COMPLIANCE DETERMINATION STRATEGY

RRT 3.2.3.2 FAVORABLE CONDITION: GEOCHEMICAL CONDITIONS

APPLICABLE REGULATORY REQUIREMENT(S):

10 CFR 60.21(c)(1)(ii)(B)
10 CFR 60.21(c)(1)(ii)(F)
10 CFR 60.122(b)(3)

TYPES OF REVIEW:

Acceptance Review (Type 1)
Safety Review (Type 3)
Detailed Safety Review Supported by Analysis (Type 4)

RATIONALE FOR TYPES OF REVIEW:

Acceptance Review (Type 1) Rationale:

This regulatory requirement topic is considered to be license application-related because, as specified in the license application content requirements of 10 CFR 60.21(c) and the regulatory guide "Format and Content for the License Application for the High-Level Waste Repository (FCRG)" it must be addressed by the U.S. Department of Energy (DOE) in its license application. Therefore, the staff will conduct an Acceptance Review of the license application for this regulatory requirement topic.

Safety Review (Type 3) Rationale:

This regulatory requirement is considered to be related to containment or waste isolation. It is a requirement for which compliance is necessary to make a safety determination for construction authorization as defined in 10 CFR 60.31(a) (i.e., regulatory requirements in Subparts E, G, H, and I). Therefore, the staff will conduct a Safety Review of the license application to determine compliance with this regulatory requirement.

This regulatory requirement topic focuses on the favorable condition (FAC) that considers geochemical conditions that (1) promote precipitation or sorption of radionuclides; (2) inhibit the formation of particulates, colloids, and inorganic and organic complexes that increase the mobility of radionuclides; or (3) inhibit the transport of radionuclides by particulates, colloids, and complexes. The use of the word "or" in the regulatory requirement topic means that the contribution of geochemical conditions to any one of the three characteristics (1 through 3) would constitute a favorable condition. The effect of geochemical conditions on each of the characteristics must be evaluated, as set forth in 10 CFR 60.122(a).

In order to evaluate information concerning the presence or absence of the favorable condition, the NRC staff had to define the term "geochemical conditions." For regulatory purposes the term is defined as any condition or property in the repository environment that could affect or be affected by the geochemistry or chemistry of the system.

It is noted that a geochemical condition could exist that would inhibit the transport of radionuclides by particulates, colloids, and complexes, even though noncomplexed radionuclides dissolved in the groundwater could migrate unretarded (i.e., no sorption or precipitation) through the system. In this situation DOE could take credit for the presence of a favorable condition.

Various geochemical conditions, singly or in combination, may promote radionuclide precipitation or sorption, inhibit the formation of particulates, colloids or complexes that increase radionuclide mobility, or inhibit the transport of radionuclides by particulates, colloids or complexes. Table 1 contains a list of possible geochemical conditions.

Table 1. Possible geochemical conditions that may promote precipitation or sorption, inhibit the formation of particulates, colloids or complexes that increase radionuclide mobility, or inhibit the transport of radionuclides by particulates, colloids or complexes.

composition/activity	distribution of phases	reactivity (rates)
equilibrium (chemical and physical)	nonequilibrium (supersaturation or undersaturation)	metastability
crystallinity	gradients (chemical and physical)	heterogeneity
steady state	dynamic	open system
closed system	temperature	pressure (isotropic and anisotropic)
volume	mass	density
surface area	viscosity	internal energy
heat capacity	compressibility	interconnectivity
conductivity (electrical and hydraulic)	cation exchange capacity	surface charge

Material properties are included in the list on geochemical conditions, as properties and conditions are considered synonymous. Also, conditions may overlap, such as gradients and heterogeneity or pressure and stress. The emphasis in selecting entries to the table was to identify as many conditions as possible that may affect the geochemistry at Yucca Mountain with little concern for eliminating potentially inappropriate entries. In that way, there was less chance for a condition to be omitted. This list should, however, be considered incomplete as other currently unidentified conditions most likely exist.

The geochemical conditions considered in this regulatory requirement topic are those that have occurred in the past, are occurring now, or may reasonably be expected to occur in the future. Those conditions that have occurred in the past or are occurring now are significant only if they are also expected to exist in the future, for the rule discusses these conditions relative to radionuclide migration, a process limited to the future. However, conditions in the future will not include those that apply to perturbation of the site by the repository, only those that occur naturally.

Some geochemical conditions may have opposite effects on the same characteristic but involving different radionuclides. For example, increasing temperature may favor the sorption or precipitation of some radionuclides while inhibiting the sorption or precipitation of others.

Given the complex nature of this regulatory requirement topic, it is prudent to divide the requirement topic into its parts and describe the rationale for each separately.

Promote radionuclide precipitation or sorption

Reducing conditions are recognized as ones that can promote precipitation for radionuclides with multivalent states, e.g., uranium. Solubilities of certain radionuclides in reducing conditions are often less than those in oxidizing conditions [e.g., uranium (Langmuir, 1978)]. Supersaturation is another condition which when applied to radionuclide-bearing solid phases, promotes radionuclide precipitation. In addition, supersaturation with respect to nonradionuclide-bearing phases can lead to precipitation of those phases, which, in turn, can lead to the coprecipitation of radionuclides as trace components.

