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*Invited paper
SESSION JJ1: CONTAINER MATERIALS AND ENGINEERED BARRIER

Chair: David W. Shoemith and Paul R. Rebok
Monday Morning, November 26, 2001
Republic B (Sheraton)

8:30 AM *JJ1.1
TWENTY-FIVE YEARS OF MATERIALS RESEARCH IN NUCLEAR WASTE - PROGRESS AND REMAINING CHALLENGES. Rodney C. Ewing, Univ of Michigan, Dept of Nuclear Engineering and Radiological Sciences, Ann Arbor, MI

The MRS symposium, “Science Underlying Radioactive Waste Management”, was first held in Boston, in November of 1976. This years symposium is the 25th in the series that now has had meetings around the world. During the past 25 years of international effort, substantial progress has been made in the development, characterization and understanding of materials that are used for the processing, transport, containment and disposal of radioactive waste. The development of materials for long-term performance applications has required a uniquely interdisciplinary effort. I will identify some of the major innovations and contributions during the past 25 years and provide a list of remaining challenges for materials scientists.

9:00 AM *JJ1.2
CORROSION PERFORMANCE PROJECTION OF YUCCA MOUNTAIN WASTE PACKAGES. Alberto A. Sagues, University of South Florida, Department of Civil and Environmental Engineering, Tampa, FL

The proposed high level nuclear waste repository at Yucca Mountain relies heavily on the corrosion resistance of waste packages (WP), employed in turn protected through tuffaceous rock, for its performance during the anticipated 10,000 years regulatory period. Present WP design uses an ~20 mm thick outer shell of Alloy 22 as the main corrosion resistant barrier. The operating conditions may include a pulse of above-boiling temperatures that will last several hundred years. External shields are envisioned to prevent direct water dripping on the WP. However, recent findings suggest that delamination salts and other contaminants on the WP surfaces may cause liquid water to form there, even at high temperatures. Current performance predictions predict that during the anticipated regulatory period localized corrosion modes will be unlikely, and that the Alloy 22 layers will degrade primarily by very slow uniform dissolution, essentially under passive surface conditions. A review is presented of the assumptions and experimental findings leading to these projections, as well as a discussion of the challenges involved in extrapolating limited information on corrosion behavior over an extremely long service period that extends beyond the time frame of common engineering experience. Potential mechanisms for deterioration of the passive regime that may be encountered under those circumstances are discussed.

9:30 AM *JJ1.3
WASTE PACKAGE ENVIRONMENT FOR THE YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT. G. E. Golisow, T.J. Wilery, and N.D. Rosenbek, Lawrence Livermore National Laboratory, Livermore, CA

Characterization of the waste package environments is necessary for understanding and modeling the degradation modes that will effect the waste package material. These environments are considered in the context of the potential repository at Yucca Mountain, Nevada. This potential repository site is located above the local water table and is barometrically coupled with the environment outside the mountain. Waters that will evolve on the waste packages will be brines due to the low relative humidities at these components. These brines will be either high-pH sodium carbonate brines or near neutral pH waters, which may contain soluble magnesium or calcium. The brines are characterized with respect to those parameters that will effect the waste package degradation. These include water chemistry, pH, electrochemical potential, and hygroscopic salt content. The hygroscopic salt constituents determine the temperature-relative humidity conditions where aqueous solution formation can occur. The presence of corrosively aggressive anions [e.g. halide ions] and corrosion inhibitors [e.g. nitrates, sulfates, and carbonates] in the different brines are examined in terms of mixed ion solutions that may evolve. Minor constituents, such as lead (Pb), which may effect corrosion processes, are also considered. Occasional-reduction complexes in the mineral waters and those introduced by the degradation of the waste packages are considered in terms of the electrochemical potential that they may impose on the waste package.

9:45 AM *JJ1.4
DELIQUESCENCE BEHAVIOR OF MULTICOMPONENT SALTS: EFFECTS ON THE DRIP SHIELD AND WASTE PACKAGE CHEMICAL ENVIRONMENT AT THE PROPOSED NUCLEAR WASTE REPOSITORY AT YUCCA MOUNTAIN, NEVADA. Roberto T. Palahniuk, Lieta 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 soil 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 conditions associated with highly concentrated brine sources 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. Hygroscopic salts on drip shield/waste package surfaces will absorb moisture from the atmosphere, generating small volumes of highly corrosive brines. This wetting is expected to occur after the repository temperature falls below the boiling point for the salt mixture and the equilibrium humidity, or deliquescence, has been reached. The U.S. Department of Energy (DOE) performance assessment abstraction of in-drift chemical environment assumes that deliquescence 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 abstract. 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 *JJ1.5
INFLUENCE OF THERMAL AGING ON THE MECHANICAL AND CORROSION PROPERTIES OF GTAW WELDS OF ALLOY N80022. Radl B. Rebok, Sumanta S. Edgcombe, Todd A. Palmer, Lawrence Livermore National Laboratory, Livermore, CA; Paul Crow, Hughes International Inc., Kokomo, IN

A Ni-Cr-Mo-W alloy (N80022) 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 N80022 in gas tungsten arc welds (GTAW) was studied by aging samples at 427, 482, 538, 564, 649, 704, and 760°C 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, the degradation of the impact toughness of welded specimens begins at shorter aging times than that seen for non-welded specimens. However, Arseniuk extrapolations showed that the degradation rates were similar for both welded and non-welded specimens.

10:45 AM *JJ1.6
LOCALIZED CORROSION SUSCEPTIBILITY OF ALLOY 22 AS A WASTE PACKAGE CONTAINER MATERIAL. D.S. Dunn, C.S. Brossia, L. Yang, Y.-M. Pan, N. Shihrar, and G.A. Cragin-Gmelin, Center for Nuclear Waste Regulatory Analyses - Southwest Research Institute, San Antonio, TX

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 anodic species, such as nitrate, and potentially aggressive cathodic species, such as lead, were also determined in laboratory testing. In addition to the accelerated material tests, were also 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 the 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 deliquescent salts. 

Disclaimer: This paper was prepared to document work performed for the Nuclear Regulatory Commission under Contract No. NRC-92-97-009. 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.

11:00 AM J11.7 INTEGRATED ANALYSIS FOR LONG-TERM DEGRADATION OF WASTE PACKAGE AT THE POTENTIAL YUCCA MOUNTAIN DEPOSITORY. J.H. Lee, Sandia National Laboratories, Las Vegas, NV; N.G. Mon, Duke Engineering & Services, Las Vegas, NV; D.E. Longhine, Duke Engineering & Services, Austin, TX; B.E. Ballard, Duke Engineering & Services, Las Vegas, NV; A.M. Month, Bechtel-SAIC, Las Vegas, NV.

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 systems (EBS) components. The SR waste package design has two layers: a 25-mm thick Alloy 22 outer barrier and a 50-mm thick 3108G stainless steel inner shell. The waste package is encased under a Titanium Grade 7 closure shield. 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 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 induced corrosion (MIC) aging and phase stability, and pre-existing manufacturing flaws on the outer barrier degradation. The exposure conditions of 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, cracks by SCC, pits by localized corrosion, and large openings by general corrosion) and number of waste package and drift shield penetrations. Results show waste packages and drift 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 120,000 years after the waste has been placed in the package. The failure curves to the waste package first crack failure and first pit failure curves indicate that the initial failures are due to SCC that has initiated at one or more pre-existing manufacturing flaws in the closure weld region.

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. Shewan, 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 with 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 dissolution; (iii) enhanced passive corrosion due to heterogeneous processes; (iv) accumulation of damage and increased susceptibility to localized corrosion due to accumulated corrosion products.


Titanium Grade 7 (Ti-6Al-4V) is considered for use as a construction material for drift shields to be used to protect nuclear waste packages in a geologic repository. The study investigates the interaction between Ti-6Al-4V and groundwater containing fluoride and chloride. The temperature where liquid water can 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 stainless 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 fluoride and chloride 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 108-120°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, fissuring of these 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 scribing.

11:45 AM J11.10 EVOLUTION OF WATER CHEMISTRY THROUGH INTERACTIONS WITH WASTE PACKAGE. Ying Pan, Darrell Dobson, Shannon Brossin, Gustavo Craginolino, Vijay Jamani, Narasi Sridhar, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX. The chemistry of water dripping into the waste packages for HAW 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 concentrations using a specimen of type 310L stainless steel with a predrilled 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 capillary electrophoresis and the pH was measured using a microelectrode. Preliminary results indicate that the cation concentrations inside the pit due to nitric dissolution of type 310L 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.

SESSION J12: CERAMIC STRUCTURE
Chairs: Barry B. Ford and Martin Stuart
Monday Afternoon, November 26, 2001
Republic B (Sheraton)

1:30 PM J12.1 A GLASS-ENCAPSULATED CERAMIC WASTEFORM FOR THE IMMOBILIZATION OF CHLORIDE-CONTAINING HLW. FORMATION OF HALITE CRYSTALS BY REACTION BETWEEN THE GLASS ENCAPSULANT AND CERAMIC HOST. I.W. Donald, R.B. Metcalf, R.S. Greenhew, Chemistry Research Div, Aldermaston, UNITED KINGDOM.

We have developed a calcium phosphate ceramic based on the mineral phases hydroxyapatite and chlorapatite which, on the basis of evidence from non-active simulated studies, is expected to provide an effectively hermetic host for immobilizing the chloride constituents that result from the pyrochemical processing of Pu. The
immobilized product is in the form of a free-flowing non-hygroscopic powder in which the chlorides are chemically combined within the mineral phase. It was envisoned to provide a monolithic 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 aluminium phosphate glass 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 testing of sintering glass the Na and potassium in the glass recombine with the chlorosparite and chloropyroxene phases to form a dispersion of halite 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 highlighted and discussed.

1:45 PM J12.2

STUDY OF NATURAL MINERALS OF PYROCHLORITE TYPE STRUCTURE AS ANALOGUES OF plutonium CERAMIC WASTE FORM. Roman Bogdanov, Yuri Baturin, Elena Puchkova, St. Petersburg Univ, Dept of Chemistry, St. Petersburg, Russia; Andrey Sergeev, Yelena Puchkova, Institute of Geology, St. Petersburg, Russia; Boris Burnakov, V. K. Kikoin Radiation Institute, St. Petersburg, Russia.

At present, crystalline ceramic based on titane pyrochlore, Ca$_3$Gd$_3$(HPO$_4$)$_2$O$_{10}$, is considered as US candidate waste form for the immobilization of weapons grade plutonium. Naturally occurring uranium bearing minerals with pyrochlore type structure: 

- Hexagonal: U$_3$O$_8$ (HIU, U$_3$O$_8$), Na$_2$U$_3$O$_8$ (O$_2$I$_4$) (OH)$_2$, 180, Ca$_3$Sr$_2$(U,Ta)$_2$O$_7$ (O$_2$I$_4$) (OH)$_2$, 180, Ca$_3$Sr$_2$(U,Ta)$_2$O$_7$ (O$_2$I$_4$) (OH)$_2$, 180.

The formal calcium in the oxide-coated U$_3$O$_8$+ ion was confirmed as UO$_2$ based on the X-ray beam spectroscopy technique. The calculations were performed on the basis of the two-dimensional La$_3$O$_4$ and La$_3$O$_4$. The conversion of the initial La$_3$O$_4$ ion in the structure of natural pyrochlore to UO$_2$+ due to metamict decay causes significant increase of uranium mobility. Data of uranium leach rate (10$^{-8}$ g/cm$^2$/day) from hexachloride 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 UO$_2$+ and as assumed, (UO$_2$)$_2$+ and (UO$_2$)$_2$+ in pyrochlore structure makes doubt that pyrochlore is a feasible host phase for the immobilization of actinides such as U, Pu, Np.

2:00 PM J12.3

THE FORMATION ENTHALPY OF 4M ZIRCONOLITE, Ca$_2$Gd$_2$O$_7$(OH)$_2$.12H$_2$O, 0.78, 0.55, 0.82, K.B. Helcom, T. Lee, A. Nawrotsky, Thermochromatic Facility, Dept. of Chemical Engineering and Materials Science, University of California-Davis, Davis, CA; J. Liang, L. Wang, F. Wang, Dept of Radiological Sciences and Nuclear Engineering, University of Michigan, Ann Arbor, M. B. Ebbinghaus, Lawrence Livermore National Laboratory, Livermore, CA.

Zirconolite, nominally ABC$_2$O$_7$ and the structurally related pyrochlore, nominally B$_2$C$_2$O$_7$ (where A = Ca, Na, REE, Th, B zr, Hf, Ce, U, REE, CaZrTiFe, or Al), is primary components of SYNOIC. The pyrochlore structure becomes the stable phase when the Ba:Th molar ratio (and primary Ca:Ba ratio) by calcination is substantially larger than Zr:Th = 0.85 (0.08 mm). Substituting cations such as Ca:Th (0.10 mm) or Ba:Th (0.105 mm) stabilize the pyrochlore structure by forcing the zirconolite B-site to become c-oriented and, hence, crystallographically equivalent to the zirconolite A-site. At approximately 30 mol% occupancy of the B-site by Gd, a mixture at the unit cell scale of half zirconolite and half pyrochlore motifs, the so-called zirconolite-4M is formed. Zirconolite-4M with stoichiometry Ca$_2$Gd$_2$O$_7$(OH)$_2$, lies outside of the pseudo-binary defined by CaHf$_2$O$_7$+Gd$_2$O$_7$, two of the end-member compositions for the proposed waste form for excess weapons plutonium. The formation enthalpy of zirconolite-4M is, therefore, of interest. High resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (XRD) and electron microprobe analysis (EMPA) were used to characterize the zirconolite-4M sample. High temperature oxide melt solution calorimetry using two solvents, (T$_{2}$O$_{4}$.SIO$_{2}$:T$_{2}$O$_{4}$, T = 111°C) was used to measure the heats of solution for CaCO$_3$, FeO, TiO$_2$, Gd$_2$O$_3$ and Ca$_2$Fe$_2$O$_4$. Applying the appropriate thermodynamic cycles to our gravimetric and calorimetric data, the enthalpy of formation of the 4M zirconolite at 298 K was calculated [k J/mol]: Pb-halate derived CH$_2$ = -233 +2.53, Na-molybdate derived CH$_2$ = -81.7 +3.9. These two values are equal within error, supporting satisfactory dissolution of samples in both solvents. The calculated formation enthalpy from two pyrochlores assuming ideal mixing is (0.33Gd$_2$O$_3$.0.67CaHf$_2$O$_7$.0.344[CaHfO$_7$]) CH$_2$ = -83 k J/mol. This suggests a small positive entropy of mixing (approximately 8-4.5 k J/mol).

2:15 PM J12.4

ELEMENTS/PARTITIONING IN A PYROCHLOR-INFUSED PLUTONIUM CERAMIC WASTE FORM. Beto Gries, Carrie Hattier, Earth & Atmospheric Sciences, Purdue University, West Lafayette, IN; Edgar Buck, Pacific Northwest National Laboratory, Richland, WA.

Tritium-based ceramic waste forms, designed for immobilization of plutonium, contain as major constituents pyrochlore [Al$_2$Ti$_2$O$_7$], zirconolite [Al$_2$Ti$_2$O$_7$] and brannerite [Bi$_2$TiO$_2$]. 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$_2$ strongly partitions into the pyrochlore phases, while the zirconolite phases contain no U. The brannerite and pyrochlore incorporate in a site that is distinct from that occupied by Hf. Incorporation of Gd into zirconolite takes place via a coupled 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 phase and an Al-rich (Al-oxide) 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., Pu-233) might be needed in the future.

2:30 PM J12.5


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$_2$Gd$_2$O$_7$.6Al$_2$O$_3$ and Ca$_2$Zr$_2$O$_7$.6TiO$_2$, with Al and Ce, and Ce and Hf, and Ce and Zr to mimic minor excess hafnia plus rutile or zirconia. Samples of these zirconates and titanates with up to 15 wt % of potential Pu-process waste have also been prepared. The titanates tend to form pyrochlore as the major phase, whereas the zirconates form a fluoro. Very little of the impurities are accommodated in the fluoro with powellite, a spinel and a silicate glass appearing as extrinsic phases. In the titanates samples the pyrochlore incorporates more impurities, with the remainder forming zirconolite, silicate glass, magnetoplumbite, perovskite and leveringite. The oxide-route zirconate required sintering temperatures of about 1500°C to produce a dense product, 200°C higher than the sintering temperature required for the titanates. Silicate impurities reduce the sintering temperatures appreciably in both titanates and zirconates. Extended annealing of all the Ti- and zirconate at ~1100°C had no effect on the composition or microstructure. However the Ti- and zirconate zirconate was transformed to pyrochlore. The results of 1 MeV Kr$^+$ and 8 MeV Au$^{+}$ ion irradiation experiments performed at the IThem and EML accelerators at ANL and PNNL, respectively, will be discussed.

2:45 PM J12.6

IONIC SIZE LIMITS FOR A IONS IN BRANNERITE/Al$_2$O$_3$ AND PYROCHLORIE/Al$_2$O$_3$ TITANATE STRUCTURES. (A = TETRAVALENT RARE EARTH AND ACTINIDES). Eric Vance, Molly Carter, Martin Stewart, Arthur Dany, Cliff Ball,.
The lower limit of the size of the octahedral ion in the A2O6
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 tenivalent U ions for three A ions or (b) substituting one
Ba plus one hexagonal ion for two A ions did not succeed. Ge, Sn,
and Zr substitutions in the Ti site of brannerite do not exceed 0.2 formul
units in ceramic preparations. Various attempts at single and coupled
experiments in the A site of Th-brannerite (though several showed that
the average size could tolerate deviations of \(1\%\)). Tetranivalent
Ce is unusually stabilized in air at temperatures close to the
melting point of 1409°C in the A site of brannerite. Lattice
parameter data on different endmember brannerites are given. The
lower and upper size limits for the eightfold A ions in the pyrochlore
structure are around 0.10 and 0.117 nm, respectively. A BaTl2O5
stochiometry did not produce a pyrochlore structure, and when fired
in either argon or air yielded a mixture of BaF2O6, whose structure is
still uncertain, plus brannerite and rutile.

