SYMPOSIUM JJ
Scientific Basis for Nuclear Waste Management XXV

November 26 – 29, 2001

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Symposium Support
Applied Metamix, Ltd.
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U.S. Department of Energy
U.S. Nuclear Regulatory Commission
Westinghouse Savannah River Company

Proceedings to be published in both book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as Volume 713
of the Materials Research Society
Symposium Proceedings Series

*Invited paper
WASTE REPOSITORY AT YUCCA MOUNTAIN, NEVADA.

Roberto T. Patahan, Letai Yang, Lauren Browning, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

Groundwater seeping into the proposed Yucca Mountain nuclear waste repository would be subjected to evaporation and salt formation processes that may enhance corrosion of metal drip shield/waste package surfaces. Because corrosion may increase with increasing brine concentrations, we have initiated a study to characterize the processes associated with highly concentrated brine solutions at Yucca Mountain. In a hot repository setting, evaporation may lead to the accumulation of dry, multicomponent salt deposits on drip shield/waste package surfaces. This accumulation may also result from deposition of salts entrained in ventilation air. Halloysite salts on drip shield/waste package surfaces will absorb moisture from the atmosphere, generating small volumes of highly corrosive brines. This rewetting is expected to occur after the repository temperature falls below the boiling point for the salt mixture and the equilibrium humidity of the drip shield, and has been reached. The U.S. Department of Energy (DOE) performance assessment abstraction of in-drift chemical environment assumes that desiccation begins at a relative humidity of 50 percent and aqueous corrosion of the drip shield or waste package does not occur until this value is reached. The threshold relative humidity is based on the deliquescence behavior of pure NaNO3 salt. In this study, thermodynamic modeling of multicomponent salt mixtures is used to demonstrate that the deliquescence point of Yucca Mountain waters is lower than that of pure NaNO3 implying that initiation of drip shield or waste package aqueous corrosion can occur at lower relative humidities and at earlier times than predicted by the DOE abstraction. This abstract is an independent product of the Center for Nuclear Waste Regulatory Analyses and does not necessarily reflect the views or regulatory position of the U.S. Nuclear Regulatory Commission.

10:30 AM AII1.5

INFLUENCE OF THERMAL AGING ON THE MECHANICAL AND CORROSION PROPERTIES OF GTAW WELDS OF ALLOY N00922. Radh B. Rokhok, Sumit S. Edgcombe-Summers, Todd A. Palmer, Lawrence Livermore National Laboratory, Livermore, CA; Paul Crook, Haynes International Inc., Kokomo, IN.

A Ni-Cr-Mo-W alloy (N00922) is being considered as a major component in the design of the containers for the current Yucca Mountain Site Characterization Project. The fabrication of these containers will require significant amount of welding. The phase stability of alloy N00922 gives tungsten arc welds (GTAW) was studied by aging samples at 427, 482, 538, 649, 704, and 760°F for times up to 40,000 hours. The tensile properties and the Charpy impact toughness of these samples were measured in the as-welded condition as well as after aging. The corrosion resistance was measured using standard immersion tests in acidic ferric sulfate (ASTM G 28 A) and 2.5% hydrochloric acid solutions at the boiling point. The microstructures of welded samples were examined using scanning electron microscopy (SEM). The mechanical and corrosion properties were compared to volume fraction measurements in order to determine the level of precipitation where degradation begins. Also, the effect of annealing on weld properties and precipitation kinetics was investigated. Some of the results show that, for example, degradation of the impact toughness of welded specimens begins at shorter aging times than that seen for non-welded specimens. However, Arseniust extrapolations showed that the degradation rates were similar for both welded and non-welded specimens.

10:45 AM AII1.6


The susceptibility of Alloy 22 to localized corrosion is important in the evaluation of the waste package outer barrier and overall performance of the proposed repository at Yucca Mountain, NV. Factors significant to localized corrosion susceptibility include the chemical composition of the waste package environment, temperature, and fabrication processes. Environmental chemical composition and temperature effects were examined by measuring the repassivation potential for crevice corrosion in chloride containing solutions at temperatures in the range of 80 to 150°C. The effects of potentially inhibiting micronic species, such as nitrate, and potentially aggressive cationic species, such as lead, were also determined in laboratory tests. In addition to the immersed material tests, were conducted on both welded and thermally aged material to evaluate the effects of waste package fabrication processes. The Alloy 22 localized corrosion susceptibility increased when temperature and chloride concentration were increased. Welding and thermal aging also decreased localized corrosion resistance of the alloy. Results of both short term
and long term tests indicate that localized corrosion can be initiated on Alloy 22 in chloride containing environments at temperatures less than those at which a liquid film can be formed on the container surface by the presence of degradable salts.

Disclaimer: This paper was prepared to document work performed for the Nuclear Regulatory Commission under Contract No. NRC-02-97-009. This work is an independent project of the Center for Nuclear Waste Regulatory Analyses and does not necessarily reflect the views or regulatory position of the Nuclear Regulatory Commission.

11:00 AM J11.7

The Site Recommendation (SR) of the potential repository for high-level nuclear waste at Yucca Mountain, Nevada is in progress. Long-term containment of the waste and subsequent slow release of radionuclides from the EBS into the geosphere will rely on a robust waste container design, among other Engineered Barrier System (EBS) components. The SR waste package design has two layers: a 28-mm thick Alloy 22 outer barrier and a 50-mm thick 310N stainless steel inner shell. The waste package is emplaced under a Titanium Grade 7 weld. No barrier performance credit is taken for the inner shell. The waste package outer barrier has two Alloy 22 closure lids: one 25-mm thick lid and one 18-mm thick inner lid. The lids are welded to the outer barrier after the waste is loaded.

The Waste Package Degradation (WAPDEG) stochastic simulation model was developed to analyze long-term degradation of waste packages in the potential repository. For the SR analysis, the WAPDEG model simulates the waste package degradation considering general corrosion, localized corrosion and stress corrosion cracking (SCC) of the outer barrier. The current model also includes effects of microbiologically influenced corrosion (MIC), aging and phase stability, and pre-existing manufacturing flaws on the outer barrier degradation. The exposure conditions the WAPDEG model uses are temperature and relative humidity at the waste package surface as a function of time and the bounding corrosive chemistry of aqueous solutions contacting the waste packages.

This paper discusses the WAPDEG stochastic simulation model and the waste package degradation model results for the SR reference case. Results of the WAPDEG simulation using multiple realizations (typically 100 realizations) are presented by summary statistics for the time histories of the type (i.e., cracks by SCC, pits by localized corrosion, and large openings by general corrosion) and number of waste package and drip shield penetrations. Results show waste packages and drip shields are not subject to localized corrosion under the exposure conditions expected in the potential repository. The waste package failure in the 95th percentile confidence interval case occurs after approximately 90,000 years. Comparing the waste package failure curves to the waste package first crack failure and first punch failure curves indicates that the initial failures are due to SCC that has initiated at one or more pre-existing manufacturing flaws in the closure weld regions.

11:15 AM J11.8
EVALUATION OF THE LONG-TERM STABILITY OF PASSIVE CORROSION ON THE WASTE PACKAGE AND DRIP SHIELD UNDER YUCCA MOUNTAIN CONDITIONS. David W. Shesmost, Department of Chemistry, University of Western Ontario, London, Ontario, CANADA.

A number of possible passive corrosion scenarios are considered for the Titanium Grade-7 drip shield and the Alloy-22 waste package under Yucca Mountain conditions. The primary aims are to evaluate how passive corrosion processes might change in environmental conditions within the repository evolve with time. The effect of a period of dry thermal oxidation on the following possible scenarios is discussed: i) oxide film fracture and spalling; ii) enhanced passive corrosion due to inorganic processes; iii) enhanced passive corrosion and increased susceptibility to localized corrosion due to materials aging; iv) accumulation of damage and increased susceptibility to localized corrosion due to thermal cycling and other candidate corrosion events. Only the last of these scenarios seems capable of influencing the long term corrosion process on the waste package, but only if extremely aggressive chloride-dominated environments are produced. Under these circumstances are rare, the probability that a metastable event on Alloy-22 will lead to stable crevice propagation. Providing the drip shield performs its design function such events should be very rare. Metastable events have not been reported on titanium under oxidizing conditions.

11:30 AM J11.9
EFFECTS OF FLUORIDE AND CHLORINE IONS ON CORROSION OF TITANIUM GRADE 7 IN CONCENTRATED GROUNDWATERS. April L. Pulvirenti, Karen M. Needham, Mohammad A. Adeli-Hadi, Charles R. Marks, Jeffrey A. Gorman, and Aaron Burdett. Catholic University of America, Dept of Chemistry, Washington, DC; Dominion Engineering, Inc., McLean, VA.

Titanium Grade 7 (Ti-6Al-4V) is considered for use as a construction material for drip shields to be used to protect nuclear waste packages in a geologic repository in contact with groundwater. In sites such as Yucca Mountain, Nevada, groundwater contain significant levels (several parts per million) of chloride and fluoride. The temperature where liquid water can first form in the vicinity of the waste package is expected to be at least around 120°C and the water in this region is expected to undergo concentration by factors exceeding 1000 due to evaporation.

Experiments have been carried out on titanium Grade 7 disks and U-bend samples at temperatures ranging between 90°C and 160°C. The solutions are based on the composition of water from the J.13 well in the vicinity of Yucca Mountain, with chloride and fluoride concentrations enhanced by factors of up to 1000 to simulate the effect of evaporation. Optical metallography and SEM/EDS observations show that even at temperatures as low as 108.1°C significant corrosion can be observed at the end of test periods as short as 15-30 days. The corrosion is highly localized, involving considerable pitting and, possibly, mechanical defects. The corrosion is particularly noticeable near the circumference of the samples, at corners, and in places where the samples have been marked using techniques such as vibroetching.

11:45 AM J11.10
EVALUATION OF WASTE PACKAGING INTERACTIONS WITH WASTE PACKAGE. Yiming Pan, Darrell Dombrowski, Gustavo-Craginolino, Vijay Jam, Juan Seidman, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

The chemistry of water dripping into the waste packages for HLW disposal is important to the performance of engineered barriers and the subsequent release of radionuclides to the environment. A corrosion test cell that simulates the internal geometry of the waste packages has been designed to investigate changes to the in-package solution chemistry. A series of tests was conducted to evaluate solution chemistry variations as a function of applied potential, temperature, and chloride concentration using a specimen of type 316L stainless steel with a pre-drilled hole as a simulated pit. A micro-syringe was used to extract solutions from inside and outside the pit. The solutions were analyzed for cation concentrations using a capillary electrophoresis and the pH was measured using a micro-pH probe. Preliminary manganese and cationic chloride concentrations inside the pit due to mobile dissolution of type 316L stainless steel. The solution pH became significantly acidic reaching a value of 2.6. These results suggest that interactions of waste package internal structural components with the incoming water may have significant influence on the evolution of water chemistry and the subsequent corrosion of waste forms such as spent nuclear fuel.

Disclaimer: This paper was prepared to document work performed for the Nuclear Regulatory Commission under Contract No. NRC-02-97-009. This work is an independent product of the Center for Nuclear Waste Regulatory Analyses and does not necessarily reflect the views or regulatory position of the Nuclear Regulatory Commission.
immobilized product is in the form of a free-flowing non-hygroscopic powder in which the chlorides are chemically combined within the mineral phase. This powder provides an encapsulated wasteform suitable for long-term storage, the feasibility of encapsulating this product in a compatible glass is being assessed. The final wasteform will be manufactured by a pressureless sintering route and sodium alumino-silicate glass forms are currently being developed for this purpose. These glasses are of particular interest due to a combination of useful properties which include good sintering characteristics, together with excellent chemical durability. We have noted, however, that during the process of sintering the Na present in the glass reacts with the chlorosilicate and chloroaluminophosphate to form a dispersion of halide crystals within the final wasteform. If the sintering temperature is high enough, some of these crystals volatilize to leave a void of well-defined voids within the wasteform. The formation of free halite within the wasteform is clearly undesirable, but can be minimized by careful control over the processing parameters, in particular the sintering temperature. The implications of these findings are being highlighted and discussed.

At present, crystalline ceramic based on titanate pyrochlore, Ca$_2$Ga$_2$(OH)$_6$UO$_2$, is considered as US candidate waste form for the immobilization of weapons grade plutonium. Naturally occurring uranium bearing minerals with pyrochlore type structure: 

- Uraninite, (HeU$_2$, U$_2$, Ti$_2$, Th$_2$, U$_3$)$_2$O$_{8}$ (O, OH), betafite, (U,Ca,Sc,$^{3+}$Ta,Fe)$_2$(O,OH)$_3$ and elbertite (Ca,Sr,Fe)$_2$(Nb,Ta)$_2$O$_6$ (O,OH), containing 20, 15, 25 wt.% U, respectively, were studied in order to understand the long-term behavior of pyrochlore type waste forms and its relationship with geological environment. Chemical shifts [4] of the following X-ray emission lines: U(L$_{1,2}$3) and U(L$_{1,3}$), were determined by X-ray spectrometry method. The calculations were performed on the basis of the two-dimensional L$_{1,2}$3 and L$_{1,3}$ correlation diagram. It was shown that 100% of uranium in harchetohéite and, probably, 95-100% of uranium in betafite are in the forms of $\text{UO}_2^{2+}$ and $\text{UO}_4^{2+}$ and the rest is $\text{U}^{4+}$. The conversion of the initial $\text{U}^{4+}$ ion in the structure of natural pyrochlore to $\text{UO}_2^{2+}$ due to metamict decay causes significant increase of uranium mobility. Data on uranium leach rate [10] $10^{-7}$ g/cm$^2$ day from harchetohéite in distilled water at 25°C for 7 days are approximately two orders of magnitude higher than corresponding actinide leach rates from Synroc ceramic under the same conditions. The weak bonding of $\text{UO}_2^{2+}$ and as assumed, $\text{PuO}_2^{2+}$ and $\text{NpO}_2^{2+}$ in pyrochlore structure makes doubt that pyrochlore is a feasible host phase for the immobilization of actinides such as U, Pu, Np.

Zirconate, nominally ABC$_2$O$_7$ and the structurally related pyrochlore, nominally Ba$_2$Zr$_2$O$_7$ and Ba$_2$Y$_2$Zr$_2$O$_7$, are primary components of SYNROC. The pyrochlore structure becomes the only stable phase when the solid phase of the primary solid solution ends by conversion into the secondary substantially larger than Zr$_2$O$_7$ (0.228 nm). Substituting cations such as Ce$^{3+}$ (0.107 nm) or Gd$^{3+}$ (0.1053 nm) stabilize the pyrochlore structure by forcing the zirconate B-site to become 8-coordinated and, hence, crystallographically equivalent to the zirconate B-site. At approximately 30 mol.% occupancy of the B-site by Gd, a mixture at the unit cell scale of half zirconate and half pyrochlore motifs, the so-called zirconate-4M is formed. Zirconate-4M with stoichiometry Ca$_3$Ga$_2$O$_7$ tetragonal, lies in the pseudo-binary defined by CaHfO$_2$-Gd$_2$O$_3$, two of the end-member compositions for the proposed waste form for excess weapons plutonium. The formation enthalpy of zirconate-4M is, therefore, of interest. High resolution transmission electron microscopy (HRTEM) and electron microprobe analysis (EMPA) were used to characterize the zirconate-4M sample. High temperature oxide melt solution calorimetry using two solvents, $\text{Na}_2\text{O}_4$-$\text{Na}_2\text{O}_3$. T = 750 K and $\text{K}_2\text{O}$. $\text{BaO}$. T = 1075 K, was used to measure the heats of solution for CaCO$_3$, HfO$_2$, TiO$_2$, Gd$_2$O$_3$ and Ca$_3$Ga$_2$O$_7$ to $\text{Ti}_2$O$_3$ + $\text{Gd}_2$O$_3$. Applying the appropriate thermodynamic cycles to our presented thermodynamic data, the enthalpy of formation of zirconate-4M at 298 K was calculated ($k$J/mol): P6$_{3}$-hborate derived $\Delta H_{\text{f,298}}$ = -81.4 ± 5.3 J/mol. This value is equal within error, supporting satisfactory dissolution of samples in both solvents. The calculated formation enthalpy from two pyrochlore assuming ideal mixing is (0.363+0.07g) 0.7CaHfO$_2$ + 0.34Ti$_2$O$_3$, $\Delta H_{\text{f,298}}$ = -83 ± 8 kJ/mol. This suggests a small positive enthalpy of mixing (approximately 8 ± 8 kJ/mol). Additional experiments are being conducted to refine these data.

2:15 PM 112.4 ELEMENT/PARTITIONING IN A PYROCHLOR-E-BASED CERAMIC WASTE FORM. Beto Goire, Carrie Hatchet, Earth & Atmospheric Sciences, Purdue University, West Lafayette, IN; Edgar Buck, Pacific Northwest National Laboratory, Richland, WA. 

Titanate-based ceramic waste forms, designed for immobilization of plutonium, contain as major constituents pyrochlore, $\text{Al}_2\text{Ti}_2\text{O}_7$, zirconate [$\text{AB}_2\text{O}_4$], and brannerite [$\text{Bi}_2\text{Ti}_2\text{O}_7$], where A = Ca$_2$, actinides, and lanthanides, and B = actinides, lanthanides, and Hf. This study reports data for a ceramic containing 0.14 wt% Al and 0.33 wt% Mo in addition to the major components present in the baseline ceramic (Ti, U, Ca, Hf, Gd, and Ce oxides; Buck et al. 1999). Hafnium and Gd are added as neutron absorbers. Al and Mo represent impurities. An electron microprobe was used to generate X-ray maps in order to reveal element distributions and textural relationships between the different phases. The data demonstrate that UO$_2$ is strongly partitioned into the pyrochlore structure, whereas most of the Mo and Al is found as euhedral crystals with inclusions of unreacted UO$_2$. Pyrochlore forms the groundmass and has an average UO$_2$ content of 28 wt%. Zirconate contains only 1.5 wt% UO$_2$, but is significantly more effective in accommodating U and Gd than both brannerite and pyrochlore, as demonstrated by the much higher U/Hf and Gd/U ratios. Zirconate accommodates U together with Hf in one structural site, whereas brannerite and pyrochlore incorporate U with Hf in a site that is distinct from that occupied by Hf. Incorporation of Gd into zirconate takes place via a coupling substitution involving Al, thus explaining the high Al$_2$O$_3$ contents (3 wt%). The Ti and Al distribution maps reveal the presence of additional phases, a Ti-rich ($\text{Ti}_2\text{O}_3$) and an Al-rich ($\text{Al}_2\text{O}_3$) phase. Transmission electron microscopy is currently used for identification and characterization. Molybdenum was not detected in the major oxides, and is probably present in these minor phases. Although the studied waste form was designed to incorporate Pu, the present dataset is valuable because immobilization of highly fissile U (e.g., U-233) might be needed to be considered in the future.


Zirconates have recently been proposed as hosts for Pu and other actinides due to their cubic (fluorite) structure, which renders them less susceptible to radiation damage than their pyrochlore/zirconolite structured titanate counterparts. Zirconates and titanates have been prepared with the nominal composition, Ca$_3$Gd$_2$O$_7$, $\text{Sr}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_7$ with Al and Ce, and Sr and Hf as minor excess hafnia plus rutile or zirconia. Samples of these zirconates and titanates with up to 1.5 wt% of potential Pu-process waste elements have also been prepared. The titmates tend to form pyrochlore as the major phase, whereas the zirconates form a fluorite. Very little of the impurities are accommodated in the fluorite with powellite, a spinel and a silicate glass appearing as extra phases. In the titmate samples the pyrochlore incorporates more impurities, with the remainder forming zirconolite, silicate glass, magnetoplumbite, perovskite and leucite. The oxide-route zirconate required sintering temperatures of about 1500°C to produce a dense product, 250°C higher than the sintering temperature required for the titmate. Silicate impurities reduce the sintering temperatures appreciably in both titmates and zirconates. Extended annealing of all the Ti-pyrochlores and the Ce-Ce-zirconate at ~1100°C had no effect on the composition or microstructure. However the Ti-pyrochlores were significantly transformed to pyrochlore. The results of $\text{Fe}$- and $\text{Mg}$-ion irradiation experiments performed at the 1VEM and 4EMS accelerators at ANL and PNL, respectively, will be discussed.

2:45 PM 112.6 IONIC SIZE LIMITS FOR A IONS IN BRANNERITE/Al$_2$O$_3$ AND PYROCHLOR-E/CA$_2$Ti$_2$O$_7$ TITANATE STRUCTURES. (A TETRAVALLANT RARE EARTHS AND ACTINIDES). Eric Vance, Molly Carter, Martin Stewart, Arthur Day, Cliff Ball,
The lower limit of the size of the octahedral ion in the $A_2O_2$ brannerite structure is just smaller than that of $Ce/Pu$. Attempts to expand the $A$ ion size beyond that of $Th$ by (a) substituting a $Ba$ ion plus two pentavalent $U$ ions for three $A$ ions or (b) substituting one $Ba$ plus one hexavalent ion for two $A$ ions did not succeed. $Ge$, $Sn$, and $Zr$ substitutions in the Ti site of brannerite do not exceed 0.2 formula units in ceramic preparations. Various attempts at single and coupled pressure synthesis data on different endmember brannerites are given. The lower and upper size limits for the eightfold $A$ ions in the pyrochlore structure are around 0.100 and 0.117 nm respectively. A BaTi$_2$O$_5$ stoichiometry did not produce a pyrochlore structure, and when fired in either argon or air it yielded a mixture of BaF$_2$O$_3$, whose structure is still uncertain, plus brannerite and rutile.

SESSION 33: RADIATION EFFECTS
Chairs: William J. Weber and Katherine L. Smith
Monday morning, November 26, 2001
Republic B (Sheraton)

3:30 PM #113.1
RADIATION EFFECTS IN CRYSTALLINE OXIDE HOST PHASES FOR IMMOBILIZATION OF ACTINIDES
William J. Weber
Pacific Northwest National Laboratory, Richland, WA, Rodney C. Ewing, The University of Michigan, Dept. of Nuclear Engineering & Radiological Sciences, Ann Arbor, MI,

Radiation effects from alpha decay in crystalline oxide host phases for the immobilization of actinides generally leads to amorphization, macroscopic swelling and increases in dissolution rates for nearly all phases currently under consideration. The results of computer simulations, new models, and experimental studies using short-lived actinides and ion-beam simulations over the past 20 years will be presented to highlight the state-of-the-art understanding and predictive models on amorphization, spontaneous, induced pyrochlores, and pyrochlore/fluorite structures of current interest. One of the successes of these studies is the discovery of a glass of radiation-resistant pyrochlore/fluorite structures that can serve as highly durable, radiation resistant host phases for the immobilization of actinides.

4:00 PM #113.2
ION-INDUCED AMORPHIZATION OF MURATAITE
Jie Liu, University of Michigan, Ann Arbor, MI, Sergey V. Yadudin, IGI RAS, Moscow, Russia, Sergey V. Stefanovskiy, Olga I. Kirsanov, SIA Radon, Moscow, Russia, Rodney C. Ewing, University of Michigan, Ann Arbor, MI,

Murataite $A_2B_2C_3O_{22-}$ where $A = Na^+$, $Ca^{2+}$, $REE^{3+}$, $An^{4+}/An^{5+}$, $B = Sr^{2+}$, $Zr^{4+}$, $C = Ti^{4+}$, $Fe^{3+}$, $Al^{3+}$, $0 < g < 1$, is cubic fluorite-structured phase potentially suitable as phase for rare earths and actinides with actinides as $B$-site elements. The compound is $B$-site metal rich and similar to the $A_2B_2O_4$ fluoride structure. Amorphization of murataite by $1 \text{MeV}$ $Kr^+$ ion irradiation in three ceramic samples proposed for actinide waste immobilization was studied. The $1 \text{MeV}$ $Kr^+$ ion irradiations were performed at room temperature using IVEF interfaced with a Trumbin ion accelerator at Argonne National Laboratory. Radiation damage was observed by in-situ TEM. Initially, the irradiation caused disordering of the murataite structure. Murataite was rendered fully amorphous at doses of $(1.7 \pm 0.1) \times 10^{17} \text{ions} / \text{cm}^2$ (approximately 0.2 dpa). Similar observations were obtained in the cold crucible melted sample. The susceptibility of murataite ceramics to ion irradiation induced damage increases in this order: murataite-$SC^\prime$ $\leq$ murataite-$SC$ $\leq$ murataite-$SC^\prime$. The pyrochlore structure phase is slightly more radiation resistant to ion irradiation than the murataite structure phase with similar chemical compositions. $Ce$ ($\geq$11 wt % in murataite and $\geq$28 wt % in pyrochlore) ion has significant effects on the radiation resistance of pyrochlore and murataite phases and the critical amorphization doses ($x \times 10^8 \text{ions/cm}^2$) from $2.4 \sim 1.8$ for pyrochlore and from $1.8 \sim 1.7$ for murataite.