Large surface areas and high cation exchange capacities of solids exposed to groundwater containing radionuclides would tend to promote the sorption of radionuclides. Congruently, high hydraulic conductivity in the matrix would contribute to porous medium flow as opposed to fracture flow and result in the exposure of large surface areas possibly capable of sorbing radionuclides.

Inhibit formation of particulates, colloids, and complexes that increase radionuclide mobility

Particulates are solids capable of being moved under certain hydrologic conditions. The maximum size of particulates carried by flowing groundwater depends on the hydrologic conditions. Particles ranging in diameter from 0.24 μm to 4 μm are called "clay." Particles having diameters of 4 to 62 μm are termed "silt" and from 62 μm to 2 mm are "sand." In the slow-flow conditions likely to exist at Yucca Mountain, the particulates must be small to be carried. Large particles settle too fast under gravitational force to be carried great horizontal distances in slow-flowing groundwater. In vertical fractures, however, large particles could move at rates that exceed groundwater flow. Colloids are a subset of particulates in that they are solid particles of very low water solubility ranging in size from 0.001 μm to 1 μm (Stumm and Morgan, 1981). Also, flow through small pores may filter small particles from suspension.

Particulates and colloids have been identified at Yucca Mountain. Water from well J-13 was pumped and sampled: 9300 L were passed through a 0.4 μm filter and 5300 L were passed through a 0.05 μm filter. The concentration of particulate/colloid was 2.7×10^{-5} g/L (Kerrisk, 1987).

Some actinides readily form colloids through the processes of hydrolysis and condensation. Plutonium, for example, forms colloids under conditions expected at Yucca Mountain. These colloids are "solution like sols that are optically clear, show a characteristic absorption spectrum, and do not settle out of solution" (DOE, 1988, p.4-93). Their size is estimated to range from 0.002 to 0.003 μm. Experimental evidence suggests plutonium colloids are not produced under equilibrium conditions but are a result of alpha radiolysis. Other elements known to form radiocolloids are americium, thorium, and praseodymium.

The term "formation of particulates" is assumed to refer to both natural formation of particulates and manmade formation of particulates. Natural formation of particulates can occur as a result of precipitation of solids. For particulates that increase the mobility of radionuclides, these particulates would be either

radionuclide-bearing crystallites or initially nonradionuclide-bearing crystallites to which radionuclides have subsequently sorbed. Particulates also can be formed by weathering processes, both chemical and mechanical. These weathering processes can be naturally occurring or anthropogenic. For example, volcanic glass can chemically alter to form clay particles, or the waste form can undergo spallation during oxidation, or drilling operations and underground facilities construction can produce rock flour.

The formation of particulates is not traditionally simulated in existing geochemistry codes. However, it is possible to model systems with ranges of crystal size (e.g. Stumm and Morgan, 1981). Due to surface energy contributions, small particles are less stable than large particles, as exemplified in Ostwald ripening. It should be possible in the future to modify existing geochemical codes to include algorithms that simulate thermodynamic and kinetic effects of particle size distributions. Key parameters such as mean surface tension and surface-area-dependent rate constants would be required for each phase that could exist as a particle.

Geochemical conditions that would inhibit the formation of particulates by precipitation processes are aqueous solutions with compositions that are undersaturated with respect to the particulate phase and with nucleation reaction rates that are slow. For particulates formed by weathering processes, geochemical conditions that would inhibit particulate formation are aqueous solution compositions that suppress chemical alteration, and reaction rates that are slow.

The term "colloid" refers to both natural colloids such as clay minerals, metal oxides, and microbes or bacteria, and repository-related colloids such as radionuclide-bearing (Pu and Am) waste form alteration products. The lower size limit for colloids is about 1 nm. Smaller sizes are normally indistinguishable from dissolved species. Colloids can be divided into two classifications: lyophilic (strong affinity for solvent) and lyophobic (weak affinity for solvent) depending on the ease with which the system can be redispersed after it has been allowed to dry out (Hunter, 1986). Lyophilic colloids redisperse spontaneously on rewetting whereas lyophobic colloids do not. As an example, montmorillonite will disperse spontaneously in water if its negative charge is neutralized by strongly hydrolyzable cations (e.g., Li^+) but not if the cation is weakly hydrolyzable (e.g., Cs^+) or highly charged (e.g., Ca^{2+}). The wetting and drying conditions of the unsaturated zone may be a significant factor controlling colloid stability.

The processes that lead to the formation of colloids can be described as either dispersion or condensation. Dispersion processes involve mechanical grinding of the material to be dispersed. Condensation processes involve dissolution and reprecipitation. Supersaturation promotes the colloid formation. Chemical reactions such as reduction, oxidation, and double decomposition also can produce colloids. Geochemical conditions that would inhibit the formation of colloids by condensation processes include aqueous solution compositions that are undersaturated with respect to the colloid phase and nucleation reaction rates that are slow. For colloids formed by dispersion processes, geochemical conditions that would inhibit colloid formation include aqueous solution compositions that would promote coagulation. Coagulation is dependent on surface chemistry and geometry of the colloids as well as on pH, ionic strength, and composition of the groundwater. Coagulation, in the absence of interparticle forces, is dependent on the rate of collision of colloid particles due to Brownian motion. The collisions per time increase as temperature increases, viscosity decreases, colloid concentration increases.

