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**CHEMICAL AND MINERALOGICAL CONCERNS
FOR THE USE OF MAN-MADE MATERIALS
IN THE POST-EMPLACEMENT ENVIRONMENT**

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CHEMICAL AND MINERALOGICAL CONCERNS FOR THE USE OF MAN-MADE MATERIALS IN THE POST-EMPLACEMENT ENVIRONMENT

INTRODUCTION

In a radioactive waste repository, materials will be introduced for a variety of reasons. Some materials such as metals, bonding agents, and concrete will serve as active parts of the designed engineered barrier system (EBS). Other materials will be introduced to serve a number of purposes that include any or all of the following: surveillance (thermocouples, gauges), construction and operation (drilling rigs, roadbeds, exhaust fumes, chemical toilets, concrete, grout, rebar), lubrication (petroleum-based products, rope dressing) and other functions. Some materials will be present as waste. The materials may also be present during a relatively short time (during construction and testing), or stay permanently in the near-field environment. Compounds which could be introduced can be classified into broad categories depending on their physical state (solid, liquid, gas), chemical reactivity (soluble, insoluble), as well as reactivity with the rock and whether the compounds are organic or inorganic. Some of the compounds that need to be considered are:

- insoluble metals (stainless steel): these include measurement devices and electrical accessories
- insoluble organic solids (neoprene, plastic): these include packing and rubber
- soluble inorganic solids (LiBr, LiCl, NaBr): tracers
- inorganic liquid (water with tracers)
- miscible organic liquids (ethylene-glycol): these include antifreeze and fluorescein dye
- immiscible organic liquids (petroleum based oils): these include brake fluids, lubricants, oils, paints, grease and fuels
- organic gases: H_2 , N_2 , O_2 , CO , CO_2 , C_2H_2

Water chemistry will directly affect the corrosion of containers, the dissolution of spent fuel and waste glass and the concentration of dissolved or suspended radionuclides in water that exits breached containers. To predict the water quality requires a knowledge of the dissolution kinetics of the phases present in man-made materials, and the precipitation kinetics of product phases. The chemical evolution of man-made materials of interest to the Yucca Mountain project are by and large not presently known. Prediction of the long-term behavior (10,000 years) required of our modeling efforts is an additional layer of complexity that is not addressed by current models of water chemistry. It is known that the variation of the repository environment through time will be complex. Computer modeling of the thermal behavior of the waste package near-field environment has demonstrated that there will be a rapid increase in temperature immediately after package emplacement (O'Neal et al., 1984) to an estimated maximum of 230°C, depending on the repository design. As a consequence, a dehydration zone is expected to develop around the waste package as water vaporizes in the vicinity of the waste packages. The duration and extent of the dehydration zone will be a complex function of the local and areal power density, and the thermal properties of the rock. The near-field environment may rehydrate as the rock cools. For some scenarios under unanticipated conditions, saturation of the waste package host rock may occur. Chemical reactions under saturated conditions may differ in magnitude and nature from those that might occur under unsaturated conditions. This effort involves not only long term data on each material in the repository that participates in complex chemical reactions due to thermal and radiation affects, but also an accurate accounting of the stability of each material as the conditions in the repository change through time.

Man-made modifications to the environment may significantly alter the thermal, chemical and radionuclide transportation attributes of the natural environment that are presently being considered in order to determine a waste package design. These alterations may compromise the lifetime of the waste packages, or affect the transport of radionuclides from breached containers. Adequate chemical data

are thus a major requirement for the development of the predictive geochemical, hydrological and mechanical models of the waste package environment that will be used as input to a waste package design and performance assessment. The man made materials task activities are intended to satisfy the requirements for chemical data regarding man-made materials as they relate to the water quality and water quantity that may contact waste containers for specific environmental scenarios. The evolution of secondary phases that will result from interaction, possibly at elevated temperatures, between tuff, water, water vapor, radiation, and waste package and introduced materials are included in this evaluation. Without this data we must rely on our best judgment based on incomplete published work and data collected for the International Program. Unfortunately, most of these data sets represent specific groups of materials rather than reactions between groups of materials, which may drastically alter the chemical environment. At present the quantity, location and identity of man-made materials to be used at the proposed waste repository site is unknown. Therefore it is impossible to determine whether potential detrimental modifications of the environment will be produced by man-made materials.

