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September 15, 1994
SP307:091594:01

Mr. Andy Ledford
EG&G Rocky Flats, Inc.
Rocky Flats Environmental Technology Site
P.O. Box 464, Building 080
Golden, Colorado 80402-0464

Subject: MTS 343756 GG
OU4 Solar Ponds IM/IRA
Request for Chemical Analysis of Waste Materials Being Dispositioned Beneath
the Engineered Cover

Reference: Record of Telephone Conversation (September 7, 1994) SP307:090894:02 - Soil
Strength Discussions

Dear Mr. Ledford:

Enclosed for review and comment is a request to perform batch leaching tests and chemical analysis on the various waste forms that will be consolidated beneath the engineered cover. The waste forms include:

- 1) Unamended soils,
- 2) Soil and sludge mixtures,
- 3) Soil and pondcrete mixtures, and
- 4) Soil and liner mixtures.

In general, ES recommends that in the case of #1 above, batch testing using existing core samples be performed. This will eliminate the need for additional drilling to obtain samples.

Prototypes of other waste forms will be formulated using existing drill cuttings for the soil component. Batch tests will be performed with clean water to simulate the actual field conditions. The results will be used as input data to the VS2DT vadose zone model to determine if leachate concentrations from the consolidated materials will be protective of human health and the environment.

Please review this plan and indicate if this program can be implemented in the near future so that the IM/IRA-EA Decision Document can be revised for submittal to the regulatory agencies and the public. It should be noted that physical testing for compaction and strength characteristics will also be required. These tests have been previously identified.

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Please call me at 764-8811 or pager 687-2551 if you have any questions.

Sincerely,


Philip A. Nixon
Project Manager: Solar Pond IM/IRA

cc:

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**PROPOSAL FOR ENHANCED PERFORMANCE MODELING OF
INTERIM MEASURES/INTERIM REMEDIAL ACTION COVER
(INCLUDING PROPOSAL FOR ACQUIRING ADDITIONAL CHEMICAL DATA)**

1.0 BACKGROUND AND OVERVIEW

Recent changes in the proposed method of incorporating Solar Evaporation Pond (SEP) sludge and existing pondcrete beneath the interim measures/interim remedial action (IM/IRA) engineered cover, and increased dependence on long-range performance modeling of the overall structure to demonstrate protection of human health and the environment, necessitate upgrading current modeling efforts. This proposal describes measures required to accomplish that upgrade.

Specifically, VLEACH (Lawson, 1991), a computer code based on a relatively simple model for solute transport in the vadose zone, and which has been used to date is proposed for replacement in favor of a more sophisticated and comprehensive code and model. The increased model sophistication requires input data currently not available for the materials to be placed beneath the engineered cover. Accordingly, this proposal also includes the acquisition of those data.

2.0 JUSTIFICATION FOR PROPOSED ACTIVITIES

The fundamental objective of the long-term performance modeling of IM/IRA enclosure contents is to predict the stability of contaminants of concern (COCs) within the confines of the enclosure and ultimately to predict the potential for release of COCs. The conceptual model for a release involves 1) infiltration of meteoric water through the engineered cover; 2) percolation of that water, with or without residual soil moisture, (the mobile liquid phase) through the unsaturated waste materials; 3) transfer of contaminants from the waste materials into the mobile liquid phase (by liquid mixing, dissolution, desorption, or ion exchange); and finally 4) leakage of the mobile liquid phase from the base of the closed unit into the subsurface environment. The overall complexity of the physical and chemical processes involved is sufficiently great to merit the application of the most appropriate model and to acquire the necessary data for that model.

2.1 Justification for Model and Code Upgrade

The model and computer code (VLEACH) which has previously been applied to the IM/IRA materials is not ideally suited for dealing with the variably saturated and otherwise heterogenous nature of the proposed mounded aggregate of waste material. Waste materials proposed for inclusion are:

- 1) Contaminated native soils and unconsolidated vadose zone materials - at least three types exist based on physical characteristics;

- 2) SEP sludge and chemically fixed sludge water - chemical and physical properties to be determined, ultimately to be mixed with contaminated soil;
- 3) Previously prepared "pondcrete" - existing in various physical and chemical conditions, to be disaggregated and combined with contaminated soil; and
- 4) SEP construction materials - mainly asphaltic liners.

