field environment and may increase relative humidities in the drift. If the water content of the concrete can be kept to amounts comparable to the natural water content of the host rock, this should not be a major effect. The final water content of the concrete may be minimized by using pre-cast concrete, which would reduce free water via curing/hydration of cement paste and water migration out of the concrete before placement.

In the plan below, the Performance Assessment analysts will work in close cooperation with the Scientific Program investigators to bound both the potential *effects* (Section II-A) of the evolution of large quantities of cementitious materials in a potential repository environment and the level of *impacts* (Section II-B) to the Performance Parameters that are currently included, or planned to be incorporated in the near future, in the Total System Performance Assessment model. This cooperative effort will be facilitated by concurrent model development/evaluation of the evolution of cementitious materials in the in-drift environment by both Performance Assessment analysts and Scientific Program investigators. Strategic experimental work will allow testing of process-level modeling accuracy and precision. This effort will also include incorporation of the contributions of outside experts regarding the expected evolution of cementitious materials in the potential repository environment and the probable geochemical effects of the evolving materials.

#### II-A. Constraints on Geochemical Effects

The cementitious materials (or precast concrete) to be focussed on in this portion of the study are classified into two types according to their pore solution pH: 1) precast concrete based on ordinary portland cement (OPC) which commonly generates a highly alkaline pore solution with a pH between 13 and 13.5; and 2) precast concrete based on a specially designed cement to lower the pH of the pore solution to about 11. The pore solution pH of the ordinary portland cement-based concrete is dominated initially by the alkalis (Na and K) at a pH 13 and 13.5, and later from the equilibration of portlandite ( $\text{Ca(OH)}_2$ ) setting the pore solution to a pH of about 12.5. To assuage potential problems associated with high pH solutions, cement

for precast concrete can be engineered by adding additional silica that reacts with portlandite to produce calcium silicate hydrate phases ( $x\text{CaO}\cdot\text{SiO}_2\cdot y\text{H}_2\text{O}$ ) which are characterized as having "gel-like", quasi-crystalline structures and high specific surface area. The calcium silicate hydrate phases contain some of the alkalis by adsorption and incorporation into their structure. The resulting solutions of this engineered precast concrete commonly have pH values between 11 and 11.5. This analysis should identify if the use of such engineered concretes requires the use of organic admixtures in order to be effective.

**Activity 2. Constraints on the potential effects of evolving cementitious materials on in-drift (near-field) geochemistry as a function of time and space.**

This activity will involve documenting applicable constraints from existing literature, expert elicitation, and modeling studies of the system using reaction path and reactive transport programs (e.g., EQ3/6, AREST-CT, OS3D/GIMRT). In addition, strategic experiment(s) will be conducted to generate a data set with which to evaluate the accuracy and precision of the modeling studies. At least one such experiment will be completed by the beginning of December 1996 because they are short term (1-3 months), and it will be designed to test the ability of the modeling programs to predict pH and selected ionic concentrations that result from water contacting cement affected by high temperatures at low relative humidities. Elicitation of contributions from outside experts regarding the physico-chemical characteristics of cementitious materials and evolution of these in the potential repository environment will provide inputs with which to more precisely identify the major effects for consideration and to sharpen the scope of modeling studies of cementitious materials evolution and experimental tests of the models. In addition, this activity would include documentation of the available thermochemical data for cement-system phases, assessment of the uncertainty in model results resulting from data limitations, and comparison between model calculations and experimental results. Both Performance Assessment analysts and Scientific Programs investigators will work cooperatively to ensure consistency of process-level analyses and abstraction of bounding parameters into scenarios for Performance Assessment analyses. These studies will focus on providing data on constraining:

- a. In-drift fluid composition (e.g., pH, ionic strength, sulfate, alkalis, silica)
- b. Colloid abundances generated from cementitious materials
- c. In-drift mineralogic changes

Comparison of the changes observed relative to a "base-case" of ~J-13 fluid will allow identification of the major variables of concern (e.g., pH, ionic strength, etc.).

Primary 1.2.3 investigators: A. Meike  
W. Glassley  
B. Vianni

Primary 1.2.5 investigators: D. Sassani  
J. Lee

**Activity 3. *Potential effects of cementitious materials on geosphere (far-field) geochemistry as a function of time and space.***

This activity will be essentially an extension of the in-drift effects study outlined above. In this case the focus is on the interaction of the resulting fluid composition with the tuffaceous host-rock of the geosphere. This activity will summarize existing information concerning reaction of cementitious fluids in the geosphere (including natural analogue, experimental, and modeling studies) and provide results of modeling studies of the system using reaction path and reactive transport code packages (e.g., EQ3/6, AREST-CT, OS3D/GIMRT). Such modeling will provide constraints on the extent to which cement fluids may migrate through the geosphere, how such fluid compositions change, and how the host rock mineralogy alters during reactive of the fluid phase. Assessment of the uncertainty in the model results will also be performed. This activity will focus on providing data on:

- a. Extent of migration of perturbed fluid compositions (alkaline plume)
- b. Compositional evolution of fluids with migration
- c. Mineral alteration of host rock

Primary 1.2.3 investigators: W. Glassley  
B. Robinson

Primary 1.2.5 investigators: D. Sassani  
J. Lee

**II-B. Impacts of Geochemical Effects on Performance Parameters**

In order to evaluate the consequences to performance of cementitious materials, connections should be established between geochemical effects and how performance parameters change as a result. The values of impacted performance parameters allow evaluation of the expected perturbation of the system. The activities outlined below are intended to develop constraints on both the in-drift and geosphere performance parameters.

**Activity 4. *Potential impacts of changes in-drift geochemistry on performance-assessment related parameters (e.g., solubility-limited concentrations, colloidal radionuclides, and stability, corrosion degradation).***

This activity will involve documenting the existing knowledge concerning how the potential geochemical effects could impact the dissolved concentrations of radionuclides (solubility-limits, etc.), or provide other sources of mobile radionuclides (e.g., colloidal radionuclides). Thermochemical modeling of phase stabilities and the changes in their solubilities under these conditions will allow comparison of these values to those in ~J-13 fluid. Assessment of model uncertainties will be performed. In addition, this activity will include preliminary assessments of the impacts (possible benefits) of these geochemical effects on waste package degradation rates using constraints surveyed from the literature or available models. In this

case also, model uncertainties should be assessed. Impacts to waste-form (spent fuel and vitrified high-level waste) degradation rates may also be included, but the current performance assessment model for spent-fuel dissolution is viewed as sufficiently conservative because it is based on the far-from equilibrium values. This activity should reexamine this assessment by a rapid survey of existing knowledge. This activity will focus on providing data on:

- a. Changes to radionuclide solubility-limits for perturbed fluids.
- b. Sorbed masses of radionuclides on cementitious material-derived colloids.
- c. Changes to container degradation rate.

Primary 1.2.3 investigators: C. Palmer  
D. Tait  
A. Meike

Primary 1.2.2 investigators: G. Henshall  
D. McCright  
R. Stout

**Activity 5. Potential impacts of changes in far-field geochemistry on geosphere performance assessment related parameters.**

This activity would include a summary and an assessment of the applicable data for distribution coefficients of radionuclides under the conditions of the plume fluid composition, particularly the high pH effect. Estimation/extrapolation may be required using available data with constraints from theoretical/modeling studies where directly applicable measurements are not available. Assessment of uncertainties should be performed for constraints provided. This activity should focus on providing data for:

- a. Changes to radionuclide sorption coefficients for plume fluids

Primary 1.2.3 investigators: I. Triay  
B. Robinson

**III. Schedule and Resources:**

**III-A. Fiscal Year 1996:**

In the remainder of Fiscal Year 1996, each of the five activities in the study will be started, although it is not expected that any aspect of the above plan will be completed within that time. The initial focus is on better constraining the geochemical effects. A letter report will be issued at the end of FY96 (September 30, 1996) detailing the status of the progress in each of the 5 activities. It is planned that this will include preliminary input elicited from two experts on cementitious materials regarding expected geochemical effects. For the remainder of this fiscal year, the effort will be focussed on beginning the highest priority studies using

resources totaling \$100 K. These resources will be divided among the 5 activity areas in the following manner:

- Activity 1:** *\$15K for consequence analyses assuming ranges of potential impacts to the geosphere transport (\$15K for 1.2.5).*  
To start, this activity would address the consequences of having decreased (possibly to zero)  $K_d$  for radionuclides along a portion of the geosphere pathway using the RIP code. These sensitivity analyses will be used to evaluate the consequence to peak doses of such decreased retardation along the first 10 m and the first 100 m of geosphere pathway (1.2.5).
- Activity 2:** *\$45K for developing constraints on effects to in-drift geochemistry (\$15K for 1.2.3; \$15K for 1.2.5; and \$15K for outside experts).*  
Summary report on current thermochemical data available for modeling evolution of solid phases in the cement system (1.2.3).  
Meeting (in August) between PA and SPO staff to exchange information on modeling cement/water evolution, coordinate modeling effort, and plan modeling strategy (1.2.3 & 1.2.5).  
Meeting with Experts (early September, or sooner) on cementitious materials to get initial constraints for expected geochemical effects and define content of Experts' Report. Summarize meeting discussion/findings (1.2.3 & 1.2.5).  
Initiation of modeling studies (scenario development), definition of inputs, and preparation of materials for experiments (1.2.3 & 1.2.5).  
Letter Report advising on status of all activities at the end of FY96 provided by September 30, 1996 (1.2.5).
- Activity 3:** *\$15K for developing constraints on the effect to the geochemistry in the geosphere (1.2.3).*  
Begin summary of existing literature concerning reaction of cementitious fluids in the geosphere (including natural analogue, experimental, and modeling studies).  
Formulate strategy for modeling studies of the system using reaction path and reactive transport code packages (e.g., EQ3/6, AREST-CT, OS3D/GIMRT).
- Activity 4:** *\$15K for developing impacts to radionuclide solubility-limited concentrations from major geochemical effects (1.2.3).*  
Begin review and summary of existing experimental and modeling studies for high pH conditions (i.e., >10) focussing initially on actinides (Np, Pu, Am, U). Include an outline of other radionuclides that should also be evaluated. This summary report should assess the potential under these conditions for formation of more-stable phases for which data are lacking (1.2.3).

**Activity 5. \$10K for developing impacts to sorption in the geosphere from major geochemical effects (1.2.3).**

Begin review and summary of existing experimental and modeling studies for high pH conditions (i.e., >10) focussing initially on those radionuclides that are highly sorbed for base-case (i.e., J-13-like) fluids and that could contribute largely to dose if not sorbed effectively (e.g., Pu). Include an outline of other radionuclides that should also be evaluated (1.2.3).

**III-B. Fiscal Year 1997:**

In the first quarter of FY1997 (October through December), work will progress within each of the five activities culminating in a Performance Assessment Department Report completed for January 15, 1997. Many of the activities will be concurrent and, because of the interdependencies, will be ongoing throughout the period. For example, much of the work to be performed within Activity 1 will depend upon information derived from Activities 2 through 5. Similarly, scopes within Activities 4 and 5 may change as information is provided from Activities 2 and 3 (or even Activity 1). Given these uncertainties, estimates of schedules and resource needs are listed below for each of the five (5) activities, in terms of fractions of Full-Time Employees (FTE-where 3 months is equivalent to 0.25 FTE). In order to fulfill the overview study in this time-frame the resources needed are:

**Activity 1: *Performance Assessment Analysis of Impacts and Consequences (1.2.5).***

- a. Assessment of impacts to in-drift performance parameters  
status of sensitivity studies by October 31, 1996  
status of impact assessments by November 15, 1996  
completed by December 31, 1996
- b. Assessment of impacts to geosphere performance parameters  
status of sensitivity studies by October 31, 1996  
status of impact assessments by November 15, 1996  
completed by December 31, 1996
- c. Assessment of consequences at the accessible environment  
status of consequence analyses by November 15, 1996  
completed by 1st week of January, 1997
- d. Generate final report  
completed January 15, 1997

**Activity 1 Total Resources: 0.625 FTE in 1.2.5**

**Activity 2. *Constraints on the potential effects of evolving cementitious materials on in-drift (near-field) geochemistry as a function of time and space (1.2.3 & 1.2.5).***

- a. In-drift fluid composition (e.g., pH, ionic strength, sulfate, alkalis, silica)  
status by November 15, 1996

- completed by December 15, 1996
- b. Colloid abundances generated from cementitious materials  
status by November 15, 1996  
completed by December 15, 1996
- c. In-drift mineralogic changes  
status by November 15, 1996  
completed by December 15, 1996

*Activity 2 Total Resources:* 0.750 FTE in 1.2.3  
0.375 FTE in 1.2.5

*Activity 3. Potential effects of cementitious materials on geosphere (far-field) geochemistry as a function of time and space (1.2.3 & 1.2.5).*

- a. Extent of migration of perturbed fluid compositions (alkaline plume)  
status by November 15, 1996  
completed by December 15, 1996
- b. Compositional evolution of fluids with migration  
status by November 15, 1996  
completed by December 15, 1996
- c. Mineral alteration of host rock  
status by November 15, 1996  
completed by December 15, 1996

*Activity 3 Total Resources:* 0.500 FTE in 1.2.3  
0.125 FTE in 1.2.5

*Activity 4. Potential impacts of changes in-drift geochemistry on performance-assessment related parameters (e.g., solubility-limited concentrations, colloidal radionuclides, and stability, corrosion degradation) (1.2.3 & 1.2.2).*

- a. Changes to radionuclide solubility-limits for perturbed fluids  
status by November 30, 1996  
completed by December 31, 1996
- b. Sorbed masses of radionuclides on cementitious colloids  
status by November 30, 1996  
completed by December 31, 1996
- c. Changes to container degradation rate (include assessment of waste-form impacts)  
status by November 30, 1996  
completed by December 31, 1996

*Activity 4 Total Resources:* 0.500 FTE in 1.2.3  
0.125 FTE in 1.2.2

**Activity 5. Potential impacts of changes in far-field geochemistry on geosphere performance assessment related parameters (1.2.3).**

- a. Changes to radionuclide sorption coefficients for plume fluids  
status by November 30, 1996  
completed by December 31, 1996

**Activity 5 Total Resources: 0.250 FTE in 1.2.3**

**Total Resources for Fiscal Year 1997**

1.125 FTE in 1.2.5

2.000 FTE in 1.2.3

0.125 FTE in 1.2.2

3.250 FTE total

# RIP SIMULATIONS TO INVESTIGATE THE POSSIBLE CONSEQUENCES OF CEMENT PLACEMENT WITHIN THE POTENTIAL YUCCA MOUNTAIN REPOSITORY

Tim F. Dale

## 1. INTRODUCTION

Simulations using the Repository Integration Program (RIP) were generated to investigate the change in dose to man, measured at the accessible environment (AE), due to a change in groundwater chemistry as a result of dissolution of concrete surrounding the drifts within the repository. As the groundwater infiltrates into and through the repository, the concrete is dissolved into solution resulting in an increase in the pH of the groundwater. Several effects of having a groundwater with a higher pH in contact with the waste forms were investigated and the results are presented below.

The increase in pH was incorporated into the RIP base-case model by increasing the pH of the infiltration water to a constant value of 11 and specifying the solubility limits for Americium, Neptunium, and Plutonium as a function of pH. The dissolution of the waste forms was maintained as a function of pH as specified within the base-case model. The change in each radionuclide solubility limit as a function of pH was calculated within RIP during each simulation.

The increase in the groundwater pH was also assumed to decrease the distribution coefficient ( $K_d$ ) of the radionuclides within the geosphere, thereby decreasing the retardation of the radionuclide. Because no transport processes were specified as a function of pH within the base-case model, the decrease in the  $K_d$  values was incorporated into the geosphere module by setting all  $K_d$  values to zero (retardation = 1) for various distances away from the waste package. The three distances selected were 10 and 100 m away from the repository, and, *as an extremely unlikely bounding case*, for the entire unsaturated zone.

The RIP base-case model was simulated to provide the base-case results to which all modified runs were compared. The changes to the RIP base-case model were conducted by first modifying the  $K_d$  values for the various distances within the geosphere (initial pH scenario). Following the analysis of these runs, the increase in the pH and the solubility characteristics of the groundwater within the repository was incorporated (modified pH scenario).

## 2. BASE-CASE MODEL

A RIP input data file (83YHCB0.RP) based on the TSPA-1995 case for 83 MTU/acre, high infiltration, climate model, drips on waste package, and backfill was renamed 83.RP and was considered the base-case model for this study. The base-case waste-package model assumed a pH of 7 for the infiltrating water at a temperature of 25°C. The dissolution of the spent fuel and

defense high level waste packages was defined by the coded functions CSFDIS and CGLDIS as in TSPA-1995. The solubility-limited values for all radionuclides were not specified as a function of pH in this case.

The thickness of each geologic unit or layer within each of the six unsaturated-zone columns represented in RIP is presented in Table 1. The Kd value for each radionuclide, and thus the retardation for each radionuclide, was assumed to be constant across the entire length of each simulated geological layer. Table 2 lists the expected-value retardation values for each chemical element group per geologic material.

The longitudinal dispersivity value assigned to each matrix flow mode was assigned a value of one-tenth of the pathway length ( $L/10$ ). The Poisson's transition ratio for the fracture flow mode was assigned a value of one divided by the pathway length ( $1/L$ ).

### 3. MODEL MODIFICATIONS

The base-case model was modified for two different scenarios. The first scenario involved maintaining the base-case standard pH value for the infiltrating water and modifying the Kd values for each radionuclide within the unsaturated-zone pathways. The second scenario involved increasing the pH for the percolation flux within the repository, and specifying the solubility-limits of several radionuclide families to be functions of the increased pH.

#### 3.1 INITIAL pH SCENARIO

The initial pH scenario consisted of the base case standard temperature (25°C) pH of 7 for the water infiltrating through the repository. The solubility and dissolution of all radionuclides were not modified from the base-case values.

An assumed change in the pH of the groundwater beneath the repository was incorporated into the model by modifying the Kd values for all radionuclides to three finite distances within the unsaturated zone. These distances were specified as 10 m, 100 m, and the entire length of the unsaturated-zone columns. In order to determine the maximum change in the dose measured at the accessible environment, the Kd values were set to zero, resulting in no radionuclide retardation within the modified unsaturated-zone pathways.

To incorporate the Kd modifications for a distance of 10 m, the unsaturated-zone pathways were modified such that the first pathway downgradient from the repository invert layer was 10 m in length for each column. This required the first geologic layer (TSw) to be split into two pathways. Table 3 shows the changes to the pathway lengths which were incorporated into the 10 m model (KD10.RP). The shaded areas in the Layer Thickness column of Table 3 denote the pathways in which the retardation of each radionuclide was set to 1.0 ( $K_d = 0$ ) within the matrix flow mode. For each of the models in which pathways were modified, the relationship between

the pathway length and the longitudinal dispersivity and the Poisson's transition ratio was maintained.

To incorporate the Kd modifications for a distance of 100 m, the unsaturated-zone pathways were modified such that the first 100 m downgradient from the repository invert layer could be specified with a retardation of 1.0. Table 4 shows the changes to the pathway lengths which were incorporated into the 100 m model (KD100.RP). For columns 1, 2, 4, and 6, the upper geologic layer (TSw) thickness was greater than 100 m, so these layers were modified in a similar fashion as to the 10 m model. For columns 3 and 5, the combined thickness of the upper two geologic layers (TSw and TSv) was less than 100 m. The thicknesses of these two layers were not modified but it was necessary to modify the third layer (CHnv) to obtain a series of pathways which total 100 m. Table 4 shows how the CHnv layer was divided. The shaded areas in the Layer Thickness column of Table 4 denote the pathways in which the retardation of each radionuclide was set to 1.0 within the matrix flow mode.

The model in which the Kd values were set to zero for the entire unsaturated zone was generated by only changing the parameter values for the retardation within the RIP input deck (KDALL.RP). No modifications to the pathway lengths were required. The layer thicknesses are the same as presented for the base case in Table 1, however, the retardation for all radionuclides was set to 1.0 for each layer.

The base-case and the three modified models were simulated with results generated for a single-realization expected-value dose to man at the accessible environment at time frames of 10,000 years, 100,000 years, and 1,000,000 years. A CCDF plot of dose to man at the accessible environment, based on 100 realizations, was also conducted for time frames of 10,000 years and 100,000 years.

### 3.2 MODIFIED pH SCENARIO

The second pH scenario consisted of taking the three previously modified cases (KD\*.RP) and incorporating the increased pH value within the waste package. The modifications consisted of increasing the standard temperature pH to 11, and by specifying that the solubility limits of Americium, Neptunium, and Plutonium were defined by the coded function CAMSOL, CNPSOL, and CPUSOL, respectively. The coded functions specify that the solubility limits of these radionuclides depend on the pH of the water infiltrating through the repository.

The three modified models (PK10.RP, PK100.RP, and PKALL.RP) were simulated to show the single-realization expected-value dose to man at the accessible environment at time frames of 10,000 years, 100,000 years, and 1,000,000 years. A CCDF plot of dose to man at the accessible environment, based on 100 realizations, was also conducted for time frames of 10,000 years and 100,000 years.

## 4. RESULTS

The simulation results generated from the base-case model and the six modified models are included at the end of this report as plots of dose to man, measured at the accessible environment, versus time, and as CCDF plots of probability of exceeding versus peak dose to man measured at the accessible environment. This section will present the results from the individual models. Section 5 will present comparisons of the results and discuss the major points and observations obtained from this study.

### 4.1 EXPECTED-VALUE SINGLE-REALIZATION SIMULATIONS

#### 4.1.1 10,000 years

The results presented for a time frame of 10,000 years were generated from the RIP input files used to simulate a total time of 100,000 years. The 100,000 year simulations were run with 1000 timesteps at 100 years per time step. Therefore, the plots for 10,000 years present the first 100 data points of the total 1000 data point file generated over 100,000 years.

The single-realization expected-value plots of dose to man, measured at the accessible environment, over 10,000 years are presented in Figures 4.1.1-1 through 4.1.1-7 for the base case and the six modified cases, respectively. These results show that the non-retarded radionuclides ( $^{129}\text{I}$ ,  $^{99}\text{Tc}$ , and  $^{14}\text{C}$ ) are the primary dose contributors with dose greater than  $1\text{E-}8$  rem/yr. The modified pH scenario plots show  $^{237}\text{Np}$  dose greater than  $1\text{E-}8$  rem/yr for all cases. For the case where there is no retardation within the entire column, Figures 4.1.1-4 and 4.1.1-7 show that  $^{237}\text{Np}$ ,  $^{233}\text{U}$ , and  $^{229}\text{Th}$  also contribute to the dose above  $1\text{E-}8$  rem/yr.

#### 4.1.2 100,000 years

The single-realization expected-value plots of dose to man, measured at the accessible environment, over 100,000 years are presented in Figures 4.1.2-1 through 4.1.2-7 for the base case and the six modified cases, respectively. For all cases, except the base case and the 10 m  $\text{Kd}=0$  case, the highest dose is contributed by  $^{237}\text{Np}$  over the 100,000 year time frame. For the base case and the 10 m  $\text{Kd}=0$  case, the highest dose is contributed by  $^{129}\text{I}$ .

#### 4.1.3 1,000,000 years

The single-realization expected-value plots of dose to man, measured at the accessible environment, over 1,000,000 years are presented in Figures 4.1.3-1 through 4.1.3-7 for the base case and the six modified cases, respectively. For all cases, except the entire column cases, the peak dose is attributed to  $^{237}\text{Np}$  over the 1,000,000 year time frame. The second highest dose contributor was  $^{229}\text{Th}$ . For both entire column cases, the peak dose was contributed by  $^{135}\text{Cs}$  with  $^{237}\text{Np}$  the second highest dose contributor.

## 4.2 MULTIPLE REALIZATION SIMULATIONS

The input files for the base case and the modified files for the 100 m and the entire column cases were simulated with 100 realizations over time frames of 10,000 and 100,000 years. Separate simulations were conducted for each time frame investigated.

The peak dose results for each of the 100 realizations generated for the simulation of a 10,000 year time frame are presented in Figure 4.2-1. The peak dose results of the 100 realization simulations over a time frame of 100,000 years are presented in Figure 4.2-2.

The CCDF plots in Figures 4.2-1 and 4.2-2 present the peak dose results of 100 realizations for the base case, 100 m case, and the entire column case based on time frames of 10,000 years and 100,000 years, respectively. The 10,000 year results (Figure 4.2-1) show that the base-case model (solid circles) yields the highest peak dose values for greater than 85 percent of the simulations. The results for the initial pH scenario for  $K_d = 0$  for the entire column (open triangles) are identical to the base case. This is due to the peak dose within 10,000 years being primarily from non-retarded radionuclides ( $^{129}\text{I}$ ,  $^{99}\text{Tc}$ ). The results for the initial pH scenario for  $K_d = 0$  for 100 m (open squares) should also be identical to the base case since the non-retarded radionuclide  $^{129}\text{I}$  is the peak dose contributor (Figure 4.1.1-3), but is lower due to the effects of pathway discretization. The two simulations for the modified pH scenario show that for the majority of the simulations, the peak dose values are less than that of the base case.

The results from the 100,000 year simulations for the base case and the four modified cases (Figure 4.2-2) show that the peak dose for each of the modified cases is greater than the base case. The results from the modified pH scenario show higher peak doses for the modified cases, than do the initial pH scenario results. The higher peak dose results are due to decrease in the retardation within the pathways, and the subsequent increase in radionuclide release at the accessible environment. As expected, the results from the "entire column" cases are the highest for the cases presented.

## 5. DISCUSSION

The results from the 10,000 year simulations presented in Section 4.1 are not significantly affected by the  $K_d$  and pH modifications because the significant dose contributors within 10,000 years are the non-retarded radionuclides ( $^{129}\text{I}$ ,  $^{99}\text{Tc}$ , and  $^{14}\text{C}$ ). The dose per radionuclide should not change solely due to setting all retardation values to 1.0. However, the 10,000 year results do show a change in peak dose. This change is attributable to the modification of the pathway lengths when the 10 and 100 m pathways were incorporated into the model. As the new pathways are encountered, the radionuclides are redistributed between the fracture and matrix flow mode. This redistribution of radionuclides has a tendency to delay the arrival time of the radionuclides. Comparison of these results was not presented due to this model effect. This effect is not significant for the 100,000 year results.

The results for the 100,000 year simulations were compared using the  $^{237}\text{Np}$  expected value dose time histories. Figure 5-1 presents the dose due to  $^{237}\text{Np}$  for the base case and the three modified models from the initial pH scenario. The results show that the base case and the 10 m case results are almost identical, therefore, the incorporation of no retardation within 10 m of the repository did not have a significant effect on the results. However, there are significant increases in dose in the 100 m and the entire column case results. The peak dose for the 100 m case increased by over one-half an order-of-magnitude. The peak dose for the entire column case increase by over one-and-a-half orders-of-magnitude from the base case.

Figure 5-2 presents the dose due to  $^{237}\text{Np}$  for the base case and the three modified models from the modified pH scenario. The 10 and 100 m cases resulted in an increase in the peak  $^{237}\text{Np}$  dose by approximately one order-of-magnitude over the base case. The entire column case shows a very significant increase in the peak dose. The peak  $^{237}\text{Np}$  increased by approximately two-and-one-half orders-of-magnitude over the base case. As with the previous entire column case, the magnitude of the  $^{237}\text{Np}$  dose was higher at early time, peaked at approximately 60,000 years, and decreased for the remainder of the simulation due to the depletion of the source term.

Figures 5-3 through 5-5 present a comparison of the base-case model results with those generated from both of the 10 m, 100 m, and the entire column modified cases, respectively. These results show that except for the 10 m case, all of the modified cases yield higher peak doses than the base case and the inclusion of the radionuclide solubility as a function of pH results in the highest  $^{237}\text{Np}$  peak dose values.

Figure 5-6 presents the  $^{237}\text{Np}$  dose time histories over a 1,000,000 year time frame for the base case and the modified case simulations under the initial pH scenario. These results are similar to the 100,000 year results presented in Figure 5-1. The 10 m case is almost identical to the base case and the entire column case has the highest  $^{237}\text{Np}$  peak dose value.

Figure 5-7 presents the  $^{237}\text{Np}$  dose time histories over a 1,000,000 year time frame for the base and modified case simulations under the modified pH scenario. These peak dose results are also similar to the 100,000 year results presented in Figure 5-2. The peak dose for  $^{237}\text{Np}$  is greatest for the entire column case with the 10 and 100 m cases showing similar magnitude of results. Both the 100,000 and 1,000,000 year simulations for the entire column case yields the highest peak  $^{237}\text{Np}$  dose values with the time history curve showing the peak dose within 100,000 years. The 1,000,000 year case shows the  $^{237}\text{Np}$  dose decreasing by several orders of magnitude over the remainder of the simulation with significant climate change effects on the time history curve.

Figures 5-8 through 5-10 present a comparison of the base-case model results with those generated from both of the 10 m, 100 m, and the entire column modified cases, respectively, over a 1,000,000 year time frame. These results show that except for the 10 m case for the initial pH scenario, all of the modified cases yield higher peak doses than the base case and the inclusion of the radionuclide solubility as a function of pH results in the highest  $^{237}\text{Np}$  peak dose values.

Figure 5-11 presents the 1,000,000 year expected-value dose time history for  $^{135}\text{Cs}$  based on the initial pH scenario. The peak dose for  $^{135}\text{Cs}$  is two to three orders-of-magnitude less than  $^{237}\text{Np}$  for the base, 10 and 100 m cases. However, for the entire column case, the peak dose for  $^{135}\text{Cs}$  is approximately two-and-a-half orders-of-magnitude higher than the peak dose for  $^{237}\text{Np}$ . Therefore, decrease in the retardation within the unsaturated zone has a very significant effect on the arrival time for  $^{135}\text{Cs}$  and thus the peak dose to man measured at the accessible environment.

Figures 5-12 and 5-13 present the 1,000,000 year expected-value dose time history for  $^{239}\text{Pu}$  based on the initial and the modified pH scenarios, respectively. Figures 5-14 and 5-15 present similar results for  $^{242}\text{Pu}$ . The peak dose values for both of the plutonium isotopes ( $^{239}\text{Pu}$ , and  $^{242}\text{Pu}$ ) were within about one-half an order-of-magnitude of each other for the base case and all modified cases. However, the time at which the peak dose occurred and the overall shape of the time history curves are significantly different between the two isotopes. The results from the modified pH scenario (Figures 5-13 and 5-15) show that the peak dose values for both  $^{239}\text{Pu}$  and  $^{242}\text{Pu}$  increased by about 1.0 to 2.5 orders-of-magnitude relative to the initial pH case (Figures 5-12 and 5-14).

Table 1. Base-Case Layer and Column Thicknesses

Unsaturated-Zone Column	Geologic Unit	Layer Thickness (m)	Total Column Thickness (m)
1	TSw	105	344
	TSv	8	
	CHnv	92	
	CHnz	24	
	PPw	115	
2	TSw	176	344
	TSv	8	
	CHnv	72	
	CHnz	50	
	PPw	38	
3	TSw	87	358
	TSv	8	
	CHnv	105	
	CHnz	32	
	PPw	126	
4	TSw	147	360
	TSv	8	
	CHnv	87	
	CHnz	57	
	PPw	61	
5	TSw	35	372
	TSv	7	
	CHnv	132	
	CHnz	40	
	PPw	158	
6	TSw	113	370
	TSv	7	
	CHnv	102	
	CHnz	43	
	PPw	105	

Table 2. Base-Case Expected-Value Retardation Factors for each Chemical Element Group per Geologic Layer

Chemical Element Group	Geologic Layer					Chemical Group Elements
	TSw	TSv	CHv	CHz	PPW	
1	17603	12616	3386	3228	6116	Ac227, Am241, Am242m, Am243, Cm244, Cm245, Cm246, Nb93m, Mb94, Sm151, Th 229, Th230, Th232, Zr93
2	8551	1735	466.5	16139	2996	Cs135
3	1677	1577	424.2	587.8	588.2	Ni59, Ni63, Pd107
4	17.76	32.54	9.464	3.934	6.872	Np237
5	839.2	1578	424.2	294.4	294.6	Pa231
6	5030	9462	2540	17.1	1762	Pb210
7	1677	3155	847.4	587.8	588.2	Pu238, Pu239, Pu242, Pu241, Pu242
8	5030	2366	635.8	17606	1762	Ra226, Ra228
9	1745	3470	932.1	1174	646.9	Sn126
10	34.53	32.53	9.464	42.08	12.74	U233, U234, U235, U236, U238
11	1	1	1	1	1	C14
12	1	1	1	1	1	C136, I129, Tc99
13	51.29	95.61	26.39	12.74	18.61	Se79

Att. II

Table 3. Layer Thicknesses for the  $K_d = 0$  for 10 m Modified Case

Unsaturated-Zone Column	(a) Geologic Unit	(b) Layer Thickness (m)	Total Column Thickness (m)
1	TSw-1	10	344
	TSw-2	95	
	TSv	8	
	CHnv	92	
	CHnz	24	
	PPw	115	
2	TSw-1	10	344
	TSw-2	166	
	TSv	8	
	CHnv	72	
	CHnz	50	
	PPw	38	
3	TSw-1	10	358
	TSw-2	77	
	TSv	8	
	CHnv	105	
	CHnz	32	
	PPw	126	
4	TSw-1	10	360
	TSw-2	137	
	TSv	8	
	CHnv	87	
	CHnz	57	
	PPw	61	
5	TSw-1	10	372
	TSw-2	25	
	TSv	7	
	CHnv	132	
	CHnz	40	
	PPw	158	
6	TSw-1	10	370
	TSw-2	103	
	TSv	7	
	CHnv	102	
	CHnz	43	
	PPw	105	

(a) shaded area denotes modified layers

(b) shaded area denotes layers with  $K_d = 0$

Table 4. Layer Thicknesses for the  $K_d = 0$  for 100 m Modified Case

Unsaturated-Zone Column	(a) Geologic Unit	(b) Layer Thickness (m)	Total Column Thickness (m)
1	TSw-1	100	344
	TSw-2	5	
	TSv	8	
	CHnv	92	
	CHnz	24	
	PPw	115	
2	TSw-1	100	344
	TSw-2	76	
	TSv	8	
	CHnv	72	
	CHnz	50	
	PPw	38	
3	TSw	87	358
	TSv	8	
	CHnv-1	5	
	CHnv-2	100	
	CHnz	32	
	PPw	126	
4	TSw-1	100	360
	TSw-2	47	
	TSv	8	
	CHnv	87	
	CHnz	57	
	PPw	61	
5	TSw	35	372
	TSv	7	
	CHnv-1	58	
	CHnv-2	74	
	CHnz	40	
	PPw	158	
6	TSw-1	100	370
	TSw-2	13	
	TSv	7	
	CHnv	102	
	CHnz	43	
	PPw	105	

(a) shaded area denotes modified layers

(b) shaded area denotes layers with  $K_d = 0$

Att. II

BASEVDAE.GRF  
85IDAE.DAT  
85TCDAE.DAT  
85NPDAE.DAT  
85THDAE.DAT  
85CDAE.DAT  
85U3DAE.DAT  
09/11/96

10,000 yr Expected-Value Dose History  
'BASE' Case (83E5.RP)  
83/yes/hlq/clime/drips on WP

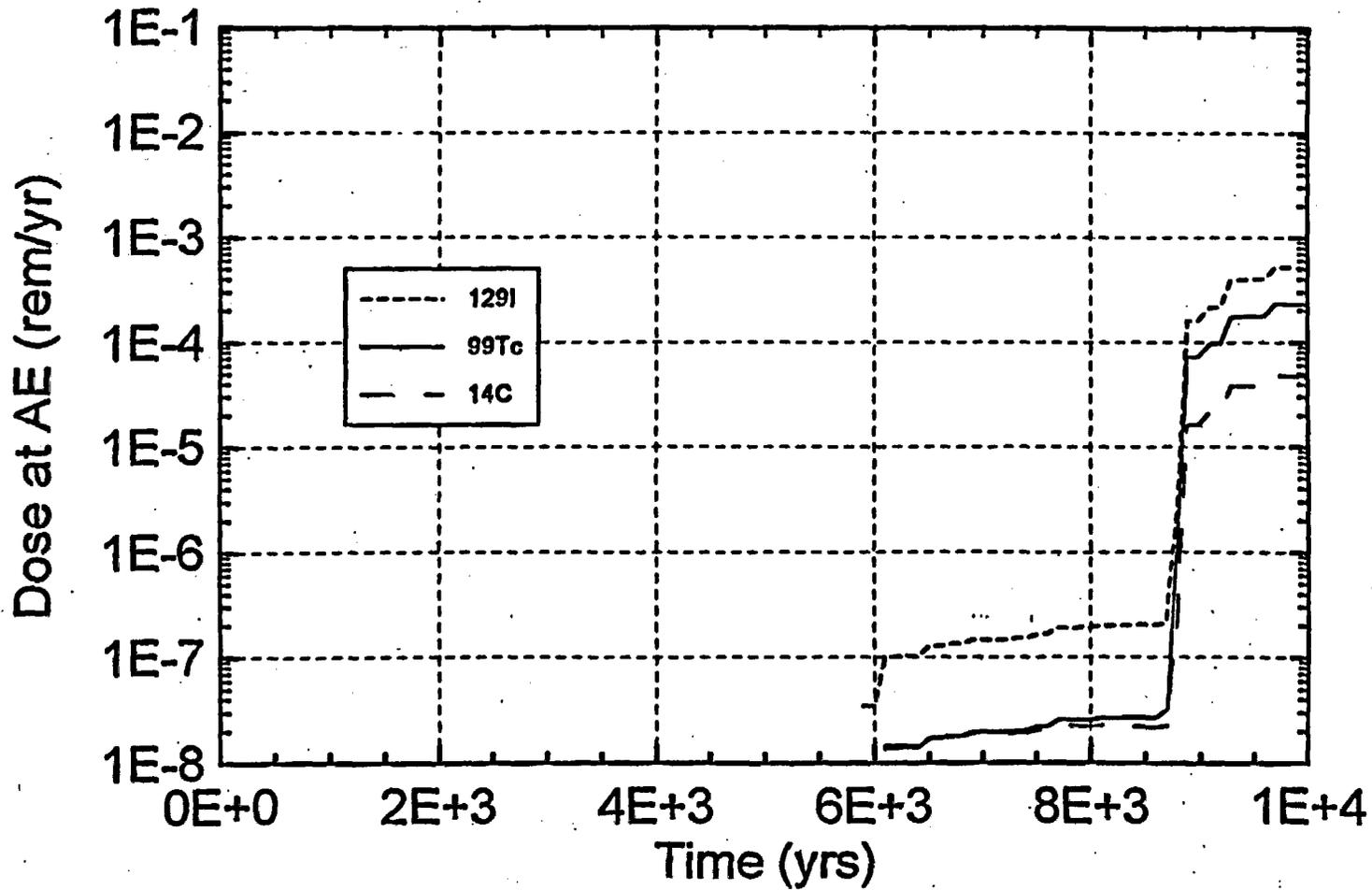


Figure 4.1.1-1 Expected-value dose time history for the base-case model over 10,000 years.

BVDAE.GRF  
B5IDAE.DAT  
B5TCDAE.DAT  
B5NPDAE.DAT  
B5THDAE.DAT  
B5CDAE.DAT  
B5U3DAE.DAT  
09/11/96

10,000 yr Expected-Value Dose History  
Kd = 0 for 10 m (KD101E5.RP)  
83/yes/hlq/clime/drips on WP

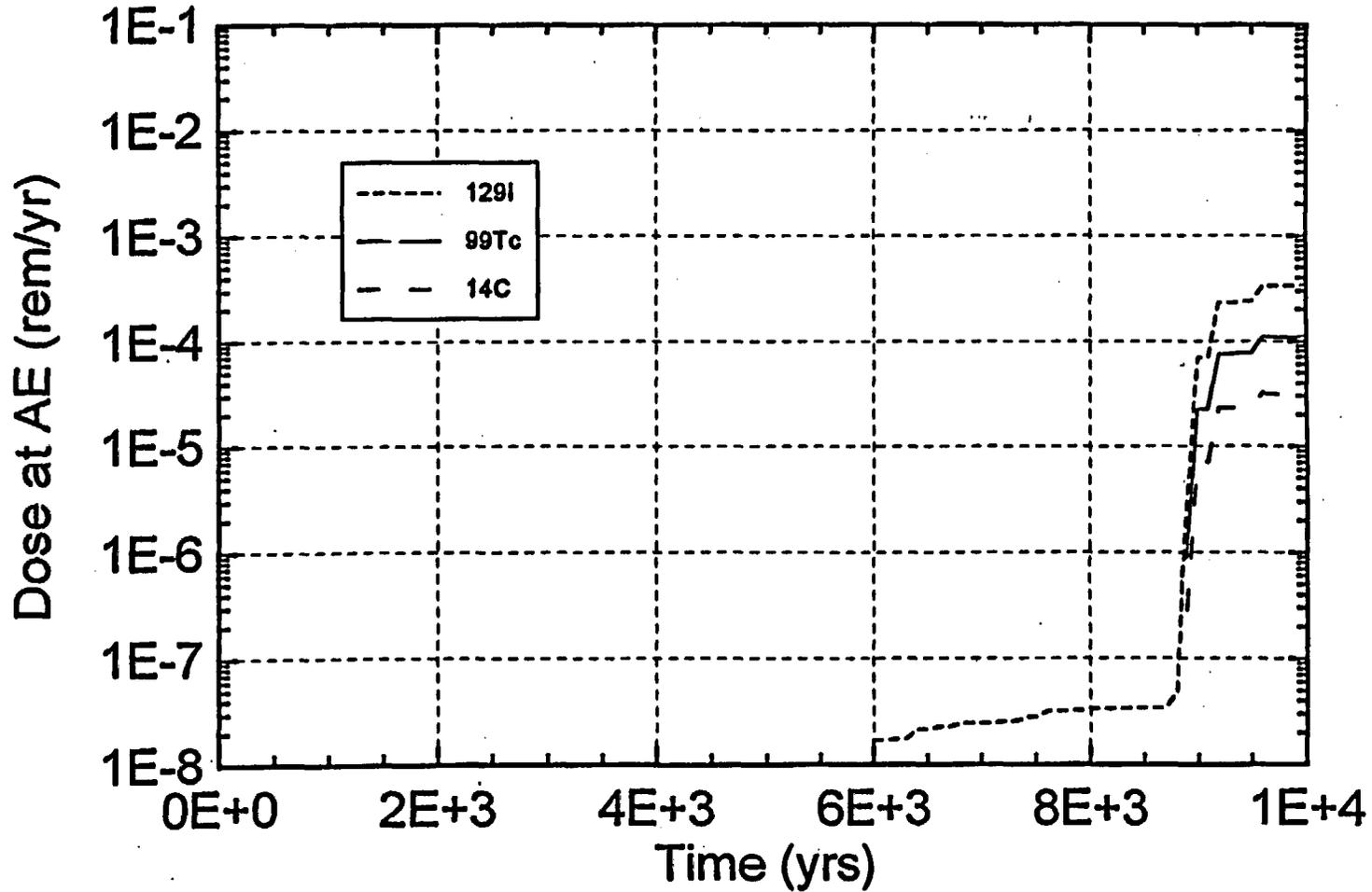


Figure 4.1.1-2 Expected-value dose time history for the  $K_d = 0$  for 10 m and the initial pH scenario over 10,000 years.

CVDAE.GRF  
C5NPDAE.DAT  
C5IDAE.DAT  
C5TCDAE.DAT  
C5THDAE.DAT  
C5U3DAE.DAT  
C5CDAE.DAT  
09/11/96

10,000 yr Expected-Value Dose History  
Kd = 0 for 100 m (KD1001E5.RP)  
83/yes/hq/clime/drips on WP

Att. II

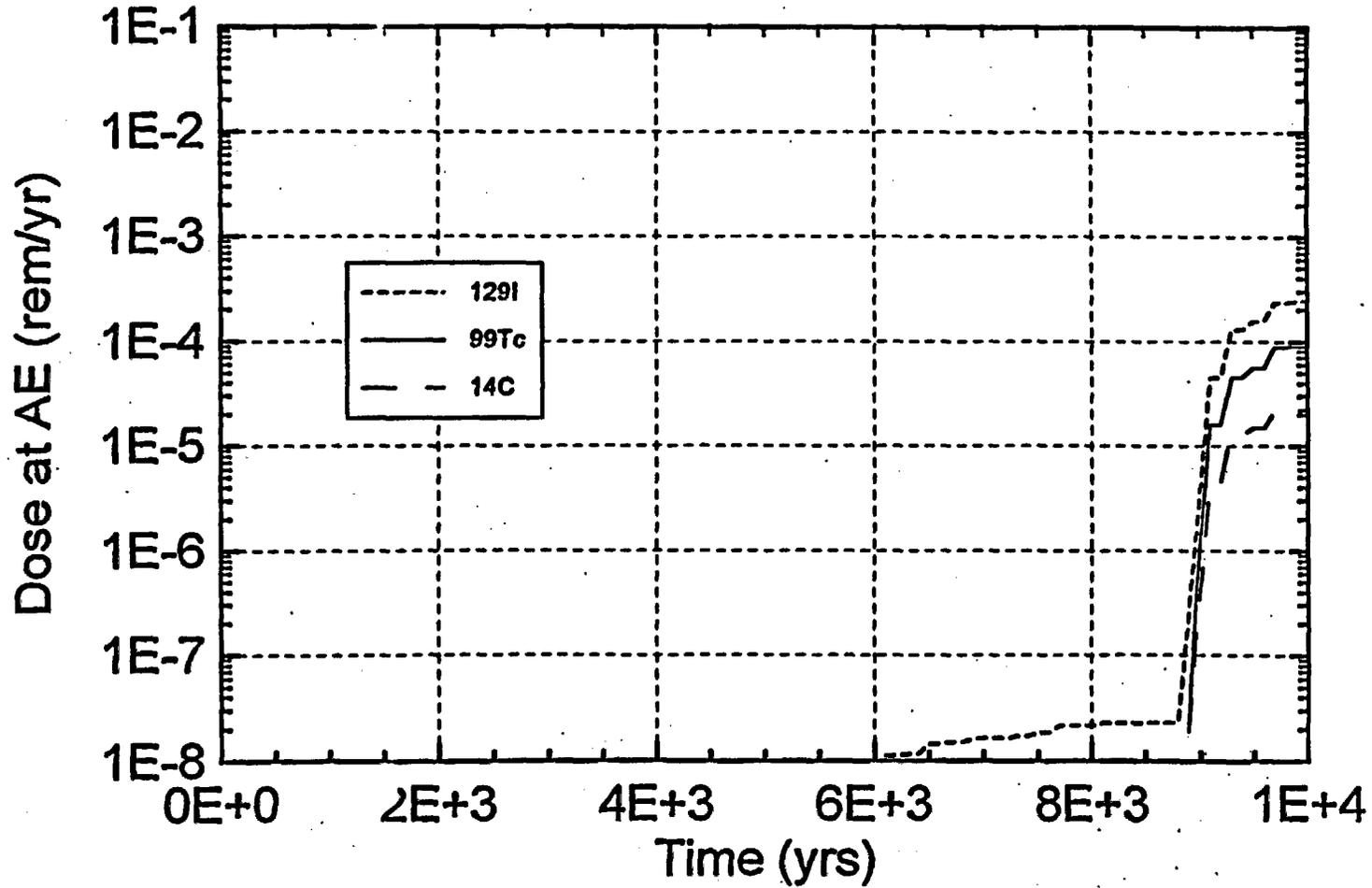


Figure 4.1.1-3 Expected-value dose time history for the Kd = 0 for 100 m and the initial pH scenario over 10,000 years.