SESSION J33: RADIATION EFFECTS
Chair: William J. Weber and Katherine L. Smith
Monday afternoon, November 28, 2001
Republic B (Sheraton)

3:30 PM J33.1
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 lead 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 current state-of-the-art understanding and predictive modeling of amorphization, spall, swelling, decomposition and pyrochlore/fluorite structures of current interest. One of the successes of these studies is the discovery of a glassy transition in crystalline phases with soft structures that can serve as highly durable, radiation-resistant host phases for the immobilization of actinides.

4:00 PM J33.2
ION-INDUCED AMORPHIZATION OF MURATAITE
Jie Liu
University of Michigan, Ann Arbor, MI, Sergey V. Yudin鞑ev, IGEM RAS, Moscow, Russia; Sergey V. Stafinskiy, Olga I. Kiryakova, SIA Radon, Moscow, Russia; Rodney C. Ewing, University of Michigan, Ann Arbor, MI.

Masutana A2B2C2O922−, where A = Na+, Cs+, REE3+, An+4/4+;
B = Al3+4/3+, Zn2+, C = Ti4+, Fe3+, Al3+, 0g ≤ 1.5; cubic fluoro-
structurally-structured phase potentially suitable as phase for rare earths and actinides with actinides with three (A,B,C) sets (5c), and eight-
fold (8c) elementary fluorous unit cells were found.

Amorphization of masutana by 1 MeV Kr+ ion irradiations performed at room temperature using IEME interfaced with a Tennion ion accelerator at Argonne National Laboratory. Radiation damage was observed by in situ TEM. Initially, the irradiation caused disordering of the masutana structure. Masutana was rendered fully amorphous at doses of 1.72-1.01 \(10^{16}\) ion/cm² (approximately 0.2 ppi). Similar observations were obtained in the cold crucible melt sample. The susceptibility of masutana ceramics to ion irradiation induced damage increases in this order: masutana-SC ≤ masutana-5C ≤ masutana-8C.

The pyrochlore structure phase is slightly more radiation resistant to ion irradiation than the masutana structure phase with similar chemical compositions. Cs (≈ 11 wt % in masutana and ≈ 28 wt % in pyrochlore) has significant effects on the radiation resistance of pyrochlore and masutana phases and decreases the critical amorphization doses (\(10^8\) ion/cm²) from 2 to 2 to 1 if pyrochlore and from 1.8 to 1.7 if masutana.

4:15 PM J33.3
MOLECULAR DYNAMICS SIMULATIONS OF VOID STABILITY
IN AMORPHOUS Si
Maria Onokwezie, Brent J. Heney, Yvon Ashkenzay, Robert S. Asenjo; 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 (a-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 nuclear waste yields a 5.6 MeV alpha
particle and a 54.100 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 glassy waste forms could reduce
the lifetime of this storage medium. The nature of the radiation damage
process in glasses is unknown, particularly the influence on this 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 code
PARCAS. Discussion of our results will focus on i) void stability 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-FG05-98ER14121.

4:30 PM J33.4
STRUCTURAL INVESTIGATION OF ION IRRADIATED SIMULATED HIGH-LEVEL WASTE GLASS
S.K. Sundaram, D.A. Haller,*, Y. Su, V. Shukhratman, J.S. Young and T. Thethivin,
Pacific Northwest National Laboratory, Richland, WA. *ERL.

Radiator effects of HLW glasses containing crystalline phases have not been extensively studied. In this study, heat-treated MS-7 glasses that is a simplified version of a typical Hanford HLW glass with a TL of 1.0 for incorporating imbedded spinel crystals was used to investigate the aggregate radiation effects. The composition of the base glass was (mass%): 8.00 Al2O3, 7.00 B2O3, 0.3 CaO, 11.50 Fe2O3, 4.54 Li2O, 0.69 MgO,
0.50 MnO, 13.60 Na2O, 0.35 Al2O3, 45.31 SiO2, and 6.02 ZrO2. These glass samples were irradiated using 2.0 MeV Au+ ions to the fluences ranging from 3.4x1016 to 1.25x1017 ions/cm² at room temperature. After the irradiation, the samples were characterized using Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), and X-ray spectroscopy at Pacific Northwest National Laboratory (PNL) 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 transient oxidation state where a larger number of non-bonding oxygen atoms exists in the base glass matrix. On ion irradiation, tetrahedral 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 correlated 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 J33.5
RADIATION DAMAGE IN TITANATE CERAMICS USED FOR PLUTONIUM IMMOLIBIZATION
D.M. Strachan, R.D. Scheele, W.C. Buchmiller, R.L. Sell and R.J. Elvick,
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% \(^{238}\)Pu and approximately 100 sister specimens that contain about 10 mass% \(^{239}\)Pu. 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 materials were irradiated at various temperatures and carbonic of the constituents and by sintering the mixture at 150°C for a minimum of 4 hours. Some specimens of pyrochlore and zirconolite were sintered at an additional 100 hours at 1500°C to enhance the crystalline grains. The specimens were stored at 20°C, 100°C, and 250°C with the \(^{238}\)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 NDA test, photography, and X-ray microanalysis. Analysis 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 239Pu-bearing ceramics is about 100 times higher than from the 239Pu-bearing ceramics. The densities of the ceramics have been decreased due to the zirconolite-rich ceramic at 250°C than at 25°C, an unexpected result.

SESSION JJ4: PERFORMANCE ASSESSMENT
(H.W.)

Tuesday Morning, November 27, 2001
Republic B (Sheraton)

8:30 AM #J4.1

TOTAL-SYSTEM PERFORMANCE ASSESSMENT FOR THE YUCCA MOUNTAIN SITE. Michael L. Wilson, Peter N. Swift, Sandia National Laboratories, Albuquerque, NM; Jerry A. McNelis, S. David Sevougian, 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) have 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 (1) identify and screen potentially relevant features, events, and processes to develop scenarios, (2) develop models, (3) estimate parameter ranges and uncertainties, (4) perform calculations, and (5) 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, a site characterization project is recommended, further TSPA analyses will 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, Nuclear Site Characterization Project. 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 #J4.2

THE SR 97 PERFORMANCE ASSESSMENT OF A KBS 3 REPOSITORY FOR SPENT NUCLEAR FUEL. - OVERVIEW. Review Comments and New Developments. Allan Hedin, Ulf Kränsky, Lenn Muren, Patrik Sellin and Jan-Olof Schröer, SKB, Stockholm, SWEDEN.

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 isolated copper-coated stainless steel high-strength iron insert. 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, initially defective canisters, climate change, greenhouse gases and future inadvertent human intrusion. The principal conclusion of the assessment is that the repository is a safe 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 concept and siting of future repositories. 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 next stages. The authorities were in principal consistent with those of the NEA. Since SR 97, the methodology for probabilistic consequence analyses and for earth quake simulations have been improved. The authors of SR 97 investigated the zirconolite-rich ceramic at 250°C than at 25°C, an unexpected result.
FOR SPENT FUEL, HLW AND LONG-LIVED HLW IN SWITZERLAND L. H. Johnson, J. W. Schneider and P. Zaidema, Nagra, Zrich, SWITZERLAND, and AMEC Environment Management Ltd., UNITED KINGDOM; Peter Grbi, Vilo-Consult AG, Brugg, SWITZERLAND.

Nagra, the national co-operative for the disposal of radioactive waste, is responsible for research and development, geological investigations, design studies and safety assessment studies leading to the development of facilities for the disposal of radioactive waste in Switzerland. For identified high-level and long-lived intermediate-level waste, the present focus is on developing the safety case for a proposed repository site in the Opalinus Clay in the Zrich Weinland (northern Switzerland). The methodology to develop a safety case will include: a systematic and comprehensive 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; a procedure to present 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 this may introduce into results; a means of drawing together the different lines of argument so that well-supported and relevant conclusions are drawn, that provides 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 applied to the Opalinus Clay repository is outlined in order to illustrate the decision-making 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 for the repository in Opalinus Clay is then presented, and examples are given of arguments that are being formulated, based on independent lines of evidence, to illustrate the important safety functions (safety 'pillars') of the repository system.

11:30 AM #J34.6 GENERAL APPROACH USED IN THE PERFORMANCE ASSESSMENT FOR THE WASTE ISOLATION PILOT PLANT Bob P. Ruchti, 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 of 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 1998. The EPA's decision was primarily based 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 1992. This paper discusses the technical approach and rationale of the PA components contributed to the PA, including the WIPP certification. For these PAs, Sandia mostly used detailed models for evaluating the performance of the repository under the stimulated conditions specified by the EPA (i.e., the use of models based on partial differential equations in several dimensions). In addition, Sandia used most of these detailed models directly in the probabilistic synthesis of the repository behavior. This challengeing approach to PA was facilitated by the use of a database, which all codes needed, to store model parameters; a neutral file format that was used to store and pass results between codes; and a suite of analysis tools 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 results of these models (e.g., using response surfaces): First, accepted mathematical formulations and implementations, as represented by the various numerical procedures, could be used without truncation. Second, more interaction between investigators and PA analysts occurred as both parties worked to jointly produce an acceptable process model. Third, when changes occurred in the repository design or regulatory constraints (e.g., over the course of several years, the first generation of the mining portals in strata above the WIPP repository), the detailed models could rapidly accommodate this requirement without necessitating a new series of simplified model building for PA analysis. Fourth, the process model was decreased since only one model had to be described, verified, and validated under the stringent quality assurance procedures required for certification in the legal environment of the United States rather than documenting both a process model and analysis results. Fifth, the number of parameters to be developed was decreased since two models of the same phenomenon (but with possibly slightly different meanings) were not needed. It was important to avoid confusion and avoid unduly burdening the regulator with descriptions of numerous models and the process of EPA was required, Safety, Assurance, and Performance Assessment, to review the 1996 PA in one year. This paper concludes with the presentation of a few results of the PA over the years. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

SESSION J15: CONTAMINANT TRANSPORT I
Chair: Roberto T. Poblete and John A. Berry
Tuesday Afternoon, November 27, 2001

1:30 PM J15.1 RADIONUCLIDE INCORPORATION IN SECONDARY CRYSTALLINE MINERALS FROM CHEMICAL WEATHERING OF GLASS L. V. Legere, Pacific Northwest National Laboratory, Richland, WA

A performance assessment (PA) is being conducted at the Hanford site in Washington for long-term disposal of vitrified low-activity waste in unconsolidated sediments. The (PA) consists of analyses that predict the transport of radionuclides and/or contaminants from a source to a receptor via pathways that are considered credible. It is expected that pore water intermixing with the glasses disposed in the immobilized low-activity waste (ILAW) facility will have moderately high ionic strengths and will be slightly alkaline. Under such conditions, several chemical reactions are known to occur in waste forms, neighboring engineered structures, and surrounding sediments that include dissolution of several carbonate and silicate minerals, precipitation of secondary and tertiary mineral phases, radionuclide adsorption onto minerals (primary, secondary, and tertiary phases), and incorporation of radionuclides into secondary and tertiary mineral phases. Currently, data are lacking on the tendency of key radionuclides to be sequestered into secondary crystalline mineral structures. This lack of knowledge could adversely affect waste-disposal activities by increasing the uncertainty and requiring unrealistically conservative estimates be used as inputs to dose calculations. To fill this gap, we conducted a series of tests on three different waste glasses to determine the potential sequestration of 99m-Tc, Cs-137, and I-129 in secondary and tertiary mineral phases. Weathering experiments conducted at 90°C with radionuclide-spiked Hanford Site groundwater indicated that substantial fractions of the total activity (~50% of Se-79, ~8% of Se-79, ~19% of I-129, and ~10% of U-238) were retained by the secondary zeolitic minerals that formed during weathering of LDD4512 glass. Tests conducted at 160°C on LDD4512 and LA203 glasses indicated that ~8% of Se-79, ~1% of Cs-137, and ~10% of I-129 were incorporated into the secondary crystalline phases such as hectorite and smectite. Additionally, both glasses exhibited a greater degree of sequestration of stable isotopes (70 - 85% of I, ~58 - 69% of Se, and ~36% of Cs). Implications of these findings toward integrating the radionuclide mobilization aspects of ILAW performance assessment will be presented.

1:45 PM J15.2 LIQUID-SOLID PARTITION COEFFICIENTS (KD) OF ANONIC AND CATIONIC SPECIES OF RADIONUCLIDES PRESENT IN CONTAMINATED GROUNDWATER, F. K. Haas, Edward L. Cooper, Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, ON; Dave J. Robertson, Pacific Northwest National Laboratory, Richland, WA

Radionuclides present in contaminated groundwater have varying interactions with aquifer materials, which can be represented using the solid-liquid partition coefficient (Kd). Standard procedures for determining this coefficient lump together several surface-driven processes at the solid, and provide limited information on radionuclide speciation. It is possible, however, to obtain better information using preparation techniques that reveal differences in liquid-solid interactions between the predominant aqueous species of radionuclides. In this work, we used contaminated groundwater from a former liquid waste discharge area at the Chalk River Laboratories. The groundwater was treated with ion exchange resins to isolate anionic and cationic aqueous forms of selected radionuclides (90Sr, 137Cs, 99Tc, 137Cs, 90Sr, 241Am, 226Ra). Separate, liquid-solid partitioning values for the anionic and cationic forms were measured on unconsolidated aquifer materials, and these results were compared to those obtained with spikes of radioisotopes of some of these elements, not present in the contaminated groundwater. The comparison also included separate determinations for unconsolidated groundwater and aquifer materials, spiked with 239/240Pu and 241Am. The dominant aqueous species of 90Sr, 137Cs, 239/240Pu, and 241Am were...
and 241Am present in the contaminated groundwater were negatively charged. The solid-liquid partitioning of these negatively charged species was found to be 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 ‘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 are quite strong and apparently exist in some sort of sorption, 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 J15.3
PREDICTION OF METAL PARTITIONING BETWEEN MINERAL AND AQUEOUS SOLUTIONS: AN IMPLICATION TO CONTAINMENT MATERIAL SELECTION FOR RADIOACTIVE WASTE DISPOSAL
Yifeng Wang, Sandin National Laboratories, Carlsbad, NM; Hufang Xu, Dept of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM; Charles Bryan, Anna C. Siinder, Sandin National Laboratories, Carlsbad, NM.

Metal partitioning between inorganic 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 in situ structural 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. Magnesite 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.

2:15 PM J15.4
EFFECTS OF REACTOR DECONTAMINATION COMPLEXING AGENTS ON SOIL ADSORPTION. COLUMN STUDIES
R. Jeff Seme, Kirk. J. Castrell, I. V. Kutyniok, and Chick W. Hinderliter, Applied Geology and Geochemistry Section, Pacific Northwest Laboratory, Richland, WA.

Organic complexes of radionuclides have been implicated in several instances of mobility and migration of radionuclides into groundwater percolating through sediments. Organic chemicals have also been shown to leach from nuclear power plant decontamination wastes that are up being buried in shallow land burial grounds. Column experiments were performed using two sediments, two organic compounds and two contaminants [Ni²⁺ and PuO₂⁺⁺]. The influent solutions were a simplified groundwater. The organic and metal concentrations were picolinate 18-4, EDTA 10-5, Ni 18-5, and Pu 10-7 M, respectively. The organic compounds were spiked with radiolabeled 14C and 35S and 239Pu. The columns were equilibrated with background electrolyte for 2 pore volumes. Then solutions containing the metal, complexant, and tracer were injected for up to 10 PVL through glass columns and 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 sliced 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 >1 kM to significantly lower the sorption 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 dissolve. After migration, radionuclides migrate from the disposal facility, dilute and interact with competing cations and adsorption reactions will result in dissociation of all but the strongest or most kinetically recalcitrant complexes. Conditions that enhance 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 Co²⁺ is very significant and adsorption by sediments is essentially zero. Thus, we recommend that mixtures of metal/educts and EDTA should not be co-disposed with high pH materials. For weaker organic complexes [picolinate, citrate and oxalate], co-disposal of decontaminants wast concrete and should be acceptable.

2:30 PM J15.5
DIFFUSION AND SORPTION OF RADIOACTIVE CESIUM AND COBALT IN REGOLITH MATERIALS OF CENTRAL Australia. Takashi Ikegaki, Gordon D. McInnis, Timothy E. Purser, Australian Nuclear Science and Technology Organization, Environment Division, Menai, 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 and vadose 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 sample container 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 J15.6
STUDIES OF NEPTUNIUM(V) SORPTION ON CALCITE. F. Paul Bertetti and Bradley A. Werling, 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 key technical support 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 concentration of 2.5 × 10⁻⁶ 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 large role in the sorption behavior. Differences in sorption are 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. CRC-02-97-0008. It is an independent product of the CNWARA and does not necessarily reflect the views or regulatory position of the NRC.