Nitsche et al., 1993 observed that "with increasing temperature, the Pu(IV) polymer (colloid) peptizes to become more thermodynamically stable and therefore less soluble; over long times it may possibly convert to crystalline PuO_2 of much lower solubility."

"Colloids are subject to basic forces brought on by their fundamental properties of mass and electrical charge. The property of mass gives rise to the gravitational force and the van der Waals force. The property of charge gives rise to the electrostatic force and indirectly the solvation force. The first two forces cause a colloidal suspension to be unstable, whereas the second two cause it to remain stable" (Sposito, 1989). Gravity tends to pull colloids out of suspension by sedimentation processes. Van der Waals force tends to attract nonpolar molecules to each other when they are brought close together. This attraction results from the induced fluctuation of the dipole moment of one molecule by the fluctuation of the dipole moment of the other. Electrostatic force due to like charges on the surfaces of colloidal particles tends to keep them apart, dispersed and suspended. The solvation force is the strength with which water molecules are associated with exchangeable cations. When exchangeable cations are combined with colloidal particles reducing their surface charge, it is necessary to break the water-cation bonds. Thus solvation force tends to stabilize colloids. The critical coagulation concentration is the smallest concentration of electrolyte at which a colloidal suspension becomes unstable. Thus, high ionic strength solutions tend to destabilize colloidal suspensions.

The formation of colloids is not traditionally simulated in existing geochemistry codes. For example, the database DATA0.COM.R7 for EQ3/6 contains no colloid entries. However, this database does contain thermodynamic information on phases that can exist as colloids if their size is small enough. This information would have to be modified due to increased contribution of surface properties to particle stability.

The methods of characterization of colloids are somewhat limited. From the SCP (DOE, 1988), for example, methods of colloid characterization include separation techniques like filtration and centrifugation and size distribution by autocorrelator photon spectrometry. X-ray diffraction also can be used as exemplified by the characterization of Pu colloid described above. The small concentrations of colloids in the solutions expected at Yucca Mountain make current analytical techniques inappropriate or uncertain. Field techniques to obtain representative samples of natural colloids are also in development, and introduce additional uncertainty.

Existing geochemical computer codes contain algorithms that allow for simulation of organic complexation. These codes are limited by the accuracy and completeness of the databases containing thermodynamic parameters describing the complexes. Generally, the databases are more complete with respect to inorganic as opposed to organic complexes of radioactive waste elements (Serne et al., 1990). For example, the database for EQ3/6, DATA0.COM.R7, contains thermodynamic data for approximately 30 inorganic complexes of plutonium, but no data on organic complexes of plutonium. In fact the only organic complex included in DATA0.COM.R7 is iron acetate. This database is one of the most extensive of existing geochemical codes.

Geochemical conditions that would inhibit the formation of complexes are low concentrations of complexing ligands, and slow reaction rates of complexation.

<u>Inhibit transport of particulates, colloids, and complexes that increase radionuclide mobility</u>

Geochemical conditions that inhibit transport of particulates, colloids, and complexes could include compositions that promote precipitation of various solid phases that might plug flowpaths or reduce flow tube diameters such that particles and colloids are filtered. These conditions might also cause coprecipitation, removing radionuclide-bearing particulates, colloids, and complexes from the flowing groundwater. J. Wan from New Mexico Tech presented her work on the effect of hydrologically

unsaturated conditions on colloid transport at the Yucca Mountain Site Characterization Project Colloid Workshop, May 3-5, 1993. Initial results indicate that hydrophilic colloids are preferentially sorbed at the gas/water interface while hydrophobic colloids sorb at both the gas/water and solid/water interfaces.

Other geochemical conditions might be the distribution of phases including sorptive phases having high cation exchange capacities along flowpaths capable of removing charged particulates, colloids and complexes. High temperature, above the boiling point, can dry out the rock. Without water moving in the liquid phase, particulates, colloids, and complexes of radionuclides cannot move. High density of particulates or colloids contribute to the settling.

Detailed Safety Review Supported by Analyses (Type 4) Rationale:

The staff considers that there may be a high potential risk of noncompliance with the applicable regulatory requirement(s) because, for the Yucca Mountain site, there are several Key Technical Uncertainties.

These Key Technical Uncertainties are considered to require a Type 4 review because there is a high risk of noncompliance with the performance objectives specified below. This concern of high risk of noncompliance will necessitate analysis above and beyond that required for a Type 3 Safety Review in order to assure that the uncertainties and potential effects on performance have been minimized to the extent practical.

Key Technical Uncertainty Topic: Uncertainty in identifying geochemical conditions that would inhibit particulate and colloid formation.

Description of Uncertainty: Different processes could potentially contribute to the formation of particulates and colloids. Particulates and colloids can be produced by precipitation or condensation processes or by weathering or dispersion processes. These phases can be originally composed of radionuclides (termed radiocolloids) as, for example, particles from the spallation of waste form or Pu(IV) colloid. These phases can also be natural or manmade to which radionuclides sorb. When the phase is a colloid to which radionuclides sorb, the phase is often called a pseudocolloid. In addition to the processes described above, other processes not normally considered by geochemists can result in particulate formation. Nitsche et al., 1993 described for americium experiments how steady-state conditions were not attained because the soluble americium formed pseudocolloids together with Teflon particles that were dislodged from the container material by α-radiation. Given the various processes that could contribute to the formation of particulates and colloids, it is uncertain which geochemical conditions would inhibit formation of particulates and colloids that could increase radionuclide mobility.