SPECIFIC CHEMICAL CONCERNS

Man-made materials are, by definition, modified from their natural forms and therefore unstable. Materials could modify the water chemistry through the contribution of organic compounds, alkali metals, or halogen elements to solution, or through the formation of silicon compounds or through the modification of pH or Eh. The extent to which a reaction can modify the water chemistry will depend on a variety of parameters that include temperature, composition, the rate of thermal fluctuation, and the quantity and character of radiolysis products. Gradients in water chemistry can also drive chemical reactions. These gradients may exist because the concentration of man-made materials at specific sites within the repository and the relative man-made modifications of the repository as a whole, change the local pH and temperature significantly.

A wide range of materials, about which we have little information, may be present in the repository. This includes thermal stability of materials that are well characterized at room temperature but are not well characterized at the 200° to 250°C temperatures and in the chemical microenvironments that will be experienced in the repository. Concretes will possibly be present in large volumes (thousands of cu. ft.), with the capability of changing the pH of water to values as high as 11.5 at 100°C. The oxidation of metals, such as iron, if present in large volumes, could consume large quantities of oxygen and influence the atmosphere around waste containers. In addition, hydrocarbons that may be present from diverse sources such as vehicle exhaust, rubber abrasion, and paint and epoxy fumes, have the potential for generating ligands that may enhance radionuclide transport. And finally, organics and microbial activity may alter chemical reactions, increase reaction rates and promote the formation of colloids.

Man-made materials can alter predicted natural chemical reactions. The extent to which chemical reactions proceed will depend upon rates of material dissolution, precipitation, and diffusion. These rates are, in turn, influenced by temperature, the degree of water saturation, composition, and the ratio of material surface area to fluid volume. Possible product phases include oxidized metals, sulfides, chlorides, carbonates and silicates. Some products, especially of the interactions between organic compounds and other chemical species, are unknown. Of the known products, some are known to be chemically aggressive. For example, borehole liner corrosion products, which include oxides, hydroxides and chlorides, have the potential to alter the pH, ionic strength, and elemental composition of water that enters and exits breached containers. Kinetics data are unavailable over a broad pH and temperature range for many of these phases and must, therefore, be obtained through laboratory study and the study of historical analogs. The potential moderation of those effects by natural zeolites in rock adjacent to the repository environment must also be evaluated.

Solubility and Stability of Solid Phases

Repository materials such as concrete, grout, other construction materials, metal containers, and possibly borehole liners, are expected to age, react chemically with water and humid air, and to disintegrate or corrode during the life time of the repository. It is likely that the disintegration of these materials will modify the chemistry of water that may be present at some time in the vicinity of the waste packages. The stability of the constituent phases of solid man-made materials such as metal, resin, paint and concrete, over the range of temperatures, ionic strengths, pH and surface areas that bracket anticipated and selected unanticipated repository conditions are unknown. For example, concrete, cured nine years at ambient conditions may continue to undergo volumetric changes. Such relatively short-term aging and disintegration effects in the concrete must result from mineralogical changes, but they have not been described. The disintegration of concrete, grout, and other construction materials in the presence of water may produce an aggressive chemical environment, and may exceed the expected boundary conditions to water pH (as measured, for example in studies conducted for the Reference Waste Package Environment report (Glassley, 1986)).

