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January 7, 1982

Ms. Julia Corrado
Nuclear Regulatory Commission
Mail Stop 697-S
Washington, D.C. 20555

Dear Ms. Corrado:

As you requested, enclosed please find a reworked "Executive Summary" for the report entitled "Status of Geochemical Problems Relating to the Burial of High-Level Radioactive Waste, 1982." Please let me know when we can discuss its contents.

Very truly yours,

Bill

Bill Stromdahl
Program Manager

BS:rmr

Enclosure

"Status of Geochemical Problems Relating to the Burial of High-Level Radioactive Wastes, 1982" 11/85

EXECUTIVE SUMMARY

This report was written at the request of the Nuclear Materials Safety and Safeguards Division of the Nuclear Regulatory Commission. Its purpose is to provide an independent evaluation of geochemical research supporting underground high-level waste disposal. The evaluation aims at identifying future research needs and the priorities under which this research should be carried out. Both the evaluation and the identified research needs are based on the technical criteria proposed in 10 CFR Part 60 (U.S. NRC, 1981).

Geologic waste repositories are presently considered appropriate disposal sites for commercial high-level radioactive waste, either as spent unreprocessed fuel or as reprocessed waste. Some of the most important unanswered questions pertaining to this means of disposal relate to geochemical processes. These questions focus ~~center~~ on the problem of predicting which radionuclides will be contained should they be released from the waste package. However, other questions not directly related to radionuclide migration also require consideration of geochemical processes.

It has long been recognized that predicting radionuclide migration is essential to the design of a safe repository and to the choice of a repository site. The Department of Energy and its predecessors, as well as foreign governments, have sponsored research in this area for a number of years. An extensive body of literature therefore already exists on this and other subjects pertaining to underground waste isolation. Various committees and individuals have produced several review documents, that specify the research needed to resolve issues relating to radioactive waste disposal. However, the broad scope of the technical subjects requiring study has made it difficult until now to devote the time and effort necessary to critically review and prioritize the research needs of each subject.

In this report, an attempt is made to address important issues pertaining to geochemical processes in a waste repository. These issues were identified through review of the available literature by experts familiar with the geochemical aspects of geologic waste repositories. Each issue was examined and evaluated in terms of the state of knowledge concerning the issue and by means of preliminary heuristic calculations and modeling where time and resources permitted. This approach differs from previous assessments of research needs in that the focus of the effort was to resolve the issue rather than determine the current status of research progress. Hence exhaustive reviews of the current literature were deemphasized in favor of identifying the principal hindrances to solution of the problems. However, regardless of whether the issue could be resolved with the resources available, each evaluation nevertheless permits conclusions to be reached and recommendations to be made for further research.

The organization of the report centers on the evaluation of the issues. Chapter 1 is a general introduction. It specifies the approach used in defining the current status of geochemical problems and summarizes the contents of the report. Chapters 2 and 3 contain the discussions of the major issues. Two broad categories are covered in Chapter 2: bounding problems and general problems relating to radionuclide migration through the repository barriers. Chapter 3 covers specific problems relating to the barriers ~~are~~ (subdivided into backfill, near field, and far field). Chapter 4 assembles in summary form the conclusions and recommendations of all issues addressed in the preceding two chapters and assigns priorities to the recommendations. The recommendations are used as the basis for formulating specific projects, which are tabulated in Chapter 4.

Section 2.2 reviews the bounding geochemical conditions and radionuclide compositions. The purpose of these evaluations is to set limits on the scope of subsequent evaluations by restricting them to only those conditions or radionuclides that may reasonably be expected to be relevant to a waste repository. Among the conditions discussed in Section 2.2.1 are pressure, temperature, host rock mineralogy, groundwater composition, and host rock physical parameters such as porosity, permeability, and effective surface area.

Recommendations include further study on the effect of pressure on backfill compaction, investigation of the effect of long-term changes on the chemical and physical properties of backfill and host rocks at temperatures to 300°C, restriction of radionuclide sorption and complexation studies to 175°C, restriction of the study of sorption substrates to specific minerals, investigation of a satisfactory means of characterizing surface area in relation to radionuclide sorption, improvement of groundwater sampling methods, and development of a definitive means of characterizing groundwater oxidation state.