Performance Objective at Risk:

10 CFR 60.112
10 CFR 60.113(a)(1)(i)(B) and 60.113(a)(1)(ii)(B)

Explanation of Nature of Risk: Numerous processes can lead to the formation of particulates and colloids that could increase radionuclide mobility. The construction of a repository in an unperturbed geologic system such as the unsaturated zone at Yucca Mountain could create significant amounts of particulate material. Many dissolved radionuclides are strongly attracted to solid surfaces. If the solid surfaces to which these radionuclides are attracted are particles moving with groundwater, these radionuclides would not be retarded by sorption processes. Given the uncertainty in identifying the

geochemical conditions that could inhibit the formation of these phases, demonstration of compliance with 10 CFR 60.113(a)(1)(i)(B), 10 CFR 60.113(a)(1)(ii)(B), and 10 CFR 60.112 may be at risk.

Description of Resolution Difficulty: Geochemical modelling efforts traditionally do not include consideration of particulates and colloids. Evidence for this omission is indicated by the limitations of current geochemical computer codes (e.g., EQ3/6). They do not have the capability to simulate the formation of particulates and colloids. Furthermore, the databases associated with these geochemical codes do not contain information on particulates and colloids. As phases get smaller the contribution of surface interactions to the overall energetics of the system studied becomes more important. The science of surface interactions and characterizations is still in its infancy. Lacking thermodynamic and kinetic data on these phases, the geochemist is hard pressed to predict their effect on performance of the repository. Existing codes will have to be modified to take into account the effect of surface tension on the stability of small particles. It may be possible to include surface complexation models to describe the surface charge of colloids and particulates. Surface charge helps stabilize the small particles, keeping them dispersed through electrostatic repulsion. Furthermore, different size particles settle at different rates. If coupled flow and transport modeling is attempted, consideration of particle size on diffusivity and rate of gravitational settling at various flow rates would be required. Experimental data will have to be collected on the surface tension of phases expected at the repository site.

The number of combinations of processes, components, and conditions is so great at Yucca Mountain as to make it unlikely that all will be considered in detail prior to submittal of a License Application. In order to minimize the number of possible combinations of processes, components and conditions expected at Yucca Mountain, but not evaluated by DOE, the NRC staff and CNWRA personnel will need to continue geochemical modelling exercises in efforts such as iterative performance assessment and auxiliary analyses utilizing existing and modified computer codes.

Key Technical Uncertainty Topic: Uncertainty in characterizing the chemistry of the groundwater in the partially-saturated hydrologic zone of Yucca Mountain, Nevada.

Description of Uncertainty: Little information is available on the groundwater chemistry for the hydrologically partially-saturated zone of Yucca Mountain, Nevada. Although some efforts to extract aqueous solutions by triaxial compression ('high pressure') of rock samples taken from the partially-saturated zone of Yucca Mountain are underway (e.g., Yang et al, 1988; Peters et al., 1992), there are large variabilities in the chemical compositions of solutions derived using this technique. Aqueous samples have also been extracted from partially-saturated soils and sands by ultracentrifugation techniques (e.g., Edmunds et al., 1992; Puchelt and Bergfeldt, 1992). It is uncertain whether compositions of water extracted from rock pores by ultracentrifugation or by high-pressure 'squeezing' techniques accurately represent the compositions of *in situ* water. The compositions of *in situ* water extracted in these manners are likely to be different due to several possible processes (Peters et al., 1992): 1) dilution of pore solutions by water desorbed from hydrated minerals like zeolites and clays; 2) dissolution reactions due to increased mineral solubility and/or higher carbon dioxide concentration at higher pressures; 3) membrane filtration by clays and zeolites; and 4) ion exchange with the zeolites and clays. In addition, colloids which may be present in pore waters are likely to be altered, destabilized, or filtered out of solution during the extraction process. No method is currently known to give unambiguous, accurate data on the chemistry of pore waters in partially-saturated crystalline rock.

Performance Objective at Risk:

10 CFR 60.112
10 CFR 60.113(a)(1)(i)(B) and 60.113(a)(1)(ii)(B)

Explanation of Nature of Risk: Geochemical processes such as radionuclide precipitation, sorption, and complexation, as well as formation of colloids, are strongly influenced by groundwater chemistry (e.g., pH, ionic strength, solute composition and concentration). For example, experimental data for various types of sorbents indicate that uranium sorption is strongly dependent on pH (Tripathi, 1984; Payne et al., 1992; Pabalan et al., 1993). The presence of complex-forming species reduces the amount of radionuclide sorbed on mineral surfaces; this represents an unfavorable geochemical condition. The presence of colloids, which may enhance transport of radionuclides, is also a potentially unfavorable condition. Therefore, without knowledge of the groundwater chemistry in the partially-saturated zone, including the presence and characteristics of colloids and particulates, it is not possible to determine whether geochemical conditions present at the proposed repository are favorable or unfavorable to inhibition of radionuclide migration.

