APPENDIX A

EXAMPLES OF POTENTIAL EXPERIMENTS FOR ACRSL

The specific experiments that would be performed in the proposed Actinide Chemistry and Repository Science Laboratory (ACRSL) would be determined and prioritized in discussions with the Carlsbad Field Office, Los Alamos National Laboratory, Sandia National Laboratories, Westinghouse TRU Solutions LLC, and New Mexico State University. The potential experiments would be expected to include a subset of those described below (Mercer 2002).

Research on Oxidizing Effects of Radiolysis

- Generation rates of radiolysis by-products (e.g., H_2O_2, ClO^-, Cl^-) in typical Waste Isolation Pilot Plant (WIPP) alpha and gamma irradiation fields
- A kinetic model for hypochlorite and peroxide production rates, including a complex reaction mechanism
- Quantification of radiolysis-related changes in radionuclide solubilities and speciation
- Define conditions to possibly affect actinide oxidation state

Research on the Reducing Effects

- Mild steel and aluminum corrosion
  - Influence of mild steel and aluminum corrosion on the Eh–pH system of WIPP brine, with respect to brine salinity, temperature, and pressure provided by the repository, and as a function of typical WIPP contact-handled waste and remote-handled waste irradiation fields
  - Reaction mechanism producing surface passivation and the associated agglomerations of solid inorganic phases onto the waste drum steel surfaces
- Complexing and chelating agents
  - Effects of organics on the solubility of actinides under WIPP conditions
  - Effects of organics on actinide speciation under WIPP conditions

Research on Actinide Demobilization

- Waste form and waste package corrosion
  - Corrosion mechanism and corrosion rates of WIPP-typical waste packages
  - Influence of waste form degradation on the geochemical Eh-pH system within the near field
  - Influence of reactive waste sub-components on corrosion rates and secondary phase formation in aged Source-Term Waste Test Program brines
  - Determination of co-precipitation mechanism and the formation of possible host phases in waste form corrosion
    - Pu-$SrSO_4$ solid solution as co-precipitation mechanism in the Source-Term Waste Test Program
    - Barite-type solid solution, smectite-type solid solution, and powellite-type solid solution in waste glass corrosion
  - Compare corrosion mechanism and secondary phase formation of transuranic (TRU) waste forms to those of advanced waste forms
    - phosphate-based waste glass
    - silicate-based waste glass
    - borosilicate-based waste glass
    - ceramic phosphate-based and titanate-based (Synroc II, pyrochlore) waste forms
    - sintered waste-forms (glass-ceramic composite materials)
    - advanced Portland cement-based (e.g., improvements caused by fly ash admixtures)

- Evaluation of the role of colloids on radionuclide transportation and migration
  - The formation, characterization, and quantification of colloidal and nano-crystalline particles which influence the migration of radionuclides and the total radionuclide concentrations in the aqueous phase
  - The sorption mechanism of positively charged radionuclides onto a negatively charged colloid surface area in order to complete the current geochemical repository model, which assumes equilibrium conditions by introducing the thermodynamically non-equilibrium behavior that describes colloidal formation and radionuclide transportation and migration.
  - Investigation of the ability of colloids to influence the migration of radionuclides in the following pathways:
    - radionuclide sorption/desorption from solid phase
    - radionuclide sorption/desorption from colloid
    - colloid radionuclide sorption/desorption from solid phase
  - Readjust or replace current model that is based on radionuclide sorption to sediment using sorption distribution coefficients by a model based on colloidal transport of radionuclides in the geochemical system of WIPP

Characterization of the Radioactive Inventory

- Waste characterization in solid state
  - Non-destructive characterization of radionuclide inventory
    - Alpha counting
    - Gamma counting
    - X-ray fluorescence
    - Laser ablation mass spectroscopy
  - Characterization of the solid phase constitution
    - X-ray diffraction
    - Microscopy (Optical SEM)
    - EXAFS (optional)
  - Determination of radionuclide oxidation state
    - X-ray diffraction
    - EXAFS
- Destructive waste characterization for quantification and specification of radionuclides (including beta emitters) in the liquid phase
  - Design appropriate digestion procedure (e.g., microwave digestion)
  - Apply effective separation technique for individual quantification of beta emitters
    - Liquid-liquid extraction
    - Chromatographic column extraction
    - Supercritical CO_2 extraction (to be applied preferably in Japan, France, and United Kingdom)
  - Analysis of each beta emitter by liquid scintillation counting
  - Quantification of the total TRU waste inventory by ICP-MS
  - Determination of the radionuclide oxidation state within the TRU waste
    - Photoacoustic laser spectroscopy
    - Time resolved laser fluorescence spectroscopy
    - UV-VIS spectrophotometry
    - Vibrational spectroscopy (FTIR, Raman)
    - Electron spray mass spectroscopy
    - Analysis of Eh-pH and the concentration of radiolysis by-products (e.g., hypochlorite, peroxide, oxygen, hydrogen)
    - Actinide speciation in TRU waste and under repository conditions
    - Solubility behavior of radionulides in TRU waste under repository conditions

- Characterization of the radioactive content in the free-standing liquid
  - Quantification of the total TRU waste inventory by ICP-MS
  - Electron spray mass spectrometry
  - Extraction technique, if applicable
  - Potentiometric titration and the concentration of radiolysis by-products (e.g., hypochlorite, peroxide, oxygen, hydrogen)
  - Analysis by UV-VIS (radiolysis by-products), laser spectroscopy

Improvement of Waste Forms, Model Conditioning, and Model Stabilization of Waste Streams Without Viable Disposition Path

- Set-up treatment test unit for waste forms that do not meet regulations and for waste forms with high possibility to fail certification procedure
  - Extract hazardous organic components *in situ* and without further repackaging. A possible secondary waste stream should be destroyed (oxidized) or stabilized.
  - Determine mineralogical phase constitution and the chemical composition of the waste package in order to define the appropriate treatment procedure.
  - Establish extraction capabilities for waste forms containing disallowed amounts of freestanding liquid and/or hazardous organic components
  - Adopt extraction technologies from real-scale deployments and industrial processes. Typical candidates might be:
    - Supercritical CO_2 treatment ($SCCO_2$) to extract free liquid and organic solvents with low dipolar moments and molar mass not greater than 500 grams per mole. $SCCO_2$ can furthermore improve leach resistance of Portland cement-based waste forms.
    - Apply pyrolysis and thermal desorption to extract and destroy (oxidize) any non-stabilized organic components like solvents and volatile combustible organics. Pyrolysis might successfully treat waste forms like Oasis sludge (Rocky Flats, IDC 801).
    - Convert mixed waste streams into combustible pyrolysis (carbonization) gas and dry residue at temperatures of 400°C to 500°C and in a low-oxygen atmosphere by applying the latest pyrolysis technology.

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