4:15 PM #113.3
MOLECULAR DYNAMICS SIMULATIONS OF VOID STABILITY IN AMORPHOUS Si, Maria Okonowski, Brent J. Heusler, Yixin Anderkman, Robert S. Averback, University of Illinois, Urbana, IL,

We have begun a research program to investigate the effect of radiation damage and helium (He) production in simple borosilicate glasses. As part of this program, molecular dynamics (MD) simulations of the radiation damage process in amorphous Si has been performed. A Si was chosen as a model material that will capture the salient features of the radiation damage process and the effect of He. The decay of Pu in a nuclear waste yields a 5-6 MeV alpha particle and a 50-100 keV heavy-ion recoil, both of which can create significant damage. It is well known that He stabilizes voids against collapse in metals; a similar scenario in glass waste forms could reduce the lifetime of this storage medium. The nature of the radiation damage process in glasses is unknown, particularly the influence of the evolution of He bubble formation. We have performed MD simulations of void stability during displacement cascade formation, with and without He. These simulations also provide information on pressure during localized heating in the vicinity of the cascade. MD simulations have been performed with the parallel MD code PARCAS. Discussion of our results will focus on i) void stability with and without He and ii) temperature/pressure evolution during the displacement cascade process.

This work was funded by the DOE NEER program under grant DE-FG05-99ID14121.

4:30 PM #113.4
STRUCTURAL INVESTIGATION OF ION IRADIATED SIMULATED HIGH-LEVEL WASTE GLASS

Radiation effects of HLW glass containing crystalline phase have not been extensively studied. In this study, heat-treated MS-7 glass that is a simplified version of a typical Hanford HLW glass with a TL of 1000 is incorporated into a number of spinel crystals was used to investigate the unique radiation effects. The composition of the base glass was (mass%); 8.0 $Ar_203$, 7.0 $B_203$, 0.3 $Zr_203$, 11.5 $Zr_203$, 5.4 $Li_203$, 0.6 $MgO$, 0.5 $Na_20$, 13.5 $So_20$, 0.35 $SiO_2$, 45.3 $SiO_2$, and 6.0 $Zr_2O$. These glass samples were irradiated using 2 MeV $A=24$ ions to the fluences ranging from $3.4 \times 10^{16}$ to $1.25 \times 10^{17}$ ions/cm² at room temperature. After the irradiation, the samples were characterized using Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), and Raman spectroscopy at Pacific Northwest National Laboratory (PNNL) and x-ray absorption spectroscopy (XAS) using the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). Preliminary XAS results indicate that Fe occupies a tetrahedral site in a radiation induced amorphous state where a larger number of non-bonding oxygen atoms exists in the base glass matrix. On ion irradiation, a second Fe is partially reduced to divalent Fe and occupies an octahedral site. The Fe is more loosely bound to oxygen atoms and hence the number of non-bonding oxygen is smaller, as seen from a reduction in the pre-edge peak in the oxygen K-edge spectra. The change in the oxidation state significantly shifts the Fe L-edge to lower energy in the irradiated glass compared to the base glass. These results will be discussed and compared to other results from RBS, SEM, and Raman spectroscopy.

Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences and Biological and Environmental Research, and the Environmental Management Science Program.

4:45 PM #113.5
RADIATION DAMAGE IN TITANATE CERAMICS USED FOR PLUTONIUM IMMobilization
D.M. Strachan, R.D. Scheele, W.C. Buchmüller, R.L. Sella, and R.J. Ekelund, Pacific Northwest National Laboratory, Richland, WA.

As part of the waste form qualification activities for plutonium immobilization, radiation damage experiments are being conducted. One of the assumptions in the safety case for the repository is that a criticality will not occur after the material has been exposed to water. In 1999, approximately 100 specimens were made that contain approximately 10 mass% $^{239m}PuO_2$ and approximately 100 sister specimens that contain about 10 mass% $^{239}PuO_2$. The Pu was incorporated into five minerals or mineral mixtures: pyrochlore, zirconolite, pyrochlore-rich (some zirconolite and brannerite), zirconolite-rich (some pyrochlore and brannerite), and pyrochlore-rich mineral with many of the impurities expected in the feed to the immobilization plant. These minerals were made from the mixtures of oxides and carbones of the constituents and by sintering the mixture at 1350°C for a minimum of 4 hours. Some specimens of pyrochlore and zirconolite were sintered at an additional 100 hours at 1350°C to enhance the crystalline grains. The specimens are stored at room temperature with the $^{239}Pu$ specimens characterized every six months to determine the effects of radiation and temperature. Characterization consists of density measurements, determining releases during a 3-day MD test, photography, and X-ray diffraction. X-ray diffraction results to date show that the pyrochlore mineral has been rendered amorphous in one year, size and dissolution test results indicate that
the zirconolite-rich ceramic is most affected. Zirconolite appears to be less susceptible to structural damage. The radiation damage results are different from what was expected from the heavy ion bombardment experiments reported in the literature. The release of Pu from the \(^{239}\)Pu-bearing ceramic is about 100 times higher than from the \(^{239}\)Pu-bearing ceramic. The densities of the ceramics have been decreased by the neutron exposure. The zirconolite-rich ceramic at 250°C than at 25°C, an unexpected result.

**SESSION J14: PERFORMANCE ASSESSMENT**

**HLW**

Chair: David W. Esh and Allan B. Hedin

Tuesday Morning, November 27, 2001

Republic B (Sheraton)

8:30 AM *J14.1*  
**TOTAL-SYSTEM PERFORMANCE ASSESSMENT FOR THE YUCCA MOUNTAIN SITE.** Michael L. Wilen, Peter N. Swift, Sandia National Laboratories, Albuquerque, NM; Jerry A. McNabb, S. David Sevcougin, Duke Engineering and Services, Las Vegas, NV.

Yucca Mountain, Nevada, is being studied as a potential site for disposal of high-level radioactive waste. The site has been the subject of an extensive site characterization effort, and a series of total-system performance assessments (TSPAs) has been conducted over the past decade, with increasing complexity and detail in the models used for the assessment. A general approach for conducting a TSPA is to identify and screen potentially relevant features, events, and processes to develop the scenario, develop models, estimate parameter ranges and uncertainties, perform calculations, and interpret results. Some of these steps can be carried out in parallel, and the procedure generally must be repeated iteratively as knowledge is gained. The TSPA model for Yucca Mountain includes numerous submodels for natural systems, engineered systems, and the interactions between them. Disruptive events are also modeled (primarily igneous activity, but with consideration of other possible disruptive events as well). As implied by step [3], we use a probabilistic approach, in which uncertainties are propagated through the system so that the effects of uncertainties on the final results can be analyzed. The most recent TSPA analyses have been conducted in support of a preliminary site-suitability evaluation. If the site is found to be suitable, it is recommended that further TSPA analyses be conducted to support the license application. Results to date show that risk is dominated by igneous activity at early times because the robust waste-package design prevents significant nominal (non-disruptive) releases for tens of thousands of years or longer. The peak dose in the model occurs hundreds of thousands of years in the future, and is dominated by nominal processes, including waste-package corrosion, infiltration and seepage of water, and radionuclide dissolution.

This work was supported by the Yucca Mountain Site Characterization Office as part of the Civilian Radioactive Waste Management Program, which is managed by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94-AL85000.

9:00 AM *J14.2*  

In preparation for coming site investigations for siting of a deep repository for spent nuclear fuel, SKB in 1999 reported the long-term safety assessment SR 97, requested by the Swedish Government. The repository is of the KBS-3 type, where the fuel is placed in glassed ceramic high-strength canisters. The canisters are surrounded by bentonite clay in individual deposition holes at a depth of 500 m in granite bedrock. Geological data are taken from three sites in Sweden to shed light on different conditions in Swedish granite bedrock. The future evolution of the repository system is analyzed in five scenarios, treating the unperturbed evolution, initial disruptive canisters, climate change, earthquakes and future inadvertent human intrusion. The principal conclusion of the assessment is that the safety aspects of building a deep repository for spent nuclear fuel in Swedish granite bedrock are good. The results of the assessment have also served as a basis for formulating requirements and preferences regarding the design and construction of a site investigation for and for prioritization of research. SR 97 has been reviewed both by an international group of OECD/NEA experts and by Swedish authorities. The NEA reviewers concluded that SR 97 provides a sensible illustration of the potential safety of the KBS-3 concept, and no issues were identified that need to be resolved prior to proceeding to the investigation of possible sites. The authors have worked in principal consistent with those of the NEA. Since SR 97, the methodology for probabilistic consequence analyses and for earthquake simulations have been further developed. Also, uncertainties and lack of knowledge were identified in SR 97 have strongly influenced the contents and structure of SRBs most recent research programme, RD&D-Programme 2001.

9:30 AM *J14.3*  
**OVERVIEW OF THE H12 PERFORMANCE ASSESSMENT IN PERSPECTIVE.** Kazunori Miyahara, Hitoshi Miyake, Tetsuo Kato, Keihiro Wakisagi, Atsushi Sawada, Yuki Iijima, Aki Takasa, Moritama Nagae, Hiroshi Uno, Japan Nuclear Cycle Development Institute (at present, 

*Tokai Corporation* 

*Nuclear Safety Research Association* 

*Nuclear Waste Management Organization of JAPAN*.)

The second progress report, H12, documented research and development progress for high-level waste disposal made since the publication of the earlier first progress report (H1) in 1999. The concept of geological disposal in Japan is similar to that considered in other countries, being based on a system of multiple passive barriers consisting of the geological environment and an engineered barrier system. The disposal system considered is generic, as neither host rock type nor siting area has so far been identified. The H12 performance assessment (PA) provided a test for the robustness of a system concept based on structural siting and design, taking account of a wide range of potentially suitable Japanese geological environments. The generic nature of the host rock in the H12 assessment means, however, that emphasis is placed very much on the strong near field performance. The assessment included a comprehensive evaluation of uncertainty and potential detrimental factors, including perturbations due to external events and processes. Uncertainty is addressed by a combination of alternative scenarios, alternative conceptual models and parameter variations used in deterministic calculations. This allows the significance of various types and scales of uncertainty to be investigated to improved system understanding. This can, in turn, include where effort is most concentrated in order to increase the reliability of future assessments and, possibly, reduce the level of conservatism in the analysis. Despite the considerable uncertainty at the current stage of the Japanese program, a safety case that is adequate for the aims of the assessment can be made by a strategy of employing conservatism where there is uncertainty and stressing the reliability and effectiveness of the performance of the near field. The aim of this paper is to present the H12 PA in a way which makes the PA process clearer and the implications of the results more meaningful both to workers within the PA field and to a wider technical audience.

10:30 AM *J14.4*  
**PERFORMANCE ASSESSMENT OF GEOLOGICAL DISPOSAL OF HIGH-LEVEL WASTE IN A PLASTIC CLAY FORMATION.** Jammont, Didier Maillot, Belgoscarc, Research Centre SCK-CEN, Waste & Disposal Dept., Mol, BELGIUM.

In Belgium the possibilities to dispose of high-level waste in the plastic Boom Clay formation are studied since 1975. Consequently many results of the site characterisation programme are already available. Various performance assessments have been carried out dealing with the disposal of high-level waste types arising from reprocessing and from direct disposal of spent fuel. The scenario analysis is based on a catalogue of features, events and processes (FEPs) having the potential to influence the behaviour of the repository system. Two main groups of scenarios are distinguished. The normal evolution scenario, of which a number of variants are considered, treats the FEPs that are about sure to take place. Altered evolution scenarios focus on FEPs having a probability of occurrence lower than one but that might drastically influence the performance of the repository system. For the consequence analyses a robust concept approach is introduced, which allows focusing the analyses on a limited number of well-characterised barriers and processes. The consequence analyses are completed with sensitivity and uncertainty analyses based on deterministic and probabilistic approaches. The main output variable of the consequence analyses is the dose. However, because it can be expected that future biodegradation will be very different from the present ones, alternative output variables are considered as safety indicators. Performance indicators help evaluating the contribution of each barrier to the performance of the integrated repository system. Clearly defined basic safety functions contribute to explain the functioning of the repository system to non-technical audiences and facilitate the interfacing between the performance assessment and the repository design.

11:00 AM *J14.5*  
**BUILDING THE SAFETY CASE FOR A DISPOSAL FACILITY**
FOR SPENT FUEL, HLW AND LONG-LIVED HLW IN SWITZERLAND. L. H. Johnson, J. W. Schneider and P. Zaisner, Nagra (Switzerland), United Kingdom, Management Ltd., UNITED KINGDOM; Peter Grabi, Vibiro-Consult AG, Brugg, SWITZERLAND.

Nagra, the national co-operative for the disposal of radioactive waste, is responsible for research & development, geological investigations, design studies and safety assessment studies leading to the development of facilities for the disposal of radioactive waste in Switzerland. For discharge of spent fuel and long-lived intermediate-level waste, the present focus is on developing the safety case for a proposed repository site in the Oppolzin Clay in the Zurich region (northern Switzerland). The methodology to develop a safety case requires an extensive evaluation of scientific understanding relevant to the disposal system under consideration, with particular attention to the issues of completeness and the justification for the inclusion or exclusion of phenomena from consideration. The methodology is designed to process and prepare information in order to develop arguments for the safety of the system that takes account of the known limitations in scientific understanding, including the issues of the evolution and treatment of uncertainties and the bias that may influence these. Based on the review, results are drawn that provide feedback to guide future stages of the programme, and a presentation of the safety case in which key assumptions and arguments are visible, transparent and traceable. The performance assessment methodology being developed for the Oppolzin Clay repository is outlined in order to illustrate the technical reasoning, the process, the synthesis of information on the components of the disposal system and their interactions, the management of uncertainty and the important elements of feedback that occur during the application of the methodology. The concept of the repository in presented, and examples are given of arguments that are being formulated, based on independent lines of evidence, to illustrate the important safety functions (safety functions) of the repository system.

11:30 AM *E34.6 GENERAL APPROACH USED IN THE PERFORMANCE ASSESSMENT FOR THE WASTE ISOLATION PILOT PLANT Bob P. Rechel, Sandia National Laboratories, Albuquerque, NM.

In 1978, only three years before the Materials Research Society began their special sessions on nuclear waste management, the citizens in southern New Mexico invited the Atomic Energy Commission (AEC) to explore the salt beds in the Delaware Basin for a site for disposal of radioactive waste. A year later, the AEC drilled two boreholes at a potential location. By 1976, a suitable site had been found for more detailed characterization. This site eventually became the Waste Isolation Pilot Plant (WIPP), a repository for disposal of transuranic (TRU) waste that was certified by the U.S. Environmental Protection Agency (EPA) in 1988. The EPA's decision was based primarily on the technical results of the performance assessment (PA) conducted by Sandia National Laboratories in 1996. This performance assessment was the culmination of four preliminary PAs conducted between 1989 and 1993. This paper discusses the technical approach and rationale of the PA conducted to support the performance of the WIPP certification. For these PAs, Sandia used detailed models for evaluating the performance of the repository under the USL conditions specified by the EPA. The use of models based on detailed descriptions of the system (in several dimensions). In addition, Sandia used most of these detailed models directly in the probabilistic synthesis of the repository behavior. This approach was facilitated by the use of a database, which allows access to detailed models. A neutral file format was used to store and process results between codes, and a suite of analysis that could process results from all codes once results were stored in the neutral file format. Several advantages were gained by using detailed models directly in the PA rather than using simplified models of these codes (e.g., using response surfaces). First, accepted mathematical formulations and algorithms, rather than simple response surfaces, are used. Second, more information about the behavior of the WIPP occurs at both the repository behavior level and at the regional level. Finally, the use of detailed models in the design of the repository behavior analysis is gaining increasing importance. The detailed models could rapidly accommodate this requirement without necessitating a new series of simplified models. In the future, the performance assessment results will be used to further improve the design of the repository behavior analysis. This approach was successful in that it could accommodate this requirement without necessitating a new series of simplified models. In the future, the performance assessment results will be used to further improve the design of the repository behavior analysis.
and 241Am present in the contaminated groundwater were negatively charged. The solid-liquid partitioning of these negatively charged species was significant to two orders of magnitude, compared to the values obtained with the tracers, 57Co, 134Cs, 239/240Pu and 241Am. The measurements with tracers are typical of conventional short-term laboratory Kd determinations, and they could overestimate contaminant retention, because the important 'active' aqueous species are not all represented in these measurements. The negatively charged species in the contaminated groundwater were stable over the duration of the experiments, which suggests that these aqueous species remain strongly adsorbed on the oxidized Fe oxides in solution. The adsorption, and can explain some of the radionuclide mobility observed in the field. This work was supported by a US-NRC subcontract through the Pacific Northwest National Laboratories.

2:00 PM I15.3
PREDICTION OF METAL PARTITIONING BETWEEN MINERAL/SOLUTION PHASES: AN IMPLICATION TO CONTAINMENT MATERIAL SELECTION FOR RADIOACTIVE WASTE DISPOSAL. Yifeng Wang, Sandia National Laboratories, Carlsbad, NM; Huijuan Qu, Dept of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM; Charles Bryan, Anna C. Siuder, Sandia National Laboratories, Carlsbad, NM.

Metal partitioning between authigenic minerals and aqueous solutions is an important chemical process for radioactive waste containment. In this communication, a linear free energy correlation model is developed to correlate metal partition coefficients with metal cation properties. Host minerals from an interstratified family have the same linear free energy relationship, as long as the relationship is expressed as a function of the differences in cation properties between substituent and host metals. The model has been applied to both isomorphous and non-isomorphous metal partitioning in carbonate minerals, and it closely fits the existing experimental data, thus demonstrating the robustness of the linear free energy relationship. Using this model, the partition coefficients of divalent and trivalent metals between various carbonate minerals and aqueous solutions are calculated. Magnesium is predicted to have the largest partition coefficients among the carbonate minerals with a calcite structure and therefore can be a good scavenger for toxic metals and radionuclides. The implication of model predictions to the Waste Isolation Pilot Plant (WIPP) is discussed. The fraction of radionuclides that can be potentially immobilized by magnesium carbonate minerals in the WIPP as a result of using MgO as a chemical backfill is evaluated. The model developed in this communication provides a useful tool for predicting unknown partition coefficients and thus helps select effective containment materials and waste forms for radioactive waste disposal.

2:15 PM I15.4
EFFECTS OF REACTOR DECONTAMINATION COMPLEXING AGENTS ON SOIL ADSORPTION. COLON STUDIES. R. Jeff Seime, Kirk J. Castrell, J. V. Kutrynak, and Chuck W. Fendlerman. Applied Geology and Geochemistry Section, Pacific Northwest Laboratory, Richland, WA.

Organic complexes of radionuclides have been implicated in several instances of unusual mobility of radionuclides in soils, especially percolating through sediments. Organic chelates have also been shown to lead to nuclear power plant decontamination efforts that end up being buried in shallow-buried landfills. Column experiments were conducted using two sediments, two organic complexants, and two contaminants [Ni²⁺ and PuO₂(bh₄)]. The influent solutions were a simplified groundwater. The organic and metal concentrations were picolinate 10⁻⁴, EDTA 10⁻⁵, Ni 10⁻⁵, and Pu 10⁻⁶ M, respectively. The organic complexants were spiked with radionuclides, CO₂, and 239Pu 2³⁹Pu. The columns were equilibrated with background electrolyte for 2 pore volumes. Then solutions containing the metal, complexant, and tracers were injected for up to 10 pore volumes through a large container with pore volume taken every few hours. Flow rates were held constant at 3 pore volumes per day. In some cases, injection of the metal/ligand was stopped and flushing was continued with the background electrolyte. After each column experiment was finished, the column was cut into 2 cm thick sections and extracted overnight with 1 M nitric acid to determine mass balance. The results show that picolinate concentrations have to be >10⁻⁴ M to significantly lower the adsorption of divalent transition metals [Ni and Co]. EDTA forms strong complexes with divalent transition metals and can stop adsorption of Ni and Co when EDTA concentrations are >10⁻⁵ M. Most other picolinate and EDTA-metal complexes appear to readily dissociate. As complexants migrate from the disposal facility, dilution and interaction with competing cations and adsorption reactions will result in dissociation of all but the strongest or most kinetically recalcitrant complexes. Conditions for enhanced migration include high concentrations of organic ligands, low concentrations of competing cations, alkaline pH, organic ligands with slow biodegradation rates and kinetically inert or very strong ligand-metal complexes. At high pH values such as that created by cementitious wastes, mobilization of Ni²⁺ and Ce⁴⁺ by EDTA becomes very significant and adsorption by sediments is essentially zero. Thus, we recommend that mixtures of metal/complexants and EDTA should not be co-disposed with high pH materials. For weaker organic complexants [picolinate, citrate and oxalate], co-disposal of decontamination wastes and concrete should be acceptable.

2:30 PM I15.5
DIFFUSION AND SORPTION OF RADIOACTIVE CESIUM AND COBALT IN REGOLITH MATERIALS OF CENTRAL AUSTRALIA. Takashi Ikeda, Gordon D. McGrath, Timothy E. Pedr, Australian Nuclear Science and Technology Environment Division, Menari, NSW, AUSTRALIA; Chin Jian Leo, University of Western Sydney Nepean, School of Engineering and Industrial Design, Kingswood, NSW, AUSTRALIA.

The movement of radionuclides in geological media can be driven by advection and diffusion. Diffusion can be the dominant process in clays and under arid zone conditions where advection is not significant. Preliminary studies have been performed to describe the diffusion and sorption of ¹³⁷cesium and ⁶⁰cobalt without the influence of advection, using saturated reconstituted samples of regolith materials from an arid region in Southern Australia. A simple column and two reservoirs made of polycarbonate resin were used to measure the transport of the selected radionuclides through the samples. A curve fitting procedure employing one-dimensional contaminant equations was used to estimate diffusion and sorption coefficients from measured concentration-time profiles. Results are compared with those obtained from batch sorption tests undertaken with the same samples under a range of chemical conditions. The application of transport parameters to the prediction of radionuclide transport is briefly discussed.

2:45 PM I15.6
STUDIES OF NEPTUNIUM(V) SORPTION ON CALCIUM FERROXASEROLITE ANALYSIS. F. Paul Bertetti and Bradley A. Welinger, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

The U.S. Department of Energy (DOE) is currently investigating Yucca Mountain (YM), Nevada as a potential site for geologic disposal of high-level nuclear waste. Delay of radionuclides during transport within groundwater has been identified as a principal factor in the DOE safety case, and is a key technical issue for the U.S. Nuclear Regulatory Commission (NRC). Neptunium-237 has been identified as a radionuclide of concern in analyses of performance of the proposed YM repository because of its relatively high solubility and the sensitivity of its saturated zone transport time to retardation factors used in modeling. Studies have suggested that Np-237 sorption on calcite, a mineral with widespread occurrence at YM, is enhanced relative to sorption on other common mineral phases. Nevertheless, little is known regarding the mechanism and potential for uptake of Np-237 on calcite. Batch experiments were conducted using a calcite substrate in solutions at or near saturation with respect to calcite over a pH range of 7 to 9, in equilibrium with atmospheric carbon dioxide, and with an initial Np concentration of 5.6 x 10⁻⁵ M Np-237. Results of the experiments indicate that sorption of Np-237 is significant below pH of ~8.2. The dependence of sorption on solution pH suggests that the speciation of Np-237 in solution plays a major role in the sorption behavior. Differences in sorption observed depending on the experimental protocol used (e.g., less sorption at pH 7.8 when calcite was added to solution after Np-237). A comparison of results from previous studies and considerations for modeling of the Np-calcite system are discussed. This work was conducted for the NRC under Contract No. NRC-02-97-0008. It is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.

SESSION I36: CERAMICS CORROSION

Chair: Boris B. Burakov and David B. Chamberlain

Tuesday Afternoon, November 27, 2001

Republic B (Sheraton)

3:30 PM I36.1
DURABILITY OF Pd-DOPED ZIRCONATE AND TITANATE CERAMICS FOR Pu DISPOSAL. Yuang Chang, King Ho, Bruce Begg, Zaiphan A. Al, Alan Brownstone, Arthur Day, Martin Stewart, ANSTO, AUSTRALIA.

Zirconates have recently been proposed as hosts for Pu and other actinides due to their cubic (fluorite) structure, which renders them less susceptible to radiation damage than their pyrochlore/rutile structured titanate counterparts. T₆ and Z₆ versions of the pyrochlore-rich ceramic [50wt% Ca₁₀₋₅Ga₂₋₅Hf₆₋₅Pu₂₋₅Ca₁₀₋₅] were synthesised in reducing conditions to lower the probability of Pu solubility. Complexing of Pu with Cl⁻ during synthesis was indicated by the incorporation of 129I as a tracer, the results of which were consistent with the formation of a stable Pu(IV)/Cl⁻ complex. Irradiation induced changes in the lattice parameters and cell volume for the T₆ and Z₆ phases were consistent with radiation damage models.
(Zr/Ti) 2O 5 1 wt% HEO 4 2 wt% (Zr/Ti)2O 5 prepared for Pu disposal were prepared by the standard alkoxide route. The final material was calcined as a powder in a range of argon atmospheres for 4 hours at temperatures between 1300 and 1500°C. An addition of 5 wt% of mixed impurities was made to some of the samples. Samples were characterised by XRD, SEM, alpha-spectrometry and leaching at 30°C in deionised water. The titanic preparations that were free of impurities consisted of brannerite and pyrochlore whilst the zirconate preparations had formed a single-phase leucite thorite. The zirconate preparations were sintered in argon at 1450°C for 20 h. Impurities were detected by TEM at some 150°C, higher temperature to achieve equivalent level of closed porosity. SEM indicated that there were more impurities in the pyrochlore-prepared sample than in the titanate-prepared sample. No impurities were detected in the pyrochlore-prepared sample. The leucite-doped sample was sintered at 1300°C and with impurities sintered at 1350°C. The lowest Pu leach rates were measured for the titanate and the pyrochlore impurities sintered at 1300°C and with impurities sintered at 1400°C, with impurities, and 1500°C, without impurities.