DVDAE.GRF  
D5NPDAE.DAT  
D5TCPDAE.DAT  
D5IDAE.DAT  
D5TCDAE.DAT  
D5ACDAE.DAT  
D5PDAE.DAT  
09/11/96

10,000 yr Expected-Value Dose History  
Kd = 0 for Entire Column (KDALL1E5.RP)  
83/yes/hiq/clime/drips on WP

Att. II

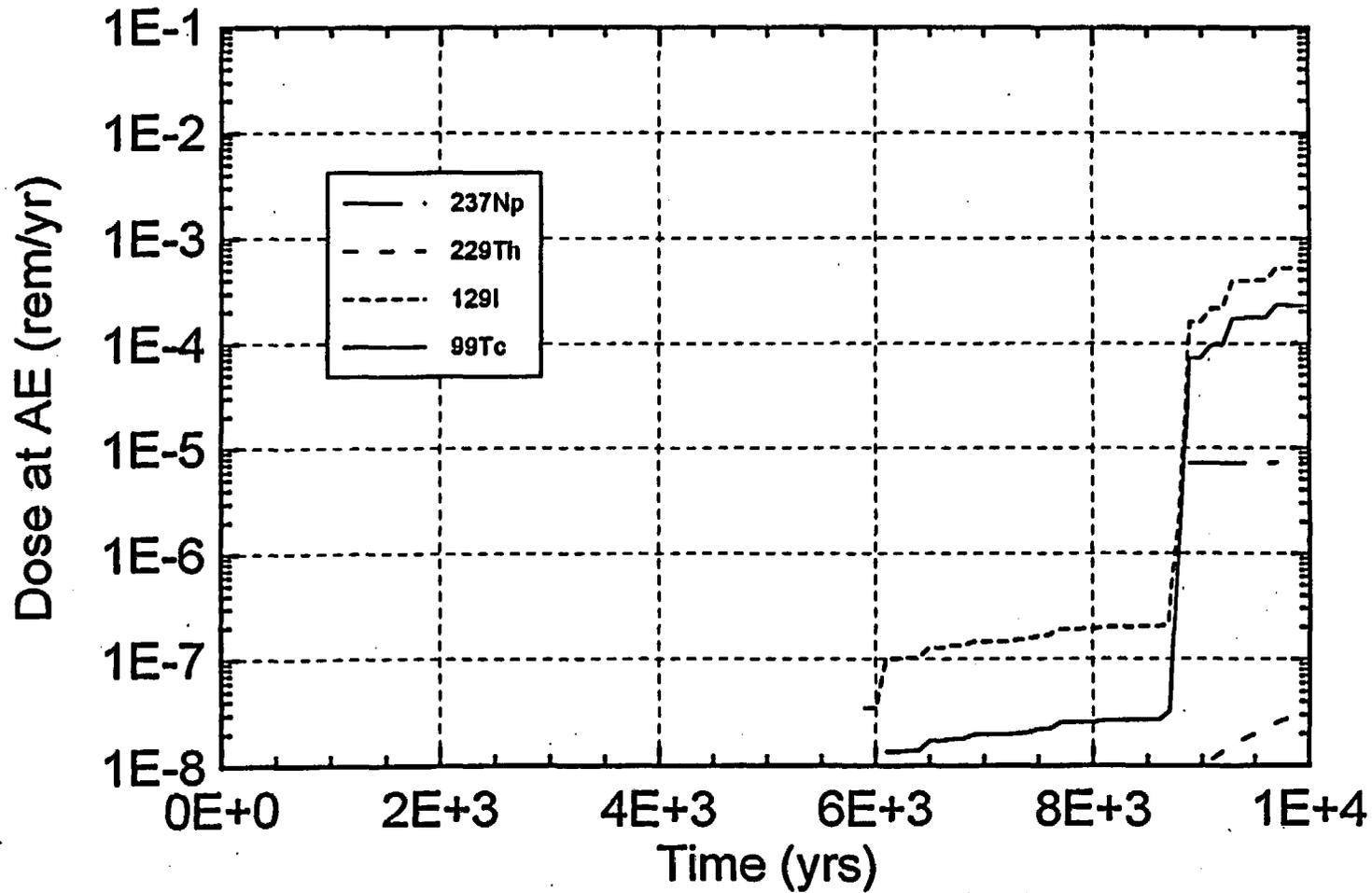


Figure 4.1.1-4 Expected-value dose time history for the Kd = 0 for entire column and the initial pH scenario over 10,000 years

QVDAE.GRF  
Q5NPDAE.DAT  
Q5IDAE.DAT  
Q5TCDAE.DAT  
Q5THDAE.DAT  
Q5U3DAE.DAT  
Q5CDAE.DAT  
09/27/86

10,000 yr Expected-Value Dose History  
SOL = f(pH = 11); Kd = 0 for 10 m (PK101E5.RP)  
83/yes/hlq/clme/drips on WP

Attachment II

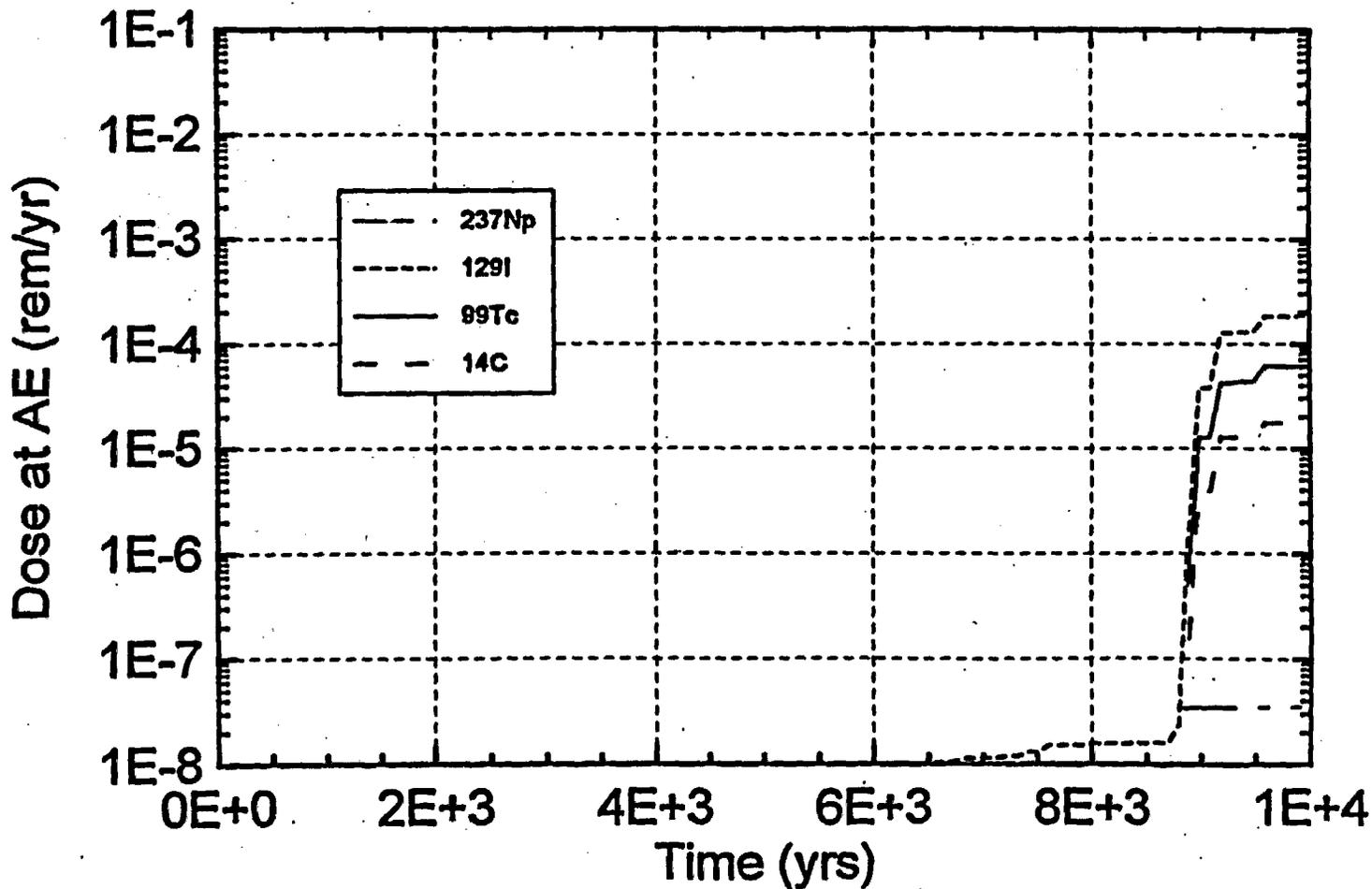


Figure 4.1.1-5 Expected-value dose time history for the  $K_d = 0$  for 10 m and the modified pH scenario over 10,000 years.

RVDAE.GRF  
R5NPIDAE.DAT  
R5IDAE.DAT  
R5TCDAE.DAT  
R5THDAE.DAT  
R5U3DAE.DAT  
R5CDAE.DAT  
09/27/96

10,000 yr Expected-Value Dose History  
SOL = f(pH = 11); Kd = 0 for 100 m (PK1001E5.RP)  
83/yes/hiq/clime/drips on WP

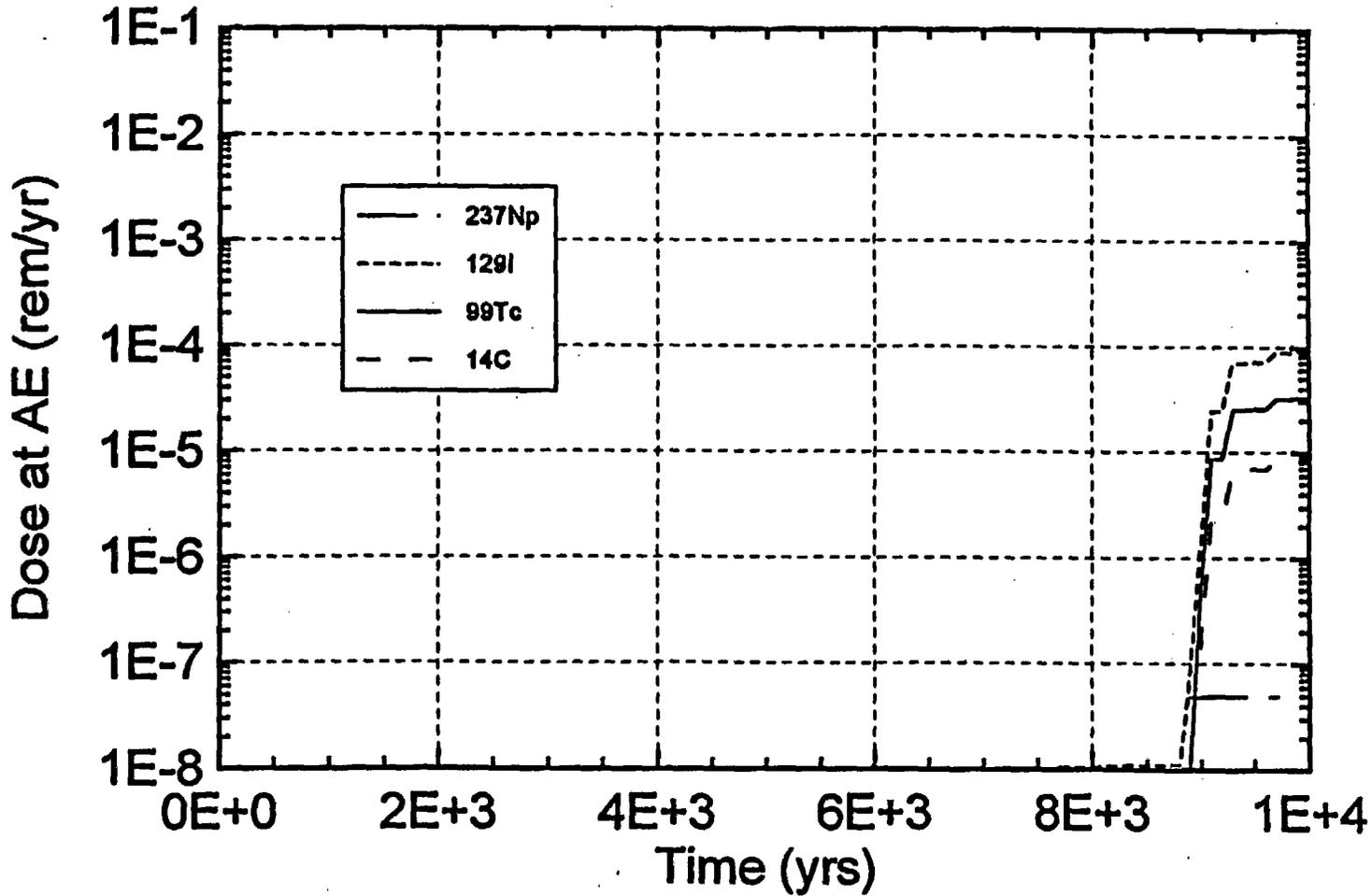


Figure 4.1.1-6 Expected-value dose time history for the ( 0 for 100 m and the modified pH scenario over 10,000 ye(

SVDAE.GRF  
S5NPDAE.DAT  
S5THDAE.DAT  
S5P39DAE.DAT  
S5U3DAE.DAT  
S5IDA.E.DAT  
S5TCDAE.DAT  
09/27/96

10,000 yr Expected-Value Dose History  
SOL = f(pH = 11); Kd = 0 for Entire Column (PKALL1E5.RP)  
83/yes/hlq/clme/drips on WP

Att. II

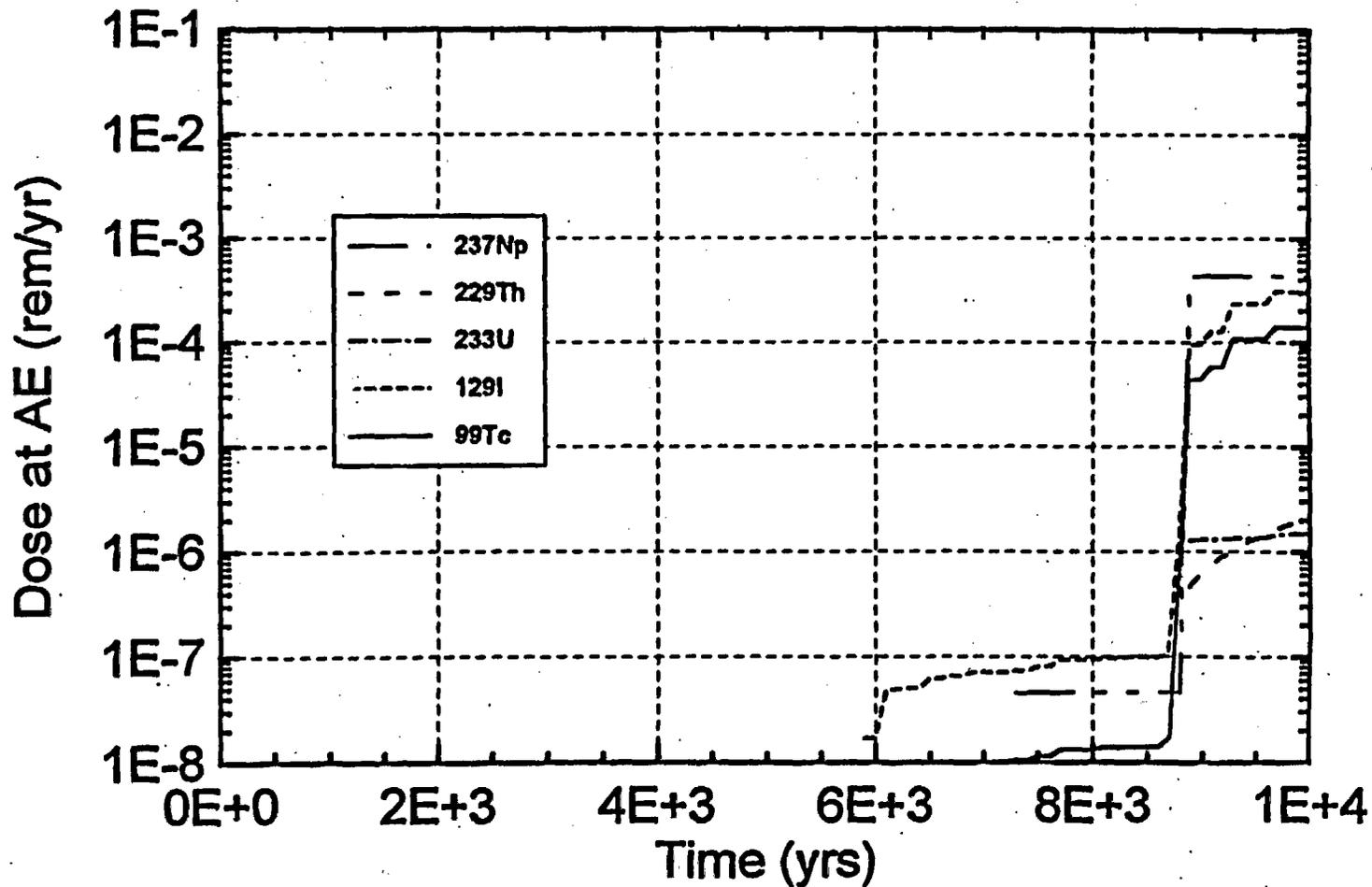


Figure 4.1.1-7 Expected-value dose time history for the Kd = 0 for entire column and the modified pH scenario over 10,000 years.

BASE5DAE.GRF  
851DAE.DAT  
85TCDAE.DAT  
85NPDAE.DAT  
85THDAE.DAT  
85CDAE.DAT  
85U3DAE.DAT  
09/11/96

100,000 yr Expected-Value Dose History  
'BASE' Case (83E5.RP)  
83/yes/hiq/clime/drips on WP

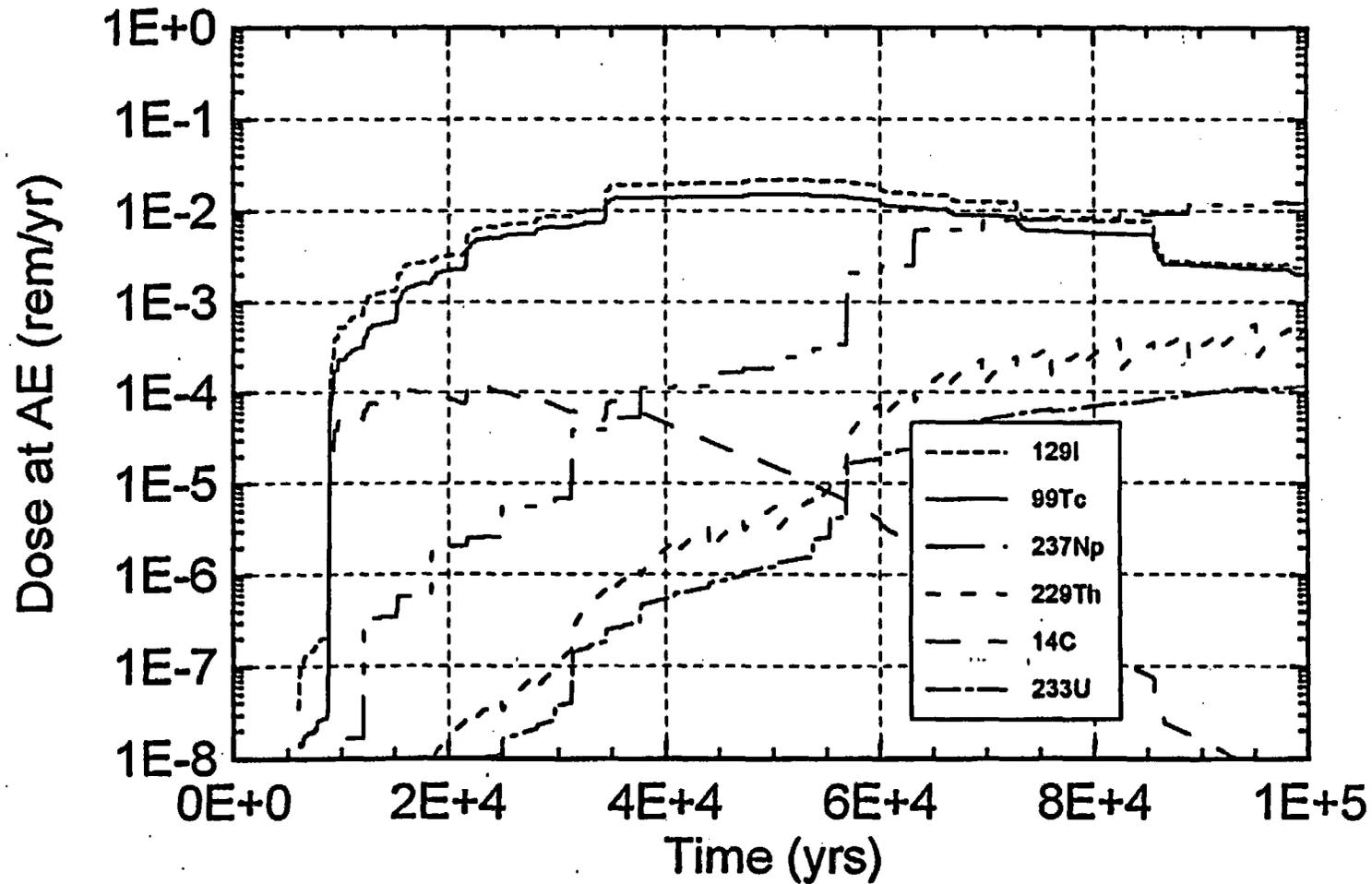


Figure 4.1.2-1 Expected-value dose time history for the base-case model over 100,000 years.

B5DAE.GRF  
B5IDAE.DAT  
B5TCDAE.DAT  
B5NPDAE.DAT  
B5THDAE.DAT  
B5CDAE.DAT  
B5U3DAE.DAT  
09/11/96

100,000 yr Expected-Value Dose History  
Kd = 0 for 10 m (KD101E5.RP)  
83/yes/hlq/clime/drips on WP

Att. II

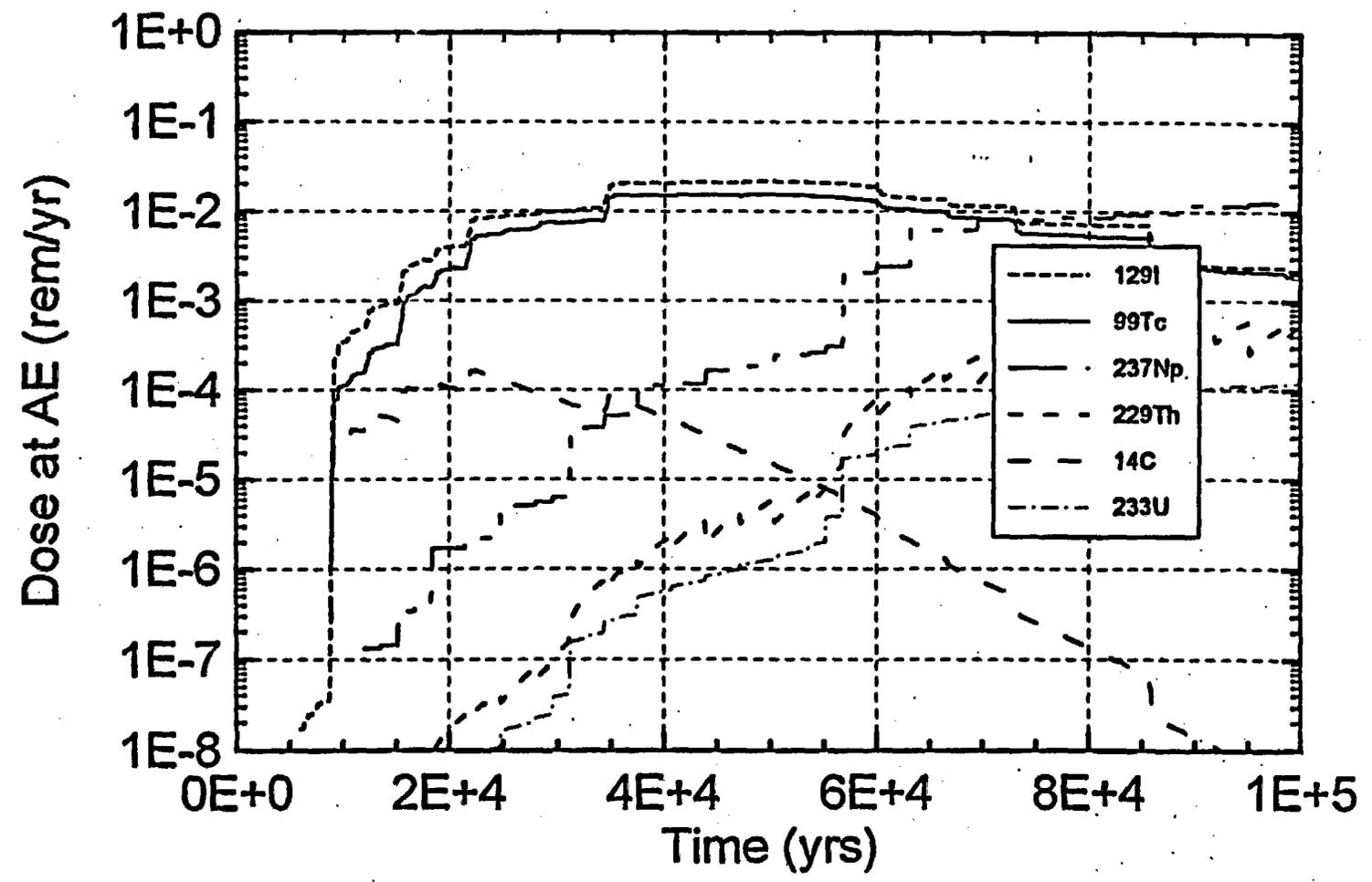


Figure 4.1.2-2 Expected-value dose time history for the Kd = 0 for 10 m and the initial pH scenario over 100,000 years.

C5DAE.GRF  
C5NPDAE.DAT  
C5IDAE.DAT  
C5TCDAE.DAT  
C5THDAE.DAT  
C5U3DAE.DAT  
C5CDAE.DAT  
09/11/96

100,000 yr Expected-Value Dose History  
Kd = 0 for 100 m (KD1001E5.RP)  
83/yes/hiq/clime/drips on WP

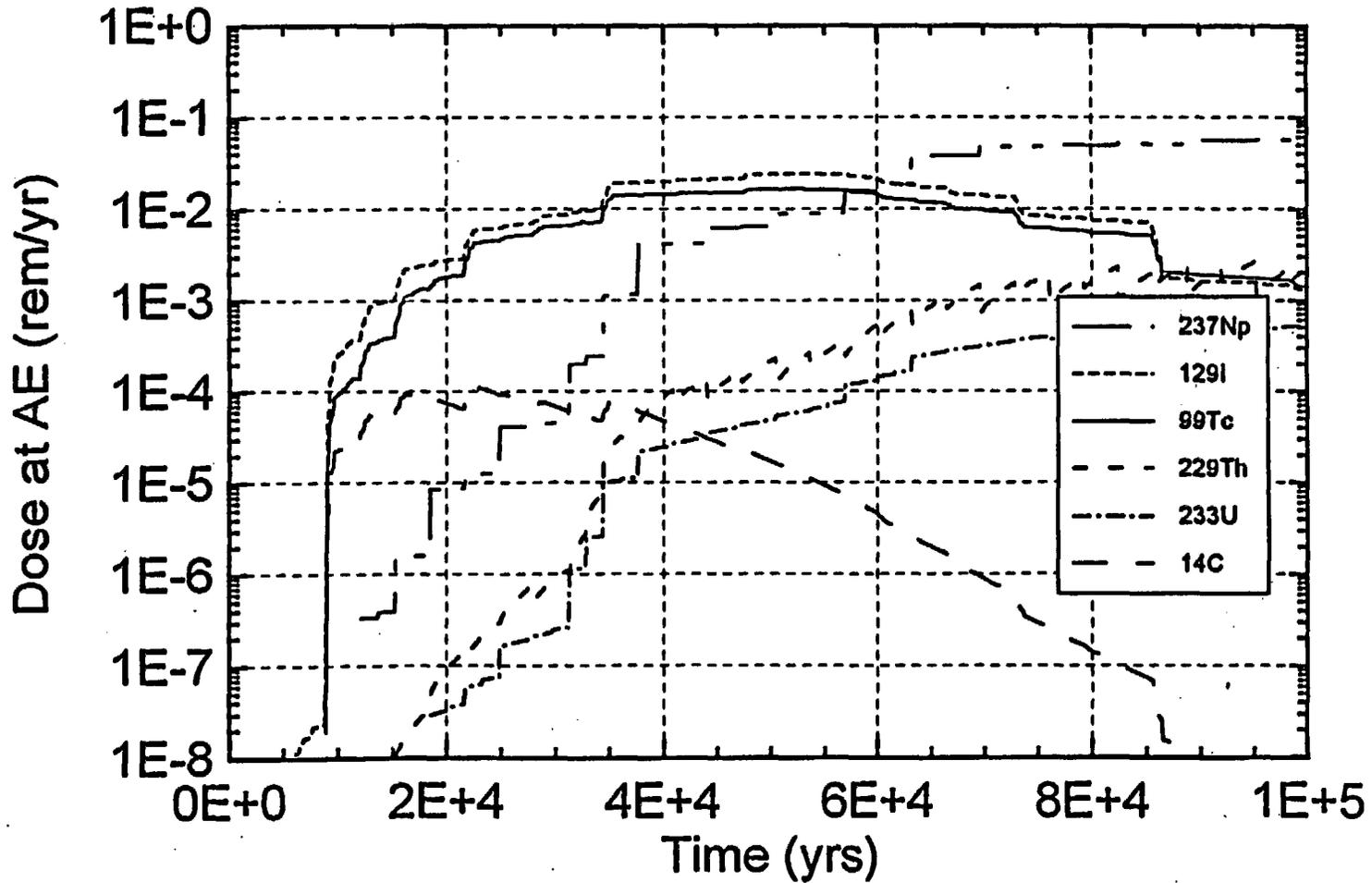


Figure 4.1.2-3 Expected-value dose time history for the Kd = 0 for 100 m and the initial pH scenario over 100,000 year

D5DAE.GRF  
D5NPDAE.DAT  
D5TCPDAE.DAT  
D5IDA.E.DAT  
D5TCDAE.DAT  
D5ACDAE.DAT  
D5PDAE.DAT  
09/11/96

100,000 yr Expected-Value Dose History  
Kd = 0 for Entire Column (KDALL1E5.RP)  
83/yes/hiq/clime/drips on WP

A44. II

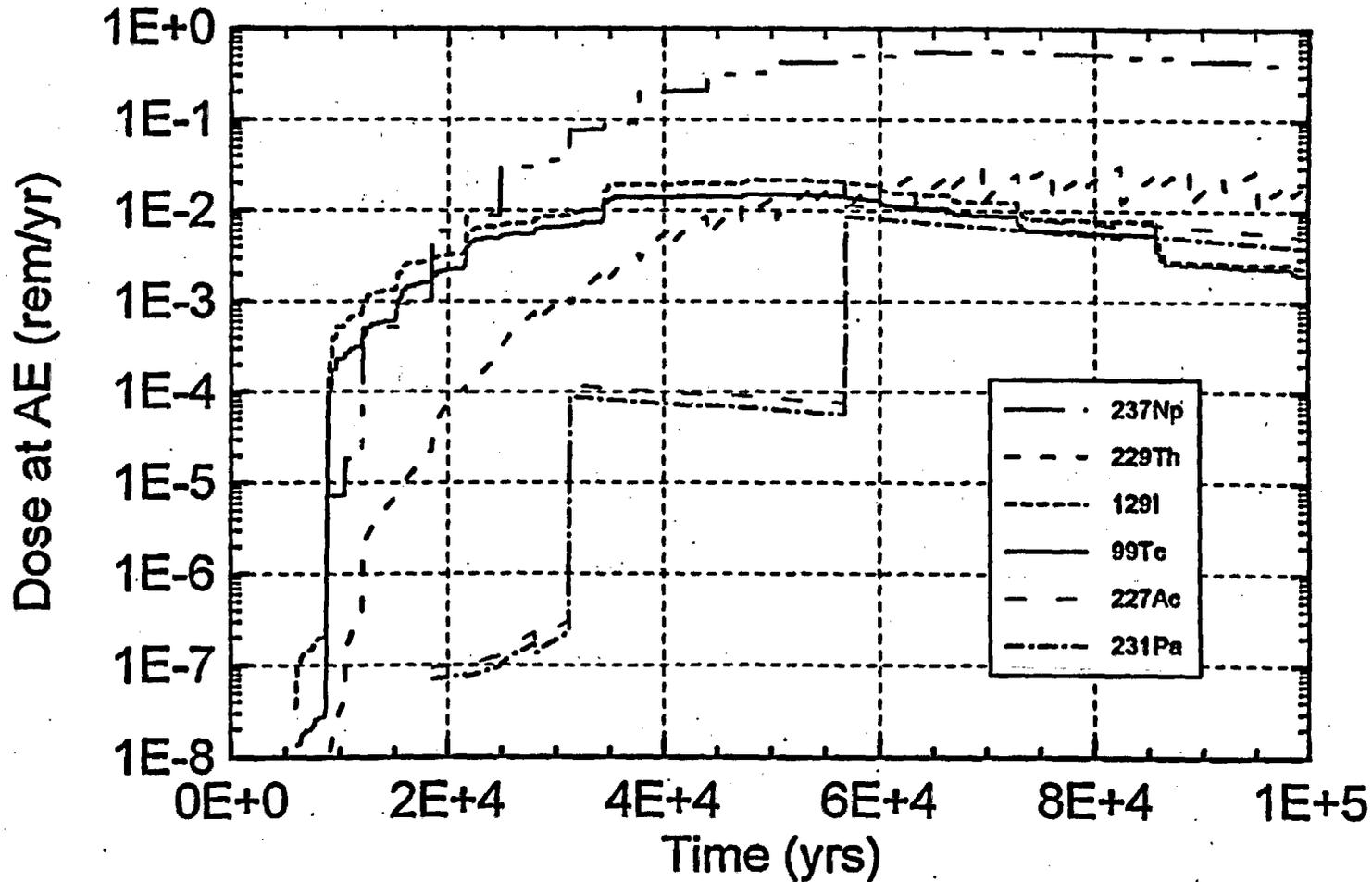


Figure 4.1.2-4 Expected-value dose time history for the Kd = 0 for entire column and the initial pH scenario over 100,000 years.

Q5DAE.GRF  
Q5NPDAE.DAT  
Q5IDAE.DAT  
Q5TCDAE.DAT  
Q5THDAE.DAT  
Q5U3DAE.DAT  
Q5CDAE.DAT  
09/27/96

100,000 yr Expected-Value Dose History  
SOL = f(pH = 11); Kd = 0 for 10 m (PK101E5.RP)  
83/yes/hiq/clime/drips on WP

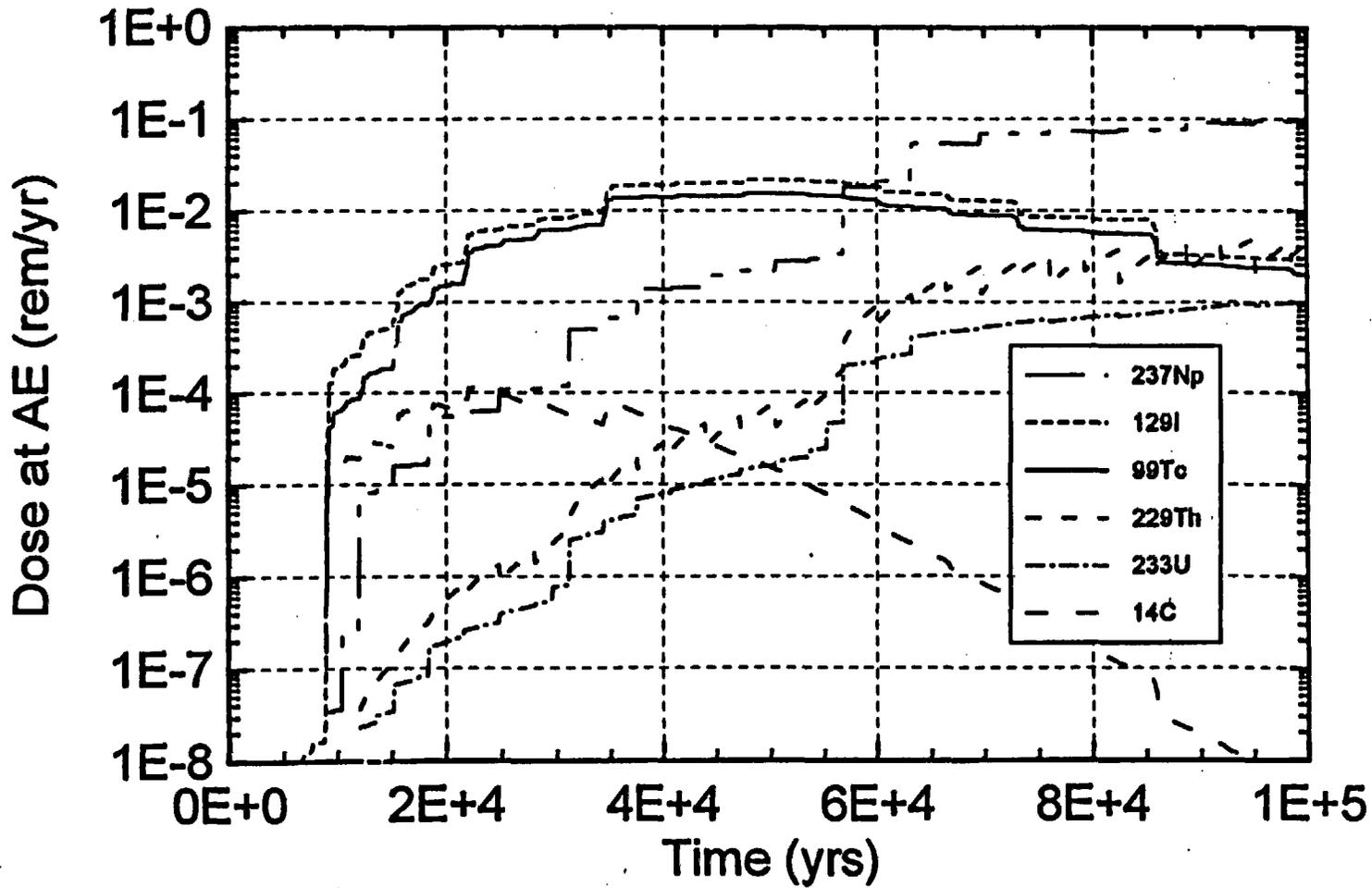


Figure 4.1.2-5 Expected-value dose time history for the  $K_d = 0$  for 10 m and the modified pH scenario over 100,000 years

R5DAE.GRF  
R5NPIDAE.DAT  
R5IDAE.DAT  
R5TCDAE.DAT  
R5THDAE.DAT  
R5U3DAE.DAT  
R5CDAE.DAT  
09/27/96

100,000 yr Expected-Value Dose History  
SOL = f(pH = 11);  $K_d = 0$  for 100 m (PK1001E5.RP)  
83/yes/hlq/clime/drips on WP

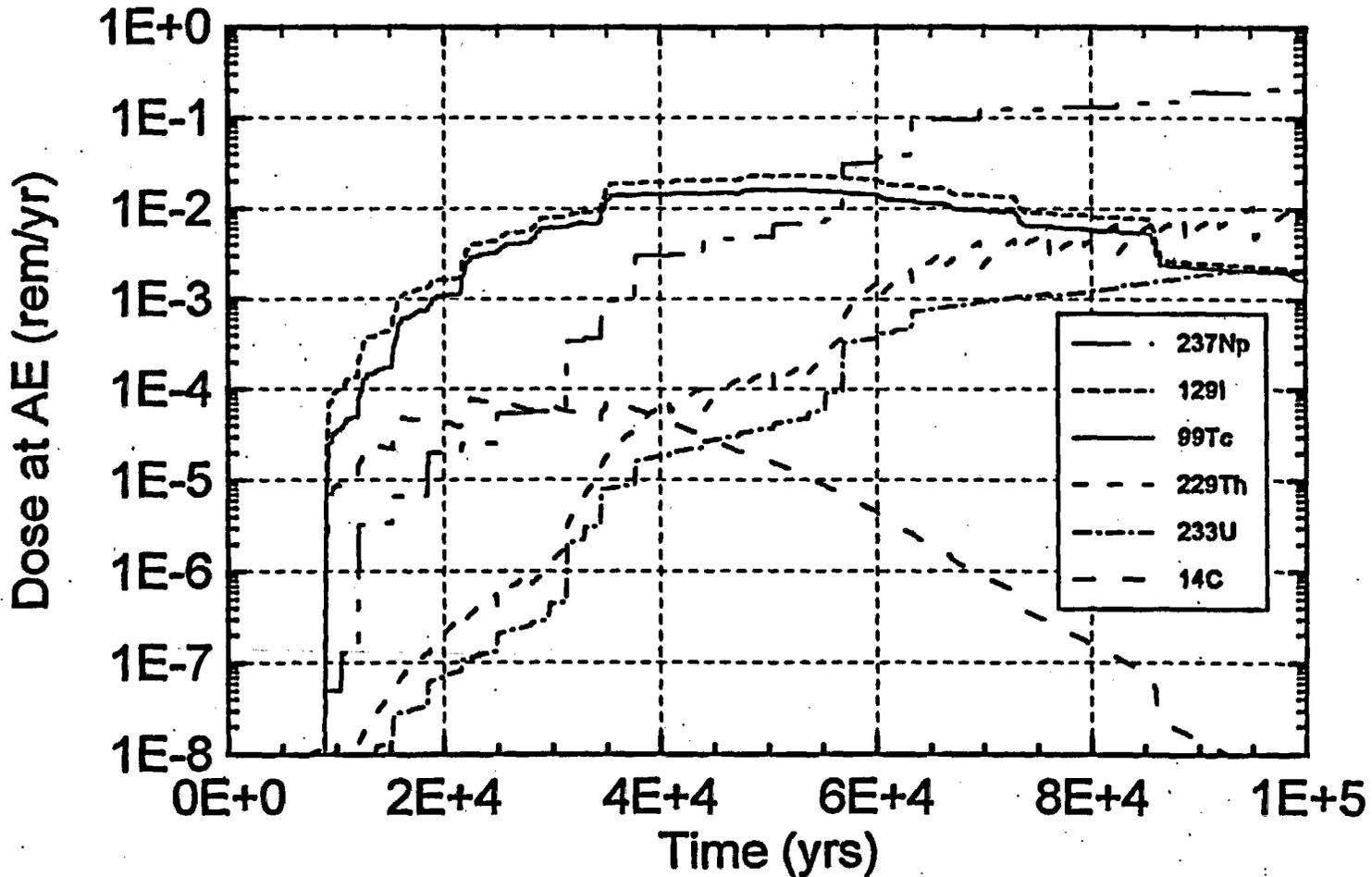


Figure 4.1.2-6 Expected-value dose time history for the  $K_d = 0$  for 100 m and the modified pH scenario over 100,000 years.

S5DAE.GRF  
S5NPDAE.DAT  
S5THDAE.DAT  
S5P39DAE.DAT  
S5U3DAE.DAT  
S5IDA.E.DAT  
S5TCDAE.DAT  
09/27/96

100,000 yr Expected-Value Dose History  
SOL = f(pH = 11); Kd = 0 for Entire Column (PKALL1E5.RP)  
83/yes/hiq/clme/drips on WP

Att. II

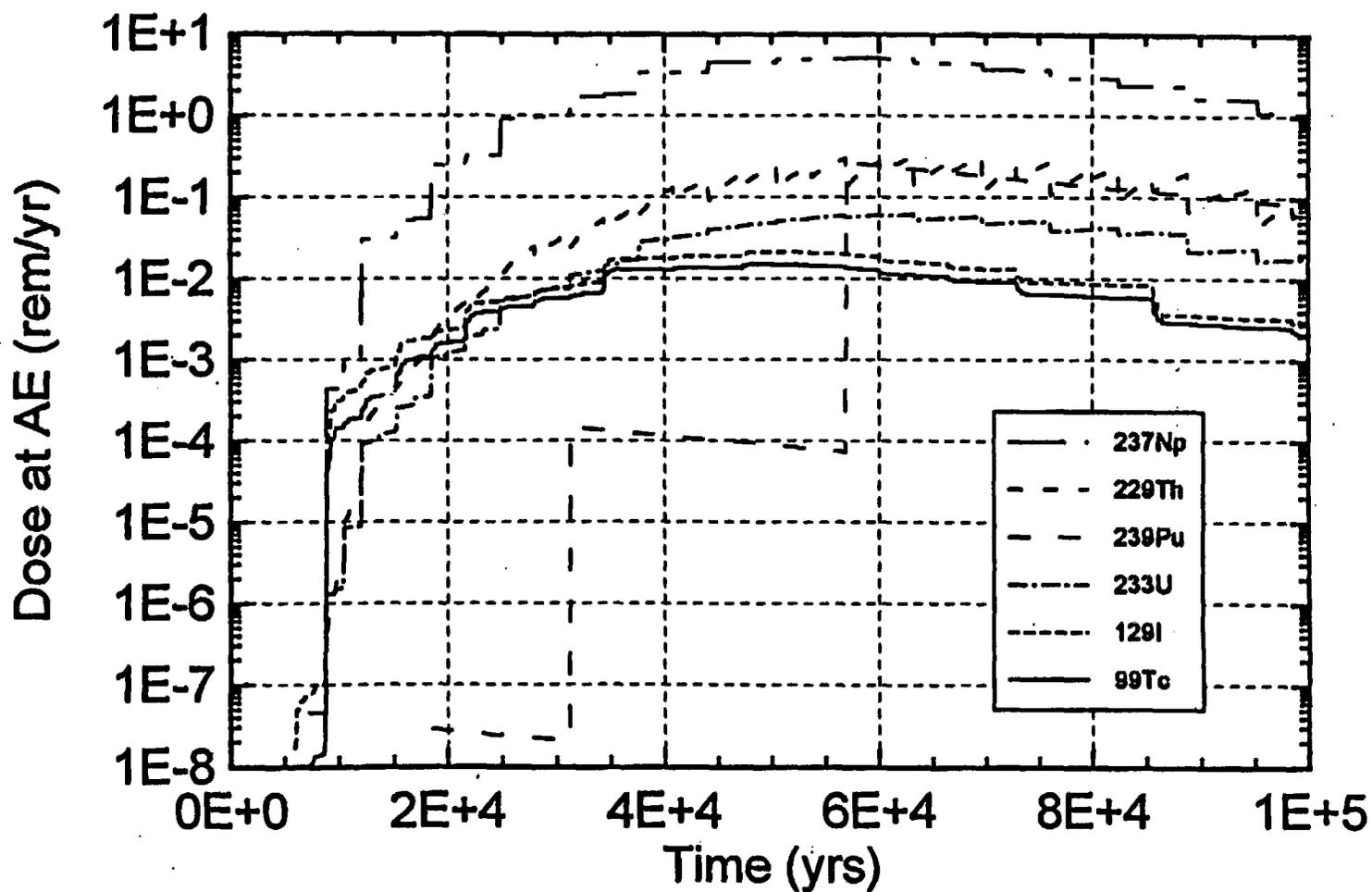


Figure 4.1.2-7 Expected-value dose time history for the Kd = 0 for entire column and the modified pH scenario over 100,000 years.

BASE.GRF  
NP\_BASE.DAT  
TH\_BASE.DAT  
I\_BASE.DAT  
TC\_BASE.DAT  
U\_BASE.DAT  
CS\_BASE.DAT  
09/11/96

1,000,000 yr Expected-Value Dose History  
'BASE' Case (83.RP)  
83/yes/hq/clime/drips on WP

Att. II

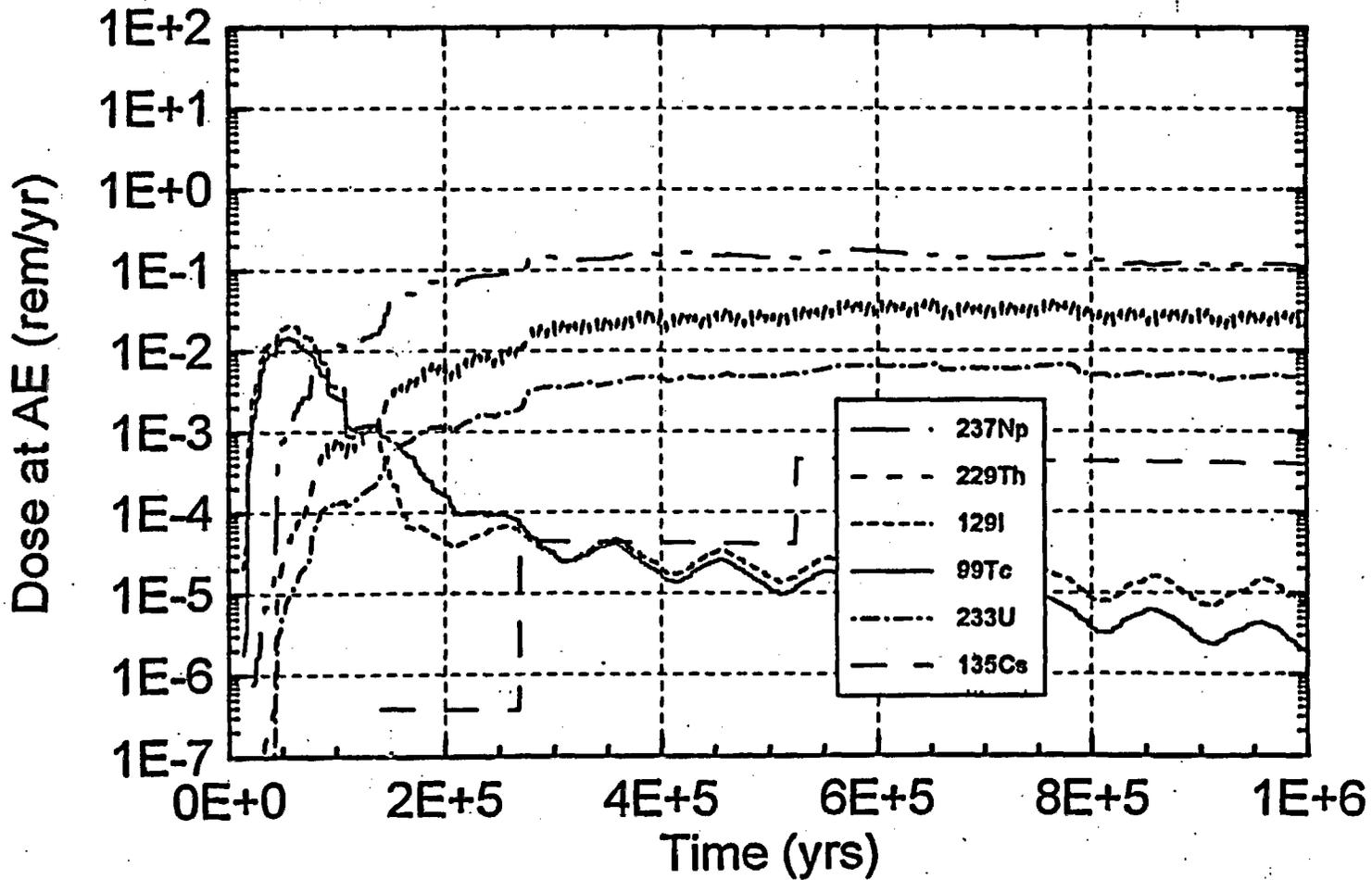


Figure 4.1.3-1 Expected-value dose time history for the base-case model over 1,000,000 years.