SESSION 3:06 CERAMICS CORROSION
Chair: Boris E. Baturin and David B. Chamberlain Tuesday Afternoon, November 27, 2001
Republic B (Sheraton)

3:30 PM J36.1

Zircons 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/fozocelite structured titanate counterparts. Ti₆+ and Zr⁺⁺ versions of the pyrochlore-rich ceramic (50wt% CeO₂ 50ZrO₂ 22HfO₂ 23CeO₂ 22ZrO₂ 44)
(Zr/Ti)_{2}O_{4} 1 wt % HFO 2 wt % (Zr/Ti)_{2}O_{4} powder for Pu dissolution was prepared by the standard alkoxide route. The final precipitate was rinsed with "hot" water in a Schlenk apparatus 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, and X-ray powder diffractometry (XRD) and leaching at 100°C in deionised water. The titania preparations that were free of impurities consisted of anatase and pyrochlore whilst the zirconium formations had formed a single phase of a phase mixture. The zirconate formations were studied by XRD and XRF spectrometry at the University of Antwerp and H. H. W. van der Wiel at some 150°C temperature to achieve equivalent level of closed porosity. SEM indicated that the impurities were readily incorporated into the pyrochlore-stabilised titanian, which had also formed a minor pyrochlore matrix. No impurities were present in the defect-fluorite structured zirconate which had formed a glassy phase along with the magnetostructural. The presence of impurities aided sintering in both matrices. Leaching results are available for the titania and zirconium formations impurities sintered to 1300°C and with impurities sintered to 1500°C, with impurities.

3.45 PM J16.2
Dissolution of A12Ti5O12 (A = Y, Gd, or Lu) Pyrochlore By Experiment at pH = 2. 50°C: Evidence for

Recent theories for dissolution of solids into aqueous solutions focus on analogies with ligand-exchange reactions between aqueous complexes and the solids. Some of these theories have also been extremely 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 A12Ti5O12, where A = Y, Gd, or Lu, and pH = 2 solutions at 50°C. Analysis by XRD showed that all three compositions are chemically stoichiometric, as revealed by electron microprobe analysis. Analysis by Raman spectroscopy, however, indicates that the Y12Ti5O12 specimens are more disordered compared to the other materials. The thermodynamic stability of the three solids was performed using a linear free-energy model and reported enthalpies and entropies of formation. The calculations indicated that the most stable phase should follow in the progression Lu2Gd2Y3, as observed in the dissolution experiments. Although the relatively greater disorder detected in the Y12Ti5O12 sample probably contributes to the faster dissolution rate observed, the relative thermodynamic stability of the solids could, itself, explain the trend in dissolution rates. Our data indicate, therefore, that dissolution models based on ligand-exchange reactions may not be strictly applicable to simple pyrochlore minerals.

4.00 PM J16.5
A STUDY OF Pd-DOPED ZIRCONIUM ALTERATION UNDER HYDROTHERMAL CONDITIONS, Boris Barikova, Elena Nikolenko, Maria Yakovleva, the V.G. Khlopin Radium Institute, St. Petersburg, RUSSIA; Rodney Ewing, Michigan Univ, Ann Arbor, MI; Werner Latzke, Univ of New Mexico, Albuquerque, NM.

Phosphon doped ceramic based on zircon structure, (Zr-Pd)SO4, is the subject of investigation as a durable ceramic waste form for the immobilization of weapons grade plutonium and other actinides. Currently irradiated waste from the Zr, Si, and Pu fuels is prepared from solution with insignificant excess of Zr to provide a final yield of zircon phase not less than 95 wt %, with the remainder as zirconin, avoiding formation of silic or PuO2. This material was dried at 120°C and calcined at 750°C for 2 hours. 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 diffractometry analysis, the ceramic consisted of in [wt %]: zircon-95-96; monoclinic zirconia-1-3; tetragonal zirconium-3-5. Electron probe microanalysis of EPMA has shown that zircon contained 6.1 wt % Pd. The sizes of zircon grains were too small [less than 2 microns] and provided samples,respectively. Although the decrease of Pd amount was detected, no traces of Pd-oxide were found on XRD spectrum of altered material. The results obtained confirmed the high resistance of Pd-doped zircon-based ceramic under hydrothermal conditions.

4:15 PM J16.4
ALTERATION OF A ZIRCONOLITE GLASS-CERAMIC MATRIX UNDER HYDROTHERMAL CONDITIONS. Christelle Martin, Isabelle Ribet, SESC/UCF CEA Valbrio, Thierry Advocato, SCDV/IWMA CEA Valbrio, FRANCE.

Glass-ceramic matrices based on zirconolite (Ca2Ti5O12) are being considered for specific conditioning of plutonium or the minor actinides. This application is contingent upon a demonstration of the long-term aqueous corrosion resistance of the material. The investigatory method consists in leaching zirconolite glass-ceramic specimens under hydrothermal conditions to accelerate the dissolution kinetics and obtain data on advanced stages of reaction progress in a relatively short time. The principle is as follows: both the residual glass matrix was altered, and the alteration film formed on the specimen surface. The film thickness varied according to the alteration conditions, from about 0.7 µm in the vapor phase to 2 µm in the liquid phase. The reference glass altered for 40 days in the liquid phase also formed a gel 2 µm thick. The film thickness was constant over the surface of the glass, but variable on the glass-ceramic alteration was observed to a depth of several tens of micrometers along the zirconolite grain boundaries. The dissolution results indicated greater mass losses for the glass-ceramic than for the glass. Microprobe analysis showed composition differences between the glass specimens and the vitreous matrix of the glass-ceramic, resulting in a more intense alteration of the former. Tests are now underway to verify that this different behavior affects only the initial alteration period.

4:30 PM J16.6
COUGROSION OF GLASS-BONDED SODALITE AND ITS COMPONENTS AS A FUNCTION OF pH AND TEMPERATURE, S. Y. Jeong, L.R. Mora, A.J. Morgan, and W.L. Elbert, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

Glass-bonded sodalite is the ceramic waste form (CWF) that is being developed to immobilize electrolyte mixer salt waste from electroplating allurgical treatment of sodium-bonded spent reactor fuel for disposal. In order to provide parameters (pH and temperature dependence of CWF forward dissolution rate) for the waste form degradation model, MCC-1 tests were conducted with sodalite, binder glass, and CWF. Tests were conducted in pH-buffered solutions in the pH range of 5-10 at temperatures of 296-30°C using conventional buffers. The normalized forward dissolution rates of sodium from sodalite, glass, and CWF have negative slopes in acidic solutions and positive slopes in basic solutions, with minimum neutral pH. Similar results were obtained at 70°C using purely characterized noncomplexing buffers, confirming that the complexation of conventional buffers with released waste form species is not significant. The forward rates increased with increasing temperature; the temperature dependence is therefore not a significant factor. The pH and temperature dependences for CWF are similar to those calculated from high-level waste glasses. MCC-1 tests in buffer solutions at 70°C were also conducted with a simple five-component hydroxide glass for comparison; the results were previously calculated from flow-through tests. The dissolution...
trends whereas current practice involves disposal to concrete vaults. Disposal is carried out under an authorization from the UK Environment Agency (the Agency). Periodically the Agency 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, BNFL and the Agency conduct an information exchange process on the development of the PCSC. This process has led to notable improvements, as well as affording a mechanism for providing clarifications and building confidence in the PCSC. BNFL undertakes a new communication activity following scientific conference, presentation, participation in international programmes (such as those of IAEA and NEA) and liaison with local communities. The PCSC will also benefit from peer reviews. The central to the safety case is a systematic examination of the mechanisms that control radioactive transport and for modeling radionuclide migration in a repository.

SESSION JJ7: PERFORMANCE ASSESSMENT (LLW)

Chairs: Charles Kincad and Christy Polkene
Wednesday, Morning, November 28, 2001
Republic B (Sheraton)

8:30 AM #117.1 DEVELOPMENT OF A PERFORMANCE ASSESSMENT METHODOLOGY FOR DESIGN AND STAGING OF A LLW REPOSITORY IN ITALY. Piero Risibaldi, Giancarlo Ventura, ENEA Waste Disposal Program, Rome, ITALY.

Since 1998, a general site selection process covering the whole Italian territory is under way to comply with the governmental policy of promoting candidates on possible voluntary siting of a LLW repository. A GIS (Geographic Information System) methodology has been developed to identify suitable areas for locating the repository, based on exclusion criteria derived from performance assessment principles and on a suitability index calculation for the selected areas. This methodology was implemented in three steps using the ESRI ARC/INFO and GRASS 4.1 platforms. The GIS screening analysis identified approximately 1% of the Italian territory as suitable for locating the LLW Repository. The performance assessment (PA) procedure used an upgraded version of the AMBER code, which was applied and tested for four sites. Scenario definitions used for the PA coupled the use of the GIS methodology based on the exclusion criteria with the FEPs (features, event and processes). The PA activities were primarily directed at: Σ evaluating suitability of the identified areas, Σ evaluating the long-term efficiency of the EBS system; Σ identifying a standard procedure to integrate the AMBER code with data from a calibrated groundwater flow model of aquifers and unsaturated zones.

9:00 AM #117.2 DEVELOPMENT OF THE POST-CLOSURE SAFETY CASE FOR THE LOW LEVEL WASTE DISPOSAL SITE AT DRUGG, UNITED KINGDOM (Low Level Waste Disposal Programme, Environment Risk Assessment, Research & Technology, British Nuclear Fuel plc, Risley, Warrington, UNITED KINGDOM).

This paper provides an overview of the development of the post-closure safety case (PCSC) for Drigg. The paper outlines the background to the site, the implementation of a systematic approach to understanding the site and undertaking a post-closure radiological safety review (PCRCSA), continuous monitoring programmes and the contribution of these in the PCSC, including issues to be investigated further in the forward programme. Drigg is the UKs near-surface facility for disposal of solid low level radioactive waste. Disposals commenced in 1993 to
ASSOCIATED WITH THE TONO URANIUM DEPOSIT, JAPAN.
R. Adachi, Mentor Scientific, LLC, Denver, CO; T. Iwasaki, K. On, Tono Uranium Research Center, Japan Nuclear Cycle Development Institute, Taki, JAPAN.

Field investigations supporting the Tono Natural Analogue Project are aimed at characterizing hydrogeological and chemical processes that have effectively immobilized uranium within the Tono uranium deposit in Gifu Prefecture, central Japan, for about 10 million years. An unconformably underlying the deposit represents the approximate location of a redox front separating relatively oxidizing pore waters (Eh ~ 0 mV) in the weathered, fractured Tokie granite from strongly reducing pore fluids (Eh ~ -360 mV) in sedimentary rocks of the overlying Lower Tokie Lignite-bearing Formation (TL), which hosts the uranium oxide body. Groundwater samples from boreholes drilled through these overlying strata have encountered relatively high concentrations of uranium 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, upward 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 restricted any significant change in the reducing nature of this formation for millions of years. Stable and irreversible in situ redox potential measured in boreholes penetrating the granite and sedimentary rocks appear to be controlled by the Fe(III) redox system. Fe(III) oxyhydroxide precipitation and redox potential in the oxidized zone of the groundwater system may be important in limiting the availability of uranium from the granite basement as well as the continental aquifer and the overlying strata. As such, the immobilization of uranium in the Tono deposit may be a consequence of the unique redox environment (Eh ~ -360 mV) that characterizes the lower Tokie Formation, a setting that is currently absent in the basin-wide oxidizing groundwater bodies that have developed at greater water depths than about 100 m. This is consistent with previous laboratory data indicating the dependence of ionic strength on the redox stability.
the long-term performance of radioactive waste forms because uranium (UO₂) is structurally and chemically similar to the UO₂ in spent nuclear fuel. The environments that host the Oklo-Oklahoma U deposits, Giton, 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 (millions of km). The natural fissure reactors associated with the Oklo-Oklahoma 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-sowing radiation damage, and because these processes are manifested in 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 microscale. Secondary ionisation 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 uraninite from all reactor zones are highly discordant with Pb-Pb ages ranging from 40 Ma to 1880 Ma. Oxygen isotopic analyses show that uraninite 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 = -10.2% to +7.3%). These data show that important information can be obtained from natural analogues studies provided that high spatial resolution analysis techniques are utilized.

11:45 AM J18.6
APPLICATION OF SYSTEMS ANALYSIS TO A NATURAL ANALOGUE PROJECT. M.J. Stenhouse*, R. Arthur*, T. Inwamura, K. Otz*, H. Takase.1, 2, 3 Monitor Scientific, Denver, CO, 2UNC Tsu Geodynamics Center, Japan Nuclear Cycle Development Institute, Tsukuba, JAPAN. 3Queen's Japan, Yokohama, JAPAN.

System Analysis provides the framework for most performance / safety assessments addressing radioactive waste disposal, but is also being applied successfully to a natural analogue project. The Toho 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 Toho uranium deposit. System 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 water in the characteristic instruments, 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 Toho uranium deposit. System Analysis provides a convenient framework for this project, being used to:
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an environment of 100% relative humidity at temperatures up to 200°C for varying time intervals. Condensation onto the test specimen then induced transformations between the specimen and this elevated temperature. The results of the exposures of hydroceramic waste forms contrasted to EA glass will be discussed.

2:45 PM J110.5/KKS.5
Abstract Withdrawn.

SESSION J110: CONTAMINANT TRANSPORT II
Chairs: Shad V. Mattigod and Joon-Hong Ahn
Wednesday Afternoon, November 28, 2001
Republic B (Sheraton)

3:30 PM J110.1
USING LINEAR/FREE ENERGY RELATIONSHIP TO PREDICT ACTINIDE PARTITIONING BETWEEN GEOTHIATE AND AQUEOUS PHASE. Haining Xu, Exc. Dept. of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM; Xing Wang, Sandia National Laboratories, Carlsbad, NM.
Coprecipitation of trace metals and actinides in authigenic minerals of geothite, 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 described by Wang and Xu (Geochimica et Cosmochimica Acta, 65 (2001), 1529) is extended to predict trivalent metal partitioning between geothite (alpha-FeOOH) and aqueous solution. 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 geothite 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 J110.2
INFLUENCE OF HUMIC COLLOIDS ON THE CONTAMINANT TRANSPORT IN NATURAL SYSTEMS. Wolfram Schirmer, Robert Artinger, Bernhard Kieneser, Horst Geckens, Thomas Rahung, Jee-Hil Kim, Institut fur Nukleare Entsorgung, Forschungszentrum Karlsruhe, Karlsruhe, GERMANY; Dietmar Kloz, Institutfur 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 colloid-borne contaminant transport. As an example in this paper these questions are addressed with respect to the humic colloids-borne contaminant transport. It is shown, that a thermodynamic equilibrium approach is not suitable to describe consistent laboratory batch and migration experiments with Cu(II) and Am(III) in humic rich groundwater and systems. In contrast, a kinetic model of the humic colloidal interaction (KICAM) enables the consistent description of static and dynamic experiments in the time frame from several hours up to several months. The experiments show that the humic colloid borne metal ion migration can be up scaled from 0.5 m to 10 m. Furthermore, the fraction of humic colloid borne metal ions correlates with the migration time. This enables the simplification of the formulation of the humic colloid borne metal ion transport in PA. i.e. metal ion surface interactions have not to be regarded in detail. Furthermore, due to the strong sorption of trivalent metal ions to humic colloids and sediment surfaces only the uncomplexed humic colloid 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 J110.3
RADIOACTIVITY UPTAKE AND TRANSPORT ON MICROBES IN REPOSITORY DRIFTS AT YUCCA MOUNTAIN, NEVADA. Darren M. Mobley, Duke Engineering and Services, Las Vegas, NV.
Radioactivity 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 sorption term for these calculations was derived using MINERVA 1.0 software code (EBCOM and JSL). Multiple modeling input parameter uncertainties were abstracted into a set of equations representing one meter segments of repository drift containing either commercial spent nuclear fuel (CSNF) or defense high level waste (DHLW) packages. These equations represent the average cumulative microbial biomass (MB) g dry/m generated in the EBS at time t.

\[
MB_{\text{cum}}(t) = \begin{cases} 
(1) & \text{CSNF or DHLW packages} \\
(2) & \text{EBS transported as a microbial colloid}
\end{cases}
\]

A distribution for uranium uptake onto microbes was applied to MB. The distribution was derived from the dataset in Suzuki and Brefield (1999) representing 45 different species of bacteria and fungus covering uranium uptake at optimum pH values from 1 to 7. The mass of uranium sorbed onto the biomass was either measured in the EBS or transported as a microbial colloid based on a regression of data from Jewett et al. (1999) representing microbial sorption onto air-water interfaces in unsaturated column experiments. Over one million years, it is estimated that EBS microbes may sequester from 77 to 2102 kg of uranium per meter of waste package depending on the saturation of the inter and type of waste package. Over the same period, microbial colloids may transport from 8 to 1250 kg of uranium per meter of waste package. The same model may be used to estimate uptake and transport of plutonium and thorium by microbes.

4:15 PM J110.4
SOLUBILITY EVALUATION FOR YUCCA MOUNTAIN TSPA SR. Yueting Chen, Amy Loch, Duke Engineering & Services, Terry Steinberg, Management Solutions; Patrick Brady, Christine 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 (NRC), a systematic solubility evaluation has been conducted. This paper gives a summary of this effort. In this study, a conventional thermodynamic approach was employed and geochemoal model calculations were used to estimate radionuclide solubilities. The study uses the computer code EQ3NR as the major geochemoal 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, Tt, C, Ra, Cs, Pb, Sr) and each solubility is presented as either functions 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 J110.5
A QUANTITATIVE KINETIC MODEL FOR PLUTONIUM OXIDE SOLUBILITY. John M. Hisschke, 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 solution. The model is based on the recently reported observation that plutonium dioxide spans an exceedingly wide range of Pu. The equilibrium of the higher oxide is implied by diffusion data shown that lattice parameters of the face-centered-cubic solid formed by both dioxide and hydroxide at steady state correspond with those 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 tetrahidroxide precipitation. Pu(V) and Pu(VI) concentrations are a function of the higher-oxide 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 PM JJ11.4
IODINE RELEASE FROM SILVER IODIDE UNDER REDUCING CONDITIONS WITH IRON-BEARING MINERALS. X. Xin, Y. Inagaki, A. Haruto, K. Idemitsu, T. Arima, Department of Nuclear Engineering, Kyushu University, Fukuoka, JAPAN.

