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FROM: Seth M. Coplan (Return to WM, 623-SS)
High-Level Waste Technical
Development Branch
Division of Waste Management

SUBJECT: NTS GEOCHEMISTRY

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The attached report summarizes the status of the geochemistry investigations being conducted by DOE and Los Alamos National Laboratory LANL, its geochemistry contractor, as part of the NNWSI. The report is based on information obtained by an NRC contractor (Sandia National Laboratory) during the May 17-19, 1982 NRC-DOE meeting and by the NRC staff during subsequent telephone conversations with LANL staff. The information summarized in the report together with information published in LANL reports and information supplied by DOE on December 22, 1982 will be used by NRC staff and contractors in preparing for the January 12-13, geochemistry workshop.

"ORIGINAL SIGNED BY"

Seth M. Coplan
High-Level Waste Technical
Development Branch
Division of Waste Management



cc: w/enclosure
D. L. Vieth, DOE
T. Longo, DOE

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SUMMARY OF NRC-DOE MEETING
MAY 17-19, 1982
LAS VEGAS, NEVADA
GEOCHEMISTRY ADDENDUM

On May 17 through May 19, 1982 NRC staff and consultants met in Las Vegas, NV with U. S. Department of Energy (DOE) staff and contractors. May 17 was devoted to a tour of the Nevada Test Site (NTS) that included stops at the Yucca Mountain Site, G-Tunnel, and the core library. On May 18 and 19, meetings were held at DOE's office. The purpose of the site visit and meetings was to bring NRC up to date on the status of the Nevada Nuclear Waste Storage Investigations (NNWSI), to allow for a technical exchange concerning those investigations, and to discuss questions concerning the scope and level of detail of the Site Characterization Report (SCR).

The two day technical discussion centered on questions regarding hydrology, repository design, geologic stability, and geochemistry. On August 10, 1982 a summary of the discussions and observations made by the NRC group regarding hydrology, repository design, and geologic stability was transmitted to the DOE. The present addendum addresses geochemistry. As was noted in the August 9 summary, the May meeting was planned to include a broad scope of topics even though it was recognized that depth of discussion might be sacrificed in some instances. It was planned that future meetings would be more focused and limited to specific topics and issues so that an opportunity would be provided for detailed discussion and review of data and bases of interpretation.

On the basis of the information presented and follow-up telephone conversations, several questions have been identified as subjects for

follow-up meetings regarding geochemistry. The most significant is the following:

- o What are the speciation and solubilities of waste elements between waste packages at the Yucca Mountain site and the accessible environment?

  Different molecular species have different solubility and sorption properties. It is these properties that, together with groundwater flow, largely determine the rates at which radionuclides migrate or are retarded along the path to the accessible environment.

Additional and related questions are the following:

- o What is the mineralogy of the tuffs and other rocks along possible groundwater flow paths between waste packages at the Yucca Mountain site and the accessible environment?

  The ability of a rock substrate to bind and thereby retard the transport of molecular and ionic constituents of groundwater is related to its chemical composition and the crystalline structure of the minerals that comprise the rock. Thus, the petrology of the rock units along likely flow paths from a repository to the accessible environment must be well characterized.

- o What is the chemistry of the groundwater between waste packages at the Yucca Mountain site and the accessible environment?

  To evaluate solubilities and chemical retardation of radionuclides within a repository system it is necessary to

know the chemical composition and properties of the groundwater.

- What are the effects of 1) precipitation reactions, 2) sorptive processes, and 3) physical processes on the radionuclide inventory in transit to the accessible environment from the Yucca Mountain site?

  Precipitation reactions, sorption processes and diffusional processes can each serve to retard the rate at which radionuclides are transported by the groundwater flow system. The concern is with what the relative contribution of each is and how these processes are to be represented and measured for the purpose of predicting radionuclide transport.

## Progress in the Technical Investigations

### 1. Retardation

Geochemical processes (i.e., retardation) could have a significant effect on radionuclide travel times from the Yucca Mountain site to the accessible environment. In order to determine to what extent radionuclide transport times to the accessible environment will be increased by geochemical processes, the following questions must be addressed:

- What is the mineralogy of the tuffs and other rocks along possible groundwater flow paths between waste packages at the Yucca Mountain site and the accessible environment?

- What is the chemistry of the groundwater between waste packages at the Yucca Mountain site and the accessible environment?