Similar aging of other man-made materials remain unknown or uncharacterized for virtually all materials of concern. Even relatively well studied materials such as metals (Lucey, 1971; Mor and Beccaria, 1975; Hedges, 1976; Scott, 1985; Pollard et al., 1989; McNeil et al., 1990) remain poorly understood. As a result, the near-field environment may encompass conditions that are outside the bounds presently under consideration. Some of these conditions may be aggressive and influence container performance, waste form dissolution rate, and radionuclide concentrations in solution. The bare minimum of data required includes behavior under water saturated conditions, ($T < 95^{\circ}\text{C}$) and in the presence of a water vapor ($T > 100^{\circ}\text{C}$). Stoichiometric and non-stoichiometric dissolution and saturated and unsaturated environments need to be addressed. In summary, information about the long term degradation of materials is incomplete and about interactions between the very diverse potential chemical influences of introduced materials is almost completely nonexistent. Therefore, to guess chemical consequences or trends for the introduction of any materials to the repository at this time would not only be injudicious but also misleading.

Liquid and Gas Phase Stability

The stability of fluids and gases that may be present in the repository (e.g. oils, greases, exhaust and solvent fumes) at elevated temperatures over long periods of time are poorly known. Preliminary investigations to determine high temperature and pressure phase relationships within a selected group of organic liquids have demonstrated that these liquids are not stable and can break down to more aggressive components. The example below is taken from experiments conducted for chemical waste remediation purposes. However, it demonstrates the potential for catastrophic results of combining two materials which, by themselves, are known to be relatively benign at high temperatures.

Preliminary experiments were conducted using a typical cutting/tapping fluid based on a chlorinated hydrocarbon solvent. In this case the composition was:

1,1,1-trichloroethane (TCA)	76%
1,4-dioxane	16.3%
dichloromethane	4.2%
1,2-epoxy ethane	3.5%

A 5:1 mixture (distilled water : cutting fluid, by weight) was heated in the Dickson bombs to 150°C and 200°C . The Dickson bombs were expected to be suitable for these experiments, because the Au and Ti parts are relatively nonreactive. The Ti is thoroughly passivated (converted to TiO_2) and, even

in relatively reducing environments (e.g., hydrous pyrolysis of a kerogen-rich oil shale that produced significant amounts of organics and H_2S) it performs well in HCl. Presumably, this is due to the thick rind of rutile (TiO_2) formed over the Ti metal.

No prior experimental results for water and cutting fluids were available from the literature. This much was known. Cutting fluids usually are one of two general formulations. One comprises a mixture of mineral oil (short to medium length alkanes - distillates of petroleum), waxy compounds (longer length alkanes) and fatty acids (aliphatic carboxylic acids). The other consists predominantly of one or more chlorinated-hydrocarbons plus other hydrocarbons. In order to model the chemical behavior of these compounds in an aqueous environment, we need to know their solubility, their rate and mechanism of thermal decarboxylation, etc. For example, at relatively low temperatures the fatty acids will cleave to produce a short-chain carboxylic acid and a shorter alkane molecule. Similarly, glycols and ethers can react with water in the presence of acid to form carboxylic acids. The short chain carboxylic acids are very soluble and have significant complexing capabilities for metals. For example under steam conditions, it might mobilize the Pu (as a complex with the organic acid anion - OAA). At higher temperatures the OAA decarboxylate to produce short chain alkanes (ultimately methane) and CO_2 .

Some production of HCl from the TCA and carboxylic acids (from several possible reactions with the organic components involving H_2O and H^+), was expected. However, although the cutting fluids are relatively stable thermally in the absence of water (after all, they perform their function at the tool face, which can be very hot), quite unexpectedly, the fluids react readily and extensively in hot water. Without going into great detail, the experiments were a disaster. Conditions were extremely reducing (the Ti^{+4} was reduced to Ti^{+3} and formed $TiCl_3$), the solution pH was extremely acid (<0.1), the gas phase was dominated by molecular H_2 gas, etc. Enormous amounts of carboxylic acids (e.g., 30,000 ppm acetate), even more Cl^- (82,000 ppm), and F^- (8,000 ppm) were produced. The Ti head was completely corroded and the Au reaction cell was partially dissolved, too. The bottom line, however, is that Siskin and Katritzky (1991) are correct. Organic compounds are extremely reactive in hot water.