During reprocessing of spent fuel in Japan, radiiodine(I-129) is collected in a form of silver iodide (AgI) in adsorbents to be one of the most difficult issues. 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 a long-term safety assessment of the disposal because of its high radioactivity and weak adsorption of 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. In-situ tests were performed by employing a thiol solution to provide a reducing environment that maintained the presence of iron-bearing minerals, goethite(FeOOH), magnetite(Fe3O4) and wustite(FeO) in a glove box purged with gas mixture (Ar 98.5%, H2 1.5%) and concentrations of Ag+ and AgI in the solutions were measured in a function of time by using ICP-MS. The undulating concentrations of Ag+ were stable at 4.0 × 10^-8, 4.5 x 10^-8 mol/l for the tests with FeOOH and Fe3O4 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^-7 mol/l, which value was five orders of magnitude higher than those for other tests. Solid phase analyses by using XRD and SEM/EDS indicated that AgI(metal) and AgI precipitated on the surface of original AgI only for the tests with FeO and Fe3O4. 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 D (Hynes)

JJ11.1
STUDY ON VIBRATIONAL SPECTRA OF INTERLAYER WATER IN SODIUM-MICHEITE BY MOLECULAR DYNAMICS SIMULATIONS. Satoru Suzuki, Japan Nuclear Cycle Development Institute, Waste Isolation Research Division, Tokai-mura, Ibaraki-ken, JAPAN; Kunio Iwashita, 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 3560 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 [O_H2O-O_H2O = 3.0 Å] was larger than that between water molecules [O_H2O-O_H2O = 2.8 Å]. These results suggest that interaction between water molecules 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. Anke, T. Chiesa, H. Kumpulainen, J. Lehtokoski, A. Mäkinen, 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 contacted bentonite diaphragm and a contacted iron coater and the spent fuel matrix. The barriers mutually interact with the groundwater and tend towards a thermodynamic equilibrium with each other and with their geochronological environment. In order to study experimentally the chemical interactions between the groundwater, bentonite and iron coater, 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 geochemistry and repository chemistry, and on b) the results from modelling of the chemical interactions using the thermodynamic computer codes HYDRAQL /CE and EQUIL/6. In short, the experimental set-up consists of a geological column, each of which contains a copper cylinder in a solution that is initially either distilled water or an 0.5 M NaCl solution. The copper cylinder contains water-saturated MG-80 bentonite, which stays 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 (N2 atmosphere) at ambient room temperature (about 20°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 Shikida, G. Dougall, Gute, Andrew Greenhalgh, Brittan E. Hill, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

The proposed Yucca Mountain repository site has a 1.1000 to 1.10,000 probability of discovery by basaltic magma during the next 10,000 years. Basaltic magma has temperatures of approximately 1100°C, a density of 2600 kg/m3, and fluid velocities on order 0.1-1.0 m/s. Basaltic magma enters the groundwater plume on order 1.0 m/s. 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 homologous temperature (temperature divided by melting point) and homologous stress (stress divided by elastic modulus). Deformation maps and high temperature creep data of alloys similar to 99 and type 316 SG 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, 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 magma can cause high temperature corrosion. Depending upon gas chemistry, high temperature corrosion can be in the form of oxidation, sulfidation, and metal salt corrosion. The rate of corrosion for different materials in hot gases will be estimated based on effects of gas chemistry and temperature on alloy compositions similar to the proposed container material. Reported experiment with magnesium interactions will be used as an additional source of information in this evaluation.

This work, supported by U.S. Nuclear Regulatory Commission (Contract NRC02/970109), is an independent product of CNWRA that does not necessarily reflect NRC views or regulatory positions.

JJ11.4

Evaporation and aerosol deposition may lead to the accumulation of hygroscopic salts on dry sheet (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 identified iron coaters on DS and WP as critical to the observation of the environment on the surfaces of the DS and WP considers that aqueous corrosion begins when the relative humidity reaches 50%. This relative humidity is based on the minimum dewpoint pressure of NaNO3 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 adsorption of water on the surface of the dry salt. Because of the increase in conductivity, the initial increase in 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-Hadj, Charles R. Marks, Jeffery A. Gorman and Aaron Burkett.

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

Dominion Engineering, McLean, VA.

A Titanium Grade 7 (Ti-0.3Pd) 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 waste package. 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 the effects of three radionuclides - 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-Hadj, Charles R. Marks, Jeffery A. Gorman and Aaron Burkett.

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

Dominion Engineering, Inc., McLean, VA.

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 affects the general, localized, and stress corrosion behavior of C-22 in concentrated 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 long-term service conditions. The test methods used included dissolution tests of disks at temperatures up to 680°C and U-bend tests at temperatures up to 500°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 test 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 and mercury, the onset of pitting is slowed down when the pH is raised for 1 to 3 or 5 when the temperature is lowered from 295°C to 210°C to 210°C, but within a few weeks significant pitting takes place even under the mildest of these conditions. These extrapolative tests 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 GEOLGIC REPOSITORY AT YUCCA MOUNTAIN**


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) plates and Ti Gr 24 support beams. The intended function of the drip shield is to divert water from dripping onto the waste packages and prevent damage to the waste packages from roof falls. Because the repository tunnels are expected to gradually collapse over time, NRC evaluation of the drip shield includes an examination of the effects of roof fall under both dynamic and static load conditions. For the purpose of this study, the finite element model was used to predict the residual static loads and concomitant stress levels remaining in the drip shield after dynamic roof 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 plus beta Ti 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 YS. 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.**

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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 steel 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 catholyte film formation of carbon steel, whereas it inhibits pitting at a nobler potential. The FT-IR and XRD structural analysis of the modified film showed that siderite (FeCO₃) was formed in 0.5 - 1.0 mol/L bicarbonate solution, FeOH CO₃ was formed in 0.1 - 0.2 mol/L bicarbonate solution, while Fe(OH)₃ CO₃ was formed in 0.02 - 0.05 mol/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.**

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Carbon steel is one of the candidate overpack materials for high-level radioactive waste disposal and is expected to be contaminated with high-level waste glass during an initial period of 150 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 the corrosion oxygen introduced by repository construction after closure of repository and then will keep the reducing environment in the vicinity of repository. The reducing corrosion of carbon steel is expected to speed up 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 bentonite 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 bentonite used in this study; the first path has low amount of iron, ca. 0.1 wt%, and large apparent diffusion coefficient, ca. 10⁻¹² m²/s and the second path has high amount of iron, ca. 0.0.1 wt%, and small apparent diffusion coefficient, ca. 10⁻¹⁴ m²/s.

**J1110**

Transferred to J1.10
The precursors were cold pressed at 200 MPa and sintered at 1500-1550°C for 4-8 hours. The products were examined with XRD, SEM, EDS, and TEM. In the X-ray scattering experiments with Ca$_2$Zr$_5$O$_7$ and Ca$_2$Gd$_5$O$_7$, Zr$_2$O$_4$-specimens were not formed. In the other ceramics (with bulk compositions Ca$_2$Zr$_5$O$_7$, Ca$_2$Gd$_5$O$_7$), Zr$_2$O$_4$ was found to be a minor phase, but minor fluorite-structured oxide was also present. Crystal-chemical reasons for the phase assemblages in the samples are discussed.

**J11.14**
XRD, SEM AND TEM STUDY OF THE Gd-DOPED ZIRCONOLITE. Sergey V. Stepanovskiy, Albert Y. Troele, SIA "Rudon", Moscow, RUSSIA; N. I. Logovanskaya, B. N. Nekhodov, Anatoly V. Sintsov, IGEM RAS, Moscow, RUSSIA

Ceramic samples with formulations Ca$_3$-Gd$_2$Zr$_{1-x}$Al$_x$O$_{12}$ (0 ≤ x ≤ 1) were prepared by cold pressing the powders followed by sintering at either 1400 or 1550°C for 5 hours. All the samples produced were single phase with rare grains of cubic zirconia based solid solution in the samples with high Gd and A1 contents (x = 0.5 and 1.0). The samples produced at 1550°C were higher homogeneous and less porous than the samples sintered at 1400°C. From SEM/EDS data average compositions of zirconolite in the samples varied within 0.5 compositions of zirconolite with x = 0.8. One phase with the other has higher symmetry, orthorhombic or tetragonal.

**J11.15**
CHARACTERIZATION AND DISSOLUTION OF ZrTiO$_4$ and Ti$_3$O$_4$ CERAMICS. V. Kurran, Y. Seveste, W. Ratry, P.G. Allen*, K. Czerwinski, Nuclear Engineering Department, Massachusetts Institute of Technology, Cambridge, MA, Massachusetts Institute of Technology, Lawrence Livermore National Laboratory, Livermore, CA

Thoria-rare oxide ceramics were studied in order to investigate the long-term behavior of potential thorium fuels in a repository environment. The ceramics were prepared by co-sintering. Zirconia was added to determine if further stabilization of the thoria-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 ZrTif, 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 synchrotron X-ray absorption spectroscopy (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 zirconium-oxide based phase and an actinide-based phase with low mutual affinity of thorium and zirconium, as well as partial solubilization of uranium in zirconia. The comparison of EELS spectra collected for the ceramics with spectra collected for UO$_2$ and UO$_3$ reference materials allowed the assessment of uranium oxidation state 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 NPZ STRUCTURE. Albert Troele, Sergey Stepanovskiy, SIA "Rudon", Moscow, RUSSIA

Incorporation of paramagnetic species in NaZr$_2$(PO$_4$)$_3$ (NPP) single crystal made possible to investigate local distortion of the NPZ structure from EPR data. Ca$^{2+}$ and Fe$^{3+}$ ions were used as paramagnetic probes. We monitored cubic components of the fourth rank tensor of crystal field, the indicative surface of the B$_{4a}$ element of this tensor as well as 2$^e$, 3$^d$, and 4$^d$ orders axes of the cubic component of the same tensor. From these data the combination 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$_{3v}$ (initial symmetry of the Zr$_2$Al$_4$O$_7$ polyhedron) to C$_3$ (Z$3$ aggregate probe). A comparison of dynamics of the structure occurring at lowering the symmetry with allowed dynamics of the NPZ structure (Roy-Aland-Agrawl model) makes easily explainable why the dynamics observed results in an instability of the NPZ structure and breaking the symmetry from R$3c$ to C$2/c$.
J111.17
MICROSTRUCTURE AND DISSOLUTION OF U AND H3B6EH16Y PYROCHLOR AND ZIRCONOLITE: HRTF AND AEM INVESTIGATION. Hai-feng Xu, Transmission Electron Microscopy Lab, Department of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM; Jinfeng Wang, Sunil National Laboratory, Carlsbad, NM; Phong Zhao, Lawrence Livermore National Laboratory, Livermore, CA.

Transmission electron microscopy results from a sintered ceramics with stoichiometry of Cs2(U0.57T0.12H2O)2Ti2O7 show the material contains both pyrochlore and zirconolite phases and structural intergrowth of zirconolite-harnequin in pyrochlore. [001] plane of pyrochlore is parallel to (111) plane of pyrochlore because of their structural similarities. The pyrochlore is relatively rich in U, Ce, and Ca with respect to the coexisting zirconolite. Average U/U ratios for the coexisting pyrochlore and zirconolite at 1350°C are 0.72 and 0.38, respectively. Dissolution experiments indicate that the dissolution rate decreases as dissolution time increases. High-resolution TEM results show that a He- and Ti-rich layer formed on the surface of the pyrochlore/zirconolite. The thickness of the layer ranges from 5 to 10 nm in a sample which was leached for 1.5 years at pH 4. The leached layer is depleted in U and Ca, and it is amorphous like in structure. It is proposed that the leached layer limit the further dissolution rate of the pyrochlore and zirconolite. The waste form of U and Pu-bearing pyrochlore/zirconolite is a stable ceramic form in geological repository that is depleted in aqueous silica and carbonates, such as WIPP site (Wang and Xu, 2000).

J111.18
INVESTIGATION OF Pu-DOPED CERAMICS USING MCC-1 LEACH TEST. Elena Nikolayeva, Boris Barakov, The V.G. Khlopin Radium Institute, St. Petersburg, RUSSIA.

Leach testing is an important tool for the investigation of chemical durability of radioactive waste forms. The data obtained from these tests allows for the selection of the most durable ceramics for the immobilization of weapons-grade plutonium. Ceramics based on cubic zirconia, (Zr,Gd,Pu)O2, doped with 10 wt. % 239Pu, zircon, (Zr,Pu)SiO4 doped with separately 5.6 and 10 wt. % 239Pu pyrochlore, (Ca,Pu,Gd,Hf)UO2, doped with 10 wt. % 239Pu, were studied using MCC-1 leach test. Ceramic samples were placed in test vessels with deionized water and set temperatures of 25°C and 90°C in an oven for 28 days. The leaching solution was removed and replaced with fresh deionized water after 3 and 14 days from the start of the test. Only data obtained after 14 and 28 days were used for the interpretation. No saturation of leach solution with Pu was observed in any experiments. It was found that formal (without correction on porosity) normalized Pu mass loss in g/cm² after 14 and 28 days were - for the zirconic ceramic - 2L-2E/2, at 90°C and 8E-3/8E-3 - at 25°C, for zircon doped with 5.6 wt. % Pu - 7E-3/8E-3/8E-3 - at 90°C and 1.0E-3/1E-3 - at 25°C, for zircon doped with 10 wt. % Pu - 0.0E-2/0.0E-2/0.0E-2 - at 90°C and 3.0E-2/2.5E-3 - at 25°C, for pyrochlore - 1.0E-3/1.3E-3 - at 25°C and 2.0E-3/3.0E-3 - at 25°C. It was shown that the high leach rate for zircon doped ceramic doped with 10 wt. % Pu was caused by the presence of the separated inclusion of PuO2 phases observable in the ceramic matrix. The data allows us to conclude that ceramics based on zirconia, zirconolite and pyrochlore are characterized by similar chemical resistance to leaching in deionized water. Based on its low porosity, zirconolite may be most durable ceramic phase for Pu.

J111.19
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, Idaho Falls, ID.

We have evaluated the possible use of the Product Consistency Test (PCT), that was developed to monitor the product consistency of boric acid glass waste forms, to monitor the consistency of ceramic waste forms (CWFs) made with waste salts from conditioned spent sodium bonded nuclear fuel. The CWF is a high-pH waste form comprised of about 70% sodalite, 25% boric acid glass binder, and small amounts of halite and carbonate debris inclusion. It must be encased for disposal as a non-standard high-level waste (HLW) form. Use of the PCT is being considered based on the similar dissolution behaviors of boric acid HLW glasses and the sodalite and glass binder phases of the CWF. Tests have been conducted to measure the within-laboratory and laboratory-to-laboratory test precision and the sensitivity of the PCT response to the composition of the CWF and to a range of processing conditions. This paper provides a summary of the approach taken for selecting a composite test that can be used to monitor glass production and the results of tests conducted to measure the precision and sensitivity of PCT conducted with the CWF. This approach can be used for other non-standard HLW forms.

J111.20
THERMODYNAMIC FUNCTIONS OF ZIRCONOLITE AND THEIR USE IN COMPUTER THERMODYNAMIC SIMULATION CODES. OLGA I. Ovchinnikov, S. S. Klimov, Olga K. Karlina,

Zirconolite is of considerable interest as a host material for transuranic elements. Synthesis of zirconolite simultaneously with immobilizing of radionuclides in its matrix is proposed, using exothermic reaction of precursors. Thermodynamic functions of precursors and zirconolite are necessary for thermodynamic analysis. Nawrotzky and co-authors has made an important contribution to determination of thermodynamic properties of zirconolite. In present work, the enthalpy of melting and the specific heat of liquid zirconolite have been estimated equal to 200 J/mol/dgr and 350 J/mol/dgr (J/mol/k) respectively. Using these data and results of A. Nawrotzky et al., thermodynamic functions of solid and liquid zirconolite are calculated. The data obtained are introduced in the database on thermophysical properties and thermodynamic properties of the thoria group. Computational thermodynamic simulation of thermochemical synthesis of zirconolite-bearing materials is performed based on these thermodynamic functions by the example of systems early proposed by A. Nawrotzky. 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.

J111.21
PRELIMINARY STUDIES OF THE DISPOSITION OF CESIUM IN A CERAMIC WASTE FORM. Marshall J. Lambregt, Steve M. Frank, Tom P. O’Holleran, Argonne National Laboratory, West, Idaho Falls, ID.

Argonne National Laboratory has developed an electrometallurgical treatment for spent DOE metallic fuel. This process produces a LiOCl/electretic salt mixture with low activation levels 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 critically dependent on the mobility of cesium 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/EBS, and NMR data exploring the disposition of the cesium in cesium-doped ceramic waste forms similar to the actual ceramic waste form.