Recent theories for dissolution of solids into aqueous solutions focus on analogies with ligand-exchange reactions between aqueous complexes and the solid surface. Some of these theories have been found to be useful in providing insights into the reactivity of solids in a homologous series containing mono- or divalent cations. The applicability of these theories to a family of solids containing cations of higher valence is not clear, however. We performed a series of dissolution experiments with well-characterized pyrochlore ceramics with the formula A2Ti4O8, where A = Y3+, Gd3+ or Lu3+ in pH 2 solutions at 90°C. By XRD analysis showed that all three compositions are chemically stoichiometric, as revealed by electron microprobe analysis. Analysis by Raman spectroscopy, however, indicates that some of the Ti4+ ions are replaced by Ti3+ ions, and that the three compositions are not chemically stoichiometric. Evaluation of the thermodynamic stability of the three solids was performed using a linear free-energy model and reported enthalpies and entropies of formation. This indicates that the thermodynamic stability of the samples could, by itself, explain the trend in dissolution rates. Our data indicates, therefore, that dissolution models based on ligand-exchange reactions may not be strictly applicable to simple pyrochlore minerals.

4:00 PM JIE6.3 A STUDY OF Bi-DOPED ZIRCON ALTERNATION UNDER HYDROTHERMAL CONDITIONS. Boris Barnev, Elena Nikoleva, Maria Yavogkina, the V. K. Kholkin Radon Institute, St. Petersburg, RUSSIA; Rodney Ewing, Michigan Univ, Ann Arbor, MI; Werner Latzke, Univer New Mexico, Albuquerque, NM.

Plutonium doped ceramic based on zircon structure, (Zr-Pu)SO4, is the subject of investigation as a durable ceramic waste form for the immobilization of weapons grade plutonium and other actinides. Complexes of Pu4+ and Pu3+ with Zr4+ in samples prepared from solution with insignificant excess of Zr to prepare a final yield of zircon phase less than 95 wt. % with the remainder as zirconium metal formation of silicon or PuS2Cate. The material was dried at 70°C and calcined at 700°C for 12 h. The obtained material was milled in a agate mortar and cold pressed into pellets of 10 mm in diameter. Then the pellets were sintered in air at 1450°C for 4 hours followed by 1500°C for 3 hours. In accordance to X-ray powder diffraction analysis (XRD), the materials consisted of [in wt. %]: zircon-95.06; monoclinic zirconia-1.3; tetragonal zirconia-3.5. Electron probe microanalysis (EPMA) has shown that zircon contained 6.1 wt % Pu. The sizes of zirconia grains were too small (less than 5 microns) to provide precise XRD and electron diffraction data. The solution of ceramic was milled in agate mortar and split off two equal parts. One part of ceramic powder was placed in special teflon vessel into water and set at 120°C for 48 days. Then the initial and altered powders were characterized by magnetic susceptibility, THz and powder diffraction. The determination of zircon unit cell parameters. No differences of XRD spectra of initial and altered samples were observed. Zircon unit cell parameters were determined using synchrotron X-ray diffraction for present sample. Although the decrease of parameter was detected, no traces of resolved Pu-oxide were found on XRD spectrum of altered sample. The results obtained confirm the high resistance of Pu-doped zirconium ceramic under hydrothermal conditions.
trends whereas current practice involves disposal to concrete vaults. Disposals are carried out under an authorization from the UK Environment Agency (the Agency) which reviews the authorization to ensure consistency with current regulatory requirements. BNFL will produce in 2002 an updated PCSC. In preparation for this, BNFL published in March 2000 a status report on the development of the PCSC. The Agency conducted an information exchange process on the development of the PCSC. This process has led to notable improvements, as well as offering a mechanism for providing clarifications and building confidence in the PCSC. The BCNPL undertakes communication activities including scientific conferences, conference presentations, participation in international conferences (such as those of IAEA and NEA) and liaison with local communities. The PCSC will also benefit from peer review mechanisms of the Central to the safety case, is a systematic process that promotes transparency and traceability and demonstrates a rigorous treatment of relevant uncertainties. The approach aligns with international best practice for near-surface disposal facilities and includes the assessment of features, events and processes and the use of tools such as conceptual model uncertainty forms. This formulation helps to identify and understand the key factors for the PCSC. Additional qualitative or simple quantitative information is used to augment the PCSC so as to provide a wider context to inform decision-making.

9:30 AM *#117.3 IMMOBILIZED LOW-ACTIVITY WASTE PERFORMANCE ASSESSMENT. 2001 VERSION. Frederick M. Mann, Ciem Hill Hanford Group, Inc.; Raymond J. Feigh, S.H. Fabrik, R. Khaleel, Fluor Federal Services, D.H. Bacon, M.P. Heggen, A.G. McGrail, S.K. Wartman, Pacific Northwest National Laboratory, Richland, WA. At the U.S. Department of Energy Hanford Site, 1.77 underground tanks hold over 54 million liters of high-level-radioactive, mixed waste. The current plans are to recover over 99% of this waste, separate it into two streams (the high-level waste stream and the low-activity waste stream), and vitrify both streams. The immobilized high-level waste will be stored at the Hanford Site until it is shipped to a federal geological repository. The immobilized low-activity waste (ILAW) will be disposed on the Hanford Site. Before the ILAW can be disposed or disposed facilities constructed, the Office of Environmental Management must issue a permit, known as a Disposal Authorization Statement (DAS). A major basis for this decision is a performance assessment (PA) that needs to show with reasonable assurance that the public health and safety and the environment will be protected. In 1998, an ILAW PA was issued on regional environmental information. A DAS for the entire Hanford Site was issued in 1999 and it included the disposal of ILAW. However, since 1998, important changes have occurred to the ILAW program: different facility concept (concrete vaults to trenches), different waste forms (high-temperature glass to low-temperature glass), and the collection of disposal site-specific geotechnical information. Based on these new data, 16 new data packages have been released. New calculations have been performed, resulting in an estimated reduction in groundwater impact of over a factor of 10 since the 1998 ILAW PA. The 2001 version of ILAW PA is now undergoing review by the Low-Level Disposal Facility Federal Review Group (with a final decision promised by September 2001).

10:00 AM #117.4 STOCHASTIC ASSESSMENT OF NUCLEAR WASTE MANAGEMENT PRACTICES AT THE HANFORD SITE. Washington, Charles T. Kincade, Paul W. Fislinger, William Nichols, Robert Bryce, and Amoreta Bunn, Pacific Northwest National Laboratory, Richland, WA. Waste management and disposal decisions at the Hanford Site, Washington, depend in part on an understanding of the risks and impacts associated with alternative disposal and remedial actions. An initial proof-of-principle site-wide assessment of the risks and impacts associated with all past, present, and future related to the Hanford Site has been performed for the first time. It simulates contaminant release, migration, and fate from today forward, and thus illustrates near-term influences on long-term risk and impact. A stochastic simulation tool capable of addressing 1000 waste disposal and disposal sites and 10 contaminant transport for a period of 100 years has been created and applied. Risk and impact are estimated in four dimensions: human health, ecological health, socioeconomic impact, and cultural impact. The methodology developed is known as the System Assessment Capability (SAC). An initial assessment based on the planning baseline of the Department of Energy (Richland Field Office and Office of River Protection) has been completed. Results of the assessment reveal the relative significance of the release, migration, and fate of waste practices: liquid and solid, known impacts to unknown, current and planned practices of solid waste and vitrified tank waste disposal, and
ASSOCIATED WITH THE TONO URANIUM DEPOSIT, JAPAN. R. Arthur, Monitor Scientific, LLC, Denver, CO; T. Iwasaki, K. Ueno, T. Kota, T. Kato, Japan Nuclear Cycle Development Institute, Tokai, JAPAN.

Field investigations supporting the Tono Natural Analog Project are aimed at characterizing hydrogeological and geochemical processes that have effectively immobilized uranium within the Tono uranium deposit in Gifu Prefecture, central Japan, for about 10 million years. An unconformity underlying the deposit represents the approximate location of a redox front separating relatively oxidizing waters (Eh > 0 mV) in the weathered, fractured Toku granite from strongly reducing pore fluids (Eh < -300 mV) in sedimentary rocks of the overlying Lower Toku Lignite-bearing Formation (TL), which hosts the uranium ore body. Groundwater models and recent ages of groundwater from the granite basement rocks and overlying sedimentary formations suggest that pore solutions in the TL are derived in part from groundwater that has migrated over long distances along the unconformity. The associated, upwelling transport of uranium across the redox front, followed by reduction of U(VI) to U(IV) in the TL, may have been continuous during the past 10 million years, but there is little or no evidence of concurrent front movement into the sedimentary formation. This suggests that oxidation-reduction reactions involving pore fluids, minerals, organic matter and microbes in the TL generate an intrinsic redox-buffering intensity and redox-buffering capacity that has effectively resisted any significant change in the reducing nature of this formation for millions of years. Slightly and reversible in situ redox potential measured in boreholes penetrating the granite and sedimentary rocks appear to be controlled by the Fe(III)-Fe(II) redox couple. Fifty micron-scale crystallinity of the oxyhydroxide varies from freshly precipitated amorphous Fe(OH)3 to fine-grained goethite, or to a mixture of Fe(OH)3 and goethite. Equilibrium of the strongly reducing groundwaters with pyrite appears to control dissolved Fe(II) concentrations in these solutions. Irreversible weathering of biotite/diopside may control Fe(III) concentrations in the relatively oxidizing groundwaters.

11:15 AM J18.4

NATURAL COLLOIDS IN GROUNDWATER FROM A BENTONITE MINE - CORRELATION BETWEEN COLLOID GENERATION AND GROUNDWATER CHEMISTRY

Hiroshi Kuno, Gento Kanei, JNC, Waste Isolation Research Div., JAPAN; Hiroki Otani, Kumime Industries Co., Ltd., Research Lab., JAPAN.

Colloids caused by erosion of compacted bentonite by groundwater flow might enhance the transport of radionuclides from the radioactive waste repository. As a natural analogue of the colloidal generation process, we investigated the groundwater dripped at the interface between bentonite bed and argillaceous rock bed (Tertiary age), cropped out at four galleries (depth range from 30 to 180 m above the sea level) in the Tsukinomori bentonite mine, northern Japan. Groundwater and filtrates separated by ultrafiltration (MWCO 10 kDa) were analyzed to determine the size, concentration, and chemical composition of colloidal particles. The major ions in groundwater are free Na (4-10 mM), carbonate (0-3 mM) and sulfate (0.2-1.2 mM). The colloidal particles were not detected in the groundwater sample 1 (collected at 180 m above the sea level) and 4 (similarly, at the same depth). The groundwater suspension was collected in case of the samples 2 (at 90 m) and 3 (at 30 m), whose concentrations of the suspended particles corresponded to 100 and 800 mg/L, respectively. Most of the particles in these samples consist of hematite, goethite and maghemite, identified by magnetic measurements. The concentrations of the particles that are similar to those of brown carbonatite, which are unstable in groundwater due to ion strength, increase to a larger value than about 0.01. This is consistent with previous laboratory measurements indicating the dependence of ionic strength on the colloidal stability.

11:30 AM J18.5

IN SITU ISOTOPIC ANALYSIS OF URANIUM MICROTEXTURES FROM THE OKLO AND OKLOBONO NATURAL FISSION REACTORS

Mustafah Engel, University of Tennessee, Dept of Geological Sciences, Knoxville, TN; Keld A. Jensen, National Institute of Occupational Health, Denmark; John Rudolph, Rodney C. Ewing, Dept of Nuclear Engineering & Radiological Sciences, University of Michigan, Ann Arbor, MI; Lee R. Rigguti, ORNL, Oak Ridge, TN.

Uranium deposits, by analogy, can provide important information on
the long-term performance of radioactive waste forms because uranium (UO₂+X) is structurally and chemically similar to the UO₂ in spent nuclear fuel. The environments that host the Oklo-Oklohbondo U deposits, Gohan, serve as important natural laboratories where the long-term (thousands to billions of years) migration of uranium and other radionuclides can be studied over large spatial scales (m to km). The natural fission reactors associated with the Oklo-Oklohbondo U deposits occur over a range of depths (100 to 400 m) and provide a unique opportunity to study the behavior of uranium in near surface oxidizing environments versus more reducing conditions at depth. Previously, it has been difficult to constrain the timing of interaction between U-rich minerals and post-depositional fluids. These problems are magnified because uranium is susceptible to alteration, continuously self-screening radiation damage, and because these processes are manifested on the mm scale. However, uranium, lead and oxygen isotopes can be used to study fluid-uraninite interaction, provided that the analyses are obtained on the micro-scale. Secondary ionization mass spectrometry (SIMS) permits in situ measurement of isotopic ratios with a spatial resolution on the scale of a few mm. Preliminary results show that uranium from all reactor zones are highly discordant with Pb-Pb ages ranging from 40 Ms to 1800 Ms. Oxygen isotopic analyses show that uranium from reactors that occur in near surface environments (δ¹⁸O = -14.4% to -8.5%) have reacted more extensively with groundwater relative to reactors located at greater depths (δ¹⁸O = -10.9% to -7.3%). These data show that important information can be obtained from natural analogue studies provided that high spatial resolution analysis techniques are utilized.

11:45 AM J18.6
Systems Analysis provides a framework for most performance/analytical assessments addressing radioactive waste disposal, but is also being applied successfully to a natural analogue project. The Tono uranium deposit (Gifu Prefecture, central Japan) was formed about 10 million years ago and available evidence suggests that this deposit has been preserved in its host sedimentary formation, i.e., uranium has not migrated significantly since then. Substantial field and modeling work is being carried out to better understand the hydrogeological and geochemical processes of uranium migration and retardation in and around the Tono uranium deposit. Systems Analysis provides a convenient framework for this project, being used to:
- develop possible scenarios for how the deposit developed,
- link field characterization and the data gathered from these activities with predictive modeling, and
- identify gaps in data and, hence, additional characterization needs.
Interesting differences exist between predictions associated with this project and those obtained for repository evolution. For example, predictions for the latter are made into the future, the uncertainty in such predictions increasing with time. On the other hand, the state of the Tono uranium deposit is being investigated back from the present, the corresponding uncertainty increasing in the reverse direction. The common factors are the same, however, is the starting point is the present day, at which time most is known about the site. The key elements of the Systems Analysis approach, as they relate to the Tono Natural Analogue Project, are discussed in this paper, viz. definition of the system to be analyzed; identification of features, events and processes (FEPs) associated with this system; identification of external factors (EFs) which are likely to have influenced the area involving the Tono uranium deposit; interactions between pairs of FEPs; and development of credible scenarios for site evolution.

SESSION J39/KK8: JOINT SESSION CEMENTS IN RADIOACTIVE WASTE MANAGEMENT
Chair: Kenneth A. Snyder Wednesday afternoon, November 28, 2001
Republic B (Sheraton)
130 PM #190.1/KK8.1
CHARACTERIZATION OF THE BARRIER PERFORMANCE OF CEMENTS. P. P. Glassier, Univ. of Aberdeen, Aberdeen, Scotland, UNITED KINGDOM
Anniversaries are a good time critically to review progress, in this instance, quantifying the barrier performance of cement materials in nuclear waste repositories. Portland cement has intrinsic advantages in this application: persistence in nature, low solubility and ease of fabrication, either in situ or precast. Its disadvantages include inherent brittle properties and possible reactions with other types of encased barrier materials. Research leads to the conclusion that the principal advantage of cements lies in their chemical properties: they complex and react with waste species forming solubility-limiting solids. Examples are given to show how cements can be tailored to enhance their long-term immobilization potential for specific radionuclides. However, after 25 years it is still not possible to give a comprehensive and quantitative description of reaction sequences and their evolution with time and temperature. A wish list to address missing or incomplete data is presented. The present showdown in activity affords opportunity to research the next generation of chemical barriers and quantify their performance.

2:00 PM J39.2/KK8.2
PRACTICAL MODEL TO EVALUATE DURABILITY OF CEMENT-BASED MATERIALS UNDER LEACHING, COUPLING WITH INTERNATIONAL DATA BASE. Shou Kamal Laboratory of Mechanics and Technology, Cachan, FRANCE. 2. LEAF/Onondah, Laboratory of Mechanics and Technology, Cachan, FRANCE, Electricité de France, Moret sur Loing, FRANCE. Michelonne Moreauville, Laboratory of Mechanics and Technology, Cachan, FRANCE.
The concrete leaching by water damages and reduces the service life of structures like radioactive waste repositories, water pipes and dams. This study develops a practical model to provide decision making in design and diagnosis of concrete structures which may be submitted to leaching. It consists on the prediction of the leaching kinetics according to material and environmental characteristics. The model assumes that the leaching kinetics follows a square root-law as a function of time. Each parameter is introduced as a weight function. The model is based on international experimental published data dealing with the effect of water-to-binder ratio, silicate fume content, aggressive solution pH, temperature. These data are compiled by other authors in order to introduce the effect of the cement type (Portland cement, silicate fume cement, fly ash cement, blast furnace slag cement) and of the interaction between the cement and water-to-binder ratio. Finally, the model is analysed and applied to practical recommendations.

2:15 PM J39.3/KK8.3
A SOLID SOLUTION MODEL FOR SORPTION OF RADIONUCLIDES IN CEMENT. Andre T. Enoki, Chalmers University of Technology, Dept of Nuclear Chemistry, Goteborg, SWEDEN.
Cement consists of a considerable number of phases, the two most important of which are the gel phase and a phase that is almost pure portlandite, calcium hydroxide. Both can be considered as solid solutions. This means that they are able to have a variable chemical composition. This also gives a possibility for the phases to incorporate different elements into their structure. Of these two phases, portlandite is rather compact while the gel phase has a very irregular structure, probably fractal. This suggests that sorption essentially takes place as adsorption in the gel phase. When this is correct, the sorption capacity could be expected to be large enough to make the contribution from other mechanisms, e.g., adsorption, negligible. In the present work, a model for multi component solid mixtures has been developed, essentially following the Guggenberger's enthalpy approach. Measurement of Kd for one gel composition makes it to calculate Kd values during the entire process of cement degradation. The main limitation is that the concentration of the radionuclide has to be low enough for all higher terms in the series expansion to be negligible. The model is mostly valid for elements forming cations and it also requires the sorbed element to form a compound of reasonably low solubility with one of the ions in cement (hydroxide or silicate). This means that it can be used essentially for metals. Kd values from the literature have been used to calculate thermodynamic properties of some solid mixtures.

3:30 PM J39.4/KK8.4
STABILITY OF HYDROCERAMIC WASTE FORM DURING VHT TESTING. Barry E. Schenck, Michal W. Gutrecht, Johnson Oronzwu, Delil M. Roy, Materials Research Institute, The Pennsylvania State University, University Park, PA; D. Daryll Siemer, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.
Immobilization of INEL waste by the reaction of alkali and an aluminosilicate zeolite to form a hydroceramic waste form has been developed over the past ten years by this research team. Subsequent research has documented the rate of formation as well as the stability of the resulting waste form and its ability to sequester the hazardous radionuclides and RCRA elements contained in the calcine. Typical hydroceramic formulations were prepared and subjected to testing following the VHT protocol developed at Argonne National Laboratory - East. This test protocol maintains the test specimen in
SESSION JJ10: CONTAMINANT TRANSPORT II
Chairs: Shao V. Muttigod and Joong Ho Ahn
Wednesday Afternoon, November 28, 2001
Republic B (Sherron)

3:30 PM JJ10.1
USING LINEAR FREE ENERGY RELATIONSHIP TO PREDICT ACTINIDE PARTITIONING BETWEEN GEOThETIC AND AQUEOUS PHASES. Hai-Fu Yang, Du, Dept. of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM; Xing Wang, Sandia National Laboratories, Carlsbad, NM.
Coppertization of trace metals and actinides in authigenic minerals of goethite, hematite and calcite will incorporate ("freeze") trace metals into stable solid phases. However, there are no such data for partitioning coefficients of actinides. It is of great interest to predict the partitioning coefficients based on theoretical model. In this paper, a linear free energy relationship describing Yang and Xu (Geochimica et Cosmochimica Acta 65 (2001), 1529) is extended to predict trivalent metal partitioning between goethite and aqueous phase. The partitioning coefficients for REE, trivalent actinides and other cations have been calculated. High-resolution transmission electron microscopy results show that as the crystallization rate increases, crystallinity of goethite also decreases. It is predicted that the partitioning coefficients for trivalent REE and actinides increase. Similar relationship can be also derived for the metal partitioning between hematite and aqueous solution. The constrained relationship can be used to systematize the existing experimental data and to predict unknown metal partitioning coefficients.

3:45 PM JJ10.2
INFLUENCE OF HUMIC COLLOIDS ON THE CONTAMINANT TRANSPORT IN NATURAL SYSTEMS. Wolfgang Busch, Robert Artinger, Bernhard Kienzler, Horst Geckens, Thomas Rahung, Jo-He Kim, Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, Karlsruhe, GERMANY; Dieter Klotz, Institut für Hydrologie, GSF Forschungszentrum, Neuherberg, GERMANY.
Applicability of laboratory results to natural systems is a crucial point in safety assessment of waste disposal. The problems arising using laboratory results to predict real repository situations are discussed on the basis of the humic collloid-borne contaminant transport. As an example this paper these questions are addressed with respect to the humic collloid-borne contaminant transport. It is shown, that a thermodynamic equilibrium approach is not suitable to describe consistent laboratory batch and migration experiments with Ca(II) and Am(III) in humic rich groundwater and in systems. In contrast, a kinetic model using the total colloidal humic colloidal interaction (KICAM) enables the consistent description of data and migration experiments in the time frame from several hours up to several months. The experiments show that the humic colloidal borne metal ion migration can be up scaled from 0.5 min to 10 m.

Furthermore, the fraction of humic colloids borne metal ions correlates with the migration time. This enables the simplification of the formulation of the humic colloidal bore metal ion transport in PA, i.e. metal ion surface interactions have to be not to be regarded in detail. Furthermore, due to the strong sorption of trivalent metal ions to humic colloids and sediment surfaces only the unengaged humic colloidal borne migration has to be considered in PA. However, the investigations revealed the fundamental problem of the temporal up scaling of laboratory data to PA relevant time scales. In some cases the investigation of natural samples or natural analogues can be a way out of this problem. In case of humic colloid bound migration of trivalent metal ion sorption experiments of metals bound to natural humic substances allows to define an upper limit for the worst case scenario in PA modeling. This does not solve the up scaling problem but it enables conservative PA calculations.

4:00 PM JJ10.3
RADIONUCLIDE UPTAKE AND TRANSPORT ON MICROBES IN REPOSITORY DRIFTS AT YUCCA MOUNTAIN, NEVADA. Darren M. Molloy, Duke Engineering and Services, Las Vegas, NV.
Radionuclide sorption onto microbes, microbial retention in the engineered barrier system (EBS), and their potential release from the EBS as microbial biomass has been investigated. The microbial source term for these calculations was derived using MINC V 1.0 software code. The sorption between the EBS and beneficial microorganisms at this elevated temperature. The results of the exposure of hydroceramic waste forms contrasted to EA glass will be discussed.

4:15 PM JJ10.4
SOLUBILIZATION EVALUATION FOR YUCCA MOUNTAIN TSPA-SR. Yueting Chen, Amy Loth, Duke Engineering & Services; Terry Steinborn, Management Solutions; Patrick Birdy, Christian Stockman, Sandia National Laboratory, Las Vegas, NV.
U.S. Department of Energy (DOE) has prepared a total system performance assessment for a site recommendation (TSPA-SR), if suitable, of Yucca Mountain, Nevada, for disposal of radioactive waste. Fundamental inputs to TSPA-SR are the solubility limits of radioactive elements, which limit the release of radionuclides to the environment. In the previous TSPAs, solubility values from an expert elicitation were used. To meet the acceptance criteria set forth by U.S. Nuclear Regulatory Commission (NRC), a new solubility evaluation has been conducted. This paper gives a summary of this effort. In this study, a conventional thermodynamic approach was employed and geochemoical model calculations were used to estimate radionuclide solubilities. The study uses the computer code EQNIR the major geochemoical modeling tool. A thermodynamic database compiled from the literature and other sources by the Project is the major input for model calculations. The water composition and environmental conditions are based on the results of in-package chemistry and in-drift chemistry studies. One key factor in solubility evaluation is the selection of solubility-controlling phases, because the result can impact the calculated solubility by orders of magnitude. Field observations, laboratory measurements, and thermodynamic and kinetic considerations are utilized to ensure the resulted solubility is conservative. Fourteen radioactive elements have been studied (U, Np, Pu, Am, Th, Ac, Pa, Ra, Tc, I, C, Cs, Sr, Ba, and Rb) and different solubilities are presented for various combinations of environmental conditions or statistical distributions. Further studies include quantifying the uncertainties associated with some important elements from various sources so that the impact on dose calculation can be estimated.