In Section 2.2.2, radionuclide compositions in both spent reactor fuel and reprocessed waste are determined for periods of 10^3, 10^4, 10^5, and 10^6 years after removal from a reactor. It is recommended that an evaluation be made of the specific biological toxicity of several fission product radionuclides and actinide decay chains.

The remainder of Chapter 2 is devoted to the evaluation of issues relating to the transport of radionuclides through repository barriers. These issues form three categories: the forms in which radionuclides are transported (Section 2.3), retardation mechanisms (Section 2.4), and transport models incorporating chemical reactions (Section 2.5).

Radionuclides may be transported as simple ions or molecules dissolved in the groundwater, as complexes, as colloids, as pseudocolloids, or as ions adsorbed on suspended particulate material. The relative importance of these various forms must be established. Furthermore, deficiencies regarding the stability and thermodynamic properties of the various radionuclide species must also be identified. With respect to inorganic complexation, it is recommended that the formation constants be determined for complexes of the most toxic radionuclides with common groundwater liquids, such as OH^-, Cl^-, HCO_3^-, CO_3^{2-}, and F^-. Furthermore, the formation constants of the most important complexes should be determined up to 175°C. Better methods should be developed for correlating and predicting stability constants as a function of temperature.

The complexing of radionuclides with organic ligands may enhance radionuclide migration. It is recommended that migrating organic species be identified and studied. Furthermore, the stability constants, electrochemical data, and chemical characteristics of radionuclide/humic-fulvic acids and related carboxylic acid complexes should be determined for the purpose of future analysis, identification, and assessment of chemical reactions under geological conditions. Finally, the interaction of radionuclide-organic complexes with mineral surfaces should be studied at specific sites.

Colloids, pseudocolloids, and particulates may also cause significant enhancement of radionuclide transport, because they may preferentially concentrate radioelements, diffuse much more slowly, and adsorb less strongly than molecular or ionic species. Investigation of the nature, radiocolloid content, and migration properties of degradation products of high-level waste forms is recommended. Attempts should be made to produce true colloidal forms of insoluble species of important waste radionuclides under simulated repository conditions. It is recommended that the chemical, physical, and mineralogical properties of naturally occurring particulates be investigated. This will entail development of suitable sampling procedures.

A modeling evaluation of the diffusion of uncharged colloidal particles between 10^{-9} and 10^{-6} m in size indicated that such particles would be subject to removal by gravitational settling and physical entrainment on mineral surfaces. It is recommended, however, that models accounting for charged particles be developed in order to assess the magnitude of the effect of charge on colloid transport. Furthermore, the relative importance of colloidal diffusion transport in the overall analysis of radionuclide release and transport through the backfill should be evaluated.

Section 2.4, on mechanisms by which radionuclides might be retarded, opens with a discussion of the solubility constraints on significant fission and actinide decay products. This is an important retardation mechanism because it defines the source term for the release of radionuclides from the waste form. Several long-lived fission and actinide decay products in spent reactor fuel and high-level waste are present in sufficient quantity that their containment in a waste repository is necessary. These include ^{79}Se, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{210}Pb, and ^{226}Ra. These radionuclide elements will form insoluble compounds and solution species with local groundwater constituents. It is recommended that the behavior of selenium in groundwater be investigated and that the most stable oxidation state of technecium in groundwater be established. The relative importance of tin and palladium solution species and their effect on tin and palladium solubility in the natural environment should be determined.

Insoluble compounds and solution species of actinides (i.e., Ac, Th, U, Np, Pu, Am, and Cm) will similarly provide major controls on their groundwater concentrations and migration rates. As with fission products, the identities and solubilities of compounds and solution species will depend on the oxidation state of the system and the amount of complexing ligands present in the groundwater.

Investigation of the solubilities of the trivalent actinide phosphates and carbonates is recommended. Moreover, the formation constants for trivalent and tetravalent actinide carbonates should be measured. Efforts should be directed toward measurement of actinide compound solubilities as a function of temperature to determine whether solubilities decrease with increasing temperature. Hydrolysis constants for tetravalent actinides should be measured. In addition, the importance of UO_2^+ and PuO_2^+ to the solubilities of UO_2 and PO_2 in natural environments should be established experimentally. Finally, a few trivalent and tetravalent actinide silicate solubilities should be measured to assess their importance in limiting radionuclide transport.