Description of Resolution Difficulty: No technique is known that provides unambiguous, accurate measurements of the chemistry of pore waters in partially-saturated media. The methods of extracting pore waters by high-pressure compression and by ultracentrifugation most likely impose some change in solution composition and are susceptible to contamination problems. *In situ* methods, such as low-vacuum electron microscopy and X-ray analysis, do not yet have the resolution to quantitatively measure solute concentrations in relatively dilute groundwater and remain to be tested for analyzing pore water chemistry in unsaturated media. Moreover, solution pH, which is a key parameter that controls radionuclide precipitation, sorption and complexation, cannot be determined by *in situ* methods, and the pH of extracted pore water is likely different from that of *in situ* pore water. The chemistry of the groundwaters in the partially-saturated zone of Yucca Mountain are therefore extremely uncertain. One way of testing techniques of extracting and analyzing pore water chemistry from partially saturated rock is to apply these techniques to rocks containing minerals and groundwater whose equilibrium interactions can be modelled using existing codes. For example, a rock containing the zeolite used in the ion exchange experiments by Pabalan (1991) could be partially saturated with a water of known composition, allowed to equilibrate, and then treated in the extraction and analytical methods proposed by DOE. The results of the analysis could then be compared with the calculated composition. This possible method of resolution would require a collaborative effort between CNWRA personnel and investigators from the USGS.

Key Technical Uncertainty Topic: Understanding the effects of degree of saturation on geochemical processes such as radionuclide sorption and precipitation and formation of particulates and colloids, and on the transport of radionuclides by particulates, colloids and complexes.

Description of Uncertainty: The proposed repository is located in a hydrologically partially-saturated horizon underneath Yucca Mountain. However, it is uncertain on how the degree of hydrologic saturation will affect sorption, precipitation, colloid formation, and transport of radionuclides by particulates, colloids and complexes. All batch sorption experiments and most column sorption studies are conducted under conditions where the sorbing medium is fully-saturated with water. It is not known if radionuclide sorption coefficients determined using fully-saturated experiments can be extrapolated to conditions of variable saturation. It is not clear whether undersaturated conditions will inhibit radionuclide migration more than fully-saturated conditions, or whether it can actually enhance migration of certain

radionuclides. It is not known what the effect of degree of saturation is on the formation of particulates and colloids, and on the transport of radionuclides by particulates, colloids, and complexes.

J. Wan from New Mexico Tech presented her work on the effect of hydrologically unsaturated conditions on colloid transport at the Yucca Mountain Site Characterization Project Colloid Workshop, May 3-5, 1993. Hydrophilic colloids are preferentially sorbed at the gas/water interface while hydrophobic colloids sorb at both the gas/water and solid/water interfaces.

Performance Objective at Risk:

10 CFR 60.112
10 CFR 60.113(a)(1)(i)(B) and 60.113(a)(1)(ii)(B)

Explanation of Nature of Risk: Current approaches to modeling radionuclide retardation and transport in partially-saturated media treat chemical interactions (e.g., sorption) in a way identical to that of fully-saturated rock, except for modifying the effective porosity. However, it is uncertain if radionuclide sorption coefficients determined using fully-saturated experiments can be extrapolated to conditions of variable saturation. Certain conditions may exist where partially-saturated conditions enhance migration of radionuclides compared to fully-saturated conditions. For example, at lower saturation the amount of solid surface-area in contact with the liquid phase may be reduced, thus diminishing sorption as a retardation mechanism for radionuclide transport. Therefore, it is uncertain whether the geochemical conditions in the partially-saturated zone of Yucca Mountain are favorable or unfavorable for inhibition of radionuclide transport.

Description of Resolution Difficulty: It is not clear whether partially-saturated experiments will allow one to resolve the effects of sorption processes from the effects of medium heterogeneities and complex fluid flow systematics (Turner, 1991). For reactive solutes, e.g., uranium, plutonium and neptunium, their aqueous chemistries are complex due to hydrolysis and complexation reactions and oxidation state changes, which in turn strongly affect sorption, precipitation, and colloid formation. It is not known how synergistic effects of different parameters, as well as complications due to kinetic effects, can be resolved by partially-saturated experiments.

The number of combinations of processes, components, and conditions is so great at Yucca Mountain as to make it unlikely that all will be considered in detail prior to submittal of a License Application. In order to minimize the number of possible combinations of processes, components and conditions expected at Yucca Mountain, but not evaluated by DOE, the NRC staff and CNWRA personnel will need to continue geochemical modelling exercises in efforts such as iterative performance assessment and auxiliary analyses utilizing existing and modified computer codes.

Key Technical Uncertainty Topic: Parametric representation of retardation processes involving radionuclide-bearing particulates, colloids, and complexes.