4:30 PM JJ10.5
A QUANTITATIVE KINETIC MODEL FOR PLUTONIUM OXIDE SOLUBILIZATION. John M. Hinchke, Actinide Science Consulting, Waco, TX; Virginia M. Oversky, V&M Konsult, Stockholm, SWEDEN.
A quantitative model for kinetically controlled dissolution of plutonium oxide is described and applied in predicting Pu concentrations and speciation in aqueous solutions. The model is based on the recently reported observation that plutonium dioxide spontaneously reacts with water to form a fluorine-reduced higher oxide solid solution, PoOx fluor, with PuOx ratios approaching or exceeding 2.3 and on extensive literature data for dissolution of plutonium dioxide and tetrahydroxide. Results suggest that dependences of Pu concentration on pH, time, Eh, and other parameters, as well as consistent appearance of Pu(V) and Pu(VI) as the dominant steady-state species over the pH 1-9 range, are most consistent with kinetic control of dissolution, not with equilibrium control. Involvement of the higher oxide is implied by difference data showing that lattice parameters of the fluor-carbonate-cubic solid formed by both dioxide and hydroxide at steady-state correspond with those of higher oxide and by coincidence of the observed oxide dissolution rate with the measured rate of Pu(V) formation in the
higher oxide. According to the conceptual model, $Pu(V)$ and $Pu(VI)$ accumulate in solution and a steady state is established when their rates of formation and disproportionation become equal. $Pu(VI)$ formed by disproportionation accumulates until the concentration is fixed by tetrahydroxide precipitation. $Pu(V)$ and $Pu(VI)$ concentrations are a function of the higher-oxides area to solution volume. Values predicted using kinetic data from literature sources accurately account for observed oxidation-state distributions and total $Pu$ concentrations in near-neutral solutions.

4:45 P.M. JJ10.6
IODINE RELEASE FROM SILVER IODIDE UNDER REDUCING CONDITION WITH IRON-BEARING MINERALS. X. Xin Y. Inagaki, A. Hartt, K. Iidemitsu, T. Arima, Department of Nuclear Engineering, Kyushu University, Fukuoka, JAPAN.

During reprocessing of spent fuel in Japan, radiiodine (I-[I-129]) is collected in a form of silver iodide (AgI) in adsorbents to be disposed of as part of the intermediate waste. The waste form is planned to be incorporated into more durable forms for geological disposal. Evaluation of iodine release from the waste form is essential for long-term safety assessment of the disposal because of its long half-life and weak adsorption on many geological minerals. Although AgI is the most stable form among iodine compounds, redox potential calculations show that it can be reduced to release iodine under reducing conditions. However, there is no empirical data on its reduction under real disposal conditions where the redox conditions may be controlled by a redox couple of Fe(II)/Fe(III) from iron-bearing minerals. The purpose of this study is to evaluate the effects of iron-bearing minerals on reduction of AgI to release iodine. Tests were performed in the presence of iron-bearing minerals, goethite (FeO(OH)), magnetite (Fe$_3$O$_4$), and wustite (FeO), in a glove box purged with gas mixture (Ar 95%H$_2$), and concentrations of I$^-$ and Ag$^+$ in the solutions were measured as a function of time by using an ICP-MS. The stirred concentrations of I$^-$ were 4.0 x 10$^{-4}$, 4.3 x 10$^{-5}$ M/ml for the tests with FeO(OH) and Fe$_3$O$_4$, respectively, which values were almost the same as that for the tests without the minerals. While for the test with FeO it was 5.0 x 10$^{-5}$ M/ml, which value was five times of magnitude higher than those for other tests. Solid phase analyses by using XRD and SEM/EDS indicated that Ag(I) and Ag(I) precipitated on the surface of original AgI only for the tests with FeO(OH) and Fe$_3$O$_4$. These results suggested that only FeO among the minerals can reduce AgI effectively to release iodine rapidly.

SESSION JJ11 POSTER SESSION
SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT

Wednesday Evening, November 28, 2001

8:00 PM
Exhibition Hall E (Hynes)

JJ11.1
STUDY ON VIBRATIONAL SPECTRA OF INTERLAYER WATER IN SODIUM-MICETITE BY MOLECULAR DYNAMICS SIMULATIONS. Sator Suzuki, Japan Nuclear Cycle Development Institute, Waste Isolation Research Division, Tokai-mura, Ibaraki-ken, JAPAN; Kunio Kawanami, Tokyo Institute of Technology, Tokyo, JAPAN.

Interactions between water and clay are of scientific and practical interest for the modeling of physical or chemical properties of compacted bentonite as an engineered barrier for the HLW disposal. A vibrational feature of water is a good probe for the microscopic interactions with smectite, the major constituent of bentonite. We studied correlation between a vibrational spectrum and molecular structure simultaneously obtained by the molecular dynamics simulations. The simulated results were in good agreement with IR spectroscopic observations. A stretching vibrational spectrum of interlayer water consisted of a broad band with a peak top at around 3400 cm$^{-1}$ and a sharp peak around 3650 to 3700 cm$^{-1}$. The former broad band was assigned to O-H vibrations between water molecules as bulk water, while the latter band was attributed to O-H ones oriented to silicate surface through hydrogen bonding. The hydrogen bond distance, determined as the shortest O-O distance by the radial distribution function (RDF), revealed that hydrogen bond distance between water and silicate surface ($r_{H_{2}O-O_{SiO}_{4}} < 3.0$ Å) was larger than that between water molecules ($r_{H_{2}O-O_{H_{2}O}} < 2.8$ Å). These results suggest that the interaction between water molecule and silicate surface is weaker than that between water molecules, although they were forced to be oriented.

JJ11.2
CHEMICAL INTERACTIONS IN THE NEAR-FIELD OF A SPENT FUEL REPOSITORY. PRELIMINARY RESULTS FROM A LONG-TERM LABORATORY EXPERIMENT. H. Asko, T. Ciellew, H. Kumpulainen, J. Lehikoinen, A. Marrinen, VTT Chemical Technology, Industrial Physics, Espoo, FINLAND.

It has been planned to dispose of spent nuclear fuel in Finland in a repository at a depth of about 500 m in crystalline bedrock. The near-field barriers in the excavated space of the repository comprise a compacted bentonite layer, a so-called concrete iron-cement, and the spent fuel matrix. The barriers mutually interact via the groundwater and tend towards a thermodynamic equilibrium with each other and with their geochemical environment. In order to study experimentally the interactions between the groundwater, bentonite, and the spent fuel matrix, a long-term laboratory-scale feasibility study was recently started. Its planned duration is 10 years. The design of the long-term experiment is based on a) two extensive literature surveys, focusing on the state-of-the-art concerning relevant aspects of the geochemical conditions and the chemical interactions, and b) the results from modelling of the chemical interactions using the thermodynamic computer codes HYDRAUL/CE AND EQ4.6. In short, the experimental set-up consists of two laboratory cores, each of which contains a copper cylinder in a solution that is initially either distilled water or 0.5 M NaCl solution. The copper cylinder contains water-saturated MS-80 bentonite, which wraps in contact with the solution via metallic filter-plates. The bentonite contains in six cases an iron cylinder, while the remaining samples are reference samples containing no metallic iron. The experiments are performed under anoxic conditions (N$_2$ atmosphere) at ambient temperature and pressure (40°C). The parameters that are determined during the course of the experiment are the water chemistry, the extent to which surface corrosion occurs on the iron cylinders, and the identity of the corrosion products (equipment XRD). The paper presents the experimental arrangements and preliminary results of the first samples.

JJ11.3
PRELIMINARY ANALYSES OF HLW CONTAINER RESPONSE TO BASALTIC MAGMATIC EVENTS. Narumi Sridhar, G. Douglas Gute, Andrew Grohmann, Brittain E. Hill, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

The proposed Yucca Mountain repository site has a 1.1 to 1.10,000 probability of disruption by basaltic magma during the next 10,000 years. Basaltic magmas have temperatures of approximately 1100°C, a density of 2700 kg/m$^3$, and fluid velocities of order 0.1-1.0 m/s in the nearest recharge areas. Basaltic magmas have Reynolds numbers of order 1.0 x 10$^3$. Integrity of HLW containers will be affected by basaltic magmatic events in several ways. High temperature exposure of the materials can result in creep and stress rupture. Creep rate and mode of stress rupture is determined by the homogeneous temperature (temperature divided by melting point) and homogeneous stress (stress divided by elastic modulus). Deformation maps and high temperature creep data of alloys similar to alloy 22 and type 316 SS stainless steel will be used along with preliminary calculations of stress levels and temperatures of the container wall to determine the potential for creep and stress rupture. Exposure to high temperatures (600 to 1100°C) for days to months also will precipitate secondary phase particles in the alloy (carbides, nitrides, and intermetallics) that can cause loss of ductility upon cooling to ambient temperatures. Secondary phases may then adversely affect corrosion performance and mechanical integrity of containers during sequentially induced loading. Finally, acidic gases produced by basaltic magmas can cause high temperature corrosion. Depending upon gas chemistry, high temperature corrosion can be in the form of oxidation, sulfidation, and molten salt corrosion. The rate of corrosion for metallic materials in hot gas streams will be estimated based on effects of gas chemistry and temperature on alloy compositions similar to the proposed container material. Reported experience with magnesium alloy interactions will be used as an additional source of information in this evaluation.

This work, supported by U.S. Nuclear Regulatory Commission (Contract NRC-82-97-0010) is an independent product of CNEVA that does not necessarily reflect NRC views or regulatory positions.

JJ11.4
EXPERIMENTAL DETERMINATION OF THE CONDUCTIVITY BEHAVIOR OF A MULTICOMPONENT HLW DEPOSITION MELT DEPENDING ON FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY. Lien Yang, Roberto T. Pabalan, Lauren Browning, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

Evaporation and aerosol deposition may lead to the accumulation of hygroscopic salts on drip shield (DS)/waste package (WP) surfaces. These hygroscopic salts will absorb moisture from the atmosphere, potentially causing aqueous corrosion of the DS and WP. The U.S. Department of Energy (DOE) has investigated iron-cement concrete as an iron-based model of the environment on the surfaces of the DS and WP considering that aqueous corrosion begins when the relative humidity reaches 50%. This relative humidity is based on the minimum deactivation point of the Na$_2$CO$_3$ salt. As aqueous corrosion is directly related to the conductivity of the electrolyte, the objective of this study was to...
measure the conductivity of salts as a function of relative humidity at constant temperatures. At low relative humidities, the initial results show that the conductivity of the salt is lower than the detection limit of the instrument. With increasing relative humidity, the conductivity of the salt starts to increase after reaching a humidity value that is significantly lower than the deliquescence point of the salt. When the deliquescence point is reached, the conductivity increases dramatically as an aqueous phase is formed. The increase in conductivity at humidities below the deliquescence point is likely attributed to the sorption of water on the surface of the dry salt. Because of the increase in the sorption reaction, the conductivity may occur at a relative humidity that is significantly lower than the minimum deliquescence point of the salt mixture deposited on the DS or WP. This implies that the time for aqueous corrosion is earlier and the duration is longer than predicted by the DOE. This abstract is an independent product of the Center for Nuclear Waste Regulatory Analyses and does not necessarily reflect the views or regulatory position of the U.S. Nuclear Regulatory Commission.

**J1115**

**EFFECTS OF HEAVY METAL IONS ON CORROSION OF TITANIUM GRADE 7 IN CONCENTRATED GROUNDWATERS.**

April L. Pulvirenti, Karen M. Needham, Mohammad A. Adel-Hakadi, Charles R. Marks, Jeffrey A. Gorman and Aaron Burkat.

Catholic University of America, Dept. of Chemistry, Washington, DC.

Titanium Grade 7 (Ti-30Pd) drip shield is being considered for use in the potential nuclear waste repository at Yucca Mountain, Nevada. The purpose of the drip shield is to keep water from reaching the surface of the contained nuclear waste. It is therefore expected that the drip shield will be in contact, intermittently or continuously, with water of various concentrations of mineralogical species. Among the species that may be expected to be present in the water contacting the drip shield are heavy metals, which may accelerate the corrosion of titanium. This paper presents the results of an investigation of aqueous radiocative waste contamination of three types of lead, mercury, and cadmium, on the dissolution rate of Titanium Grade 7. These tests were deliberately carried out at extremes of pH and heavy metal ion concentration in order to identify the conditions under which titanium dissolution would be most rapid. The results of these tests indicated that lead, mercury, and cadmium ions do not significantly accelerate the general corrosion of Titanium Grade 7 under the conditions studied, and that the presence of these species in the potential repository is not likely to affect the long-term utility of the drip shield through acceleration of general corrosion.

**J1116**

**EFFECTS OF LEAD AND MERCURY ON CORROSION OF C-22 IN CONCENTRATED GROUNDWATERS AS A FUNCTION OF pH AND TEMPERATURE.**

April L. Pulvirenti, Karen M. Needham, Mohammad A. Adel-Hakadi, Charles R. Marks, Jeffrey A. Gorman and Aaron Burkat.

Catholic Univ. of America, Dept. of Chemistry, Washington, DC.

Corrosion tests have been carried out on Alloys C-22 in environments contaminated by lead or mercury. The tests explore how the presence of lead and mercury augment the general, localized and stress corrosion behavior of C-22 in contaminated groundwaters. The conditions of most tests are accelerated with regard to temperature and pH compared to expected waste repository service conditions. These accelerated test conditions provide results from short-term tests that can be extrapolated to longer-term service conditions. The test methods used included dissolution tests of disks at temperatures up to 160°C and U-bend tests at temperatures up to 250°C. The water used in the tests approximated the chemistry of thermally concentrated J-13 well water. Room temperature pH values ranged from 1 to 14. Various aggressive species were added. Several potentially aggressive species tested, including lead and mercury, affected the corrosion of C-22 specimens. Results of the tests for both dissolution and SCC were extrapolated to waste repository service conditions using trends developed from the technical literature for alloys 600 and 690 with regard to temperature and pH. Thus, it has been observed that in the presence of lead the onset of pitting is slowed when the pH is raised for 1 to 3 to 5 or when the temperature is lowered from 250°C to 210°C to 200°C, but within a few weeks significant pitting takes place even under the mildest of these conditions. These extrapolative data indicate that the service life of the C-22 may be limited by the presence of the aggressive species.

**J1117**

**CREEP ANALYSES OF TITANIUM DRIP SHIELD SUBJECTED TO ROCKFALL STATIC LOADS IN THE PROPOSED GEOLOGIC REPOSITORY AT YUCCA MOUNTAIN.**

Brett W. Neugenher.

Charles A. Greene, U.S. Nuclear Regulatory Commission, Washington D.C.; G. Douglas Gate, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

The U.S. Department of Energy (DOE) has included a Titanium drip shield as a principle component of the post closure safety case for the proposed high-level nuclear waste repository at Yucca Mountain. As currently designed by DOE, the titanium drip shields will be fabricated from Titanium grade 7 (Ti Gr 7) plate and Ti Gr 24 support beams. The intended function of the drip shield is to divert water from seeping out of the waste packages and prevent damage to the shielded packages from the incoming water. Because the repatriation tunnels are expected to gradually collapse over time, NRC evaluation of the drip shield includes an examination of the effects of rockfall under both dynamic and static load conditions. For the purpose of this study, the finite element method has been used to determine the residual static loads and constant stress levels remaining in the drip shield after dynamic rock block impacts. These static loads and stress levels, when expressed as a fraction of the Ti alloy yield strength [YS], can be used to assess the potential effects of creep on drip shield performance in terms of the impacting rock block size. It has been shown in the literature that alpha and alpha delta titanium alloys are subject to creep at temperatures below those normally required in other alloy systems, i.e., less than 30 percent of the melting temperature, and at stresses markedly below the VYS. The technical bases established by the results of this study will assist the NRC in evaluating the risk significance of these degradation mechanisms on the ability of the drip shield to perform as intended. The views and opinions expressed in this paper reflect those of the authors and do not necessarily reflect the views or regulatory position of the U.S. NRC.

**J1118**

**CORROSION BEHAVIOR OF CARBON STEEL IN BICARBONATE SOLUTIONS.**

J. H. Do, T. Nishimura, T. Kodama, Natl Inst of Materials Science, Tsukuba, Ibaraki, JAPAN.

Carbon steel is one of the candidate materials for overpacks for high-level radioactive waste disposal. Effects of bicarbonate solutions on the corrosion behavior and corrosion products of carbon steels were investigated by electrochemical measurements, FT-IR spectra and XRD pattern analysis. The results of the anodic polarization measurements showed that bicarbonate accelerates the anodic dissolution and the out layer film formation of carbon steel, whereas it inhibits pitting at a nobler potential. The FT-IR and XRD analyses of the anodized film showed that siderite (FeCO₃) was formed in 0.1 - 0.1 mol/L bicarbonate solution, Fe₃O₅(OH)₂CO₃ was formed in 0.1 - 0.2mol/L bicarbonate solution, while Fe(OH)₂CO₃ was formed in 0.02 - 0.05mol/L bicarbonate solution. In all cases the pH value was around 8.3. The stability of these chemical compositions was discussed using a potential – pH diagram.

**J1119**

**DIFFUSION BEHAVIOR OF IRON CORROSION PRODUCTS IN BUFFER MATERIALS.**

Kazumasa Kido, Seiichi Yamauchi, Yachiyo Inagaki, Yasuhiro Arima, Kiyosato University, Dept. of Applied Quantum Physics and Nuclear Engineering, Fukushima, JAPAN.

Toshiki Mizusawa, Mieko Hara and Yoshimitsu Suzuki, Tokohu University, Institute for Materials Research, Ibaraki, JAPAN.

Carbon steel is one of the candidate overpack materials for high-level radioactive waste disposal and is expected to cause complete contamination of vitrified waste glass during an initial period of 100 years. The lifetime of the carbon steel overpack will depend on its corrosion rate. The corrosion rate of carbon steel is reduced by the presence of buffer material such as bentonite and seems to be affected by the diffusion of corrosive materials and corrosion products through the buffer material. Carbon steel overpack will be corroded by assuming oxygen introduced by repository construction after closure of repository and then will keep the reducing environment in the vicinity of repository. The reducing condition expected to result in the migration of redox-sensitive radionuclides by lowering their solubilities. Therefore, the diffusion of corrosion products of iron in buffer material is important to discuss the corrosion rate of overpack, migration of redox-sensitive radionuclides and properties of buffer material. The purpose of this paper is to study diffusion behavior of a corrosion product of iron in compacted bentonites under a reducing condition with a carbon steel. The diffusion mechanism of iron in the compacted bentonite was discussed by estimation of iron species in the bentonite pore water. It seems that there are two diffusion paths of iron in the compacted bentonites used in this study: the first path has low capacity of iron, ca. 1 wt%, and large apparent diffusion coefficient, ca. 10³-12 m²/s and the second path has large capacity of iron, ca. 10 wt%, and small apparent diffusion coefficient, ca. 10⁻¹⁴ m²/s.

**J1110**

Transferred to J11.10
The precursors were cold pressed at 200 MPa and sintered at 1500–1550°C for 4–8 h. The products were examined with XRD, SEM, and TEM. In the glass-ceramic and ceramics with Ca$_{2}$Al$_{2}$Zr$_{2}$O$_{7}$ and (Ca$_{2}$Gd$_{2}$U$_{5}$)$_{2}$Zr$_{2}$O$_{7}$ specific compositions pyrochlore was not formed. In the ceramics with bulk compositions Ca$_{2}$Zr$_{2}$O$_{7}$, (Ca$_{2}$Gd$_{2}$Th$_{3}$)$_{2}$ZrTi$_{2}$O$_{0}$, (Ca$_{2}$Gd$_{2}$U$_{5}$)$_{2}$Zr$_{2}$O$_{7}$, and Zr$_{2}$Ti$_{2}$O$_{7}$ pyrochlore was not observed, but minor fluoride-structured oxide was also present. Crystal-chemical reasons for the appearance of the phase assemblages in the samples are discussed.

**J11.14**

XRD, SEM AND TEM STUDY OF THE Gd-DOPED ZIRCONOLITES. Sergey V. Štefánovský, Albert Y. Trocole, SIA “Radon”, Moscow, RUSSIA; Maria I. Lapina, B.S. Nokolov, Anatomy V. Štefánovský, IGMEM RAS, Moscow, RUSSIA.

Ceramic samples with compositions Gd$_{2}$O$_{3}$-Zr$_{2}$Ti$_{2}$O$_{7}$ (0 ≤ x ≤ 1) were cold pressed at 200 MPa and sintered at 1400°C for 5 h. All the samples produced single phase with rare grains of cubic zirconia based solid solution in the samples with high Gd and Al contents (x = 0.9 and 1.0). The samples produced at 1500°C were higher homogeneous and less porous than the samples sintered at 1400°C. SEM/EDS data average compositions of zirconolite in the samples are very close to specified formulation (within experimental error), for example, zirconolite formula in the ceramic with x = 1 was found to be Gd$_{10}$Ti$_{2}$Al$_{8}$O$_{34}$ [probably Gd$_{10}$Ti$_{2}$Al$_{8}$O$_{34}$. XRD and TEM patterns showed monoclinic (2M) structure for zirconolites within 0 ≤ x ≤ 0.5 compositional range. Zirconolites with x = 1.0 are two phases. One of them, x = 1, has higher symmetry, supposedly orthorhombic or tetragonal.

**J11.15**

CHARACTERIZATION AND DISSOLUTION OF ZrTiO$_{4}$10 and Th$_{3}$UO$_{7}$ CERAMICS. V. Curran, Y. Svetova, W. Ruttrey, P.G. Allen*, K. Czerwinski, Nuclear Engineering Department, Massachusetts Institute of Technology, Cambridge, USA. University of Lebedev Institute, Lawrence Livermore National Laboratory, Livermore, CA.

Thoriuroaritic-zirconia ceramics were studied in order to investigate the long-term behaviour of potential thorium fuels in a repository environment. The ceramics were prepared by co-pressing. Zirconia was added to determine if further stabilization of the thorium-uranium system could be achieved. In addition, 0.5 wt% MgO was added to some samples to increase stability and density. The ceramics with the inclusion of Zr were shown not to dramatically enhance the stability of the matrix. Comparison of ceramics with higher Zr stoichiometry, up to a metal ratio of Zr/Th=1:2, also showed no enhanced stability against dissolution.

Material properties of the ceramics were analyzed using electron microscopy techniques such as Energy Dispersive X-ray (EDX) analysis and Electron Energy Loss Spectroscopy (EELS). X-ray diffraction and x-ray absorption spectroscopy including EXAFS and XANES were also used to reveal elements of the phase structure and chemistry of the ceramics. XRD and EDX show that these ceramics separate into a zirconia-based phase and an actinide-based phase with low mutual affinity of thorium and zirconium, as well as partial solubilization of uranium in zirconium. The comparison of EELS spectra collected for the ceramics with spectra collected for UO$_{2}$ and UO$_{3}$ reference materials also allow the assessment of uranium oxides in zirconium independently in the two separate phases. Assessment of the bulk oxidation state using XANES correlated well with the EELS analysis. Interatomic distances and the bulk crystal structure were determined using EXAFS.

**J11.16**

INSTABILITY MODEL OF THE ZP STRUCTURE. Albert Trocole, Sergey Štefánovský, SIA “Radon”, Moscow, RUSSIA.

Incorporation of paramagnetic species in Na$_{2}$Zr$_{2}$PO$_{7}$ (ZP) single crystal made possible to investigate local distortion of the ZP structure from EPR data. Cr$^{3+}$ and Fe$^{2+}$ ions were used as paramagnetic probes. We mapped out a cubic component of the fourth rank tensor of crystal field, the indicative surface of the B$_{4}$ element of this tensor as well as $2^{	ext{nd}}$, $3^{	ext{rd}}$, and $4^{	ext{th}}$ orders axes of the cubic component of the same tensor. From these data the coordination polyhedron of the ion-probe has been modeled and direction to change compensator has been determined. Based on the coordination polyhedron model obtained it has been shown how would the local symmetry be lowered from C$_{4}$ (initial symmetry of the ZP polyhedral) to C$_{1}$ (Z$_{4}$ structure unit). A comparison of dynamics of the structure occurring at lowering the symmetry with allowed dynamics of the ZP structure (Roy-Alamo-Agrafal model) makes easily explainable why the dynamics observed results in an instability of the ZP structure and breaking the symmetry from R$3c$ to C$2/c$.
synthesis of zirconolite-bearing materials is performed based on these thermodynamic functions by the example of systems early proposed by Nakrowski. It is demonstrated that the synthesis of zirconolite-bearing materials is possible using the self-sustaining exothermic reaction.

Some preliminary experimental results indicate the same.

