NEW MEXICO ENERGY, MINERALS
& NATURAL RESOURCES DEPARTMENT

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Jennifer A. Salisbury
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July 3, 1996

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NM ENVIRONMENT DEPARTMENT
OFFICE OF THE SECRETARY

Mr. George Dials, Manager
Carlsbad Area Office
U.S. Department of Energy
P.O. Box 3090
Carlsbad, New Mexico 88221

Subject: **ACTINIDE DISTRIBUTION COEFFICIENTS (K_d) FOR WIPP PERFORMANCE ASSESSMENT**

Dear Mr. Dials:

This is in response to your letter of June 7, 1996, regarding the Consultation and Cooperation (C&C) meeting held May 21 in Carlsbad. Thank you for your efforts in fulfilling the U.S. Department of Energy's (DOE's) obligation to consult with the State of New Mexico on the issue of experimentally derived actinide distribution coefficient values to be used in the WIPP performance assessment calculations.

The issue of radionuclide transport retardation at WIPP has long been a matter of considerable interest to both DOE and the State of New Mexico. Indeed, it is my understanding that the extent of such retardation in the Culebra Member of the Rustler Formation may be a critical factor in determining whether WIPP complies with the applicable disposal standards, 40 CFR Part 191, assuming future inadvertent human intrusion into the repository (*e.g.*, through exploratory drilling for hydrocarbon or potash resources). For this reason, it is imperative DOE continue its efforts to minimize, to the greatest extent possible, the degree of uncertainty surrounding chemical and physical retardation of radionuclides in the Culebra aquifer.

Enclosed for your review and consideration is a copy of some recent correspondence from Robert H. Neill, Director of the Environmental Evaluation Group (EEG), dated June 10, 1996. Attached to that correspondence is EEG's technical analysis and recommendations for K_d values to be used in the WIPP performance assessment. Also included as attachments to the EEG letter are the individual reports of Dr. Donald Langmuir, Dr. Leslie Smith, and Dr. John Bredehoeft on this important subject; these highly respected scientists served as consultants to the EEG (Langmuir, Smith) and the New Mexico Attorney General's Office (Bredehoeft) in addressing the retardation issue.

The State generally concurs in the conclusions and recommendations of the EEG, as outlined in their enclosed correspondence and attachments. In particular, we strongly agree with EEG's conclusion that, based on the results of the batch and column experiments, "...it is reasonable to expect that the actinides will sorb to some degree on the solid surfaces that are encountered along the flow path from the repository to the site boundary." However, we also agree with EEG and the three consultants that the K_d estimates derived from the batch tests may not accurately represent the extent to which radionuclide retardation will occur in the field. For this reason, we believe EEG's corresponding recommendations are reasonable and should be seriously considered for implementation by DOE.

Notwithstanding this belief, I would like to clarify our position on two of those recommendations put forward by EEG. First, we do not suggest it is necessary to perform any new column tests. K_d values obtained by using gamma ray tomography on cores with no breakthrough, or determining the progress of radionuclides in the column by slicing the cores, are appropriate in lieu of conducting new tests. Second, we believe DOE should continue and intensify its contingency planning efforts with respect to engineered barriers so that time will not be lost should the current iteration of the WIPP long-term performance assessment indicate such barriers may be necessary to comply with the applicable disposal standards.

In conclusion, I greatly appreciate the excellent briefings and corresponding detailed documentation provided to staff by DOE, Sandia National Laboratories, and others at the C&C meeting in Carlsbad on May 21. It is apparent from the information presented that you are committed to an open and scientifically based process for determining WIPP's long-term suitability as a permanent disposal facility. We look forward to future such candid discussions and consultations on other technical issues surrounding WIPP's performance.