Description of Uncertainty: Performance assessment calculations typically use a single retardation factor (R_f) to represent the attenuation of radionuclide transport. This factor is frequently based on an experimentally measured sorption coefficient (K_d), which is assumed to represent equilibrium sorption/desorption processes alone. However, other processes may contribute to retardation, including diffusion, dispersion, and precipitation. Although using R_f simplifies transport calculations, it is empirical in nature and has no theoretical basis for extrapolation beyond the particular conditions of the initial

experiments. It is well-known that sorption of radionuclides on rock and mineral substrates is influenced by the physical and chemical characteristics of the groundwater (e.g., pH, composition, temperature) and of the substrate (e.g., mineralogy, surface area, surface properties). R_f (K_d) tends to be assigned as a "property" of the medium. This does not accurately reflect the role of systematic chemical variations in determining the extent of retardation of radionuclide migration. The use of R_f also does not allow discrimination between the contributions of various processes involved in retardation. Therefore, it is not clear how quantitative representation of retardation processes can be done.

Performance Objective at Risk:

10 CFR 60.112
10 CFR 60.113(a)(1)(i)(B) and 60.113(a)(1)(ii)(B)

Explanation of Nature of Risk: The geochemical characteristics of the groundwater and the rocks/minerals will likely vary along the flow-paths from the repository to the accessible environment. Sorption reactions and other processes such as diffusion, dispersion and precipitation/dissolution are dependent on those characteristics. Parameters that are used to represent retardation processes in performance assessment calculations must allow accurate extrapolation to varying geochemical conditions. At present it is not known how this can be done. Thus it is not clear how to determine whether favorable geochemical conditions exist for inhibiting radionuclide transport.

Description of Resolution Difficulty: There are many physical and chemical parameters that affect retardation processes, many of which have synergistic effects. Simple representations of sorption and retardation, such as K_d and R_f, do not allow extrapolation to conditions other than those of the initial experiment. More robust models, such as surface-complexation models, require more parameters. The latter represents state-of-the-art, but model parameters are available for only a few radionuclides and a few sorbents. Surface-complexation approaches are also not currently applied to modeling transport of particulates and colloids.

The number of combinations of processes, components, and conditions is so great at Yucca Mountain as to make it unlikely that all will be considered in detail prior to submittal of a License Application. In order to minimize the number of possible combinations of processes, components and conditions expected at Yucca Mountain, but not evaluated by DOE, the NRC staff and CNWRA personnel will need to continue geochemical modelling exercises in efforts such as iterative performance assessment and auxiliary analyses utilizing existing and modified computer codes.

Summary: The following assumptions have been made in assigning Type 4 level of review to this CDS:

(1) All probable combinations of geochemical conditions that could inhibit the formation of particulates and colloids can not be identified because of the intrinsic complexity of the systems.

(2) The quantitative determination of radionuclide-bearing particulate and colloid formation can not be accomplished for all chemical conditions expected at Yucca Mountain because of the intrinsic complexity of the systems.

REVIEW STRATEGY:

Acceptance Review:

In conducting the Acceptance Review of favorable conditions related to geochemical conditions which favor inhibition of radionuclide migration, i.e., those that (1) promote precipitation or sorption of radionuclides; (2) inhibit the formation of particulates, colloids, and inorganic and organic complexes that increase the mobility of radionuclides; or (3) inhibit the transport of radionuclides by particulates, colloids, and complexes, the reviewer should determine if the information present in the license application and its references for determining compliance with the applicable regulatory requirements in the regulatory guide, Format and Content Regulatory Guide (FCRG), is complete in technical breadth and depth as identified in the FCRG. The reviewer should determine that all appropriate information necessary for the staff to review the favorable geochemical conditions is presented such that the assessments required by the regulatory requirement(s) associated with total system and subsystem performance objectives or other technical criteria can be performed.

The information contained in the license application should be presented in such a way that the assumptions, data, and logic lead to a clear demonstration of compliance with the requirement. The reviewer should not be required to conduct extensive analyses or literature searches. The reviewer should also determine whether an appropriate range of alternative interpretations and models has been described.

Finally, the reviewer should determine if the U.S. Department of Energy (DOE) has either resolved all the NRC staff objections that apply to this requirement or provided all the information requested in Section 1.6.2 of the FCRG, for unresolved objections. The reviewer should evaluate the effects of any unresolved objections, both individually and in combinations with others, on: (1) the reviewer's ability to conduct a meaningful and timely review; and (2) the Commission's ability to make a decision regarding construction authorization within the three-year statutory period.

Safety Review:

This regulatory requirement is limited to consideration of favorable conditions related to geochemical conditions that (1) promote precipitation or sorption of radionuclides; (2) inhibit the formation of particulates, colloids, and inorganic and organic complexes that increase the mobility of radionuclides; or (3) inhibit the transport of radionuclides by particulates, colloids, and complexes. It is not concerned with potentially adverse conditions relating to groundwater conditions in the host rock, including chemical composition, high ionic strength or ranges of Eh-pH, that could increase the solubility or chemical reactivity of the engineered barrier system. These topics will be covered separately in Section 3.2.3.4 "Groundwater Conditions and the Engineered Barrier System" of the License Application. It is also not concerned with potentially adverse conditions relating to geochemical processes that would reduce sorption of radionuclides, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system. These will also be covered separately in Section 3.2.3.5 "Geochemical Processes" of the License Application.

Following the Acceptance Review, the first step will be to evaluate DOE's analyses to determine if the following basic assumptions are correct:

(1) All probable combinations of geochemical conditions that could inhibit the formation of particulates and colloids have not been identified.

(2) The quantitative determination of radionuclide-bearing particulate and colloid formation has not been accomplished for all chemical conditions expected at Yucca Mountain because of the intrinsic complexity of the systems.