VLEACH assumes that the moisture profile within the unsaturated interval is constant and the model is restricted to steady-state conditions with respect to water movement. Construction specifications for placing the materials will likely require 90% Proctor compaction which, due to the heterogeneity of the proposed waste materials, will therefore require different moisture contents, thus violating the assumption of a uniform moisture profile. This may be particularly true for the lifts containing sludge and chemically fixed sludge water. Furthermore, incorporation of non-soil components [i.e., items 2), 3), and 4) above] will alter the porosity, permeability, and moisture retention characteristics necessitating use of a stratified model. VLEACH assumes vertically homogenous physical properties and thus would not allow adequate modeling of the various layers of waste material.

Regarding the transport of contaminants of concern: the VLEACH model does not include a diffusion term and is one-dimensional and thus does not allow for dispersion, a potentially important component of solute mass transport. Additionally, VLEACH has only a limited capability to model the transfer of contaminants from the solid phases of the waste material to the mobile liquid phase. VLEACH was intended to deal with neutral organic solutes and thus considers soil concentrations of organic matter and K_{om} values for various compounds. Inorganic contaminants of concern in the IM/IRA waste materials are better modeled through solubility and linear or non-linear sorption isotherms. Finally, some highly soluble components of the wastes (e.g., nitrate) are largely contained in soil moisture. To consider the transport of these components, mixing of soil moisture with percolating waters is required and is not possible with VLEACH.

2.1.1 Model Requirements/Code Selection

For the above reasons, an alternative model and computer code is proposed to replace VLEACH. An acceptable model and computer code would allow (minimally) for the following:

- 1) Variable initial soil moisture contents (VLEACH assumes homogenous moisture contents.),
- 2) Non-steady state advection of fluid phase (VLEACH is steady state.),
- 3) Dispersion (VLEACH does not include dispersion.),
- 4) Two dimensions (VLEACH is only one dimensional.),

- 5) Linear (Freundlich) K_d terms and nonlinear Langmuir isotherm parameters to describe equilibrium adsorption and desorption processes (VLEACH is strictly linear.),
- 6) Chemical mixing of soil moisture and percolating waters (VLEACH does not allow such mixing.), and
- 7) Equilibrium dissolution of limited solubility solids (VLEACH does not allow for equilibrium dissolution.).

A computer code, VS2D/VS2DT (VS2DT) (Healy, 1990 and Lappala et al., 1987), is proposed as the replacement for VLEACH. According to the documentation accompanying VS2DT and conversations with the author of the code, VS2DT meets all the requirements set forth above with the exception of 7). However, the modular, subroutine-oriented structure of VS2DT should allow modification of this public-domain code to account for dissolution-limited contaminant solubility.

2.2 Justification for Additional Data

The model on which VS2DT is based requires input data above and beyond those required by VLEACH. The additional required data are physical and chemical data as described below.

2.2.1 Physical Data Requirements

Modeling of liquid flow in a heterogenous, variably saturated mound of materials requires the following input parameters for each class of material:

- 1) Saturated hydraulic conductivity
- 2) Porosity, and
- 3) Unsaturated moisture contents and associated pressure heads (collectively known as soil moisture characteristic or moisture retention curves).

Although all these parameters have been determined for Operable Unit 4 (OU4) soils representative of those to be included in the waste mound, those determinations were made under *in situ* conditions. None of these parameters have been determined on the same or similar soils under the compaction conditions (90% Proctor) and moisture contents (design conditions) anticipated for the waste mound materials. Furthermore, none of these determinations have been made on non-soil wastes including soil and sludge mixtures, soil and pondcrete mixtures, and liner and soil mixtures.