KD10DAE.GRF  
BNPDAE.DAT  
BTHDAE.DAT  
BIDAE.DAT  
BTCDAE.DAT  
BU3DAE.DAT  
BCSDAE.DAT  
09/11/96

1,000,000 yr Expected-Value Dose History  
Kd = 0 for 10 m (KD10.RP)  
83/yes/hiq/clime/drips on WP

A.H.  
II

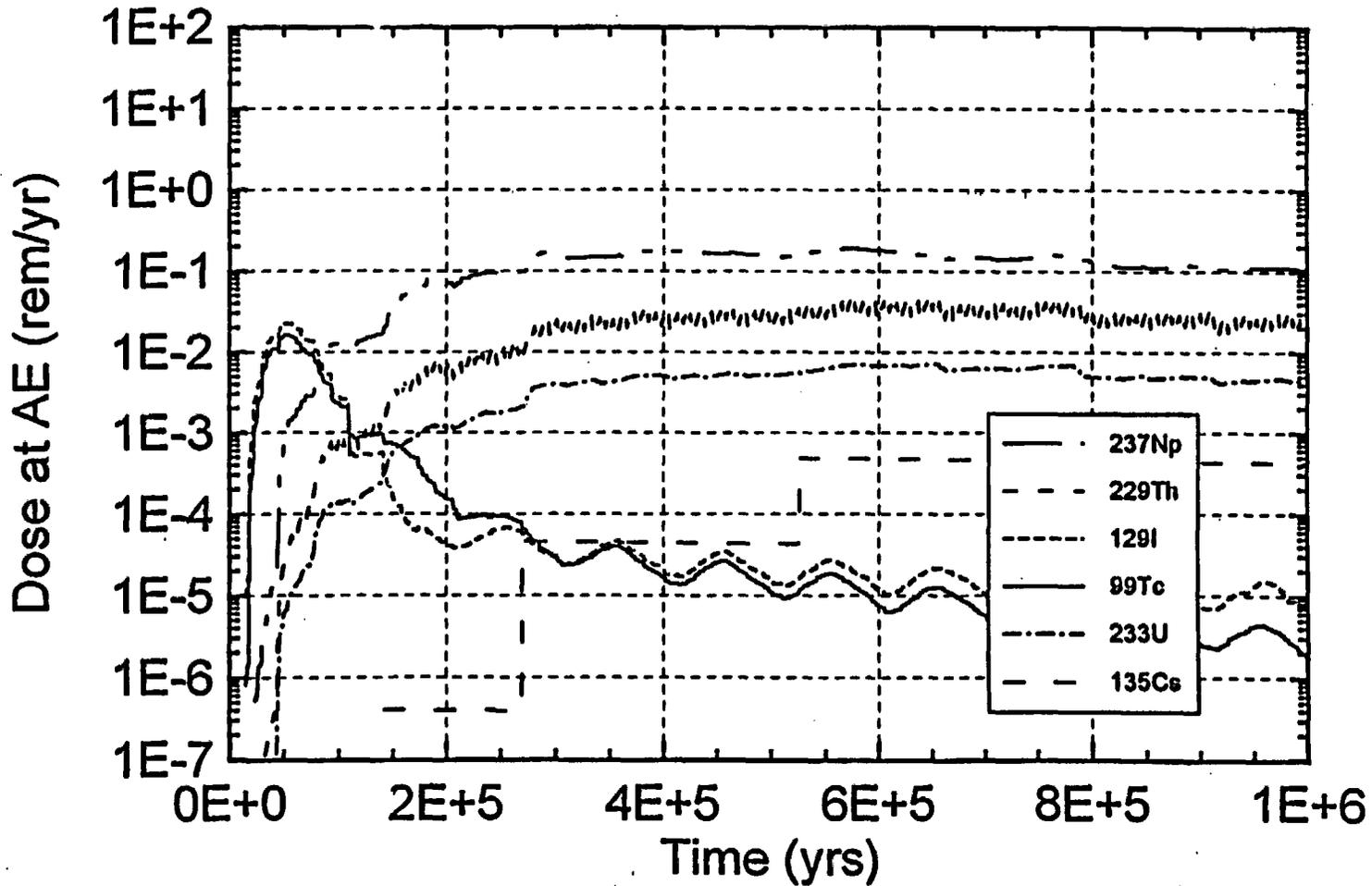


Figure 4.1.3-2 Expected-value dose time history for the  $K_d = 0$  for 10 m and the initial pH scenario over 1,000,000 years.

K100DAE.GRF  
CTCDAE.DAT  
CNPDAE.DAT  
CIDAE.DAT  
CTHDAE.DAT  
CU3DAE.DAT  
CCSDAE.DAT  
09/11/96

1,000,000 yr Expected-Value Dose History  
Kd = 0 for 100 m (KD100.RP)  
83/yes/hlq/clime/drips on WP

Att. II

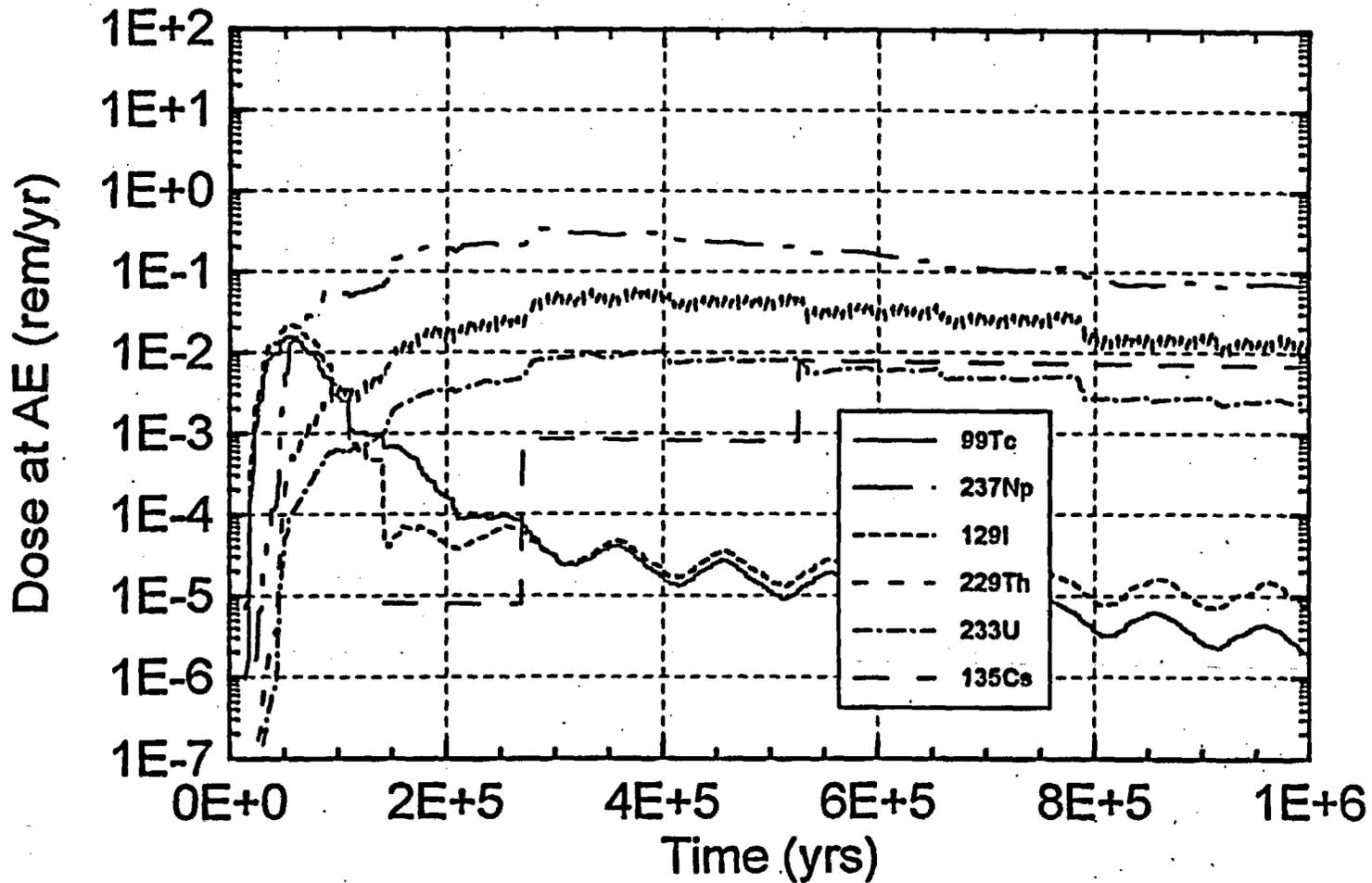


Figure 4.1.3-3 Expected-value dose time history for the Kd = 0 for 100 m and the initial pH scenario over 1,000,000 years.

KALLDAE.GRF  
DCSDAE.DAT  
DNPDAE.DAT  
DTHDAE.DAT  
DACDAE.DAT  
DPADAE.DAT  
DIDAE.DAT  
09/11/96

1,000,000 yr Expected-Value Dose History  
Kd = 0 for Entire Column (KDALL.RP)  
83/yes/hiq/clime/drips on WP

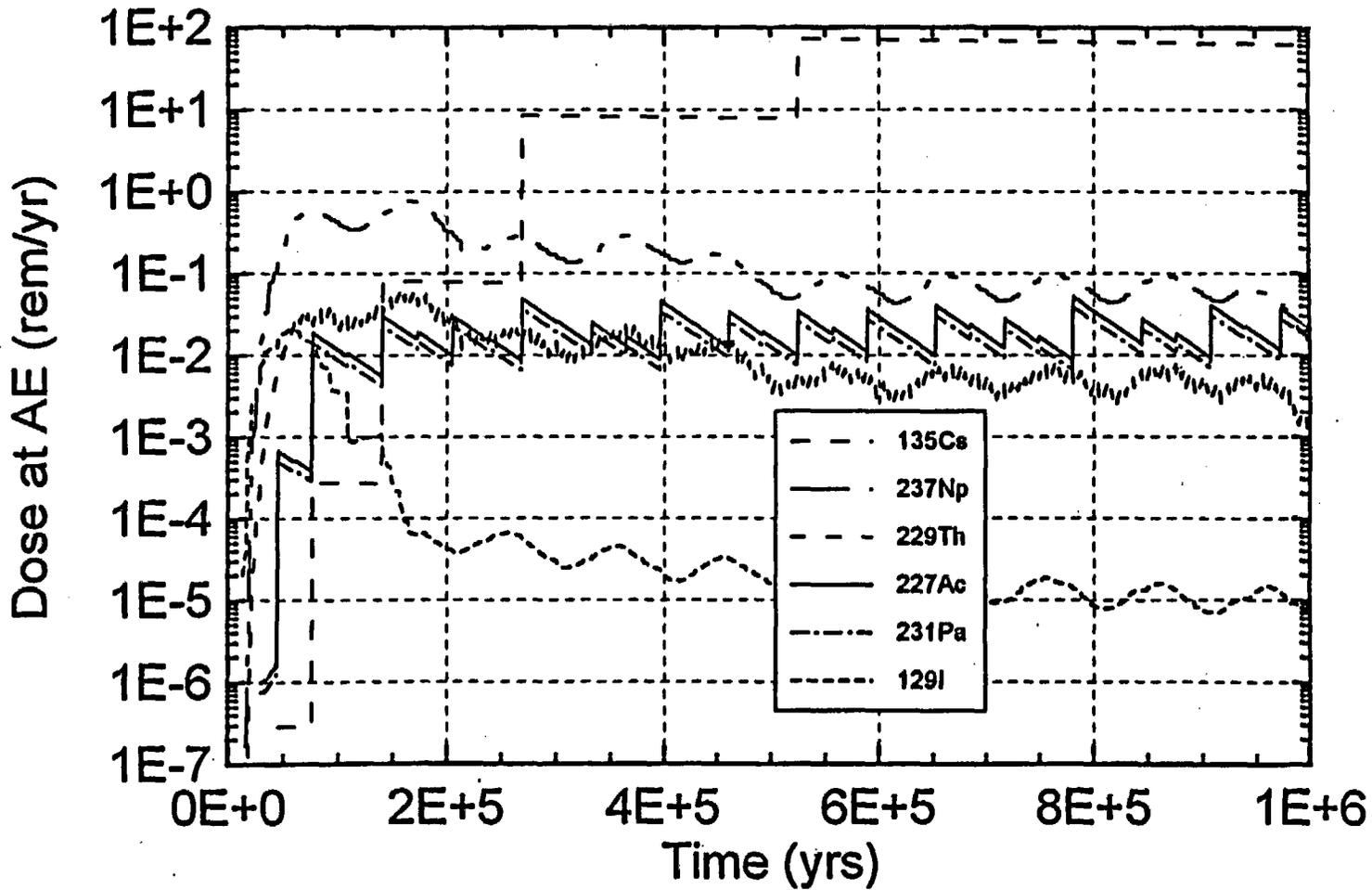


Figure 4.1.3-4 Expected-value dose time history for the  $K_d = 0$  for entire column and the initial pH scenario over 1,000,000 years.

PK10DAE.GRF  
QNPDAE.DAT  
QTHDAE.DAT  
QIDAE.DAT  
QTCDAE.DAT  
QU3DAE.DAT  
QCSDAE.DAT  
09/27/96

1,000,000 yr Expected-Value Dose History  
SOL = f(pH = 11); Kd = 0 for 10 m (PK10.RP)  
83/yes/hlq/dlme/drips on WP

Aff. II

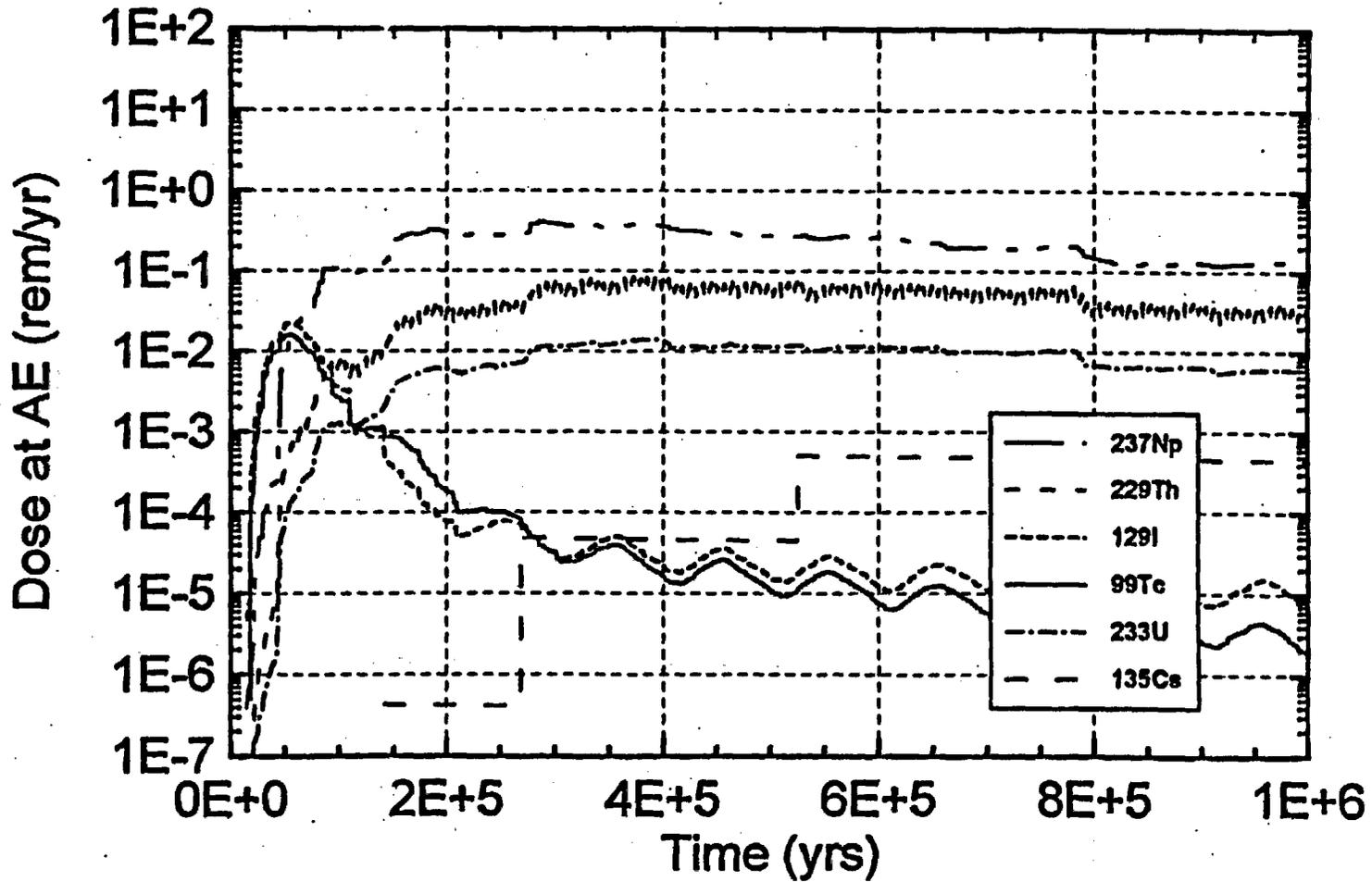


Figure 4.1.3-5 Expected-value dose time history for the Kd = 0 for 10 m and the modified pH scenario over 1,000,000 years.

RDAE.GRF  
RNPDAE.DAT  
RTHDAE.DAT  
RU3DAE.DAT  
RIDA.E.DAT  
RTCDAE.DAT  
RCSDAE.DAT  
09/27/96

1,000,000 yr Expected-Value Dose History  
SOL = f(pH = 11); Kd = 0 for 100 m (PK100.RP)  
83/yes/hq/clime/drips on WP

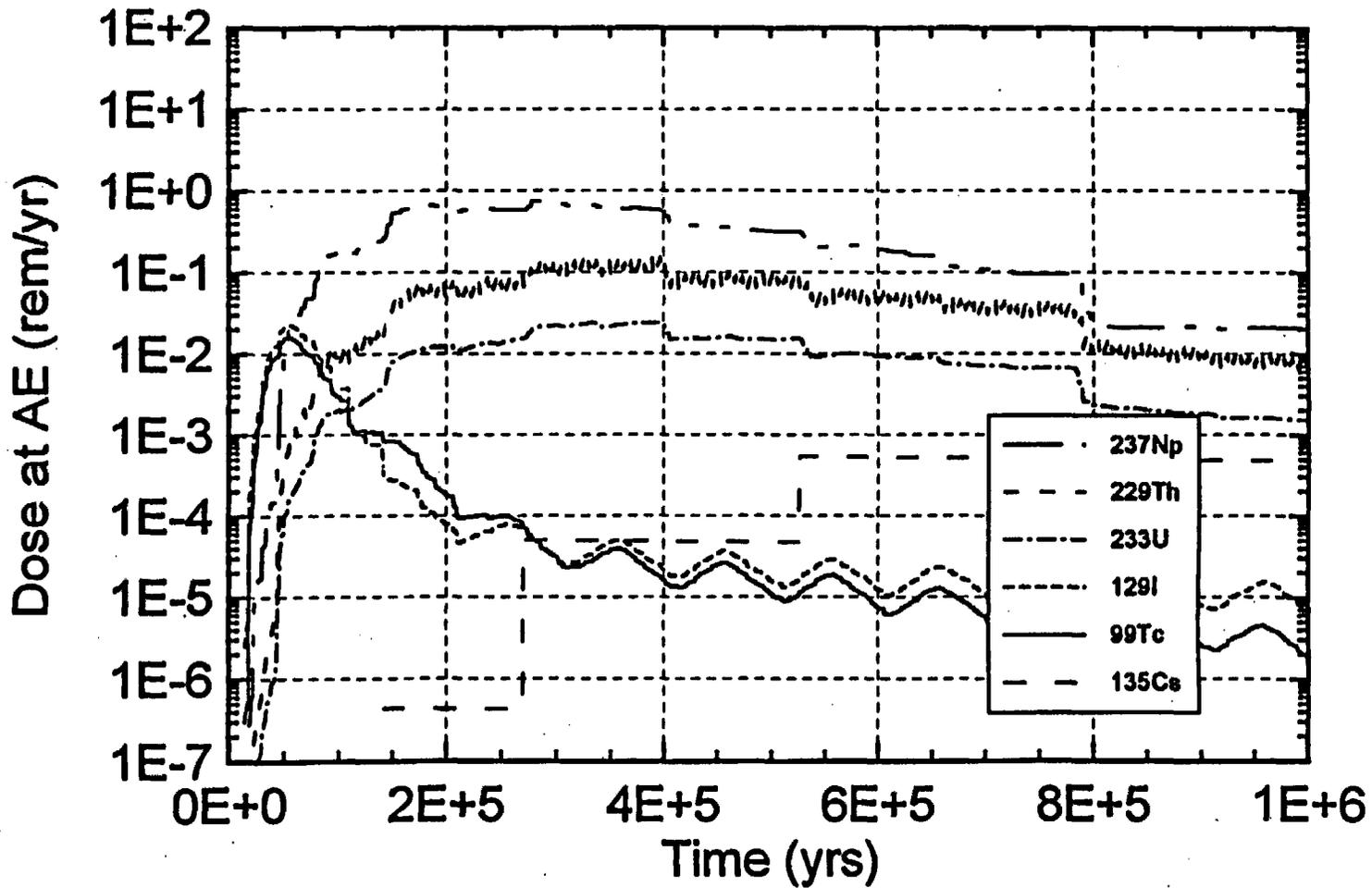


Figure 4.1.3-6 Expected-value dose time history for the Kd = 0 for 100 m and the modified pH scenario over 1,000,000 years.

SDAE.GRF  
SCSDAE.DAT  
SNPDAE.DAT  
SPU39DAE.DAT  
SPU42DAE.DAT  
STHDAE.DAT  
SU3DAE.DAT  
09/27/96

1,000,000 yr Expected-Value Dose History  
SOL = f(pH = 11); Kd = 0 for Entire Column (PKALL.RP)  
83/yes/hiq/clime/drips on WP

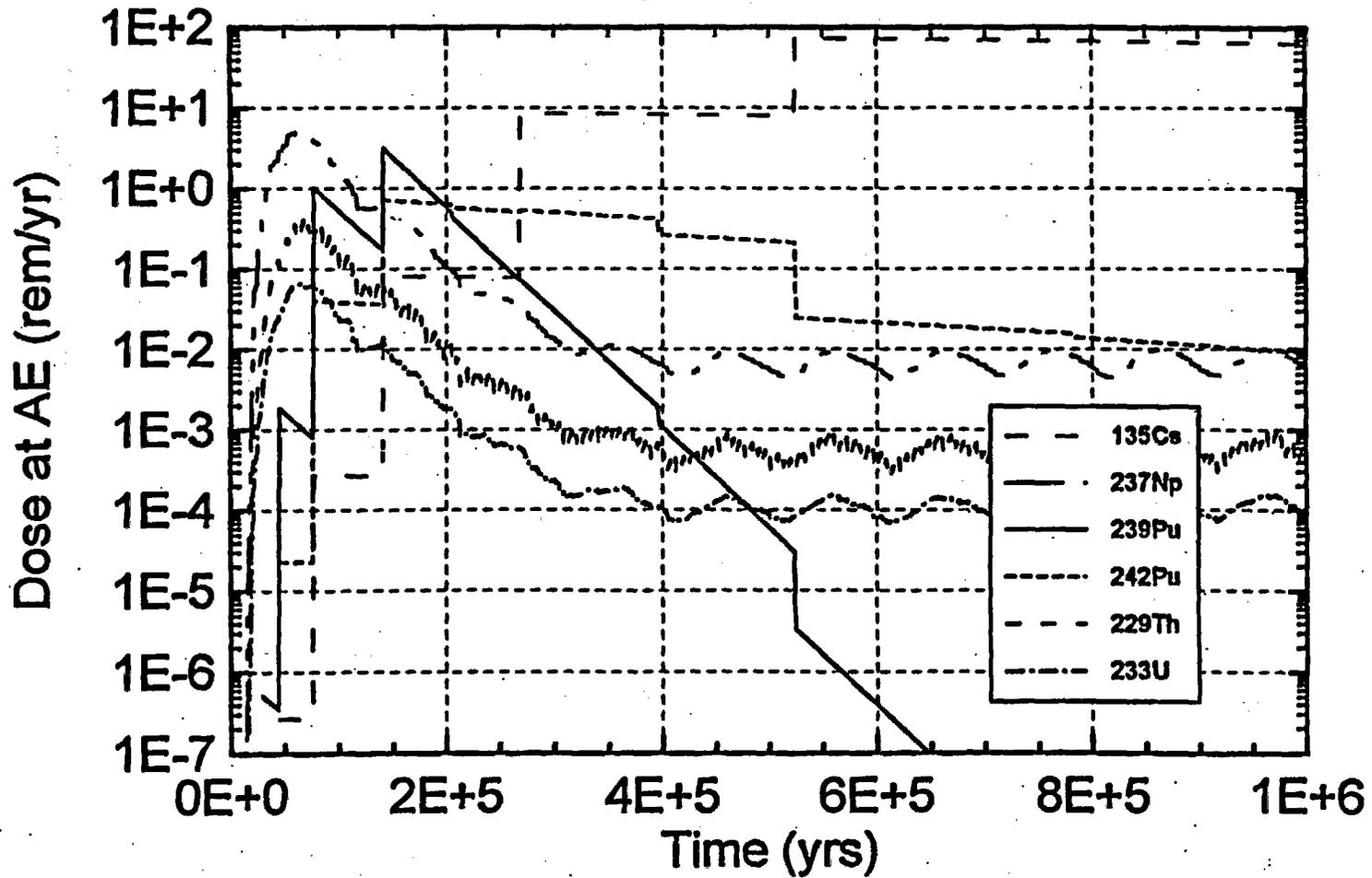


Figure 4.1.3-7 Expected-value dose time history for the Kd = 0 for entire column and the modified pH scenario over 1,000,000 years.

CCDF1E4.GRF  
83CC.DAT  
KD100CC.DAT  
KDALLCC.DAT  
PK100CC.DAT  
PKALLCC.DAT  
09/28/96

### 'BASE' Case vs 100 m and Entire Column Modified Cases 10,000 yr CCDF Based on 100 Realizations

83/yes/hq/clime/drips on WP

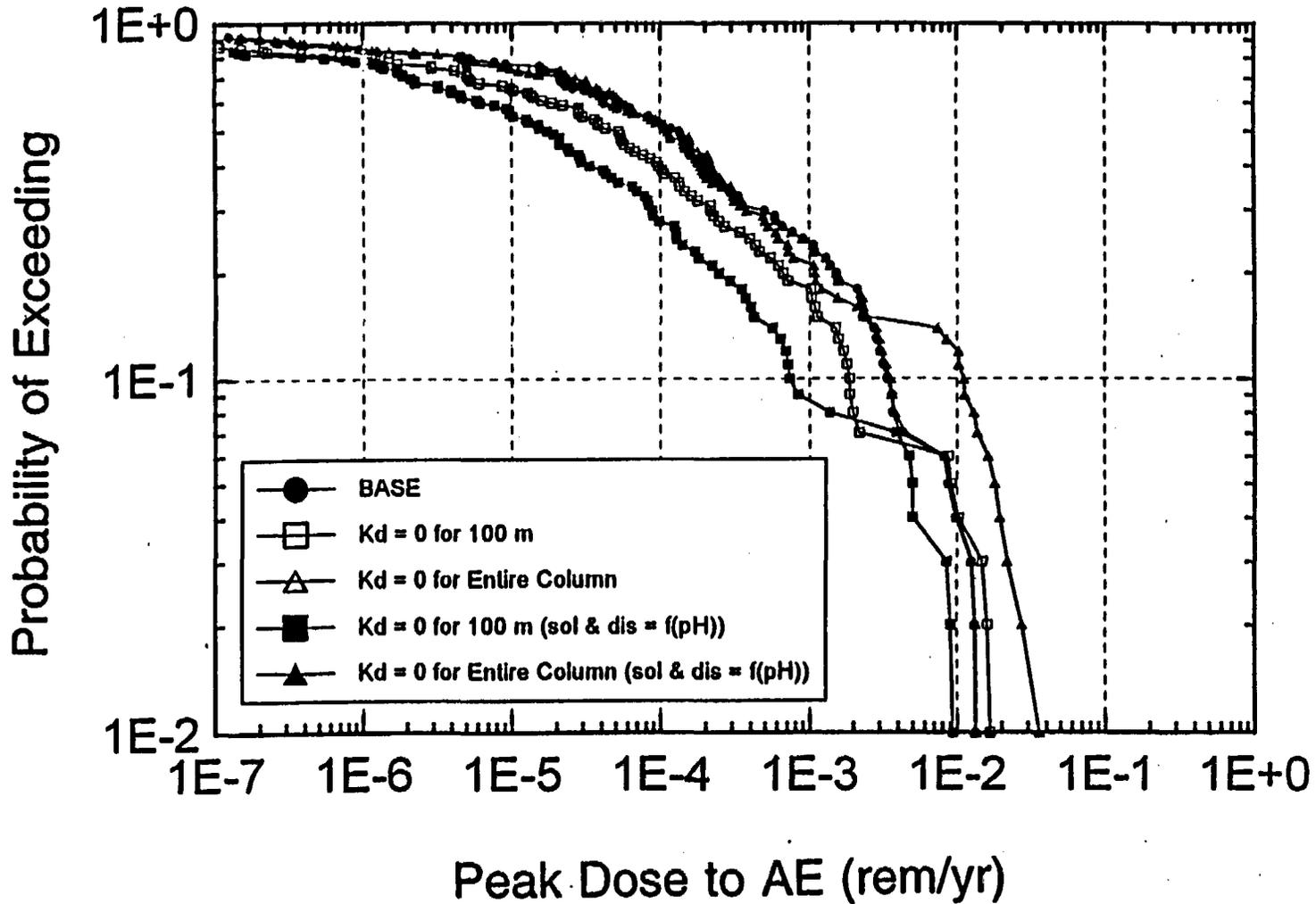


Figure 4.2-1 CCDF of peak dose for the base case model and all six modified models over 10,000 years.

CC...5.GRF  
83E5CC.DAT  
KD1005CC.DAT  
KDALL5CC.DAT  
PK1005CC.DAT  
PKALL5CC.DAT  
09/28/96

'BASE' Case vs 100 m and Entire Column Modified Cases  
100,000 yr CCDF Based on 100 Realizations  
83/yes/hlq/clime/drips on WP

Att. II

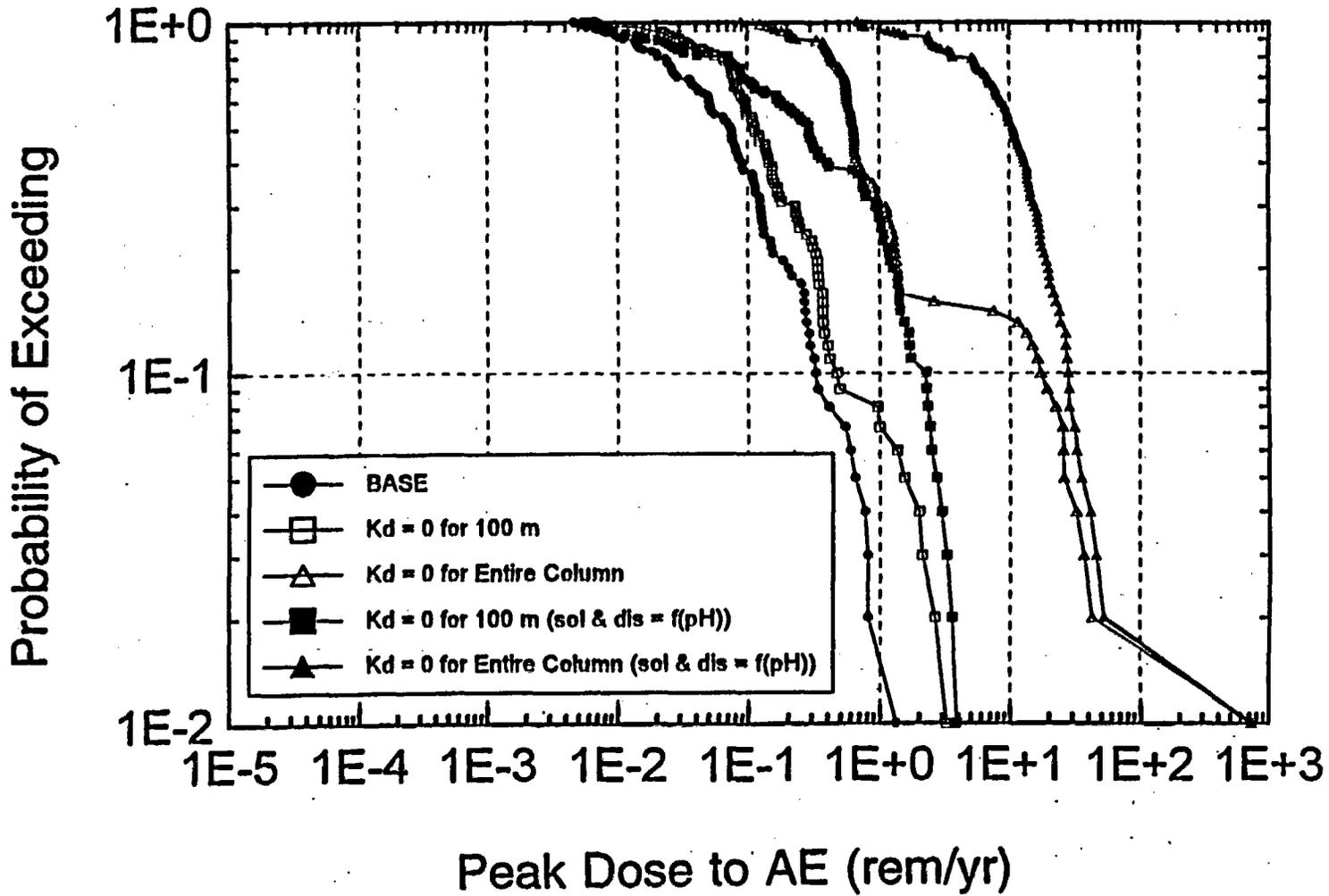


Figure 4.2-2 CCDF of peak dose for the base-case model and all six modified models over 100,000 years.

NP5DAE.GRF  
85NPDAE.DAT  
B5NPDAE.DAT  
C5NPDAE.DAT  
D5NPDAE.DAT  
09/24/86

### 237Np

## 100,000 yr Expected-Value Dose History

83/yes/hlq/clime/drips on WP

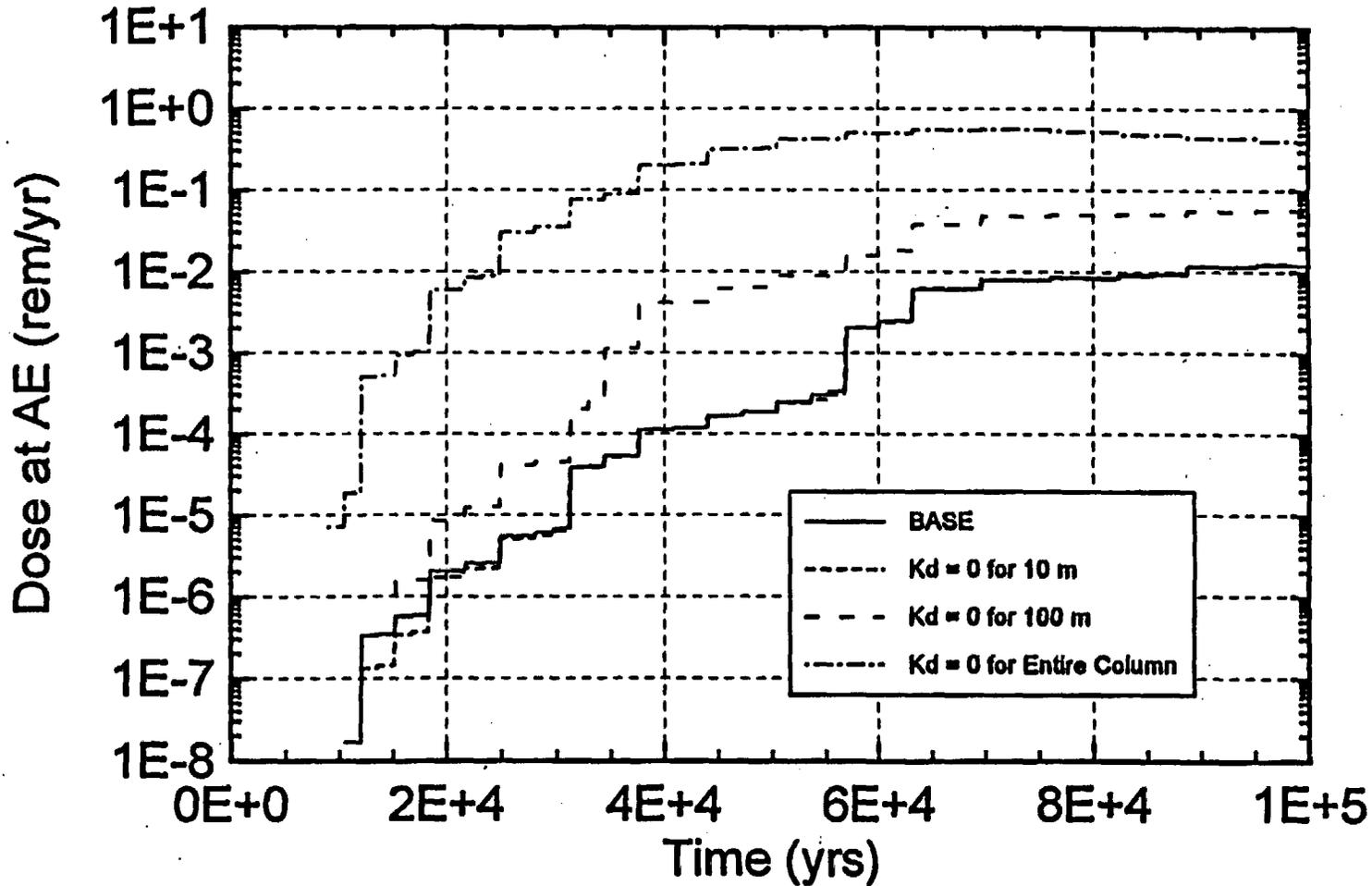


Figure 5-1

Expected-value <sup>237</sup>Np dose time history for the base-case model and the three initial pH scenario models over 100,000 years.

PK5NPDAE.GRF  
85NPDAE.DAT  
Q5NPDAE.DAT  
R5NPDAE.DAT  
S5NPDAE.DAT  
09/27/96

### $^{237}\text{Np}$

## 'BASE' Case versus $K_d$ and pH Modified Cases 100,000 yr Expected-Value Dose History

83/yes/hq/clme/drips on WP

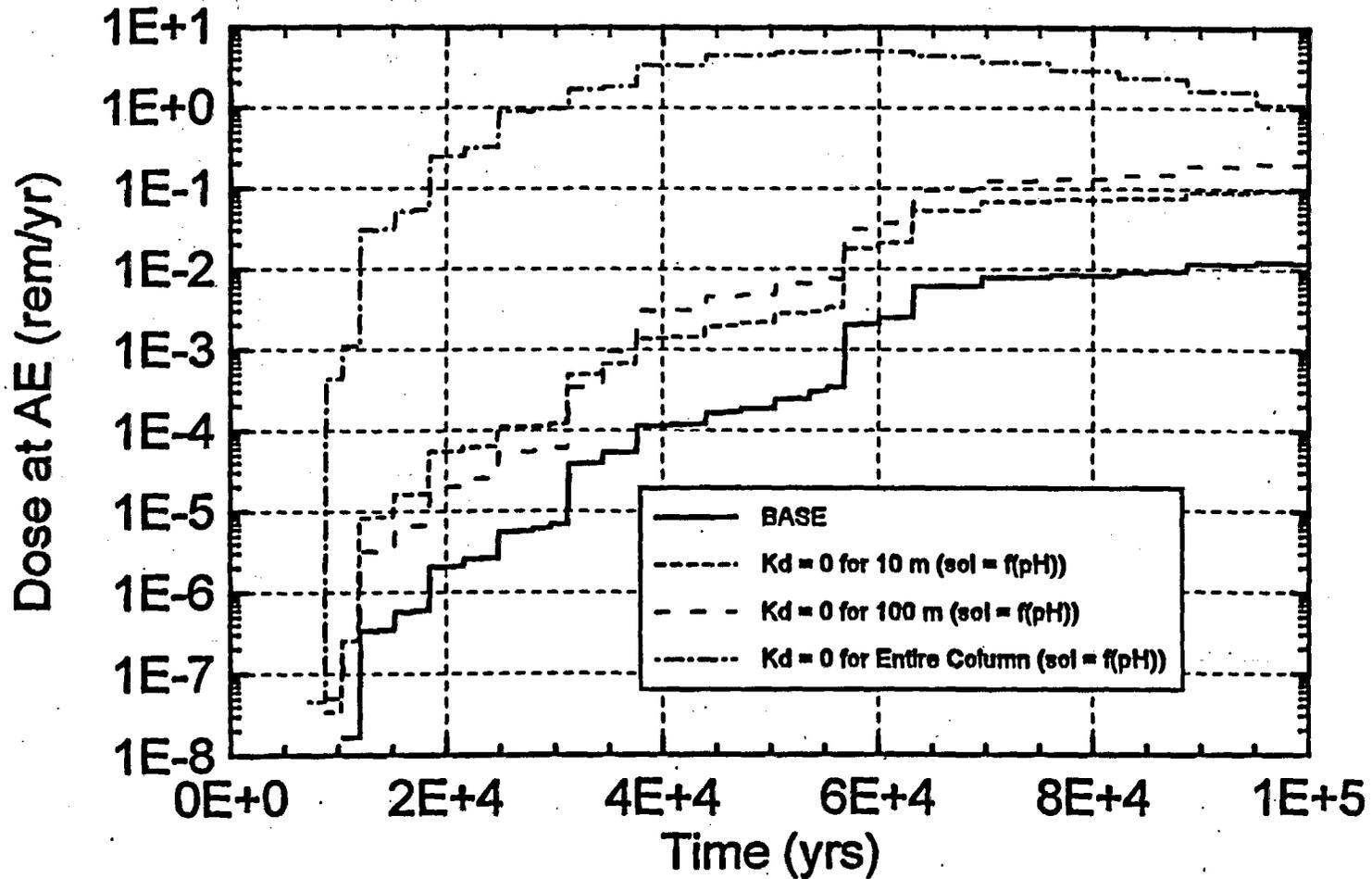


Figure 5-2 Expected-value  $^{237}\text{Np}$  time history for the base-case model and the three modified pH scenario models over 100,000 years.

105NPDAE.GRF  
85NPDAE.DAT  
B5NPDAE.DAT  
Q5NPDAE.DAT  
09/27/96

$^{237}\text{Np}$

'BASE' Case vs 10 m Modified Cases  
100,000 yr Expected-Value Dose History  
83/yes/hiq/clime/drips on WP

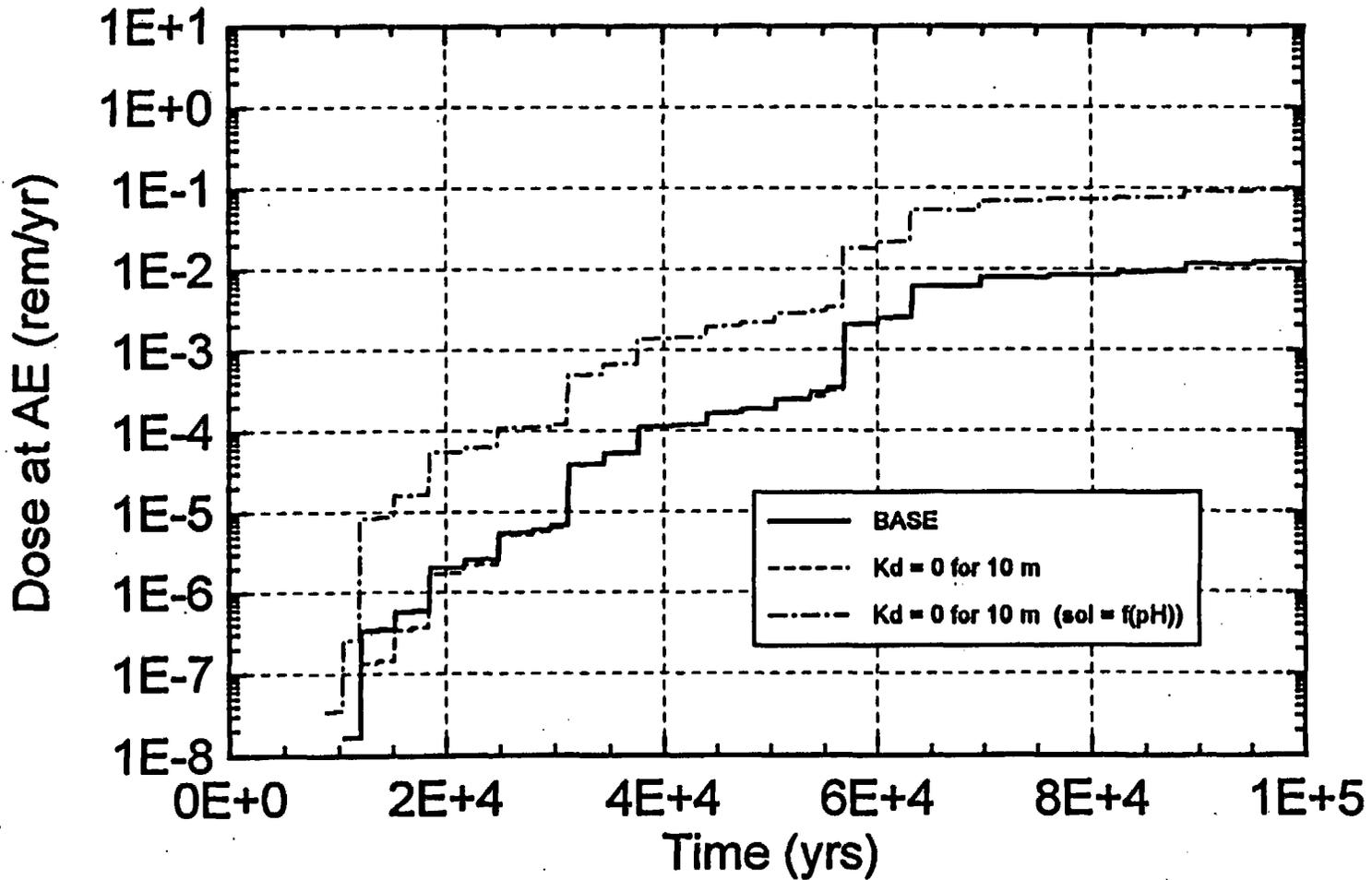


Figure 5-3

Expected-value  $^{237}\text{Np}$  time history for the base model and the  $K_d = 0$  for 10 m for both the initial and the modified pH scenario models over 100,000 years.

model and the  $K_d = 0$  for 10 m for both the initial and the modified

1005NDAE.GRF  
85NPDAE.DAT  
C5NPDAE.DAT  
R5NPDAE.DAT  
09/27/96

$^{237}\text{Np}$

'BASE' Case vs 100 m Modified Cases  
100,000 yr Expected-Value Dose History

83/yes/hlq/clme/drips on WP

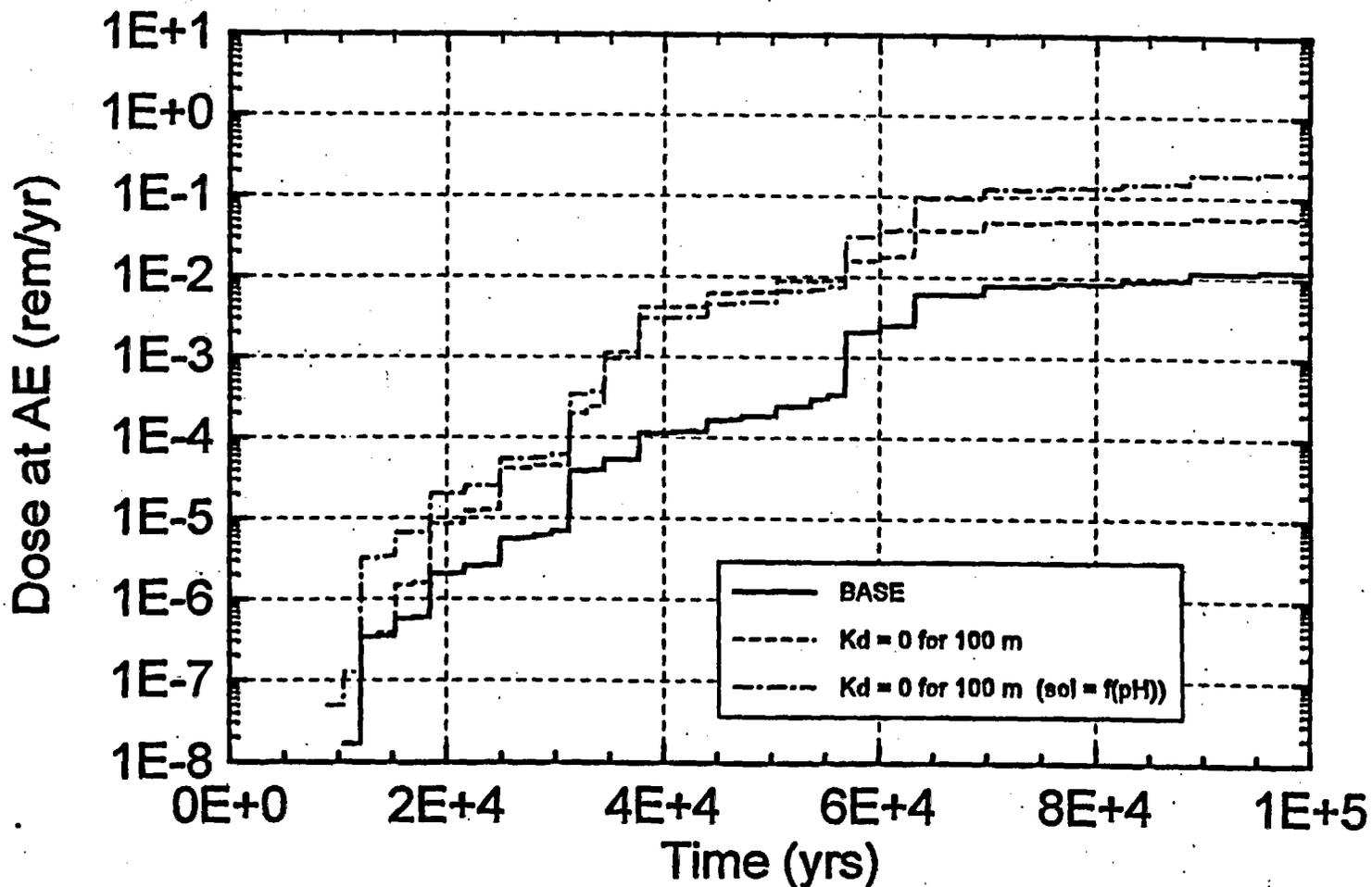


Figure 5-4

Expected-value  $^{237}\text{Np}$  time history for the base-case model and the  $K_d = 0$  for 100 m for both the initial and the modified pH scenario models over 100,000 years.