Long Term Effects

Man has been using metal for thousands of years since the Bronze and Copper Ages and concrete at least since Roman times. Studies of metal artifacts from a variety of ages demonstrate that some phases that form cannot be predicted from our present knowledge of material degradation (Lucey, 1971; Mor and Beccaria, 1975; Hedges, 1976; Scott, 1985; Pollard et al., 1989). Some of the unpredictable phases even involve the activity of micro-organisms (McNeil et al., 1990). This information is not accessible through laboratory experiment. Therefore analysis of the decomposition of ancient materials is the key to the validation of man-made material-rock-water interaction simulations because they provide the most significant verification of the man-made material decomposition over long periods of time. For example studies of concrete from early Roman times can offer constraints for up to one tenth of the time this study is required to predict, whereas a year long laboratory experiment can provide constraints that may apply to only one ten thousandth of the required time.

Radiolysis Effects on Man-made Material - Water Chemistry

Deciphering the complex chemical history of the waste package environment will also require evaluation of radiolysis. Ionizing gamma radiation can interact with the air-steam atmosphere and pore water to form radiolysis products in the waste package environment and may interact with man-made material in the vicinity of waste packages. These products may then interact with the repository rock and with each other to influence mineral dissolution and precipitation and

waste package performance. The composition of the radiolysis products will change during the thermal evolution of the package environment. Radiolysis products are poorly characterized at present. These interactions are as yet undocumented. Of particular concern for container and waste form performance is whether a bicarbonate-buffered aqueous solution (such as J-13 water) in contact with air will form a formate (a compound that contains an H-C-O-O radical) or an oxalate (a compound that contains a C₂O₂ radical). Neutron radiation will be low, and alpha and beta radiation will not noticeably penetrate the waste package container (Van Konynenburg, 1986).

Colloids

The study of colloids involves a distinct set of chemical considerations. Organics can complex radionuclides in a far more soluble form than inorganic complexes or single ions (Laxen and Chandler, 1983). Other evidence strongly suggests that colloids may carry adsorbed radionuclides in suspension (Christenson, 1962; Fried et al., 1975; Fried et al., 1976; Rogers, 1977; Abee et al., 1981; Nyhan, 1984; Raloff, 1990). Therefore, colloids present in water that contacts and enters waste containers can significantly enhance transport of radionuclides from the engineered barrier. Studies of the effects of pseudocolloid formation (238Pu, 241Am, 244Cm) have shown that actinides can associate with colloids resulting in solubilities which may be enhanced by three orders of magnitude (Kim et al., 1984a, 1984b from (Ramsay 1985)). As a consequence, the movement of radionuclides may not be predictable through inorganic chemistry alone. Little is also known about the sorption of radionuclides onto colloids. The contact of the radionuclide with the colloid, fixation and retention of the radionuclide on the colloid, and mechanical breaking away of the particle in the event of collision are not well understood. The kinetics of the particles, which depend on the velocity of the flow are also not well known. In still fluid, diffusion, sedimentation and Brownian motion dominate; in flowing fluids, the movements are due to laminar and turbulent flow, entrainment, fluid drag, dispersion. Fracture-matrix relationships, the formation of new minerals (e.g. zeolites), the hydrochemistry, the temperature, the hydraulic gradients, the electrical field, and the effect of the saturation state of the rock, and gas flow have yet to be understood. All of these parameters are ultimately required to perform the numerical simulations that will be required to extend predictions to 10,000 years. However, this is not the purpose of the man-made materials task.