It is currently anticipated that the requisite tests on unamended soils under design conditions will be performed as part of an amendment to the geotechnical investigation currently underway at OU4. The proposed inclusion of the above tests in that program is described in a separate work plan. Complementary testing of final design waste forms (e.g., soil and sludge mixtures, soil and pondcrete mixtures) will be performed following development of the final waste form.

2.2.2 Chemical Data Requirements

COCs have been found in SEP-proximal surficial and vadose zone materials, SEP construction materials (liners), and SEP sludges and associated liquids. These contaminants include uranium, radium, the transuranic actinides plutonium and americium, as well as certain stable metals (of greatest concern is cadmium). The processes by which these contaminants can transfer from the above solids to mobile liquid phases within the consolidated waste mound, and the extent to which such transfer might take place are extremely complex issues (Stumm, 1992). Plutonium probably represents the worst case with respect to these complexities because of its multiple valence states, strong sorption characteristics, and tendency for complexation and polymerization (Langmuir 1994). For reasons attendant to these complexities, it is common practice to determine operational, empirical coefficients which relate concentrations of a given compound in solid phases to equilibrium concentrations of that compound in the associated liquid phase. These relationships take many forms, the most elementary of which is $K_d = \frac{C_s}{C_l}$ where K_d is the partition coefficient, and C_s and C_l are the concentrations in the solid and liquid phases, respectively.

K_d values, or coefficients for one of the more complex relationships (e.g., Freundlich or Langmuir isotherm equations), is mandatory for VS2DT to operate.

It must, however, be emphasized that K_d s are notoriously condition specific (i.e., highly dependent on the experimental conditions under which they were determined). Among the operational variables which are well documented and known to affect partitioning are the following:

- 1) Exact chemical and physical nature of the solid phase;
- 2) Identity of the compound (contaminant) and its chemical form (oxidation state and complexation), which is a function of some of the other variables listed below;
- 3) Solution pH (affects both the contaminant form and surface conditions of the solid);
- 4) Other components of the liquid phase, (i.e., matrix solutes affect contaminant complexation and solid surface conditions); and

5) Initial concentration of the contaminant in the solid or liquid phase.

Numerous workers have determined the extent of partitioning of various elements between various solids and liquids (typically aqueous solutions) of various compositions. Many exhaustive compilations exist (Thibault et al., 1990; Ames and Rai, 1978; Rai and Zachara, 1984; and others). Obviously the matrix of experimental conditions and associated partitioning coefficients is huge and accordingly the range of K_d values for any given contaminant is very large. It is not atypical for K_d s to range over three to five orders of magnitude.

It has frequently been suggested that literature values be used as input for modeling of the IM/IRA waste performance. However, an examination of the literature quickly reveals the difficulty of selecting a value that may be representative of the IM/IRA wastes with any degree of confidence. It is true that there is typically little difference in the mobility of a contaminant whether its $K_d = 100$ or 100,000 (In both cases the contaminant is strongly associated with the solid and thus essentially immobile.); however, there is an enormous difference in mobility between K_d s = 100 and 10. The danger in assuming that some typical or apparently relevant literature value actually represents conditions of the IM/IRA is that some aspect of the real site-specific environment may cause K_d s to be unexpectedly low. For example, OU4 vadose zone pore waters collected with lysimeters (exclusive of deep lysimeters which may have collected true saturated-zone ground water) reveal pH values as high as 11.53, specific conductances as high as 19,990 microsiemens per centimeter ($\mu\text{S}/\text{cm}$), high nitrate concentrations and high U-238 activities [671 picocuries per liter (pCi/L)]. Column leach experiments on OU4 vadose zone soils confirm elevated pH values and pore water nitrate concentrations as high as 16,000 milligrams per liter (mg/L) (NO_3 as N). These conditions are outside the "norms" typically used for K_d determinations and therefore invalidate the assumption that "average" K_d values are automatically representative of OU4 conditions. Furthermore, literature summaries of K_d values which attempt to "average" elemental K_d values for various soil types etc. (e.g., Thibault et al., 1990, which is largely based on Baes and Sharp, 1983) are suspect because they attempt to represent highly disparate data (by author's own admission) with ordinary parametric statistics thus ignoring the inherent complexity of the population of K_d values being sampled.