If the above assumptions are met, the staff will follow the review strategy described here. If these assumptions are not met, the staff's review may require a different review strategy for evaluating DOE's demonstration of compliance with the applicable regulatory requirements. It is expected, however, that any deviation from these assumptions will be known well in advance of the time a license application is submitted, and this strategy shall be revised in accordance with such new information as it becomes available to the staff.

In conducting the Safety Review, the reviewer will, at a minimum, determine the adequacy of the data and analyses presented in the license application to support DOE's demonstration of compliance with this regulatory requirement. Specifically, DOE will need to: (1) provide information to determine whether, and to what degree, this favorable geochemical condition is; (2) assure the sufficiency of the lateral and vertical extent of the data collection; and (3) evaluate the information presented under item (1) above using assumptions and analysis methods that adequately describe the presence of favorable geochemical conditions and ranges of relevant parameters. The specific aspects of the license application on which the reviewer will focus are discussed below, and the Acceptance Criteria will be identified in Section 3.0 of this Review Plan.

In conducting the Safety Review, the staff should confirm that DOE has submitted the following: (1) information regarding geochemical conditions that would promote precipitation or sorption of radionuclides, (2) information on geochemical conditions that inhibit formation of particulates, colloids, or complexes that could increase radionuclide mobility, and (3) information on geochemical conditions that inhibit the transport of radionuclides by particulates, colloids, or complexes. This information is expected to include adequate data concerning hydrology and geology to allow assessment of relevant geochemical conditions.

DOE will also need to explain how models are supported that are used to assess the presence or absence of the favorable condition. Analyses and models that will be used to predict future conditions and changes in the geologic setting shall be supported by an appropriate combination of methods such as field tests, laboratory tests that are representative of field conditions, monitoring data, and natural analog studies. For purposes of determining the presence or absence of the favorable condition, investigations should extend from the ground surface to a depth sufficient to determine critical pathways for radionuclide migration from the underground facility. Investigations should be sufficient to demonstrate a suitable understanding of effect of geochemical conditions on radionuclide precipitation or sorption, on formation of particulates, colloids and complexes, and on transport of particulates, colloids, and complexes such that reasonable bounds can be placed on the different conceptual models.

In conducting the aforementioned evaluations, the reviewer should determine that DOE uses: (1) analyses that are sensitive to evidence of the Favorable condition; and (2) assumptions that are not likely to underestimate its effects. In general, the reviewer should assess the adequacy of DOE's investigations of favorable geochemical conditions, both within the controlled area and outside the controlled area, as necessary, in the manner defined in 10 CFR 60.21(c)(1)(ii)(B).

Reviewers will rely on staff expertise and independently acquired knowledge, information, and data such as the results of research activities being conducted by the NRC's Office of Nuclear Regulatory Research,

in addition to that provided by the DOE in its license application. The reviewer should focus on additional data which can refine knowledge of the favorable geochemical conditions for inhibition of radionuclide transport, and should perform, as necessary, additional analyses to confirm the resolution capabilities of the methodologies. The reviewer must have access to a body of knowledge regarding these and other critical considerations in anticipation of conducting the review to assure that DOE investigations to resolve the presence or absence of the favorable geochemical conditions that promote precipitation and sorption, inhibit formation of particulates, colloids or complexes, and inhibit the transport of radionuclides by particulates, colloids, and complexes are sufficient in scope and depth to provide the information to resolve the concerns. Research undertaken in the CNWRA Geochemistry, Sorption, Engineered Barrier System, and Geochemical Natural Analogs research projects is expected to provide data relevant to the assessment of information regarding favorable geochemical conditions that promote precipitation and sorption, inhibit formation of particulates, colloids or complexes, and inhibit the transport of radionuclides by particulates, colloids, and complexes. For example, published data including those generated for NRC by the CNWRA (e.g., Pabalan et al., 1993) demonstrate that uranium sorption on minerals depends on solution pH and solute concentration.

Finally, investigations in the following DOE site characterization program study plans are expected to produce data and analyses needed to help in the review described above to address the presence or absence of this favorable condition:

STUDY PLAN NO.	TITLES
8.3.1.2.2.7	Hydrochemical Characterization of the Unsaturated Zone (DOE, 1990a)
8.3.1.2.3.2	Characterization of the Yucca Mountain Saturated-Zone Hydrochemistry (DOE, 1992d)
8.3.1.3.2.1	Mineralogy, Petrology, and Chemistry of Transport Pathways
8.3.1.3.2.2	History of Mineralogic and Geochemical Alteration of Yucca Mountain (DOE, 1992b)
8.3.1.3.3.4	Conceptual Model of Mineral Evolution (in preparation)
8.3.1.3.4.1	Batch Sorption Studies
8.3.1.3.4.2	Biological Sorption and Transport (DOE, 1993)
8.3.1.3.5.2	Colloid Behavior
8.3.1.3.6.1	Dynamic Transport Column Experiments
8.3.1.3.7.1	Retardation Sensitivity Analysis (DOE, 1992)
8.3.1.5.1.4	Analysis of the Paleoenvironmental History of the Yucca Mountain Region (DOE, 1991e)
8.3.1.5.1.5	Paleoclimate-Paleoenvironmental Synthesis (in preparation)
8.3.1.5.2.1	Characterization of the Quaternary Regional Hydrology (DOE, 1992g)

Reports presenting the results from additional study plans related to this favorable condition, when available, should also be reviewed.