Sincerely,

Jennifer A. Salisbury
Cabinet Secretary and Chair
N.M. Radioactive Waste Consultation Task Force

Enclosure (1)

c: Robert H. Neill, EEG
Task Force Cabinet Secretaries (NMED)

ENVIRONMENTAL EVALUATION GROUP

AN EQUAL OPPORTUNITY / AFFIRMATIVE ACTION EMPLOYER

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June 10, 1996

Ms. Jennifer A. Salisbury
Cabinet Secretary and Chair
N.M. Radioactive Waste Consultation Task Force
N.M. Energy, Minerals & Natural Resources Department
2040 South Pacheco Street
Santa Fe, NM 87505

Dear Ms. Salisbury:

This letter is to convey the Environmental Evaluation Group's analysis and recommendations on the actinide sorption values selected by the Department of Energy (DOE) for use in the performance assessment of the Waste Isolation Pilot Plant (WIPP). The 1988 modification to the DOE/State Consultation and Cooperation (C&C) Agreement requires the DOE to consult with the State of New Mexico prior to selecting the actinide retardation values for the Culebra aquifer in performance assessment modeling. The most likely breach of the WIPP repository sometime during the future 10,000 year assessment period will be through a human initiated event, such as drilling for resource exploration. A scenario being analyzed by the DOE is that radionuclide contaminated brine may enter the Culebra aquifer that overlies the WIPP repository horizon in the subsurface. As the contaminated water flows to the WIPP boundary, radionuclides may sorb onto the rock surfaces of the aquifer, thus slowing down the arrival of radionuclides at the boundary. A parameter known as the *distribution coefficient,* or K_d is used in the calculation of transport of radionuclides during postulated flow of contaminated water through an aquifer. Since the value, or a range of values, of this parameter is expected to significantly affect the outcome of performance assessment and thus the WIPP's compliance with the EPA's disposal standards, only an experimentally justified set of values may be used in the calculations.

In fulfillment of the C&C agreement, on May 21, 1996, the DOE presented the basis of the range of K_d values selected by the department to members of the EEG, Chris Wentz representing the Governor's Task Force on WIPP and Lindsay Lovejoy of the New Mexico Attorney General's office. In addition, Dr. Don Langmuir, professor of geochemistry emeritus

of the Colorado School of Mines and a member of the Nuclear Waste Technical Review Board, and Dr. Leslie Smith, professor and chair of the Department of Geological Sciences of the University of British Columbia and a renowned expert on fracture-flow hydrology, attended the meeting as EEG consultants. Dr. John Bredehoeft, a retired research hydrologist with the U.S. Geological Survey and a member of the National Academy of Engineering, attended the meeting as a consultant for the Attorney General's office.

The EEG staff met with the consultants and Mr. Wentz and Mr. Lovejoy on May 22 in the EEG Albuquerque office to discuss the DOE presentations. Subsequently, the three consultants provided brief written reports. After serious consideration of all the information, the EEG has reached conclusions on this matter and has prepared recommendations for the State to communicate to the DOE. Our conclusions follow:

Conclusions

- The K_d used for calculations of radionuclide transport in ground-water is a bulk parameter that must capture the randomness of the ground-water velocity field at the field scale.

- The batch and column experiments indicate that it is reasonable to expect that the actinides will sorb to some degree on the solid surfaces that are encountered along the flow path from the repository to the site boundary.

- The batch tests on crushed rock samples are conducted under artificial conditions, very different from the field, so that the contaminants contact the rock mass uniformly. On the other hand, complex and variable flow patterns exist in the field. Calculation of the surface area as a function of grain size is too simplistic to capture the conditions within the intact rock fabric and the fracture system. We are not questioning the validity of the K_d estimates as they apply to the material on which they were measured, but only the use of these values as representing the field conditions.

- No evidence of the occurrence of corrensite or other clays in the fractures or in the matrix of the Culebra along the postulated flow paths has yet been presented. The samples for the batch tests came from the VPX25 core from the Air Intake Shaft (AIS) and no corrensite clay above the detection limit was detected in these samples in the X-Ray diffraction tests performed at the Los Alamos National Laboratory. Also, the acid treatment of the samples does not remove clays.

- The batch tests overestimate actinide retardation in the field, but there is no known method to estimate the degree of overestimation.