Of equal importance to the solubility constraint in retarding the release of radionuclides is radionuclide sorption on mineral substrates. When radionuclide species dissolved in groundwater are transported through the fractures and pores of host rocks, they may adsorb on the surfaces of exposed minerals. Adsorption may be either a reversible equilibrium process or an irreversible nonequilibrium process. Depending on the extent to which adsorption occurs, radionuclides may be retarded either slightly or significantly. This subject is the most extensively studied of all geochemical aspects of nuclear waste isolation, and abundant literature is available.

In order to quantify sorption processes in a repository, chemical conditions in the backfill and near-field host rock should be experimentally determined under conditions of expected loss of canister integrity. Sorption studies should also be expanded to include the full range of anticipated host rock types and secondary minerals. Both theoretical and experimental studies should be extended to 175°C. The results of all such activities should be incorporated in models of chemical interaction and transport in the backfill region.

Although much research has already been undertaken with respect to reversible sorption processes, little attention has been paid to the effect of long-term nonequilibrium water-rock or irreversible radionuclide interactions on radionuclide retardation. These interactions could be important because nearly all water-rock interactions are in a state of disequilibrium. The question whether they seriously affect estimates of radionuclide adsorption based on laboratory measurements must therefore be answered.

It is recommended that a laboratory and theoretical program be conducted to determine the effect of long-term nonequilibrium rock-water reactions on radionuclide retardation. Slow diffusion rates should be quantified using the latest surface analytical techniques, and a mechanistic model should be formulated to extrapolate to long-term conditions. Confirmatory field tests should be conducted, and the chemistry and mineralogy of expected near- and far-field host rocks should be characterized.

Section 2.5 discusses transport models incorporating chemical reactions. Because radionuclide transport may occur over periods of up to 10^5 years or more, direct experimental verification is impractical, and reliance must be placed upon transport models incorporating both radionuclide decay and chemical reaction. The levels of sophistication required of chemical algorithms describing radionuclide transport must be addressed, especially with respect to complex chemical reactions in the near field. Furthermore, an adequate treatment of precipitation, including reversible dissociation, must be incorporated in radionuclide transport models. Finally, if such transport processes are deemed necessary to the understanding of radionuclide migration, transport models must be validated using dynamic column experiments.

Chapter 3 addresses geochemical problems as they relate to specific barriers in a waste repository. These include the backfill, near field, and far field.

Section 3.2 is devoted to the backfill. Because the backfill can be engineered, the materials used and the thickness of the barrier can be varied to suit the conditions of the repository site. An attempt should therefore be made to determine the potential of the backfill to contain given radionuclides. The first subsection concerns the selection and properties of low-permeability backfill materials, such as smectitic clays. It is recommended that the hydraulic conductivity and porosity of specific backfill materials as a function of compaction pressure and chemical saturation state should be defined experimentally. Better estimates are required of parameters related to repository conditions. Hydraulic gradients should be measured under site specific temporal variations in hydraulic, thermal, and chemical gradients. The diffusivities of specific radionuclides should be measured in clays as a function of compaction pressure and electrolyte concentration.

Because the permeability of backfill barriers will be so low that only diffusional processes will be significant, it is worth exploring further how nonsorbing nuclides will diffuse from a nonsorbing barrier in spherical geometry. This was simulated by analytical expressions derived in the course of the present work. As a result, it was determined that the source term must be defined and that data should be acquired on dissolution rates of the waste form, degree of congruity of dissolution, identities of possible solid secondary phases formed in the source region, and identities and concentrations of solute species produced in dissolution and equilibration with secondary phases. The transport properties pertaining to engineered barriers should also be measured, i.e., diffusion coefficients of solute species and tortuosities. If convective transport is included, estimates of barrier dispersivities, porosities, and permeabilities will be required.

Modeling of transport processes through multiple layered media should be undertaken. Further investigation should be made of transport modeling in the temporal domain following disappearance of the source term. Transport modeling should be extended to arrays of waste canisters surrounded by barrier materials. Finally, cross-diffusional coupling and coupling of mass fluxes to thermal fluxes should receive more attention.