Miner et al. (1982) investigated plutonium soil/water interactions in soils from various DOE facilities, including the Rocky Flats Environmental Technology Site (RFETS). For three RFETS soil samples, K_d values ranged from 43 to 2,200 milliliters per gram (ml/g) as determined in adsorption mode experiments with plutonium concentrations in water ranging from 10^{-8} to 10^{-6} M (or 0.146 pCi/L to 14.6 pCi/L - maximum observed OU4 value for dissolved plutonium is 0.04 pCi/L). The possibility of values less than 100 ml/g is of particular interest for transportability. The fact that relatively low K_d values have been measured under some conditions for at least one RFETS soil gives rise to concern about using the values recommended by Thibault et al. (1990) (550; 1,200; 5,100; 1,900 ml/g for sand, silt, clay, and organic soils, respectively). Desorption-mode experiments performed by Miner et al. (1982) gave a K_d value of 1,180 milligrams per gram (mg/g) for a starting plutonium concentration of 367,000 pCi/g in native soils. This latter value is probably not relevant because of the extremely high initial plutonium concentration.

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In conclusion, there is no defensible substitute for determining site-specific, condition-specific partitioning coefficients for each of the IM/IRA waste materials to be included beneath the engineered cover, including unamended soils, and any engineered waste form. It is therefore proposed that K_d s be determined on selected representative soils (see laboratory procedures below) and any waste forms proposed for inclusion beneath the IM/IRA engineered cover.

3.0 LABORATORY TESTING

3.1 Physical Property Determinations

The required physical testing has been proposed elsewhere as part of an ongoing program and is therefore not proposed here.

3.2 Chemical Property Determinations

It is proposed that laboratory determinations of desorption-mode partition coefficients be made on all materials anticipated for inclusion beneath the IM/IRA engineered cover. To simplify the laboratory procedure, all tests will be conducted as batch tests. A description of the materials to be tested and their sources follows.

- 1) Four samples of SEP-proximal, contaminated, unconsolidated vadose zone material (three different and one duplicate). Soil samples would be retrieved from existing cores obtained during RCRA Facility Investigation/Remedial Investigation (RFI/RI) Phase I investigations and selected on the basis of physical properties (e.g., soil moisture characteristic curves) and contamination levels. The selection process would attempt to identify a) samples representative of the range of soil types present in the vicinity of SEPs and b) soils with optimal contaminant concentrations (i.e., relatively high) for laboratory batch desorption experiments. Approximately 1 kilogram (kg) of selected intervals will receive radiological screening and be shipped to the selected testing laboratory.
- 2) Mixture(s) of soil, sludge, and chemically fixed sludge moisture. This is the recently proposed waste form now being considered by HNUS. This mixture will be prepared by HNUS using OU4 unconsolidated vadose material in the form of drill cuttings (the "soil" retrieved from storage drums) and the sludge/chemically fixed sludge water solid mixture designed by HNUS. All components will be mixed in the proportions anticipated for the final IM/IRA structure. If more than one candidate recipe for the mixture is designed by HNUS, a sample of each mixture should be tested. A 1-kg sample of each mixture will be shipped to the selected testing laboratory.
- 3) Mixture(s) of soil and pondcrete. This mixture will be prepared from soils [as described in 2) above] and existing pondcrete. The mixture will simulate the proportions and final pondcrete aggregate size anticipated for the final IM/IRA

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structure. If more than one candidate recipe for the mixture is designed, a sample of each mixture should be tested. A 1-kg sample of each mixture will be shipped to the selected testing laboratory.

- 4) Mixture(s) of soil and asphaltic pond liners. This mixture will be prepared from soils [as described in 2) above] and representative samples of pond liners. The availability of pond liners is currently in question and should be discussed.

The experimental design will be developed in cooperation with the selected analytical laboratory with the objective of simulating, as closely as possible, the conditions expected beneath the IM/IRA engineered cover. In addition the requirements of trace metal and radiochemical analyses will be considered. The following design criteria will be used.