- The column tests on carefully collected rock cores have the potential of providing better understanding of retardation in the intact rock matrix even though they do not simulate the field conditions of in situ rock mass. For this reason, the State included these tests in the 1988 modification of the Consultation and Cooperation Agreement. Work on these column tests started in 1992. Cores were obtained with great care from the Air Intake Shaft and scoping tests were conducted. However, the program inexplicably and suddenly came to an end in the summer of 1994 and appears to have been without proper direction since. Results are not available for several species because the tests have not been conducted or the breakthrough has not occurred. We expected to see complete results from these tests by now as agreed in the 1988 C&C agreement.

- Identification of a sampling distribution for K_d values based on the batch tests or a combination of the batch and column experiments is, in our opinion, not a reasonable method. If retardation in the Culebra is identified as an important factor in meeting the WIPP's compliance with the EPA standards, there is no alternative but to conduct field sorbing tracer tests.

Based on the above conclusions, we make the following recommendations:

Recommendations

- To get a sense of the importance of the K_d parameter in performance assessment calculations, use the values listed in Table 1, and also compare the results to those obtained using K_d=0.

- For Th(IV), U(IV), Np(IV), Pu(IV), Pu(III), and Am(III), perform new column tests. Since time is a factor, K_d values obtained by using gamma ray tomography on cores with no breakthrough, or determining the progress of radionuclides in the column by slicing the cores may be used; we believe this can be readily accomplished.

- Focus on including engineered barriers such as an engineered backfill and fixing the waste through treatment to avoid taking credit for retardation in transport through the Culebra.

- Start planning now to conduct a field sorbing test, so that if a decision is made to conduct it, additional time is not lost. The EEG has recommended it since 1979.

A technical analysis by the EEG and the letter reports from the three consultants are enclosed. We will be pleased to provide a briefing to yourself and/or the Task Force on this subject, if you so desire.

Sincerely,

Robert H. Neill
Director

RHN:LC:js

cc: Tom Udall, N.M. Attorney General

Enclosures: Table 1
EEG Technical Analysis and Recommendations for K_d values
Reports of Dr. Langmuir, Dr. Smith, and Dr. Bredehoeft

Table 1. Recommended K_d (ml/g) values for the actinide elements, based on information provided by the DOE and its contractors on May 21, 1996. Listed values are lowest reported or average reported K_d's based on column test results only. DB and CB denote values obtained in experiments using deep brine and Culebra brine, respectively. Parenthetic values for Pu(V) have been estimated assuming they equal the measured column test values for analogous Np(V)).

Actinide					
Oxidation State	**Th**	**U**	**Np**	**Pu**	**Am**
VI	NA	0.03 DB 0.0 CB	NA	NA	NA
V	NA	NA	2 DB 1 CB	(2) DB (1) CB	NA
IV	#	#	#	#	NA
III	NA	NA	NA	#	#

No column test results were reported for Th(IV), Pu(V) or Am(III), since breakthrough had not been observed for any of these radionuclides after about 80 days of experiments. We recommend that gamma emission tomography be used to determine the progress of Th(IV), Am(III) and Pu(V) in the columns and to calculate K_d values for these radionuclides. In the absence of a column K_d for Pu(V), its value may be set equal to that measured for Np(V) as indicated in the table.

ENVIRONMENTAL EVALUATION GROUP
TECHNICAL ANALYSIS AND RECOMMENDATIONS FOR THE APPLICATION OF K_d MEASUREMENTS TO PERFORMANCE ASSESSMENT OF THE WIPP

(Attachment to R.H. Neill letter to J. Salisbury, 6/10/96)

BACKGROUND

MODELING ACTINIDE RETARDATION

How does one estimate the time it would take for radionuclides introduced into the Culebra aquifer to reach the land withdrawal boundary? The approach in performance assessment is to form a computer model of the pertinent hydraulic phenomena occurring in the Culebra to calculate actinide transport. The hydrologic phenomena can be separated into individual components through the use of a computer model. The model domain can be separated into many small components with each having individual parameter values representing the various phenomena. The model can not be broken down so finely that the physics of what is occurring can be represented. The hydrologic phenomena representations are abstractions of the system [*Beckie et al* 1994; *Neuman and Orr* 1993]. The parameters used in the model are effective and appropriate for a particular use of the models.