Colloids can occur as organic materials, oxides, and clays and can adsorb ions. Water that transports colloids in suspension also transports the adsorbed ions. Colloids exist naturally, as fracture lining materials, clays, bacteria, algae and humic acid but can also be the product of degradation of man-made materials and debris, such as glass, fuels and greases, metals, and organic waste. The processes that are known to form colloids: release from bulk material (dissolution of matrix, chemical reactions such as degradation, hydrodynamic forces, mechanical stress), aggregation by collisions, electrical or Van der Waals forces, nucleation in case of supersaturation, activity of microorganism, and introduction can involve materials introduced into a radioactive waste repository or interaction between man-made materials and the host rock. At Yucca Mountain, interactions between man-made materials and groundwater could lead to the formation of colloids in the form of oxy(hydr)oxides, clays, organic particles, polysilicates. The processes that have been identified to date are only a few of the many possibilities. They include: leaching of the waste form, corrosion of canister material, degradation of backfill material, naturally occurring colloids such as clays, organics and precipitates, and introduced organic materials (Olofsson et al., 1981, 1982a and b).

Additional areas of concern regarding colloids include degradation and chemical interactions of the following classes of materials: inorganic complexants such as acids and batteries, organic complexants and nutrients for microbes such as alcohol, antifreeze, bituminous materials, fuel, hydrocarbons, some gases, clothes, lubricants, plastic, paint and wood, and groundwater pH modifiers such as acids, concrete, grout, lime and plaster. Physical (size, bulk charge, density)

also influences colloid formation, transport, and stability. Colloids that could be generated from the degradation of introduced materials, cover the whole range of sizes. Small (<10 nm) colloids include hydrated metal ions, small organic particles, polyhydroxo-complexes, polysilicates and fulvic acids. Medium (10 - 100 nm) sized colloids include clays and metal-hydroxides. Large (> 1 μ m) sized colloids include inorganic and organic particles.

The following synopsis not only illustrates the adsorption of a radionuclide to colloids that could be generated by man-made materials (e.g. rust), but also the chemical complexity of predictive modeling. Uranyl adsorption (dissolved uranyl $10E-05$ to $10E-08$ M) was measured from aqueous solutions onto well-characterized goethite, amorphous ferric oxyhydroxide and hematite sols at 25 C as a function of solution pH, ionic strength, electrolyte concentration and of competing cations and carbonate complexation. It was found that all the iron oxide materials strongly adsorbed dissolved uranyl species at pHs above 5 to 6. The presence of Ca or Mg ($10E-03$ M) did not significantly affect uranyl adsorption. However, uranyl carbonate and hydroxy-carbonate complexing severely inhibited adsorption (Hsi and Langmuir 1985). Even at very low concentrations marked effects may be caused by organic additives to cement (aliphatic and aromatics at 20mmol/l, saccharides at even 5 mmol/l). They will likely degrade to give fragments containing hydroxyl, carboxyl, and phenolic groups. It is also possible that association of actinides with other components leaching from cement ($Si(OH)_4$, $Fe(OH)_4^-$) may subsequently give rise to pseudocolloids as the pH falls and colloidal hydroxide formation is favored. Polymers, silica fume and pulverized fuel ash, may contribute to pseudocolloid formation, if they are prone to dissolution in the alkaline pore water, (Ramsay, Avery et al. 1988).