J111.22

A baseline formulation based upon a target mineralogy of 95 wt. % pyrochlore (Cs0.46Gd0.39H2O2Pu0.28U0.24Ti0.2); plus 5 wt. % H3B6EH16Y rutile (approximately Ti0.66Hf0.34O2) has been developed for the disposal 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 3.7% hydrogen in argon) and temperature on the mineralogy of the pyrochlore/Ce/U/TiO2 ceramic. 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.

J111.23
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, Idaho Falls, ID.

We have evaluated the possible use of the Product Consistency Test (PCT), that was developed to monitor the product consistency of boric acid glass waste forms, to monitor the consistency of ceramic waste forms (CWFs) made with waste salts from conditioned spent sodium bonded nuclear fuel. The CWF is a high-pH waste form comprised of about 70% sodalite, 25% boric acid glass binder, and small amounts of halite and carbonate debris inclusions. It must be encased for disposal as a non-standard high-level waste (HLW) form. Use of the PCT is being considered based on the similar dissolution behaviors of boric acid HLW glasses and the sodalite and glass binder phases of the CWF. Tests have been conducted to measure the within-laboratory and laboratory-to-laboratory test precision and the sensitivity of the PCT response to the composition of the CWF and to a range of processing conditions. This paper provides a summary of the approach taken for selecting a composite test that can be used to monitor glass production and the results of tests conducted to measure the precision and sensitivity of PCT conducted with the CWF. This approach can be used for other non-standard HLW forms.
Until now, previous calorimetric investigations of zirconolite and HZirconolite used Pb-borate (2PbO·4SiO₂) near 973 K as a solvent. As was noted in previous studies, dissolving zirconolite in this reagent was very slow. Calorimetric experiments for the H5-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 impossible to test. However, a second calorimetric investigation was undertaken using an alternative molten oxide in which the samples appear to dissolve more readily. High-temperature oxide melt solution calorimetry experiments employed lead nitrate (Pb(NO₃)₂) solvent to measure the heats of solution for Ce₂O₃·2H₂O, ZrO₂, and HfO₂, respectively. The results of these experiments are consistent with those previously reported.

**J11.25**

**ENERGETIC TRENDS IN REE-TITANATE AND ZIRCONITE PYROCHELORS**

K. B. Helou, E. Y. Udishakov, A. Niewrotski

Thermochromy Facility, Department of Chemical Engineering and Materials Science, The University of California at Davis, CA; J. Lian, L.M. Weng, R.C. Ewing, Department of Geological Sciences and Nuclear Engineering, The University of Michigan, Ann Arbor, MI, L.A. Boxner and J. M. Farmer, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Rare-earth-element-bearing titanate and zirconate pyrochlores, nominally RE₂M₂O₉, where RE = 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 radioactive 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 RE₂-REE and zirconate pyrochlore samples. High-temperature oxide melt solution calorimetry experiments were used to measure the heats of solution, ΔHₚ, using NaNO₃·4MoO₃ solvent at 973 K for RE₂O₃ (REE = Y, La, Nd, Sm, Eu, Gd, Ho, Er, Tm), RE₂Ti₂O₇ (REE = Y, Ti, Er, Ho, Gd, Eu, Sm) and RE₂Zr₂O₇ (REE = La, Nd, Sm, Gd). These data were used to calculate enthalpies of formation from the oxides, ΔH_f, at 298 K (kJ/mol), for example: Gd₂Zr₂O₇ [218 ± 1.5], Nd₂Zr₂O₇ [226 ± 0.5], and Sm₂Zr₂O₇ [240 ± 2.5]. These data, plotted against the ionic radii (RE/REE) of the RE₂O₃ or RE₂Ti₂O₇, shows a linear trend, ΔH_f = -186.84[R(REE)/R(M)] + 221.6. Approximately 94% of the variation in the data is defined by this trend. As [REE/RE]/M decreases, the pyrochlore phase becomes less stable. Structural data plus the complete calorimetric data set will be presented.

**J11.26**

**THE USE OF CERIUM VALENCE STATE FOR EVALUATION OF ACCESSORY MINERALS DURABILITY TO RADIATION DAMAGE**

Roman Bogdashov, Yuri Zvyetsev, State Petersburg Univ. Dept of Chemistry, St. Petersburg, RUSSIA; Andrey Sergeev, St. Petersburg State University, Dept of Geology, St. Petersburg, RUSSIA.

Cerium-actinide bearing natural minerals which demonstrate their physico-chemical durability for long time (>10⁶ years) would be considered as the analogues of actinide ceramic waste forms. Radiation damage due to the materials usage can be defined as oxidation of cerium from initial Ce⁴⁺ to Ce³⁺. Therefore, cerium valence state in actinoid-actinoid bearing natural minerals reflects in some cases the resist against 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,Tb)UPO₄ [4 samples]; britholite (Ce,Tr,Cu,Fe,Ti)₂(OH,F) [2 samples]; nesocshite, (Ce,Tr,Tb,U,Ca)(Ni,Ti,Fe,Al)₂(OH,F) [2 samples]. 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 Ce⁴⁺ and Ce³⁺, respectively. The following contents of Ce⁴⁺ were observed: more than 30% in britholite; 11% in nesocshite; 0% in monazite. The results obtained allow to conclude that these actinoid host phases decreases in the raw monazite-nesocshite-britholite.

**J11.27**

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

**METACITIZATION**

Christopher S. Paleik, University of Michigan, Dept. of Geological Sciences, Ann Arbor, MI; Jie Lian, Rodney C. Ewing, University of Michigan, Department of Nuclear Engineering and Radiological Sciences, Ann Arbor, MI.

Zircon (ZrSiO₄) has been proposed as a potential waste form for actinides, particularly transuranium elements. 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 degradation is not understood. This work uses microanalytical techniques to relate the accumulation of radiation damage to micro-scale 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 can be calculated for each zone. When the calculated doses, 1.6 × 10¹⁴ to 1.7 × 10¹⁵ 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 significant change occurs between zones of varying radiation damage. The decrease in photon frequencies and peak intensities with increasing dose for both internal and external modes implies a rotation of the SiO₄ tetrahedra and/or 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 omega domains, with some suggestion of the formation of Zr₂O₃ nanoparticles.

**J11.28**

**ISOMORPHIC CAPACITY AND RADIATION STABILITY OF THE GARNET-STRUCTURED ACTINIDE HOST. S.V. Yudinsev, M.I. Lagina, Institute of Geology of Ore Deposits, Moscow, RUSSIA; T.S. Yudinsev, Moscow State University, Moscow, RUSSIA.**

From chemical-physical point of view prospective actinide waste form should retain its crystalline lattice under wide variations of waste streams chemical composition. One of the most promising host is garnet-structured phases of general formula AB₂O₄·SO₂. In order to evaluate feasibility of usage of the garnet for actinide waste immobilization research of synthetic phases formed in the system: CeO₂·Fe₂O₃·Al₂O₃·SiO₂·ZrO₂·Gd₂O₃·UO₂ was carried out. Experiments were performed in air medium at 1400K. At 100 C all of the garnets produced have high capacity in regard of Gd and Zr, while incorporation of U in the structure was found to be greater dependent on the phase overall composition. Solubility of uranium varied from 1.6 ± 0.8 weight % to 6.0 ± 0.8 weight % within the range of different garnet compositions. The garnet phase most resistant to radiation damage is the Gd-doped garnet. The other actinide-bearing phase observed in sample [(fluorozirconate-structured oxide) did not become amorphous even at a dose of three times higher of critical fluence for garnet. The critical amorphization temperature above which the garnet structure could not be amorphized was determined to be 1040K.

**J11.29**

**A CATHODOLUMINESCEENCE INVESTIGATION OF THE ZIRCONOCHLORIDE, (Ca,Gd,H,U,Pu)₂Ti₂O₇, DOPED WITH ²⁵⁹Pu AND ²³⁵Pu. Maria Zvyatcseva, Yury Zvyatsev, The V.G. Khlopin Radium Institute, St. Petersburg, RUSSIA; Roman Bogdashov, Dept of Chemistry, St. Petersburg State University, St. Petersburg, RUSSIA; Andrey Sergeev, Dept of Geology, St. Petersburg State University, St. Petersburg, RUSSIA.**

Crystalline ceramic based on the pyrochlore structure (Ca,Gd,H,U,Pu)₂Ti₂O₇ has been proposed in the U.S. as a waste form for the immobilization of actinides. To date, no samples of polycrystalline pyrochlore doped separately with ²⁵⁹Pu and ²³⁵Pu were studied using cathodoluminescence (CL) immediately after synthesis and then after 175, 245 and 405 days. Cathodoluminescence allows for the observation and identification of defects in crystalline materials and to determine in some cases the valence state of different ions. All starting precursors for the pyrochlore synthesis were loaded with 10.5 weight % Pu and 20.9 weight % U. The Pu and U contents determined by electron probe microanalysis.
[EMPA] in single pyrochlore grains, however, were variable. Pyrochlore doped with Pu contained [in wt %] Eu: Pu=0.9-1.7 and U=26.1. Pu-239 doped pyrochlore was obtained after 245 days and a synthesis revealed that pyrochlore doped with 239Pu became inhomogeneous and contained [in wt %] Eu: Pu=3-4, 26.8 and U=22.4. The CL spectra of pyrochlore doped with 239Pu and 233U showed similarities in a dark field and characterized a typical broad band emission with a maximum peak at 2.5 eV. New CL peaks with maximum intensities at 2.5, 2.4 and 2.3 eV in the emission spectra of 239Pu-doped pyrochlore were observed after synthesis was done later. Also, the same peaks were observed in the CL spectra of natural U-pyrochlore containing approximately 20 wt % U in the form of the uranyl ion. The results obtained allow us to conclude that the radiation damage of pyrochlored-based ceramic waste form is not converted into pyrochlore structure from the mobile uranyl ion.

J111.30
ALPHA-DECAY RADIATION DAMAGE STUDY OF A GLASS-BONDED SODALITE CERAMIC WASTE FORM
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Effects of alpha decay on the ceramic waste form used to immobilize actinides and fission products were studied using electron beam treatment of spent DOE fuel. 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 oxides. 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, microstructural 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
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Garnet is an orthosilicate, ideally $A_2B_2O_7$. The isotropic structure consists of a corner-sharing framework of $A_2O_4$ tetrahedra, $A_2O_6$ dodecahedra and $BO_6$ octahedra. Because both the $A$- and $B$-sites can be occupied by actinides, garnet is a candidate nuclear waste form. In this project, we investigate the radiation susceptibility of several synthetic garnet compositions as candidates for waste forms. The compositions of the synthetic garnets are [normalized by 24 oxygen]: N56: Ca4.93Eu0.07Fe2.75Ga0.65Na0.44Sc0.44; N77: Ca4.03Eu0.07Fe2.95Ga0.41Na0.30Sc0.69; Ca4.02Eu0.15Fe2.95Ga0.41Na0.30Sc0.69; Ca4.01Eu0.15Fe2.95Ga0.41Na0.30Sc0.69; G3: Ca4.93Eu0.07Fe2.75Ga0.65Na0.44Sc0.44; Ca5.93Eu0.07Fe2.95Ga0.41Na0.30Sc0.69; G4: Ca4.93Eu0.07Fe2.75Ga0.65Na0.44Sc0.44; N56 and N77 are silicate garnet, while G3, G4 and N56 are alumino-silicate garnet. IRR experiments [1.0 MeV Kr] have been completed in these synthetic garnets and natural garnet (mandrite: Ca3Fe2Si1.5O7.5). The critical amorphization temperature ($T_a$), above which amorphization does not occur, were determined to be 1050 K for N77, 1130 K for N56, 1100 K for G3, 890 K for G4 and 1000 K for mandrite, respectively. $T_a$ increases as the total cation weight in the formula increases. Although the garnet structure has different cation-sites, the relationship between $T_a$ and atomic mass is consistent with previously reported $T_a$-mass relationships for A-site cations in zirconia-stabilised phases. At high temperatures, nano-crystals formed with dopings consisting with a unit cell in which the parameter lattice is close to half of the original garnet. This suggests that the garnet structure is converted into cation-dissordered garnets.

J111.32
COMPUTER STUDY OF THE EFFECT OF POINT DEFECTS ON X-RAY DIFFRACTION SPECTRA OFIRRADIATED

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The presence of defects in crystals can cause severe problems for standard 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 results in changes of the integrated diffraction line intensities, the key parameter for structure refinement or quantitative phase analysis. It is clear that correct structure determination from pattern information is only possible, and 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 molecular dynamic models. The dependence of this factor to the 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 few cases, and it is discussed under what conditions the K-dependence of the factor can be sufficiently simple for use in practical structure refinement.

J111.33
ABSTRACT WITHDRAWN

J111.34
STRUCTURAL CHANGES OF TITANITE PYROCHLORES INDUCED BY ION IRRADIATION: XPS INTERPRETATION
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Titanate pyrochlores are expected to be used for the isolation of weapons plutonium; they also have potential in solid electrolytes and oxygen gas sensor. The radiation-induced microstructural evolutions of titanate pyrochlores have been characterized using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Following the irradiation of $\text{Gd}_2\text{Ti}_2\text{O}_7$ with 1.5 MeV Xe ions at a fluence of $1 \times 10^{14} \text{Xe}^+ \text{cm}^{-2}$, a 300-nm-thick amorphous layer was formed at the specimen surface by cross-sectional TEM XPS analysis before and after amorphization shows that the main reasons for amorphization are the decrease in coordination number of titanium and the changes of bond-type properties of Gd-O. These structural features found indicate that titanium acts as glassy network former in ion-beam-amorphized $\text{Gd}_2\text{Ti}_2\text{O}_7$. This is similar to those characteristics of titanium glasses. A model based on this glassy network structure was developed and predictions to the relative susceptibilities to amorphization of other titanate pyrochlores have been given. These predictions are coincident with our recent experimental results.

J111.35
ION IRRADIATION OF ZIRCONATE PYROCHLORES
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Zirconate pyrochlores, $\text{Ln}_2\text{Zr}_2\text{O}_7$, are important potential nuclear waste forms for Pu immobilization. Previous study of the binary series $\text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$ showed that resistance to amorphization increased with the increasing Zr content, and $\text{Gd}_2\text{Zr}_2\text{O}_7$ is radiation resistant to 1 MeV Kr ion irradiation. A 1.5 MeV Xe$^+$ at 500 keV Au$^+$ irradiation were performed for different $\text{Ln}_2\text{Zr}_2\text{O}_7$ pyrochlores compositions (A: Eu, Sm, and Gd) and titanate-zirconate series $\text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$ (x=0.25 and 0.5). The critical amorphization temperature $T_a$ for $\text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$ series increase with the cascade size resulting form different incident ion sources, and the increasing radiation resistance with the increasing cascade size was further evidenced. Only partial amorphization was observed in $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Zr}_2\text{O}_7$ irradiated by 1.5 MeV Xe to 34 dpa at 25 K. $\text{Ln}_2\text{Zr}_2\text{O}_7$ is the only zirconate pyrochlore that can be amorphized with a critical amorphization temperature of ~310 K. The susceptibility to amorphization of $\text{Ln}_2\text{Zr}_2\text{O}_7$ is related to the fact that it has the largest structure deviation from the ideal fluorite structure, and the highest energy barrier for ion-impact enhanced recrystallization.

J111.36
ATOMIC SIMULATION OF DISPLACEMENT CASCADES IN ZIRCONIA.
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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 of ceramic glass from which UO₂ is precipitated. 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 atomic defect formation processes, such as interstitial- and vacancy-type point defects, and subsequent defect migration. These processes play a vital role in determining the radiation response of ZrSiO₄ and can be elucidated by realistic computer simulations of displacement cascades. However, very few similar calculations 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 simulation using a Coulombic model for long-range interactions, Buckingham potentials for short range interactions, and Ziegler-Biersack-Littmark potentials for close-pair interactions. The simulations showed that radiation damage in crystallographic parameters, point defect formation, interstitial and vacancy point defects, and self-interstitial and self-vacancy point defects have been reproduced by the model. The temperature dependence of the radiation damage was then used to estimate the time scale of the radiation damage. The results showed that the time scale is on the order of 100 years, which is consistent with the current waste management practices.

A study of temperature distribution for an in-floor type nuclear waste repository in granite rock for high-level nuclear waste (HLW) bearing granite is presented. Transient calculations for a 3-D model have been carried out for both 20 weight percent and 10 weight percent HLW bearing granite, for the surface cooling periods between reactor discharge and geological disposal varying from 5 to 40 years. The hypothetical 'in-floor' type repository is assumed to consist of a tunnel network at a depth of 500 m below the surface. This study investigates the temperature distribution in one of the boreholes of the hypothetical tunnel for a basic geometrical setting as well as the effect of varying the distance between the adjacent boreholes and the distance between the adjacent tunnels. The temperatures in the repository were found to be sensitive to surface cooling conditions as well as the amount of waste loaded. For the base geometry (tunnel spacing 30 m and casier spacing 6 m), the maximum temperature reached at the waste centreline was calculated to be 210°C for 10 weight percent HLW bearing granite, with a faster initial cooling period. On the other hand, for similar centerline temperatures, initial cooling period for 20 weight percent HLW containing granite was predicted to be about 20 years. In comparison to the base geometry, decreasing the spacing between the casiers was found to have a more pronounced effect on the temperature field than decreasing the space between the adjacent tunnels.
Depleted uranium dioxide (DUO2) waste packages (WPs) for spent nuclear fuel (SNF) are being investigated to reduce radiocesium release from WPs. Decrease of potential for repository nuclear criticality events, and 3) provide means to naturally use excess D-excess. Conceptually, the DUO2 WP with SNF is similar to a small (100 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) fill for all void space, 2) WP-specific design, and 3) component as a component of a DUO-steel cement. Ceramics are a mechanism to create a ductile form of DUO2. The cement, containing up to 65 vol. % DUO2 embedded in steel, substitutes for the steel components (shell and base) of the WP. The WP contains an outer non-oxide layer of a more corrosion-resistant alloy such as C22. 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 these radionuclides trapped in the fuel pellets. The WP material of construction are chosen for geochemical reasons. Mechanisms for delayed release of radionuclides include: elimination of void space to prevent early WP collapse with failure of radionuclide release barriers (outer corrosion resistance 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 DU, reduced fluid flow (air, oxidizing groundwater) inside 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 DUOx oxides, and long-term buildup of uranium silicate surfaces.