- 1) All tests will be conducted in a desorption mode. Because the conceptual model for long-term performance of IM/IRA wastes includes contact of wastes with clean (initially meteoric) water and subsequent transfer of contaminants to the liquid phase, soil samples will be mixed with clean (contaminant-free) water. This contrasts with the more commonly performed adsorption-mode experiments in which contaminants are initially placed in the liquid phase and equilibrated with clean soils.
- 2) Existing ("native") levels of contamination will be used, i.e., no contamination will be added (spiked) to the soil. This procedure ensures that the desorption mode partitioning of contaminants will occur under actual field conditions rather than those of artificially highly contaminated soils.
- 3) Existing cores will be brought back to original soil moisture levels by the addition of pure water and homogenized. Because some highly soluble contaminants (e.g., nitrate) are expected to exist in vadose zone soils principally as solutes in soil moisture, an attempt to replicate the original conditions will be made.
- 4) Homogenized, rehydrated soils will be analyzed for all contaminants of concern prior to experimentation. The RFI/RI Phase I practice of analyzing a 6-foot interval aggregate of core will not provide adequate data for calculating partitioning coefficients.
- 5) Soil/water ratios will be estimated on the basis of starting soil concentrations and conservative (high) estimates of K_d values so as to achieve 10x minimum detection limit (MDL) concentrations in the liquid phase. This will ensure the greatest likelihood of obtaining liquids with sufficient contaminant concentrations to be analyzed.

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- 6) Liquid volumes will be sufficiently large (2,000 to 2,500 ml) to allow adequate concentrations of radionuclides for standard counting procedures. Smaller volumes will force laboratories to extend counting times and increase minimum detection limits.
- 7) Batch tests will be performed in an NBS rotary extractor to ensure comparability with other data (Roy et al., 1991).
- 8) Equilibration times will be no less than 24 hours (Roy et al., 1991).
- 9) Equilibrated batch slurries will be allowed to settle and the solutions will be decanted and filtered through a 0.1- μ m filter.
- 10) All filtered equilibrated solutions will be analyzed for all COCs, pH, total dissolved solids (TDS), and a full suite of water quality parameters. COCs and desired MDL are as follows:

Am-241	0.01 pCi/L †
Cs-134	§
Cs-137	§
Pu-239/240	0.01 pCi/L †
Ra-226	§
Sr-89	§
Sr-90	§
U-233-234 *	0.6 pCi/L †
U-235 *	0.6 pCi/L †
U-238 *	0.6 pCi/L †
Cd #	0.005 mg/L
Be #	0.0003 mg/L

* Although total uranium should be sufficient, isotopic determinations improve sensitivity and are consistent with existing analytical protocol.

Cd and Be appear to be the only metals of concern, a multi-element inductively coupled plasms (ICP) analysis would be appropriate.

† Isotopic analyses by microprecipitation or electrodeposition followed by alpha spectrometry.

§ Feasibility of determining these analytes is dependent on exact analytical scheme (to be determined) because of volume requirements.

- 11) All filter membranes will be analyzed by radiochemical methods to detect the possibility of suspended-matter associated contaminants.

- 12) All batch procedures will be repeated on the same solid mass to establish trends in partitioning. Ideally, K_d values would be identical for successive batch experiments (as long as K_d s are relatively high and contaminant concentrations in the solid material are not limiting (i.e., so small that the contaminant is completely removed). It is very possible that initial batch runs will be atypical of (lower than) successive runs because of anomalous initial dissolution or particulate releases. K_d values may thus only be indicative of initial mobility of contaminants in the IM/IRA structure and could over estimate long-term mobility. It is proposed that batch experiments be repeated until some level of consistency (repeatability) is obtained.