PRELIMINARY STUDIES OF THE DISPOSITION OF CESIUM IN A CERAMIC WASTE FORM, Marshall J. Lambrecht, Steve M. Frank, Tom P. O'Holleran, Argonne National Laboratory-West, Idaho Falls, ID

Argonne National Laboratory has developed an electrochemical treatment for spent DOE metallic fuel. This process produces a LiOCl solvent containing fissile solutions and low levels of actinides. The salt is immobilized in a durable ceramic waste form suitable for long term storage in a geological repository. The waste form chosen was a glass-bonded sodalite. The behavior of cesium in the waste form is an important characteristic of this glass mobility within the environment. The amount of cesium found in the waste form is approximately 0.1 wt.%. Because of the small amount of cesium present, it was unaccounted for in previous studies and thought to be uniformly distributed throughout the waste form. This paper presents preliminary XRD, SEM WDS/EDS, and NMR data exploring the disposition of the cesium in cesium-doped ceramic waste forms similar to the actual ceramic waste form.

ATMOSPHERE PROCESSING EFFECTS ON TITANATE CERAMICS DESIGNED FOR PLUTONIUM DISPOSITION, M. A. Stewart, E.R. Vance, A. Justman, K. Finnie, H.A. Day, ANSTO, Lucas Heights, NSW, AUSTRALIA; B.B. Ebbinghaus, Lawrence Livermore National Laboratory, Livermore, CA

A baseline formulation based upon a target mineralogy of 95 wt. % pyrochlore (Ca0.85Gd0.15Hf2O7P2O7U2O8 and 44 wt. % Hf-doped rutile (approximately Ti0.6Hf0.4O2)) has been developed for the disposition of excess weapons plutonium. In experimental work Ce and Th have been used as an analogue for Pu and Ce as an analogue for U. Zr can also replace Hf for testing purposes. We discuss the effect of sintering atmosphere (air, argon and 3.5% hydrogen in argon) and temperature on the mineralogy of Pu/U, Th/U, Ce/U and CeO2-baseline compositions. The pyrochlore ceramics produced proved to be extremely flexible with charge compensation mechanisms allowing the production of a desirable mineralogy under a variety of processing conditions. The redox state of U has been examined using diffuse reflectance spectroscopy. The limitations of each analogue and the effects of processing impurities will also be discussed.

APPLICATION OF PCT TO THE EIR II CERAMIC WASTE FORM W.L. Ebert, M.A. Lewis, and S.G. Johnson, Argonne National Laboratory-East, Argonne, IL, Argonne National Laboratory-West, Idaho Falls, ID

We have evaluated the possible use of the Product Consistency Test (PCT) to characterize the pyrochlore phase of the EIR II waste form, C2Fe2P2O7. C2Fe2P2O7 is the PCT matrix. This allows us to conclude that the pyrochlore phase is not present in the EIR II waste form. The presence of pyrochlore in the EIR II waste form was confirmed by X-ray diffraction analysis. The presence of pyrochlore in the EIR II waste form is consistent with the results of previous studies. The presence of pyrochlore in the EIR II waste form is consistent with the results of previous studies.

THE THERMODYNAMIC FUNDATIONS OF ZIRCONOLITE, CaZr2O4 AND HF-ZIRCONOLITE, CaHf2O4 REVISITED, K.B. Helgeson, T. Lee, A. Nakrowski, Thermodynamics Facility Department of Chemical Engineering and Materials Science, The University of California at Davis, Davis, CA, R.I. Putnam, Los Alamos National Laboratory, Los Alamos, NM, B. Ebbinghaus, Lawrence Livermore National Laboratory, Livermore, CA

Zirconolite, nominally CaMg4Ti4O12, 0.8 x<1.37 and MgZr, Hf, Ce, U, REE, is a primary component of SYNROC. As such zirconolite has been the subject of ongoing study. Despite the complex nature of the thermodynamic properties of zirconolite, its fundamental thermodynamic properties were unknown.
unaided. Previous calorimetric investigations of zirconolite and Hfzirconolite used Pb-zirconate (2PbO·6HfO2) near 973 K as a solvent. As noted in previous studies, dissolved Hf or Zr oxide was slow. Calorimetric experiments for the Hf-bearing compounds were conducted by mixing the materials with powdered solvent to aid in the dissolution. This introduces additional uncertainty in the data and makes it difficult to measure accurately the thermodynamic strengths of formation reactions. Therefore, a second calorimetric investigation was undertaken using an alternative molten oxide solvent in which the samples appear to dissolve more readily. High-temperature oxide melt solution calorimetry was conducted using 5 mol % of Na2O in a PbO·2SiO2 solvent to measure the heats of solution for CaCO3, ZrO2, HfO2, TiO2, Gd2O3, CaZrTiO5, CaHfTiO5, and Ca(Gd1-xHfx)TiO5. Applying the approximate thermodynamic cycles to our preliminary results, the enthalpies of formation for these oxides are
\[ \Delta H_f^\text{ZrO}_2 = 298 K \text{ were calculated} \] (kJ/mol) for CaZrTiO5 (-889.4 ± 3.5 kJ/mol) and CaHfTiO5 (-77.7 ± 2.7 kJ/mol). The enthalpy of formation derived from solution in the 3NaO·4MgO·SiO2 solvent for CaZrTiO5 was calculated to the previously published value derived from 2PbO·6HfO2 solution data. However, the preliminary results for CaHfTiO5 indicate that its \( \Delta H_f^\text{ZrO}_2 \) is as much as 34 kJ/mol more endothermic than previously reported.

**J11.25**

**ENERGETIC TRENDS IN REE-TITANATE AND ZIRCONATE PYROCHLORIDES.** K.B. Hellen, S.Y. Ushakov, A. Nowotny, Thermochimistry Facility, Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA; J. Lian, L.M. Wang, R.E. Ewing, Department of Geological Sciences and Nuclear Engineering, University of Michigan, Ann Arbor, MI; L.A. Banter, J.M. Farmer, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Hans-ehrlich element-bearing titanate and zirconate pyrochlores, nominally REE2M2O12, where REE = lanthanides plus Y and M = Ti, Zr, are used as solid ionic conductors and oxygen sensors in numerous industrial applications. In addition, Gd2Ti2O7 and Gd2Zr2O7 are potential hosts for actinides in radiocative waste ceramics such as SYNROC. Numerous studies have investigated the structural details and radiation resistance properties of these pyrochlore phases. This study presents the preliminary results of a calorimetric investigation into the crystal chemical controls of formation enthalpies. X-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) were used to characterize a suite of REE-titanate and zirconate pyrochlore samples. High-temperature oxide melt solution calorimetry was used to measure heats of solution, \( \Delta H_f \), using 5 mol % of Na2O in a PbO·2SiO2 solvent at 973 K for REE2O5 (REE = Y, La, Nd, Sm, Eu, Gd, Ho, Er, Tm), REE2Ti2O7 (REE = Y, Tm, Er, Ho, Gd, Eu, Sm) and REE2Zr2O7 (REE = La, Nd, Sm, Eu). These data were used to calculate enthalpies of formation from the oxides, \( \Delta H_f^\text{REE2M2O12} \), for example: Gd2Zr2O7 (-528.4 ± 8.1 kJ/mol), Nd2Zr2O7 (-668.4 ± 4.0 kJ/mol), Gd2Tl2O7 (-860.6 ± 4.5 kJ/mol) and Sm2Ti2O7 (-1154.2 ± 5.0 kJ/mol). These data, when plotted against the atomic radii of REE, yield a linear trend, \( \Delta H_f = -1868.4[R(\text{REE})/R(M)] + 221.06 \). Approximately 94% of the variation in the data is defined by this trend. As \( R(\text{REE})/R(M) \) decreases, the pyrochlore phases become less stable. Structural details plus the complete calorimetric data set will be presented.

**J11.26**

**THE USE OF CERIUM VALENCE STATE FOR EVALUATION OF ACCESSORY MINERAL DURABILITY TO RADIATION DAMAGE.** Roman Bogdanov, Yuri Zygatev, S. Petersburg Univ, Dept of Chemistry, St. Petersburg, RUSSIA; Andrey Sergeev, S. Petersburg Univ, Dept of Geology, St. Petersburg, RUSSIA.

Cerium-actinide bearing natural minerals which demonstrate their physico-chemical durability for long time (>10^4 years) would be considered as the analogues of actinide ceramic waste forms. Radiation damage induced by all natural actinides could be oxidized by cerium from initial Ce^3+ to Ce^4+. Therefore, cerium valence state in actinoid-cerium bearing natural minerals reflects in some cases the resistant of such minerals to radiation damage. Cerium valence state was determined in the following natural minerals of similar age and similar U-contents: monazite, (Ce,Tr,Th,U,VPO4 [4 samples], britholite (Ce,Tr,Cn,Tr,Th,Us)[Si04,PO4,3]O1F [2 samples], nesancyite, (Ce,Tr,Cn,Us,Cn)[Si04,PO4,4]O1F [1 sample]. The method of chemical shifts of X-ray emission (Ce Kα line) was used. The Ce(NO3)3 and Ce2O3 were used as standards of Ce^3+ and Ce^4+, respectively. The following contents of Ce^3+ were observed: more than 30% in britholite, 11% in nesancyite, 0% in monazite. The results obtained allow us to conclude that the Ce^3+ content of these actinide host phases decreases in the raw “nonsitic-nesancyite-britholite”.

**J11.27**

**MICROANALYSIS OF RADIATION DAMAGE ACROSS A ZONED ZIRCON CRYSTAL: STRUCTURAL CHANGES INDUCED BY...**

**METACALIZATION.** Christopher S. Palejik, University of Michigan, Dept. of Geological Sciences, Ann Arbor, MI; Jie Liu, Rodney C. Ewing, University of Michigan, Dept. of Nuclear Engineering and Radiological Sciences, Ann Arbor, MI.

Zircon (ZrSiO4) has been proposed as a potential waste form for actinides, particularly the "monazite" phosphates. The chemical and physical durability of zircon is well established because of its use in geologic age-dating. Radiation damage due to alpha decay events is known to decrease the chemical durability of zircon; however, the mechanism of damage accumulation and measurement of phosphates has been under active investigation. In this work, an oxygen-zoned single crystal of zircon from St.虏ng (570 Ma) has been studied using a variety of microanalytical techniques in order to relate the accumulation of radiation damage to monazite structural changes. An electron microprobe traverse across optical zones shows that variations in birefringence reflect changes in the U and Th content (0.10 < UO2 + ThO2 < 0.62 wt.%). Based on these concentrations, a cumulative alpha decay dose could be calculated for each traverse. When the calculated doses, 1.6x10^3 to 1.1x10^7 alpha-decay events/mg, suggest that zones within the crystal represent crystalline, transitional and amorphous regions. A traverse across these zones using micro-Raman spectroscopy confirmed that a structural change occurs between zones of varying radiation damage. The decrease in phonon frequencies and peak intensities with increasing dose for both internal and external modes implies a transition of the SiO4 tetrahedra and for an increase in bond length. These results are consistent with the physical swelling associated with amorphization. High resolution transmission and analytical electron microscopy was used to study zones showing the full range of radiation damage states. Highly damaged zones show an increased frequency and size of uranium oxide domains, with some suggestion of the formation of ZrO2 nanoparticles.
MATERIALS. Stephan Grigull, European Synchrotron Radiation Facility, Grenoble, FRANCE.

The presence of defects in crystals can cause severe problems for most methods of extracting structure information from X-ray diffraction measurements. Point defects as observed in materials exposed to radiation environments are much more difficult to account for than dislocations since their presence result in changes of the integrated diffraction line intensities - the key parameter for structure refinement or quantitative phase analysis. It is clear that correct structure refinement becomes difficult in the presence of significant distortions caused by the defects are somehow included in the model used for structure evaluation, for example as a K-dependent correction factor to the line intensities in analogy to the temperature factor used in crystallography. The K-dependence of this factor is determined by details of the spatial rearrangement of the lattice atoms surrounding the defects which to date cannot be calculated with sufficient accuracy by analytical methods. In the present work the Molecular Dynamics simulation technique is used to generate defective crystal structures in the computer for which X-ray diffraction spectra can be easily calculated. Intensity correction factors are evaluated for different defect types and concentrations in a for metal, and it is discussed under what conditions the K-dependence of the factor may be sufficiently simple for use in practical structure refinement.

J111.30
ALPHA-DECAY RADIATION DAMAGE STUDY OF A GLASS-BONDED SODALITE CERAMIC WASTE FORM. Steven M. Frank, Thomas DiSanto, K. Michael Goff, Stephen G. Johnson, Junsung Joo, Tanya L. Masotti, Mariann Noy, Thomas P. O’Hollen, Argonne National Laboratory, West, Idaho Falls, ID.

Effects of alpha decay on the ceramic waste form used to immobilize actinides and long-lived fission products accumulated from electromagnetic treatment of spent DOE fuel has been studied. This involved the preparation of a surrogate ceramic waste form containing two-weight percent plutonium-238 and monitoring changes to the waste form resulting from alpha-decay damage. The phase assembly of the ceramic waste form consists of glass-bonded sodalite granules with small quantities of nepheline, halite and plutonium oxide. The surrogate waste form has been monitored for four years and has acquired an internal alpha-decay dose of approximately 1.18 disintegrations per gram of material. Methods used to monitor the material include: density determination to measure possible macroscopic swelling, chemical durability measured by leach testing, microstructure analysis by scanning and transmission electron microscopy and phase composition by powder X-ray diffraction. The investigation has, to date, found little alteration to the waste form due to alpha-decay damage. X-ray diffraction analysis has detected a unit cell volume increase of 0.6% of the Pu-bearing phase. Furthermore, possible bubble formation has been observed by transmission electron microscopy in the sodalite phase; however, these findings remain inconclusive.

J111.31
ION IRRADIATION EFFECTS IN THE GARNET-BASED WASTE FORM. Makoto Tanaka, Li-Min Wang, Rodney C. Ewing, University of Washington, Seattle, WA, Sergey Yulitsine, Russian Academy of Sciences, Inst. of Geology of Ore Deposits, Moscow, RUSSIA.

Garnet is an orthosilicate, ideally A3B2Si3O12. The isometric structure consists of a corner-sharing framework of A3O6 tetrahedra, A2O4 dodecahedra and BO6 octahedra. Because both the A- and B-sites can be occupied by actinides, garnet is a candidate nuclear waste form. In this work we investigated the susceptibility of several synthetic garnet compositions to radiolytic processes.

The compositions of the synthetic garnets are:[Ca16O24(Na12O35Fe12O35)16; Ca16O24(Si8O24)16; Ca8Si8O24] and [Ca16O24Fe12Fe12O35; Ca16O24Fe12Si12O35; Ca8Si8O24] and [Ca16O24Si12Fe12O35; Ca8Si8O24]. The results showed that the garnet is resistant to irradiation by X-rays and that the garnet is resistant to irradiation by neutrons.

J111.32
COMPUTER STUDY OF THE EFFECT OF POINT DEFECTS ON X-RAY DIFFRACTION SPECTRA OF IRRADIATED...
Zircon (ZrSiO₄) is a potential ceramic host material for the immobilization and disposal of excess weapons-grade plutonium and high-actinide wastes, and it is one of the crystalline phases that form during devitrification from glassy ceramics when glass is heated. Previous experimental studies have shed light on radiation effects, thermal decomposition, and recrystallization of ZrSiO₄, but such studies have not yielded much-needed information on the radiological behavior of this phase. Because of the need for long-range coherence and subsequent defect migration, these processes play a crucial role in determining the radiation response of ZrSiO₄ and can be elucidated by realistic computer simulations of displacement cascades. However, very few simulations of cascades in ZrSiO₄ have been performed because of the long range of the Coulombic interaction and lack of reliable potentials. In the present work, energetic displacement cascades in ZrSiO₄ have been investigated by molecular dynamic simulations using a Coulombic model for long-range interactions, Buckingham potentials for short-range interactions, and Ziegler-Biersack-Littmark potentials for close-pair interactions. The calculated defect production and evolution of the partially amorphous state will be presented to shed light on displacement damage produced by energetic Zr recoils in ZrSiO₄. Polymorhization of Si, and distributions of bond length and bond angles in the crystal will be compared with those in amorphous zircon.

**J11.37**

**RADIOACTIVE TRANSMUTATION EFFECTS IN A CRYSTALLINE ALUMINOSILICATE CERAMIC: A TEM STUDY**

Jeffrey Fontenot, Scott Aune, and Don Reed, Argonne National Laboratory, Argonne, IL.

We demonstrate the use of TEM to study the effects of the radioactive (β-decay) of 137Cs to 137mCs in crystalline polycrystalline (CaSiO₄). Most prior work on radiation effects in materials has focused on structural damage from alpha radiation. Betaradiation, on the other hand, causes little structural displacement but the decay radiation results in progeny with different valence and ionic radius. Cerium-137 is a fission product of uranium and is a major contaminant at U.S. Department of Energy production facilities. Polycrystalline alumino-silicate ceramics were being used to store the 137Cs. We focused on one of several available forms of 137Cs. These samples were initially fabricated in the 1970s and 1980s for tumor treatment. These sources were small, sealed, stainless steel capsules containing polycrystalline in which the amount of radioactivity GAS had been replaced by radioactive 137Ca (t1/2 = 30.13 years). The sample chosen for TEM examination had aged for nearly 20 years and contained the most radiogenic boron. Only 1% of the total cesium had been exchanged by the 137Ca. Transmission electron microscopy revealed a homogeneous, crystalline matrix, with no evidence of distinct Si phases or exsolution phenomena resulting from the 137Cs transmutation. Electron diffraction patterns were obtained from several areas of the sample and were consistent with literature values for polycrystalline Ce. These data suggest that the structural damage was done to the crystal structure of the sample, despite the transmutation of nearly 100% of the cesium to barium over the elapsed 20 years. Although these results are, to our knowledge, the only available data that the transmutation effects have been isolated from other radiation damage phenomena.

**J11.38**

**EXPERIMENTAL DETERMINATION OF THE DISSOLUTION KINETICS OF PLUTONIUM AND URANIUM BEARING CERAMICS AT 90°C**


Titanate-based ceramics have emerged as the leading candidate for a matrix for disposal of excess weapons-grade plutonium in a deep geologic repository. Concern remains, however, that accumulation of radiation damage will compromise the chemical durability of the titanate matrix. As a first step toward understanding the effects of radiation damage on element release rates, we performed single-pass flow-through (SPFT) experiments with 239Pu and 238U-bearing ceramics over a solution pH-interval of 2 to 10 m 90°C. The ceramics tested include chemically complex ceramics (Ca₂Ti₄O₉), betafriederite (Ti-rich pyrochlore, Ca₂Fe₃O₉), and titanate (239PuO₂, 238UO₂). B, Cr, Ca, and Sr, respectively) betafriederite-rich ceramics, and beta-friederite-rich samples that were transmutated at pH 2, 90°C. The experiment with the 238Pu-bearing ceramic utilized a platinum-lined Tellon reactor to eliminate radiation damage to the Tellon from direct contact with the ceramic powder. The 238Pu-bearing specimens showed a release of Pu to solution (rate = 8.3 x 10⁻⁷ g m⁻² d⁻¹), even at pH = 2. At higher pH values, the dissolution rate decreased by a factor of 10 and then increased nearly 100% above the release of uranium, which is type of 10²X faster and is inconsistent with rates based on other elements. Compared to results from 238Pu-bearing materials, the 239Pu-bearing specimen released Pu nearly 10²X faster (rate = 3.2 X 10⁻⁵ g m⁻² d⁻¹), and the 238Pu-bearing ceramic was also faster from the 238Pu-bearing ceramic compared to the specimen containing 238Pu. Although preliminary, the data can be interpreted to indicate that accumulation of radiation damage may result in faster release of Pu and U to solution than previously suspected.

**J11.40**

**SUCCESSFUL RADIOACTIVE WASTE MANAGEMENT APPROACHES AND METHODS AT THE WASTE ISOLATION PLANT**

Ines Traney, Mark Matthews, P.E., US DOE, Carlsbad, NM; Leif Eriksson, GRAM, Albuquerque, NM.

On March 26, 1999, the U.S. Department of Energy (DOE), supported by its local contractors, achieved a global milestone by opening the world’s first deep geologic repository for radioactive wastes at the Waste Isolation Pilot Plant (WIPP) site in New Mexico. The WIPP repository is situated approximately 1,000 feet (m) below the groundwater surface in a 250-meter (m) by 250-meter (m) by 600-micron-thick, undisturbed, virtually impermeable salt bed, known as the Salado Formation. A 24-year-long site selection, site characterization, and repository-development process preceded the opening of the WIPP repository. During the last seven years of this process, the DOE had to overcome considerable challenges posed by evolving laws, regulations, and legal actions. The establishment of the DOE Carlsbad Field Office, and its successful development and implementation of the WIPP Disposal Decision Plan, the Systems Prioritization Method, and the performance assessment studies and development of an effective safety case, were instrumental to the successful resolution of these challenges. They were also instrumental in establishing a broad-based national acceptance and, ultimately, the certification of WIPP by virtue of the strength of the WIPP Safety Case. At the end of May 2001, 245 shipments of LLRWs had been safely received and disposed at the WIPP site. When filled to its current statutory capacity, the WIPP repository will safely contain and isolate up to 175,586 cubic meters of long-lived, transuranic radioactive waste (TRUW). The TRUW will contain between 12 and 17 metric tons of radioactive isotopes with half-lives in excess of 25,000 years, and TRUW contains 74,000 dore units. The TRUW is expected to last for up to 100 years.

Several additional challenges remain to be overcome before WIPP has accomplished its current statutory mission. The opening of the repository, its implementation of a comprehensive characterization and licensing capacities, the successful re-certification of WIPP by March 26, 2004, and the safe continued operation of WIPP are foremost among current challenges and priorities. This paper will focus upon the approaches, methods, key findings, and successes in the establishment and future directions of WIPP.
J11143

RADIOISOTOPE FRACTIONATION AND SECULAR DISEQUILIBRIUM IN PERFORMANCE ASSESSMENT. William M. Martin, Colorado School of Mines, Golden, Colorado; David A. Pickett, CNWRA, Southwest Research Institute, San Antonio, Texas.

Radioisotopes of actinides and their decay products are fractionated in natural geochemical systems and in chemical processes associated with geologic disposal of nuclear waste. Two potential applications of isotope fractionation and decay-series disequilibrium in performance assessment for geologic repositories for nuclear waste are the estimation of radionuclide release and characterization of system closure. Systems that are closed on time scales that are long relative to the half-lives of decay chain nuclides achieve secular equilibrium, characterized by unit news. Natural systems are not out of secular equilibrium. For example, U-234/U-238 activity ratios in groundwaters reach values of 5 to 10. A primary mechanism is selective release and mobility of alpha decay products because of nuclear recoil effects. Prediction of radionuclide release of uranium and thorium from nuclear waste forms or solubility limiting solid phases could affect repository performance; however, consequences of differential radionuclide release have not been regarded previously in performance assessments. For example, in DOE TSPA-37 performance assessment calculations for the proposed repository at Yucca Mountain, Pu-239 is a major dose contributor at times greater than 50,000 years. If Pu-239 were released preferentially to other Pu isotopes, dose would be underestimated.

Another possible application might come from the usefulness of decay-series disequilibrium to characterize open-system behavior in natural systems. For geologic disposal of nuclear waste, a criterion focused on chemical system closure could capture the essential performance feature of the natural system with respect to radionuclide transport and could be based quantitatively on uranium and thorium decay series isotopic equilibrium/disequilibrium. This work is supported in part by the U.S. Nuclear Regulatory Commission (NRC) under contract number NRC-82-57,009. This is an independent product and does not necessarily represent the views or position of the NRC.

J1113

DEPLETED URANIUM DIOXIDE WASTE PACKAGES FOR SPENT NUCLEAR FUEL. Charles Forsberg, Oak Ridge National Laboratory, Oak Ridge, TN.

Depleted uranium dioxide (DUO2) waste packages (WP) for spent nuclear fuel (SNF) are being investigated to [1] reduce radionuclide release from WPs, [2] decrease the potential for repository nuclear criticality events, and [3] provide a means to beneficially use excess DU. Conceptually, the DUO2 WP with SNF is similar to a small (10 ton) uranium ore deposit containing UO2. The expected behavior is described and compared with that of natural uranium ore deposits in similar environments. DUO2 in the WP is used as [1] a filter for all radionuclides present in the DUO2, inclining SNF coolant draining and [2] a component of a DUO2 steel container. Cermetics are a mechanism to create a ductile form of DUO2. The cermet, containing 40 to 65 vol% DUO2 embedded in steel, substitutes for the steel components (shell and base) of the WP. The WP includes an outer non-linear layer of a more corrosion-resistant alloy such as C-22. The same mechanisms that have preserved ore bodies containing UO2 in some areas of oxidizing groundwater are expected to help preserve DUO2 in SNF and thus delay the release of the radionuclides trapped in the fuel pellets. The WP material of construction are chosen for geochemical reasons. Cermetics for delayed release of radionuclides include: (1) elimination of void space to prevent early WP collapse if extreme radionuclide release barriers (outer corrosion resistant metal layer, diffusion barriers, etc.), maintenance of chemically reducing conditions within the WP by preferential oxidation of DUO2 and steel; saturation of fluids in the WP with DUO2, reduced fluid flow (air, oxidizing groundwater) outside the WP from plugging of void spaces by the oxidation products of iron and DUO2; sorption and ion exchange of selected radionuclides (neptunium, etc.) on hydrated DU oxides, and long-term bulkup of uranium silicate surfaces.