- What are the speciations and solubilities of radionuclides in the groundwater between waste packages at the Yucca Mountain site and the accessible environment?

- What are the effects of 1) precipitation reactions, 2) sorption processes, and 3) physical processes on a radionuclide inventory in transit to the accessible environment from the Yucca Mountain site?

Status

The ability of a rock substrate to bind molecular and ionic constituents of groundwater is related to its chemical composition and the crystalline structure of the minerals that comprise the rock. Thus, the petrology of the rock units along likely flow paths from a repository to the accessible environment must be well characterized to permit assessments of the potential for retardation of radionuclides along that pathway.

The petrology program at LANL has included mineralogic studies on core from at least four geologic boreholes on Yucca Mountain. From each borehole, the core was partitioned according to stratigraphic horizon. In this way, each stratigraphic unit could be studied at the four different sampling locations.

LANL studies indicate that the dominant sorptive phases are zeolites (clinoptilolite, heulandite, mordenite) and clays (montmorillonite [a smectite], illites). Zeolite minerals are hydrous Na, Ca, K alumino-silicates which can form as a result of hydrothermal alteration of silicate rocks (tuff, in the case of NTS). The smectites are probably the product of alteration of glass shards and pumice fragments.

Because of the sorptive properties of zeolites and smectites, it is important to be able to accurately determine the amounts present in rock

samples. The amounts of smectite and clinoptilolite in a sample can be routinely measured with a high degree of precision. Mordenite is more difficult to measure; mixtures of zeolites are still more difficult to analyse.

In general, to predict the chemical behavior of any element, it is necessary to know the chemistry of the solution in which reactions are expected. Consequently, to evaluate chemical retardation of radionuclides within a HLW repository system it is necessary to know the chemical composition and properties of the groundwater. LANL is approaching the question of groundwater chemistry by analyzing samples from the five hydrology wells on Yucca Mountain. The redox potential of groundwater in the unsaturated zone and the upper part of the saturated zone appears to be oxidizing.

At the May meeting, LANL discussed samples taken at various depths in Well USW-H1 by a thief sampler which indicated reducing waters and had measurable quantities of sulfide which are attributed to contact with pyrite in an open well. In June and July, LANL conducted a pumping test for 28 days using straddle-packers in Well UE25b-1 and found low Eh (-15mV) and no detectable oxygen after 1 day of pumping indicating that the oxygen in the drilling fluid is removed at an early stage. However, detergent was detectable, but decreasing, during the 28 day pumping test. In general, measurements of oxidation potential are subject to a large amount of uncertainty and are difficult to interpret. LANL intends to confirm preliminary data by further investigations.

It is important to investigate the speciation of radionuclides with ions in groundwater because all molecular species have different solubility and sorption properties. The degree to which radionuclides can accumulate at the accessible environment is related to the amount which is retarded by precipitation from the groundwater or sorbed onto rocks along the path from the repository to the accessible environment.

Therefore LANL is investigating speciation of radionuclides with ions in NTS groundwater.

To date, these speciation studies have involved few actual measurements of thermodynamic data for radionuclide species. The bulk of the research has involved sensitivity analyses for critical nuclides using thermodynamic data available in the literature. The final step in such sensitivity analyses is to determine a "maximum solubility". The solubility concentration of the Pu (IV) in the carbonate dominated groundwater at Yucca Mountain is estimated to be $10^{-3}$ molal when the Russian value for the Pu (IV) carbonate complex is used. LANL evaluation of the Russian data would tend to indicate use of the Russian data may result in an error of a factor of $10^{11}$ , so that the concentration is $10^{-14}$ molal.

LANL is investigating the behavior of all actinides in Yucca Mountain groundwaters, particularly with respect to speciation (i.e., oxidation state, complexes) and solubilities. These studies are only now in full swing as part of the NNWSI since the generic NWTS program was formerly charged with this responsibility. Based on these studies, LANL considers that colloidal transport is a process that may be significant in tuff systems. Therefore, LANL has been investigating this as a site specific concern.

In addition, LANL is investigating anionic species such as $I^-$, $TcO_4^-$, and anionic carbonate complexes as important non-sorbing species. As a by-product, the investigations pertaining to colloidal species have led to some refinements in the actinide data base. In particular, LANL considers that the speciation of mobile Pu (IV) is in the form of "pseudocolloidal" particles. Hence, the properties of the Pu (IV) polymer and its potential for migration through tuff as a pseudocolloid are being studied. The techniques used to study the behavior of the

polymer include micro-autoradiography, laser techniques, and artificial particulates.