There is substantial field evidence that the dolomite rock of the Culebra is bypassed by water flowing through fractures in the rock, at least in portions of the Culebra. These fractures may occur in many sizes. A dual porosity model best represents the flow and transport in the Culebra at several locations on the WIPP site. In a dual porosity model, the actual transport of solutes by the bulk motion of the flowing groundwater is through fractures. The matrix plays a role in transport only through diffusion of solutes into the matrix material. The dual porosity model represents the fractures by two orthogonal sets of fractures that are parallel, equally spaced, and of equal aperture. The effective parameters of this model must represent 1) the transmissivity of each block of the model, 2) the effective porosity, 3) the effective dispersion of the flow so that at the accessible environment (WIPP land withdrawal boundary) the spreading of the actinide concentration would be correct, and 4) the effective retardation of the actinides.

Actinides may be introduced into the Culebra aquifer through inadvertent drilling into the WIPP repository. These actinides would be in solution in brine. The solute would move through the Culebra at a slower rate than the brine because of reactions with the Culebra rock. The dominant form of these reactions is through absorption on to the surfaces of the rock. If the sorption reactions are fast and linearly related to the concentration, K_d is the ratio of the solute concentration to the amount of solute on the surface of the rock per mass of rock. Solute is retarded relative to brine movement because the portion of the solute attached

coefficient for the matrix in proximity to the fractures? Brine has been migrating through the Culebra for millions of years. One explanation for differences in Culebra transmissivity has been the dissolution of anhydrite and gypsum from the fractures [*Beauheim and Holt* 1990]. This leads to the question of whether the surfaces of the matrix in close proximity to the fractures have been altered by interaction with the migrating fluids such that K_ds calculated from the bulk rock experiments are inappropriate.

CORE COLUMN MEASUREMENTS OF K_d

Forcing actinide solutions through columns of intact core could be useful in addressing some of the concerns raised in both the modeling of retardation and in the appropriateness of batch experiments. The core column experiments are closer to the field conditions because the surfaces exposed to the solute in the matrix of the rock and in micro-fractures are representative of the surfaces that would be exposed *in-situ*. Experiments with cores mitigate the concerns of the impact of freshly exposed surfaces from rock crushing.

The limitation of the core column experiments is that the bulk rock, with fractures and heterogeneities both laterally and vertically, cannot be replicated by a core. A core is only a very small sample of the rock *in situ*.

FIELD TESTING OF RETARDATION

Maloszewski and Zuber [1990] state "It remains unknown if the field values of the reaction parameters can be predicted from laboratory batch or column experiments." Field testing of retardation in the Culebra is the only method to estimate the influence of the heterogeneous nature of the fractured dolomite on actinide retardation. While the scale of any feasible tracer test is still small compared to the distance from the repository to the land withdrawal boundary, the concern over the representativeness of the Culebra is significantly reduced in a field test compared to core column experiments. In a field test, the tracer must be a representative analog to the actinides of concern for radionuclide release. The concern over representativeness of the Culebra is replaced in some part by the representativeness of the tracer behavior.

Experiments using a non-reactive tracer provide a measure of the dispersion created by the heterogeneity of the fractures within the Culebra and by diffusion into the dolomite. These experiments are imperative in the establishment of effective aperture estimates. However, non-reactive tracers diffuse much further into the rock matrix and this could introduce significant error in understanding the behavior of sorbing tracers in the system. Comparisons of experiments with reactive tracers to those using non-reactive tracers would provide an indication of the influence of these differences on the overall transport behavior.

the contaminant plume. Although we saw these images briefly, we believe they demonstrate an uneven flow through the Culebra rock that bypasses regions of the rock.

The K_d estimates were derived from the batch tests, the column tests and the mechanistic investigations using a formal rule. In addition, because of the lack of experimental results for oxidation state +III, the results from PU(+V) were used to provide bounding estimates for Am(+III) and Pu(+III). The resulting K_d estimates are presented in Table 1.

The DOE maintains that K_d estimates are conservative for the following reasons:

1) Clay was not detected in the XRD analysis of the rock samples used. It is believed that corrensite exists in detectable quantities within the Culebra. Corrensite would significantly enhance the Culebra sorption.

2) The lowest values from the two different major brine types were used to establish the K_d values.