J11142


Recent advances in development of reactive chemical transport models have made it possible to use these tools in performance assessments for nuclear waste disposal. The Subsurface Transport Over Reactive Multiphases (STORM) code was used to evaluate the impacts of design modifications on the performance of two shallow subsurface disposal systems for low-level radioactive waste. The first site located at Hanford is for disposal of lowactivity waste glass. One-dimensional simulations showed that a new design with only three layers (versus 4 layers) of taller (2.3 m high vs. 1.4 m high) waste packages was predicted to lower (10%) normalized release. This slight decrease occurred despite a higher calculated pH (hence higher glass corrosion rate) for the new design, which resulted from greater Na ion exchange. The new 3-layer design has fewer interfaces with the bedfill, where the SO4(aq) concentration goes through a sharp transition because of mineralogical and transport property differences across the interface. Since the glass saturation index is significantly lower at these interfaces (higher corrosion rate), having one less interface with the bedfill design offers a higher pH relative to the 4-layer design. Simulations that included the effect of container corrosion products showed that they had almost no impact on glass performance when modeled as layers between the backfill and glass but increased release rates significantly when modeled as a homogeneous mixture with the glass. Under a collaborative project between Battelle and ENEA, STORM simulations were also performed for a LILW disposal facility under design in Italy that contains radionuclides mixed with concrete. The effect of containing waste packages containing spent graphite moderator assemblies at different locations in the repository was examined. Because carbonate from dissolved atmospheric CO2 and C-14 released from dissociation of the graphite moderator assemblies (the reaction product with portlandite), the simulations suggested that locating the graphite packages in portions of the facility with lower partial pressures of atmospheric CO2 would lower overall C-14 release rates.

J11145

Abstract Withdrawn

J11146

EFFECT OF REDOX CONDITIONS ON THE SORPTION OF URANIUM ONTO GEOLOGICAL MATERIALS. J.A. Berry, M. Brownwood, D.J. Ilett, C.M. Linklater, C. Mason, C.T. Tweed, AEA Technology, Didcot, Oxfordshire, UNITED KINGDOM; M. Yui, Japan Nuclear Cycle Development Institute Tokai Works, Ibaraki, JAPAN.

This paper presents the latest results from part of the JNC programme of generic studies for the performance assessment of a potential high-level radioactive waste repository in Japan. The sorption of plutonium onto basalt and sandstone was studied as a function of redox conditions ranging from strongly reducing to strongly oxidising. Initial thermodynamic modelling indicated that at pH 8, strongly-reducing conditions (using sodium dithionate, Eh ~ -950mV) would provide predominance of Cm(III) in solution, whereas at pH 7.5, Cm(IV) would dominate between 1000mV and +1500mV (e.g. using hydroxy amnonium chloride). Hydrogen peroxide was selected as an oxidising agent that would give a high redox potential without causing experimental difficulties. Batch sorption experiments were carried out at a liquid solid ratio of
5.1 for a 3-month equilibration period. Pu-238 was added to synthetic rock-equilibrated water as solutions of Pu(III), Pu(IV) and Pu(VI). Phase separation was carried out on April 30, 1968 and 20,000 and 100,000MCWO filtration. Results were as follows. Under strongly-reducing conditions (Eh = ~500mV), the distribution ratios (R) values after filtration were similar for both rock types, values being ~2.0 for 

The discussion on the sorption of plutonium in a natural environment is included under the heading "Sorption of Plutonium in Natural Environments". Further details are provided on the sorption behavior of plutonium in soil, water, and biological systems throughout the document. The text also touches upon the importance of understanding sorption processes in the context of environmental conservation and remediation efforts.
case of 0.04 M and 0.4 M NaCl solution, the thickness of the diffuse double layer are 1.64 nm and 0.48 nm respectively. Therefore, if the dry density of 0.1 M NaCl solution is over 1.4 g/cm³, then the effect of the platelets is so small that the contracted diffuse double layers are still overlapped resulting in the nearly constant hydraulic conductivity.

J114.51

THERMODYNAMIC MODELING OF BINARY AND TERNARY ION-EXCHANGE EQUILIBRIA BETWEEN AQUEOUS SOLUTIONS AND THE ZEOLITE MINERAL CLINOPTILOLITE. Roberta Thingholm, P. Alsdam. For Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

Because of their high cation-exchange capacity, zeolite minerals are potentially useful in the treatment of nuclear, municipal, and industrial wastewaters and acidic drain waters. Zeolites could also serve as barriers for radionuclide migration from geologic repositories for high-level nuclear waste. One example is the proposed repository at Yucca Mountain, Nevada, which is underlain by diagenetically altered, zeolite-rich volcanic tuffs. However, for many systems of interest there is a lack of experimental data that can be used to develop binary and ternary ion-exchange models. In this study, published experimental data on ion exchange involving the zeolite mineral clinoptilolite and several cations, including Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, are used to derive parameters for a solid solution model based on the Wilson equation, in addition to equilibrium constants for binary ion-exchange reactions. Where experimental data are not available, equilibrium constants are derived using a correlation method. The results indicate that, for the systems studied, the correlation method is successful in predicting ion-exchange equilibrium constants. The Wilson model, using parameters derived from binary systems, is applied to predictions of ternary ion-exchange equilibria.

J114.52

Abstract Withdrawn.

J114.53

Abstract Withdrawn.

J114.54

Transferred to J115.5

J114.55

MINERAL PHASE FORMATION FROM RT77 WASTE GLASS ALTERATION AND ASSOCIATED CESIUM RELEASE. Y. Iwasaki, K. Idemitsu, T. Kyogoku University, Tokyo, JAPAN, T. Maseda, H. Ogawa, F. Imagona, Japan Atomic Energy Research Institute, Tokai Research Establishment, Ibaraki, JAPAN.

A large number of studies on HLW glass corrosion have shown that the glass reacts with water to form more stable mineral phases (alteration phases) during the long-term geological disposal. The potential phases have been evaluated by use of thermodynamic calculations taking into account, amesite, smectite and depending on the conditions. Recent studies have suggested that the formation of zeolite can accelerate the glass corrosion. On the other hand, the formed phases such as zeolite and smectite are expected to have a retention capacity for some radionuclides. Therefore, the glass formation is essential to evaluate the radionuclide release from the glass during the long-term disposal. However, we don't have enough evidence to show that the potential phases by thermodynamic calculations can be formed in the real disposal conditions. In addition, we don't have sufficient data on kinetics of the phase formation and mechanism of the associated radionuclide release. The purpose of this study is to evaluate experimentally, the mineral phase formation from HLW glass and the associated cesium release. Static corrosion tests were performed on powdered RT77 glass in alkaline solutions at elevated temperatures to accelerate the reaction, and mineral phases formed were analyzed by XRD. The results showed that analcime+smectite, muscovite, and beidellite+smectite, was the dominating phase, with residual SiO₂ phases and beidellite+smectite coexisting depending on the conditions. The solution analysis indicated that most of the cesium is retained in the phases of beidellite and analcime by sorption.

J114.56

Abstract Withdrawn.

J114.57

EFFECTS OF THE URANIUM CONTENT ON THE STRUCTURE OF IRON-PHOSPHATE GLASS WASTEOFMS. Diego O. Basco, Diego Rodriguez, Mario E. Sterba, Nuclear Materials Group, National Atomic Energy Commission, ARGENTINA; Jose Mn, Rafael Lopez, Institute E.T. Tomo, Madrid, SPAIN; Carlos Gonzalez Oliver, CONICET, ARGENTINA.

In this work, we have studied and analyzed the thermal transformations that occur in iron-phosphate glass waste forms (typically 26 to 40 wt % Fe₂O₃, 50 to 74 wt % P₂O₅, 0 to 15 wt % UO₂). We have performed DTA/TG analysis as a tool to find the glass transformation temperature, heat of transformation and reaction enthalpy. We also did dilatometric tests to confirm the data obtained in the DTA/TG experiments and to get the softening point and thermal expansion coefficients. Additional data obtained from X-ray diffraction, infrared spectrometry, and Raman spectrometry, helped us to understand the role played by the polyvalent uranium in the vitreous structure of the glass. Finally, chemical durability of the glass was evaluated by water corrosion experiments (PCT Test and MCC-1 Tests).

J114.58


Glass and ceramic waste forms are proposed for the stabilization and immobilization of nuclear wastes. Recent findings show that Na ion exchange reaction has a major role in release of radionuclides from the glass matrix. Several sodium and borosilicate glasses coupons with fixed Na and variable B and Al concentrations were exposed to isotopically labeled aqueous D₂O solution to understand the process that lead to ion exchange and sodium release. Solution compositions were selected to determine equilibrium solubility and reaction equilibria. The objective has been to relate the overall ion exchange rates to Na loss and reaction layer formation that occurs near the glass surface. A combination of Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), heavy ion elastic recoil detection (heavy ion ERD) and secondary ion mass spectrometry (Dynamic SIMS) techniques along with SIMNRA simulations were used to measure the sodium removal and the deuterium and oxygen uptake in the surface and near surface regions of the reacted glass surface. RBS, heavy ion ERD and NRA experimental spectra were simulated using the SIMNRA simulation code with thin layer approximation. The results show that the Na exchange rate is much higher than the major ion dissolution rate. Although the sodium concentration is decreased in the near surface region, it is not completely removed from the outer surface. In the same region, there is also significant amount of O³⁻ incorporated demonstrating considerable interactions between the water and the glass. On the basis of the observed distributions of Na, D and O³⁻, different regions including reaction and diffusion regions were identified in the glass samples. Work was supported by the U.S Department of Energy (DOE) Environmental Management Science Program, the Office of Biological and Environmental Research and Australian Institute of Nuclear Science and Engineering.

J115.59

SENSITIVITY STUDIES OF THE EFFECT OF CLADDING DEGRADATION ON TSPA RESULTS. Eric Siegmund, Eve Devongan, Duke Engineering & Services, Las Vegas, NV.

The Commercial Spent Nuclear Fuel (CSNF) cladding directly influences the dose by reducing the release rate. Cladding degradation model was introduced in Total System Performance Assessment - Value (TSPA) and has been updated to the recently released TSPA-SR (Site Recommendation), Rev 00. The major components in the cladding model are initial cladding failure, creep, Stress Corrosion Cracking (SCC) localized corrosion, mechanical failures (seismic and rock overburden) and cladding unzipping. In the bare fuel case, the dose is controlled by the failure rate of the waste packages (WPs), the solubility limits for certain radionuclides, and the rate of dissolution of the radionuclides through the cracks in the WPs. The cladding model has improvements and more realistic modeling from bare fuel. The model occurs in two steps, perforation followed by unzipping. Results from sensitivity studies show the importance of the cladding in dose reduction is to prevent fuel dissolution (cladding not performed). If all the cladding is performed but unzipping is considered, the peak dose is within 4% of that of bare fuel. The unzipping model and UO₂ dissolution rate is sufficient rapid so that an instant unzipping increases the dose by only 12% from the bare case. Overall, the current cladding degradation model reduces the dose for the first 100,000 years by a factor of 16 when compared with bare fuel. This is because of the low initial cladding failure rate (2.1% including SCC and creep) and few failures from localized corrosion (bare WP patch opening and leak water entering the WPs). Rock overburden starts to fail the cladding after about 100,000 years and accounts for the increase in dose where the cladding model case rises. This mechanism increases the peak dose and delays the peak from approximately 200,000 to 300,000 years.
J111.00
PRECIPITATION OF CRISTALLINE NpO₂ DURING OXIDATIVE CORROSION ON URANIUM SUBMARINES. Robert J. Finch, Argonne National Laboratory, Argonne, IL.
Neptunium-237 is a radionuclide that is of special concern, because of its potential entry into the environment through the thermal-hydraulic half-life (2.14 x 10¹⁵ yr). Current thermodynamic data indicate that the crystalline Np[IV] oxide NpO₂ is the stable Np solid in YM-like groundwater systems, however, NpO₂ may be kinetically inhibited from precipitation due to its similarity to Np[III] oxide Np₂O₃ at nearambient temperatures (~253°C) [1]. Here we report precipitation of crystalline NpO₂ during the corrosion of Np-doped U₃O₈ (Np/U approximately 1.8) in humid air at 90°C and 150°C. The Np-doped U₃O₈ was reacted for several weeks in 22 mL sealed stainless-steel vessels to which 0.3 mL of water and a few drops of H₂O₂ were added. X-ray powder diffraction (XRD) of untreated solids confirmed the only crystalline solid present. Reacted solids were examined by scanning electron microscopy with energy-dispersive x-ray emission spectroscopy (SEM/EDS) and by x-ray absorption spectroscopy (XAS). The results are discussed in terms of the potential mechanism of precipitation of NpO₂ during long-term oxidation of Np-doped U₃O₈ under these conditions. The results indicate that NpO₂ does not form at low temperatures and that the reaction is controlled by diffusion of Np ions through a Np₂O₃ layer, followed by oxidation of the Np₂O₃ to NpO₂.

J111.01
ASSESSMENT OF SPENT FUEL OF ALPHA CLASS NUCLEAR SUBMARINES. J. A. Almgreen, Lawrence Livermore National Laboratory, Livermore, CA; Sviatlana Ignateva, Dmitrii Pukaratov, Ludmila Rihay, Vladimir Tchirkov, Institute of Physics and Power Engineering, Ozeninsk, RUSSIA.
The purpose of this work was to assess and analyze the radiation parameters of the spent nuclear fuel unloaded from the Alfa class Nuclear Submarines (NS) of Project 705K, to determine its radioactivity composition and set the problems on its treatment as a radioactive waste. During 1960-1988 the Institute of Physics and Power Engineering has developed an unique reactor technology that has been realized in the building of the nuclear reactors (NR) cooled by lead-bismuth eutectic alloy in the primary circuit. Such NR were in use in high-speed and maneuverable Alfa class NS. In order to support the coolest technology mastering a couple of land-based lead-bismuth test facilities have been created and operated as a prototype of such NS. All of the operated NR in question belonged to the intermediate neutron reactors: The reactor fuel composition included the iron-metallocic compound of uranium-beryllium with 90 percent of U-235 enrichment and disposed into the beryllium matrix. At present all Alfa class NS are decommissioned. Opposite to water-cooled reactors the refueling of these NR was implemented through the unloading of a single removable block, including reactor core with dropped control rods, reflector (moderator), and upper closure fitting of biological shielding. So, in fact it was the unloading of a sub-critical reactor. The unloaded and non-unloaded spent removable blocks (SRB) have been allocated for temporary storage at the coastal repository and inside the cut reactor modules at Kola Peninsula. However, the permanent storage of the SRB has not been assumed originally. In order to assess the problems of treatment of these SRB during its long-time unplanned storage the radiation parameters of this unloaded from the NS of the Project 705K are determined. Based on that determination the possible ways to make a step-by-step solution of these problems is proposed and the technological and other challenges that the project faces in its realization are considered. Our expertise has showed that: a) a higher level of humidity of Yenisei Mountain groundwater than in its long, after 100 years of cooling it belongs to the HWY form; b) the stored SRB have a relatively low sub-criticality that is sensitive to the exposure of an external adverse conditions; c) the technology of SRB storage preparation for the security of substantial security of water and air penetration into the SRB volume. Thus, the SRB stored are the source of a potential nuclear and radiation danger and must be undoubtedly removed from the reactors and coastal temporary repositories, dismantled and then finally reprocessed.

J111.02
THERMOTRANSPORT OF HYDROGEN IN MODIFIED ZIRCALOY-4 AS A FUNCTION OF HYDROGEN AND OXYGEN CONCENTRATIONS. Hyun Soo Kim, Kyung Suk Lee and Seon Jin Kim, Hanyang Univ, Dept of Material and Science Engineering, Seoul, KOREA.
The hydrogen redistribution induced by the thermotransport in modified Zircaloy-4 at temperatures likely to be encountered in nuclear power reactors (303-360°C) was investigated by means of steady state techniques. The modified Zircaloy-4 was prepared by changing the chemical compositions of Zircaloy-4, which is used widely in a nuclear fuel cladding material in pressurized water reactors. Under the influence of a temperature gradient, hydrogen in modified Zircaloy-4 moves toward the colder region. Solving the transport equation by changing the chemical compositions of Zircaloy-4, and it was confirmed by XRD, OM, SEM. In addition, the change of Q_p for hydrogen, which describes the amount of hydrogen released in the thermotransport, with increasing hydrogen and oxygen concentration was also investigated in modified Zircaloy-4. The values for Q_p for hydrogen in modified Zircaloy-4 were found to be about 0.05% and the values for Q_p for hydrogen were not affected by oxygen concentration. While the value of Q_p for hydrogen decreased with increasing oxygen concentration and it was considered to be due to the trapping of hydrogen by oxygen. Keywords: hydrogen, modified Zircaloy-4, thermotransport, oxygen, heat of transport.

J111.03
NEPTUNIUM INCORPORATION IN URANIUM(VI) COMPOUNDS FORMED DURING THE AQUEOUS CORROSION OF NEPTUNIUM-BEARING URANIUM OXIDES. Robert J. Finch, Edgar C. Buck, and Stephen F. Wolfe, Argonne National Laboratory, Argonne, IL; Battelle Pacific Northwest National Laboratory, Richland, WA.
Neptunium-237 (237Np) is an isotope relevant to evaluating the long-time performance of a geologic repository for high-level nuclear waste, because of its potential mobilility in Yucca Mountain groundwater and its long half-life (2.14 x 10¹⁵ yr). We report on the first experimental studies of Np behavior during the aqueous corrosion of unirradiated Np-bearing uranium oxides. In the experimental studies described here, Np-doped uranium oxides were reacted in humid air within sealed stainless-steel vessels, to which H₂O₂ was added. The resulting solids were reacted at 90°C and 150°C for several weeks. The reacted solids are being examined by scanning electron microscopy (SEM and TEM) with transmission electronic microscopes and x-ray absorption spectroscopy (XAS). Initial analyses of the uranium corrosion products verify that dehydrated scheelite is the predominant uranium(VI) compound formed in these tests. Dehydrated scheelite may be expected to incorporate some Np into its structure, and coexistence of NpO₂ and dehydrated scheelite may help define the miscibility of Np in dehydrated scheelite in the presence of NpO₂ under these conditions. The possibility of a partial conversion of dehydrated scheelite is below detection by conventional SEM/EDS; the results of further analyses of these crystals will be reported. [1] Buck et al. (1998) Miner. Res. Soc. Proc. Vol. 506, pp. 85-94.

J111.04
MEDIUM SURFACE AREA, TO-SOLUTION VOLUME, STATIC TEST OF EBⅡ-HIR radiated MIXED-OXIDE FUEL. J. A. Durrant, P.A. Finn, and M.M. Goldberg, Argonne National Laboratory, Argonne, IL; and Colleen Stehno-David, Idaho National Environmental Engineering Laboratory, Idaho Falls, ID.
The Department of Energy National Spent Nuclear Fuel Program [NSNP] is evaluating the long-term corrosion behavior of DOE-recovered spent nuclear fuel (DOE-SNF). Permanent disposal of the spent fuel is proposed in a repository to be located in the volcanic tuff beds near Yucca Mountain, Nevada. It is the responsibility of the NSNP to determine the release of fission products from the DOE spent fuel and the release and redistribution of fission material resulting from spent fuel corrosion. We describe batch tests on irradiated mixed oxide (MOX) fuel from the Idaho Experimental Breeder Reactor [EBⅡ-H] in Yucca Mountain groundwater. The static batch tests feature very high surface area (fuel grains) to small groundwater volume (high S/V). The objectives of the static batch tests are to examine the composition of the thin film of water that contacts irradiated MOX fuel, to evaluate the alteration-phase formation and paragenesis under conditions that maintain a high S/V, and to compare results of these tests to others performed at low S/V conditions and/or at different solution replacement rates. Under conditions of frequent replacement of the batch test solution and high S/V, the fuel released radioactivity is constant over time, even at an order of magnitude, with that in unsaturated (dry) tests of EBⅡ-H MOX which are conducted with much more frequent solution.
J111.05
INVESTIGATION OF THE OXYGEN K-EDGE IN SPENT NUCLEAR FUEL AND URANYL ALTERATION PRODUCTS.
Edgar Buck, Pacific Northwest National Laboratory, Richland, WA.

According to Pajino et al. and others, the mechanism of charge balance in UO2 involves the generation of point defects and oxidation of U4 to U5. However, direct experimental evidence for these charge balancing mechanisms is completely lacking. Experimental verification will require accurate assessment of the U-O bond length combined with modeling of the coordination environment. Calculations by Orlender suggest that uranium should be oxidized to U5 in spent UO2. Compounds containing U5 are rare and usually unstable.

Known examples include U2MoO8, U4O6, U5O7, and U5O12Cl.

Burns and Finch found crystallographic evidence for U5 in a natural mineral, [Ua4U7]2[(O)(H)]2[O4(H2O)]; however, this uranylformic phase is extremely unstable. The existence of U5 in a solid phase that was determined directly from structural arguments. In addition, evidence for U5 by most spectroscopic techniques (including X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS)) cannot distinguish, with any certainty, a mixture of U5 and U6.

In this study, the nature of the U-O bond was investigated with Electron Energy-Loss Spectroscopy (EELS) on the Transmission Electron Microscopy (TEM). Through measurement of the contrast variation in the bond, the oxidation state of the uranium in an unknown was estimated. In this paper, the O-K edge in the U-O bond from a series of uranium-bearing phases is reported. There is little covacency in the M-O bond in the spent fuel, as expected, given the much greater alteration of rare earths and actinides. In contrast, the O-K edge from [U] uranophane shows only covariant M-O bonding.

The M-O covacency shifts the O-K edge to around 510 eV.

J111.06
CEHER INCORPORATION IN A URANYL HYDROXIDE PHASE.
Cheol Whan Kim, David J. Wnekiewicz, Univ. Missouri-Rolla, Dept. Geology & Geophysics, Rolla MO; Robert J. Finch, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

The neofield migration behavior of radiocadium in a nuclear waste repository will be influenced, in part, by their equilibrium solubilities and for admixture with those of trace elements of host phases. Uranyl phases that develop on the surfaces of altered spent nuclear fuel may thus influence the mobility of released radiocamides, since by proximity, these will be the first phases that the radiocamides encounter as they leave the spent fuel matrix. The potential for incorporating rare earth elements (REE) into crystalline compounds has been evaluated by precipitating uranyl phases from aqueous solutions containing 2.1 ppm Ce4+ at a temperature of 19°C. The cerium serves both as a monitor for evaluating the potential reactive behavior of uranium in the solid state.

The crystalline compound (or compounds) that formed in the experiments has not been positively identified, but X-ray diffraction profiles match closely to a powder pattern from a uranyl hydroxide [UO2(OH) 2]; cf. JCPDS card 43104100 and several uranyl carbonate phases. An analysis of the leachable, leachate, and solid phases from sorption experiments (dissolution in deionized water; acid solution) was performed by Inductively Coupled Plasma - Mass Spectrometry. Results indicate a progressive increase in concentration of cerium in the solid from 26 to 29, and finally 11 ppm for crystals produced in 7, 35, and 180 day tests, respectively. This trend correlates with a coarsening of the crystals over the same time interval, suggesting a lowering of the potential for Ce incorporation as the overall surface area/volume ratio of the crystals decreases.

J111.07
SORPTION-REAGENT METHOD IN LIQUID RADIOACTIVE WASTE MANAGEMENT.
Valentin Avramenko, Veniamin Zhelezov, Elena Kaplan, Dmitriy Marinin, Tatiana Sokolovskaya, Anna Yukhkon, Inst of Chemistry PFLAS, Vladivostok, RUSSIA.

Methods of liquid radioactive waste (LLW) decontamination from radionuclides including their coprecipitation at specific conditions or adsorption on selective sorption materials are well known and extensively used in LWRs. This paper summarizes our ideas and work results on studies and application of a sorption-reagent method of microeludcation and radionuclides removal in which selective radionuclide sorption is provided by the sorbent reacting with components whether containing in solution or deliberately added into it. The sorption-reagent materials synthesized for decontamination purposes are the most highly selective in regard to such difficult to remove radionuclides as strontium 90 and cesium 137. It was shown by comparative analysis of radionuclide removal efficiency by traditional selective sorbents and developed sorption-reagent materials that the latter have the highest distribution coefficients in systems too complex for pure sorption/ion-exchange decontamination. For example, it was shown that the strontium distribution coefficients several dozen times higher than those of commercially available sodium tetraborate and silicotungstate. One of the main fields of the sorption-reagent materials application can be decontamination of high-salinity radioactive waste. In particular, whether as a result of ion-exchanger filters regeneration in LWR or in reverse osmosis installations. Use of sorption-reagent materials for high-salinity waste management enables to reduce several ten-fold or even hundred-fold the volume of solid radioactive waste (SWW) for be sent for final disposal and, therefore, to decrease the cost of LWR management. Data on a pilot-plant scale testing of the LLW sorption-reagent decontamination installation are presented. 385 cubic meters of LLW of complex chemical composition were decontaminated. This initial waste contained seawater, high-salinity waste remaining after the reverse osmosis process and decontaminated LLW. The degree of decontamination LLW met all the national (and international) safety standards. Total amount of SWW sent for final disposal was 0.6 cubic meters.