Chemical processes, precipitation and sorption, and physical mechanisms can increase radionuclide travel times to the accessible environment. Sorption processes (i.e., ion exchange, adsorption, substitution) are sometimes studied as a lumped parameter and designated as a $K_d$ (thermodynamic equilibrium implied) or $R_D$ (thermodynamic equilibrium not implied). Investigations at LANL have attempted to quantify the lumped parameter, $R_D$, via batch tests with sized tuff samples and column tests with crushed and intact tuff core.

LANL has found that by running batch experiments with crushed, sized tuff samples that have been pre-equilibrated with NTS water from a common well (J-13), reproducible results are obtained. LANL described the following new results at the meeting:

1. Batch experiments using sized particles (38 u) produce results which are very similar to those from crushed column experiments. This provides a relatively quick and inexpensive way of approximating the results of the generally more reliable column tests.

2. Nonlinear sorption may be important in both batch and column experiments, i.e. measured distribution coefficients ($R_D$) appear to be dependent on both the solid-to-solution ratio and tracer concentration of the experiment.

Most of the recent sorption work at LANL consists of column experiments on intact cores (both fractured and non-fractured) and batch tests using sized pellets in place of crushed rock.

Sorption experiments and physical retardation studies are being closely coordinated with modeling studies which are focusing on isotherm, kinetic effects, anion exclusion and colloidal diffusion. These models are designed to describe a particular system, in this case a tuff system.

Plans

In the area of petrology, powder X-ray diffraction techniques are being refined by LANL. By using the refined techniques, LANL expects that data from borehole G-2 will be superior to earlier published results. If so, samples from other boreholes may be re-examined using the improved techniques.

To address the question of groundwater chemistry, LANL personnel plan to pack-off, sample and measure the redox potential of water from individual units in the Crater Flat tuff and Calico Hills during the current and coming fiscal years. The data from the first borehole should be available by January, 1983. The redox potential will be measured by electrodes and by redox-sensitive chemical reactions.

With respect to speciation and solubility, LANL intends to start a program of laboratory investigations that will gather thermodynamic data on those actinides whose speciation has been shown through sensitivity analyses to have a significant impact on migration. In particular, plans are underway to study thermodynamic properties of Pu and Np. LANL plans to coordinate its efforts with similar studies in the U.S. and elsewhere in order to avoid duplication of effort.

Regarding retardation, LANL plans to gather additional sorption isotherm data for Pu, Np, Am, and U and perhaps for Ra during the coming year. LANL plans to refine its models of radionuclide transport by developing a computer program which will use the finite difference method to

incorporate nonlinear sorption into the representation of matrix diffusion.

Observations

The NRC group was favorably impressed by two aspects of LANL's approach to geochemistry as it relates to site characterization. These are (1) LANL's efforts to coordinate its laboratory test program with its development of geochemical models and (2) LANL's systematic collection of rock and water samples for laboratory testing from multiple horizons at several locations.

LANL appears to be addressing one of the NRC groups concerns that relate to repository performance, the behavior of non-sorbed radionuclides at the Yucca Mountain site. In this regard LANL is investigating the behavior of both colloidal and anionic species. While the NRC group was favorably impressed that these studies are underway, it is concerned that other non-sorbing species may also exist. LANL may be doing work with regard to such species; however, that has not been discussed during the limited interactions between LANL and NRC to date.

The NRC group was concerned that studies of radionuclide speciation at Los Alamos have as yet produced only a limited number of estimates of solubilities. Sensitivity analyses that take solubility into account could be a key consideration in determining which nuclides are critical to investigate. It is the observation of the NRC group that bounding estimates of radionuclide solubilities should be obtained soon for use in sensitivity analyses.

Interactions between the NRC group and LANL have consisted of a site visit, a meeting conducted at a relatively broad level of detail and several follow-up telephone conversations. Based on these limited interactions, it is the NRC group's impression, that with the exceptions

noted above, LANL's work has focused on the broad questions that would need to be resolved prior to licensing a repository at the Yucca Mountain site. To determine whether the more specific issues have been identified and are being addressed will require interaction at a level that allows more detailed examination of LANL's work and the results of that work to date.