3) The acid washing of the rock samples removed iron oxyhydroxides that would increase the sorption potential of the Culebra over the tested samples.

4) The test results did not include data from desorption experiments that, in some cases, resulted in larger K_d estimates.

5) The K_ds established for the +V oxidations state for Pu were used to bound the K_ds for Pu(+III) and Am(+III).

The results of non-reactive tracer tests at the H-19 and H-11 hydropads were presented. The tracer evaluations were presented as preliminary results. These presentations lacked sufficient detail to allow an evaluation of the material presented. The results of the tracer experiment could not be matched using a single porosity model of advection even using a heterogeneous transport model. It was demonstrated that a heterogeneous dual porosity model came much closer to the tracer data. A multi-rate diffusion model developed by Haggerty and Gorelick [1995] provided a close match to at least one set of tracer data from the H-19 hydropad.

EEG CONCLUSIONS

- The K_d used for calculations of radionuclide transport in ground-water is a bulk parameter that must capture the randomness of the ground-water velocity field at the field scale.

- The batch and column experiments indicate that it is reasonable to expect that the actinides will sorb to some degree on the solid surfaces that are encountered along the flow path from the repository to the site boundary.

with no breakthrough, or determining the progress of radionuclides in the column by slicing the cores may be used; we believe this can be readily accomplished.

- Focus on including engineered barriers such as an engineered backfill and fixing the waste through treatment to avoid having to take credit for retardation in transport through the Culebra.

- Start planning now to conduct a field sorbing test, so that if a decision is made to conduct it, additional time is not lost. The EEG has recommended this since 1979.

REFERENCES

Beauheim, R.L. and R.M. Holt, 1990. "Hydrogeology of the WIPP site", in *Field Trip #14, Geological and Hydrological Studies of Evaporites in the Northern Delaware Basin for the Waste Isolation Pilot Plant (WIPP), New Mexico*, by Geological Society of America, 131-180. Dallas, TX: Dallas Geological Society.

Beckie, R, A.A. Aldema and E.F. Wood, 1994. The universal structure of the groundwater flow equations. *Water Resources Research* 30 (5): 1407-1419.

Freeze, R.F and J.A. Cherry, 1979. *Groundwater.* Englewood Cliffs, N.J.: Prentice-Hall.

Haggerty, R. and S.M. Gorelick. 1995. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. *Water Resources Research* 31(10): 2383-2400.

Maloszewski, P. and A. Zuber, 1990. Mathematical modeling of tracer behavior in short-term experiments in fissured rocks. *Water Resources Research* 26(7): 1517-1528.

Neuman, S.P. and S. Orr, 1993. Prediction of steady state flow in nonuniform geological media by conditional moments: exact nonlocal formalism, effective conductivities and weak approximation. *Water Resources Research* 29(2): 341-364.

Donald Langmuir, PhD
Hydrochem Systems Corp.
129 S. Eldridge Way
Golden, CO 80401

Date: May 25, 1996

To: Robert H. Neill, Director, Environmental Evaluation Group
New Mexico Institute of Mining and Technology

From: Donald Langmuir, President, Hydrochem Systems Corp.

Subject: Letter report on the meeting in Carlsbad, May 21, 1996
between the Dept. of Energy, Sandia Natl. Labs and the EEG

I understand that my principal assignment at this meeting was to assist the EEG in evaluating the DOE's proposed basis for taking credit for chemical retardation in the performance assessment for the WIPP. I will speak chiefly to this issue, but will also comment on the colloidal transport of radionuclides, and very briefly on the solubility limits assumed for the actinides. This last topic was not considered at the meeting, but is obviously important to the definition of source term in performance assessment.

I. Retardation of Actinides

At the meeting, the DOE emphasized its intention to determine and propose conservative (lowest reasonable) K_d values for performance assessment. Three test methods were used to assess radionuclide adsorption in the Culebra dolomite. The first two (empirical batch sorption and mechanistic sorption) were both batch tests, the third employed intact core columns. All tests used relatively pure dolomites. To the extent possible, small amounts of clay (e.g. corrensite) and hydrous ferric oxides found in the Culebra were intentionally excluded from the experiments. CO_2 partial pressures in the experiments ranged from $10^{-1.5}$ to $10^{-3.5}$ bar, pH values from about 3 to 10. Fluids used were two brines from the deep

solid solution. The DOE said that both adsorption and desorption batch tests were performed, although only the adsorption results were presented. They acknowledged, however, that desorption K_d's were sometimes larger than adsorption K_d's. This is consistent with the actinides being coprecipitated at carbonate mineral surfaces, rather than simply being adsorbed.