J111.08
POHUS CRYSTALLINE SILICA (GUKBA) AS AN INORGANIC SUPPORT MATRIX FOR NOVEL SORBENTS. T.J. Traister, Idaho National Engineering and Environmental Laboratory [INEEL], Idaho Falls, ID; A.S. Aloy, N.V. Sazonovskii, Khlopin Radium Institute, St. Petersburg, RUSSIA; A.A. Tret'yakov, Mining and Chemical Combine, Zheleznogorsk, RUSSIA; A.G. Anishtin, Institute of Chemistry and Chemical Technology, Krasnoyarsk, RUSSIA; D.A. Knecht, T.A. Todd, and J. Mcclaret, INEEL, Idaho Falls, ID.

Inorganic ion exchange media typically exist as fine powders, making large-scale use impractical, unless the media can be applied to an appropriate matrix. Likewise, organic chelating agents are typically dissolved in a solvent and absorbed into porous matrices for use in extraction chromatography. The most common matrices utilized in both cases are organic materials, which are not compatible with high radiation fields or acceptable as final waste forms. Recent investigations have shown that ion exchange and chelating agents can be effectively loaded within a porous crystalline silica (Gukba) matrix. This approach allows for target radionuclides to be absorbed into a porous matrix which exchanges them onto the surface and becomes the final waste form. Subsequent to adsorption of the radionuclides, the Gukba matrix can be compressed in a hot uniaxial press, resulting in an overall volume reduction (vol. liquid/vol. final waste form) of 1:400. The porous glass matrix is produced in Russia using fly ash residue from coal combustion power generating plants. It consists of consolidated wriggles of hollow glass capillaries and is termed Gukba which is the Russian word for spittle. This paper describes a collaborative research program between the Khlopin Radium Institute [KHI], St. Petersburg, Russia, the Institute of Chemistry and Chemical Technologies, Krasnoyarsk, Russia, the Mining and Chemical Combine, Zheleznogorsk, Russia, and the Idaho National Engineering and Environmental Laboratory. Molybdenophosphate (AMP) for the removal of cesium from acidic liquid waste and Oxyphenyl). N-3-Dicyclohexylcarbodiimide-3-methylphosphonate oxime (CMPO, for the removal of lanthanides and actinides from acidic liquid) have been successfully incorporated into Gukba matrices. Test results for cesium and americium removal, using AMP-Gukba and CMPO-Gukba, respectively, will be discussed.

J111.09
DEMONSTRATION OF THE FEASIBILITY OF RECOVERING AMORPHOUS AND CURIUM IONS FROM A LANTHANE BOROSILICATE GLASS.
Tracy S. Rudall, David K. Peeler, and Thomas B. Edwards, Westinghouse Savannah River Company, Aiken, SC.

A solution containing kilogram quantities of highly radioactive isotopes of americium and curium (Am/Cm) is currently stored in a process tank at the Department of Energy's (DOE's) Savannah River Site. This tank and its vitrual support systems are old, subject to degradation, and prone to possible failure. For this reason a decision was made to vitrify the material and store the glass until
programmatic decisions on use or disposal are made by the DOE. Potentially, the glass could be shipped to the isolop production and distribution facility at the Oak Ridge National Laboratory for californium-252 production and use by the transplutonium research community. To facilitate subsequent recovery of the Am/Cm, a lanthanide borosilicate glass was selected for the vitrification process since the lanthanides are highly soluble in strong acid solutions. This demonstrates the feasibility of recovering the Am/Cm isotopes from the glasses, a series of small-scale experiments was performed as part of a compositional variability study. Glasses fabricated during the study utilized counterions that are not associated with the high specific activity of these materials. In the dissolution tests, glass formulations representative of potential uncertainties in the composition of the Am/Cm solution were fabricated, ground to a 35 to 60 mesh, and dissolved in 9 M nitric acid at 110°C. Under these conditions, at least 98% of the lanthanide oxides in the glass dissolved in less than 2 hours, a recoverability criterion established for the vitrification process and imposing no limitations on the acceptable glass composition region.

**J111.70**
SYNTHESIS, CRYSTAL CHEMISTRY AND ENERGETICS OF MICROPOROUS SILICONIANES IN THE 
\[K_2(\text{O}_6)\text{H}_2\text{Si}_3\text{O}_12\text{OH}\cdot\text{H}_2\text{O} \text{ SYSTEM} \]

H. Xu, A. Nisbet, Dept. of Chemical Engineering & Materials Science, University of California, Davis, CA; M. D. Nyman, T. M. Menoff, Catalysis & Chemical Technologies, Sandia National Laboratories, Albuquerque, NM; Y. Su, ML. Balmer, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA.

Crystalline siliconitane (CST) ion exchangers are of considerable interest because of their high selectivity for radioactive 125I Cs and their potential application in the separation of 134Cs from aqueous solutions. In this study, we synthesized a mixture of microporous phases with the compositions \[K_2(\text{O}_6)\text{H}_2\text{Si}_3\text{O}_12\text{OH}\cdot\text{H}_2\text{O} \] \((n = 4 \text{ to } 6, 0 \leq x \leq 1)\) using the hydrothermal method. Rietveld analysis of synchrotron XRD data indicates that these phases are non-stoichiometric with the mineral phanosiderite (space group P6/m) and that the lattice parameter a increases linearly with increasing Cs content. The enthalpies of formation from the oxides and from the elements were determined by drop solution calorimetry with 2-propanol as solvent at 923 K. Our results show that the formation enthalpies become more exothermic with increasing Cs/K ratio. Thus the Cs uptake in this solid solution series is largely thermodynamically driven.

**J111.71**
ANIS-Ti-Si \((A = Na, K, Rb, Cs, Sr, Ba)\) OXIDE FRAMEWORK CONDENSED AND MICROPOROUS PHASES AND THEIR APPLICATION TO RADIONUCLEIDE SEQUESTERATION AND IMMobilization.

May Nyman, Tina M. Menoff, Sandia National Laboratories, Albuquerque, NM; Robert S. Maxwell, Lawrence Livermore National Laboratory, Livermore, CA; Akeleif Tripathi and John B. Delia, Department of Chemistry and Department of Geosciences, State University of New York, Stony Brook, NY; Alexander Nisbet and Hongxu Xu, Dept. of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA.

Crystalline siliconitane (CST) is a microporous ion exchanger that has undergone extensive and advanced testing for the application of selective removal of radioactive Cs from DOE defense waste. Substitution of small amounts of Nb into the Ti framework site greatly enhances the selectivity for Cs. Since this type of heterovalent substitution in both open framework and condensed phases requires modification or compensation of the charge balance by cation vacancies, there is a counter-substitution, or addition of exchangeable protons to properties such as exchange capacity, kinetics and selectivity of porous phases and stability of condensed phases may be tailored. We have extended this strategy to the development of new ANS-Ti-Si \((A = Na, K, Rb, Cs, Sr, Ba)\) oxide framework materials in the application of radionuclide sequestration and immobilization, where condensed phases are optimized toward stability, and microporous phases are optimized toward selectivity, high capacity or rapid ion exchange. We report here two new families of niobate-based ion exchangers in which heterovalent substitutions are made. Ion exchange and stability properties are investigated as a function of framework substitution, particularly with regard to exchange of divalent cations. We also report a series of extremely stable niobate-based condensed phase materials, and stability and structure as a function of composition are reported for these materials. Special focus is given on cation balance by extra-framework ions and exchange capacity, kinetics and selectivity of porous phases.

**J111.72**
Transferred to J12.1.5

**J111.73**
RELEASE BEHAVIOR OF NEPTUNIUM, PLUTONIUM, URANIUM AND TECHNETIUM FROM THE METALLIC WASTE FORM FROM THE ELECTROMETALLURGICAL TREATMENT PROCESS.

S. G. Johnson, M. Noy, T. DiSalvo and T. J. Moeschetti, Argonne National Laboratory, West, Idaho Falls, ID.

Argonne National Laboratory is developing an electrometallurgical treatment for spent fuel from the experimental breeder reactor II. A product of this treatment process is a metal waste form that incorporates the transplutonium elements as metals or metal oxides. The fission products that are noble to the process, i.e., Te, Ru, Pd, Rh, Ag. The nominal composition of this waste form is stainless steel/15% zirconium/1-4% noble metal fission products /< 1% U. The process used the metal waste form from the cladding hulls is straightforward. The hulls after being removed from the electrometallizer are introduced to a furnace where the adhering salt from the electrometallizer is distilled off. The hulls are then placed into a crucible and, if necessary, smelted to ensure all stainless steel is added to adjust the composition to within the target bounds. The casting takes place at 1650°C with a 2 hour hold. The finished product, during this demonstration phase of the project, is an ingot approximately 20 cm in diameter and 3 cm thick. The behavior of actinides specifically, U, Pu, and Np, and Te is evaluated using a standardized test method followed by ASTM C1220. Alloys of the base composition stainless steel with 15% zirconium were produced that were doped with U, Pu, Np, and Te. Samples from these alloys were then subjected to immersion tests at 90°C for duration of 14, 34, and 91 days. The surface area of sample of volume 2.5 cm³ was 40 m². The immersion was performed in deionized water, of which the surface temperature was 90°C. The surface finish of each monolith sample was prepared to, as nearly as possible, an identical state. The tests were performed in triplicate to provide for adequate gauge of the precision. The tests were terminated at 14, 34, and 91 days and the samples removed from solution, dried and weighed. The test solutions were acidified to 2 vol.% acidity using high purity nitric acid. The test vessels were subjected to an 18 hour 90°C acid strip using 2 vol.% nitric acid solution. This acid strip solution was also analyzed. The test and the acid strip solutions were analyzed for Cs, Sr, Ni, Mg, Mn, Zr, Pu, U, Np and Te using inductive coupled plasma mass spectrometry (ICP-MS). The intent of these tests was to determine which, if any, of the actinides constitute the metallic waste form released during this type of test. These tests would also establish quantitatively the release behavior of these elements under the conditions used here. Earlier tests had shown that these various elements that constitute the metallic waste form released to solution at different rates extending over several orders of magnitude with uranium being the element released to the greatest extent. This test sequence performed in triplicate at several different times will allow for the confirmation of this behavior, as well as the establishment of the early time dependent behavior of these actinides.

**J111.74**
THERMAL BEHAVIOR OF POLYMERIC MATRICES FOR NUCLEAR WASTE IMMobilization BY DSC AND TG.

Edsia M.B. de Souza, CDTN, CNEN, Belo Horizonte, BRAZIL; Ricardo G. de Souza, Depo de Engenharia Quimica, UFMG, Belo Horizonte, BRAZIL.

The objective of the present work was to evaluate the thermal behavior of polymeric matrices used in dangerous waste immobilization. A recycled pentoxide catalyst and ion exchange resins with inorganic cesium were used in the dangerous waste. The polymeric matrices, pure and with waste, obtained by the solubilization of polyethylene recycled in isopropanol and lye scintillator, were microscopically homogeneous. The thermal behavior of all the matrices was evaluated by Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG). With the DSC curves it was possible to verify the melting and degradation temperatures of the polyethylene and matrices. From the TG curves it was possible to determine the mass variations during the heating of the samples. These curves evidenced that the processing of the polymeric matrices does not alter the thermal behavior of the polymeric matrices. The use of recycled polyethylene indicates a great potential for immobilization of dangerous waste.

**J111.75**
AGING OF BITUMEN WASTE FORM IN A WET REPOSITORY CONDITION.

Michael I. Ojovan, Natasha V. Ojovan, Zoya I. Golubeva, Irene V. Starkova, Alexander S. Barinov, SIA Radiom, Moscow, RUSSIA.

Bitumen waste form for low and intermediate level waste (LLW) immobilization is under investigation at SIA Radiom for about three decades. Bituminized waste blocks were prepared at industrial plant on base of NPP-09 waste. Physical and chemical parameters of bitumen waste form containing 31 wt. % waste were investigated.
after its long-term storage in an experimental shallow-ground repository during 12 years. Leaching behavior of bituminized waste form was evaluated. A fraction of initial radioactive inventory was released from the block during 12 years of storage. Non-homogeneous distribution was determined for both salts and radionuclides along vertical axis. Fraction composition of bitumen host matrix was studied. The similarity of microstructure, elemental composition and aromatic hydrocarbons were separated for different parts of bituminized waste block. The bitumen fractions were distributed vertically non-homogeneously as well as the radioactivity of bitumen host matrix. The amount of bitumen was maximal in the middle part of block. Ageing of bitumen waste form during 12 years is characterized mainly by the increase of asphaltene fraction content (about 4%). The changes in the bitumen waste form will be used for modelling its long-term behavior in the repository conditions.

SESSION J112: WASTE PROCESSING
Chair: Bill Holocauster and Frederick M. Mann
Thursday Morning, November 2001
Republic B (Sherron)

8:30 AM J112.1

Radioactive high level waste (HLW) sludges at Savannah River Site are stored as caustic slurries in millions gallon tanks. These slurries are being processed and immobilized into borosilicate glass in the Defense Waste Processing Facility (DWPF) for geologic disposal. A batch of feed for the DWPF is approximately 500,000 gallons of washed slurry and is obtained by combining slurries from different tanks into a single million gallon feed tank. Washing occurs in this tank. This paper discusses the washing of the next batch of feed for the DWPF. Results of a laboratory scale test with actual radioactive slurry and washing in the feed tank are presented. Prior to processing in the DWPF, the slurry must meet certain criteria. One of these is the sodium, nitrate, and nitrite concentrations in the slurry. In unwashed slurry, these concentrations are too high. They are reduced by washing the slurry several times with inhibited water (IW) (0.01 M NaOH and 0.01 M HNO3) and washing of the sodium affects glass quality and nitrate and nitrite affects NO production in the DWPF. Washing is accomplished by adding IW, mixing the slurry, and then allowing the sludge to settle. A portion of the supernate is decanted and the next wash step initiated. These steps were also completed for the laboratory test. In the laboratory test, we investigated if washing removes any actinides or U-235 fission products from the insoluble sludge. Results indicated that while the concentrations of those elements, ions, and radionuclides that were already in the supernate were reduced significantly, there was only slight solubilization of U, and fission products (U-239, Pu-239, and Pd). Results from the full scale process indicate that concentrations of Na and other soluble in the supernate decreased as predicted by a model developed from the laboratory study.

8:45 AM J112.2
THERMODYNAMIC MODELING OF DEPOSITION IN SAFFANIVER RIVER SITE (SRS) EVAPORATORS. Carol Jantzen and James Larinat, Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC.

A nitrated aluminosilicate in the soda-lime/calcium mixture (NaAl₄SiO₆·3(Al₂O₃·2NaO)·SiO₂·3NaO) and sodium diuranate (Na₂U₂O₈) formed intermittently in the Savannah River Site (SRS) HLW High Level Waste (HLW) evaporators. Thermodynamic modeling of mineral super saturation, in the form of activity diagrams, were used to develop a process control tool to prevent evaporator feed tank compositions from precipitating aluminosilicates. It was determined that reactive oxides, soluble silicates, and soluble aluminates combine in these highly concentrated solutions to form sodium aluminosilicate (NAS) hydrogel at ambient temperature. The hydrogel converts to Zeolite A (Na₂A₂S·2H₂O) under hydrothermal conditions at elevated temperature, e.g., the conditions existing in the SRS evaporator. The complete set of sequential densification (reaction) transformations is: NAS gel → Zeolite A(cubic) → aluminosilicate (cubic) → carbonate [hexagonal]. The initial step is the saturation of the evaporator feed tank solutions with respect to the parent NAS gel phase, the primary phase from which all the others are derived. The NAS gel phase formation is also the kinetically most rapid step in the formation sequence. Thermodynamic calculations were performed on the NAS gel. While thermodynamically derived activity diagrams, also known as stability diagrams, are commonly used to represent equilibria between mineral species and aqueous solutions on geochemical time scales, activity diagram representation is appropriate since the formation of the NAS gel and the sodium diuranate are kinetically very rapid compared to the evaporator residence time (3.3 hours).

9:00 AM J112.3
PROOF-OF-CONCEPT FLOW SHEET TESTS FOR CESIUM REMOVAL FROM TANK WASTE BY CAUSTIC-SIDE SOLVENT EXTRACTION. David B. Chamberlin, Scott Ams, Hassan A. Arafat, Clif Center, Ralph A. Leonard, Monica C. Regalbuto, and George F. Vandersliff, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

A caustic-side solvent extraction (CSSX) process to remove cesium from Savannah River Site (SRS) high-level waste has been developed through a joint program with Oak Ridge National Laboratory, the Savannah River Site, and Argonne National Laboratory (ANL). The CSSX solvent consists of an extractant, 0.01 M MBOClx6 CF; a modifier, 0.50 M Cs-75B; and a suppressant, 0.001 M trietylamine in a branched paraffin hydrocarbon diluent, Isopar L. In this program we have developed and demonstrated a flow sheet that can be used to process SRS tank waste. To this end, a series of flow sheet tests were completed using simulated waste in a 2-m centrifugal contactor at ANL. Three short-term (3-4 hour) tests were completed to demonstrate various aspects of the flow sheet. These tests were followed by a 71-hour test where the solvent was recycled 42 times. In each case, we met or exceeded the key process goals: (1) cesium removal from the waste to the effluent stream; (2) elimination of cesium in the stripping stream; (3) stripping the solvent sufficiently to allow it to be recycled many times. The results from these tests, and the importance of centrifugal contactor to improve extraction efficiency, will be discussed.

9:15 AM J112.4
CHEMICAL INTERACTIONS OF UOP INSY® IL-911 (CST) WITH SRS WASTE SIMULANTS. My Nyman, James L. Krumhansl, Carlos Jove, Cokon Pengzhe Zhang, Tina M. Nenoff, Thomas J. Hendry, Sandin National Laboratories, Albuquerque, NM; Yale Si and Liu Li, Pacific Northwest National Laboratory, Richland, WA.

UOP INSY® IL-911 is a bound form of crystalline silicotitanate (CST) for use in ion exchange columns that was extensively tested for removing Cs-137 from the Savannah River Site (SRS) tank wastes. In some similar tests, column plugging incidents were observed, which led to thorough investigations to determine the causes and to develop protocols to avoid future plugging incidents. A related problem was the Cs-137 producibility of the CST resin that precipitates as a poorly crystalline, hydrous sodium dihydrogen and the second is crystalline aluminosilicate zeolite, or carbonater. The source for the sodium carbonate precipitate was determined to be a minor impurity phase that is a byproduct of CST manufacturing. The mechanisms of dissolution and reprecipitation of this phase in column pretreatment fluid (2N NaOH) was investigated, and a pretreatment protocol to rid IL-911 of this impurity was devised. Further, the IL-911 manufacturing cycle (UOP) modified its production procedure in a similar manner to rid IL-911 of this impurity. On the other hand, the source material for the aluminosilicate zeolite precipitate was determined to be predominantly from the waste solution rather than the CST resin. Silicotitanate experiments coupled with a thermodynamic analysis provided a protocol to predict when aluminosilicate precipitation will and will not occur. This, in turn, suggested that dilution may be used to prevent in-service column plugging by aluminosilicate precipitation. Finally, it was also established that aluminosilicate precipitation on the surfaces of the IL-911 granules could also account for an apparent decrease in equilibrium Kₐ as well as decreasing the kinetics of Cs sorption.

9:30 AM J112.5
INVESTIGATION OF CHEMICAL AND THERMAL STABILITIES OF PRE-LOADED CRYSTALLINE SILICOTITANATE. Yai Si, Liu Li, James S. Young, Pacific Northwest National Laboratory, Richland, WA; M. Lou Balmer, Caterpillar Inc., Peoria, IL.

An inorganic ion exchanger based on crystalline silicotitanate (CST),
IONSIVIE-911, exhibits very high selectivity for Cs over alkali metals and is useful for removal of the Cs radionuclide from defense wastes such as those stored at Hanford. The performance of this ion exchanger, has been well characterized under normal operating conditions, the stability of the material at slightly elevated temperatures, such as those that may occur in a process upset, is the subject of current investigations. IE-911 was exposed to waste simulants at 55°C and 80°C for durations of 1 to 60 days to determine if irreversible desorption of Cs from IE-911 occurs and the cause of desorption, as well as the time/temperature profiles over which desorption could be prevented. The stability of Cs desorption behavior at 80°C and 100°C, is being investigated. For the aluminosilicate precipitate, the stability of the Cs source for the aluminosilicate precipitate was not obvious. The sorption on the surface of almost all the heat-treated IE-911 samples. Cation-exchange aluminosilicates have large size openings in their structure so that Cs should be able to diffuse through these pores to IE-911 when the temperature was lowered. The mechanism for irreversible Cs desorption has been investigated and will be presented in the meeting.


Organic based ion selective resins have a desirable properties as materials for the separation and treatment of nuclear wastes: ease of synthesis, high metal ion complexation ability, and flexibility for different nuclear waste management applications. For most nuclear applications, the ligand is deemed to be of primary importance for the interaction with the radionuclides in the waste matrix. The polymer matrix is usually ignored. For ion specific resins, the polymer structure is formed to a specific metal ion. Using the molecular imprinting technique, resins can be formed with functional groups and cavities for a target ion.

Ion exchange resins were created to selectively complex either uranium or thorium. The target metal ion, either UO2+ or Th4+, was dissolved in the solvent, CCl4. While the resin was created around the ions to provide a unique structure based upon each metal. These resins were synthesized by a radical polymerization method, producing a reusable organic solid. The resins were qualified by obtaining values for their proton exchange capacities and data to define their complexation kinetics. Proton exchange capacities were determined using an indirect titration and were found to be 6.40 meq/g for the uranium-based resin and 4.61 meq/g for the thorium-based resin. Data for the resins were obtained at pH 1.0, 2.5, 4.0, and 5.5. Results show that ion-exchanged resins can be recovered from aqueous solution under experimental conditions. Once loaded with metal, the ions can easily be removed with 5 M HNO3 and reused. The acid wash is thermodynamically described to allow modeling of separation schemes.

SESSION J113: GLASS STRUCTURE AND CORROSION
Chair: Neil E. Biber and Olivier Spalla
Thursday Morning, November 29, 2001
Republican B (Sheraton)


Single-pass flow through (SPFT) experiments were performed with a series of simple binary mixing glasses along the alkali-rare earth join [2.55]Na2O-xAl2O3 (0.5-x)B2O3, 0 ≤ x ≤ 1] and with a high-level waste analog glass [1.47Na2O-1.8B2O3-78.52O2] that has been tested extensively in France. Desorption rates for these glasses were determined at fixed solution pH and fixed SO2 activity up to smorphic silica saturation. At early times in the experiments (non-steady state conditions), there is no correlation between SO2 activity and the rate of glass dissolution. This occurs because of) surface artifacts introduced during sample preparation, and 2) molecular clustering in glasses where the molar B2O3 content (determined from 11B MAS-NMR) into borate units that are much more reactive than the bulk glass matrix. These factors dominate the early time behavior in static experiments, and so explain the reported strong deviation from expected behavior based on the transition state theory (TST) of chemical kinetics. In contrast, once steady state is obtained, the dissolution rates vary linearly with respect to a finite range of SO2 activity that depends on glass composition. For glasses with the NBO sites, stoichiometric values were verified with respect to SO2 activity all the way to SO2 (nm) saturation, which in direct accord with expectations from the TST rate laws. In contrast, glasses with a significant population density of NBO sites are not consistent to alkali-rich glasses, which suggests that the reaction rates of glass dissolution in silica-saturated solutions. Consequently, the behavior of these glasses deviates strongly from TST. By doping the aqueous phase with SiO2 and tracking its penetration profile in the surface layers, it was also possible to quantitatively evaluate alternative models that consider the gel layer as a significant mass transport barrier. In general, the results were more consistent with secondary reaction mechanisms as the source of deviations from TST. Consideration of these important secondary effects is critical to developing an improved kinetic theory for dissolution of silicate glasses and minerals.


The chemical and structural role of vanadium in borosilicate melts is of interest with regard to the vitrification of sulfur-bearing radioactive waste for long term storage. In this case, an important issue deals with homogeneously incorporating significant amounts of sulfur from the waste into borosilicate melts. Sulfur can be the waste-limiting constituent in this process, because of its low solubility in silicate melts. Recent investigations have suggested that adding vanadium to borosilicate formulations improves sulfur solubility in the melt. It is therefore of interest to determine if vanadium has any influence on or affinity with sulfur in the glass structure. XANES and EXAFS data were collected and analyzed to characterize vanadium in a variety of borosilicate glasses, some with and some without sulfur, that have vanadium oxide concentrations as high as 9.99%. The data for all glasses investigated indicate that, if not all, vanadium is 5 valent and is tetrahedrally coordinated by four oxygen atoms. There is no evidence from the data of V-S bonds in any of the glasses investigated. Both XANES and EXAFS also show that melt glasses synthesized under reducing conditions can have small amounts of V5+ up to approximately 20 to 25% of all vanadium present in the glass with the remainder being V4+. Increasing concentrations of peroxo-terminated V5+ can be achieved by adding sulfur to the melt, which increases the redox-reaction between the glass structure; however, vanadium bonding to S=O tetrahedra cannot be completely ruled out.