It is important to identify secondary effects of introduced materials on the formation, transport and stability of colloids in a radioactive waste repository. These secondary effects include chemical changes such as pH, redox potential, ionic strength, competing ions, organic matter and sorption, and changes in the environment such as pore aperture and temperature. For example, the formation of actinide colloids may be complicated by hydrolysis reactions, variable valence states (redox dependent), ion complexation effects, and polynuclear ion formation. The actinides form strong complexes with many oxygen-containing anions in natural waters (hydroxide, carbonate, phosphate, sulfate) as well as fluoride (Allard, 1982 from (Ramsay 1985)). Low redox potential conditions are to be expected in the near field due to cement and canister corrosion. This will generally favor the formation of Actinide(III) or Actinide(IV) species. Colloids were found with Am and Pu in the pH range 7-9 (Olofsson et al., 1983 from (Ramsay 1985)). As another example, the pH of water in contact with cement may be as high as 13, and would be expected to fall progressively to near neutral in the far field. A similar variation in Eh may occur for water in contact with cements containing reducing agents such as blast furnace slag. Variations in pH and Eh influence the solubility and speciation of colloids. In this the pH gradient is of primary importance. The original solubility of the cement components may be considerable, and then decline with decrease in pH as the water moves to the far field. The decrease in solubility may cause soluble silicates to polymerize and thus yield colloids that can incorporate radionuclides. Additives to cements are also of concern. Extensive studies of chemical additives which either retard or accelerate the setting of cement have shown that modest concentration of salt solutions (about 0.5 mol/l) can markedly accelerate or retard hydration of the C3S phase depending on the type of cation or anion present (Double, 1983 from (Ramsay 1985)).

Interactions Between Man-Made Materials, Rock and J-13 or Concentrated J-13 Water

The host rock at the proposed radioactive waste repository is a devitrified, welded, rhyolitic tuff. The tuff consists of primary minerals, such as sanidine, plagioclase, quartz, biotite, iron-titanium oxides, allanite and zircon, that formed at temperatures in excess of 600°C, and

secondary minerals, such as cristobalite, quartz, alkali feldspars, and smectite clays that formed during cooling and later alteration of the tuff at temperatures less than 500°C. In addition, the repository horizon and the adjacent horizons contain zeolites. Zeolites are used commercially as molecular sieves and sorbates. Clinoptilolite, for example, is used as a molecular sieve for the ammonium ion (Barrer, 1978; Breck, 1974) which is known to increase corrosion rates. However, other man-made materials counteract the potential beneficial effects of the zeolites, by either dissolving the mineral or by providing preferentially adsorbed ions. The balance of the effect of zeolites on the aggressive behavior of some man-made materials at the repository is unknown at present. However, it is clear that modification of the near-field environment, such as the introduction of large quantities of iron or an extreme change in pH, can alter the geochemical reactions that are currently predicted through the current geochemical models.

RECOMMENDATIONS

It is clear that the potential degradation effects of many materials that can be introduced into the exploratory studies facility (ESF) on water chemistry is unknown, especially at elevated temperatures. In addition, combinations of materials will occur that heretofore have not been considered. We are aware that some of the potential consequences that cannot yet be predicted may lead to very aggressive water chemistry or to the creation of colloids that will mobilize radionuclides. We are unable to recommend maximum tolerable levels for any introduced materials, because we are aware that chemical gradients can be as effective in promoting chemical reactions as great concentrations of a chemical substance. Therefore, at this time, we recommend that, to the extent possible, all introduced materials; solid, liquid and gas, be collected and removed from the ESF.

We recommend the removal of all gases, including diesel exhaust, by ventilation directly to the outside. Ventilation of the shaft is not sufficient because gases will escape into fractures and particulates will be deposited on the drift walls. Volatile liquids such as antifreeze, oils and fuels should be contained and retrieved. Spills should also be contained and retrieved. In other words, laying out a tarp to catch spills is not sufficient due to the release of volatiles. We cannot presently recommend the use of any type of permanent introduced material such as rock bolts of any composition; epoxy, cementitious material, or sulfur. In addition, because of the very significant role of dissolved organic material in the formation of colloids, all waste materials, including food and human waste should be retrieved.

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APPENDIX A

The capability to predict the behavior of the near-field environment is predicated on the precision and accuracy of our chemical, thermal and mechanical evolution models of the near-field. Container performance, waste form dissolution rate, and radionuclide concentrations in solution will be unpredictable if we lack knowledge of the chemical effects of these man-made materials. It is the responsibility of the near field environment technical area to identify chemical and physical processes that are important for container performance, and to specify allowable changes that can result from repository construction. The materials evaluation activities of the man made materials task are part of the near field environment effort to satisfy this responsibility.