The DOE announced that it had discarded batch adsorption data that did not plot in a linear isotherm on a plot of amount sorbed versus dissolved concentration. It was never explained to my satisfaction how this action could be justified.

After examining the experimental batch and column test results, we noted that the column test results generally gave lower K_d values than the lowest K_d values obtained through batch tests. We further concluded that the column tests more closely represented groundwater flow conditions at the WIPP than did the batch tests. We decided therefore, to recommend that only column test results be used in PA. We proposed that the DOE should adapt their lowest and average experimentally measured K_d values for U(VI) and Np(V) from the column tests, and assume the K_d for Pu(V) equalled its value for Np(V) from the column tests. However, column test results were lacking for Th(IV), Pu(V) and Am(III), because breathrough of these species had not yet occurred (after about 80 days). This led to our proposal that the DOE obtain gamma emission tomography images of the column test cores to determine the migration distance and so to compute K_d values for these actinides in the Culebra dolomite. Our conclusions as just discussed and apparently agreed to at the EEG offices in Albuquerque on May 22nd, are summarized with minor edits in Table 1.

It is important to remember that conditions at the time of waste emplacement in a WIPP repository will be oxidizing because of ventillation with air. Under such conditions Pu(V) and Pu(VI), U(VI) and Np(V) are the important oxidation states of these elements. All (except perhaps for Pu(V) -see above) have K_d's near zero and readily move with groundwater. However, once the waste has been flooded with local groundwaters in the Culebra, or comes in contact with deeper brines introduced by oil and gas activities, it will exist in a reducing environment. In the vicinity of the waste, the iron drums will poise the Eh near the $H_2O/H_2(g)$ boundary. Under such conditions, only IV and III oxidation states of the actinides are stable. Reliable K_d values for these species from column tests, which so far are lacking, are therefore especially important for PA.

them to flocculate and settle (Stumm and Morgan, 1996). For such reasons colloids are rare and unimportant in the brines at Gorleben, Germany, and in the Palo Duro Basin of north Texas. As noted in the WIPP colloid test plan of June 9, 1995 (Papenguth and Behl, 1995), "the high ionic strength of the Gorleben brines precludes the formation of colloids", and "colloids were not important in the transport of U, Th, and Ra ... in (the Palo Duro) brines".

Papenguth reported on experiments with actinide-humic colloids, which were thought to perhaps have potential importance at the WIPP site. Crushed rock column tests and intact-core column flow tests showed that humic substances did not enhance the transport of actinides. Colloidal transport of the actinides can therefore be neglected in performance assessment.

III. Summary Remarks

Assuming only column test results are valid, the DOE effort to determine conservative K_d values for performance assessment, indicates that K_d values may be low and close to zero for the V- and VI-valent actinides, which are the dominant species in a WIPP repository prior to closure. The III- and IV-valent actinides which will control actinide mobilities after repository closure, are probably highly immobile in Culebra brines or in other brines that may be introduced into the repository. In the absence of breakthrough results from column tests for these species, gamma emmission tomography should be used to compute K_d values from the column studies.

Colloid theory and field studies elsewhere in saline groundwaters, indicate that colloidal transport of radionuclides is highly unlikely at the WIPP site. Studies by DOE scientists further indicate that actinide-humic colloids will not significantly increase the mobility of actinides over their mobilities as inorganic species. Colloidal transport can therefore be ignored in performance assessment.