4.0 RECOMMENDED LABORATORIES

The logistical, licensing, and technical requirements for receiving, storing, handling, and determining radioactive isotopes places practical limitations on candidate laboratories for the proposed work. Furthermore, there would probably be significant time, schedule, and cost advantages to performing the batch desorption mode partition experiments in the same facility scheduled to perform the radiochemical analysis. This point is particularly relevant to item 12) above in which multiple batch runs are proposed with the objective of establishing K_d trends. Finally, it is necessary that all batch experiments be performed in the same facility and by the same methods.

Three laboratories are currently under contract with EG&G to perform radiochemical analyses:

TMA Norcal, Richmond, CA
Lockheed, Las Vegas, NV
Quantera, Richland, WA

One laboratory (TMA Norcal) has been contacted with regard to the feasibility of the proposed batch tests and required radiochemical analyses as well as cooperating in the design of the tests. They concurred with the overall design as described here and cited considerable experience with similar investigations.

5.0 REFERENCES

- Ames, L. L., and Rai, D., 1978, Radionuclide Interactions with Soil and Rock Media, Volume 1: Processes Influencing Radionuclide Mobility and Retention, Element Chemistry and Geochemistry, Conclusions and Evaluation, PB-292 460, EPA 520/6-78-007-a, NTIS PB292460: Richland, WA, Batelle, Pacific Northwest Laboratories, 360 p.
- Baes (III), C. F., and Sharp, R. D., 1983, A proposal for estimation of soil leaching and leaching constants for use in assessment models: *J. Environ. Qual.*, v. 12, no. 1, p. 17-28.
- Healy, R. W., 1990, Simulation of Solute Transport in Variably Saturated Porous Media with Supplemental Information on Modifications to the U.S. Geological Survey's Computer Code VS2D, Water-Resources Investigations Report 90-4025: U.S. Geological Survey, 125 p.
- Langmuir, D. 1994, Personal communication, September 8, 1994.
- Lappala, E. G., Healy, R. W., and Weeks, E. P., 1987, Documentation of Computer Program VS2D to Solve the Equations of Fluid Flow in Variably Saturated Porous Media, Water-Resources Investigations Report 93-4099: U.S. Geological Survey, 183 p.
- Lawson, P., 1991, VLEACH: A One-Dimensional Finite Difference Vadose Zone Leaching Model: Golden, CO, Internat. Ground Water Modeling Center.
- Miner, F. J., 1982, Plutonium Behavior In The Soil Water Environment. Part 1: Sorption of Plutonium by Soils, Part 2: Selected Chemical and Physical Characteristics of Aqueous Plutonium and Their Effects on the Sorption of Plutonium by Soils (Polzer and Miner), RFP-2480, UC-70 Nuclear Waste Management, DOE/TIC 4500 (Rev. 69), eds.: Golden, CO, Rockwell International, Summary of work presented at Am. Soc. Agronomy meeting, Chicago, Nov. 4, 1974.
- Rai, D., and Zachara, J. M., Principal Investigators, February 1984, Reprinted w. Corrections April 1986, Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration, Vol. 1: A Critical Review, Vol. 2: An Annotated Bibliography, EA-3356, Vol. 1, Project 2198-1: 3412 Hillview Av., Palo Alto, CA 94304, Electric Power Research Institute, Prepared by Batelle, Pacific Northwest Laboratories, D. Rai (509) 376-8641.
- Roy, W. R., Krapac, I. G., Chou, S. F. J., and Griffin, R. A., 1991, Batch-Type Procedures for Estimating Soil Adsorption of Chemicals, EPA/530-SW-87-006-F, Technical Resource Document: Washington, D.C., USEPA, Office of Solid Waste and Emergency Response, 100 p.

Stumm, W., 1992, Chemistry of the Solid-Water Interface. John Wiley & Sons, Inc., 428 p.

Thibault, D. H., Sheppard, M. I., and Smith, P. A., 1990, A Critical Compilation and Review of Default Soil Solid/Liquid Partition Coefficients, K_d , For Use in Environmental Assessments, AECL-10125: Pinawa, Manitoba ROE 1L0, Atomic Energy of Canada, Ltd., Whiteshell Nuclear Research Establishment, (204) 753-2311.

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