ALL5NDAE.GRF  
85NPDAE.DAT  
D5NPDAE.DAT  
S5NPDAE.DAT  
09/27/96

$^{237}\text{Np}$

'BASE' Case vs Entire Column Modified Cases  
100,000 yr Expected-Value Dose History  
83/yes/hlq/clime/drips on WP

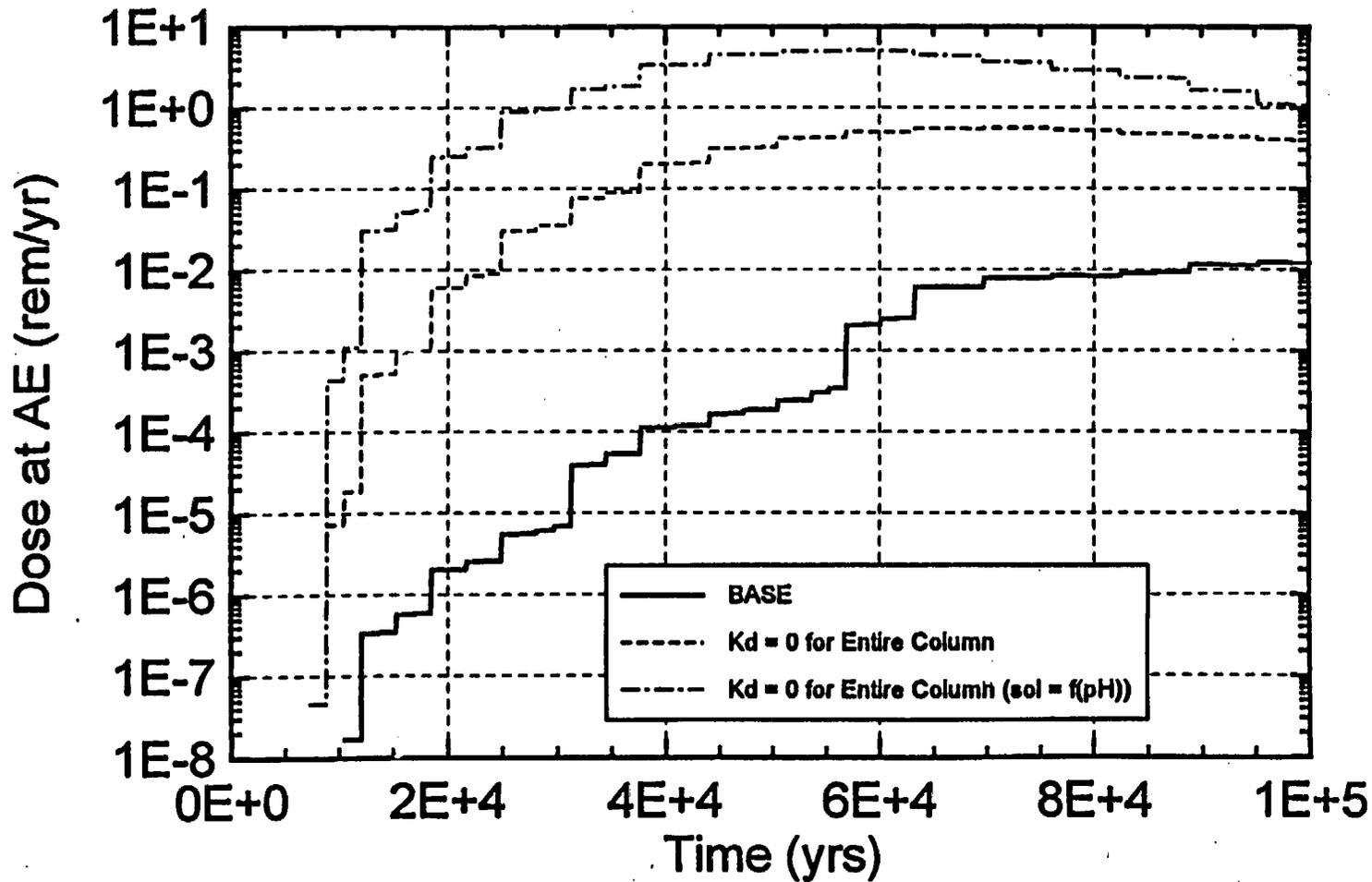


Figure 5-5

Expected-value  $^{237}\text{Np}$  time history for the base model and the Kd = 0 for entire column for both the initial modified pH scenario models over 100,000 years

model and the Kd = 0 for entire column for both the initial and the

NPDAE.GRF  
NP\_BASE.DAT  
BNPDAE.DAT  
CNPDAE.DAT  
DNPDAE.DAT  
09/11/96

237Np  
1,000,000 yr Expected-Value Dose History  
83/yes/hiq/clime/drips on WP

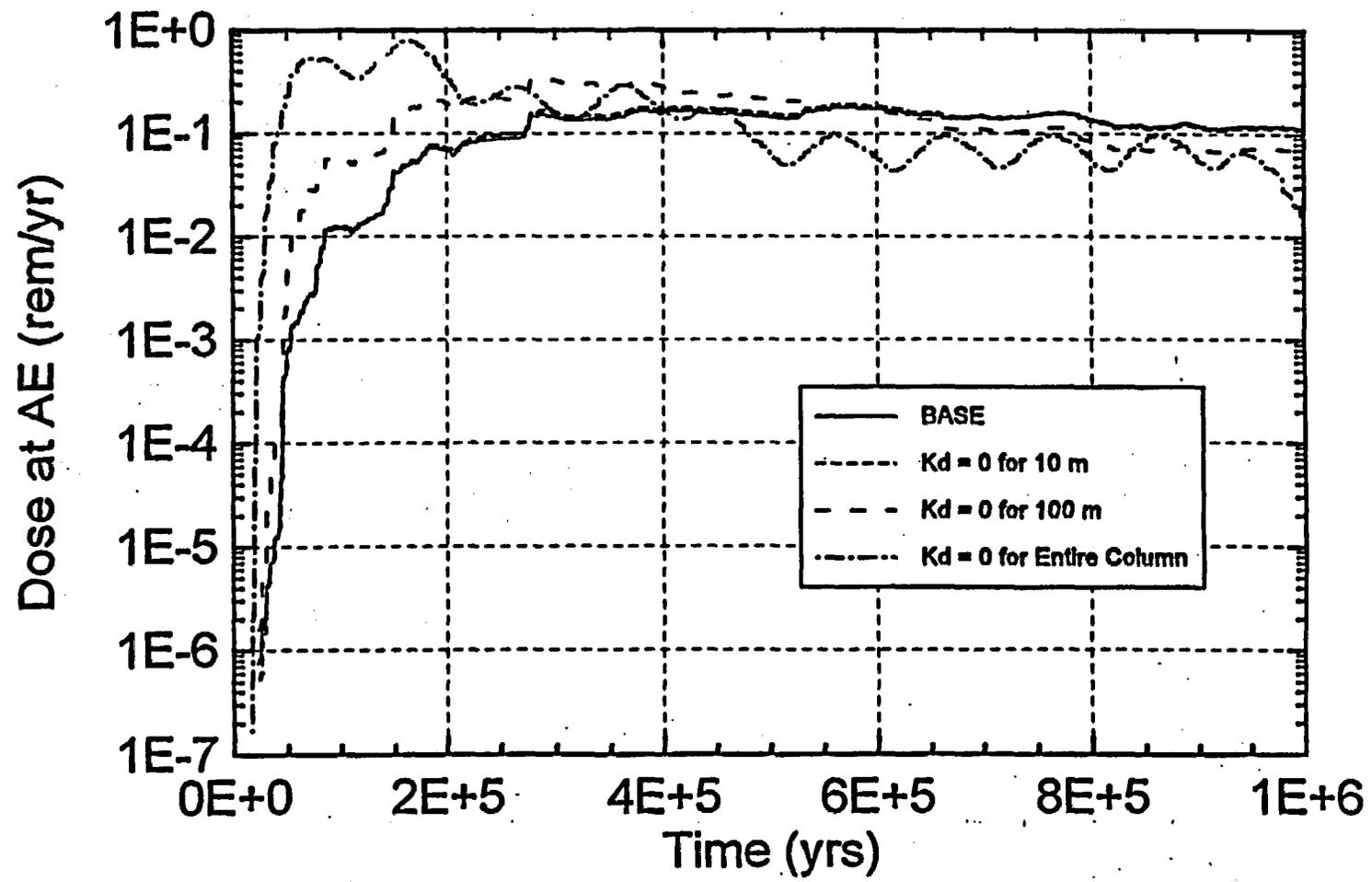


Figure 5-6 Expected-value <sup>237</sup>Np dose time history for the base-case model and the three initial pH scenario models over 1,000,000 years.

PKNPDAE.GRF  
NP\_BASE.DAT  
QNPDAE.DAT  
RNPDAE.DAT  
SNPDAE.DAT  
09/27/96

**<sup>237</sup>Np**

**'BASE' Case versus Kd and pH Modified Cases  
1,000,000 yr Expected-Value Dose History**

83/yes/hlq/clime/drips on WP

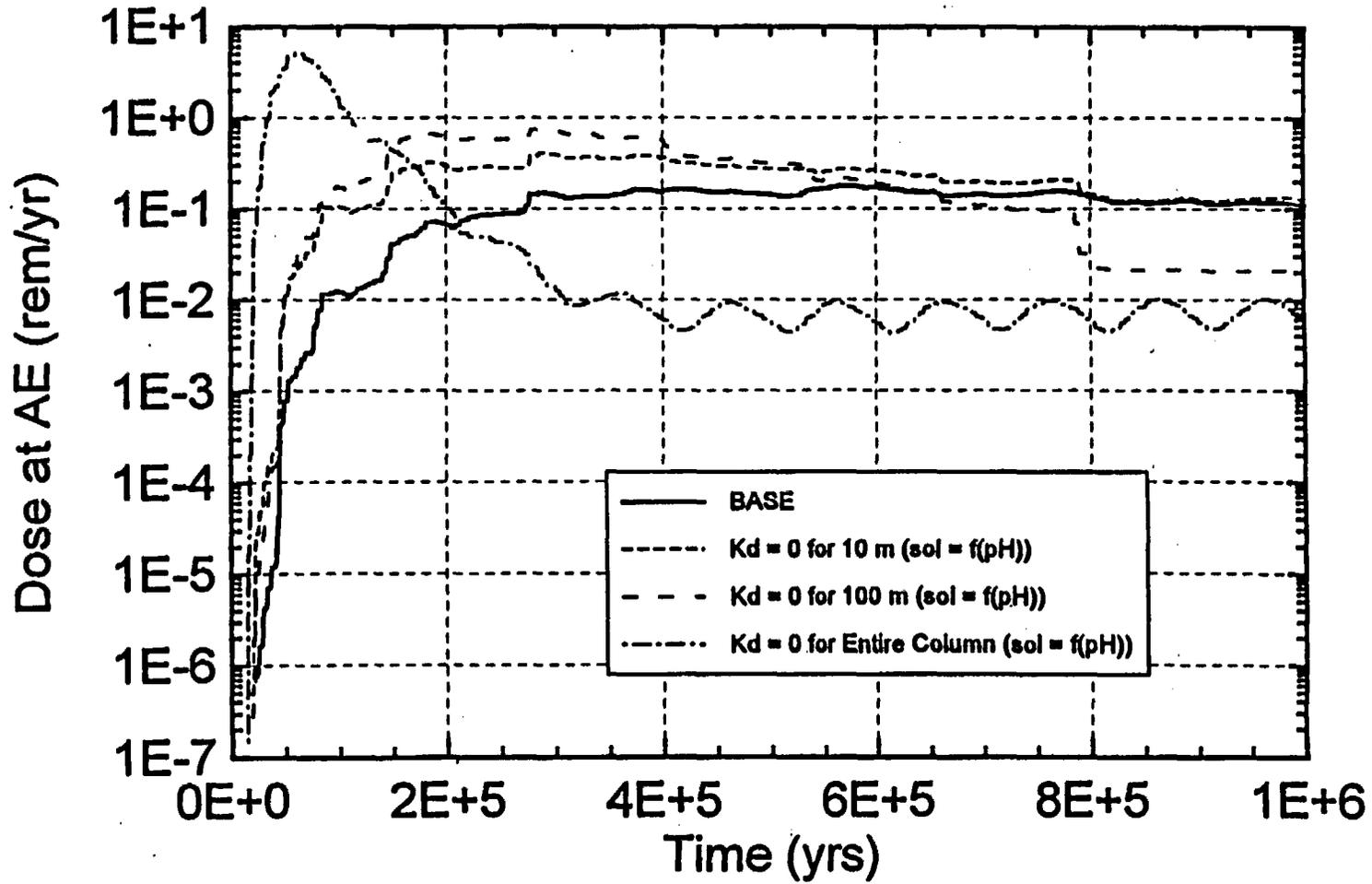


Figure 5-7

Expected-value <sup>237</sup>Np time history for the base model and the three modified pH scenario models over 1,000,000 years.

model and the three modified pH scenario models over 1,000,000 years.

10NPDAE.GRF  
NP\_BASE.DAT  
BNPDAE.DAT  
QNPDAE.DAT  
09/27/96

$^{237}\text{Np}$

'BASE' Case vs 10 m Modified Cases  
1,000,000 yr Expected-Value Dose History  
83/yes/hiq/clime/drips on WP

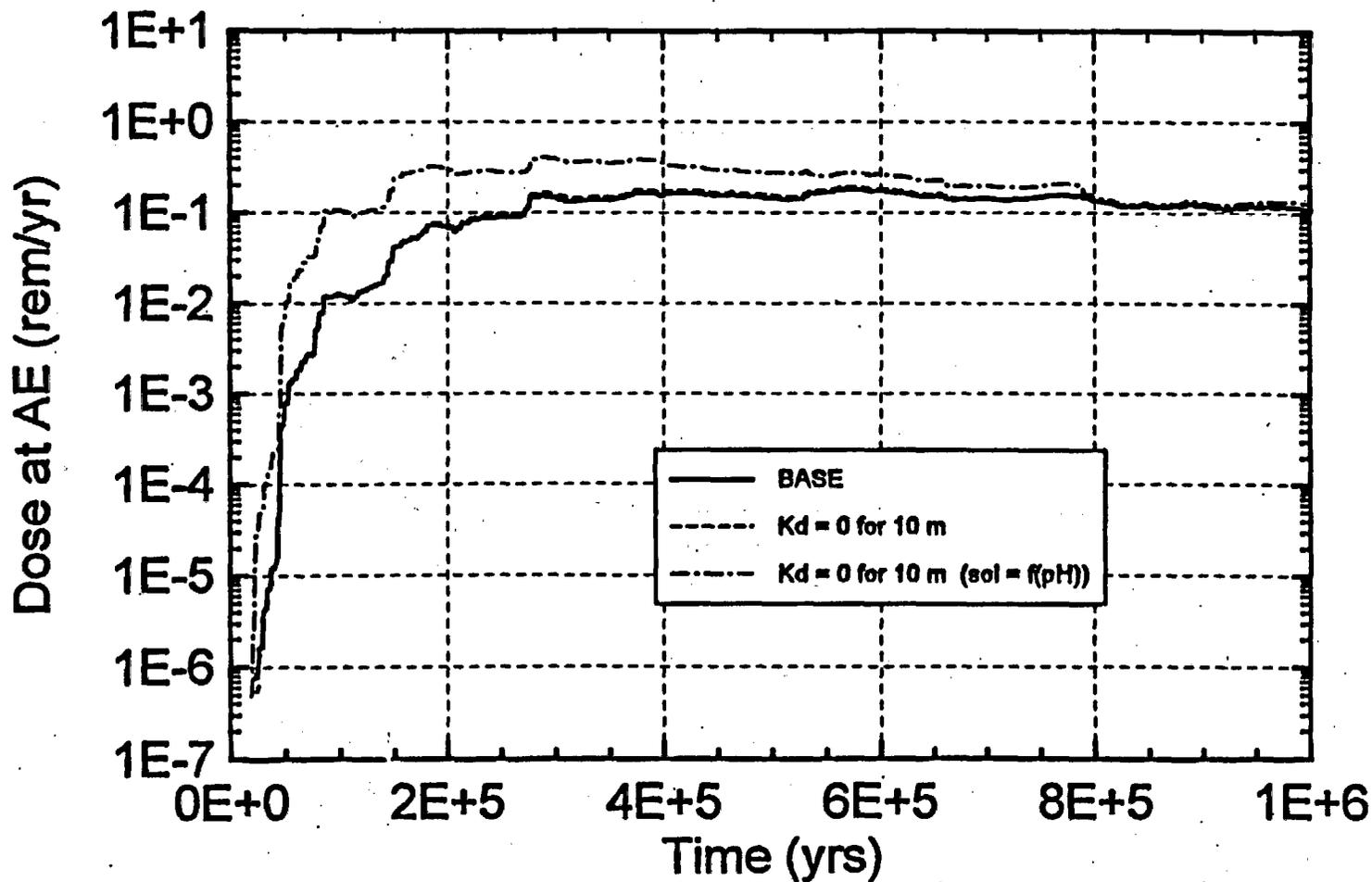


Figure 5-8

Expected-value  $^{237}\text{Np}$  time history for the base-case model and the  $K_d = 0$  for 10 m for both the initial and the modified pH scenario models over 1,000,000 years.

100NPDAE.GRF  
NP\_BASE.DAT  
CNPDAE.DAT  
RNPDAE.DAT  
09/27/96

$^{237}\text{Np}$

'BASE' Case vs 100 m Modified Cases  
1,000,000 yr Expected-Value Dose History  
83/yes/hiq/clime/drips on WP

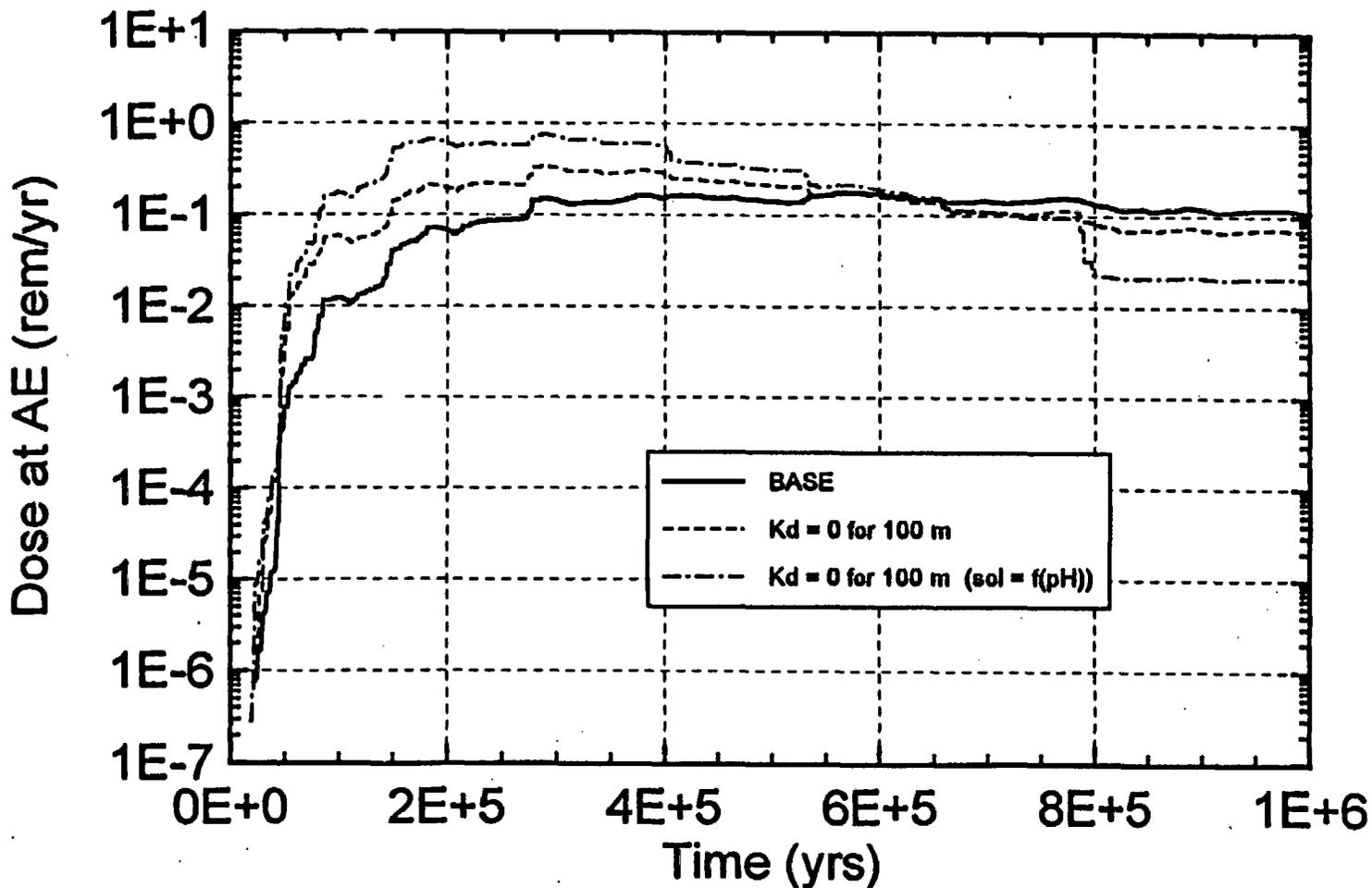


Figure 5-9 Expected-value  $^{237}\text{Np}$  time history for the base-case model and the  $K_d = 0$  for 100 m for both the initial and the modified pH scenario models over 1,000,000 y

ALLNPDAE.GRF  
NP\_BASE.DAT  
DNPDAE.DAT  
SNPDAE.DAT  
09/27/96

$^{237}\text{Np}$

'BASE' Case vs Entire Column Modified Cases  
1,000,000 yr Expected-Value Dose History  
83/yes/hiq/clime/drips on WP

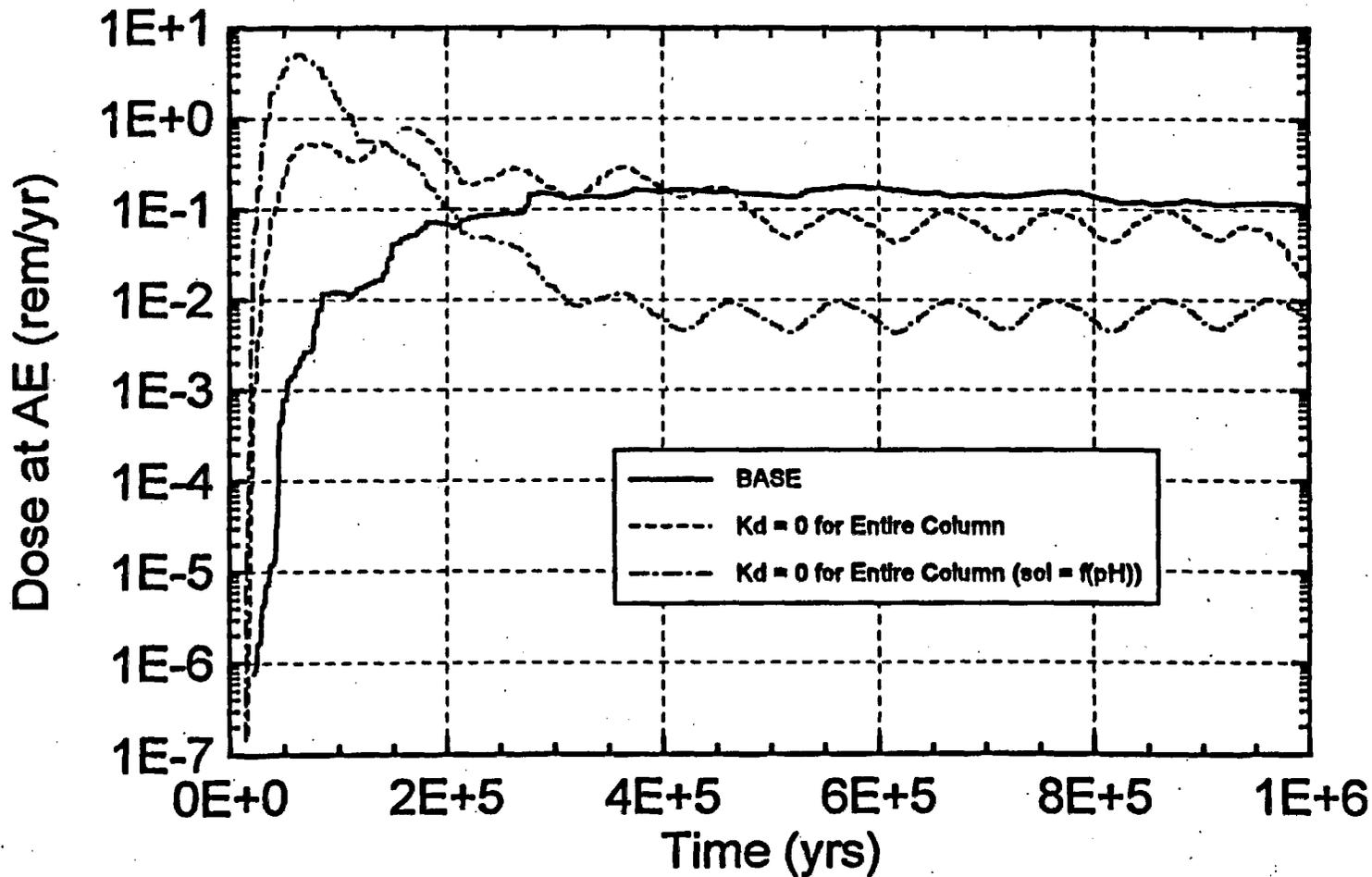
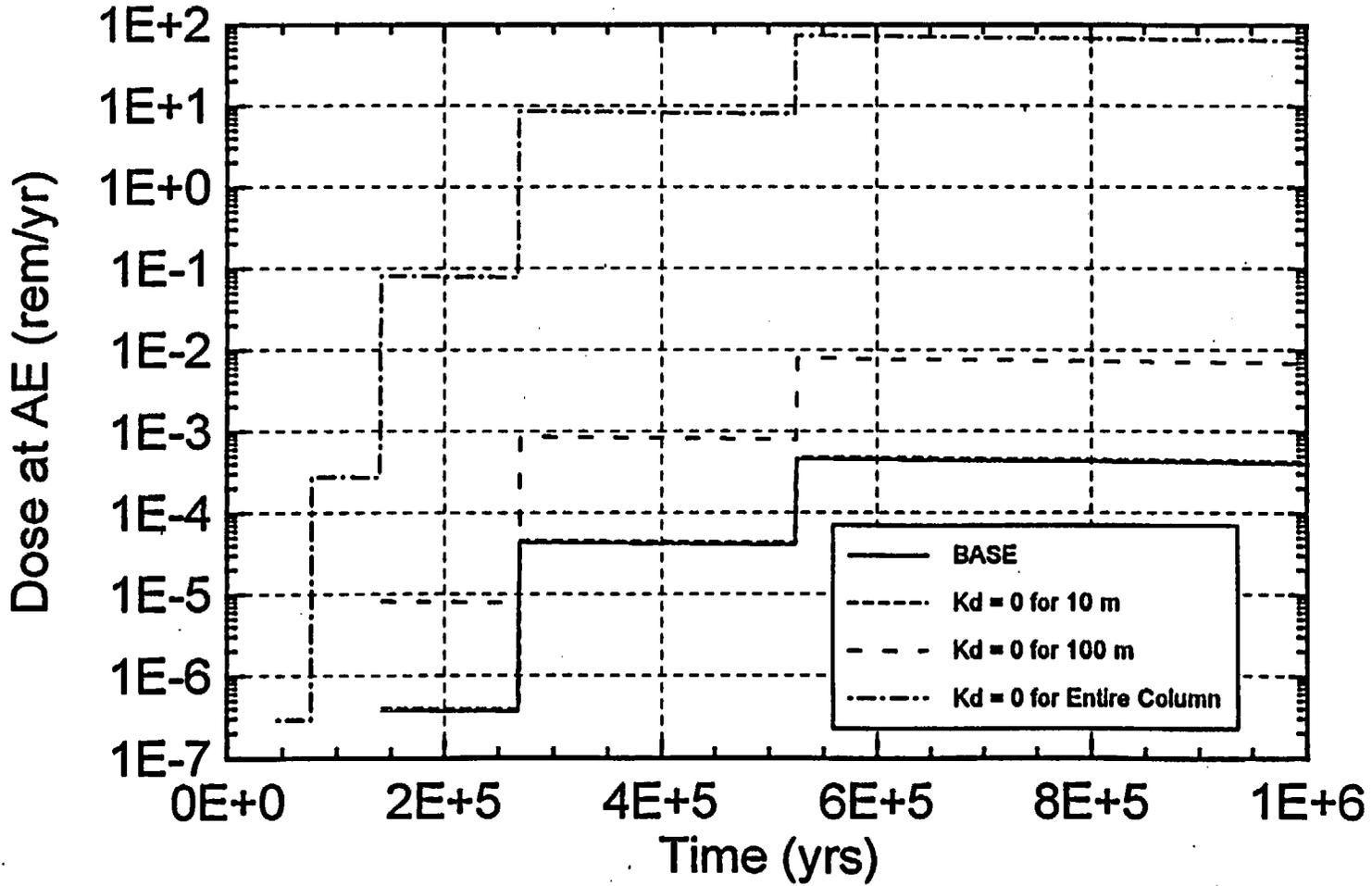


Figure 5-10 Expected-value  $^{237}\text{Np}$  time history for the base-case model and the  $K_d = 0$  for entire column for both the initial and the modified pH scenario models over 1,000,000 years.

CSDAE.GRF  
CS\_BASE.DAT  
BCSDAE.DAT  
CCSDAE.DAT  
DCSDAE.DAT  
09/11/96

135Cs  
1,000,000 yr Expected-Value Dose History  
83/yes/hiq/clime/drips on WP



re 5-11 Expected-value <sup>135</sup>Cs dose time history for the base model and the three initial pH scenario models over 1,000,000 years.

PU39DAE.GRF  
PU39\_BAS.DAT  
BPU39DAE.DAT  
CPU39DAE.DAT  
DPU39DAE.DAT  
09/11/96

$^{239}\text{Pu}$

1,000,000 yr Expected-Value Dose History

83/yes/hq/clime/drips on WP

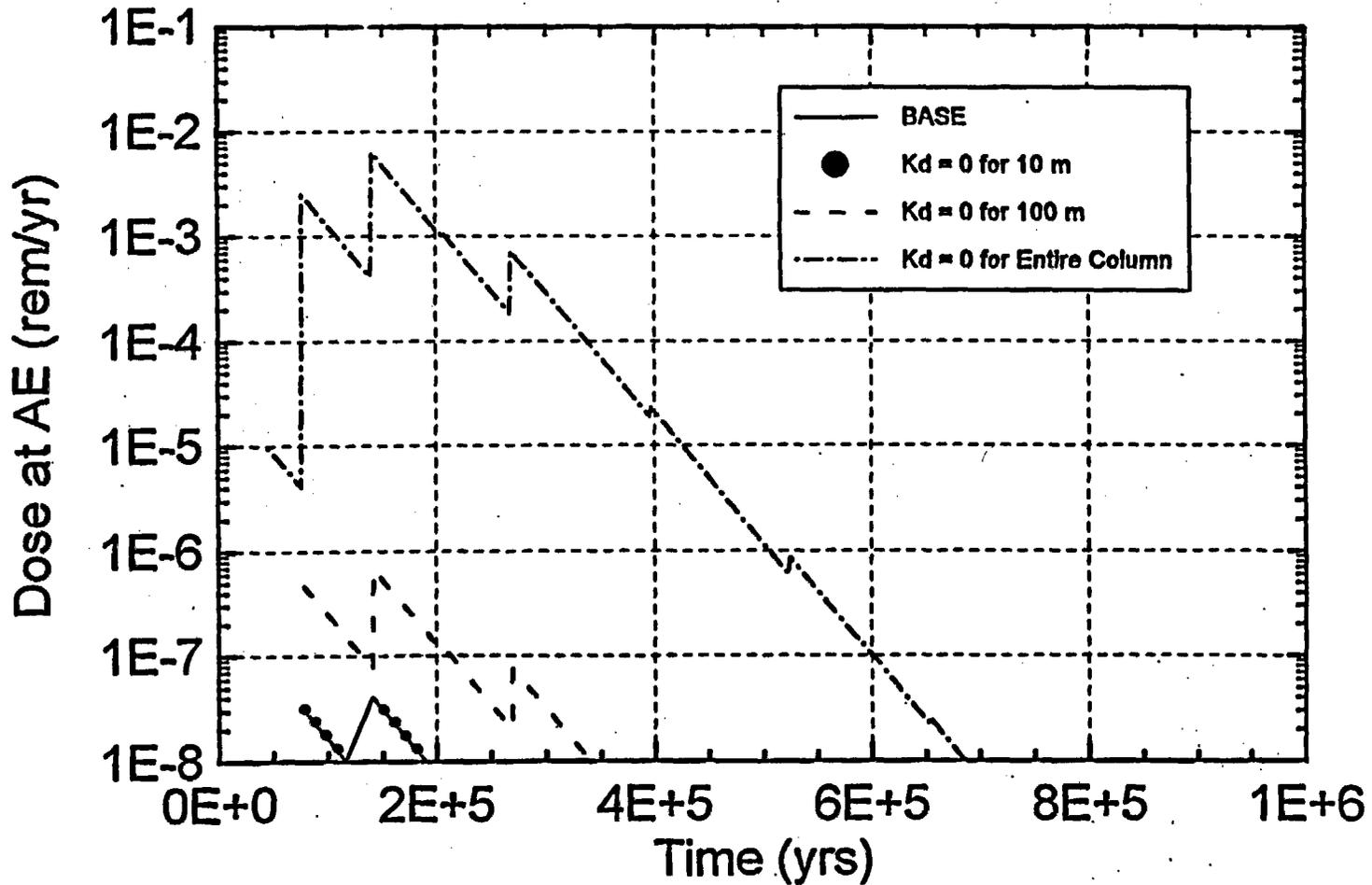


Figure 5-12 Expected-value  $^{239}\text{Pu}$  dose time history for the base-case model and the three initial pH scenario models over 1,000,000 years.

PKP9DAE.GRF  
PU39\_BAS.DAT  
QPU39DAE.DAT  
RPU39DAE.DAT  
SPU39DAE.DAT  
09/27/96

$^{239}\text{Pu}$

'BASE' Case versus Kd and pH Modified Cases  
1,000,000 yr Expected-Value Dose History  
83/yes/hq/clime/drips on WP

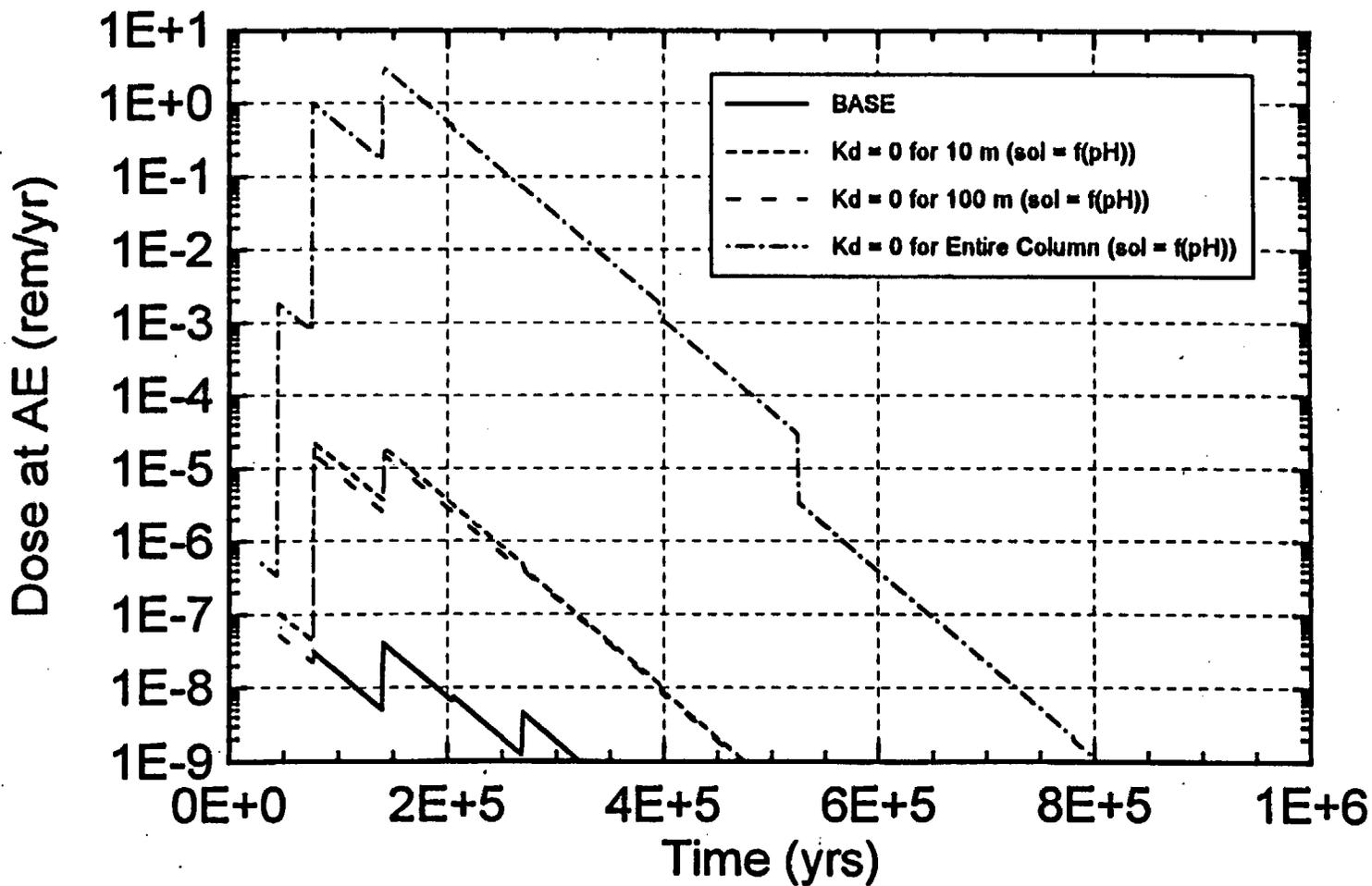


Figure 5-13 Expected-value  $^{239}\text{Pu}$  dose time history for the base case model and the three modified pH scenario models over 1,000,000 years.

PU42DAE.GRF  
PU42\_BAS.DAT  
BPU42DAE.DAT  
CPU42DAE.DAT  
DPU42DAE.DAT  
09/11/96

$^{242}\text{Pu}$

### 1,000,000 yr Expected-Value Dose History

83/yes/hiq/clime/drips on WP

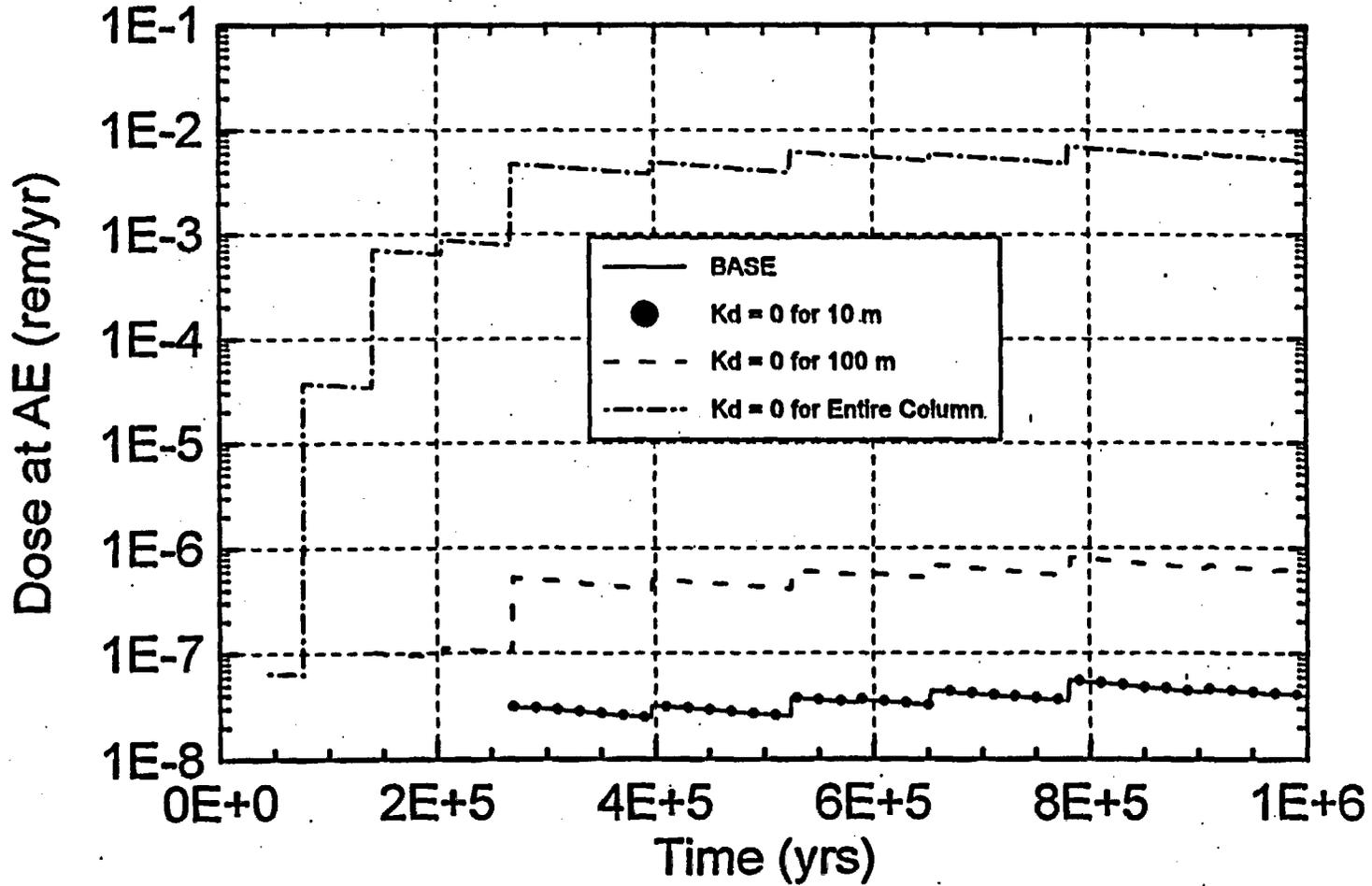


Figure 5-14 Expected-value  $^{242}\text{Pu}$  dose time history for the base-case model and the three initial pH scenario models over 1,000,000 years.

PKP2DAE.GRF  
PU42\_BAS.DAT  
QPU42DAE.DAT  
RPU42DAE.DAT  
SPU42DAE.DAT  
09/27/96

### 242Pu

## 'BASE' Case versus Kd and pH Modified Cases 1,000,000 yr Expected-Value Dose History 83/yes/hiq/clime/drips on WP

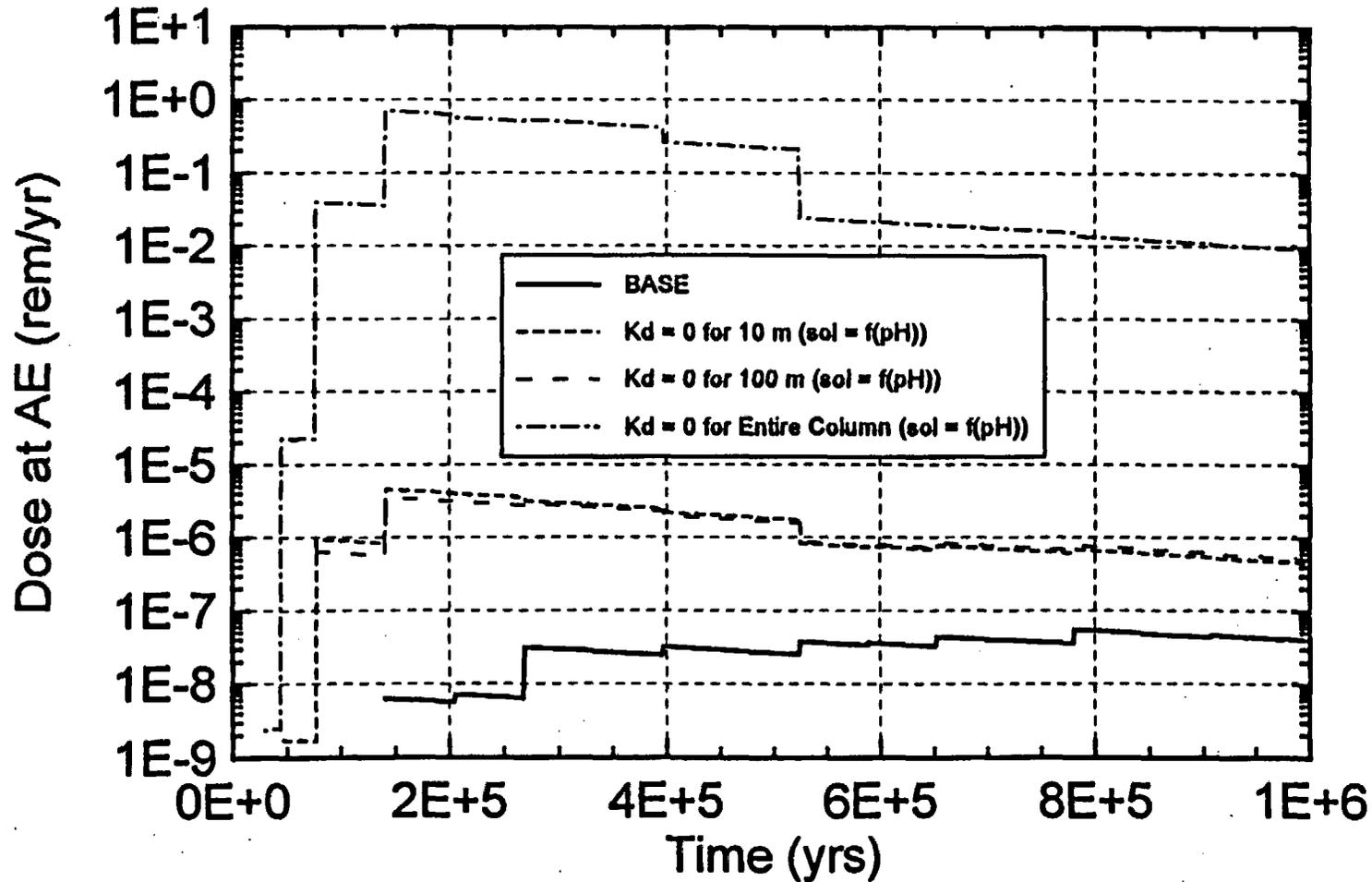


Figure 5-15

Expected-value <sup>242</sup>Pu dose time history for the base-case model and the three modified pH scenario models over 1,000,000 years.

***Performance Assessment Consequences of Cementitious Materials Scoping Study:  
Cement Expert Consultation Meeting Report***

**Summary of Expert Consultation Meeting on Potential Geochemical Effects  
of Evolving Cementitious Materials, September 5, 1996**

The Meeting between the outside experts on cementitious materials and the Yucca Mountain Project Personnel took place on Thursday September 5, 1996. A copy of the final draft agenda for the meeting is attached to the end of this report (Attachment A). The experts that were brought in for the meeting are Prof. Della Roy of The Pennsylvania State University, Dr. Maria Onofrei of the Atomic Energy Canada Ltd. (AECL), and Prof. Hamlin Jennings of Northwestern University, each of whom agreed to attend this one day meeting and to provide a short report covering their expert judgement regarding the potential geochemical effects of concrete and possible cement options that minimize those effects. The PA Cement Study Meeting with these outside cement experts involved personnel from the Waste Package group (WP), the Repository Design group (RD), the Scientific Programs organization (SPO), and the Performance Assessment Dept. (PA), all of the M&O, and personnel from the Assistant Manager of Suitability and Licensing (AMSL) organization of YMSCO. A copy of the list of participants is included at the end of this report (Attachment B). This section provides an overview and concise summary of the meeting and is followed by a detailed set of notes that document the questions and discussions of the meeting.

A number of presentations were made to introduce the outside experts to the Yucca Mountain site, the current Repository Design and Concrete formulations considered for ground support, the potential in-drift environment that materials would experience on the 10,000+ year time-frame, and the potential post-closure performance issues with cementitious materials (all in Attachment C). This material provided the context for the outside experts in which to consider the information needs of this study. Because of the working nature of this meeting, questions were permitted to flow freely. This was particularly true for queries from the outside experts who were trying to understand the information needs of the Project. As such, the actual schedule diverged somewhat from the agenda, but because the interaction was productive, and the original schedule was designed for flexibility, this was not a concern.

The afternoon was spent discussing the possible evolution of cementitious materials in the potential near-field environment and conceivable methods to assuage or eliminate the potential performance impacts. This discussion was guided by a set of questions prepared by PA covering the potential post-closure issues of large masses of cementitious materials (Attachment D). The thrust of the questions focuses on the evolution of the cementitious materials within the potential repository environment over long time periods. The experts all agreed that discussion of the evolution of the materials over such a time frame and at such extreme conditions would necessarily be speculative because of the lack of data concerning cementitious materials in such an environment. However, many aspects of what could be expected were covered and discussed at some length. In addition, a number of alternative cement mixes were addressed.

The experts were in agreement that precast concrete would allow the greatest number of possible solutions to reduce the extent of pH perturbations to extreme alkaline conditions. The options proposed included alkali activated cements, C<sub>2</sub>S-rich (lower calcium/higher silica)

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cements, or lower pH cements being developed at AECL. It was agreed that using tuff aggregate and decreasing the Ca/Si ratio in the cement would bring it closer to the host rock in terms of composition and would thereby enhance their compatibility. In addition, discussion of the evolved cementitious materials focussed on the potential benefits of carbonation reactions to mitigate any alkali generating phases in the solids. It was indicated that constraining the expected extent of cement carbonation would be key in evaluating the capacity of the evolved material to affect pH. Although a number of cement mixes were discussed as having low pH, it is not clear that these mixes would provide starting pH values below 10, which is currently considered to be the limit for PA. The experts reports will be sent in the last week of September and D. Sassani will include them in the letter status report for the PA Cement Study which is due at the end of September. This input will help guide further PA evaluation and aid in recommendations to RD for cement mix options that minimize potential impacts.

**Transcription of Detailed Meeting Notes of D. C. Sassani**

R. Barton (YMSCO) welcomed everyone to the meeting (this occurred at 8:15 a.m. because we delayed 15 minutes to see if Prof. Jennings would arrive prior to the start, but it turned out that he showed up at about 8:45. He suggested, after arrival, that signs more clearly labeling the facilities in Summerlin as part of the Yucca Mountain Project would have helped greatly). After the YMSCO welcome, D. Sassani (DCS) welcomed the cement experts on behalf of the M&O, and then requested that Project personnel give their names and organizations to briefly introduce themselves to the outside experts (there is an attached list of persons attending the meeting).

After these brief introductions, the outside experts were requested to spend about 5 minutes discussing some relevant aspects of their backgrounds to put their expertise in context for the participants in the meeting.