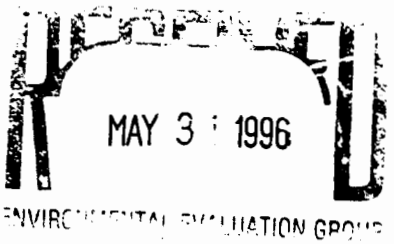
Finally, another important geochemical control on the actinide source term, is the assumed solubility of actinide solids in WIPP groundwaters. Discussion of the assumptions and thermodynamic basis for actinide solubility calculations was not presented. However, most DOE scientists are assuming the thermodynamic data for uranium published by Grenthe et al., (1992) is correct. I am convinced that the data is seriously in error for UO_2(am), and the neutral complex $U(OH)_4^\circ$, which defines the minimum solubility of UO_2 solids at low

Table 1. Recommended K_d (ml/g) values for the actinide elements, based on information provided by the DOE and its contractors on May 21, 1996. Listed values are lowest reported or average reported K_d's based on column test results only. DB and CB denote values obtained in experiments using deep brine and Culebra brine, respectively. Parenthetic values for Pu(V) have been estimated assuming they equal the measured column test values for analogous Np(V)).

Actinide					
Oxidation State	Th	U	Np	Pu	Am
VI	NA	0.03 DB 0.0 CB	NA	NA	NA
V	NA	NA	2 DB 1 CB	(2) DB (1) CB	NA
IV	#	#	#	#	NA
III	NA	NA	NA	#	#

No column test results were reported for Th(IV), Pu(V) or Am(III), since breakthrough had not been observed for any of these radionuclides after about 80 days of experiments. We recommend that gamma emission tomography be used to determine the progress of Th(IV), Am(III) and Pu(V) in the columns and to calculate K_d values for these radionuclides. In the absence of a column K_d for Pu(V), its value may be set equal to that measured for Np(V) as indicated in the table.

Leslie Smith
Hydrogeological Analysis • Groundwater Contamination Studies



Dr. Robert Neill
Director, Environmental Evaluation Group
7007 Wyoming Blvd, N.E. Suite F-2
Albuquerque, New Mexico 87109

May 24, 1996

Dear Bob,

In this letter I provide my viewpoint on DOE's radionuclide retardation model for the Culebra. The opinions expressed here reflect my consideration of the material presented at the Consultation Meeting in Carlsbad on May 21, and the meeting of EEG and its consultants at the EEG office on May 22, 1996. As the meeting with DOE and its contractors was not intended to provide detailed technical information, the conclusions expressed here are necessarily limited to a broad-based assessment of concepts and experimental approaches.

1. The hydraulic characterization indicates that it is reasonable to expect that along the preferred flow path from the repository to the site boundary, there are regions where the Culebra behaves as a double porosity medium, and actinides will migrate from fractures into matrix blocks. The suggestion I heard that it may be possible to distinguish the locations of regions with single and double porosity on the basis of transmissivity values is intriguing and should be pursued.

2. The batch and column experiments indicate that it is reasonable to expect that the actinides will sorb to some degree on the solid surfaces that are encountered along the flow path from the repository to the site boundary. These surfaces may be on fracture walls, or within matrix blocks.

3. The only rigorous way of determining Kd values for PA calculations would be to carry out sorbing tracer tests within the Culebra, at a scale large enough to characterize the influence of variable, local-scale flow paths on the effective or "bulk" Kd value. In the absence of field verification, lab-based measurements have the potential to introduce considerable uncertainty in the extent to which they capture the effect of complex local flow patterns that undoubtable exist in the Culebra. The argument DOE presented on surface area as a function of size fraction does not persuade me that the Kd measurements on crushed dolomite are representative of the sorption that could occur within the intact rock fabric of the Culebra.

4. The batch test data are of unknown reliability when used to characterize the extent of sorption that will occur in the Culebra. This viewpoint does not question the validity of

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the Kd estimates as they apply to the material on which they were measured. The idealized, double porosity hydraulic model that will be used in PA cannot describe the heterogeneity of the medium in sufficient detail to permit a simple assignment of the batch-scale Kd's throughout the matrix blocks. The viewgraphs presented to us that compare results of batch and column experiments suggest to me that the batch Kd's will overestimate actinide retardation in the Culebra. I do not support an approach that combines the results of column-scale and batch experiments to identify a sampling distribution for Kd values.