**J1114.2 PERFORMANCE ASSESSMENT OF LOW-LEVEL WASTE DISPOSAL FACILITIES USING A COUPLED UNSATURATED FLOW AND REACTIVE TRANSPORT SIMULATOR.**


Recent advances in development of reactive chemical transport simulators have made it possible to use these tools in performance assessments for nuclear waste disposal. The Subsurface Transport Over Reactive Multihyphal (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 low-activity 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 yields 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 buffer, whereas the SiO2(In) 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 design offers a higher pH relative to the 4-layer design. Simulations that included the effect of canister 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 LIW disposal facility under design in Italy that contains radioactive waste 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 dissolution of the graphite of the reactor core (the reactor product with portlandite), the simulations suggested that leaching the graphite packages in the presence of the facility with lower partial pressures of atmospheric CO2 would lower overall C-14 release rates.

**J1114.3 RADIOISOTOPE FRACTIONATION AND SEQUENTIAL DISSEQUILIBRIUM IN PERFORMANCE ASSESSMENT.**

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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 assessments for geologic repositories include: estimation of radiocesium release from radioactive waste 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 neutron fluence. Natural systems are characterized by secular disequilibrium. For example, U-234/238 activity ratios in groundwaters reach values of 5 to 10. A primary mechanism for selectivity of radionuclide release from radioactive waste includes solubility. Release of radionuclides from uranium waste forms or solubility limiting solid phases could affect repository performance, however, consequences of differential radionuclide release have not been reported previously in performance assessments. For example, in DOE-TP-407, 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 estimates may be incorrect. Another possible application is to use 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 quantitatively related to uranium and thorium decay series isotope equilibrium/disequilibrium. This work is supported in part by the U.S. Nuclear Regulatory Commission (NRC) under contract number NRC-82-97.0009. This is an independent product and does not necessarily represent the views or position of the NRC.

**J1114.4 MASS-BASED MEASURES FOR IMPACTS OF GEOLOGIC DISPOSAL.**

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In previous performance assessments, radionuclide mass released from an independent waste canister was first obtained, and then used as the initial boundary condition for the radionuclide transport into the farfield. The repository was regarded as a collection of such independent canisters. However, there can be important effects of the number and interaction of canisters on the release of radionuclides from the repository. A repository performance model that can show effects of canister multiplicity and configuration has been developed. Mass of radionuclide in the repository and the far field are proposed as performance measures. Mass balance equations for the radionuclide in the waste matrix, in the buffer, and in the near-field rock are established by considering solubility-limited release from the waste matrix to the buffer. Radionuclide diffusion in the buffer, coupled with advective transport in the NFR, is taken into account. A separate balance equation is written for the radionuclide mass in the far field. To illustrate, we consider transport of 249Pu in two extreme configurations. In configuration (A), 10 canisters are lined up in the direction parallel to the water flow in the near field rock. In configuration (B), which is the one applied in previous assessments, 10 canisters are lined up in the direction perpendicular to the water flow, and are assumed to not interact with each other. Canister multiplicity in Configuration (A) has significant effects on the release of long-lived radionuclides from the repository. As more canisters are included in the same waste canister design, the radionuclide concentration in the stream increases, but becomes independent of the number of canisters for sufficiently many canisters. Effects of reduction of radionuclide mass in one canister and reduction of the number of radionuclides from the repository performance are clearly observed if the mass-based measures are applied.

**J1114.5 Abstract Withdrawn**

**J1114.6 EFFECT OF REDOX CONDITIONS ON THE SORPTION OF URANIUM ONTO GEOLOGICAL MATERIALS.**

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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 basalts and sandstones was studied as a function of redox conditions ranging from strongly reducing to strongly oxidizing. Thermodynamic modelling indicated that at pH 8, strongly-reducing conditions (using sodium dithionate, Eh ~ 500mV) would provide predominance of Pu(III) in solution, whereas Pu(IV) would dominate between 1000mV and +1500mV (e.g. using hydroxy ammonium chloride). Hydrogen peroxide was also examined as a sorption agent that would give a high redox potential without causing experimental difficulties. Both 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 performed using separatory funnels and 10000 MWCO filtration. Results were as follows. Under strongly-reducing conditions (\( E_h = \approx 500 \text{mV} \)), the distribution ratios (\( R_p \) values after filtration) were similar for both rock types, values being \( \approx 20 \pm 2 \). Under oxidising conditions (\( E_h = \approx 400 \text{mV} \)), \( R_p \) values were greater than 20 and \( 30 \text{mLg}^{-1} \) sorption being onto clays. Under oxidising conditions, (\( E_h = \approx 490 \text{mV} \)), \( R_p \) values were in the range 1-70 \text{mLg}^{-1} \) for basalt with some variation with phase separation method, and \( 0 \text{mLg}^{-1} \) for sandstone.

A model based on sorption onto iron oxide was developed and was able to reproduce most of the experimental data within known uncertainties, but tended to predict the sorption of plutonium onto clays under intermediate and oxidising conditions.

**J11.47**
SOFTWARE FOR THERMODYNAMIC SIMULATION OF HIGH-TEMPERATURE CHEMICAL EQUILIBRIUM
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Thermodynamic computer-based simulation is an effective tool for chemical engineers and scientists engaged in thermochemical treatment of radioactive wastes. It allows investigation of systems with an arbitrary chemical composition using only reference data on thermodynamic properties of individual substances, which might arise from the waste combustion. Unquestionable, the assumption of the phase and chemical equilibrium is a limiting case, but even the simulation results are of great importance when analyzing the possible processes in an investigated system, especially containing high-level wastes. The goal of the publication is to present the thermodynamic simulation software developed for the determination of equilibrium composition and properties of arbitrary reacting systems. The software is easy in installation and employment for any scientist and investigator due to simplicity of problem formulation and convenience of data representation. The method is based on the maximal entropy principle, which is true, according to second law of thermodynamic, for any equilibrium system regardless of pathway of process to the equilibrium state. The generalized statement of the thermodynamic simulation problem has allowed development of the multi-purpose software THERA coupled with databases on the thermodynamic properties of 3000 chemical compounds in gaseous, condensed, and ionized state. In the computation, all possible compounds of the chemical elements incorporated into the system of interest are taken into consideration. The software interface has been designed in such a way as to simplify specific iteration of the starting chemical composition and description of initial conditions. The contents of chemical elements are given by their mass or molar parts or by the parts of source substances constituting the system investigated. The conditions to be required for the determination of equilibrium state parameters are given by the values of any pair of parameters among the six: the pressure, the temperature, the specific volume, the entropy, the total enthalpy, and the internal energy. Within the one task, new calculations may be conducted using up to 100 values of the initial parameters. The calculation results are represented on display in the form of plots and tables, also they may be stored as a disk file or printed. The software is BHAR-compatible, operating under the control of Windows 95/98/NT/2000. Examples of software THERA application for a number of problems relating to the radioactive waste thermochemical treatment are demonstrated.

**J11.48**
GAS CONTAMINANT MOBILITY AT SUBSURFACE DISPOSAL AREA. Chang Oh, Todd Housey, Jeff Sandrup, Idaho National Engineering Laboratory, Idaho Falls, ID; Sheldon Smith, Wayne Down, Brigham Young Univ, Dept of Civil Engineering, Provo, UT; Vance Wiking, Brigham Young Univ, Dept of Chemical Engineering, Provo, UT.

Beginning in 1952, waste materials, including VOCs contaminated with transuranic radionuclides were generated during the fabrication, assembly, and processing of nuclear weapons components in the US Department of Energy (DOE) weapons production complex at the Rocky Flats Plant (RFP). Initially, these waste materials were drummed and stored at the so-called “Mound Area” at the RFP. They were transferred to the RFP 901 Storage Area in July of 1959, and to RFP Building 724 for processing beginning in January of 1967. Processing included the mixing of the VOCs and miscellaneous cork contaminated with transuranic wastes, with calcium silicate absorbent in a ratio of approximately 30 gallons of liquid organic waste to approximately 100 lbs. of absorbent. The resulting organic mixtures or “743 Series Waste” was double or triple bagged and placed in 55 gallon drums. Following processing and contamination, 743 Series Waste drums were shipped to the SDA for burial at the Idaho National Engineering and Environmental Laboratory (INEL). On October 7, 1969, approximately 100 743 Series Waste drums were buried in the Subsurface Disposal Area (SDA). Note that beginning in November 1970, transuranic waste received at the NWMC was placed in retrievable, surface-storage in containers with direction to discontinue subsurface disposal of transuranic waste. In order to understand the phenomena controlling the transport of volatile organic compounds (VOCs) from the burial site at the INEL, we studied potential contaminant transport scenarios and evaluated the equilibrium relationship established for these VOCs in the various media in which they are found. This paper describes the history of mixed wastes buried at the SDA, phase partitioning, and computer simulation results on gas contaminant mobility in the vadose zone.

**J11.49**
RESULTS OF MODELING VADOSE ZONE FLOW AND TRANSPORT AT THE 241-SX SHELTER SITING SITE.
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The U.S. Department of Energy (DOE) has initiated a Resource Conservation and Recovery Act (RCRA) Corrective Action process to address the impacts of past and potential future tank waste releases to the vadose zone at the 241-SX single-shell tank farms at the Hanford Site in southeastern Washington. The corrective actions include evaluation of impacts to groundwater resources (i.e., the concentration of contaminants in groundwater) and long-term risk to human health (associated with groundwater use). Numerical models have been developed that consider the extent of contamination present within the vadose zone, contaminant movement through the vadose zone to groundwater, and contaminant movement in groundwater to points of compliance. The models are used to evaluate the impacts of an interim barrier to the contamination of meteoric water by contaminants from previous tank sources. The reference suite of simulations (Base Case) considered the migration of contaminants from field estimates of contaminant concentrations through the vadose zone and groundwater to the SXS Waste Management Area (WMA) boundary with no interim barriers but a closure barrier by the year 2040. The impact of an interim surface barrier was investigated by altering the Base Case simulation to include an interim barrier in place by the year 2010. Results showed that, while the peak arrival time to the WMA boundary was delayed by 15 to 18 years with the interim barrier, the peak concentration was reduced by 70%, and the peak concentrations for TrCr99, Cr, and NOS, respectively. Results suggest that an earlier placement of the interim barrier will further delay arrival times and reduce the peak concentrations at the compliance points.

**J11.50**
INFLUENCE OF SALINITY ON THE HYDRAULIC CONDUCTIVITY OF COMPACTED BENTONITE. Wen-Jin Cho, Jin-Dong Lee, Chul-Hyung Kang, Korea Atomic Energy Research Institute, Taejon, KOREA.

This study presents the results of experimental studies to investigate the effect of salinity elevation due to the seawater intrusion on hydraulic conductivity of backfill material for the underground repository. The hydraulic conductivities in the compacted bentonites with dry densities of 1.0 Mg/m³ to 1.8 Mg/m³ were measured. Potentiometric water retention tests of material were determined before the hydraulic conductivities were measured. The experimental results show that the hydraulic conductivities increase with increasing salinity only when the dry density of bentonite is relatively low. The degree of increase becomes more remarkable at lower dry density of bentonite. For the bentonites with the densities of 1.0 Mg/m³ and 1.2 Mg/m³, the hydraulic conductivities of 0.4 M NaCl solution increase up to about 7 times and 3 times, respectively as high as those of demineralized water. However, for the bentonites with the dry density higher than 1.4 Mg/m³, the salinity has no significant effect on the hydraulic conductivity. When saline water is intruded into the bentonite, the cation concentration in porewater is increased, and it causes the diffuse double layer to contract. Whether or not this contraction of the diffuse double layer will result in the increase of hydraulic conductivity depends on the relationship between the distance between the cation platelets of the nanoscale double layer. For the dry densities of 1.0 Mg/m³ to 1.8 Mg/m³, the half distance between bentonite platelets varies from 1.81 nm to 0.53 nm. In the
case of 0.0 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 the sample is over 1.45 g/cm$^3$, the sample thickness is so small that the contracted diffuse double layers are still overhung resulting in the nearly constant hydraulic conductivity.

**J111.51**

**THERMODYNAMIC MODELING OF BINARY AND TERNARY ISOTOPIC EXCHANGE EQUILIBRIA BETWEEN AQUEOUS SOLUTIONS AND THE ZEOLITE MINERAL CLINOPTILOLITE.**

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Because of their high cation-exchange capacity, zeolite minerals are potentially useful in the treatment of nuclear, municipal, and industrial wastewaters and acid mine drainage 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 $\text{Na}^+$, $\text{K}^+$, $\text{Rb}^+$, and $\text{Cs}^+$, 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.

**J111.52**

Abstract Withdrawn.

**J111.53**

Abstract Withdrawn.

**J111.54**

Transferred to J111.55

**J111.55**


A large number of studies on HLW glass corrosion have shown that the glass reacts with water to form more stable mineral phases (alterations) during the long-term geological disposal. The potential phases have been evaluated by use of thermodynamic calculations to determine, amosite, mellite, and cristobalite 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 amosite 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 will 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 R777 glass in alkaline solutions at elevated temperatures to accelerate the reaction, and mineral phases formed were analyzed by XRD. The results showed that anatase/muscovite, cristobalite, and the diagenesis between the SiO$_2$(am), and beidellite(amosite) or gibbsite coexists depending on the conditions. The solution analysis indicated that most of the cesium is retained in the phases of beidellite and amosite by substitution.

**J111.56**

Abstract Withdrawn.

**J111.57**

**EFFECTS OF THE URANIUM CONTENT ON THE STRUCTURE OF IRON-PHOSPHATE GLASS WASTEFORMS.** Diego O. Bassa, Diego Rodríquez, Mario E. Sterba, Nuclear Materials Group, National Atomic Energy Commission, Argentina; José M. Rubén López, Instituto E. Tronjo, Madrid, Spain; Carlos González 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 % $\text{Fe}_2\text{O}_3$, 50 to 74 wt % $\text{P}_2\text{O}_5$, 0 to 15 wt % $\text{UO}_3$). We have performed DTA/TA analysis so as to find the glass transition temperature, the heat of transformation, and the enthalpy content. We also did dilatometric experiments to confirm the data obtained in the DTA/TA experiments and to get the softening point and thermal expansion coefficients. Additional data obtained from X-ray diffraction, infrared spectroscopy, and X-ray fluorescence, 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 Test).

**J111.58**

**SURFACE AND NEAR SURFACE REACTIONS IN SODIUM AND BETA SILICATE GLASSES EXPOSED TO AQUEOUS SOLUTIONS.** S. Shuttmann, S. Thevuthusan, D.R. Bay, J.P. Itenhow, and B.P. McGlachlan, Pacific Northwest National Laboratory, Richland, WA; S. Molinas, University of Western Sydney, Kingswood, Australia; N. Paloo, National Nuclear Security Administration and Technology Organization, Menlo, Australia; A.A. Salk, Charles Evans and Associates, Sunnyvale, CA.

Glass and ceramic waste forms are proposed for the stabilization and immobilization of nuclear wastes. Recent findings show that ion exchange reaction has a major role in release of radionuclides from the glass matrix. Several sodium and boro silicate glass coupons with fixed Na and variable B and Al concentrations were exposed to isotopically labeled aqueous D$_2$O$_4$O$_2$ solution to understand the process that lead to ion exchange and sodium release. Solution compositions were used to determine the release of radionuclides. These studies have 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 samples. 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 sodium release. 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 $^{18}$O incorporated demonstrating considerable interactions between the water and the glass. On the basis of the depth distributions of Na, D and $^{18}$O, 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, Office of Biological and Environmental Research and Australian Institute of Nuclear Science and Engineering.