Detailed Safety Review Supported by Analysis:

A Detailed Safety Review and Analysis will be needed for evaluation of the following Key Technical Uncertainties: (1) ability to identify geochemical conditions that would inhibit formation of particulates and colloids; (2) chemistry of the groundwater in the partially-saturated hydrologic zone of Yucca Mountain, Nevada; (3) effects of degree of saturation on geochemical processes such as radionuclide

sorption and precipitation and formation of colloids, and on the transport of radionuclides by particulates, colloids, and complexes; and (4) parametric representation of retardation processes involving particulates and colloids. This will ensure that DOE has adequately demonstrated Items (1)-(3), listed in the previous section (see Section 2.2.1 "Safety Review," paragraph 2). Activities performed in the Detailed Safety Review will help to assure that DOE has adequately addressed and resolved these Key Technical Uncertainties so that they do not lead to noncompliance with the total system performance objective and the subsystem performance objective concerning the engineered barrier system.

For the Key Technical Uncertainty regarding the ability to identify geochemical conditions that would inhibit the formation of particulates and colloids that increase radionuclide mobility, examples of specific review activities that may be required include: (1) review and analysis of geochemical conditions that inhibit processes of particulate and colloid formation; (2) modification or coupling of existing codes to simulate effects of particle size on equilibrium thermodynamics and kinetics of pertinent reactions; (3) evaluation of stability of particulate and colloid phases once formed, (4) review of methods for characterization of particulates and colloids, and (5) comparison of natural analogues of colloid and particulate formation to conditions expected at Yucca Mountain. It may also be appropriate to assess the quality and traceability of data and information by utilizing staff with expertise in review of quality assurance programs.

For the Key Technical Uncertainty regarding groundwater chemistry in the partially-saturated hydrologic zone of Yucca Mountain, examples of specific review activities that will be required include: (1) review and analysis of measured chemistry of groundwaters from the site; (2) evaluation of uncertainties in the reported analytical data; and (3) determination of the potential implications of the reported groundwater chemistry for inhibition of radionuclide transport. This review will require familiarity with analytical chemistry and error propagation methods. The use of equilibrium geochemical codes such as EQ3 will be used to evaluate the analytical data on groundwater chemistry. To help determine the potential implications of the reported groundwater chemistry to inhibition of radionuclide transport, other codes such as MINTEQA2 (Allison et al., 1991) may be used. It may also be appropriate to assess the quality and traceability of data and information by utilizing staff with expertise in review of quality assurance programs.

For the Key Technical Uncertainty concerning the effects of degree of saturation on geochemical processes, examples of specific review activities that will be required include: (1) review and analysis of experiments which were conducted under partially-saturated hydrologic conditions and which studied geochemical processes such as radionuclide sorption, precipitation, colloid formation, and transport of radionuclides by particulates, colloids, and complexes; (2) review and analysis of models used to describe the above geochemical processes for partially-saturated porous media; and (3) determination of whether partially-saturated hydrologic conditions will inhibit, enhance, or not affect radionuclide migration compared to fully-saturated conditions. This determination may have to be conducted for each important radionuclide because different radionuclides may have different chemical properties and, therefore, different sorption and transport behavior. It may also be appropriate to assess the quality and traceability of data and information by utilizing staff with expertise in review of quality assurance programs.

For the Key Technical Uncertainty concerning parametric representation of retardation processes, examples of specific review activities that will be required include: (1) review and analysis of models used to represent retardation processes in radionuclide transport calculations, including the assumptions and uncertainties associated with the models; and (2) evaluation of the experimental, field, or natural analog data that were used to validate the models and to demonstrate their capability to predict

radionuclide retardation and transport under varying geochemical conditions. The NRC staff will need to independently model radionuclide retardation and transport using codes and models developed by DOE or by CNWRA for the NRC Office of Nuclear Regulatory Research. Published experimental, field, or natural analog data, including those generated for NRC by CNWRA, will be used to validate and test the predictive capability of the models. Sensitivity analyses will need to be performed to evaluate the statistical reasonableness of model parameters. It may also be appropriate to assess the quality and traceability of data and information by utilizing staff with expertise in review of quality assurance programs.

RATIONALE FOR REVIEW STRATEGY:

In view of the complexity of the key technical uncertainties addressed above, it is appropriate that the NRC conduct the independent activities described in order to (1) develop the licensing tools and technical basis necessary to judge the adequacy of DOE's license application, (2) assure sufficient independent understanding of the basic physical processes taking place at the geologic repository, and (3) maintain an independent but limited confirmatory research capability under NRC auspices.

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Date of Analysis: August 13, 1993

APPLICABLE REGULATORY REQUIREMENTS FOR EACH TYPE OF REVIEW:

Type 1:

10 CFR 60.21(c)(1)(ii)(B)
10 CFR 60.21(c)(1)(ii)(F)
10 CFR 60.122(b)(3)

Type 3:

10 CFR 60.122(b)(3)

Type 4:

10 CFR 60.122(b)(3)

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