5. The brief overview we heard on the column experiments suggests that these data may be more indicative of the retardation that could occur within the matrix blocks of the Culebra dolomite. The column tests for those actinides that have yet to breakthrough at the end of the column should be characterized using tomographic techniques to estimate a Kd value (based on the present center of mass of the sorbing tracer). I sense that insufficient data are available on cores from different hydrostratigraphic zones and locations in the Culebra to bound the range of values that may be encountered along the preferred flow path to the site boundary. The concern remains (but to a lesser degree) about the degree to which values measured on columns will reflect field behavior. Field Kd values may be lower than those reported for the column experiments. It is conceivable that the field Kd value could also be higher if the indicated low-clay content of the cores from the air intake shaft are not representative of the average condition within the Culebra.

I have struggled with the issue of maintaining a consistent approach in identifying the range of Kd values I could support in a PA, in the absence of field tests with sorbing tracers. It is my view that the table (once finalized) of column-scale Kd's that we developed in the EEG office should have some value in guiding DOE in the Kd values that could be used in PA. At the same time, I recognize the conservative approach would be to assign a Kd value of zero to each actinide. The former approach has the potential to overestimate Kd, the latter approach will underestimate Kd. The easiest resolution is to give no credit to retardation in a preliminary set of PA calculations to determine if actinide mobility in the Culebra is a significant issue. Depending upon these results, a second set of PA calculations could be performed using our tabulated values. If retardation in the Culebra is identified as an important factor in meeting the EPA compliance requirements for the human intrusion scenario, I see no alternative but to attempt field-scale sorbing tracer tests.

Sincerely,

Leslie Smith

Leslie Smith

The HYDRODYNAMICS Group
studies in mass and energy transport in the earth

JOHN BREDEHOEFT *PhD, NAE*
principal

June 1, 1996

Lindsay Lovejoy, Jr., Assistant Attorney General
Attorney General of New Mexico
PO Drawer 1508
Santa Fe, NM 87504-1508

Dear Lindsay:

The purpose of this letter is to comment on the work by Sandia in measuring distribution coefficients for use in the performance assessment (PA) calculations. These coefficients will be used to predict the transport of radio-nuclides in the Culebra Dolomite.

The PA transport calculations in the Culebra Dolomite require a lumped parameter that captures the nature of the chemical interactions between the nuclide of concern and the rock matrix in the field situation. The batch laboratory tests do not represent this interaction. While they may describe the chemical interactions in a perfect world, they do not capture the nature of the sorption reactions in the field transport calculations. Let me explain.

Batch Tests

The batch tests create a laboratory system in which, the contaminant of concern contacts all of the rock: mass uniformly. This situation is deliberately created in the laboratory. The flow system created by the hydraulics of the real system differ considerably from the laboratory. The column experiments conducted by Sandia illustrate the point.

Column Experiments

In order to calculate a distribution coefficient, K_d, from the column experiment one implicitly assumes that the contaminant has contacted the rock mass uniformly throughout the column. The radio-tomography illustrates that this is not the case. Any given scan shows a more or less random distribution of the radioactivity across the column. This reflects a heterogeneous distribution of the flow paths in the column. There are fast pathways that move some of the contaminants through the core more quickly, and other paths that are slower. This leads to a more or less random distribution of sorption in the column. The point is that the distribution is not uniform in the column as is assumed by the batch tests. For this reason one obtains smaller K_ds from the column experiments.

One can imagine that the field situation is much like the column experiment except at much larger scale. Again, the point is that in the field the contaminant of concern is moved by a highly variable flow field that moves the contaminants through the rock mass in a very heterogeneous manner.

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The K_d used for transport calculations is a bulk parameter that must capture the randomness of the ground-water velocity field at the appropriate scale--the field scale. The distribution coefficient is analogous to the dispersivity which is also a bulk parameter.

Conclusion

The batch laboratory tests do not provide any guidance for PA transport calculations for the Culebra. The column experiments are probably more meaningful. They may provide an upper bound on the appropriate K_d. If anything we would expect the numbers for the field to he smaller than the column test values. There will be even more heterogeneity in the ground-water velocity field at the field scale.

Sincerely yours,

John Bredehoeft

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