**J111.59**

**SENSITIVITY STUDIES OF THE EFFECT OF CLADDING DEGRADATION ON TSPA RESULTS.** Eric Siegmund, Eve Devonec, 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 - Voluntary Assessment (TSPA-VA) and have been updated to the recently released TSPA-9R (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 diffusion of the radionuclides through the cracks in the WPs. The cladding model improves improvements and mate-pass point modeling from bare fuel. The model occurs in two steps, perforation followed by unzipping. Results from sensitivity studies show the important effect of the cladding in dose reduction is to prevent fuel disintegration (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 $^{14}$O$_2$ dissolution rate is sufficiently rapid so that the instantaneous unzipping increases the dose by only 12% from the base case. Overall, the current cladding 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 little 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.
Neptunium-237 is a radionuclide that is of special concern, because of its potential ability in nuclear reactor environments. It has a half-life of 2.14 × 10^10 years. Current thermodynamic data indicate that the crystalline Np(V) oxides NpO_2 are stable Np solid in YM-like groundwaters; however, NpO_2 may be kinetically inhibited from precipitation in certain Np-bearing groundwaters or at near-ambient temperatures (~25°C) [1]. Here we report precipitation of crystalline NpO_2 during the corrosion of Np-doped UO_2 (Np-U approximately 1.8% in humid air at 90°C and 150°C. The Np-doped UO_2 was reacted for several weeks in 22 mL sealed stainless-steel vessels to which 0.3 mL of water and a few drops of H_2O_2 were added. X-ray powder diffraction (XRD) of unreacted solids confirmed oxide UO_2 as the only crystalline solid present. Reacted solids were examined by scanning electron microscopy with energy-dispersive x-ray emission spectroscopy (SEM/EDS) and blind analysis of a uranium (hydr)oxide precipitate using the predominant corrosion product; spherical, Np-bearing particles (~1.2 micrometer diameter) were also found. The XRD pattern from the reacted solids indicates that the degraded crystals correspond to dehydrated scheelite. In addition to a small amount of unreacted UO_2, a cubic phase is also apparent, with a diffraction pattern identical to that of NpO_2. A full-particle Rietveld refinement was performed, with alpha-UO_2, alpha-UO_2(OH)_2, and NpO_2 used as starting structural models for the three components. Refined unit-cell parameters for the cubic phase (NpO_2) are consistent with literature values for NpO_2. The refined indices indicate that the resulting crystals consist of approximately 79 mass% dehydrated scheelite, 9 mass% NpO_2, and 12 mass% UO_2 [1] Roberts et al. (1999). Abstracts volume for Migration 99. Program A10. 

**J111.03** NEUTRON INCORPORATION IN URANIUM(VI) COMPOUNDS FORMED DURING THE AQUEOUS CORROSION OF NEPTUNIUM-BEARING URANIUM OXIDES. Robert J. Finch, Edgar C. Buck, and Stephen F. Wall, Argonne National Laboratory, Argonne, IL; Battelle Pacific Northwest National Laboratory, Richland, WA.

Neptunium-237 (237Np) is an isotope relevant to evaluating the long-term performance of geologic disposal for high-level nuclear waste, because of its potential mobility in Yucca Mountain groundwaters and its long half-life (2.14 × 10^10 yr). We report on the first experimental studies of Np behavior during the aqueous corrosion of unirradiated Neptunium-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 H_2O_2 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 with energy-dispersive X-ray emission spectroscopy (SEM/EDS) and transmission electron microscopies (TEM and SEM) with energy-dispersive x-ray emission spectroscopy (EDS) and electron energy-loss spectroscopy (EELS), as well as by x-ray powder diffraction (XRD), inductively coupled plasma mass spectrometry (ICPMS), 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. Crystalline NpO_2 also precipitated during these experiments. Dehydrated scheelite may be expected to incorporate some Np into its structure, and coexistence of NpO_2 and dehydrated scheelite may help define the mobility of Np in dehydrated scheelite in the presence of NpO_2 under these conditions. The determination of stable in 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) Mater. Res. Soc. Symp. Proc. Vol 506, pp. 87-94.
replacement and at much lower 5/S. However, at long continuous times in test (3 months before solution replacement), the release rate from static batch tests is much lower than that observed in dynamic unstirred tests. These results suggest an approach to solution saturation of a dissolving species or solution depletion of a ground water species. Thus, spent oxide fuel corrosion does not experience a steady acceleration from increased fuel surface area to solution volume (5/V) effects. This is contrary to other systems where the 5/V is known to have a strong effect, e.g., alkali-aluminosilicate glass corrosion, which likely arises from a positive feedback mechanism that is absent in spent oxide fuel.

J111.65 INVESTIGATION OF THE OXYGEN K-EDGE IN SPENT NUCLEAR FUEL AND URANIUM ALTERATION PRODUCTS. Edgar Buck, Pacific Northwest National Laboratory, Richland, WA.

According to Papino 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 Ohrlander suggest that uranium should be oxidized to U5 in spent UO2. Compounds containing U5 are rare and usually unstable. Known examples include, \( \text{U}_2\text{MoO}_8 \), \( \text{UBr}_3 \), \( \text{U}_2\text{O}_5 \), and \( \text{U}_5\text{O}_{12}\text{C}_1 \). Burns and Finch found crystallographic evidence for U5 in a natural mineral, pyrite, \([\text{CaU}_5\text{UO}_2(\text{OH})_2] \) [H2O]7. However, this orthorhombic phase is extremely unstable. The existence of U5 in a solid phase has been determined directly and confirmed on 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 ocean, 258 mixture of U4 and U5. 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 complex 3-electron recombination 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 covency in the M-O bond in the spent fuel, as expected, given the high chemical stability of rare earths and actinides. In contrast, the O-K edge from [V] uranium shows only coveny M-O bonding. The M-O covency shifts the O-K edge to around 510 eV.

J111.66 CERIUM INCORPORATION IN A URANYL HYDROXIDE PHASE. Cheol-Won Kim, David J. Weckleskie, Univ. Missouri-Rolla, Dept. Geology & Geophysics, Rolla MO; Robert J. Finch, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

The neutron migration behavior of radionuclides in a mixed-waste repository will be influenced, in part, by their equilibrium solubilities and the distribution of their adsorption as trace contaminants on surfaces of host phases. Uranyl phases that develop on the surfaces of altered spent nuclear fuel may thus influence the mobility of released radionuclides, since by proximity, these will be the first phases that the radionuclides encounter as they leach from their reservoir, the 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 98°C. The cerium serves both as a monitor for evaluating the potential repository behavior of quadrivalent REE radionuclides and as a surrogate element for actinides [e.g., Ce4+ (0.94 Å for Pu4+ 0.93 Å)]. 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 \( \text{UO}_2(\text{OH})_2 \); cf. JCPDS card # 00-046-1180 and several uranyl carbonate phases. An analysis of the leachate, leachate, and solid phases, and the potential implications for radionuclide leaching and sorption (2 dilute hydrofluoric acid solution) was performed by Inductively Coupled Plasma Mass Spectrometry. Results indicate a progressive decrease in concentration of cerium in the solid from 26 to 29, and finally 11 ppm for cerium produced in 7, 35, and 180 day tests, respectively. This trend correlates with a decrease in the amount of adsorbed onto the surfaces of the crystals over the same time interval, suggesting a lowering of the potential for Ce incorporation on the surface area/volume ratio of the crystals decreases. This correlation indicates that surface adsorption is playing a key role in the immobilization of cerium by the solid phase in these experiments.

J111.67 SORPTION-REAGENT METHOD IN LIQUID RADIOACTIVE WASTE MANAGEMENT. Valentin Avramenko, Veniamin Zhelezov, Elena Kaplan, Dmitri Maminin, Tatiana Sokolotkina, Anna Yulkkun, Inst of Chemistry FELIXS, Vishnyatez, RUSSIA.

Methods of liquid radioactive waste (LRW) decontamination from radionuclides including their co-precipitation at specific conditions or adsorption on selective sorption materials are well known and extensively used in LRW processing. This work summarizes our ideas and work results on studies and application of a sorption-reagent method of microelements and radionuclides removal in which selective radionuclide sorption is provided by the sorbent reaction 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 caesium 137. It was shown by comprehensive analysis of radionuclide removal efficiency by traditional selective sorbents and developed sorption-reagent materials that the latter have the highest distribution coefficients in systems to provide for pure sorption/ion-exchange decontamination. For example, the sorbents made here have the strontium distribution coefficients several dozens higher than those of commercially available sodium titanates and silicotitanates. One of the main fields of the sorption-reagent materials application can be decontamination of high-salinity radioactive waste. The effectiveness of such decontamination is confirmed whether as a result of ion-exchanger filters regeneration in LRW treatment 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 (SWR) to be sent for final disposal and, therefore, to decrease the cost of LRW management. Data on a pilot-plant scale testing of the LRW sorption-reagent decontamination installation are presented. 350 cubic meters of LRW of complex chemical composition were decontaminated. This initial waste contained seawater, high-salinity waste remaining after the reverse osmosis process and decontaminated waste. The decontaminated LRW met all the national (and international) safety standards. Total volume of SWR sent for final disposal was 0.6 cubic meters.

J111.68 PHOSPHATE CRYSTALLINE SILICA (GUKBA) AS AN INORGANIC SUPPORT MATRIX FOR NOVEL SORBENTS. T.J. Trasker, Idaho National Engineering and Environmental Laboratory (INEL), Idaho Falls, ID; A.S. Aloy, N.V. Sapezhnikova, Khlipin Radioactive Institute, St. Petersburg, RUSSIA; A.A. Tret’yakov, Mining and Chemical Combine, Zheleznogorsk, RUSSIA; A.G. Anashit, Institute of Chemistry and Chemical Technology, Krasnoyarsk, RUSSIA; D.A. Knetsch, T.A. Todd, and J. Markert, INEL, Idaho Falls, ID.

Inorganic ion exchange media typically exist as fine powders, making large-scale use impractical, unless the media can be agitated 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 enables them to be stored as a contaminant 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 1461. The porous glass matrix is produced in Russia using fly ash residue from coal combustion power generating plants. It consists of consolidated layers of honey glass cemenophores and is termed Gukba which is the Russian word for gunk. This paper describes a collaborative research program between the Khlop Radioactive Institute [KRI], 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. Ammonium molybdozaphosphate (AMP) for the removal of cesium from acidic liquid waste and Oxyelphenyl) 4-(N,N-diethylcarbamoylmethyl)phosphonic acid (CMPO) for the removal of inorganic matrices) have been successfully incorporated into Gukba matrices. Test results for cesium and americium removal, using AMP-Gukba and CMPO-Gukba, respectively, will be discussed.

J111.69 DEMONSTRATION OF THE FEASIBILITY OF RECOVERING ACIDIC LIQUIDS AND URANIUM TOPOLOGIES FROM A LANTHANITE BOROSILICATE GLASS. Tracy S. Rudolf, David K. Peeler, and Thomas B. Edwards, Westinghouse Savannah River Company, Aiken, SC.

A solution containing kilograms 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 vital support systems are old, subject to degradation, and prone to potential leakage. For this reason, DOE’s 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 isotope production and distribution site 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 boronate glass was selected for the vitrification process since the lanthanides are highly soluble in strong acid solutions. To demonstrate the feasibility of recovering the Am/Cm isotopes from the glass, a series of small-scale experiments was performed as part of a compositional variability study. Glasses fabricated during the study utilized lanthanide oxides as surrogates for 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 8 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 meeting 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 SILICONNITRATES IN THE \( \{K_{1-x} \cdot C_8\} _2Ti_2Si_3O_15 \cdot (OH) \cdot OH \cdot \text{H}_2\text{O} \) SYSTEM H. Xu, A. Nwosu, Dept. of Chemical Engineering & Materials Science, University of California, Davis, CA; M.D. Nyman, T.M. Nenoff, Catalysis & Chemical Technologies, Sandia National Laboratories, Albuquerque, NM; Y. Su, ML. Balmer, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA.

Crystalline siliconnitrate (CST) ion exchangers are of considerable interest because of their high selectivity for radioactive \(^{137}\)Cs and their potential application in the separation of \(^{137}\)Cs from aqueous solutions of radioactive wastes as surrogate materials. In this study, we synthesized a series of microperosorous phases with the compositions \( \{K_{1-x} \cdot C_8\} _2Ti_2Si_3O_15 \cdot (OH) \cdot OH \cdot \text{H}_2\text{O} \) \((n = 4 \text{ to } 6, 0 \leq x \leq 1)\) using the hydrothermal methods. Rietveld analysis of synchrotron XRD data indicates that these phases are isomorphous with the mineral phosphosiderite (space group \( \text{Pnmm} \)) and that the lattice parameter \( a \) increases linearly with increasing \( \text{Cs} \) content. The enthalpies of formation from the oxides and from the elements were determined by drop solution calorimetry with \( 2\text{PtO} \cdot \text{H}_2\text{O} \) as the solvent at \( 973 \) K. Our results show that the formation enthalpies become more exothermic with increasing \( \text{Cs}/\text{K} \) ratio. Thus the \( \text{Cs} \) uptake in this solid solution series is largely thermodynamically driven.

**J111.71** ANS-Ti-Si \( (A = \text{Na, K, Rb, Cs, Sr, Ba}) \) OXIDE FRAMEWORK CONDENSED AND MICROPOROUS PHASES AND THEIR APPLICATION TO RADIOACTIVITY SEQUESTRATION AND IMMobilization. Myf Nyman, Tina M. Nenoff, Sandia National Laboratories, Albuquerque, NM; Robert S. Maxwell, Lawrence Livermore National Laboratory, Livermore, CA; Akhilesh Tripathi and John B. Fenn, Department of Chemistry and Department of Geosciences, State University of New York, Stony Brook, NY; Alexandr Nwosu and Hongwu Xu, Dept. of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA.

Crystalline siliconnitrate (CST) is a microperosorous ion exchanger that has undergone extensive and advanced testing for the application of selective removal of radioactive Cs from DOE defense wastes. Substitution of small amounts of \( \text{Nb}^\text{V} \) into the \( \text{Ti}^\text{IV} \) framework site greatly enhances the selectivity for Cs. Since this type of heterovalent substitution in both open framework and condensed phases requires compensation of the charge balance by cation vacancies, a counter-substitution, or addition of exchangeable cations, 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 \( (A = \text{Na, K, Rb, Cs, Sr, Ba}) \) oxide framework materials for the application of radionuclide sequestration and immobilization, where condensed phases are optimized toward stability, and microperosorous phases are optimized toward selective, high capacity or rapid ion exchange. We report here two new families of nickel-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 selective exchange of divalent cations. We also report a series of extremely stable tetracationic-based co-condensed phase materials, and stability and structure as a function of composition are reported for these materials. Special focus is given on charge balance by extra-framework ions and exchange capacity, kinetics and selectivity of porous phases.

**J111.72** Transferred to J112.5.

**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. DiSanuto and T.L. Macchetti, 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 metallic waste form that incorporates the stainless steel cladding hull, zirconium from the fuel, and the fission products that are noble to the process, i.e., \( \text{Te}, \text{Ru}, \text{Pd}, \text{Rh}, \text{Ag} \). The nominal composition of this waste form is stainless steel/15 wt% zirconium/1-4 wt% noble metal fission products / < 1 wt% \( \text{Pu} \). The process used to make the metallic waste form that contained the cladding hulls is straightforward. The hulls after being removed from the electrowinning are introduced to a furnace where the adhering salt from the electrowinner is distilled off. The hulls are then placed into a crucible and, if necessary, submerged in a molten salt solution or stainless steel are 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, \( \text{U}, \text{Pu}, \text{and Np} \), and \( \text{Te} \) is evaluated using a standardized test model as described by ASTM C1290. Alloys of the base composition stainless steel with 15 wt% zirconium were produced that were doped with \( \text{U}, \text{Pu}, \text{and Np} \). 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 to volume of immersion was \( 40 \text{ m}^2/\text{L} \). The immersion tests were performed in triplicate to provide reliable data for the prediction. 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 \( 2 \text{ M} \) citric acid using high purity nitric acid. The test vessels were subjected to an 18 hour 90 °C acid strip using a \( 2 \text{ M} \) nitric acid solution. This acid strip solution was also analyzed. The test and the acid strip solutions were analyzed for \( \text{Fe}, \text{Cr}, \text{Ni}, \text{Mo}, \text{Mn}, \text{Zr}, \text{Pu}, \text{Np} \), and \( \text{Te} \) using inductive coupled plasma mass spectrometry (ICP-MS). The intent of these tests was to determine which, if any, of the metallic constituents of the metallic waste form could be used as a measure of the material 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 are 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 alloys.

**J111.74** THERMAL BEHAVIOR OF POLYMERIC MATRICES FOR NUCLEAR WASTE IMMobilization by DSC AND TG. Edéna M.B. de Sousa, CDTN, CNEN, Belo Horizonte, BRAZIL; Ricardo G. de Sousa, Depto de Engenharia Química, 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 inative cesium were used in the dangerous waste. The polymeric matrices, pure and with waste, obtained by the solubilization of polyethylene recycled in isoparaffins oil and kerosene oil, were microscopically homogenous. The thermal behavior of all the matrices was evaluated by Differential Scanning Calorimetry DSC and Thermogravimetry TG. With the DSC curves it is 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 do not alter the thermal behavior of the polymeric matrices. Use of the recycled polyethylene indicates a great potential for immobilization of dangerous waste.

**J111.75** AGING OF BITUMEN WASTE FORM IN WET REPOSITORY CONDITION. Michael L. Ogoin, Natalyn V. Ogoin, Zeyn I. Gohbara, Irene V. Starchek, Alexander S. Barinov, SIA Radon, Moscow, RUSSIA.

Bitumen waste form for low and intermediate level waste (LILW) immobilization is under investigation at SIA Radon for about three decades. Bituminized waste blocks were prepared at industrial plant on base of NPP-operative waste. Physical and chemical parameters of bitumen waste form containing 31 wt % solids were investigated.
after its long-term storage in an experimental shallow rock repository during 12 years. Leaching behavior of bituminized waste form was studied using the thermodynamic activity inventory which was released from the block during 12 years of storage. Non-homogeneous distribution was determined for both salts and radionuclides along vertical axis. Fractionation of bitumen host matrix was studied. The main components of bitumen were alkanes, aromatic hydrocarbons, and aromatic nitrogen compounds. The bitumen fraction was separated for different parts of bituminized waste block. The bitumen fractions were divided vertically non-homogeneously as well as the radioactivity of bitumen host matrix. The fraction 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 modeling its long-term behavior in the repository conditions.