11:00 AM J113.3 STRUCTURAL ENVIRONMENT OF HAFNINUM IN BOROSILICATE GLASSES WITH VARYING SODIUM ALUMINUM RATIOS. D. L. Bader, Galler Laboratories, San Jose, CA, Linda L. Davis, Department of Geology, Northern Arizona University, Flagstaff, AZ, John G. Durall, Battelle, Pacific Northwest National Laboratory, Richland, WA, David K. Shah, Corvin H. Booth, Jerry J. Baehr, Ernest O. Lawrence Berkeley National Laboratory, Berkeley, CA; Denis M. Stranger, Battelle Pacific Northwest National Laboratory, Richland, WA.

Hafnium-bearing glass series were made in crucibles at temperatures between 1450 and 1500°C. The manner in which the Hf8+ is incorporated into the crystal-free glasses was the object of an X-ray absorption spectrometric study. Data for glasses with peralkaline to peraluminous compositions are presented here. We note an unusual feature at the white line maximum at the Hf L1 absorption edge, many of our samples exhibit a split peak, which we had not reported in the Hf L2 XANES prior to our work. Similar features have been observed in the L2 XANES of a few other samples. The effects are observed in the second derivative spectrum of the XANES as a double well. The double well is indicative of crystal field splitting of the vanadium d manifold of Hf4+ and is characteristic of Hf in an octahedral coordination environment. As the composition in a glass series changes from peralkaline (where for these compositions, Na2O to peraluminous (Al2O3Na), the double well disappears, indicating a
change in the coordination environment from octahedral to perhaps 7 or 8-fold coordination. Analysis of Hf L XANES corroborates that of the Hf K edge. The final model composed with Np and Tc found all the peralkaline glasses are essentially structurally identical to each other, and similar to a Hf silicate studied in which Hf is in octahedral coordination. The H-F bond distances are near 2.06 Å, typical for Ge coordination, and bond distances for the second shell Si [or Na, B, or Al] O are consistent with the six-membered ring structural motif observed in the Hf silicate. The data for the peralkaline glasses is consistent with the presence of two different Hf environments compared to similar to that in the Hf-alkaline silicate and, additionally, a structural motif distinct from the silicate.

In order to determine the influence of the alteration layer on the RT77 nuclear waste glass dissolution, some experiments were conducted. Alteration tests were performed in different aqueous media (pure water, siliceous and silico-phosphoric solutions) at 90°C. The S/V ratio is close to 0.5 cm-1 in order to develop quickly a high alteration (thickness) layer. After a five day alteration, the sample is taken and dropped into a new solution. This process is repeated three times. Solution (by IPC-MS) and solid analyses (by SEM, TEM and FTIR) were realized to follow the alteration process. Results show a decrease of concentration versus renewed process, producing a stabilization of the alteration rate. For comparison to studies in static condition, the glass alteration rate r diminishes in a constant way during the four tests. The surface solid analysis shows the development of microcrystalline zircon at the external part of the glass during the alteration in pure water and silico media. Chemical X-RDS analyses and electron diffraction put in evidence the presence of clay minerals with enrichment in iron and zinc. In the phosphoric media, the altered layer seems to be more homogeneous with a constant increase of phosphorus from the solution to the raw glass. Some dark nodules are observed at the external part of the gel. The chemistry of these nodules is essentially phosphatic with a high proportion of lanthanides; and HREEs show crystallization of some micro-domains.

The alteration of simplified glasses (as compared to the nuclear glasses) has been studied by X-ray scattering experiments which allow to characterize the structure of the porous layer at the mesoscopic scale (1-1000 nm). In the presentation, we will focus on glass compositions based on a ternary system (SiO2/Na2O/Al2O3 = 50/15/35) to which ZrO2 was added up to 5%. Hence, the aim of the paper is to study the effect of the initial Zr content on the morphology of the gel layer. The glass grains (35-50 micrometers) have been altered in hot water for periods lasting from one week to 4 months. Altered layers were produced at the interface, the structure of which was characterized by Small Angle X-ray Scattering (SAXS) and Anomalous Small Angle X-ray Scattering (ASAXS) at the K-edge of the hardener element Zr. The results show that the layer is nanorough. Furthermore, the size of the pores and the pores volume fraction in the altered layer both depend on the amount of Zr in the initial composition and on the time of alteration. The study with time reveals that the layer constructs in two stages. First, the thickness of the layer increases linearly with time, but the pores remain very small (1nm), then the size of the layer increases at a constant rate until it ripens and the specific surface of the pores decreases. For a given rate of alteration, the pores gets smaller as the initial Zr content increases. This decrease of pore size is very rapid from 0 to 3% in Zr. On a more general level, these results are discussed in the framework of a model of pores nucleation growth and coalescence, where the driving force for ripening of the porous morphology is the partial solubility of Si which depends on the local curvature of the gel-water interface.

11:45 AM J313.6
LEACHING OF Np AND Tc FROM DOPED NUCLEAR WASTE GLASSES IN CLAY MEDIA: THE EFFECTS OF REDOX CONDITIONS. Vera Perlot, Karel Lammens, Pierre Van Impe, SCK, CEN, Waste and Disposal Department, Mol, BELGIUM.

Boom Clay is the candidate geological formation in Belgium for disposal of vitrified high level waste for which Np-237 and Tc-99 are some of the main critical radionuclides. The results of corrosion tests involving glasses doped with Np and Tc depend strongly on the redox conditions of the media contacting the glass. Tests with the RT77 glass and the PANELLA glass doped with Np and Tc showed that all the peralkaline glasses are essentially structurally identical to each other, and similar to a Hf silicate studied in which Hf is in octahedral coordination. The H-F bond distances are near 2.06 Å, typical for Ge coordination, and bond distances for the second shell Si [or Na, B, or Al] O are consistent with the six-membered ring structural motif observed in the Hf silicate. The data for the peralkaline glasses is consistent with the presence of two different Hf environments compared to similar to that in the Hf-alkaline silicate and, additionally, a structural motif distinct from the silicate.

SESSION J314: SPENT FUEL AND TRANSPORTABLE CHEMISTRY
Chairs: Edgar Back and Christopher Poirsot
Thursday Afternoon, November 29, 2001
Republic B (Sheraton)

1:30 PM J314.1
COMPARISON OF NUCLIDE RELEASE UNDER UNSATURATED TEST CONDITIONS FROM BWR FUELS WITH A RANGE OF BUSPIS, Patricia A. Finn, Y. Tosi, S. Wulf and J.C. Cunanan
Argonne National Laboratory, Argonne, IL

The magnitude of the nuclide releases from BWR and PWR fuel was determined under conditions similar to those expected in a geological repository at Yucca Mountain. Two BWR fuels (burnup of 64 and 71 MWD/kgU) and two PWR fuels (burnup of 30 and 45 MWD/kgU) were exposed to humid air and dripping groundwater. Differences in the fuels included burnup, geometric surface area, and size of the BWR fuels, and Gd content (2% Gd in the 64 MWD/kgU BWR fuel Gd BWR). The release rates of 238 U, 239, 241Pu, 241Am, 235U, 239U, 239Pu, 237Np, 240Cm, 241Cm, 237Pa, 239Pu, and 235Pa were compared at each test interval for the first two years of reaction. The release rates for all four fuels were within an order of magnitude of each other except for 237Pa and 239Pu. For 237Pa, the release rates of the BWR fuels were two orders of magnitude larger than the release rates for the PWR fuels. The 239Pu release rate of the Gd BWR fuel was two orders of magnitude larger than the 239Pu release rates of the PWR fuels and an order of magnitude larger than the release rate of the gow BWR fuel. The nuclide concentrations of 237, 239, 241, and 239Pu in the leachates were also examined. The 238U concentrations (2x10^-6 M) were similar for the PWR and BWR fuels. This agreement was consistent with the formation of similar uranyl alteration phases in both sets of tests. The Pu concentration was between 2x10^-7 and 2x10^-6 M for the four fuels. Most of the Pu was sorbed on the glass in a transported vessel for all four tests. Up to 5% of the Pu was associated with colloidal material. The Np concentration was about 10^-8 M for the BWR fuels and 10^-10 to 10^-11 M for the PWR fuels. The Np/U mass fraction ratio was examined to determine if Np and U were released congruently, i.e., a ratio of one. At the two year test interval, the Np/U ratio was in the range of 0.1 to 0.8 for the four fuels. At longer test intervals, the Np/U ratio for the PWR fuels was 0.8.

1:45 PM J314.2
ASSESSMENT OF THE EVOLUTION WITH TIME OF THE INTERNAL RELEASE FACTOR IN GEOLOGICAL DISPOSAL CONDITIONS. Christophe Poirsot, Patrick Verona, Marie-Helene Faure, Commission d’Energie Atomique, CEA de Saclay, Nuclear Energy Direction, Department of Chemical Physics, Service for Physical and Analytical Chemistry, Laboratory for the Study of the Radiocative Behavior in Their Environment, Gif-sur-Yvette, order, FRANCE.

The aim of this paper is to give a first quantitative assessment of the potential evolution with time of the Internal Release Factor (IRF) which is a instantaneous release when water arrives in contact with spent fuel in geological disposal. We developed a model to evaluate the radionuclide (RN) inventory associated with the IRF, i.e. located in the gap zone, in the region outside the glass boundaries. The following is assumed: the rim zone is supposed to be roughly 200 µm thick outer part of the pellet (ca. 10% of the total volume of the pellet). - the burnup in the rim zone is roughly twice the average
bump. The global RN inventory located in the rim zone is about 20% of the total inventory. The part of radionuclides in the gap, grain boundary, and in the heated portion of the control volume. - the inner part of the pellet is composed of 8 μm diameter grains with a regular distribution. Diffusion process is a combination of both a Fickian diffusion and also an irradiation-enhanced diffusion (diffusion coefficient D = 1 × 10^{-25} m^2 s^{-1}). - The concentrations at the grain boundary are zero, which corresponds to an instantaneous release of the radioactive element. In this model, the RN inventory strongly increases with time reaching for example 60% of the total inventory after 2,000 years for the expected D value. Results will be presented. They enlighten (i) the significance of the irradiation-enhanced diffusion which may lead to a significant evolution of the RN locations within the rods, (ii) the necessity for a good knowledge of the representative volume element (RVE) and the diffusion coefficient D and (iii) the significant influence of RN inventory with time, to be accounted for in RN source term calculations.

**2:00 PM J114.3**

**FORMATION AND DECOMPOSITION OF HYDRATED PHASES ON NUCLEAR FUELS.** Brady Hauser, Bruce McNamara, John Atcheson, Edgar Buck, Pacific Northwest National Laboratory, Richland, WA.

Recent studies (Kinsel et al. 1998, CRIMS MoO 2000) of spent LWR fuels have demonstrated that a thin surface layer of a hydrated phase greatly accelerates the dry-oxidation process. The presence of these uranium oxy-hydroxides, such as dehydrated scheelite, may, therefore, be detrimental to the performance of spent fuel in either dry storage or a radioactive repository. This study was undertaken to determine the kinetics and mechanisms of formation of hydrated phases on both unirradiated and spent fuels under conditions experienced in typical pool storage. The conditions necessary to remove these water-hydrated phases, such as could be utilized during the drying of a storage canister, were examined. These studies appear to have implications for the models being developed for the geologic disposal of spent fuel. Alternate radionuclide release models for the proposed Yucca Mountain repository are based on a co-precipitation and solubility of secondary U(VI) mineral phases, such as scheelite (Chen 2000, Murphy 2000). Other release models rely on the incorporation of radionuclides, Np in particular as reported by Buck et al. (1998), in host thorium from their release. The present study presents evidence of oscillatory behavior for the formation and dissolution of scheelite and related uranyl oxy-hydroxide phases in batch tests between 25°C and 75°C. These findings suggest that the alternate release models may underestimate the long-term stability of these types of uranyl phases.

**2:15 PM J114.4**

**CORROSION TESTING OF A SIMULATED FIVE-METAL EPSILON PHASE IN SPENT NUCLEAR FUEL.** David J. Wrzesinski, Chase S. Watkins, Andrew C. Beugham, Uni Annex, Missouri-Rolls Dept. Geology & Geophysics, Rolls MO; F. Scott Miller, University of Nebraska-Lincoln, Nebraska, Aviation Engineering, Rolls MO; Stephan F. Wolf, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

The five-metal epsilon phase represents an important component with respect to the corrosion of spent nuclear fuel. This importance is emphasized in its being a host for 99-Tc, which in turn is a potentially high solubility radionuclide (as TcO_4^-), with a long half-life (213,000 years), that is an important source of emissions from the repository. Metal powders were mixed in a weight percent basis of 40% Mo, 30% Ru, 15% Pt, 10% Re (used as a surrogate for Tc), and 5% Rh. This mixture replicates the composition of epsilon phase particles in the Turkey Point pressurized-water spent fuel reactor (Thomas et al., 1989). The powders were melted in a Argus purged vacuum chamber using an electric arc-melter. Backscattered - scanning electron microscope images of the as-cast samples denote two separate regions with an inner zone enriched in Ru, Re, and Rh relative to the outer zone. Each zone is composed of a mixture of micron-sized crystals. Sample wafers of the simulated epsilon phase were reacted using vapor hydrolysis (200°C) and MCC-1 testing (90°C) protocols. Vapor hydrolysis results indicate the formation of Mo and Ru enriched alteration phases for test periods up to 35 days. Phase growth was enhanced when air was periodically replenished, relative to tests that were run in a static environment. This suggests that this could be used to promote the hydroxide alteration phases play a role in the corrosion process. MCC-1 tests were conducted for time periods up to 182 days in leachant solutions that were prepared with either (1) deionized water or (2) Np and 84-Tc enriched with nitric acid to pH 3.0. The deionized water tests progressively decreased in pH over time (5.5 to 4.0), while the pH values remained at a constant value of 3.0 in tests with the acidified leachant. Solutions are currently being analyzed for their metal concentrations.

**2:30 PM J114.5**


In a repository, the spent fuel could come in contact with groundwater if the canister or container has breached. The system may be quite complex with oxygen-free water, uranium dioxide, a corrodible metal, such as iron, and a radionuclide present at the same time. In an anoxic environment iron and mild steel will corrode with hydrogen evolution. The equilibrium hydrogen pressure for this reaction is very high and some time after water intrusion, there will be a hydrogen pressure in the near environment of the fuel, equivalent at least to the hydrogen pressure at 70°C. For this reason we investigated the leaching behavior of 0.5-5.0 mm sized fragments of PWR spent fuel (34 MWt/kg U) in simulated groundwater solution (10 mM NaCl and 2 mM HCO_3^-) under 5 MPa hydrogen and argon pressure. In a leaching experiment under 5 MPa hydrogen at 35°C, the total U concentration was found to be 10^{-16} M. After refilling of the autoclave with new solution at 70°C, the total U concentration first increased to 10^{-16} M, and then quickly decreased to 10^{-20} M. The leaching behavior of uranium and other fuel components indicates that under pressurized hydrogen, the spent fuel dissolution is substantially hindered. Leaching results obtained after the substitution of hydrogen at the same pressure and temperature are also presented. Finally, some results on spent fuel leaching under pressurized argon are presented and comparatively discussed.

**2:45 PM J114.6**

**EVALUATING CLOTTING CREEP DURING DRY STORAGE AND REPOSITORY PLACEMENT.** Eric Siegmann, Duke Engineering & Services, Waste Form Dept., Las Vegas, NV; Pierre Mairelet, Framatome ANP Inc., Waste Package Project, Las Vegas, NV.

Crep strain has been identified as the dominant failure mode for dry storage, including the vacuum drying phase. It could also be important during the early period of repository closure. A statistical analysis of creep failure during these three phases was performed. Starting with an assumed burnup distribution (rod range 44 MWd/kgU, range 2 to 75 MWd/kgU), a distribution of rod properties, and finally a conservative stress distribution was developed. The Mstyy creep correlation was selected after comparing 6 rod fits with correlations with respect to all parameters. It was then modified to better predict irradiated cladding creep data. Creep failure criteria is a CDF based on 52 failure tests. The fuel rods are exposed to three consecutive temperature histories: 24 hours of vacuum drying, 20 years dry storage, and 1,000 years of repository thermal history. Each phase has a peak temperature, treated as an independent variable, and temperature history taken from the literature. Uncertainties in the temperatures and strain rate are included. Radial temperature distribution across the waste package is also modeled. For the first phase, vacuum drying, rod failures start to occur at around 550°C and exceed 1% failure at 600°C. With peak temperature (10°C), rods begin to fail during dry storage when the peak temperature reaches 400°C. They approached 1% failure level at 450°C. With representative peak temperatures of 430°C for drying and 350°C for dry storage, rod failures start to occur during repository closure at a peak cladding temperature of 390°C. They reached 1% at around 420°C. In the repository design, the cladding temperatures are below 210°C and rod failures from creep are not expected. Statistical analysis is an important tool for predicting failure behavior and the distributions can be modified for specific applications.

**SESSION J115: GLASS AND ALTERNATIVE WASTE FORMS**

Chairs: Denis M. Strachan and Pierre Van Joosthem, Thursday Afternoon, November 29, 2001, Republic B (Sheraton)

**3:15 PM J115.1**

**EFFECT OF Fe AND Cd OXIDES ON THE GLASS DURABILITY.** Marie Lobanov, Aurélien Lodieu, Philippe Barboux, François Devreux, Physique de l’Univers Condensed, Ecole Polytechnique, Palaiseau Cedex, France; Olivier Spalla, Jacques Lambert, Service de Chimie Moléculaire, CEA Saclay, Gif sur Yvette, France.

We have analysed the experimental data on the dissolution of ternary sodium borosilicate glasses in the framework of a numerical model based on percolation concepts and Monte Carlo simulations. This simplified model accounts qualitatively well for the effect of soluble species (Na, B) on the dissolution kinetics, on the saturation concentrations of silica in static conditions as well as on the porous morphology of the alteration layers. The comparison with the
experimental data allows to introduce realistic dissolution parameters for the numerical calculations. In the process of searching a more quantifi- cation of this model, a more realistic glass composition has been introduced both in the simulations and in the real glasses. Some elements that increase the glass durability and that also simulate, to some extent, some radioactive elements. Borosilicate glasses were thus prepared in the composition 70 SiO₂ - 15Na₂O - 15K₂O. xMO₆ with M = Gd, Zr and x ranging between 0 and 10. The glasses were studied by conventional static leaching tests at 90°C in water and buffered solutions. The experimental data show that the introduction of Gd and Zr drastically reduces the initial dissolution rate \( V_0 \) of the glass. It also decreases the final silica solubility which is predicted by the numerical model but in a larger amount. The porous layer morphology is strongly modified in good agreement with the SEM images. Local X-ray absorption spectroscopic experiments (EXAFS, NMR, ESR, IR) have been used to assess the model's modification of configurations around Zr and Gd and to discuss their long-term diffusion and eventual phase separation in the altered layer.

3:30 PM J115.2 MECHANISM OF VAPOR PHASE HYDRATION IN HIGH SOUDIUM WASTE GLASSES FROM COMPUTER SIMULATIONS. Fernando C. Perez-Camarena, Hao Guan, Xiaoming Liu, and Ian L. Pegg, Vircuse State Laboratory, The Catholic University of America, Washington, DC.

The vapor phase hydration test (VHT) has been used as an accelerated test of the aqueous leaching of waste glasses and has recently been adopted as a product-quality requirement for Hanford Low Activity Waste (LAW) glasses. However, the mechanism of the vapor phase hydration of LAW glasses is complex and relatively poorly understood. We have recently shown that the Avrami equation, and a generalization thereof, empirically gives a very good representation of the leachate concentration, which typically shows an 'incubation' period, a period of rapid alteration, and finally, a long-term alteration-rate decrease. We have also shown that this form provides a good basis for correlation of the time, temperature, and glass compositional dependence in a single model. However, the relevance of the original derivation of the Avrami equation to the VHT process is questionable. This model, which uses data from only one set of model parameters. It is known that the basic 'stretched exponential' form of the Avrami equation can arise in many ways. In this paper, we present results from computer simulations with a cell model of the VHT process in which the key parameters are the water diffusion rate; the hydration reaction rate and stoichiometry; and the compositional miss-match between the matrix and the new surface phase. The model successfully reproduces Avrami-like behavior over most of progress to reaction completion. Furthermore, by introducing site-site cooperative effects, the reaction front can be made either planar or dendritic, reproducing the 'fingering fronts' in alteration layers that are experimentally observed for some LAW glasses.

3:45 PM J115.3 LONG-TERM CORROSION OF BOROSILICATE GLASS UNDER HYDROLOGICALLY UNSATURATED CONDITIONS. J.C. Cannane, J. Fortner, and R. Olson; 1Chemical Technology Division, Argonne National Laboratory, Argonne, IL; 2Selle Corporation, Hendersonville, NC.

The corrosion of borosilicate glass is examined under test conditions that simulate conditions to which the glass may be exposed in a potential repository underground. Monte Carlo simulations of the glass composition are conducted. In the first [vapor hydration tests], the glass was exposed to humid air environments in closed stainless steel vessels to which enough water was added to establish a range of relative humidity conditions. The matrix of tests span the temperature range of 70-200°C, relative humidity conditions from 50-100%, and test durations up to three years. In the second set of tests [leaching test], two actinide-doped borosilicate glass compositions were exposed to humid air and twice weekly injections of simulated groundwater. These tests, which were conducted at 90°C, have been running for fifteen years with periodic sampling and analysis of the solution and alteration products. The 200°C results from the vapor hydration tests show that the rate of corrosion decreases by about three orders of magnitude when the relative humidity is changed from 100 to 50%.

The temperature dependence of the initial hydration rate has an effective activation energy close to 80 kJ/mol. The average corrosion rate observed in the glass after more than a decade of operation is less than 1E-3 g/m². The results from both sets of tests are interpreted based on the conditions in the water films on the glass surface and current understanding of factors that control the rate of aqueous corrosion of borosilicate glasses.

4:00 PM J115.4 THE OXIDATION STATE OF PLUTONIUM FROM DISSOLUTION OF PYROCHEMICAL SALT WASTES IN WIPP BRINES. Virginia M. Oversby, VMO Konsult, SWEDEN; John M. Hashke, Actinide Science Consulting, Waco, TX; Matthew K. Silva, Environmental Evaluation Group, Albuquerque, NM.

Pyrochemical salt wastes from the Rocky Flats plant in Colorado contain about 1 tonne of plutonium in the form of metal and/or oxide. The concentrations of Pu in the salts can be up to 10%. Tests of similar pyrochemical salt wastes in brines at Los Alamos National Laboratory gave very high solution concentrations of Pu, Pu(V) and Pu(VI) were identified by spectroscopy in some of the solutions with high concentrations of total Pu. We have developed a model to explain the presence of higher oxidation states of Pu in brines in contact with pyrochemical salts. The model predicts that Pu(IV) will oxidize in contact with water to form PuO₂⁺, which will release Pu(V) to solution. The Pu(V) will then disproportionate to Pu(VI), which remains in solution, and Pu(IV), which precipitates as a hydrous oxide. The precipitate, as well as the original Pu(IV), will oxidize to PuO₂⁺, releasing more Pu(V) to solution. This process, which is controlled by the competing rates of oxidation, disproportionation, and precipitation will reach a steady-state concentration level of total Pu, Pu(V), and Pu(VI) in solution. If redox changes such as Fe metal or Fe(II) ions in solution are present, these may reduce the Pu(V) or Pu(VI) to Pu(IV), which will precipitate as the hydrous oxide. Once precipitation occurs, however, the process of oxidation by water will continue, generating more Pu(V) and Pu(VI) in solution. The rate of reduction will then be a factor in the final steady-state solution concentration values for each Pu oxidation state. The significance of processes controlled by competing reaction rates, rather than chemical equilibrium, for performance assessment of the WIPP facility will be discussed.


The Defense Waste Processing Facility (DWPF) at Savannah River Site (SRS) is immobilizing SRS high level waste (HLW) sludges into borosilicate glass for geologic disposal. The DWPF will operate for ~25 years to immobilize all the HLW at SRS. The ASTM 1285 standard bench test was formulated at SRS as a reliable test that could be performed remotely to demonstrate the consistency of the durability of the radioactive glass produced during the lifetime of the DWPF; hence, the name Product Consistency Test (PCT) was adopted. After refinement, the PCT was approved by the ASTM and became a consensus standard test for measuring the durability of HLW glasses. In the PCT the glass is crushed, sieved to a uniform size distribution, washed, dried, and then leached in deionized water (10 grams water per gram glass) at 90°C for seven days. The leachate is analyzed to measure concentrations of elements that were leached from the glass. Normalized releases are calculated in terms of grams of glass dissolved based on these elements and their concentrations in the glass. In the DWPF developmental program when radioactive glasses were not available, the elements B, Li, and Na in the glass were chosen as indicators of glass durability because of their solubilities in the leachate. These elements indicated the largest normalized releases compared to those based on other elements in this glass. Later radioactive glasses became available and the question arose, do any of the radionuclides have normalized releases greater than those for the above soluble elements? We used three radioactive glasses and two DWPF glasses that contained small concentrations of a glass containing Hanford HLW to answer this question. Some had releases equal to those for B, Li, or Na, but none had higher. Examples of the radionuclides are actinides U-238, Pu-238, and Np-237, and fission products Cs-137, Sr-90, and Cs-134. Deltak will be presented.