Prof. Della Roy of Pennsylvania State University began these abbreviated professional biographies, indicating that her education is in the areas of Chemistry, Mineralogy, and Geochemistry and that her research very quickly became focussed into the field of Materials Science. Within that broad area, Prof. Roy said that she has focussed on cements and their applications to waste management. She wrote a review paper in 1992 covering cementitious materials. Her work has included studying the use of cementitious materials as seal materials, waste forms, and as backfill materials and covers low-, intermediate-, and high-level radioactive waste management systems, including work performed specifically for the Waste Isolation Pilot Plant (WIPP) and for Yucca Mountain Project (YMP). The emphasis of her work has been to elucidate the stability of cementitious materials in a variety of geologic media. In particular, Prof. Roy also has experience with the use of cements/concretes used within geothermal wells up to temperatures of about 400°C.

Dr. Maria Onofrei, a Senior Scientist at the Atomic Energy of Canada Limited (AECL), then gave a synopsis of her work which has focussed on evaluating the seals materials and their performance at the AECL facility in Canada. In addition, Dr. Onofrei has

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worked on cement-based grouts to be used by the Stripa Project and has provided work to NAGRA regarding the use of porous concrete as backfill in low- to intermediate-level waste repositories. Dr. Onofrei also discussed briefly the work she had done for WIPP regarding microfine cements and indicated that for AECL she is currently working on cements/concretes which have lower pH than normal Portland-type cements.

At this point D. Stahl (DS) asked if Dr. Onofrei had any experience with microbes in concretes. Dr. Onofrei replied that she herself did not, but that another scientist (S. Gascoyne, AECL) was working on this aspect. Dr. Onofrei indicated that the AECL was evaluating the organic additives used for water reduction in the cement mix and preliminary results showed that the large molecules of these organic additives did not seem to work well to stimulate microbial action.

A. Meike (AM) suggested that we need to keep clear a distinction between the effects of organics and biotics, and indicated that they should not be viewed as the same thing. Furthermore, AM said that there are microbes which will use carbon dioxide gas (CO<sub>2</sub>) for food and that this type may be the most important ones to address.

After these descriptions of the experts backgrounds, R. Andrews (RA), made a brief overview presentation of the Yucca Mountain Site geology and potential repository layout to familiarize the outside experts with the general concepts and layout of the potential waste isolation system. After indicating the location of the mountain using maps and pictures of the site, RA gave brief descriptions of the stratigraphy and hydrology, the potential repository location within the rock layers, and the concept for waste emplacement. This was concluded with a description of the top-level strategy for waste containment and isolation in which RA focussed our attention upon near-field portions of the system. The five pieces of this strategy are (1) low ambient flux and saturations; (2) robust canisters; (3) limited mobilization of radionuclides; (4) robust engineered systems with possible diffusion barrier; and (5) slow migration through the geosphere.

Toward the end of RA's presentation, Prof. Hamlin Jennings arrived so that we performed a series of short introductions by all those present. This was followed by a brief description of Prof. Jennings' background. Prof. Jennings indicated that his beginning work focussed on structural ceramics and through this he pursued quantification of the links between microstructure and physico-chemical properties of cementitious materials. He chose to focus particularly in application of thermodynamic phase equilibria and kinetics to the understanding of how the microstructure related to the properties of these materials.

The presentation by R. Nolting (RN) covered the current repository ground support design and material compositions. The presentation covered the broad layout of the repository with emplacement oriented perpendicular to major fracture zones. The possibility of an exhaust drift 20 to 30 m below the potential repository horizon was discussed and the excavation is supposed to proceed from north to south with a barrier between the development side and the emplacement side. Emplacement will lag about 12-13 drifts behind excavation. The total drift lifetime is assumed to be about 150 yrs (including the retrieval period), which is comparable to the 120 year Channel tunnel life expectancy except that there will be a higher thermal condition in the case of the potential repository. Repairs to ground

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support may be needed during the monitoring/retrieval period.

D. Chesnut (DC) asked if the fact that the potential repository is planned to go from near the top of the TSw2 adjacent to the Exploratory Studies Facility Main Drift, to near the bottom of the TSw2 near the western margin creates any geotechnical concerns. RN indicated that there were no specific geotechnical concerns because of this. Prof. Roy asked for clarification of the orientation of connecting tunnels on the figure shown (RN-3), and RN indicated that the cross-hatched pattern was in the orientation of the potential drifts. Dr. Onofrei asked if the faults shown on the figure (RN-3) occur at the surface and RN confirmed that they did although the positions shown were those projected to the potential repository horizon. RN commented that the temperature within the drifts would reach about 150-200°C if they are not ventilated and the current plan was to not actively ventilate them because the cost involved for all drifts is very high. DC pointed out here that about 100-200 mm/yr of evaporation occurs at the ambient temperatures in the ESF with ventilation.

RN continued with his presentation of the current conceptualization of the construction showing some of the drawings for the invert and rail system and the initial Tunnel Boring Machine (TBM) launching layout for drift construction. RN indicated that within the main drift, the invert and rail system could be covered by additional systems capable to support waste package transports reliably. DCS noted that currently the ESF inverts are considered temporary items that will be removed prior to closure. The emplacement option being primarily considered is one using a gantry so that waste packages could be moved up into the gantry and pass over the remaining waste packages for relocation. The resting waste packages would sit within cradles and would perhaps have areas that could be gripped on their ends so that the gantry could lift them easily. The current plan for the pedestal is to use cast-in-place concrete with steel fiber reinforcement. At this point Prof. Jennings asked if hydrogen (H<sub>2</sub>) gas build up from corrosion of the steel fiber would be a problem in the tunnels. The general discussion on this point indicated that even with segmented linings (which have joints between segments), the tunnel would be very permeable to gas flow and that even if cast-in-place concrete would be used for the lining it would be, or could be, fractured, or even have holes drilled in it to ensure that gas flow was efficient.

RN continued into his presentation on ground support design plans giving three alternatives: (a) expanded precast segmental lining; (b) cast-in-place concrete lining; and (c) steel sets. RN indicated that the precast concrete segments were the preferred choice and would be about 150 to 200 mm thick. Prof. Jennings then inquired as to the spacing of canisters (depends on thermal load considered), and whether the gantry car would remain in the drift (no). Prof. Jennings further inquired as to the length of time to keep the drifts open (~150 years) and whether or not falling blocks were expected to fall over the time frame involved. RN replied that the block falls calculated indicated that size would be controlled by the joint spacing in the rock with blocks with diameters of ½ to 1 times the joint spacing being the most probable, and a rubble zone developing within the drift. Dr. Onofrei asked if the option of backfilling the drifts was being considered. RN responded to this to explain that although it was considered it did not currently seem feasible. DC and W. Halsey (WH) indicated that the temperature of the cladding increases dramatically if a backfill is used.

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At this point a tangential discussion was lead by DCS, DC, and W. Halsey (WH) covering the PA priorities for this study. DCS indicated that although the ground support function of the concrete was crucial for preclosure safety, this aspect was already considered by the panel of tunneling experts and that we were here mainly to address the potential postclosure PA issues resulting from concrete. DC pointed out that P. Zuidema of NAGRA who heads PA for the Swiss Program suggested that for geologic disposal the host lithology be chosen such that no cement was required for ground support. DCS and WH stressed that we are looking to better constrain the resultant effects on fluid chemistry from cement/concrete interactions with the ground water, particularly shifts to high pH. Dr. Onofrei stated that some work by Atkinson in the UK addressed aspects of the impacts of high pH on the mobility of radionuclides, and that this may be useful for our efforts.

RN continued with his description of the potential drift linings. In the current plan there are about 165 km of emplacement drifts and the liner represents about 3 cubic meters of concrete per m of drift length so that about 500,000 m<sup>3</sup> of concrete would be used within the potential emplacement drifts. In addition there will be about 13 km of ESF drifts, and a total of 196 km of tunnels altogether. This amount of concrete would probably require dedicated local facilities for providing it to the project, such as is done currently at the batch plant for production of the inverters for the ESF. The all-steel option for ground support is still possible but appears to be the more expensive of the options.

The presentation continued with discussion of possible concrete mix design for the drift linings. Repository Design is attempting to address current PA issues by evaluating low pH cement/concrete formulations. The currently preferred mix design combines type II Portland cement, limestone aggregate which appears to be relatively non-reactive with the cement, silica fume (10% by weight of concrete to get to pH of ~12), and perhaps steel fibers (nominally 0.5% by weight) for strength reinforcement. Structural reinforcement such as rebar would not be necessary. Laboratory testing of the material is planned to supplement those field tests performed in the heated drift. These tests would evaluate the concrete properties at 250°C for several years and would cover various mixes under consideration. DCS inquired as to whether or not these laboratory tests were integrated with those planned by 1.2.3. It had not yet been integrated, but it was agreed that this was a good idea.

DC and Prof. Roy then discussed the fact that some of the oil-field industry had needed used silica fume to aid in the thermal constraints on the concrete they used within wells and that there was literature covering the thermal needs of this industry. AM commented that we need to be careful regarding lifting a concrete mix from another area because, for instance, this project does not need the low viscosity that the oil-filed cement has been designed to have. M. Peters (MP) indicated that there are some 1.2.3 constraints on the ground support options. MP said that because the placement of precast liner segments may hamper the mapping of the tunnel walls, this ground support system might not be viable from the 1.2.3 standpoint. Options discussed were photo or video logging of the tunnel walls prior to placement of the concrete segments. RN finished his presentation with a summary of the ESF concrete mix composition.

AM began her presentation indicating that she would cover the natural ground water

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chemistry coming into the drift and possible effects from the thermal pulse. AM stressed that there are two considerations with the ground support, one being the mechanical performance and the other being the chemical performance. Each of these is relegated to a distinct period of time with the chemical performance being over the longer term. AM emphasized that in addition to the introduced materials, the heating event plays a major role in the environmental conditions. AM indicated that she would present some results of geochemical simulations to evaluate the thermal effects in a latter portion of her presentation.

A basic description of the saturated-zone fluid compositions (Eh, pH, major cations and anions) was presented. Dr. Onofrei asked if the water compositions for drainage from the surface through the unsaturated zone were similar to the ones to those of the saturated zone. The fact that the unsaturated-zone water compositions vary to slightly more extreme values than those in the saturated zone was noted by A. Meijer (AJ) and DCS.

AM discussed the paradigm defined by the work at LLNL which segregates the site into three regions; 1) a one-phase, above boiling zone immediately surrounding the potential repository, 2) a two-phase, boiling front which surrounds zone 1, and 3) a one-phase zone of increased saturation which results from condensation outside of the boiling front. The thermal loading used in the simulation results shown corresponded to 80-100 MTU/acre (which is approximately 114 KW/acre at the higher value). Prof. Jennings asked when the water is expected to return to the drift environment. The answer was that this depends on the thermal loading and the hydrologic properties (particularly the fractures), but that time frames from 500 to 5000 years were discussed. Again it was emphasized that the focus here was on the chemical effects not the mechanical effects, and that for the concrete the particular interest is in the phase transformations that will occur in the material through time in this near-field environment. Dr. Onofrei again stated that the predictive model of Atkinson gave about a pH of 11.8 based on the Ca/Si ratio in the cement.

Prof. Roy then indicated that she had performed some experiments for Los Alamos National Laboratory on equilibration of low-Ca cements with ground water over a period of months at temperatures of 90, 150, and 250 °C. Prof. Roy thought she recalled resultant pH values were in the range of 8 to 10, but said that she would include a summary of these studies in her report. AM indicated at this point that we need to keep in mind that there is a large difference between results from a 1 year experiment and what might occur over 1000 year time frames.

AM continued with her presentation of predictive modeling calculations of water composition evolution during evaporation of J-13 water using the EQ3/6 geochemical mass transfer software package. In these calculations the system was modeled both in equilibrium with the atmospheric oxygen and carbon dioxide gases and cut off from these gases, thus evaluating open and closed system behavior. It was seen that evolution of pH and oxidation potential in the system was sensitive to this assumption, with carbon dioxide and oxygen availabilities controlling each respectively. The dissolved concentration of many constituents increase because of the loss of water during the evaporation process, but silica and phosphate concentrations respond to the formation of solid phases also.

DCS covered briefly the PA prioritized issues regarding cementitious materials used in

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large quantities within the potential repository and the strategy that had been put together to address these issues. Many of the issues that DCS covered were discussed by this point in the meeting, however, HJ questioned what level the concern was over the amount of water introduced with the concrete. DCS indicated that it was fourth priority out of the four issues listed because from the PA perspective it is difficult to make introduced water cause an impact to performance, particularly in the case of high thermal loads because of the redistribution of water within the potential repository block. In addition, although the rock is unsaturated it still contains water in amounts that are not negligible when compared to that contained in concrete. HJ, DCS, and others pointed out that as the current design would use about 3 cubic meters of concrete per linear meter of tunnel, and one can assume that there is from 20 to 30 % water by volume in the concrete, about 1 cubic meter of water per linear meter of tunnel would be added. This is comparable to the identified limits for water loss within the ESF. Although the analyses are not directly applicable to water loss in potential repository drifts, they are conservative limits and are derived for water that is not being introduced within solid materials. In addition, it had also been indicated to PA that precast concrete can be made with lower water contents than other concretes to further minimize the concern. Finally, the evaporation rate has not been included and this would also provide additional water removal to somewhat offset the effects of introduced water. This discussion continued 45 minutes into the lunch period until DCS decided that the schedule could not tolerate further adjustments.

After Lunch MO indicated that she had some information to share regarding cement compositions being developed for the AECL program and their pore water pH values at ambient and higher temperatures. Prior to starting the directed discussion period, discussion continued regarding the water content of concretes. DR pointed out that it can be a trade off between increasing silica, decreasing water content and minimizing the use of organic admixtures. MO said that using silica fume virtually assured one of needing organic admixtures to improve rheology. HJ indicated that rheology could be fixed by using controlled particle size distributions. This he had researched using autoradiography of sulfur isotope distributions in cements formed with sulfate bearing phases.

Joon Lee (JL) led the directed discussion which began with questions of how cementitious materials might evolve in the potential repository environment, particularly what phases might be expected. DR indicated that zeolites and hydrogarnet are two likely phases. This was agreed with by HJ who also stated that the alkalis likely would form zeolites and that analcime was stable at high temperatures. HJ indicated that it may be possible to design the production of zeolites and discussed his work on preparing cements with highly alkaline fluids to start (pH~14) which resulted in cements with 5 order-of-magnitude lower permeabilities than standard Portland cement. This work was done at 100 °C, but not to 200 °C. JL then asked what was the likely evolution of the CSH phases in cement. The experts responded that crystallization of the gels would occur and then dehydration would begin resulting in phases such as tobermorite and xonotolite forming. This process is slow above 100 °C but may still continue. In this case, accelerated testing may not provide much information. HJ speculated that polymerization of the silicates would occur. It was pointed

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out that natural cement analogues may allow delineation of some of the stability fields of cement phases. MP asked if estimation of data for modeling was being considered and AM responded that the data in the Russian literature are the result of using polyhedral estimation techniques. AM said these are inadequate because many of these phases have highly irregular polyhedra and therefore the estimated free energies or enthalpies may be highly inaccurate. Phase equilibria experiments for some of these phases cannot be reproduced by the estimated data. In addition, because there was poor phase characterization in the experimental phase equilibria, it is unclear which set of data is preferable. DR indicated that wollastonite may form first at about 300 °C. HJ surmised that hydrated silica gel and calcite would be the likely products, but DR suggested that more reaction would occur with water returning to the drift. MO suggested that since cement starts with totally dehydrated materials, water returning to the drift may rehydrate the cement to form CSH gels anew. The curing time at lower temperatures will be short and the drifts would reach peak temperatures relatively quickly, depending upon the package loading and spacing. It was noted that ESF invert material would be subject to the heater test, but that the information would be at least a year or two away.

HJ asked again if we thought there would be abundant CO<sub>2</sub> and DCS responded that yes, atmospheric gases were the working base-case assumption. MO indicated that another issue with the AECL was that cast-in-place concrete added to the thermal load in the drift resulting in about 70 °C temperatures.

Next the alkalis were discussed in terms of zeolite formation. It was agreed that any additional aluminate phases would scavenge the alkalis and perhaps form zeolites. It was stated that in the Hatturim formation, low temperature feldspars are observed. Discussion on the AFm and AFt phases indicated the gypsum and anhydrite are likely to carbonate (as hydrokalumite?) and that ettringite is stable up to about 85 °C under dehydrating conditions and up to about 120 °C with water present. It was thought that there was enough data in the literature on the carbonation of these phases. The next topic was carbonation as a dominant mechanism for changing the concrete via calcite, and perhaps alkali carbonate, production. MO indicated that carbonation in many cases improved strength and acted as a self-sealer for concrete so that it was not necessarily bad for the cement.

JL then turned the discussion to aggregate reaction with the cement. It was thought that with low humidity that this would not occur much. DR indicated that it could be minimized by addition of fly ash/silica fume/silica of high surface area in order to preferentially react this material. HJ was asked about alkali-aggregate reactions and indicated that because it was a different system it was more difficult to say. DC indicated that drying and rewetting would probably not be homogeneous but rather intense precipitation once in a while would cause infiltration every so often and would result in very heterogeneous distribution of moisture.

JL then proceeded to the subject of geochemical effects from concretes starting with impacts to fluid compositions. DC raised the issue that if the potential drifts are ventilated, there may be salt buildup in the rock and drift and that initial returning fluid could be concentrated. D. Tang, RD, (DT) indicated that the drifts would be actively ventilated for

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about 5 years before loading and closing whereupon they will depend on about 10% ventilation indirectly. Much of the pH issue had been discussed earlier in the day but now there was a question as to whether or not the cement solids could isolate Cl from the aqueous phase. MO indicated that the cement may fixate some Cl without any phase precipitation, but HJ did not think that the concrete would act as a good barrier to Cl transport. DR indicated that higher temperature Ca-Si-hydrate phases may incorporate Cl into their structures.

The next topic JL raised was that of colloid generation. HJ did not think this should be much of a concern and stated that, even though CSH phases are colloidal (spherical and ~100 Å) he finds in his studies that cementitious colloids are only abundant for a short period of time in the cement pore water (10-20 days). AM stated that colloids may also be generated because of the geochemical gradients in a cement-bearing system. DR seconded HJ by saying that the silica fume reacts relatively quickly.

The discussion returned to the introduction of water issue. AM stated that because this would be a heterogeneous system this was a concern. Because concrete will contact other systems and there may be local environments in the drift that have relatively high relative humidity, which could enhance microbial processes. HJ asked what would the microbes be consuming? AM answered that there are many different microbes found at the site including sulfate reducers, and sulfur oxidizers, nitrifiers, etc., many of which acidify the entire area. There are microbes which can feed off of the CO<sub>2</sub> in the atmosphere. It is unclear what the threshold relative humidity for these microbes may be. HJ again asked if we thought that carbon dioxide would be abundant in this system and DCS answered that yes it looked like it would because of the atmosphere gas transport and because much CO<sub>2</sub> would be driven out of the aqueous phase as the system heated up.

The next discussion topic JL presented was alteration of the host rock. DC indicated that modeling work and lab data for natural systems indicate that the basal vitrophyre and that in the Paintbrush non-welded unit would be the most abundantly altered by the heat and water. Formation of clays and zeolites would be expected at about 60% relative humidity and would plug the permeability in the repository above waste packages which might be good, but doing the same within the pillars would be detrimental. Plugging under the potential repository would create a bath tub effect and perhaps could flood the repository. The solubility of most cement phases decrease at higher pH. Reactions with the aggregates have been observed up to about 80 °C, but not higher (some of these data may be relevant). AM indicated that tuff was used in the New Zealand geothermal concretes, but these may be slightly different than that intended for the potential emplacement drifts.

The next topic was for suggestions regarding mix design. JL noted that RD indicated that the current was a Type II Portland cement. MO asked why we were not considering the simplified chemistry of the Type IV, sulfate resistant cement. DT indicated that sulfate was not much of a concern because of the dilute fluid compositions, even though some water may end up with enhanced sulfate concentrations. MO said that the sulfate resistance is directly related to the mechanical performance of the concrete over long time periods. HJ said that considering the amount of concrete/cement to be used that the Project should think about having a dedicated kiln to produce the cement/concrete and to control the production directly.

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HJ suggested that previously widespread  $C_2S$  cement (30% less portlandite and easier to make) may be useful for this Project because of lowered Ca/Si ratio and high strength. DR said that cement commercially made for oil wells should be considered. The use of  $C_2S$  would be justifiable from historical data of its durability and strength. DCS queried whether anyone knew offhand what cement was used at Hoover Dam. AM said that there are steam heating ducts in the east which may provide some information. DT asked if the experts knew of any buildings using steel fibers as reinforcement. DR said that this was a common way of providing strength. HJ again question why the need for steel fibers when grain size and shape control can provide strength, and rheology control for the cement mix. MO indicated that if one wanted a low pH concrete, it may require a fiber other than steel or risk high corrosion rates for the steel. H. Kalia (HK) inquired whether or not rapid cooling (~2 weeks) of heated drifts would provide problems for the concrete.

DR said that steam-curing the precast materials which seems to benefit the formation of cement. This process may enhance the reaction of alkali with aggregate and the formation of ettringite, but other than these this seems to be beneficial. This is easy to do with precast because the longer curing time required is available. HJ said that a general rule is that if there is room for the phases to form they will. If the phases can form early then it is good, but if the phases form later after porosity is gone, the cement can crack and buckle. DT indicated that it is his experience that even using silica fume it is difficult to get much below pH of 12. MO said that the effect of pH on clay stability was the motivating factor in the AECL studies. She then presented information regarding the Low Heat High Performance Concrete (LHHPC) that they are developing. This cement has more silica fume, silica flour, and fine aggregate than the standard cement/concrete mix. This also had a lower water content than the standard mix. This concrete and the standard mix were reacted with a variety of ground waters at 25 °C and 100 °C and the resultant fluids pH analyzed. At 100 °C the LHHPC pore water had pH of from 8 to 9 compared to 10.5 to 11.5 for the standard mix. At 25 °C, the values were 9.2 to 11.5 and 12 to 12.8 respectively. There is substantial reduction of pH for this concrete, however it used 10.3 kg of superplasticizer per cubic meter of concrete (vs. 7.1 kg/m<sup>3</sup>) which is a large, undesirable mass of organics for the potential repository drifts.

The day's discussion ended by reviewing with the experts the PA priorities for addressing the issues concerning cementitious materials. Aside from asking the experts to focus of these PA priorities in general, they were each asked to address specific topics within their reports. HJ was asked to focus on the phase behavior of the evolving cements and on  $C_2S$  as alternative compositions. DR was asked to include discussion of her work from the seals program, the steam curing process and alkali activated cements. MO was requested to summarize the work on LHHPC from AECL and to provide some summary of results of investigations concerning organic admixtures.

**Yucca Mountain Site Characterization Project  
Performance Assessment Consequences of Cementitious Materials Scoping Study  
Expert Consultation Meeting on Potential Geochemical Effects  
of Evolving Cementitious Materials**

Thursday September 5, 1996

8:00 a.m. - 5:00 p.m.

Summerlin 1 Facility, Bldg #4; Room 415

1261 Town Center Drive

Las Vegas, NV

**Final Draft Meeting Agenda**

**8:00-8:45 WELCOME, BACKGROUND OF EXPERTS, AND SITE OVERVIEW**

Welcome	8:00-8:05	R. Barton, YMSCO
Prof. Della Roy, Pennsylvania State Univ.	8:05-8:10	D. Roy, PSU
Dr. Maria Onofrei, Atomic Energy Canada Ltd.	8:10-8:15	M. Onofrei, AECL
Prof. Hamlin Jennings, Northwestern University	8:15-8:20	H. Jennings, NU
Site Overview	8:20-8:45	R. Andrews, M&O/Intera

**8:45-10:00 PRESENTATIONS**

i. Potential Tunnel Support Design	8:45-9:15	R. Nolting, M&O/MK
ii. Types of Concrete Considered	9:15-9:45	R. Nolting, M&O/MK
iii. Near-Field Environment	9:45-10:15	A. Meike, M&O/LLNL

**(BREAK: 10:15-10:30)**

**10:30-11:45 PRESENTATIONS AND MORNING WRAP-UP**

iv. Performance Assessment Issues/Strategy	10:30-11:00	D. Sassani, M&O/Intera
v. Focus Questions for Afternoon Discussion	11:00-11:30	J. Lee, M&O/Intera
vi. Morning Wrap-Up and Question/Answer	11:30-11:45	ALL

**(LUNCH 11:45-1:00)**

**1:00-2:30 ISSUES DISCUSSION ALL**

**(BREAK: 2:30-2:45)**

**2:45-4:00 ISSUES DISCUSSION (CONTINUED) ALL**

**4:00-4:45 DELINEATION OF REPORTS CONTENTS ALL**

**4:45-5:00 WRAP-UP AND REVIEW OF ACTION ITEMS D. Sassani, M&O/Intera**

**5:00 ADJOURN**

Att. III

Attachment A

PA Cement Study Meeting

9/5/96

<u>Print Name</u>	<u>Organization</u>	<u>Phone</u>	<u>Fax</u>	<u>E-mail</u>
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David Tang	M&O/Repository	702/794-7701	-1844	
David Stahl	M&O/Waste, Preg. Matls	702-794-7778	702-295-9122	
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Bob Barton	DOE/AMSL	702-794-1455		
ERIC SMISTAD	DOE	702-794-1479		
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ALEND MEYER	LANL	(505) 256-3769	(505) 256-1323	
Hanlin Jennings	Northwestern U.	8474914858	8474915282	H-Jennings@nwu.edu

# IN 1987 CONGRESS TOLD DOE TO STUDY ONLY YUCCA MOUNTAIN



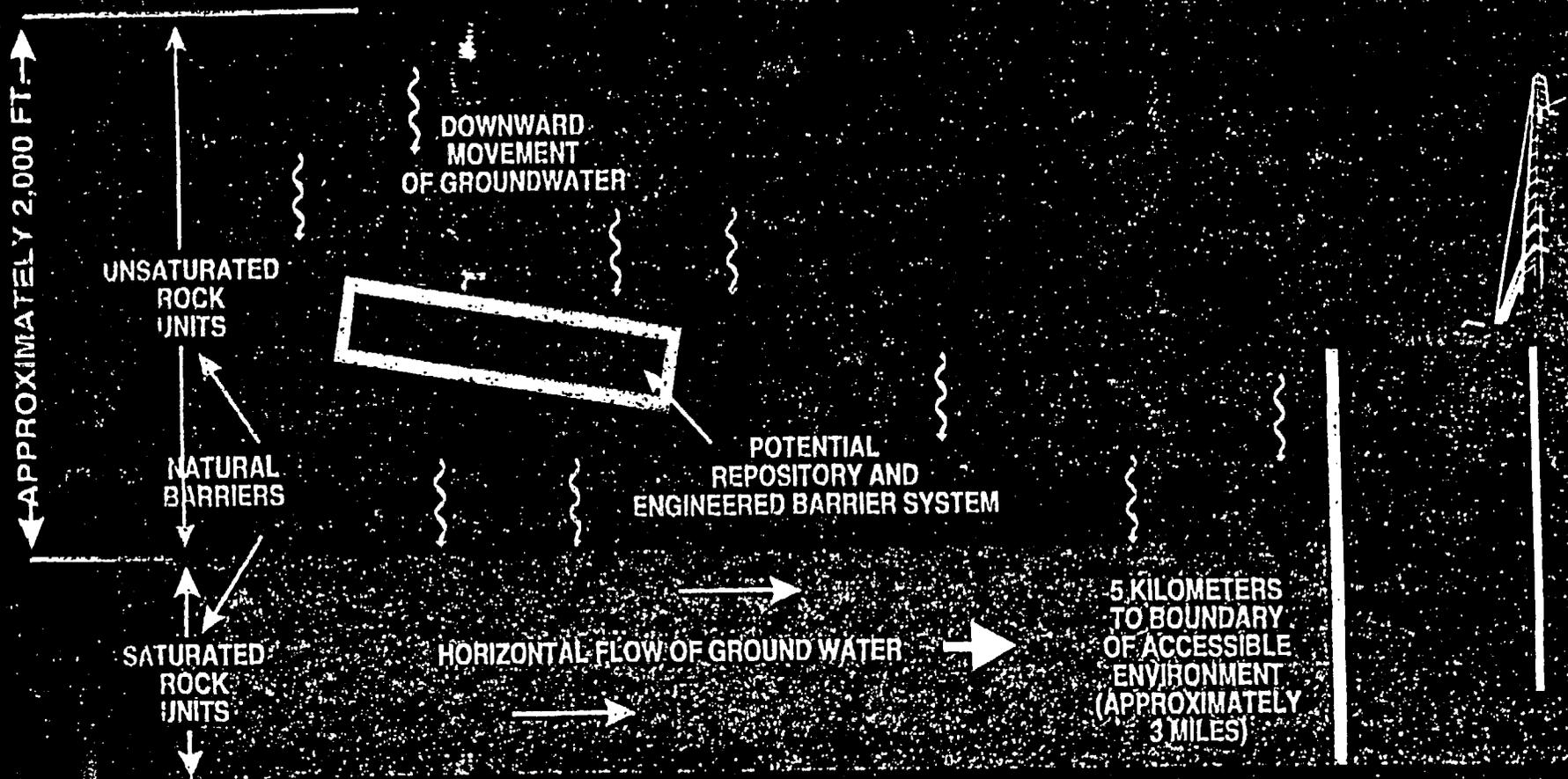
YUCCA MOUNTAIN IS APPROXIMATELY 100 ROAD MILES NW OF LAS VEGAS

9/5/96  
address - 1  
11-2-11

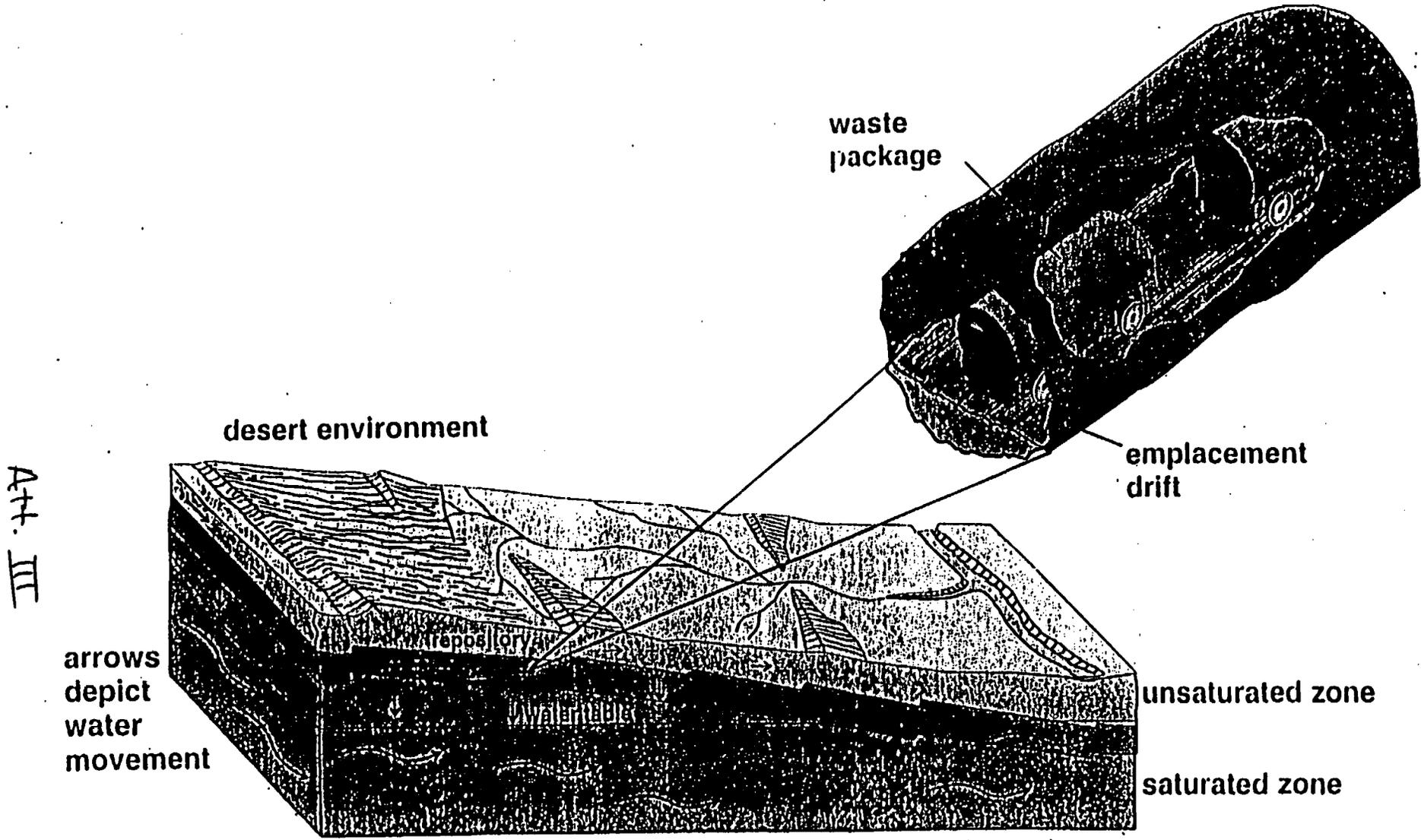


# OBJECTIVE OF SCIENTIFIC STUDIES IS TO DETERMINE IF YUCCA MOUNTAIN CAN ISOLATE RADIOACTIVE MATERIALS BY USING NATURAL AND ENGINEERED BARRIERS

Att. III

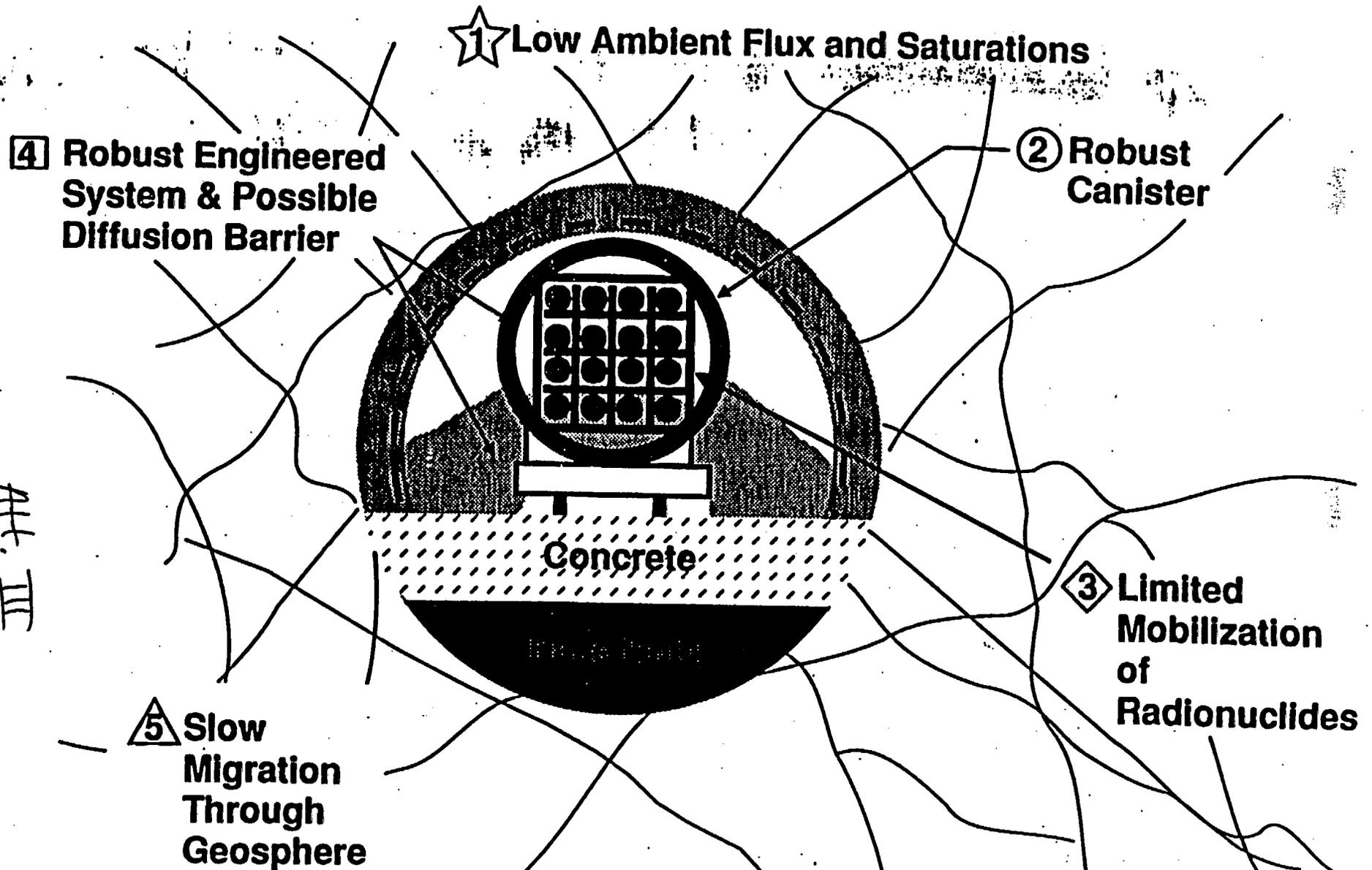


# Waste Isolation



01/15/91

# Top-Level Strategy for Waste Containment and Isolation



Attachment C Andrews-5 9/5/96

# PA Meeting on Cementitious Materials

## Repository Ground Support Design and Materials

**Dr. Rick Nolting**  
**Repository Lead Geotechnical Engineer**  
**September 5, 1996**

Att. III

R.N-1

9/5/96

Attachment c

# Discussion Topics

- **Repository layout**
- **Design of ground support**
- **Materials for ground support**

Att. III

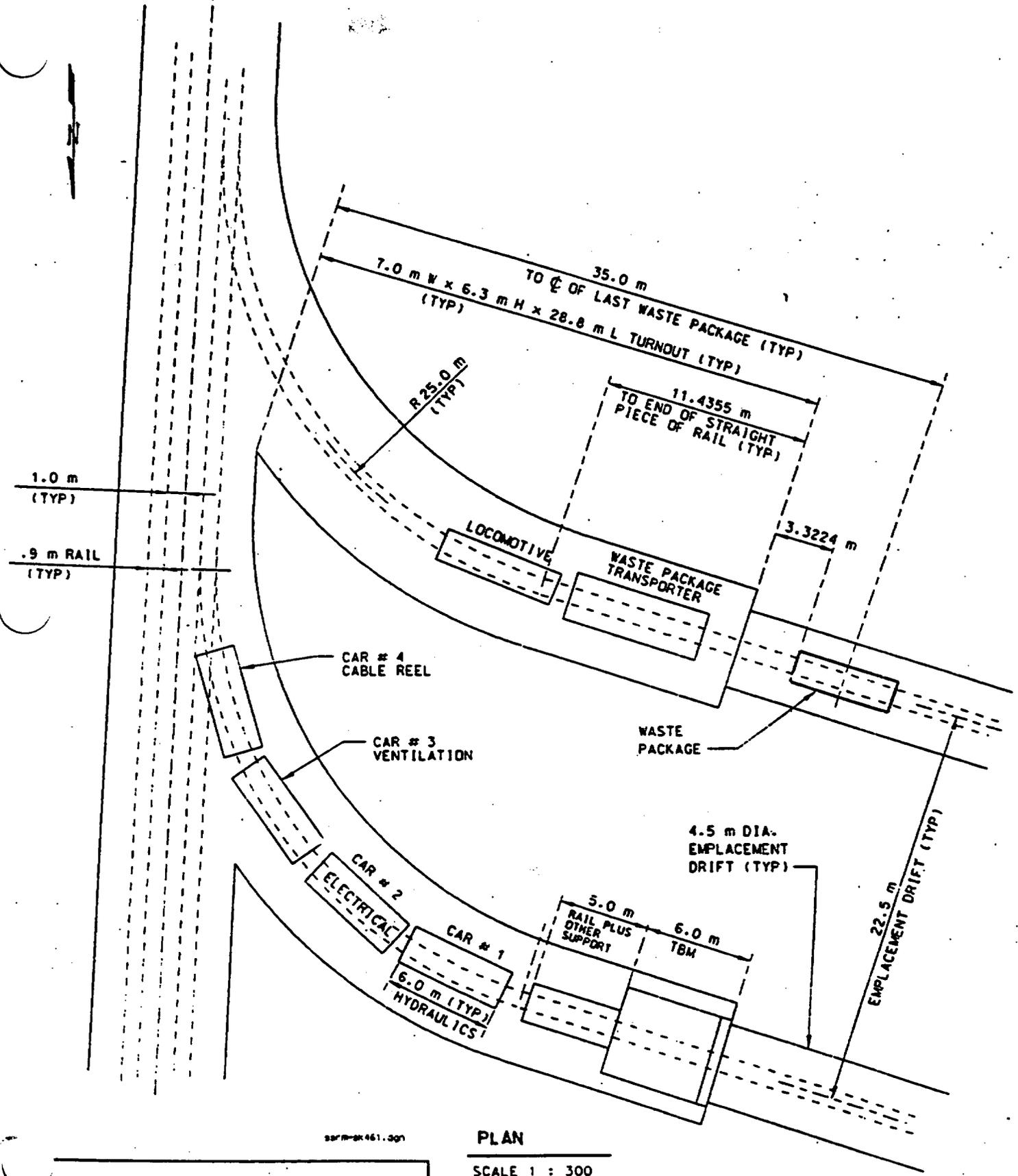
Attachment C

R.N. - 2

9/5/96



7.52 m DIA. LAUNCHING DRIFT



397-461.000

PLAN

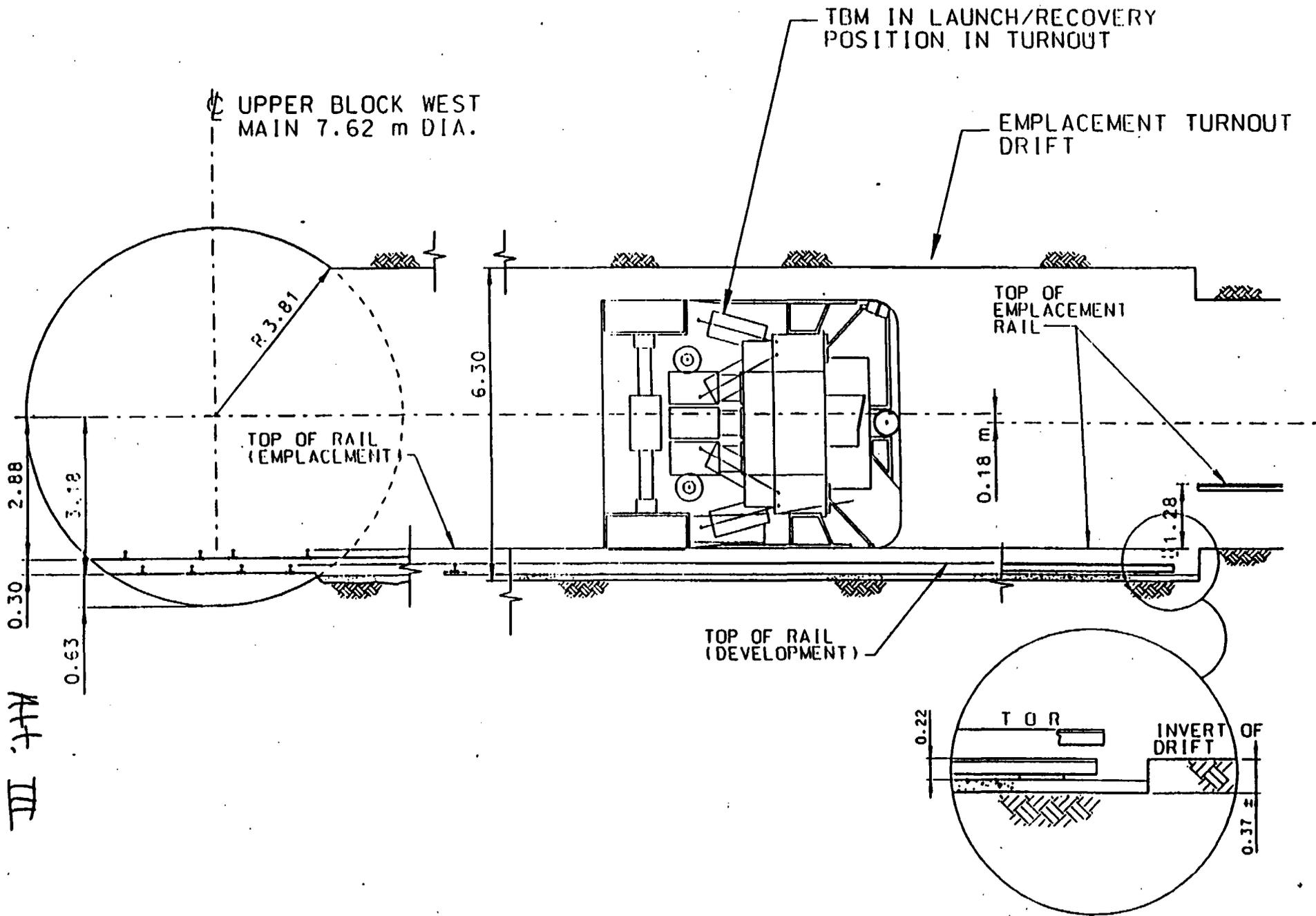
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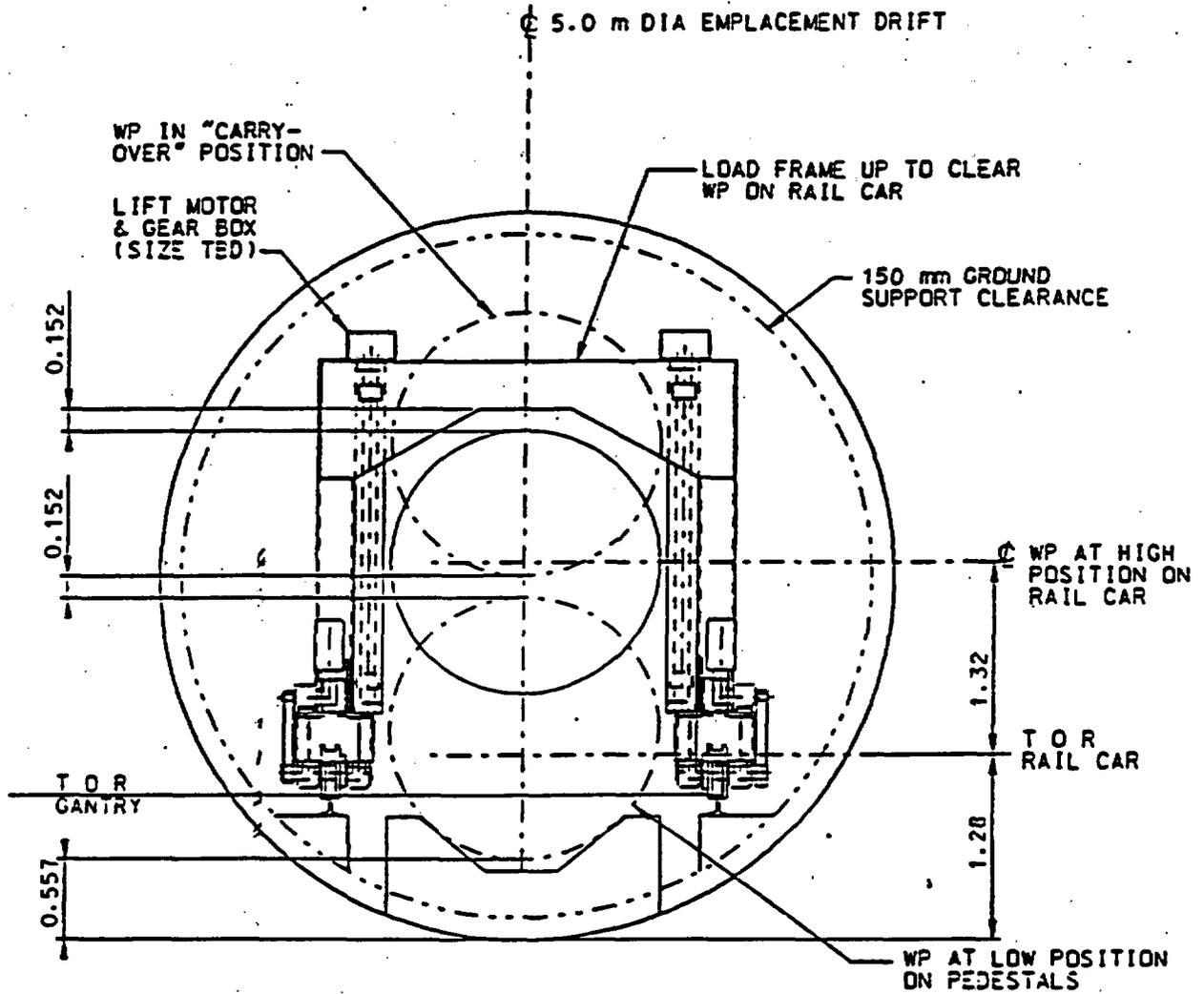
INITIAL TBM LAUNCHING LAYOUT  
ON LAUNCHING OR WEST MAINS  
(INCLUDING THE TRAILING GEAR)

25 m RADIUS TURN  
5.0 m TBM TRAILING GEAR

Att. III

Attachment C  
R.N.-4  
9/5/96

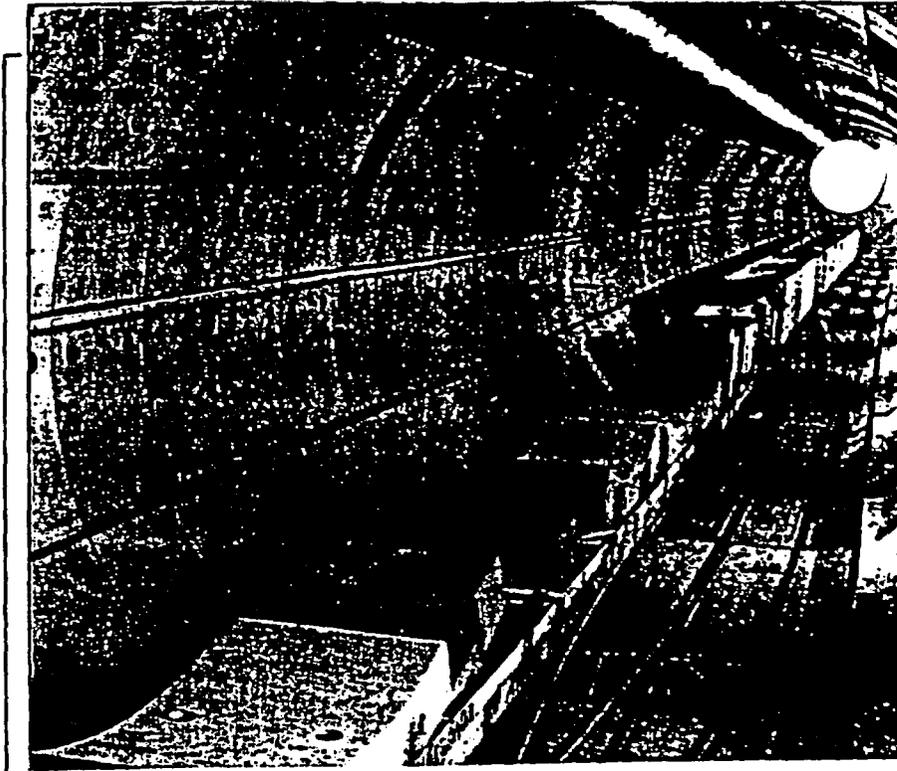




CLEARANCES OF GANTRY AND W P  
INSIDE 5.0 m DIA EMPLACEMENT DRIFT

Att. III

9/2/94  
 20-6  
 Millerham C.