Legal Issues

The man made materials task activities address the requirements contained in Section 135(a) of the NRC regulation 10 CFR Part 60, which states, in part:

Packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.

The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydration, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

The ability of the waste packages to meet these requirements will depend on the interactions between the waste package and the environment into which it is emplaced. Performance Issues 1.4 and 1.5, and their associated Information Needs (IN), address these concerns (taken from the Site Characterization Plan Chapter 8, Section 2):

Issue 1.4. Will the waste package meet the performance objective for containment as required by 10 CFR 60.113?

IN 1.4.3 Scenarios and models needed to predict the rate of degradation of the container material.

IN 1.4.4 Estimates of the rates and mechanisms of container degradation in the repository environment for anticipated and unanticipated processes and events, and calculation of the failure rate of the container as a function of time.

IN 1.4.5 Determination of whether the requirement for substantially complete containment of the waste packages is met for anticipated processes and events.

Issue 1.5 Will the waste package and repository engineered barrier systems meet the performance objective for limiting radionuclide release rates as required by 10 CFR 60.113?

IN 1.5.3 Scenarios and models needed to predict the rate of radionuclide release from the waste package and engineered barrier system.

IN 1.5.4 Determination of the release rates of radionuclides from the waste package and engineered barrier system for anticipated and unanticipated events.

IN 1.5.5 Determination of the amount of the radionuclides leaving the near-field environment of the waste package.

The design demands that pertain specifically to the attributes of the waste package environment will be addressed by gathering the information required under Information Needs 1.10.1 and 1.10.4 of Design Issue 1.10 (SCP, Chapter 8 Section 2).

Issue 1.10 Have the characteristics and configurations of the waste packages been adequately established to (a) show compliance with the post closure design criteria of 10 CFR 60.135, and (b) provide information for the resolution of the performance issues?

IN 1.10.1 Design information needed to comply with post-closure criteria from 10 CFR 60.135(a) for consideration of the interactions between the waste package and its environment.

IN 1.10.4 Post-emplacement near-field environment.

The chemical reactions that may occur over a range of saturation conditions must be characterized to satisfy the requirements for resolution of Issues 1.4, 1.5, and 1.10.

Purpose and Objective

The purpose of the man made materials task activities is to investigate the consequences of the chemical modification of the near-field environment by man-made materials. The extent to which a material modifies the chemical environment will depend on its reactivity, its distribution in the repository, and its total mass and concentration. The man-made materials task activities will identify the man-made materials of potential use in the repository and characterize their impact on chemical processes in the waste package environment for anticipated and certain unanticipated conditions. The chemical effects of man-made materials will be characterized within the range of parameter values considered appropriate to the post-emplacement environment. Specifically, these activities are intended to:

1. identify and quantify the man-made materials that will be present in the post-emplacement environment,
2. characterize chemical reactions of man-made materials and their reaction products over a range of saturation, material surface area to fluid volume ratio, pH, pore water chemistry and temperature conditions,
3. identify and characterize the processes that will occur during thermal perturbation of the tuff and man-made materials in the presence of elevated radiation doses and dose rates,

4. identify the man-made material modifications of temperature, character of the fluid phase, and pore water chemistry that will affect the near-field environment and the lifetime of critical man-made materials,
5. identify those man-made materials that should be banned from or have restricted usage in the repository,
6. identify those materials that will, through degradation or interaction with other man-made or natural materials in the repository, produce colloids capable of transporting radionuclides, and
7. identify secondary effects of introduced materials on the formation, transport and stability of colloids in radioactive waste repository.

Schedule Considerations

The integrated nature of the modeling effort indicates that delay of work outlined in this study plan may prolong completion of work in the near-field and waste package areas. As a consequence, definition of the waste package environment, as needed for waste package performance assessment, may be delayed if significant delays affect these activities.

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