Assuming that radionuclides are not retarded through adsorption by a backfill is an extremely conservative approach. It usually shows that backfills would be ineffective unless they are excessively thick. However, since most radionuclides are known to adsorb to greater or lesser extent, it is appropriate that the impact of radionuclide sorption by the backfill should be examined. This was done by use of two simplistic, one-dimensional models differing from each other in the boundary conditions set at the canister interface. It was determined that more realistic models are needed to assess the effectiveness of engineered barriers in reducing the rate of radionuclide migration. Such models should incorporate realistic boundary conditions and modeling of the host rock environment. Fractured media should be considered. The chemical interactions included should adequately predict migration rates. Acceptability criteria should also be developed that do not depend on biosphere dilution. A biosphere relevance factor should be defined and computed for each repository.

There is a remote possibility that fissionable radionuclides contained in a waste repository could concentrate in the backfill and produce a critical mass, thereby leading to a nuclear event. This subject is addressed in Section 3.2.4. It is recommended that further criticality assessments should address the physical or chemical feasibility for the accumulation of fissile isotopes in canisters or adjacent geologic and backfill materials. Such assessments should be compared with analogous natural systems.

Section 3.3 considers ~~of~~ near-field phenomena. The near field is that region bounded by the backfill on one side and by the undisturbed host rock on the other. It encompasses all ground affected by the excavation of the repository and by the heat from the decaying radionuclides. The maximum temperature of the near field may range from about 250°C at the backfill interface to ambient some 1500 feet from the canister, depending on conditions.

The important role of mechanical effects of the repository excavation on the surrounding host rocks must be taken into account in considering the geochemical processes likely to be occur in the near-field region after repository closure. The rates at which such processes occur are influenced by the physical properties of the rock, which are, in turn, affected by the mechanical and thermal stresses caused by repository excavation and waste emplacement. Several aspects of this issue were evaluated. It is recommended that further evaluation should be made of post-repository closure response of host rocks to resaturation, thermal stresses, intrusion of backfill, and backfill overpressures. The introduction of oxygen scavengers in backfills should be considered, particularly in granitic, rhyolitic, tuffaceous, or oxidized sedimentary terranes, where ferrous ion concentrations in host rock minerals are very low. The transient generation of a steam pocket adjacent to the waste canisters should be studied for chemical and physical changes that would adversely affect radionuclide containment. Spalling and chimney formation resulting from compaction of poorly consolidated backfill should be investigated and the consequences of increased groundwater circulation established. Alteration of basalts and granites under hydrothermal conditions expected in a repository should be reviewed in greater depth and expected secondary minerals predicted for given bulk chemical compositions. The mechanism of fracture sealing by secondary minerals in shales should be examined more thoroughly and techniques developed to ensure that such mechanisms might operate in the near field of a repository. Finally, further review and research is required to understand the effects of near-field mineral alteration and geomechanical changes on radionuclide transport.

A problem related to hydrothermal alteration of the near field is the effect of the temperature gradient on the transport of chemical species, which, in turn, affects ~~the affect this will have on~~ the permeability of the host rocks. ¶ However, further research on this subject is not recommended until the detailed thermal history of a repository can be calculated. If thermal gradients and maximum temperatures are large enough to induce geochemical dissolution and precipitation, then mass transport experiments will need to be conducted under simulated thermal conditions using site specific material.

Section 3.4 is devoted to the far field and covers one topic: groundwater dating. Such dating may be used to elucidate the hydrologic behavior of a repository site. Hydrological investigations may provide estimates of the rate of groundwater migration within the repository host rock. However, direct dating of the groundwater could provide an unequivocal independent estimate as a means of verifying the hydrological model.

Groundwater dating should be applied as a site evaluation method, using as many individual techniques as possible. Studies should be conducted to determine whether changes in groundwater chemistry will affect age measurements. Research should continue on the multiple application of several dating techniques to get better evidence of the applicability of each technique. More attention should be paid to groundwater sampling methods and to the size of sample realistically recoverable yet still representative. Sampling quality must be adequate for the most sensitive method. Finally, a new emphasis needs to be placed on research using water-dating techniques to detect low-volume but high-velocity paths through an otherwise slow-moving groundwater system.

Chapter 4 concludes the report by summarizing the conclusions and recommendations of the issues investigated in Chapters 2 and 3. The recommendations emerging from the conclusions and assigned priorities are presented in tabular form. Recommendations include suggestions for further research. Such suggestions are developed into research project outlines. The project outlines could help in developing a coordinated plan for geochemical research, aimed at resolving questions remaining unanswered by this evaluation.