Att. III

### EXCAVATION SUMMARY

	Length (m)	Volume (cu. m)
7.62 m Diameter TBM	13,286	605,889
5.0 m Diameter TBM	164,797	3,235,773
Roadheader	11,997	571,389
Raises	5,320	19,314
Shafts	661	23,305
<b>TOTAL</b>	<b>196,061</b>	<b>4,455,670</b>

09/04/86

02:10 PM

9/5/96  
211-8  
10

Att. III

# Ground Support Alternatives for Emplacement Drifts

- Expanded precast segmental lining
- Cast-in-place concrete lining
- Steel sets

Att. III

Attachment C R.N.-9 9/15/96

# Lining Design

**Current Approach to Accommodate Thermal Effects is to Examine Effects of:**

- Modulus reduction
- Creep
- No bond between lining and rock
- Joints between segments

**Additional Considerations:**

- Compressible elements in lining joints
- Compressible annular material

Att. III

# Use of Steel and Concrete

- **Performance Assessment (PA) uncertainty with use of concrete in the subsurface**
- **Current design requires concrete in ramps, mains, crosscuts, and turnouts**
- **We need to question PA concerns - compromise solution such as limitation on concrete use and low PH concrete**
- **We can design "All Steel" ground support and track - but expensive**
- **Long term stability of steel support questionable - steel sets generally considered temporary support**
- **Emplacement drift environment will minimize potential for steel corrosion**

Att. III

# Concrete Design

- **A goal of the concrete design is to develop an acceptable concrete formulation with low pH.**
- **Material properties will be determined for the resulting formulation and these properties incorporated into the structural design.**

Att. III

# Concrete Design, continued

- \* **Type II portland cement is the preferred cement type**
- \* **Limestone aggregate - non reactive (tuff and its constituents are potentially reactive with cement), good high temperature characteristics**
- \* **Silica fume - preliminary study indicates 30% by weight of cement (approx. 10% by weight of concrete) may be needed to reduce pH to a value of 12. The desired range appears to be greater than 11 but less than 13.**

Att. III

Attachment C

R.N. ( '3

9/5/96

# Concrete Design

(continued)

- \* **Reinforcement - structural reinforcement is not necessary, reinforcement would be specified to increase concrete toughness and tensile strength.**
- \* **Rebar is to be avoided to minimize possible long-term degradation due to differential expansion between concrete and steel. Steel fibers are the preferred alternative.**
- \* **For example, steel fibers (nominally 0.5% by volume of concrete) would be added to precast concrete segments to reduce cracking during handling and installation.**

Att. III

Attachment C

R.N. - 14

9/5/96

# Laboratory Testing

- \* **Laboratory testing is necessary because concrete properties cannot be accurately determined from field testing alone. Laboratory testing will supplement data from the drift scale heater test.**
- \* **Laboratory testing is necessary to determine the variation of concrete strength, modulus, and creep for representative repository conditions and for anticipated materials.**
- \* **These data will be used in the design of concrete linings for ground support.**

Att. III

Attachment C

R.N. 15

9/5/96

# Laboratory Testing

(continued)

- \* Test requirements include temperatures to 250 °C, test durations of several years, and variations in mix designs.
- \* An example is a series of laboratory tests to examine the effect of elevated temperature on the properties of concrete containing silica fume. Silica fume may be used to control concrete pH.

Att. III

Attachment c

R.N.-16

9/5/96

## Effects of Silica Fume in Concrete

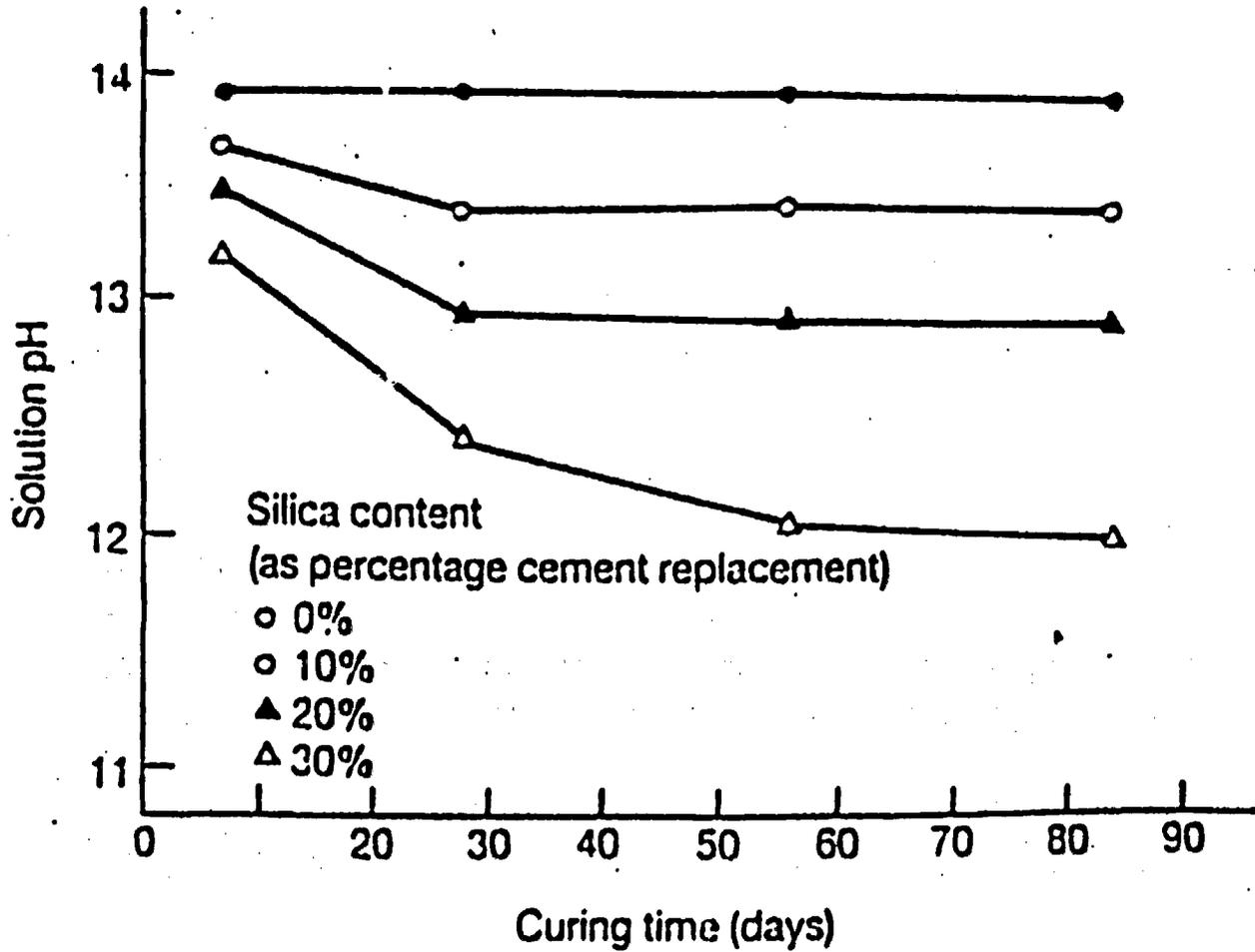
- Reduction of pH value of cement paste pore solution
- Production of low permeability concrete with enhanced durability,
- Increase resistance to sulfates
- Production of high-strength concrete

Att. III

Attachment C

R.N.-17

9/5/96



Effect of silica on the alkalinity of cement paste with  $w/c = 0.50$

Att. III

Attachment C

R.N.-18

9/5/96

## Questions About Silica Fume for Repository Use

- With addition of 30 % silica fume, the pH value does not drop below 12. Can the pH value of cement paste be reduced below 12. Do we need such a low pH ?
- Concrete containing silica fume in excess of 10 percent by weight of the cementitious materials may become sticky. Superplasticizer is required to increase the workability of cement containing silica fume. Will superplasticizer introduce too much organic material in the repository drift environment ?

Att.  
III

Attachment c R.N.-19 9/5/86

## Typical Chemical Composition of Precast Concrete in the ESF

Silicon ( as $\text{SiO}_2$ ):	22.40 %	Loss on Ignition:	1.50 %
Aluminum ( as $\text{Al}_2\text{O}_3$ ):	3.29 %	Insoluble Residue:	0.27 %
Iron ( as $\text{Fe}_2\text{O}_3$ ):	3.12 %	Total Alkali:	0.42 %
Calcium ( total CaO ):	65.07 %	$\text{C}_3\text{S}$ ( Calculated )	61 %
Magnesium ( as MgO ):	1.73 %	$\text{C}_2\text{S}$ ( Calculated )	18 %
Sulfur ( as $\text{SO}_3$ ):	1.88 %	$\text{C}_3\text{A}$ ( Calculated )	4 %
Free Lime ( CaO ):	1.70 %	$\text{C}_4\text{AF}$ ( Calculated )	9 %

Att. III

Attachment C R.N. - 20 9/5/94

## Typical Mix Design for Precast Concrete in the ESF

- Required Compressive Strength (f'c) 5000 psi
- Coarse Aggregate - 1/2" max size 1540 lb/cu yd
- Fine Aggregate 1420 lb/cu yd
- Cement - Type II portland cement 750 lb/cu yd
- Water-Reducing Admixture - Polyheed 126 oz/cu yd
- Water 37 gal/cu yd
- W/C Ratio 0.41

Att. III

Attachment C

R. N. J.

9/5/96

## Preliminary Composition of Concrete for Repository Emplacement Drifts

- Cement: Type II portland cement, 750 to 875 lb/cu yd
- Water: 300 to 350 lb/cu yd based on 3" slump and 3/4" max aggregate size
- Coarse Aggregate: 3/4" maximum size, crushed from limestone type rock
- Fine Aggregate: from same source of coarse aggregate
- Silica Fume: 15 to 30 %
- Water-Reducing Admixture: Polyheed or similar type
- Superplasticizer: Rheobuild or similar type, 15-40 oz/cwt
- $W/(C+SF)$ : < 0.4
- Steel Fiber: about 0.5 % by weight of concrete

Note: The above listed information is preliminary. Testing needs to be done to determine the optimal composition of the concrete.

Attachment C

R.N. - 22

9/5/96

Att. III

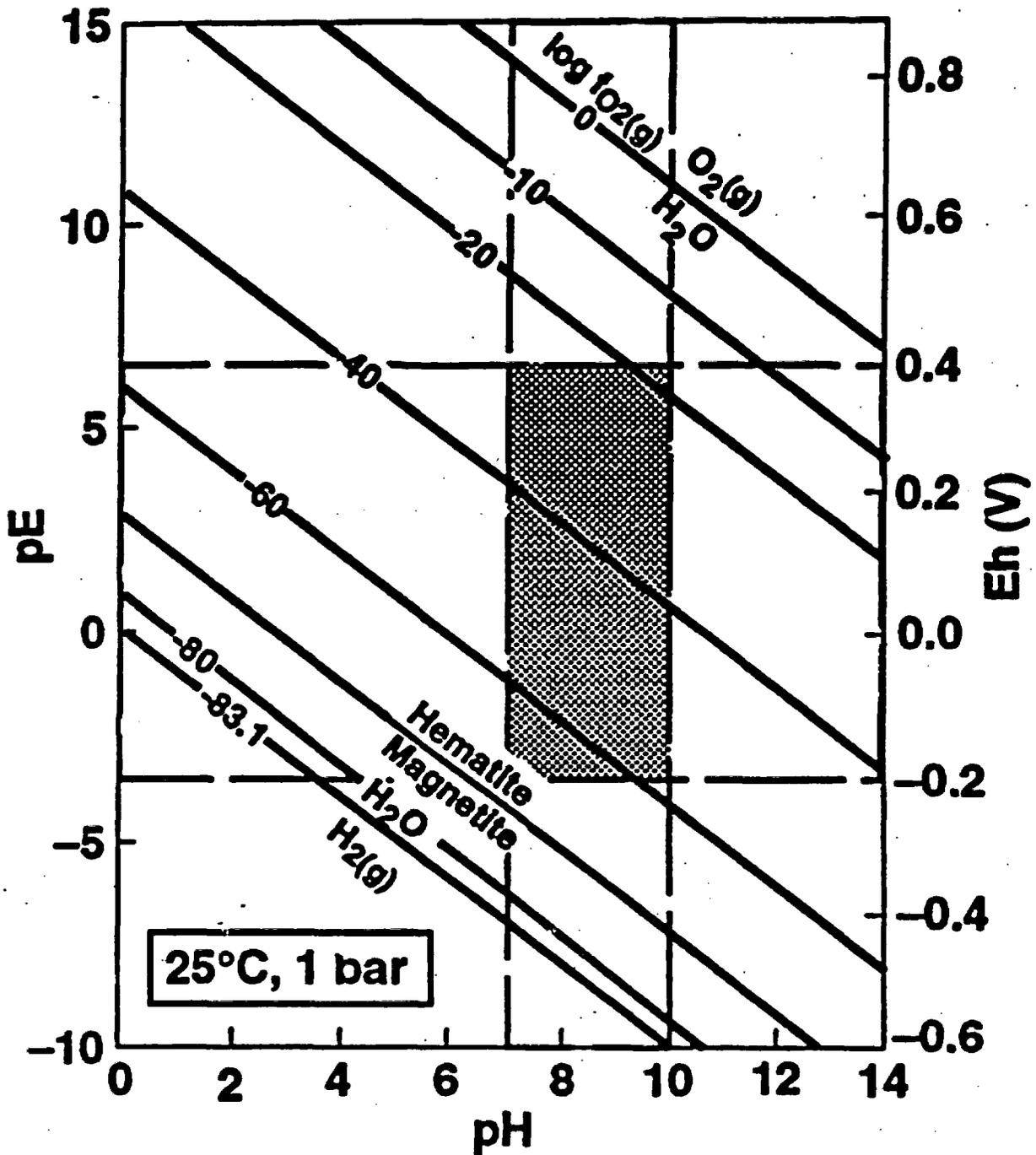


Figure 3-2. The measured ranges of Eh and pH in groundwater samples from the Yucca Mountain region (shaded area). Data from Ogard and Kerrisk (1984).

Att. III - Attachment C Meike 1; 9/5/96



COMPOSITIONS OF VARIOUS UNSATURATED-ZONE WATER FROM RAINIER MESA COMPARED WITH WELL J-13 WATER.



WHITE, ET AL. (1980)

HENNE (1982)

	<u>INTERSTITIAL</u>	<u>FRAC TURE</u>	<u>TUNNEL WATER</u>	<u>WELL J-13</u>
NA	1.73	1.53	2.30	1.96
K	0.18	0.12	0.11	0.14
CA	0.27	0.21	0.08	0.29
MG	0.10	0.06	0.01	0.07
HCO <sub>3</sub> <sup>-</sup>	1.14	1.61	2.25	2.34
SO <sub>4</sub> <sup>=</sup>	0.43	0.15	0.10	0.19
CL <sup>-</sup>	0.75	0.24	0.18	0.18
SiO <sub>2</sub>	0.97	0.88	0.73	1.07
PH	7.8	7.5	7.0	6.9

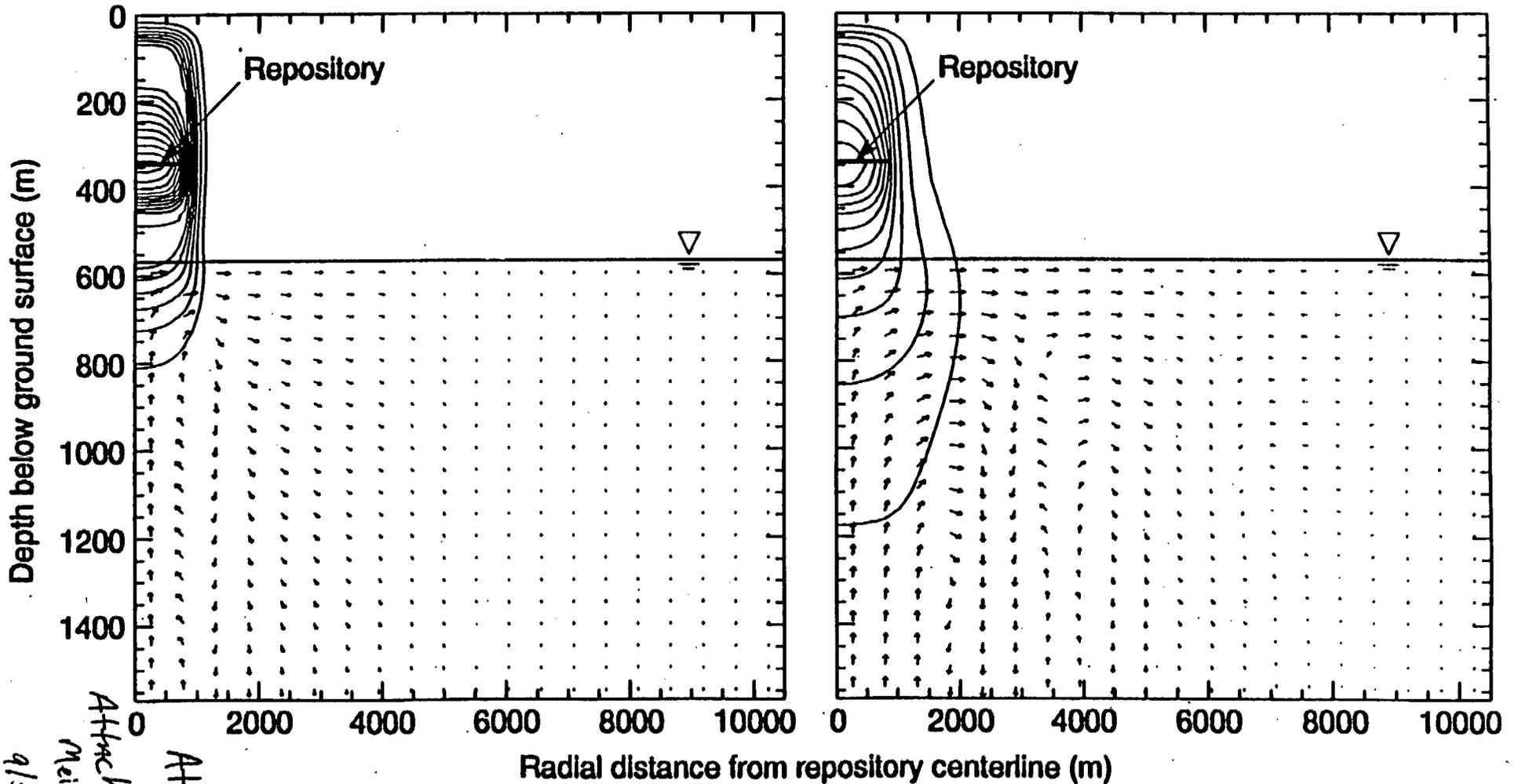
VALUES ABOVE ARE AVERAGES OF REPORTED DATA.

ALL SPECIES COMPOSITIONS ARE IN MMOLES/L.

Att. III  
 Attached  
 Meier  
 9/5/96

**Repository-heat-driven buoyancy flow in the saturated zone (SZ) becomes very significant for  $t > 1000$  yr, possibly dominating the ambient SZ flow system for tens of thousands of years**

Temperature increase above ambient (red contours) and liquid velocity field below the water table for 30-yr-old fuel, an APD of 114 kW/acre, and a recharge flux of 0.0 mm/yr; temperature contour interval is  $10^{\circ}\text{C}$ ; velocity vectors are scaled logarithmically from 0.04 mm/yr to 2 m/yr



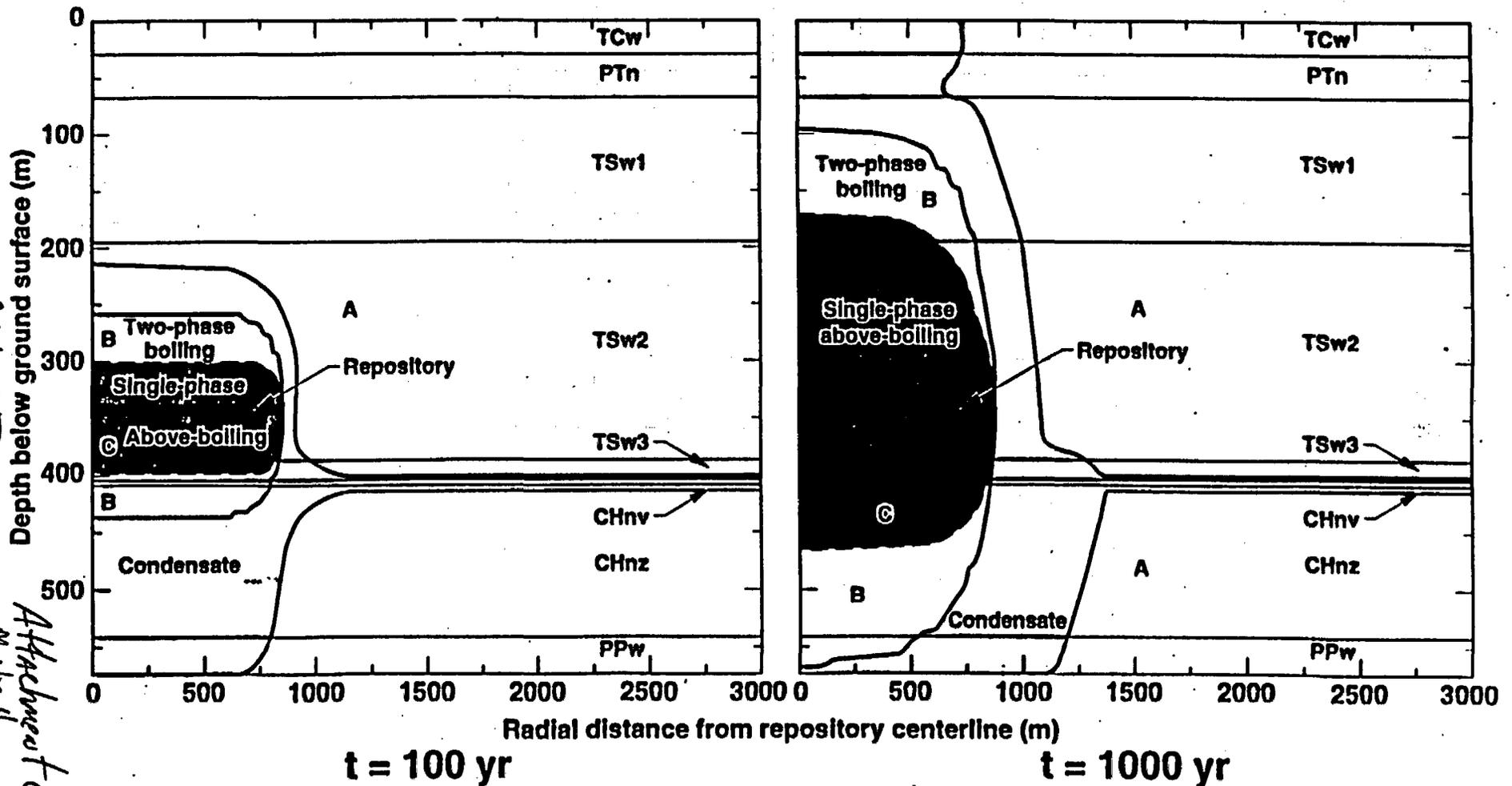
$t = 1000$  yr

$t = 5000$  yr

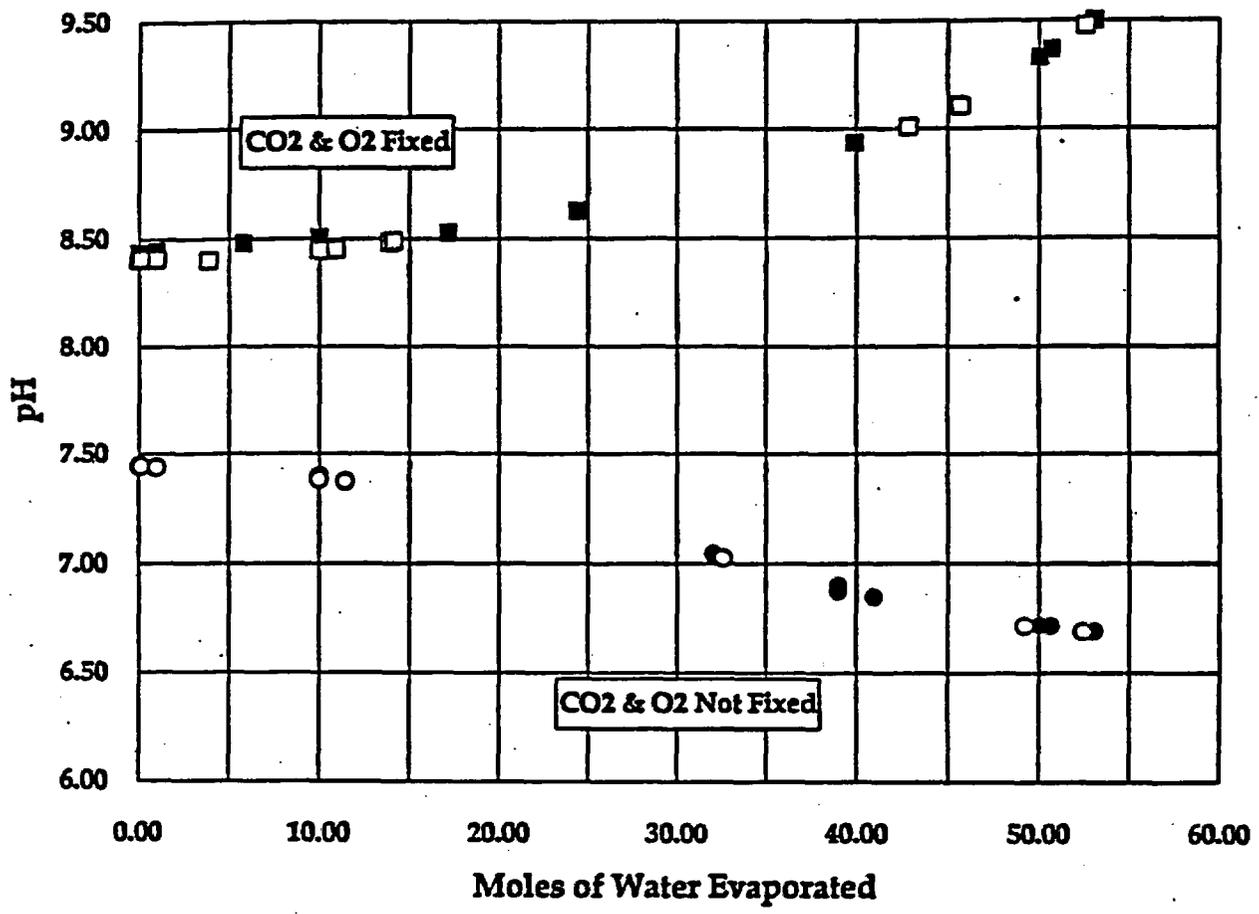
9/5/96  
 Attach  
 Meike's  
 Att. III

# Repository heating can result in a single-phase above-boiling zone, a two-phase boiling zone, and a condensate zone

dimensionless liquid saturation contours for 30-yr-old SNF, an APD of 114 kW/acre, and a AML of 154.7 MTU/acre

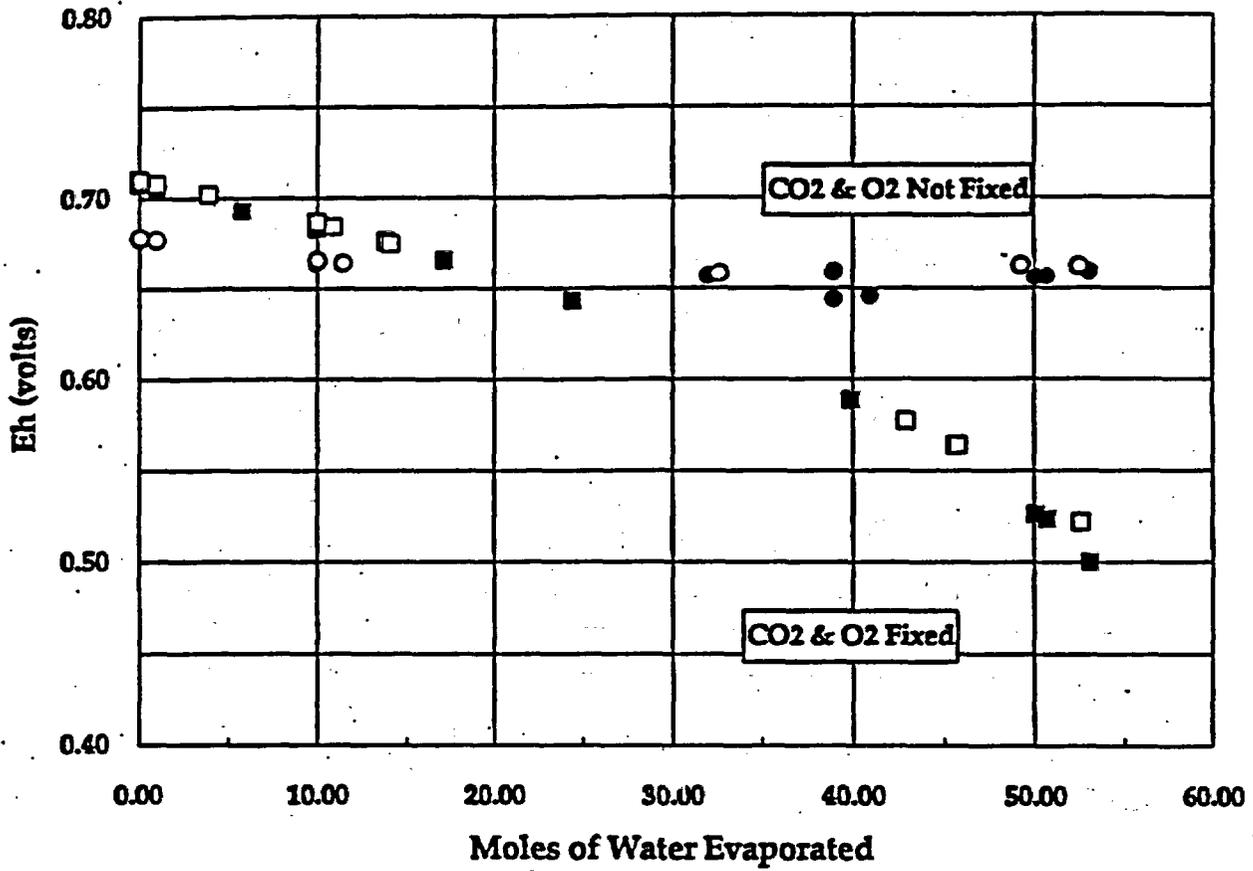


Att. III  
Attachment C  
Meike 9  
9/5/96



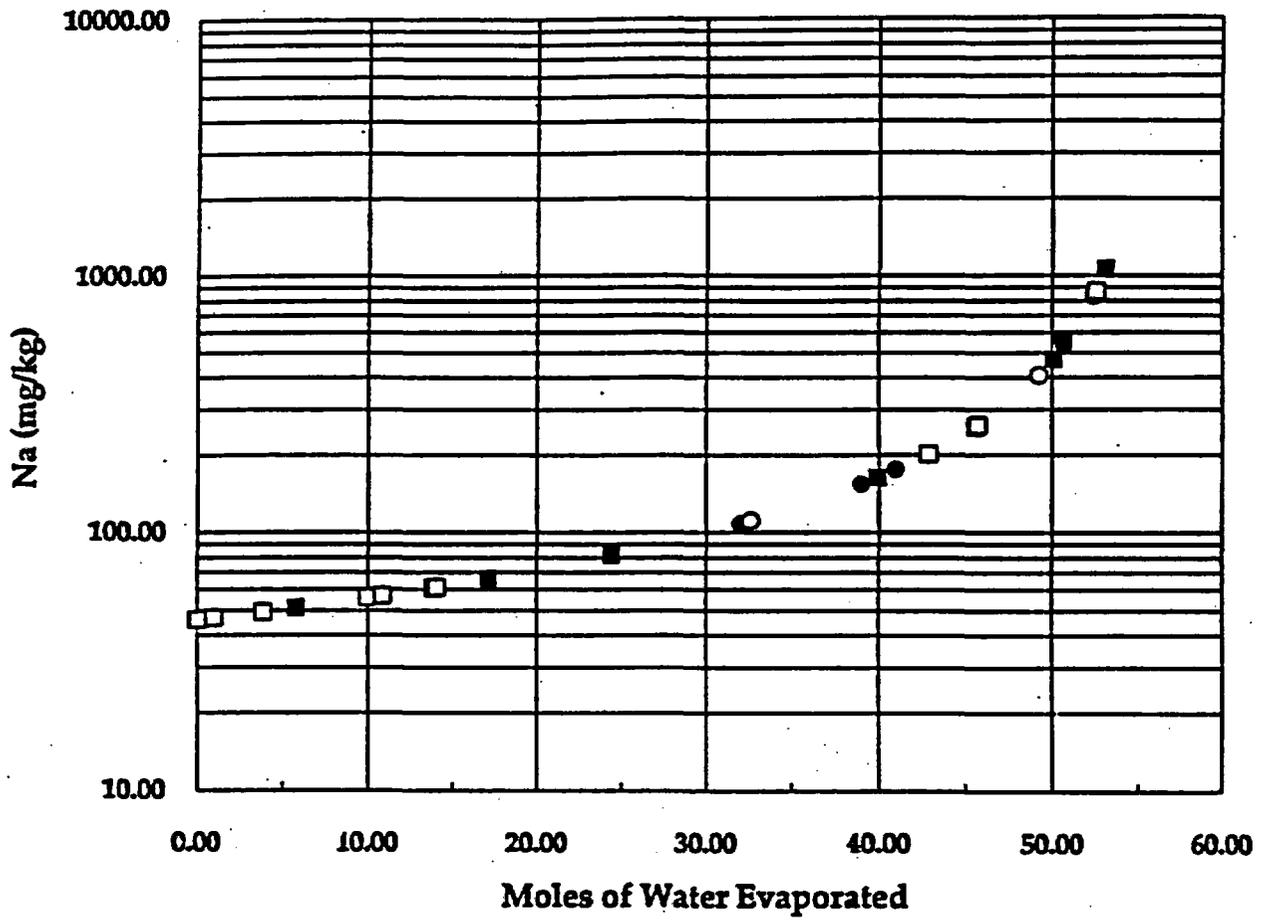
Att. III - Attachment C meike 5  
9/5/96

Fig. 2



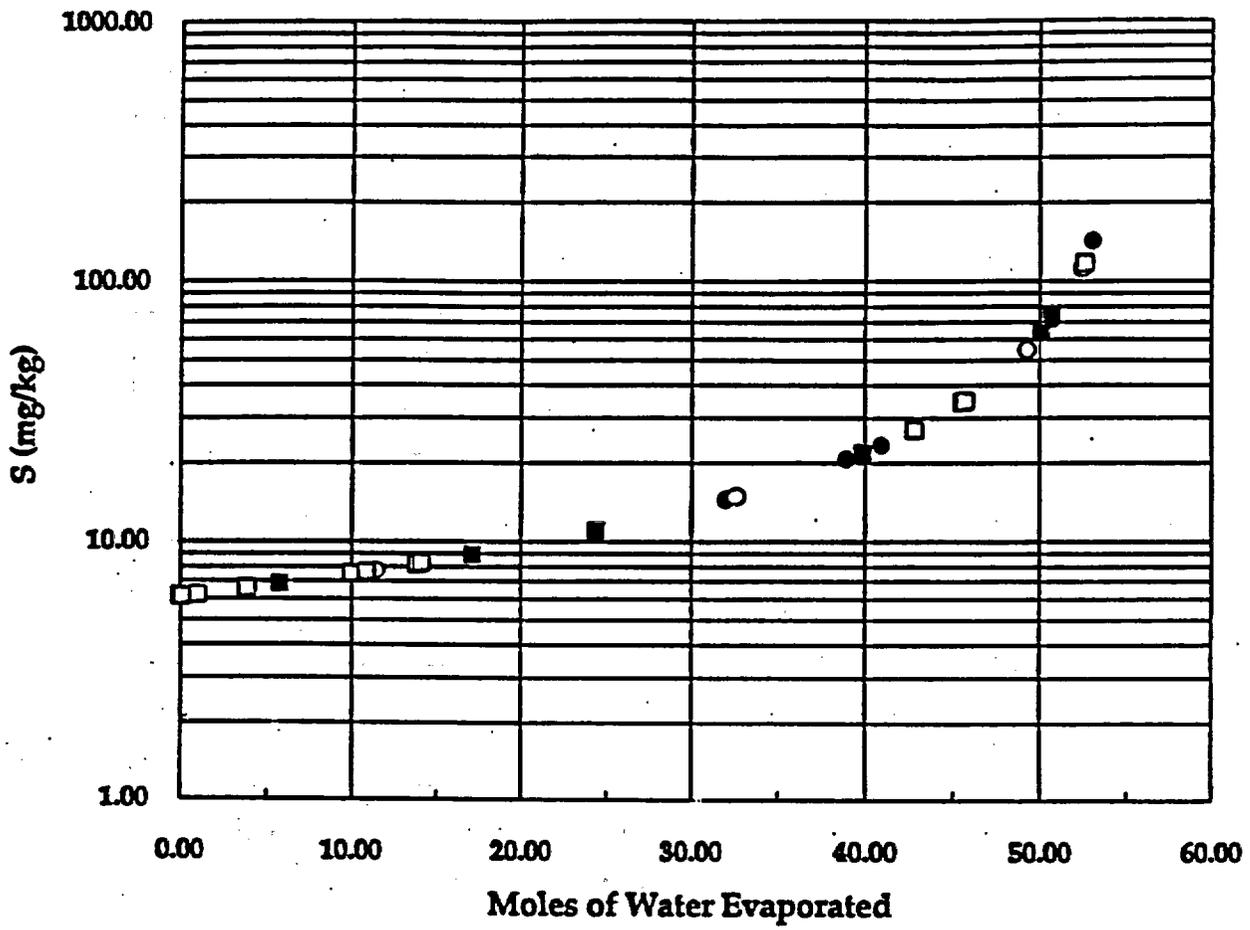
Att-III - Attachment C

Meike G  
9/5/96

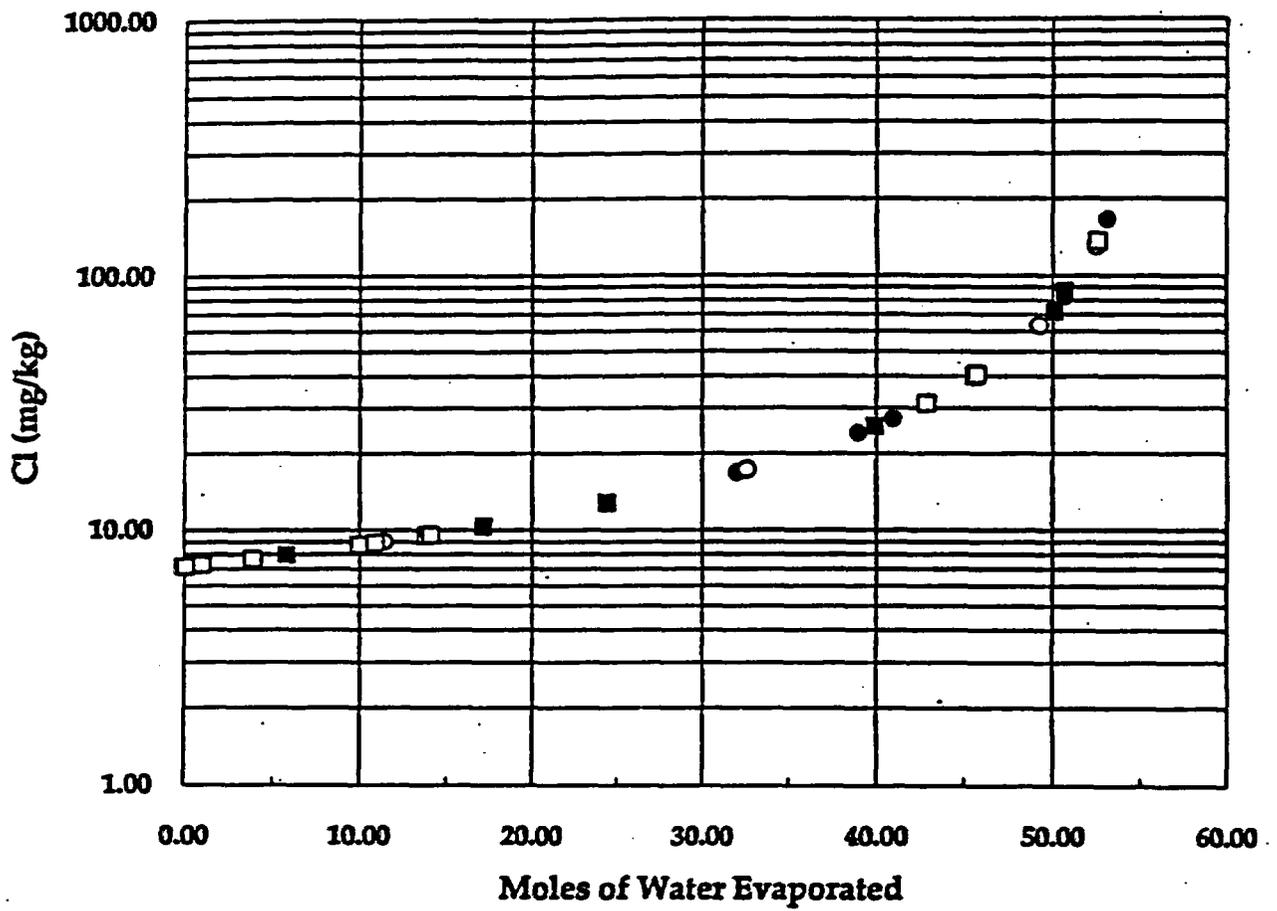


Att.-III Attachment C Meike 7 9/5/96

Fig. 4

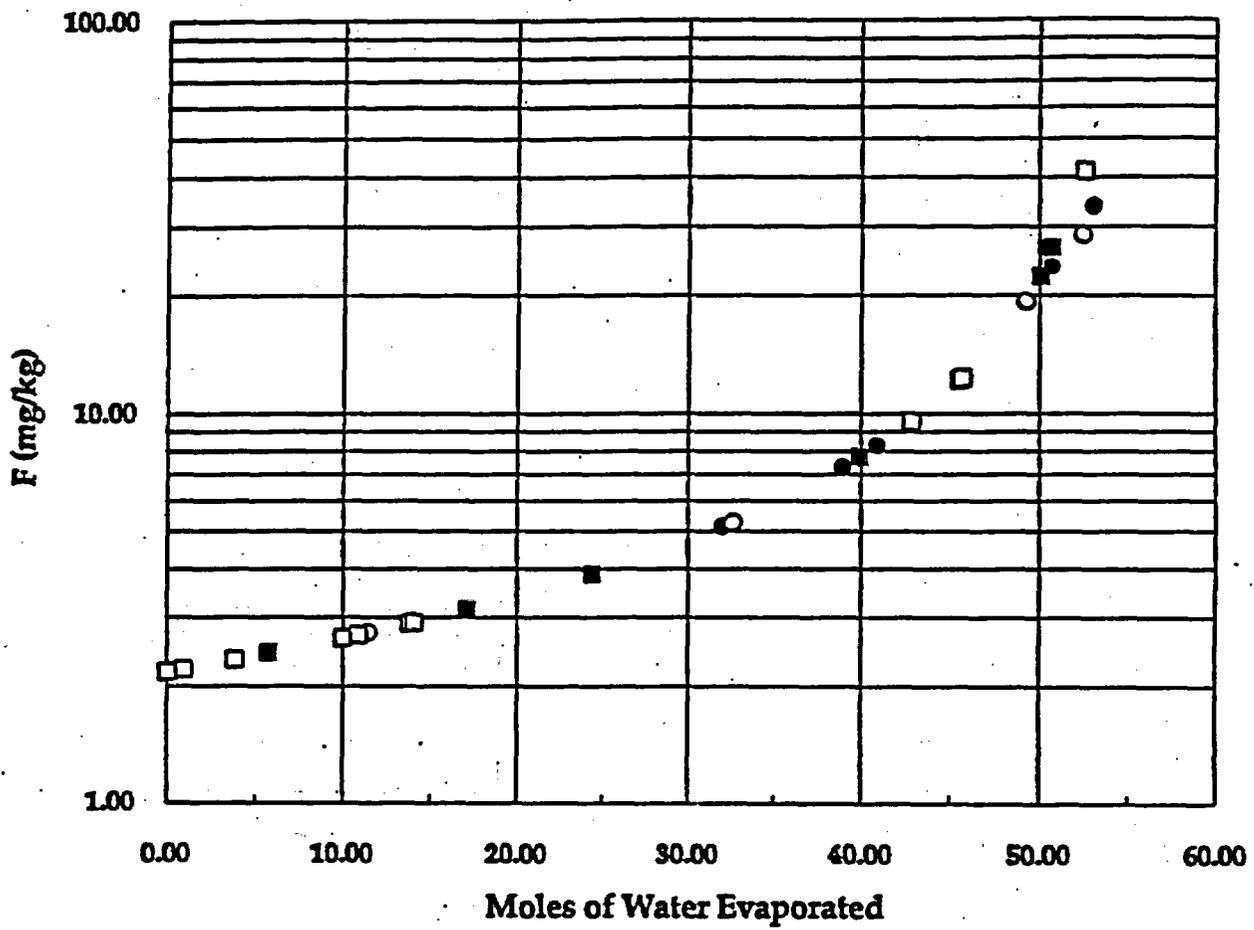


Att-III Attachment C Meike 8 9/5/96



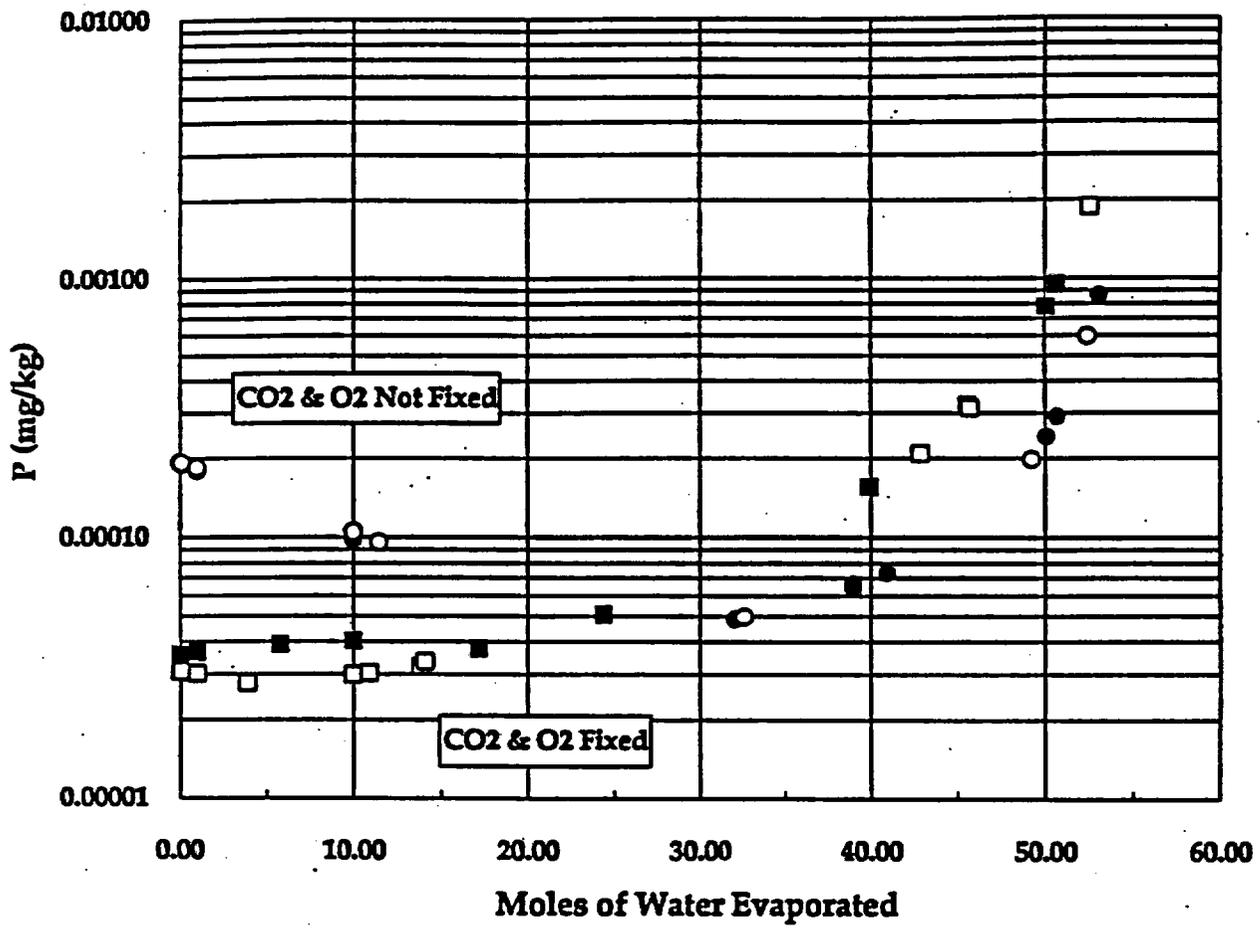
Att.-III - Attachment C Meike 9 9/5/

Fig. 6



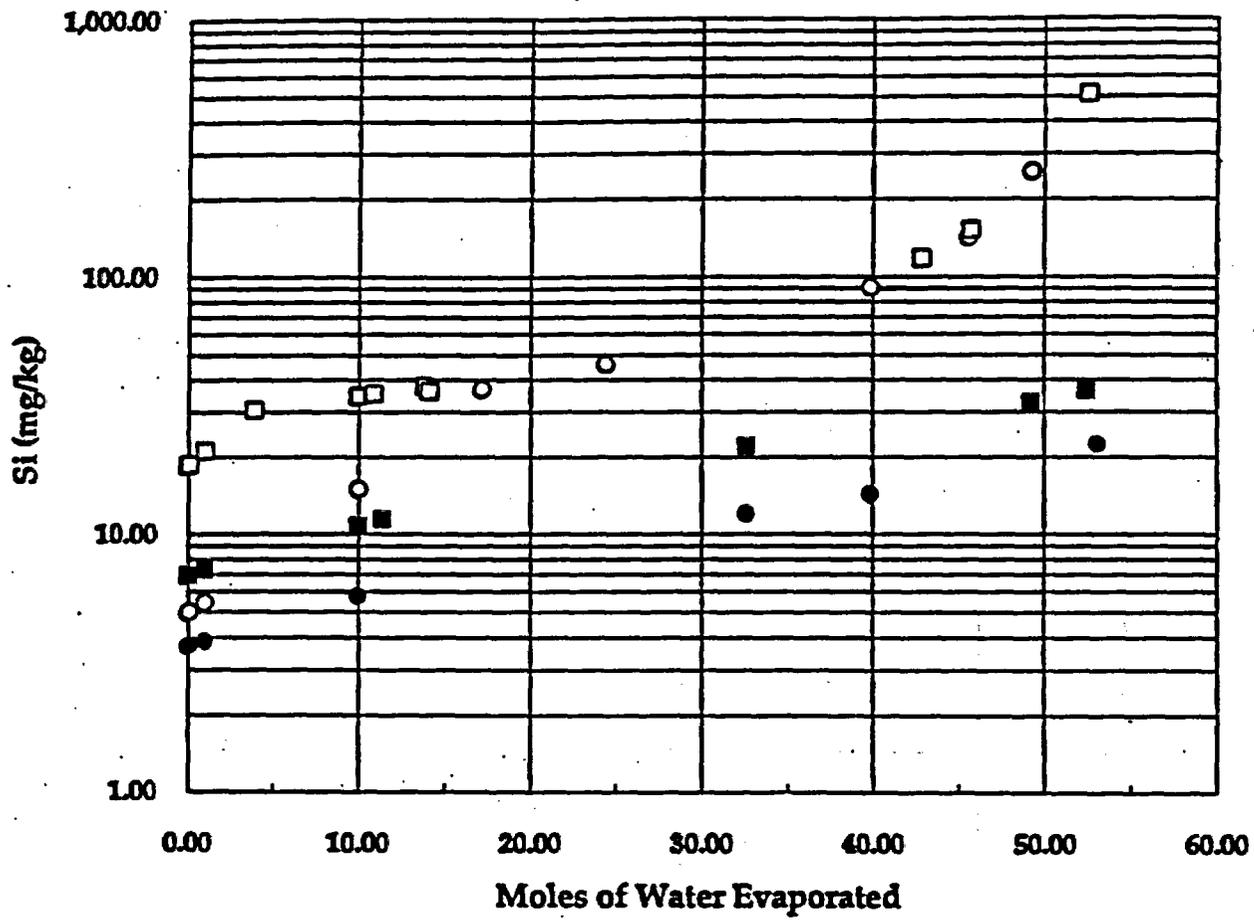
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Fig. 7



Att-III-Attachment C

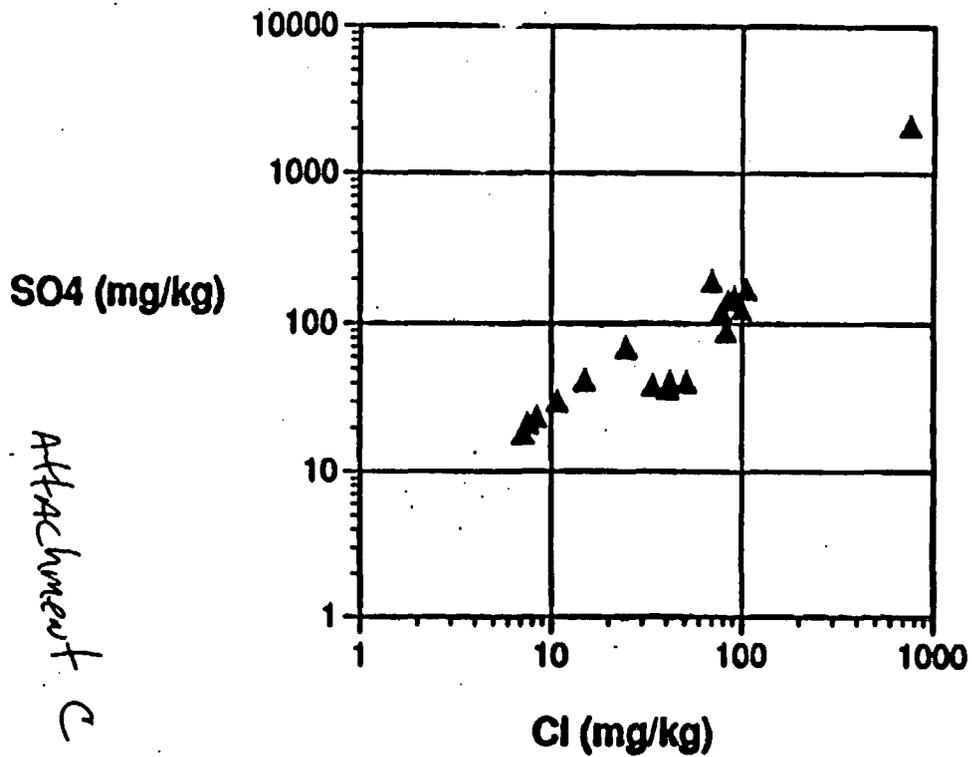
Meike 11 9/5/96



Att-III - Attachment C Meike 12 9/5/96

Fig-10

"Pore" Waters From Squeezing, J-13 Evaporation



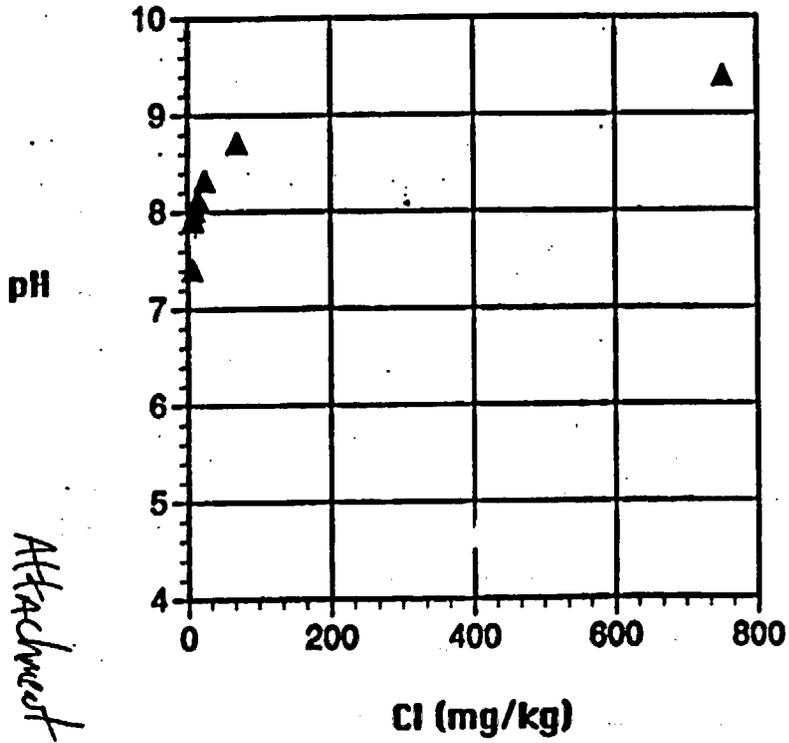
Att. III

Attachment C

Make 13

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Evaporation of J-13 at 90 C

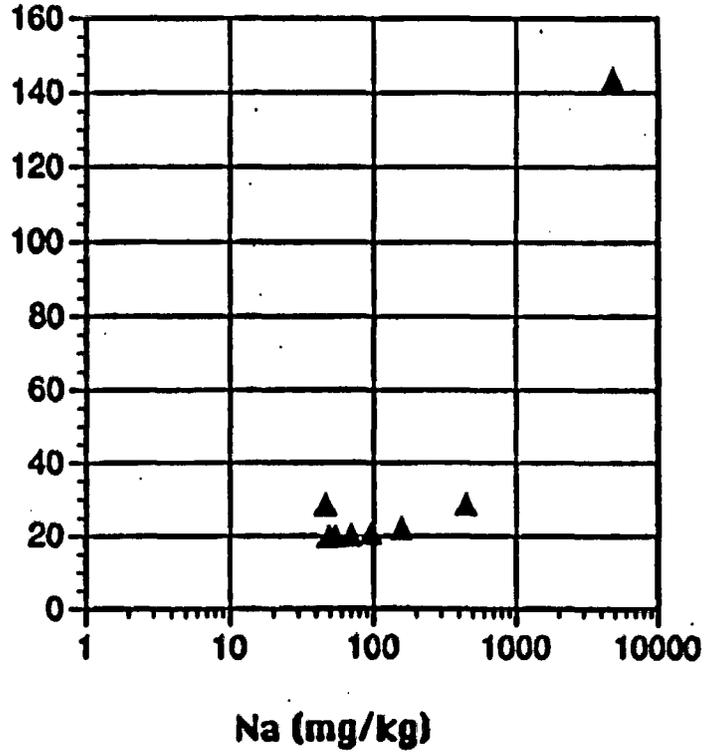


Att. III

Attachment C

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# Evaporation of J-13 at 90 C



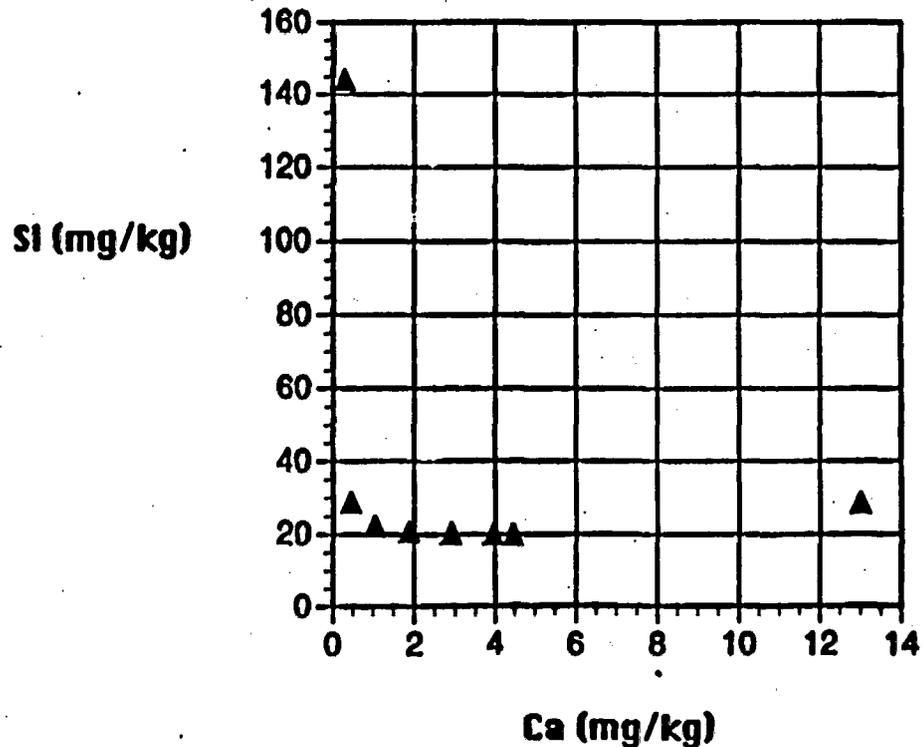
Att. III

Si (mg/kg)

Attachment c

Meike 15 2/5/96

Evaporation of J-13 at 90 C



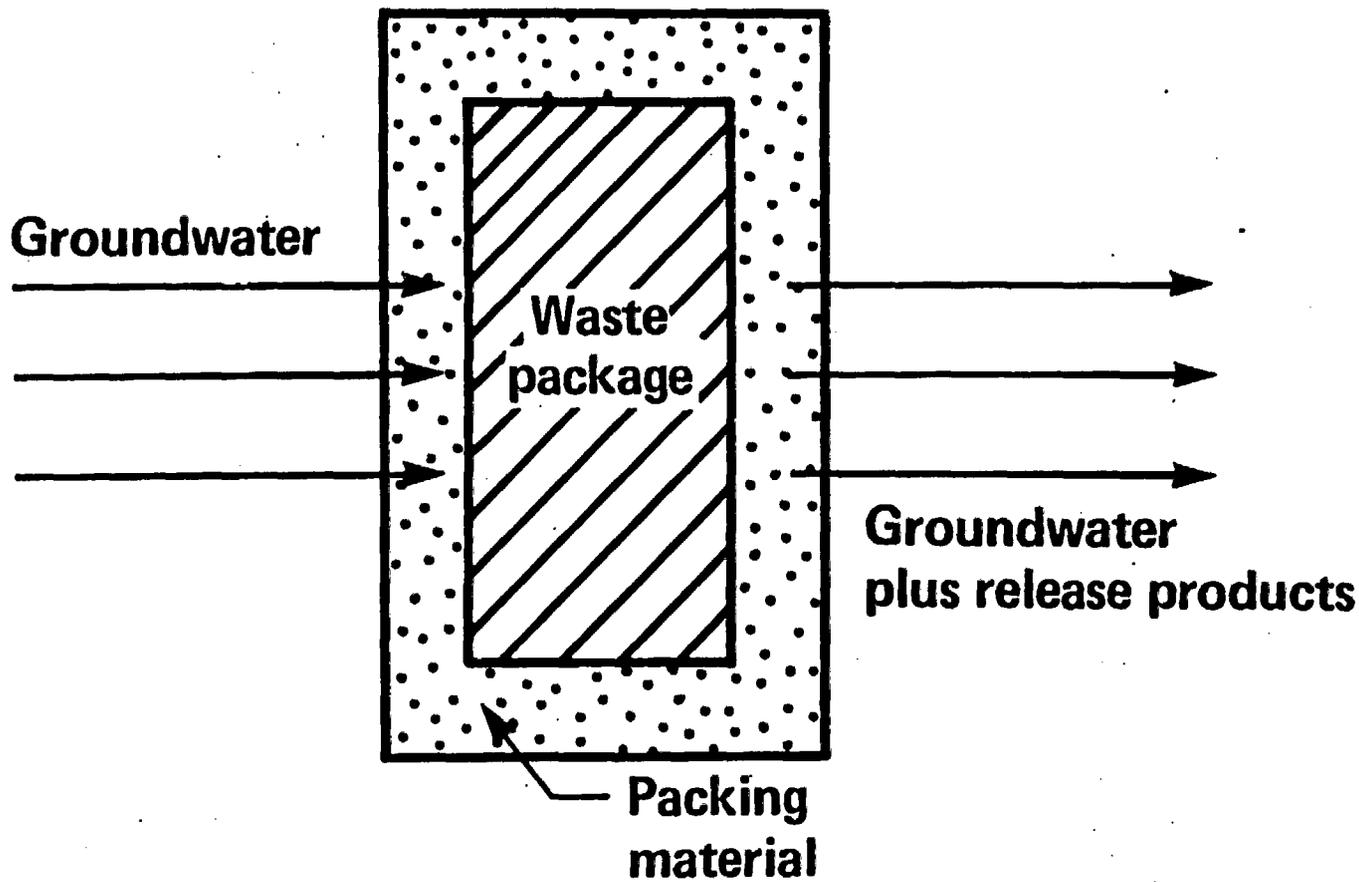
Att: III - Attachment C

Meike lb 9/5/96



Nuclear Waste  
Management  
Projects

## Generic waste package



Att. III - Attachment e

Make it 9/5/96

# Strategy to Address Potential Post-Closure Performance Impacts from Cementitious Materials

Att-III - Attachment C

# Prioritized Potential Effects and Impacts

1. Generation of High-pH (Alkaline) Fluids
  - ★ Increase Release of Radionuclides (Solubility Limited)
  - ★ Accelerate Transport/Decrease Sorption
2. Alteration of Host Rock
  - ★ Change Porosity and Permeability
  - ★ Change Transport Properties
3. Generation of Colloids
  - ★ Enhance Mobilization and Transport of Radionuclides
4. Water Source in Drift
  - ★ Increase Relative Humidity

Att. III - Attachment C

# Strategy

- ◆ Perform Sensitivity Studies at PA level for Ranges of Impacts
- ◆ Constrain Geochemical *Effects* at Process Level, both in Drift and Geosphere (SPO data need)
- ◆ Constrain *Impacts* to Performance Parameters, both in Drift and Geosphere (SPO data need)
- ◆ Assess the Impacts to Subsystem Performance (e.g., EBS release; Geosphere transport)
- ◆ Analyze Consequences to Total System Performance of Specific Impacts

Att. III - Attachment C

# Methods to Constrain Effects and Impacts

- ◆ Review and Summarize Literature Studies
- ◆ Elicit Input of External Experts on Cement System Behavior/Evolution
- ◆ Process-Level Thermochemical Modeling of Water-Cement-Rock Reaction
- ◆ Strategic Experimental Work as Tests of Reactive Transport Modeling Results

Att. III - Attachment C

# Performance Analysis of Impacts

- ◆ Sensitivity Studies for Ranges of Impacts to Source Term and Geosphere Transport
- ◆ Comparison of Impacts to Performance Parameters with Ranges Used in Total System Performance Assessment
- ◆ Perturbed-Case Consequence Analyses for Subsystems and Total System

Att. III - Attachment C

## Focus Questions on Potential Geochemical Effects of Evolving Cementitious Materials

Joon H. Lee

September 5, 1996  
Las Vegas, NV

BEW Federal Services  
Data Engineering & Services, Inc.  
Fluor Daniel, Inc.  
Framatome Cogema Fuels  
Integrated Resources Group  
INTERA, Inc.  
JMI Corporation

JK Research Associates, Inc.  
Lawrence Berkeley Laboratory  
Lawrence Livermore National Laboratory  
Los Alamos National Laboratory  
Morrison-Knudsen Corporation  
Science Applications International Corporation

Sandia National Laboratories  
TRW Environmental Safety Systems Inc.  
Woodward-Clyde Federal Services Inc.  
Winston & Strawn  
Cooperating Federal Agency:  
U.S. Geological Survey

### Areas To Be Included for Focus Questions

- Evolution of cementitious materials in emplacement drift
- Effects on in-drift water chemistry from evolving cementitious materials
- Effects on colloid generation from evolving cementitious materials
- Effects on alteration of (silica-abundant) tuffaceous host rock from evolving cementitious materials
- Suggestions for potential mix design of precast concrete for emplacement-drift linings

Attachment D

Lee

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## Evolution of cementitious materials in emplacement drift

---

- Major hydrated cement phases to be considered
  - Calcium silicate hydrate (CSH) phases
  - Calcium hydroxide (portlandite) phase
  - Alkalies (Na<sup>+</sup> and K<sup>+</sup>)
  - AFm (Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-monosulfate) phases
  - AFt (Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-trisulfate) phases
  - Other phase(s)?
- Evolution of CSH phases?
  - remain poorly crystalline or crystallized?
  - If crystallized,
    - what is its kinetics in emplacement drift conditions?
    - what are the impacts on the pore solution chemistry and the concrete physical properties?

## Evolution of cementitious materials in emplacement drift (continued)

---

- Fate of alkalies?
  - Incorporated into zeolite and/or other (Na,K)-bearing phases?
- Evolution of AFm and AFt phases?
- Carbonation of hydrated cement phases (CSH, portlandite, AFm and AFt phases)
  - assume atmospheric CO<sub>2</sub> partial pressure
  - mineralogical changes in concrete?
    - calcite precipitation and others?
  - effects on the chemistry of concrete pore water?
    - lowered pH and others?
  - physical property changes of concrete?

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8/5/96

## Evolution of cementitious materials in emplacement drift (continued)

- Long-term effects of alkali-aggregate reactions in concrete (assuming relatively sound aggregates used)
  - mineralogical changes in concrete?
  - effects on the chemistry of concrete pore water?
  - physical property changes of concrete?

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Management & Operating  
Contractor

Performance Assessment  
and Modeling

Drift cementitious materials

04/96

## Effects on In-Drift Water Chemistry

- Effects of high pH conditions from evolving cementitious materials?
- Effects of abundance of cationic species from evolving cementitious materials?
  - Ca, Si, Al, Na and K, etc.
  - mineralogical evolution within emplacement drift?
    - precipitation of calcite, calcium silicate phases, siderite ( $\text{FeCO}_3$ ) (Fe from waste package container materials)?
    - other potential phases?
- Effects of abundance of  $\text{SO}_4^{2-}$  ions from evolving cementitious materials?
- Potential incorporation of chloride ions (Cl) into hydrated cement and other phases?

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Drift cementitious materials

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Attachment D

Lee

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Att. III

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## Effects on Colloid Generation

---

- **Enhanced generation of colloids from evolving cementitious materials?**
  - provide conditions for colloid generation by large changes in pH?
  - generate colloids by gel particles spalled off from the cement paste matrix?
  - others?

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## Effects on Alteration of (Si-abundant) Tuffaceous Host Rock

---

- **Extent of mineralogical changes in host rock?**
  - mineralogical characteristics of alteration products?
  - effects on evolution of pore water chemistry in host rock?
  - accompanying physical property changes in host rock?
- **Potential plugging of pores and fractures by alteration products?**

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Page 4 9/5/96

## Suggestions for Potential Mix Design for Precast Emplacement-Drift Lining Concrete

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- What concrete mix design(s) are best suited to mitigate maximally the issues and concerns on post-closure repository performance?
  - type(s) of cement?
  - use of mineral additives (pozzolans)?
    - silica fume, fly ash, slag, etc.
  - type(s) of chemical admixtures, if necessary?
    - minimize (none if possible) organic admixtures
  - range of water to cement ratios?
  - type(s) and sizes of aggregates?
  - steel-rebar, steel fiber, and/or inorganic fiber reinforcement?
  - benefit(s) from steam-curing?
  - others?

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Meeting Report August 1996

Attachment D <sup>Lee</sup> Att. III  
Page 5 9/5/96

**POTENTIAL GEOCHEMICAL EFFECTS  
OF  
EVOLVING CEMENTITIOUS MATERIALS**

*Report To:*

Intera, Inc.  
Civilian Radioactive Waste Management System  
Management and Operating Contractor  
1261 Town Center Drive  
Las Vegas, Nevada 89134

by

Della M. Roy

September 23, 1996

*Attachment IV*

## INTRODUCTION

This report follows discussions held on September 5, 1996, at Las Vegas, concerning the probable consequences of using cementitious materials as a means of generating tunnel/drift support in the Yucca Mountain repository. The focus questions posed included: 1) Evolution of cementitious materials in emplacement drift; with T, t; 2) effects on in-drift water chemistry from evolving cementitious materials; 3) effects on colloid generation from evolving cementitious materials; 4) effects on alteration of (silica-abundant) tuffaceous-host rock from evolving cementitious materials, and 5) suggestions for potential mix design of precast concrete for emplacement-drift linings.

Because of the abbreviated time scale and limited time available to address the questions posed, this discussion will emphasize technical areas with which the author has had experience, and also those questions specifically addressed to her, insofar as time permits, and provide references to publications which may be helpful.

### A. Relevant Thermochemical Data.

#### *Introduction*

In the presentation Ms. Meike pointed out the difficulties in calculating stabilities of cementitious materials in the Yucca Mountain environment because of the incompatibility of the data sources. This is consistent with the author's experience. In an earlier study and in a report to Los Alamos, Freeborn and Roy (1983) had surveyed three types of data in an attempt to predict whether tuffs of the sort found in the Yucca Mountain vicinity were compatible (that is, could be in equilibrium) with concretes made from portland cements at low to moderate temperatures and pressures. The three types of data surveyed were thermodynamic data (free energies of formation), experimental determinations of phase equilibrium, and naturally occurring assemblages. None of these source of data was adequate in itself for the purpose.

The incomplete work by Gustafson (1974) on the relative stability of xonotlite and wollastonite has been a critical component of the interpretation for stability of high-silica calcium silicates. Gustafson was able to show that xonotlite could be converted to wollastonite plus water at temperatures as low as 225°C at 200 megapascals water pressure. He was not, however, able to show that wollastonite could be converted to xonotlite under any conditions. Taylor and Roy (1980) have pointed out some of the difficulties in establishing the upper stability temperatures for some of the hydrated calcium silicates.

Gustafson, by showing that the anhydrous wollastonite could be converted to the hydrous phase xonotlite, clearly demonstrated that between 300° and 400° xonotlite was less stable than wollastonite; the results between 225° and 300°C depend upon the interpretation of the relative strengths of the X-ray diffraction peaks, which Gustafson took to indicate that wollastonite was more stable over this interval as well. There are some reservations about these results. Wollastonite is well known for polytypism and xonotlite is susceptible to being polytypic as well, so that the reaction could have been carried out on metastable polytypes rather than the stable forms, affecting the reliability of the results.

The other work which was relied upon very heavily is the collection of work by Liou concerning zeolitic phases, which, of course, relate to the tuff compositions. The qualification attached to the work by Gustafson about the interpretation of X-ray diffraction patterns applies here as well (and perhaps even more strongly, since Liou depended upon changes in peak heights for peaks which

Att. IV

would be expected to be near the detection limit of the technique.) In addition, there is the problem of ordering of aluminum and silicon in the phases which Liou studied (1970, 1971a,b,c).

These are two sets of experimental data that provided the principal calibration for temperature in the natural assemblages, and even so, provide principally an upper limit rather than a temperature scale.

There are two classes of problems associated with the use of the thermodynamic data: the uncertainty in the data mentioned above and the paucity of data for the phases of most interest.

The only work which includes thermodynamic data for a moderately complete set of phases is that of Mchedlov-Petrossian (1972, in Russian) which is based upon an estimation technique. The German and English versions (Babushbin et al., 1985) do not improve the situation, only make the data more intelligible. The results of the calculations of the stability relations in the simple lime-silica-water system using this data resulted in no stability fields for any of the hydrous phases; this suggests that there is a systematic error in the estimation scheme, if the occurrence of these hydrated phases in natural occurrences is taken to indicate that there is a stability field at low temperature.

Among the more recent useful attempts to quantify thermodynamic models of cements has been that of Atkins et al. (1992). A computer program CEMCHEM was developed to predict stable phase assemblages in blended cements in the 6-component system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-SO}_4\text{-MgO-H}_2\text{O}$ . Solubility data are used in the model, using measured pore solutions on cements up to 5-year-age. However, the model was limited to 25°C and did not include data involving alkalis.

The natural occurrences then have been the principal source of data for estimating the probable stable assemblages at these low temperatures. As was mentioned previously, the experimental phase relations were relied upon heavily to provide the high temperature relations which the interpretation of the natural occurrences was forced to fit (the high temperature natural occurrences and the experimental results are in generally good agreement, so this is not an unreasonable approach). Shulamit Gross (1977) and colleagues have described a complex geology, the Hatrurim formation in Israel which was thermally metamorphosed by the ignition of bitumen, then undergoing retrograde metamorphism, hydrothermal mineralization and weathering. Altogether more than 40 rock types are distinguished, and the mineral assemblages have much relevance here, as they include most of the known calcium silicates and calcium silicate hydrates; calcium aluminosilicates found (some 120 listed) range from hatrurite (named from the locality) ( $\text{Ca}_3\text{SiO}_5$ ) which presumably is stable only above 1250°C, to the hydrates tobermorite, and plombierite (~60°C or less) and many zeolites, clays, tectosilicates, etc.

The principal results of this survey were that there appear to be stability fields for the crystalline phases which appear in concretes, although they are restricted to temperatures less than about 200°C (perhaps as high as 300°C). We also concluded that there are serious incompatibilities among the various phase assemblages which might appear in separate parts of the engineered repository. In particular, the aluminous clay minerals are probably not stable in contact with concretes derived from portland cements. Another probably incompatible assemblage identified in this survey is the combination of siliceous zeolites and traditional portland cement concretes. It is likely that a portland cement concrete modified to be high in silica is compatible with the range of zeolites found in Yucca Mountain or that adjustments can be made to obtain such a result. (See later discussion of high-silica concretes).

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## B. Evolution of Cementitious Materials Under Conditions Likely to be Encountered in Emplacement Drift.

### *Introduction*

Most concretes are used at room temperature or at most, the ambient generated by the exothermic heat of reaction of the cement phase when large pours of concrete are made, and there is not a large body of data on high-temperature performance. Exceptions are in precasting (steam-cured) or in specialized applications such as oil well or geothermal cements, encountering higher temperatures. In earlier studies, we undertook an evaluation of cementitious materials which might be used in an unsaturated tuff (Yucca Mountain) environment. A broad range of mechanical and physical properties (such as strength and permeability), of potential mortar and grout formulations (Licastro et al., 1990) and later concrete formulations (Roy and Scheetz, 1989) were investigated, to provide a data base.

**Preliminary screening Phase I.** This study consisted of the formulation and testing of mixes representing mortars and grouts, both expansive and nonexpansive, with bulk compositions approaching those of tuff. Short-term evaluation of these mixes included the determination of physical/mechanical properties as a function of time (up to 28 days) and curing temperatures (38 and 60°C). Ancillary data included characterization of starting materials, phase identification, and limited interface experimentation, i.e., bond strength and permeability, using a nonwelded tuff, which was available when testing was initiated. Unless otherwise noted, samples used to measure unconfined compressive strengths, bulk density, porosity, thermal conductivity, permeability of the seal material, and interface permeability, were stored by immersion in water following an initial curing time in a high-humidity room (>95% relative humidity). Samples for bond strengths were stored in a >95% relative humidity room. Viscosity and dimensional stability measurements were done on samples in a plastic state.

In preliminary screening studies (Phase I), several cementitious mortars and grouts were formulated for chemical compability with tuffaceous rocks of the Yucca Mountain area. Initial tests of physical and rheological properties of these mixes showed that desirable properties could be achieved. Expansive mixtures showed particular promise, yielding strong, high-density materials with low permeability and adequate bonding to nonwelded tuffs.

Phase II of this work concentrated on two expansive mixtures: a mortar designated (82-22) high in silica and a pumpable grout designated (82-30) with potential for use in concretes or to meet special sealing requirements. These mixtures were tested for up to 720 days of curing at 38, 60, and 90°C. In general, their physical properties continued to improve throughout the curing period, with some fluctuations in compressive strength values possibly related to curing in an unconfined condition. Strengths to 124MPa were maintained after 360 days at 90°C. Permeabilities were consistently very low, commonly less than  $10^{-8}$  Darcy.

Phase II also included long-term experiments of the properties of interfaces between these mixtures and site-specific rocks, which used welded tuff from the Topopah Spring Member of the Paintbrush Tuff. Permeabilities of these interface samples were less than or equal to those measured for the tuff alone (on the order of  $10^{-7}$  Darcy or less). A general increase of bond strength with curing time was observed for both formulations. Mixture 82-30 gave higher bond, tensile strengths, achieving over 3.45 MPa at 90 days of curing at 38°C. Pretreatment of the tuff surface before casting the cement gave higher bond strengths at 90°C with this sand-free formulation. However, this pretreatment decreased bond strength for samples cured at 38°C.

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An additional mixture, 84-12 was examined because it addressed a geochemical requirement together with maintaining the physical and mechanical properties of Mix 82-22. The geochemical requirement was reduction of the total amount of sulfate that could be released. This requirement was achieved by reducing the amount of sulfate added to the original mixture. Reducing the amount of Portland cement and using silica flour, silica fume, fly ash, and slag additives to maintain a high content of reactive silica (and alumina) with <20% (by weight) of cement in the total formulation achieved this requirement. Preliminary data for Mixture 84-12 suggest attainment of a dense, pumpable product that hydrates to a solid of very high strength (140 MPa compressive up to 360 days) and low porosity, with a chemical composition that should make it highly compatible with NTS tuffs.

### C. Potential Effects on Drift Water Composition.

#### *Introduction*

One aim of any designed cementitious material used in a geologic repository is to minimize any chemical potential gradients and prevent destabilization of the system. Compatibility of the concrete with respect to host rock can be approached in two ways. First, sands and aggregates derived from the host rock can be used in the concrete formulations. The assumption in this approach is that the bulk of the concrete is composed of rock similar to the rock of the emplacement environment. Therefore, the chemistries of the host tuff and concrete should be similar, with only a minor perturbation to the long-term compatibility caused by the relatively small amount of cement in the concrete (20 to 30%). Below are summarized experimental studies using both this and a second approach.

**Experimental Concretes, Grouts, Mortars.** Our first experimental study examined this concept through an investigation of the reactivity of a tuff-bearing concrete, CL-40 CON-14 (Scheetz and Roy, 1989a) using a partly modified cement composition, local Nevada Test Site (NTS) concrete sand, and coarse aggregates made from the Grouse Canyon Member of the Belted Range Tuff. The results of this study are described later.

The second approach to design of compatible cementitious materials is to control the bulk chemical composition of the matrix material so that it approaches the bulk chemical composition of the geologic host (Scheetz and Roy, 1985, 1989b; Scheetz et al. 1989a). Ideally, both approaches could be combined. Because of the high-silica content of the Yucca Mountain tuffs, concretes with a cementitious matrix having high silica content are likely to be more compatible with the tuff than are normal portland cement concretes with high calcium content matrices. This was also as predicted from the Freeborn and Roy (1983) studies. It is also consistent with experience with oil well and geothermal cements which must withstand higher temperatures (Langton et al., 1980).

This latter approach was followed in the design of the two grouts mortars that were evaluated. The design of the material was initially based upon the use of a commercially available shrinkage-compensating cement to minimize dimensional change, which in turn was modified with reactive silica-rich admixtures. The bulk chemistry of the grouts was carefully chosen to provide for the maximum formation of cementitious phases by reaction between the cementitious matrix and an aggregate that was a constituent of the host rock. It was also desired to minimize the impact on the waste package when used in drifts, including keeping the pH lower than in normal portland cement materials. The expansive agent which is developed in the commercial cement is ettringite, which is formed during the cement hydration by the reaction of a soluble calcium sulfate source and a source of calcium aluminate. An alternative formulation was developed that closely approximated the

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shrinkage-compensated mixture in bulk chemistry but did not contain the calcium sulfate source. This latter low-sulfate formulation was evaluated in an effort to minimize the release of sulfate to the ground water, which was considered possibly problematic.

**Observations Regarding Phase Stability and Water Chemistry.** The two formulations represent examples of an expansive (82-22) and a nonexpansive (84-12) cementitious sealing material. The expansive grout relies on the formation of ettringite to generate the expansive forces.

Phase characterization of the reaction products for the expansive grout revealed that the expansive agent, ettringite, was not stable above about 100°C (Ogawa and Roy, 1981; Satava and Veprek, 1975). Tobermorite was observed at all temperatures, even at 300°C, well above its expected stability limit. The incorporation of Al into the tobermorite structure is postulated as contributing to the enhanced thermal stability. In the longer experiments, at 200 and 300°C, the Al-tobermorite partially reacted with excess SiO<sub>2</sub> to form truscottite, another high-temperature calcium silicate hydrate. This observation is consistent with the solution analyses that suggest that the liquid phase in contact with the cementitious grout/mortar is very nearly at equilibrium with respect to quartz at 150°C and slightly undersaturated with respect to quartz at 200°C. It appears to be limited by the low solubility of the calcium silicate hydrates.

Solution analyses were made after reaction of vapor from J-13 groundwater at temperatures of 150°, 200° and 300°C. The pH values appeared to cluster near  $9.50 \pm 0.2$ , although some reached about 8.7. The pH was found to be as high as 11.6 at 150°C, and as low as 7.5 at 300°C.

Experiments, in which tuff was included along with the grout/mortar, showed a pH of 8.5 for 500 hours at 200°C, then dropping to 6.5 for one of the compositions.

Several different types of experiments were performed with tuff as coarse aggregate, studying a concrete formulation first prepared by the U.S. Army Waterways Engineering Station, in experiments exposed to J-13 groundwater (or its vapor) in both static and dynamic experiments. Concrete disc samples appeared quite intact after the experiments. However, vitreous components of the tuff showed some alteration.

Coarse powdered samples were also exposed to the solutions. It is a bit more difficult to generalize the interpretation of the results of the determinations of the solution composition with the tuff concrete because of the variety of experimental conditions used. After static hydrothermal experiments, usual phase assemblages included quartz, feldspars, zeolites, tobermorites; calcite and dolomite (residual from the concrete sand) and, surprisingly, smectite. The accompanying solutions contained Ca, Na, K, and Si at higher concentrations than in the original J-13 water, and at a relatively low pH (~5).

#### **D. Alkali-Activated Cements: Ancient and Modern**

##### *Ancient Cements and Concretes*

In recent years studies have been undertaken to determine why ancient concretes are so much more durable than their modern counterparts (Malinowski et al., 1961; Roy and Langton, 1989). In the beginning it was assumed that portland cement negatively affects the carbonation of lime resulting in a volume modification of the cement matrix (about 10 to 11%). In ancient cements, however, this high degree of carbonation has not been deleterious to the durability and strength of concrete

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Some of these concretes look like hard natural stone even after 9000 years in use (Glukowski, 1994).

Investigations (Malinowski et al., 1961) have revealed that, while ancient concrete in Roman structures has remained unaffected by severely corrosive conditions, such as flowing water and salt-laden air, in a period of 2,000 years, modern portland cement concrete has suffered extensive damage in the same localities and under the same conditions in a period of ten years. A convincing example of this is the rehabilitation of the Roman baths in Tiberia where portland cement concrete has been used. The structure restored by using portland cement concrete have been dramatically damaged by hot solutions, while the 2000 year old Roman concrete remains unaffected (Glukowski, 1994).

X-ray diffraction analyses of ancient lime-pozzolanic concretes from Italy, Greece and Cyprus, indicate that the calcite is the predominant crystalline phase together with some weak crystalline phases of analcime,  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 2\text{H}_2\text{O}$ , while some poorly crystalline phases resemble calcium silicate hydrates (Langton and Roy, 1984; Roy and Langton, 1989).

The lime-pozzolanic cements of Rome contain a significant amount of alkali ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , 4%), which was added in the form of volcanic ashes. Lime is the ingredient responsible for the properties of binding mixtures. When subjected to cation exchange with ashes, lime frees  $\text{NaOH}$  dissolving silicon dioxide ( $\text{SiO}_2$ ), and on the whole, it activates the synthetic process of the CSH-gel and synthesizes the binding system of alkaline analcime ( $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 2\text{H}_2\text{O}$ ). Free lime carbonates and, gradually, CSH-gel-type products are formed, too. The formation of analcime contributes to the long-term stability of concrete.

Langton and Roy (1984) and Roy and Langton (1989) investigated ancient concrete analogs from Italy as specifically relevant to applications in the tuff repository program because of the general similarities in the composition of materials that were incorporated in the mortars, plasters and concretes of Rome, Ostia, and vicinity to the pyroclastic rocks of the Yucca Mountain area.

#### *Modern Alkali-Activated Cements*

New binding materials were suggested by KICI (Kiev Civil Engineering Institute in the USSR) in 1957 (Glukowski et al., 1967; Glukowski, 1974). The concretes were called "soil silicate concretes", and the binders "soil cements". The soil cements are obtained by mixing well-ground mountain rock and industrial wastes dissolved in caustic alkalis and salts of sodium and potassium. They are modelling the formation of natural zeolites of the type  $\text{R}_2\text{O}\cdot\text{RO}\cdot\text{R}_2\text{O}_3\cdot (2-4)\text{SiO}_2\cdot n\text{H}_2\text{O}$ . The synthesizing of these materials, i.e. their solidifying process is practically analogous to that of the minerals in the earth's crust, like zeolites, mica, hydrous mica, which at high temperatures crystallize to nepheline and feldspars. The synthetic process is similar to the natural processes of mineral and rock formation.

Others followed in developing related materials which added only a modest amount of alkali to activate an unconventional material, including Forss (1983), who described a binder based on granulated blast-furnace slag. Further, in the development of cementitious waste forms the principle of alkali activation was found to have important application (Kaushal et al., 1986, 1987) in studies in which both high-silica fly ashes and granulated blast furnace slags were used as major components for the solidification of highly alkaline wastes. The cementitious reaction products included various zeolites, analcime and nosean.

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Davidovits (1987) discussed the relation between ancient and modern concrete, and patented alkali-activated cementitious materials which were blends of alkali-activated cements and portland cement (Heitsman et al., 1987). He also synthesized materials which he called "geopolymers" (Davidovits, 1979).

The range of alkali-activated cements vary from those with strengths some 30% higher than portland cement concrete (Forss, 1983) to commercial cements such as pyrament, with very early high strength to a number of varieties. Roy et al., (1991, 1992; Roy and Silsbee, 1995) have investigated some of the mechanisms of reaction and strength development.

The activators used in these materials may include: 1) caustic alkalis; 2) non-silicate salts of weak acids; 3) silicate salts and, 4) miscellaneous. Dosages in the range of up to 3-10% as  $\text{Na}_2\text{O}$  (used as  $\text{NaOH}$ ) are utilized but dosages in the range of 3-6% give optimum strength development. This is contrasted to the activation of ash with calcium which typically requires additions of up to 20%  $\text{CaO}$  equivalent. Relatively small quantities of alkalis in combination with lime may also provide suitable activation.

The hydration of the fly ash, and to a certain extent, glassy slag, requires the breaking of bonds and dissolution of the three-dimensional network structure of the glass. The network contains interlinked  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra and  $\text{AlO}_6$  octahedra which are attacked by the  $\text{OH}^-$  in a high pH environment. In order to maintain active hydration of the fly ash, it is necessary to supply hydroxyl, because the amounts of hydroxyl ions along with the alkali and/or alkaline earth ions derived from the fly ash alone, generally are insufficient.

The major components of the cements include fly ash (Class F or C), granulated blast furnace slag, meta-kaolin silica fume and sometimes portland cement (Roy and Silsbee, 1992). Wu et al. (1990) have discussed the effectiveness of different activators and combinations of activators.

There are many reasons to expect that such alkali-activated cements and concretes might suitably be applied in drift linings, among them the fact that many of the components of such cements undergo thermal activation (Wu et al., 1983; Forss, 1983), which also suggests their suitability for pre-casting methodology.

## **E. Performance of Specialized Concretes at Elevated Temperatures**

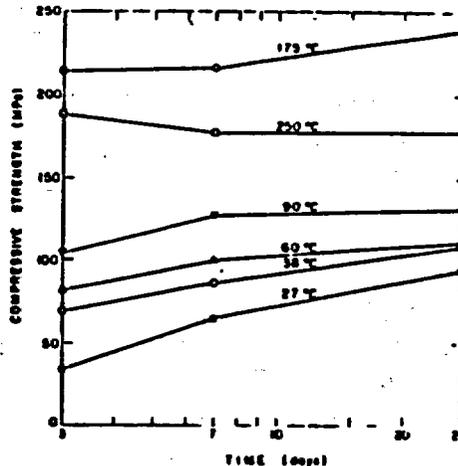
### *General Thermal Stability*

In the previous sections we have alluded to the higher temperature performance of some mortars and concretes which may be compatible with a tuff repository environment (Scheetz and Roy, 1989a, b) for which some studies were made at temperatures up to 300°C. During screening studies a number of cementitious materials were evaluated for their physical and mechanical properties at temperatures up to 250°C (Nakagawa et al., 1983, 1984). It was necessary to consider the total system; in particular, cementitious materials containing basalt sand (which is known to be refractory) were found to possess much higher strength at higher temperatures than those with quartz sand; when heated at 250°C (Nakagawa et al., 1983). As a result, chemically modified material maintained a strength of 190 MPa at 250°C (245 MPa at 175°C) while without the chemical modification the strength was only 125 MPa at 250°C (Roy et al., 1985). The following figure shows the advantage to be gained by thermal activation of the cements. There is a steady increase in the strength with time and temperature up to 175°C. Although the 250°C

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samples are not as strong as the 175°C samples, there is not a major diminishment in strength nor drop with extended time at the highest temperature studied (Roy and Idorn, 1985).

Information on the thermal stability of concrete is generally accessed through compilations such as studies related to fire exposure (short-term exposure) or geothermal well applications (longer-term exposure) or for pre-stressed concrete reactor vessels. However some studies were performed with a more specific view of the tuff repository environment (Scheetz et al., 1989b). Systematic studies have been carried out of the physical, mechanical, and geochemical properties of some



#### Thermal Stability of Potential Concrete Material for a Tuff Repository

candidate cementitious materials for use in a tuff host rock environment. One particular sanded cementitious grout (mortar) described here, was designed with substantial replacement of portland cement by low-calcium fly ash and silica fume, yet remained fluid at a low-water/cementitious solid ratio of 0.32. The ash and the fume were used in order to achieve a higher  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  content which is more compatible with the tuff geochemistry than is a plain portland cement.

It was expected that such materials might be used near waste canisters where they would be exposed to elevated temperatures. Therefore, the effects of elevated temperatures, 150°-300°C on the material properties were investigated. Initial compressive strengths of materials cured at 38°C for 7 to 900 days ranged from 100 to 125 MPa. Other properties investigated include bond strength (to tuff), water permeability, interfacial permeability, Young's modulus, density, porosity, expansive stress, and phase changes. Samples heated to 150°C for extended periods (28 days) either dry or hydrothermally, maintained their strength and well bonded microstructure, while the results of heating at 300°C were mixed, with some strengths remaining high (95-110 MPa) and others diminishing (44-51 MPa). The water permeability did not increase much at 150°C, but it did increase at 300°C.

The data obtained support the stability of this particular formulation and maintenance of its engineering properties up to approximately 300°C in a groundwater saturated environment and up to at least to 150°C in an undersaturated environment, even after a significant alteration in the bulk mineralogical composition of the solids which is associated with these temperatures. These results are encouraging and warrant the careful detailing of the rates of change of these properties as a function of time to determine the likely consequences of the degree of change observed. There is

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good reason to expect that properties/performance could be improved by more careful tailoring of the composition of the mixture, possibly along the lines, as discussed in the previous sections.

## F. GENERAL COMMENTS

### *Discussion*

Nothing has been said about the potential effect of concretes on radionuclide release. Earlier in the year it was apparent that several studies of actinide solubilities (including colloid formation) were in progress at a number of the national laboratories. Perhaps this information will be forthcoming. I might point to an earlier study of comparative waste forms regarding plutonium and americium releases (Ross et al., 1982). In that study cement waste forms performed relatively well at temperatures up to 90°C as compared to borosilicate glasses, e.g. It is also worth pointing out that other studies provide information on the solubilities of other radionuclides. The studies of Komarneni et al. (1982, 1983, 1985) have considered some interactions of cements with tuff minerals, and have also shown that some of the high-temperature cement minerals (Al-substituted tobermorite) show very significant  $K_D$  values for radionuclides such as Cs.

In the previous sections we have discussed several of the questions relevant to the performance of concrete in waste package emplacement drifts. There is by no means an unqualified consensus that all the questions have been answered, but only that there are considerable data available suggesting that use of concrete may be justified. The time has been too short to present a more coherent synthesis but only a scaffolding upon which more complete conclusions could be reached with additional directed studies.

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# **Report on Potential Geological Effects of Evolving Cementitious Materials Used in the Yucca Mountain Waste Disposal Project**

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## **BACKGROUND**

The necessity of placing cement-based materials into the storage area of Yucca Mountain, as part of the tunnel lining and base, raises several questions about the materials' long-term stability and long-term influences on the environment. It is anticipated that approximately 500,000 m<sup>3</sup> of concrete will be used. This will satisfy structural requirements until the area is sealed and afterwards for about 100 years, during which time the waste should remain retrievable in the event of an emergency.

During the first 50 years, parts of the site will experience increasing temperatures up to a peak of about 120°C. Temperatures of 100°C can be expected to last for about 2000 years. Also, during the first 50 years, the relative humidity is expected to fall from 100% RH to about 50% RH, and then it will gradually increase to about 85% RH during the next 2000 years.

The issue is: what happens to concrete in the long term when it is exposed to these conditions? Also, how will any expected changes, including deterioration of concrete, affect the performance of the repository?

During a one-day meeting on the 5th of September, 1996, a broad discussion took place that covered the tentative plan for developing the Yucca mountain site, as were some of the anticipated conditions that the concrete will be exposed to during the next 10,000 years. Towards the end of the meeting a number of topics were posed to the expert panel. These topics will be discussed in the following section. Additionally, we were asked to make general comments and to discuss any of our ideas.

Prediction of the performance of concrete in Yucca mountain is extremely complex. The first problem is to decide on the meaning of concrete; it is presently defined as a Type II Portland cement with limestone aggregate. Approximately 30% of the weight of cement will be replaced with silica fume. Steel fibers would be used for reinforcement, nominally 0.5% by weight of concrete. It is not certain whether the concrete will be precast or cast-in-place, but the agreement is that precast has several advantages. This report first deals with the questions and issues relevant primarily to precast concrete and then provides comments on special concerns and "brainstorms" the overall problem.

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## OVERVIEW COMMENTS

The primary purpose of concrete is structural. The material must maintain strength and toughness for at least 100 years, during which time the waste must be retrievable. Since the storage vaults must "breathe," allowing  $H_2$  (from corrosion) out and  $CO_2$  in, the concrete should not act as a seal. Throughout its life it should be as inert as possible, in particular, it should not alter the chemistry or physics of the mountain.

Cement is a multiminerale powder that reacts with water to produce a number of products. Soon after the reaction has started, the water phase, or aqueous phase, becomes saturated in alkali and hydroxyl ions and, therefore, has a pH typically around 13. This pH is highly buffered by undissolved phases, the most important of which is portlandite, or impure  $Ca(OH)_2$ . As the reaction products are formed the space occupied by the original water is gradually filled by reaction product and the original unreacted solid phases are replaced by hydration product. Excluding air bubbles, the volume of the largest pores, the capillary pores, decreases with time. Fig. 1 shows the volumes of the most important phases, including pores, for a typical cement paste. If the original water:cement ratio is decreased, the volume of capillary pores is also decreased, and if the ratio is too low, the reaction will stop for lack of space. Most of the water that can escape from cement paste resides in the capillary pores. Thus, reducing the water:cement ratio reduces the capillary porosity and its associated water [1].

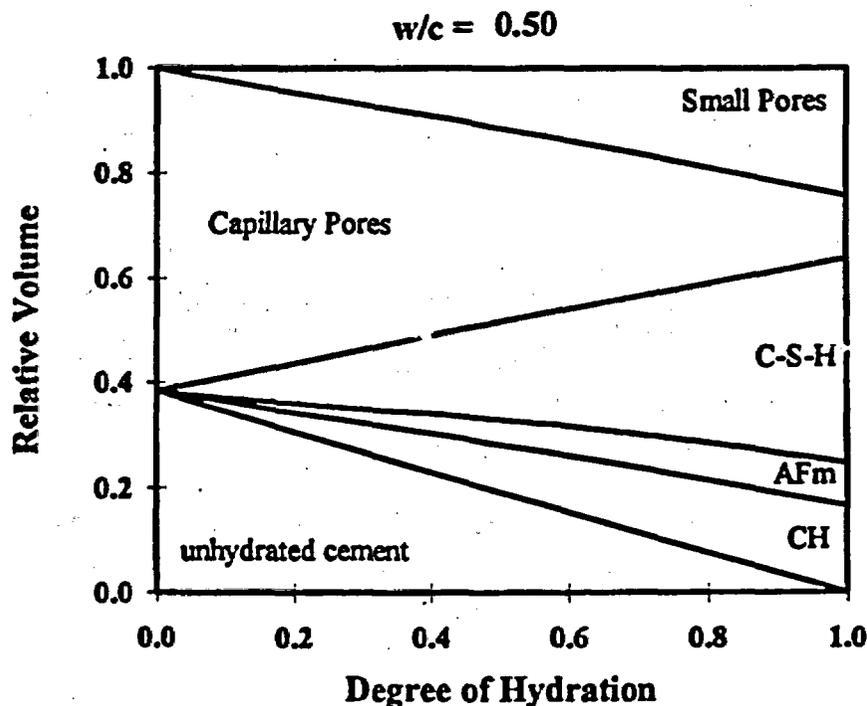


Figure 1: Model predictions (lines) for relative volumes in a Portland cement paste with a water:cement ratio of 0.5. The symbols represent experimental data [1]. Assumed cement composition: 60%  $C_3S$ , 25%  $C_2S$ , 5%  $C_3A$ , and 6%  $C_4AF$ .

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Cement-based materials are complex and the present state of knowledge is inadequate to predict their behavior over long periods of time, especially in a variety of extreme environments. A basic principle employed in the following comments is that, thermodynamically, stable phases probably will form given enough time and that, wherever possible, the concrete should be formulated in such a way as to minimize changes with time, both microstructurally and chemically.

Several concerns have been raised: 1) the water with a high pH in the pores could interact with the repository rift environment. 2) the decomposition of cement would produce water that could contribute to corrosion and 3) colloidal material and water could carry toxic waste out of the repository.

### **SPECIFIC TOPICS (comments on topics discussed in Las Vegas)**

A) In addition to the main hydration products that normally form in cement paste, including C-S-H (calcium silicate hydrate) CH (calcium hydroxide) AFm (aluminum monosulfate) and AFt (aluminum trisulfate), the high temperature conditions may produce zeolites and hydrogarnet.

B) High temperatures (200°C) and relatively dry conditions for extended periods of time will probably have several effects on the hydration products. Two or three trends may compete as follows.

At first, the higher temperatures will encourage the silicate chains in the C-S-H to polymerize. This will have the general effect of causing the phases to become slightly more crystalline. The tendency will be for zeolite and/or tobermorite to form.

High temperatures and relatively dry conditions will also mean that dehydration is possible. Thus, the general drive towards crystallinity will be countered by conditions that will remove water, including bound water, and this will cause the C-S-H to decompose as will other phases such as ettringite. Slightly hydrated silica gel and calcium hydroxide could result. It is uncertain how temperatures less than 200°C (i.e. 120°C) will affect the concrete.

Finally, it is anticipated that CO<sub>2</sub> will be available for reaction and, if this is the case, the conditions will be ideal for the formation of calcium carbonate. Silica gel, calcium carbonate, and unreacted cement could be the phases present at the end of the heating cycle.

C) The alkali in cement is highly soluble. During hydration some of the alkali can be incorporated into the products, but they are generally not tightly bound and, at the high temperatures, could be relatively easily resolubilized. The possibility of forming zeolite is

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very attractive because, if this type of phase forms, it incorporates sodium and potassium, and it efficiently incorporates other ions and is very stable.

D) The aluminates and the silicates will probably become carbonated under the anticipated conditions.

E) Carbonation will certainly lower the pH of the aqueous phase. Most of the solid reaction products will carbonate and the resulting material will probably have reasonable strength.

F) Carbonation should be considered good for both product stability and lowering of the pH, however, in an environment that contains some moisture and oxygen at elevated temperatures, steel reinforcement will be susceptible to corrosion. It is difficult to imagine that corrosion would not consume all of the steel during the first 100 years or so. Although it is noted that fiber is much more resistant to corrosion than conventional reinforcement, the high temperature and availability of CO<sub>2</sub> to decrease the pH would be particularly aggressive.

## GENERAL COMMENT ON QUESTIONS

Most questions asked at the Las Vegas meeting were related to what happens to the concrete and how its presence would affect the water chemistry of the host rock. These questions are very difficult to answer. Cement-paste plus aggregate systems are complex, the environment is complex, and the time is long. The environment is not only complex, but it is very heterogeneous. For example, the temperature and composition of the atmosphere and the local chemistry will change from place to place; some of the concrete may be exposed directly to CO<sub>2</sub> while, in other areas, it is not. Therefore, questions to do with the specifics of the phases present and how they will perform over long periods of time are very difficult to answer with confidence. There are currently too many variables and some of the following comments are related to simplifying and bounding the problem.

## RECOMMENDATIONS ON CEMENTITIOUS SYSTEMS

### *Basis for Recommendation*

The concrete must be as simple, as predictable, and as robust against the anticipated conditions as possible.

There are several exceptional differences between the Yucca mountain project and other civil engineering projects. The most important difference is that Yucca mountain must perform reliably for at least 10,000 years. It is also a project that will take decades to implement and is not a "fast-track" construction project.

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Modern cements are formulated to gain strength relatively quickly and, when all is said and done, long term durability is not always the most important consideration. Although the concrete will undergo some changes with time, any proposed formulation should maximize the following:

- 1) Predictability and simplicity
- 2) Stability with temperature, drying, and rewetting
- 3) Mechanical properties for 100 years
- 4) Compatibility with host rock

### *Cement composition*

The host rock is a Si-rich Ca-poor tuffaceous material. However, all modern cements are calcium rich to the extent that "free" calcium hydroxide almost always forms. The calcium hydroxide is relatively easily leached from concrete and, over long periods of time, this could raise the pH of surrounding water. One objective is to change the ratio of Ca to Si in the cementitious material and this can be accomplished by adding reactive silicates, in the form of silica fume, blast furnace slag, or fly ash. There are a number of advantages and disadvantages to each of these additives.

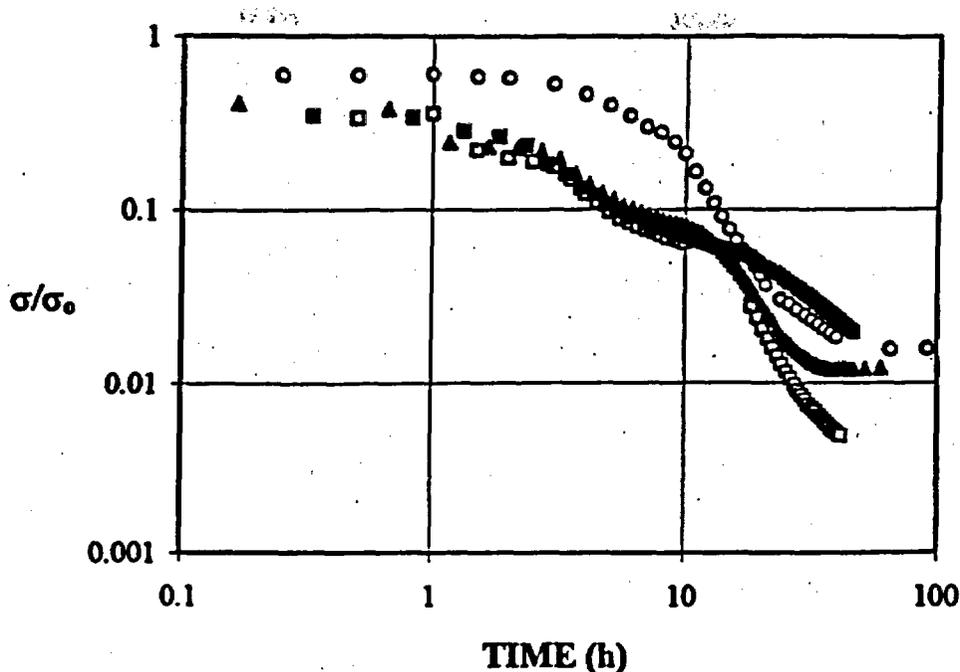
Silica fume is the purest, but it is typically a very fine-grained material requiring large amounts of superplasticiser as a dispersant. This adds organic material that may cause problems in Yucca mountain.

Blast furnace slag has a very uniform composition but is not pure. It does not require superplasticiser. The aluminates react to form AFm and AFt in the same way as they do in ordinary Portland cement, except that the reactions are much slower.

Fly ash has a variable composition, but this can be overcome with good quality control and using material from one source. It is spherical and often helps produce a workable mix.

All of these materials are reactive and consume calcium. All of these materials also are known to greatly reduce the permeability of concrete, as shown in Fig. 2. This is accomplished because the reactive silica forms product that tends to clog the pore system.

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**Figure 2:** Normalized conductivity (analogous to normalized diffusivity) versus hydration time for a cement paste composed of blended cement (68 wt% class F fly ash, 21 wt% type I/II Portland cement, and 11 wt% attapulgite clay) and a highly alkaline solution (4 molar) that simulates the low-level radioactive waste present at the Hanford site. The paste was mixed in a 1:1 solution-to-solids ratio and was cured adiabatically. Also given is the normalized conductivity of an ordinary Portland cement paste of w/c ratio 0.5.

### *Aggregate*

Using the strategy that the concrete should resemble the Tuff as closely as possible, it seems reasonable to use Tuff as aggregate. If limestone is chosen, possibly because it does not react with the alkali in cement, it should be noted that the conditions of Yucca Mountain are not favorable to alkali-silica reaction. Furthermore, since the mountain is the main defense, the paste portion of the concrete should be compatible with both the mountain and the aggregate.

### *New Special Cements*

In addition to formulating a cement paste and concrete using, as a basis, conventional commercial cements, this project may warrant the production of a special cement.

**C<sub>2</sub>S Cements:** At the turn of the century extremely good concrete was produced which had higher C<sub>2</sub>S content than cements produced today. The reason for the change in recent years is primarily related to fact that the older formulations

develop strength more slowly than modern cements and fast-reacting cements have commercial advantages. The old cements are generally considered to be equal to, or superior to, modern fast-reacting cements. Most important to this discussion is that  $C_2S$  produces 1/3 less Ca than  $C_3S$ , which may be very favorable for the Yucca mountain project.

*Strength and Toughness of Concrete:* It is very important to establish the strength requirements of the concrete. The foundation and the tunnel lining may not require the same strength. The formulation of concrete, and specifically the need to incorporate reinforcement, is sensitive to the toughness requirement. The main reason for reinforcement is to increase toughness and, therefore, toughness and strain to failure must be specified carefully. The amount of steel fiber should be chosen so that the strength and toughness meets specification, but does not greatly exceed specification.

#### *Chemical Stability—A Further Case for Low Water:Cement Ratio*

Unreacted cement clinker is chemically very stable and can easily withstand the temperatures and other conditions expected in Yucca mountain. When clinker is ground to make cement, gypsum is added to control the rate of hydration of the aluminates and this prevents premature set. Gypsum,  $Ca(SO)_4 \cdot 2H_2O$ , contains a significant amount of water as well as sulfate. If the material is cast in a factory, the issue of set may not be as important as it is in the field and, in addition, formulations incorporating little or no aluminates, or aluminates in a form that react slowly (fly ash or blast furnace slag), might be desirable anyway.

Using the philosophy that any water added to cement has the potential of becoming free water during long periods of higher temperature, it is desirable to produce concrete with very low water:cement ratio. If this is employed, in addition to achieving very high strength, the material will contain much unreacted cement that has the potential for combining with water when the temperature is lowered and/or when water is introduced into the tunnel. In other words, the unreacted material can act as a buffer to the flow of water. There are natural analogues that can be studied to determine durability of unreacted clinker.

#### *Very High Strength Non-Reinforced Concrete*

A number of strategies should be considered for producing concrete of sufficient strength for Yucca mountain without requiring reinforcement or, at least, minimizing the amount of reinforcement. Using the idea that cement-based materials are basically brittle and, therefore, have a strength determined by the size of the largest flaw, all strategies have in common the production of a dense material with exceptionally low water content. The space occupied by water eventually is the space that can be associated with the flaws. Furthermore, as stated above, low water content may be an advantage in itself. Some of the possibilities are as follows.

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There are a number of materials that use highly controlled particle size distribution (PSD) to achieve efficient particle packing. DSP (densified with small particles) is an example. Ceramics use this strategy routinely. Several advantages result.

- 1) The flow or viscosity of a particulate system can be expressed using the Krieger-Dougherty relation:

$$\eta_c = \eta_p \left[1 - \frac{\phi}{\phi_m}\right]^{-[\eta]\phi_m}$$

where  $\eta_c$  = viscosity of concrete,  $\eta_p$  = viscosity of paste,  $\eta$  = intrinsic viscosity,  $\phi$  = volume fraction of solids, and  $\phi_m$  = volume fraction of maximum packing of solids. The term of relevance here is  $\phi_m$ , which incorporates the volume of solids that can be incorporated into a box of a given size. Thus, a PSD that fills space efficiently also produces a more fluid material at a given water:cement ratio than does a PSD that is random.

- 2) Because the solid particles are tightly packed before the reaction starts, only a small amount of hydration is necessary to bind the particles together. Early strength development occurs, and very high strength is eventually achieved, even if some of the components are not highly reactive.
- 3) There is little water in the system and unreacted cement has the potential to react with water at later ages.
- 4) The concrete will be chemically very stable at the elevated temperatures of the storage site.

If pre-cast low water:cement ratio material is chosen, then there are a number of possible manufacturing strategies. In all cases the problem is to consolidate the material into the desired shape. Organic admixtures are most often employed but they may not be desirable in the Yucca mountain site. The following suggestions are based on alternate technologies.

- 1) The application of pressure during the first several hours after mixing can be a very effective way of compacting the concrete. This is especially true if the desired shape is relatively simple. Vibration can help the process.
- 2) Pressure consolidation of cement followed by infiltration of water. This technique takes advantage of powder technology to produce a dense solid mass and then the infiltration of water produces high strength concrete [2].
- 3) Warm pressed materials. Roy [3] showed that warm pressed materials can be produced with exceptional strength. The technique involves applying pressure during the early stages of hydration. Although warm pressing may be best applied to relatively small samples, it might be useful for panels that form tunnel lining and possibly rail ties.

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- 4) High temperature curing and/or steam curing might be useful ways of producing materials that are preconditioned to a high-temperature environment. Microwaves might be employed to achieve uniform heating.

#### *Pre-Cast vs. Cast-in-Place*

For the purpose of clarity, pre-cast simply means that the concrete will be cast into the relevant shape in some sort of factory, while cast-in-place means that a fluid concrete will be formed into its relevant shape in its final location.

Cast-in-place concrete must be relatively fluid and it must gain strength rapidly under ambient conditions. The advantage of this process is that the concrete may adhere to the local rock, which, for tunnel lining, simplifies the process. Also, irregular shapes can be accommodated. However, especially for the base structure, some sort of form work may be necessary, and on-site consolidation, such as vibration, and final finishing are required. Ordinary Portland cement and a normal water:cement ratio may be required, but if a low water:cement ratio is chosen, then organic admixtures will be required that fluidize the material for placement.

Pre-cast concrete is fabricated and then moved to the site for attachment (tunnel lining) or placement. Because this concrete can, in principle, gain strength more slowly than cast-in-place material, a much larger variety of materials can be considered. Furthermore, curing can be aided by high temperatures and possibly pressure and special consolidation techniques can be applied. This is the preferred technique.

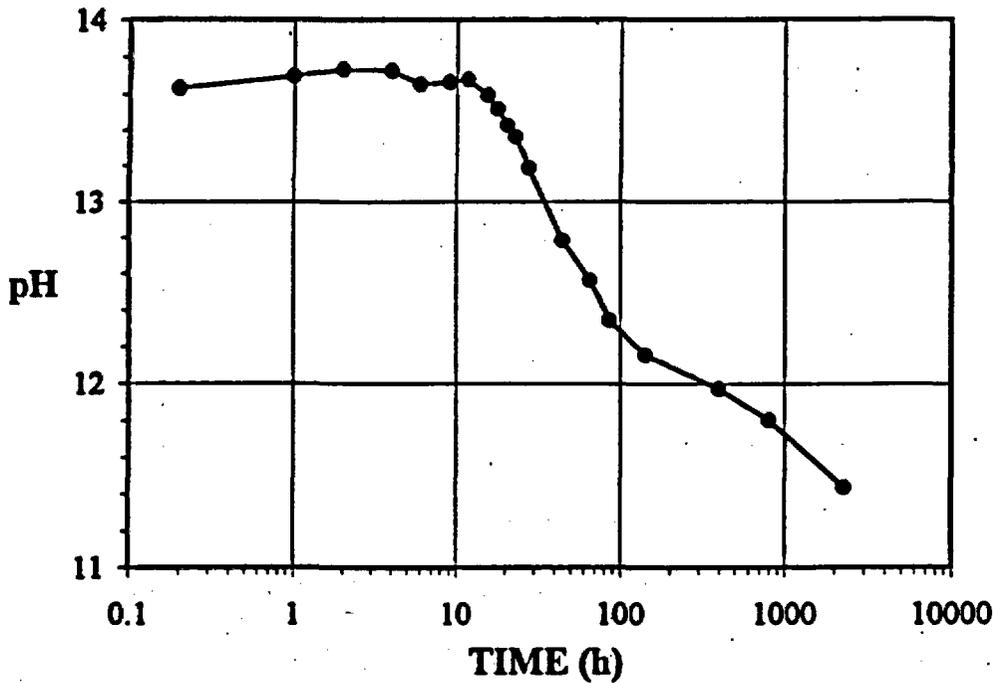
#### **Recent Relevant Research**

Even if cements are formulated to have relatively low Ca content, accomplished by increasing  $C_2S$  and adding reactive silicates, and they are formulated to contain relatively small amount of water, the aqueous phase is still of high pH. Recent unpublished research has produced some interesting and relevant results.

Research at Northwestern University (Jennings group) and at the University of Illinois (JF Young group) was intended to help define a cement system for isolation of liquid waste at the Hanford site. Portland cement was blended with fly ash and attapulgite clay and mixed with a highly alkaline solution. The material was cured at temperatures up to  $90^{\circ}C$ . The material hardened rapidly and pH of the aqueous phase was found to drop to levels well below that of a control sample prepared by mixing cement, fly ash and pure water. The pH is apparently continuing to fall even at the end of the experiments. In other words, the addition of alkali resulted in lowering the pH of the aqueous phase after several hundred hours as shown in Figure 3. Analysis of the solid phases indicated that a sodalite-type zeolite appears at about 10 h. At 30 days the stabilized crystalline composition includes

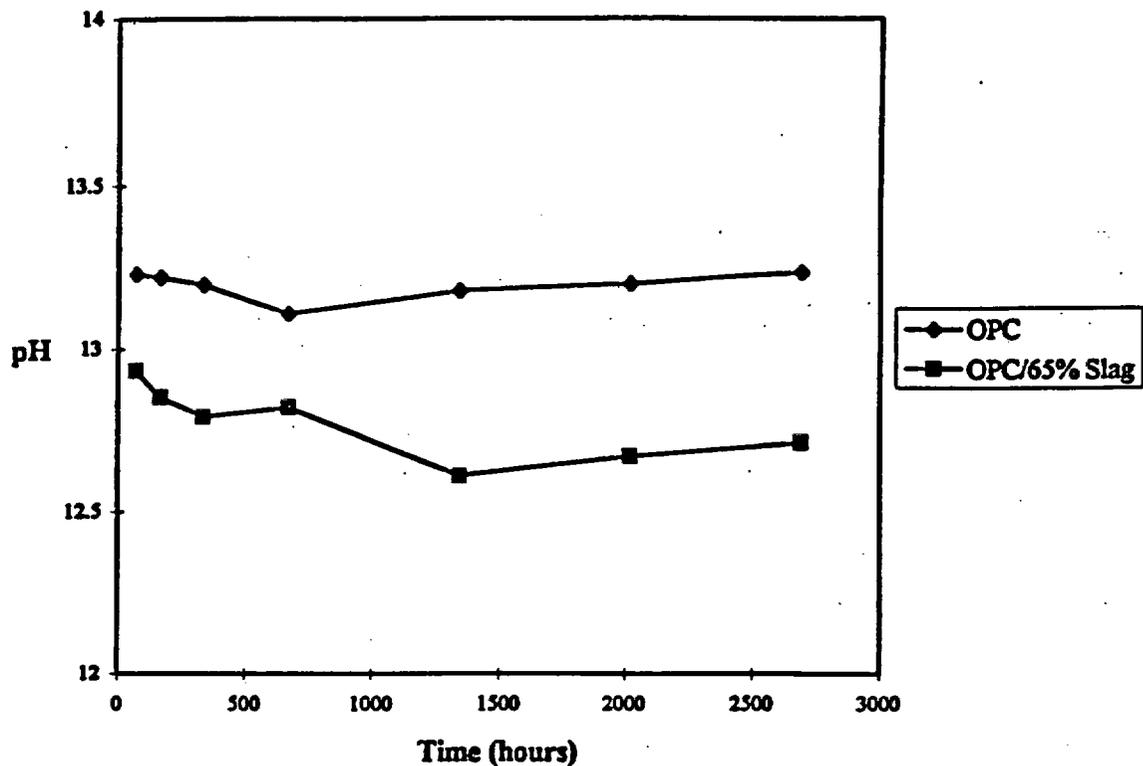
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zeolite, apatite and minor amounts of  $\text{CaCO}_3$ , quartz and monosulfate. These formulations produced material with exceptionally low permeability. The formation of zeolite at the early stages of reaction may be of particular interest if concrete is to help separate waste from the far field and this might be the subject of further research.



*Figure 3a:* pH versus hydration time for pore solutions extracted from pastes composed of blended cement (68 wt% class F fly ash, 21 wt% type I/II Portland cement, and 11 wt% attapulgite clay) and a highly alkaline solution (4 molar) that simulates the low-level radioactive waste present at the Hanford site. The paste was mixed in a 1:1 solution-to-solids ratio and was cured adiabatically.

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**Figure 3b:** pH of extracted pore solution versus hydration time for an ordinary Portland cement paste and a blended cement paste containing 65 wt% ground granulated blast furnace slag (by weight of solids). These materials are mixed with pure water.

### Postscript

Finally, long-term prediction is only possible with the development of relevant phase diagrams. Fundamental research must be supported in this area.

### References

1. "A Model for the Developing Microstructure in Portland Cement Pastes" (H.M. Jennings and P.D. Tennis) *Journal of the American Ceramic Society*, 77 [12] 3161-72 (1994). Correction published in the *J. Am. Cer. Soc.*, 78 [9] page 2575 (1995).
2. Patent "Engineered Cementitious Contaminant Barriers and Their Method of Manufacture" (with Galen Stucky and Simon Hodson). Issued December 8, 1992. Patent Number 5,169,566.
3. Roy, G.R. Gouda, and A. Bobrowsky. *Cem. Concr. Res.*, 2, 349, 1972.

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**Yucca Mountain Site Characterization Project  
Performance Assessment Consequences of Cementitious Materials Scoping Study  
Potential Geochemical Effects of Evolving Cementitious Materials**

**Independent Analysis of Issues Related  
to  
Repository Performance**

**Client :** M&O/INTERA, Inc

**For Client:**

**Technical Coordinator** Dr. David C. Sassani  
Dr. Joon H. Lee

**Administrative Coordinator** Ms. Yumi Stafford (TESS)

**For AECL-WL**

**Technical Coordinator** Dr. Maria Onofri  
**Administrative Coordinator** Mr. G. McCrank

**Report Prepared by:** Maria Onofri

27 September 1996

Attachment VI

## 1. BACKGROUND AND SCOPE

In 1996, September, TRW Environmental Safety Systems Inc. issued contract RFQ No.LV CS.YS.8/96-21 to AECL WL who was required to assist in M&O PA staff to assess long-term evaluation of cementitious materials in the anticipated near-field conditions and their effects on the near-field performance parameters. This draft letter report, which is an independent analysis of issues related to repository performance, arises from the contract instructions and various issues raised in the technical meeting with M&O/INTERA, Inc and DOE Staff . The technical briefs are presented in Appendix I of this draft letter report.

Through the contract directions, AECL-WL was advised that the Performance Assessment and Modeling (PA) group of the Civilian Radioactive Waste Management System Management and Operating Contractor (CRWMS M&O) is leading scoping study efforts to evaluate the long-term impacts of the cementitious materials on the repository system performance.

As part of the geological investigations of potential site at Yucca Mountain and associated developments for a deep geological repository for radioactive wastes, precast concrete segments is considered the primary option for ground support in the emplacement drifts. The lining is intended to enhance the stability of the emplacement drifts and to reduce the potential rock falls on the waste packages in the early post-closure stages. The cementitious materials will constitute a major part of the near-field. The accessibility of cementitious materials to groundwater means that it will have great influence on the chemical environment of the repository. Concrete may provide a physical barrier to radionuclides transport. However, because of the favourable geosphere (i.e., above watertable), this role is of secondary importance.

Geological disposal of radioactive wastes is recognized internationally as probably the only viable method of ensuring protection from the hazards presented by these materials to man

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and environment. Nearly all countries that produce radioactive waste have ongoing programs to develop concepts for the waste disposal repository. The wide variety of geologic formations under investigations in which repositories can be constructed reflects the range of geologies of the countries involved. In all cases, once the repository is closed and sealed, the most likely mechanism through which waste can escape to the biosphere is through dissolution in and movement groundwater. It is generally accepted that the materials used to seal repositories must be affordable, emplaceable, and effective in a wide range of environments. Moreover, in view of the fact that the hazardous materials in radioactive waste are very long-lived, the probable performance of the sealing materials and systems over very long time has to be understood.

## 2. Issues Related to Repository performance

### 2.1 Evolution of cementitious materials in emplacement drift

Concrete in many engineering applications can suffer undesirable degree of changes with time as the result of aging and/or environmental factors. However, these changes are not always detrimental to the point that the concrete structure/ component has deteriorated and is unable to meet its functional and performance requirement.

Concrete is a versatile structural building material, manufactured by mixing cement, aggregates, water, and admixtures. Cement when mixed with water, reacts to make a cohesive mixture which binds together the aggregate to form concrete. Admixtures are added to the mixture to produce concrete with desired properties such as consistency, setting time, strength, amount of heat of hydration and the reactivity with the alkali in aggregates.

It is generally accepted that there are physical and chemical causes of concrete degradation. The physical causes of concrete degradation have been divided in two groups: a) surface wear or loss of mass due to abrasion and erosion and b) cracking due to temperature and humidity gradients, crystallization pressures of salts in pores and structural loading. The chemical causes

of the deterioration includes reactions leading to formation of expansive products (i.e., sulphate expansion, carbonation, alkali-aggregates expansion, corrosion of reinforcement), leaching and cation-exchange reaction between aggressive fluids and the cement paste. In practice these causes are frequently superimposed on each other. For example, cracking and loss of mass by surface wear increases the permeability of the concrete, which is one of the most important factors controlling the rate and extent of chemical degradation.

It is generally agreed that engineered systems are subject to a phenomenon known as aging. This is related to time-dependent changes that occur in a system. Aging has been defined as a gradual and cumulative degradation that occurs with the passage of time in a component, system or structure due to environment and service conditions that can lead to a loss of function and an impairment of safety. Gradual change assumes that changes occur under normal operation conditions. It does exclude degradation produced by the sudden and short-term environmental and service extremes conditions (i.e., high temperature).

Exposure of concrete structures/components above ambient temperature for prolonged time can degrade the concrete in several ways. Internal stresses could result from differences in the thermal expansion coefficients of concrete constituents and from restrained movement of concrete by reinforcement. Recrystallization and precipitation of dissolved salts in the pores of the concrete as the result of water evaporation can also occur. Further crystal growth can result also in the development of internal stresses. If the internal stresses exceed the tensile strength of the material, cracking can occur.

Elevated temperature in excess of 100°C are known to cause decreases in compressive strength, tensile strength and modulus of elasticity. However, there is no evidence that long-term exposure of concrete at moderate temperatures leads to degradation in compression strength. Thermal cycling are considered to be more damaging than constant elevated temperature.

The effects of increasing temperature on concrete will depend on the degree of hydration and

the moisture state in the cement phase. A saturated cement paste contains large amounts of free water and capillary water in addition to adsorbed water. These types of water are readily lost on raising the temperature of concrete. However, if the vapour pressure inside the material increase at a faster rate than the pressure release of the steam into the atmosphere, spalling occurs. The interlayer CSH (calcium silicate hydrate) water and some of the chemically combined water from the CSH and sulphoaluminate hydrates are lost when the concrete is subjected to temperature up to 300°C, contraction associated with the water loss, occurs. Further dehydration of concrete due to decomposition of  $\text{Ca}(\text{OH})_2$  begins at about 500°C. Temperature on the order of 900°C are required for complete decomposition of CSH (Mehta, 1986). At high temperature (> 300°C), the normal aggregate will continue to expand, and resultant stresses lead to loss of strength, spalling and cracking (Lea, 1970, Philleo, 1959).

Experience of prolonged intermediate temperature, in the range between 15°C and 65°C, exposure of concrete materials is limited. Cements, hydrate to produce first a dominantly very short range ordered phases, calcium silicate hydrate phase, which is more amorphous (i.e., gel-like in nature) than crystalline. It is known that temperature in excess of 100°C convert the amorphous calcium silicate hydrate, one of the major phase in the cement phase, into  $\alpha$  dicalcium silicate hydrates giving rise to a weak porous matrix. However, there are evidence that the amorphous calcium silicate hydrate can persist to about 60 °C except at low Ca/Si ratios, where partial crystallization occur. Therefore, there is the potential for possible volume changes resulting in change in permeability on transition from amorphous state to a crystalline state (Taylor, 1964 Beaudoin and Feldman, 1979).

A temperature gradient across the concrete structures/components will increase the moisture transport in the concrete. The effects of temperature on moist movement is particularly significant at lower degree of saturation, situation which is more likely to exist in the concrete structure/components in repository. The rate of movement of water through concrete has an important bearing on the resistance of concrete to deterioration by deleterious chemicals (carbonates, chlorides, sulphates). Moisture movement in concrete occurs when there is enough differences in moisture content between layer of concrete to cause a hydraulic gradient. Water

vapour movement takes place by condensation at the higher vapour pressure surface and evaporation from the low vapour pressure surface. The increase in moisture transport through concrete will accelerate degradation processes such as carbonation and corrosion of the rebars.

Cement exposed to air will show extensive carbonation. The  $\text{CO}_2$  is quickly consumed by the reaction with the  $\text{Ca}(\text{OH})_2$  as air enters the capillary pores of the concrete. It cannot move past the barriers of the uncarbonated concrete until all  $\text{Ca}(\text{OH})_2$  is consumed.

The hydrated silicate and aluminate phases decompose as carbonation continues and the free  $\text{Ca}(\text{OH})_2$  is depleted because the normal thermodynamic phase equilibrium is upset by the absence of the free  $\text{Ca}(\text{OH})_2$ . The aluminate phases,  $\text{C}_4\text{AH}_3$  converts to  $\text{CaCO}_3$  and hydrous alumina. The monosulphate and ettringite decompose to yield  $\text{CaCO}_3$ , hydrous alumina and gypsum. The CSH is decalcified, initially by lowering the Ca/Si ratio, and ultimately by converting it into a highly porous and hydrous form of silica. The final carbonated structure is a framework of silica, alumina, and iron dioxides filled with calcium carbonate (Taylor, 1990).

Carbonation is affected by the moisture condition of the concrete; the reaction is much faster and more complete when a surface film of water (50% rh) is present. If the pores of the cement paste are completely filled with water (75% rh), the  $\text{CO}_2$  gas must first diffuse through the water. Consequently, the diffusion rate is considerably less than through the air.

The products of carbonation block the pores in concrete and impede the further ingress of  $\text{CO}_2$ . They stabilize the depth of carbonated layer. In the case of good quality concrete, this process occurs fairly early and the depth of carbonation rarely exceeds a few millimetres even after several decades of exposure. Concrete of low strength develops deeper carbonated layers and takes much longer for stabilization of the carbonate layer. In this case, cracks are developed in the concrete, and the process of carbonation starts along the sides of the cracks. This may destroy the passive film on the steel reinforcement and initiate corrosion (Neville, 1990).

The examination of the Roman concretes show no evidence of crystalline CSH and that both the CSH and  $\text{Ca(OH)}_2$  have been converted to  $\text{CaCO}_3$  and  $\text{SiO}_2$ . However, studies of other ancient structure indicate that crystalline CSH phases have been formed as the minerals tobermorite, hillebrandite, afwillite, gyrolite and reversidaite. These minerals can normally only be synthesised in the laboratory under hydrothermal conditions. There exists the possibility that they may be formed under ambient conditions over very long timescale in absence of carbonation (Roy and Langton, 1982, Nichevlov-Petrosian et al, 1968, 1967)

## 2.2 Suggestions for Potential Mix Design for Precast Emplacement-Drift Lining Concrete

The advancement of disposal strategies led to the development of a new generation of cement-based materials designed for fluidity, penetrability, low permeability, low heat of hydration, volumetric stability and resistance to chemical attack, to seal fractures and for use as massive seals.

The Canadian concept for the disposal of heat generating nuclear waste requires that the cement-based materials must be able to maintain their performance under a range of physical and chemical conditions to which they may be subjected over the life of a repository. The longevity of the seals to be used in underground disposal vaults is a unique feature; ensuring this longevity requires estimation of the long-term properties and performance of cement-based grouts materials for periods longer than those considered for classical engineering structures.

Members of a new class of portland cement-based materials (high performance grouts and concretes) are being considered for possible use in the construction of seals for underground repositories for heat-generating, radioactive, nuclear wastes (Johnson et al. 1994, Onofrei et al, 1992, 1993). With rapidly expanding data-base on the properties of high-performance cements, grouts and mortars ( Onofrei et al, 1992, 1993, Onofrei, 1994, Onofrei, 1995, Onofrei, 1996) there is an increasing confidence that the new materials (i.e., high performance grouts and concretes) possess many of the physical, mechanical and chemical properties

required of repository sealants.

Studies have been shown that in underground repository in granitic rock, such as that being considered by the Canadian Nuclear Fuel Waste Management Program (CNFWMP), high-performance cement-based grouts are durable: hydraulic conductivity can remain very low ( $<10^{-12}$  m s<sup>-1</sup>) for very long time (Alcorn et al. 1992). In light of these observations, high-performance concrete for use in the underground construction of, possibly unreinforced mass, concrete plugs, or possibly to completely backfill underground openings, are being developed and investigated for the CNFWMP.

New genera, high-performance, portland cement based grouts and concretes are more durable, less permeable, of high strength and otherwise preferable to the cementitious materials currently used in civil and structural engineering practice. Typically, current generation of high performance concretes with low *W/CM* ratio have cement contents between 450 and 500 kg m<sup>-3</sup>. The new materials have higher heats of hydration than the more conventionally used materials and, hence, like conventional concretes, without special procedures, cannot be used in mass concrete structures or other forms where the high curing temperatures reached during the cement hydration adversely influence performance. This make the materials unsuitable for use in mass-concrete structures. The materials shrink endogenously and crack as the limited amount of water in the concrete is consumed by the cement hydration reactions. Moreover, the materials change volume with significant changes in temperature that occur as heat is generated by the cement-hydration reactions and the heat is congruently and subsequently dissipated (Mehta and Aïcin, 1990; Lanard et. al. 1987; Springenschmidt and Breitenbächa, 1987; Neville and Brooks, 1987; Mehta, 1986 ).

Low heat concretes are currently produced by decreasing the cement content. To do this, the proportion of the aggregate in the concrete is increased. Moreover, the cement content is further decreased by partial replacement of the cement by materials (pozzolans) such as pulverized fuel and fly ash.

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A high-performance concrete with a cement content of  $97 \text{ kg m}^{-3}$  has been developed at AECL-WL. The Low-Heat High-Performance Concrete (LHHP) was specifically developed for high mass structures that are being proposed for use in the geological isolation and disposal of radioactive wastes. The mix proportion and the properties of the fresh and hardened concrete are presented in Table 1, 2 and 3 respectively. The properties of LHHP are being compared with those of Standard High-Performance Concrete (SHPC). Less mineralogically complex and, hence, more amenable to thermodynamic analysis than PFA-based low-heat concretes, the new material has an unconfined compressive strength of 100 MPa at 90 days after casting, exhibits a maximum temperature increase of only  $15^\circ\text{C}$  during the hydration and, compared to both conventional and high-performance concretes, is volumetrically stable. LHHP shrinks less than SHPC and normal portland cement-based concretes, cured continuously under water the LHHP expands. The concrete possesses the additional advantages of high-performance concretes such as low permeability ( $10^{-12} \text{ m s}^{-1}$ ) and also has a low pH in the range of 7.8 to 9.5.

#### pH

A problem of concern is the possible effect of hyperalkaline plume from cement materials on the surrounding host rock. Interaction between groundwater and the concrete could potentially mobilize a strong alkaline fluid from repository. Under such conditions the primary mineral assemblage is likely to be thermodynamically unstable, thus significant alteration of the rock could result. Changes in porosity and permeability are expected to occur as the rock minerals become unstable and dissolved. Development and the use of cementitious materials that establish significantly lower pH when in contact with water (i.e., LHHP Figure 1) may significantly reduce the alteration of the surrounding host rock. The pH rise observed on LHHP/water systems is small, reaching values as low as 7.8 in the case of crushed concrete reacted with groundwater (i.e., Whiteshell groundwater (WN-1), Standard Canadian Shield Saline Solution (SCSSS)). The suppression of pH excursion in LHHP/water systems may be attributed to the low cement content ( $97 \text{ kg m}^{-3}$ ) in the LHHP. Moreover, the cement content was decreased in the mix by partial replacement of the cement with inert silica floss

and silica fume (pozzolan). Supplementary cementing material (i.e., silica fume) reacts with portlandite, consequently the content of  $\text{Ca(OH)}_2$  in the hardened material will decrease.

### *Superplasticizer*

Concrete was known for a long time as a mixture of cement, water and aggregates, whose workability was essentially controlled by the amount of water added during mixing. The importance of the water/cement ratio was rapidly recognized as the most important factor governing strength properties, but was necessary to use excess water, more than that required for cement hydration, in order to obtain a workable mix. To improve the workability of concrete at a given water cement ratio, several admixtures were introduced in the concrete industry. Such admixtures, designated as "water reducers" could achieve remarkable effects on concrete, they could yield a gain in strength by allowing less water to be used, while maintaining workability. One particular type of water reducer was shown to be extremely effective in controlling workability of concretes; these were water soluble organic polymers designated as "superplasticizer". Superplasticizers are highly efficient dispersing admixtures when they are properly used. By using superplasticizer it is possible to: 1) increase concrete workability at will without any addition of water 2) produce hydrated cement paste stable and dense enough to bond very strongly to aggregates and reinforcing steel in order to produce a very strong composite material 3) make concrete so dense that it can be stronger, and more durable than many natural rocks.

However, it may be realized that the introduction of superplasticizer in concrete involves a new chemical component in a complex hydraulic binder system which already contain several added chemicals such as: grinding aid that may have been used during cement grinding, water reducer, an air-entraining agent, and sometimes, a retarder or accelerator. In such complex systems, in which each component has been individually optimized, incompatibility problems may develop.

While the implications of superplasticizers on the engineering properties of high performance grouts and concretes are understood, several important issues related to their use in nuclear

waste disposal applications were not clear. Superplasticizer are organic materials. Will these materials enhance the mobility of radionuclides by increasing the quantity or changing the quality of organic matter in a repository?

Studies carried out to address this question (Onofrei et al. 1992) revealed that superplasticizer can be leached from grouts but the observed cumulatively released quantities are very small ( $10^{-16}$  kg m<sup>-2</sup>). The release is derived from the unadsorbed fraction of superplasticizer in the pore space and concomitant gradual dissolution of the C<sub>3</sub>S and C<sub>3</sub>A hydrated phases. Analyses, using electron-microautoradiography and scanning electron microscopy, indicated that the majority of adsorbed superplasticizer resides on C-A-H and C-S-H phases in the hardened cement. It is now certain that superplasticizers will increase the total organic load in the groundwater around a repository. The significance of this increase can only be judged when realistic assessment of the quantity and the type of naturally occurring organic materials in a repository are available. The exact structure of the organic materials released from the high-performance cement-based materials remains uncertain as does the influence of the material on radionuclide mobility in the groundwater. Further studies are required to clarify these problems.

Other associated work (Onofrei et al. 1990) strongly indicate that the low-water-content, high-performance materials are significantly more durable than normal cement and concretes with high water content. The durability of high performance cement-based materials is enhanced by the ability of the materials, if mechanically disturbed, to seal autogenously (Onofrei, 1996).

#### *Belite rich cements*

Many research groups in a variety of countries (Chatterjee, 1996; Stark et al. 1986 Gies and Knofel, 1986, Muller et. al 1985) have pursued the development of belite-rich cements, and in some countries cement of this type are being used. Such cements offers several potential advantages:

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- saving energy in their manufacture,
- use of low grade calcareous raw materials,
- improvement in durability.

These advantages arise from the fact that  $\text{Ca}_2\text{SiO}_4$  forms at a lower temperature and the lower lime requirements not only allow more impure limestone to be used, but also reduces the amount of heat required to calcine it.

The principal drawback to belite cements is the lower reactivity of dicalcium silicate compared to tricalcium silicate. However, various techniques have been proposed to overcome this disadvantages, such as: reduction in crystallite size, addition of other components to offset the low early strength gain, sol-gel and spray-drying techniques, and control of polymorphism through solid state substitution.

Despite that promising cements have been produced in several laboratories, inability of belite cements to become a commercial alternative to conventional Portland cement reflect the high development costs that will be incurred to bring any of these cements to the market place.

Table 1. Mix Proportions in LHHPC\* (kg m<sup>-3</sup>)

Materials	Standard High Performance Concrete	Low Heat high-performance concrete
Portland Cement (Canadian Type 50 cement)	497.00	97.02
Silica Fume	49.7	97.02
Silica Flour	0.00	193.85
Fine Aggregate	703.20	894.74
Coarse Aggregate	1101	1039.59
Superplasticizer	7.1	10.32
Water	123.9	91.86

\* LHHPC is protected under US Patent 08/384,645 and Associated ARIPO, European and QAPI Applications

Table 2. Properties of fresh concrete

	SHPC	LHHPC
W/C	0.25	0.98
W/CM	0.23	0.49
Slump (mm)	230	170
Air Content (%)	1.8	2.75
Density (Mg.m <sup>-3</sup> )	2.482	2.121
Inert Mineral Content (vol%)	68	80
Temperature rise during curing (°C)	>10	<14

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Table 3. Properties of hardened concrete

	SHPC	LHPC
Unconfined compressive strength (MPa) 28 days , 23 °C	122	75
Unconfined compressive strength (MPa) 28 days , 50 °C	87	68
Unconfined compressive strength (MPa) 28 days , 90 °C	77	67
Hydraulic conductivity ( $m s^{-1}$ )	$<10^{-11}$	$\sim 10^{-12}$
90 day drying shrinkage ( $\mu\epsilon$ )	440	330
Linear coefficient of thermal expansion ( $\mu\epsilon / K$ .at 28 days)	6.00	8.5
Secant Young' modulus at $4\sigma$ (GPa, unconfined, 23°C)	40	36

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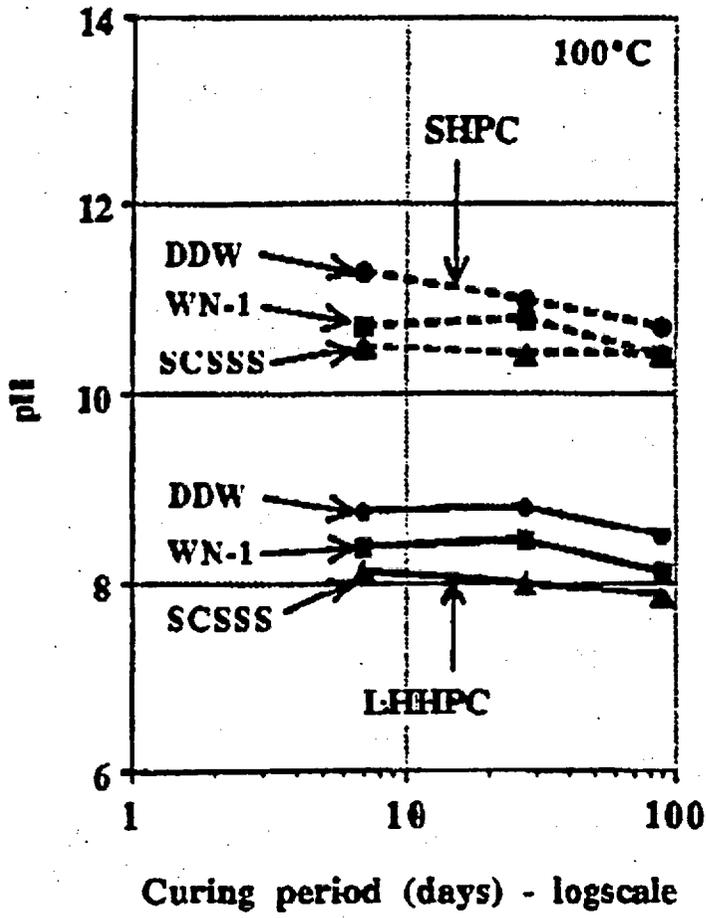


Figure 1. Evolution of pH in the concrete / water systems at 100 °C

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APPENDIX I

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08/23/96

## STATEMENT OF WORK

### BACKGROUND

Currently, precast concrete is the primary option for ground support in the emplacement drifts of the potential Yucca Mountain repository. Using precast concrete lining segments for tunnel excavation and construction provides an efficient means of developing the vast lengths of emplacement drifts in the potential repository. Lining of the emplacement drifts with precast concrete may enhance the stability of the emplacement drifts, possibly throughout the pre-closure period. These linings may also help to assuage potential rock falls on the waste packages in the early post-closure stages. However, the potential geochemical effects of the long-term evolution of cementitious materials in the potential repository drift environment may result in both beneficial and adverse impacts to post-closure waste isolation capabilities of the system.

Based on the current design base for the thermal loading of 83 metric tons of uranium per acre (MTU/acre) and without backfill over the waste package (1.8-meter diameter), the drift-scale thermo-hydrologic modeling results predict that the wall of emplacement drift (5.5-meter diameter) is heated to a peak temperature of about 120°C about 50 years after waste packages were emplaced, and the drift wall temperature remains above 100°C for about 2,000 years. The relative humidity at the drift wall decreases from the ambient relative humidity (100% RH) to about 50% at 50 years, then increases gradually to about 85% at 2,000 years. It may be assumed that precast concrete in emplacement drifts is exposed to similar temperature and humidity conditions. This prolonged exposure of concrete to such dry, elevated-temperature conditions may cause the cementitious materials to evolve in different ways from what is understood for concretes employed in conventional civil applications (i.e., dam, power plant, tunnel, bridge, etc.).

Performance Assessment and Modeling (PA) Group of Civilian Radioactive Waste Management System, Management and Operating Contractor (CRWMS M&O) is leading scoping study efforts to evaluate the long-term impacts of the cementitious materials on the repository system performance. As part of the current PA efforts, and also valuable inputs to the initiation of this scoping study activity, positions of noted experts in cementitious materials outside this project regarding long-term evolution of the cementitious materials and their impacts to the near-field environment are being solicited.

## SCOPE

In two separate tasks that are detailed below, the cement/concrete experts are asked to assist in the M&O PA staff to assess long-term evolution of cementitious materials in the anticipated near-field conditions and their effects, *emphasizing geochemical effects*, on the near-field performance parameters such as corrosion of waste container, waste form (spent fuel and vitrified high-level waste glass) alteration/dissolution, solubility of radionuclides, sorption of radionuclide, alteration of host rock, etc.

### Task I: Technical Meeting with the M&O and DOE Staff

The experts are requested to actively participate in a technical meeting with the M&O and DOE staff and provide their positions on various issues raised in the meeting. The meeting will be a one-day meeting, and is tentatively scheduled to be held in Las Vegas in the first week of September. In the meeting, each expert is asked to take a note for specific questions related to the repository performance for their follow-up independent analysis. The list of the issues to be addressed by the experts will be finalized at the end of the meeting.

### Task II: Independent Analysis of Issues Related to Repository Performance

Each expert is asked to conduct independent analysis to address the issues which are generated from Task I. As more specific issues will be discussed in the meeting of Task I, the issues expected to be addressed by the experts are as follows:

- 1) Long-term evolution of cementitious materials in expected emplacement drift environments; and
- 2) Effects of cementitious material evolution on near-field performance parameters such as
  - corrosion of waste container materials (carbon steel and Fe-Ni-Cr alloy);
  - alteration/dissolution of waste form (spent fuel and vitrified high-level waste glass);
  - solubility of radionuclide;
  - sorption and transport properties of radionuclide;
  - alteration of (silica-abundant tuffaceous) host rock; etc.

Each expert's analysis is expected to provide *defensible bounds* for these near-field performance parameters, which are based on their expert knowledge and judgement. Each expert is asked to provide a technical document for their analysis, and the supply of data and reference(s) used to support their analysis is required.

**DELIVERABLES**

Each expert is asked to document their independent analysis in a draft letter report (about 10 pages) and deliver the letter report to the M&O by September 23, 1996.

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