SESSION JJ12: WASTE PROCESSING
Chair: Bill Holzhaeuser and Frederick M. Mann
Thursday Morning, November 2001
Republic B (Sheraton)

8:30 AM JJ12.1

Radioactive high level waste (HLW) slurges at Savannah River Site are stored as ceramic slurges in million gallon tanks. These slurges are being processed and immobilized into borosilicate glass in the Defense Waste Processing Facility (DWPF). A batch of feed for the DWPF is approximately 500,000 gallons of washed slurry, and is obtained by combining slurges from different tanks into a single million gallon feed tank. Washing occurs in this tank. The 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 unswashed slurry, these concentrations are too high. They are reduced by washing the slurry several times with inhibited water (IW) (0.01 M NaOH and 0.3 M CaSO4) from the slurry feed tank. A wash of feed in the DWPF is necessary because the sodium affords glass quality and nitrate and nitrite affect NO3 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 Tc-99, and Pd. Results from the full scale process indicate that concentrations of Na and other soluble ions in the supernate decreased as predicted by a model developed from the laboratory study.

8:45 AM JJ12.2
Thermodynamic Modeling of Deposition in Savannah River Site (SRS) Evaporators. Carol Janzen and James Lauriat, Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC.

A nitrated ammonium nitrate in the solid/saline/ceramic mineral family (NaAl(SO4)2(NO3)2) and sodium diuranate (Na2UO2) formed intermediately in the Savannah River Site (SRS) high level waste (HLW) processing operation. Previously, the aluminosilicate scale deposits called the SRS 2H Evaporator to become completely incinerable. Accumulation of the sodium diuranate phase, which appears to have co-precipitated with the aluminosilicate phase, has caused technical concerns. Understanding the chemistry causing the formation of the sodium aluminosilicate scale and the sodium diuranate is critical to the safe and efficient operation of the HLW evaporators. Thermodynamic calculations 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 active solutions to form sodium aluminosilicates (NAS) hydroxyl at ambient temperature. The hydrogel converts to Zeolite A (Na2Al2Si2O8·2H2O) under hydrothermal conditions at elevated temperature, e.g., the conditions existing in the SRS evaporators. The complete set of sequential densification (liquefaction) transformations is: NAS gel → Zeolite A(cubic) → solid (cubic) ⇒ ceramic (hexagonal). The initial step is the saturation of the evaporator feed tank solutions with respect to the parent NAS gel.

9:00 AM JJ11.23
Phosphate Removal from Tank Waste by Caustic-Side Solvent Extraction. David B. Chamberlain, Scott Asse, Hasane M. Arafah, Cliff Conat, Ralph A. Leonard, Monica C. Regalbuto, and George P. Vandegrift, 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 MBOCAcycH6; a modifier, 0.50 M CaSO4; and a suppressant, 0.001 M triethylamine in a branched paraffinic hydrocarbon diluent, Isopar L. In this program we have developed and demonstrated a flowsheet that can be used to process SRS tank waste. To this end, a series of flowsheet tests were completed using simulated waste in a 3-cm centrifugal contactor at ANL. Three short-term 24-hour tests were conducted to demonstrate various aspects of the flowsheet. These tests were followed by a 72-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 solution, [2] complete solvent regeneration, and [3] efficient recovery of cesium in the aqueous strip effluent by a factor of 15 using dilute nitric acid, and [4] stripping the solvent sufficiently to allow it to be recycled many times. The results from these tests, and the improved performance in the in-plant centrifugal contactors to improve extraction efficiency, will be discussed.

9:15 AM JJ11.24
Chemical Interactions of UOP INSYS® IL-911 (CST) with SRS Waste Simulants. My Nyman, James L. Krumhansl, Carlos Jove-Cocom, Pengsheng Zheng, Tina M. Nenoff, Thomas J. Hendeky, Sandia National Laboratories, Albuquerque, NM; Yali Su and Lui Li, Pacific Northwest National Laboratory, Richland, WA.

UOP INSYS® IL-911 is a bound form of crystalline silicotitanate (CST) for use in ion exchange columns for treating high level waste on 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 recent problem was the Cs precipitate, which was determined in some long-term tests. Our studies revealed that both column plugging precipitates could form as a result of the interaction of IL-911 with the highly basic, high ionic strength, average salt simulant (simulant of averaged SRS tank waste composition). A Cs precipitate is a poorly crystalline, hydrous sodium nitrate and the second is a crystalline ammonium zeolite, or carbonite. The source for the hydrous sodium nitrate precipitate was determined to be a minor impurity phase in a byproduct of CST manufacturing. The mechanism of dissolution and reprecipitation of this phase in column pretreatment fluid (5N NaOH) was investigated, and a pretreatment protocol to rid IL-911 of this impurity was devised. Further, the IL-911 manufacturing protocol (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 ammonium zeolite precipitate was determined to be predominantly from the waste solution rather than the IL-911. Solubility experiments coupled with a thermodynamic analysis provided a protocol to predict when ammonium precipitate will and will not occur. This, in turn, suggested that dilution may be used to prevent in-service column plugging by ammonium nitrate precipitation. Finally, it was also established that ammonium nitrate precipitation on the surfaces of the IL-911 granules could also account for an apparent decrease in equilibrium $K_W$ as well as increasing the kinetics of Cs sorption.

9:30 AM JJ11.25
Investigation of Chemical and Thermal Stabilities of Load-Crystalline Silicotitanate. Yali Su, Lui Li, Junjian Cao, Young, Pacific Northwest National Laboratory, Richland, WA; M. Louis Balmer, Caterpillar Inc., Peoria, IL.

An inorganic ion exchanger based on crystalline silicotitanate (CST),
IONSIV 1.911, 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 the Hanford site. In 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 evaluations. IE-111 was exposed to simulated steam at 55°C and 80°C for durations of 1 to 60 days to determine if irreversible adsorption of Cs from IE-111 occurs and the cause of desorption, as well as the time/temperature profiles over which desorption could be observed. In addition, column capacity tests were conducted by XRF, Raman spectroscopy, and SEM/EDS. High Cs loading, high simulant/IE-111 ratio, and high-temperature heat treatment could cause irreversible Cs adsorption. SEM results showed that a crystalline sodium sulfide solution on the surface of IE-111, which had been exposed to the simulated steam at 55°C and 80°C. The morphology of the coating depends on the heat-treatment temperature, heat-treatment time, IE-111-simulant ratio, and simple simulation. IE-111 contains a Si source for the aluminosilicate precipitation. The coating should not be the major reason for the irreversible Cs adsorption because it was found on the surface of almost all the heat-treated IE-111 samples. Cationic-type aluminosilicate has large size openings in its structure so that Cs ions should be able to diffuse through these pores to IE-111 when the temperature was lowered. The mechanism for irreversible Cs desorption is under investigation 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 waste due to their ease of synthesis, high metal ion complexation ability, and flexibility for different nuclear waste management applications. For most applications, the ligand is deemed to be of primary importance for the interaction with the radwaste metal ion. The role of 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 targeted 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, CCI4H2, while the resin was created around the ion to provide a unique structure based upon each metal. These resins were synthesized by a radical polymerization method, producing a reusable organic solid. These resins were purified 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 kinetics were obtained at pH 1.0, 2.5, 4.0, and 5.5. Results show that the resins retained radioactivity from aqueous solution under experimental conditions. Once loaded with metal, the ions can easily be removed with 5 M HNO3 and reused. The actinide removal is thermodynamically described to allow modeling of separation schemes.

SESSION 1113: GLASS STRUCTURE AND CORROSION

Chair: Neil E. Bilder and Olivier Spaulla
Thursday Morning, November 29, 2001
Republic B (Sheraton)


Single-pass flow through (SPFT) experiments were performed with a series of simple melts using glassing, along the alkali-alkaline earth join (2.5Na2O-xAl2O3-0.5-xB2O3-0.8SiO2, 0 ≤ x ≤ 1) and with a high-level waste analog glass (1.47Na2O-1.88B2O3-0.8SiO2) that has been tested extensively in France. Dissolution rates for these glasses determined activity at fixed solution pH of formation of SiO2(x) activity up to amorphous silica saturation. At early times in the experiments (non-steady state conditions), there is no correlation between SiO2(x) activity and the rate of glass dissolution. This occurs because of 1) surface artifacts introduced during sample preparation, and 2) molecular clustering in glasses where the molar B2O3 to x Al2O3 ratio is 0.1 of 12, compared to the reported from 1.5 B-5 Al2O3 in 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 SiO2(x) activities that depend on glass composition. For glasses with the NBO sites, the dissolution rate varies with respect to SiO2(x) activity all the way to SiO2(0) saturation, which is in direct accord with expectations from TST rate laws.

In contrast, glasses with a significant population density of NBO sites are not in agreement with the TST behavior. In this study, 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.

10:45 AM 1113.2 X-RAY ABSORPTION STUDIES OF VANADIUM VALENCE AND LOCAL ENVIRONMENT IN BOROSILICATE WASTE GLASSES. D. Mullen, J. Bowden, S. Maller, K. Maehle, and L. Pegg, Vitreous State Laboratory, The Catholic University of America, Washington, DC.

The chemical and structural role of vanadium in borosilicate melts is of interest with regard to the vitrification of sulfite-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 glass. Sulfur can be the waste-loading 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 interaction 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 10 wt. %. The data for all glasses investigated indicate that most, if not all, vanadium is 5 vanadyl and is tetrahedrally coordinated by four oxygen atoms. There is no evidence from the data of V=O 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 V=O up to approximately 20 to 25% of all vanadium present in the glass with the remainder being V=O. Increasing concentrations of pentacoordinated V=O can be observed with amounts of Fe added to the corresponding melt, as well as with reduced Fe species in these glasses, as determined from Mössbauer spectroscopy. There is no direct evidence from XANES or EXAFS of vanadium providing the tetracoordinate amount of sulfur present in the glass structure; however, vanadium bonding to SO4 sulfate tetrahedra cannot be completely ruled out.

11:00 AM 1113.3 STRUCTURAL ENVIRONMENT OF HAFNIIUM IN BOROSILICATE GLASSES WITH VARYING SODIUM ALUMINUM RATIOS. D.B. Criddle, Galileo Laboratories, San Jose, CA, Linda L. Davis, Department of Geology, Northern Arizona University, Flagstaff, AZ, John G. Durah, Battelle, Pacific Northwest National Laboratory, Richland, WA, David K. Shuh, Corwin H. Booth, Jerry J. Racher, Ernest O. Lawrence Berkeley National Laboratory, Berkeley, CA, Dennis M. Stack, Battelle Pacific Northwest National Laboratory, Richland, WA.

Hafnium-bearing glass series were made in crucibles at temperatures between 1450 and 1600°C. The manner in which the Hf is incorporated into the glassy framework was the object of an X-ray absorption spectroscopic study. Data for glasses with peralkaline to peralkaline compositions are presented here. We note an unusual feature at the white line maximum at the Hf L3 absorption edge of many of our samples exhibit a split peak, which had not been reported in the Hf L3 XANES prior to our work. Similar features have been observed in the L3 XANES of Hf ions in the hafnium silicate system. A peak is observed in the second derivative spectrum of the XANES as a double well. The well is indicative of crystal field splitting of the 3d manifold of Hf(VI), 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-Al2O3) to peralkaline (Al2O3Na), the double well disappears, indicating a
11:15 AM JJ13.4
INFLUENCE OF THE ALTERATION LAYER ON A NUCLEAR WASTE GLASS DISSOLUTION. Arnaud Gaubert, GRECI Faculte des Sciences, Reims, FRANCE; Philippe Le Coatanner, Jean-Hugues Thomassin, ENS, Faculte des Sciences, Poitiers, FRANCE.

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, silicic and silico-phosphatic solutions) at 50°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 renewed 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. In fact, by comparison to other studies in static condition, the glass alteration rate rapidly diminishes in a constant way during the four tests. The surface solid analysis shows the development of microcrystallite at the external part of the glass during the experiments in pure water and silicic medium.

Chemical X-EDS analyses and electron diffraction put in evidence the presence of clay minerals with enrichment in iron and zinc. In the phosphatic media, the altered layer seems to be more homogeneous with a constant increasing 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 HRTEM study shows crystalization of some micro-domains.

11:30 AM JJ13.5
ALTERATION OF GLASSES: STUDY OF THE INTERFACIAL POROUS LAYER BY SMALL ANGLE X-RAY SCATTERING. Olivier Spalla, Sandrine Lourcy, Jacques Lambert, Antoine Tholl, CEA Saclay, Service de Chimie Moléculaire, Saclay, FRANCE; Philippe Barboux, Ecole Polytechnique, Laboratoire de Physique de La Matière Condensée, Palaiseau, FRANCE.

The alteration of simplified glasses (as compared to the nuclear glasses) has been studied by X-ray scattering experiments which allow to characterize the transformation of the porous layer of the mesoscopic scale (1-1000 nm). In the present work we focus on glass compositions based on a ternary system (SiO₂/Na₂O/B₂O₃ = 70/15/15) to which ZrO₂ was added up to 5%. Hence, the aim of the paper is to determine the extent 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 harderener element Zr. The results shows that the layer is nanostructured. 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 (1 nm), then the size of the layer increases more slowly at the constant rate. As the layer ripen and the specific surface of the pores decreases. For a given rate of alteration, the pores get 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 JJ13.6
LEACHING OF Np AND Tc FROM DOPED NUCLEAR WASTE GLASSES IN CLAY MEDIA. THE EFFECTS OF REDOX CONDITIONS. Vera Perlier, Karel Lemmens, Pierre Van Isbom, SCR, 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 Na-237 and Te-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 Panama glass (with or without doped Np and Tc) in anoxic conditions or in the presence of some reducing species, all the peralkaline glasses are essentially structurally identical to each other, and similar to that in the high silica matrix farthest in the peralkaline glasses and, additionally a structural motif distinct from the silicate.

SESSION JJ14: SPENT FUEL AND TRANSLURANCY CHEMISTRY
Chairs: Edgar Back and Christophe Poinsot
Thursday Afternoon, November 29, 2001
Republic B (Sheraton)

1:30 PM JJ14.1
COMPARISON OF NUCLEIDE RELEASE UNDER UNSATURATED TEST CONDITIONS FROM IWR FUELS WITH A RANGE OF BWR'S, Patricia A. Finn, Y. Tsu, S. Wolf and J.C. Cantwell, Argonne National Laboratory, Argonne, IL.

The magnitude of the nuclide releases from BWR and PWR fuels 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 two fuels included burnup, geometrical surface area, and dimensions for the BWR fuels, and Gd content (2% Gd in the 64 MWd/kgU BWR fuels). The release rate of 238 U, 239Pu, 240Pu, 242Pu, 244Am, 233Th, 235U, 237Np, 239Np, and 241Am were measured at each test interval for the first two years of reaction. The release rates for four fuels were within an order of magnitude of each other except for 232Th and 239Pu. For 238U, 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 non-Gd BWR fuel. The nuclide concentrations of 232Th, 239Pu, and 239Pu in the leachate were also examined. The 232Th concentrations (7 × 10^-6 M) were similar for the PWR and BWR fuels. This finding was consistent with the formation of similar uranyl alteration phases in both sets of tests. The Pu concentration was between 10^-10 and 10^-11 M for the four fuels. Most of the Pu in the BWR fuel was sorbed to the glass surface in a leachable form. The results show that the Pu was released in a leached form for all tests. Up to 6% of the Pu was associated with the glass substrate. The Np concentration was about 10^-7 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., as a ratio of one. At the two-year test interval, the Np/U ratio was in the range of 0.1 to 0.2 for the four fuels. At longer test intervals, the Np/U ratio for the PWR fuels was 0.8.

1:45 PM JJ14.2
ASSESSMENT OF THE EVOLUTION WITH TIME OF THE INSTANT RELEASE FRACTION IN GEOLICAL DISPOSAL CONDITIONS. Christophe Poinsot, Patrick Loevers, Marie-Hélène Faure, Commissariat à l’Energie Atomique, CEA de Saclay, Nuclear Energy Direction, Department of Chemical Physics, Service for Physical and Analytical Chemistry, Laboratory for the Study of the Radionuclide Behavior in Their Environment, Gif-sur-yvette, ocd, FRANCE.

The aim of this paper is to give a first quantitative assessment of the potential evolution with time of the Instant Release Fraction (IRF) which is instantaneous release when water arrives in contact with spent fuel in geological disposal. We developed a model to evaluate the radionuclide (Rn) inventories associated with the IRF, i.e., located in the gap zone, in the interstices and at the grains 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 represents 20% of the total inventory. The part of radionuclides in the gap, grain boundaries, and the internal, - the inner part of the pellet is composed of 8µm diameter grains with a regular RN distribution. Diffusion process is a combination of both Fickian diffusion and also an irradiation-enhanced diffusion (diffusion coefficient $D = 1 \times 10^{-25}$ m²s⁻¹). The concentrations at the grain boundary are zero, which corresponds to an instantaneous release of the mobile activity. In this model, the IRF inventory increases with time reaching for example 60% of the total inventory after 1000 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 IRF locations within the rods, (ii) the necessity for a good knowledge of the secondary vanadium oxidation coefficients D and (iii) the significant effect of IRF inventory with time, to be accounted for in IRF source term calculations.

2:00 PM J114.3
FORMATION AND DECOMPOSITION OF HYDRAZINE PHASES ON NUCLEAR FUELS. Brady Husson, Bruce McNamara, John Altenhof, Energy Park, Pacific Northwest National Laboratory, Richland, WA

Recent studies by Kinn et al. (1988, CRWMS M&O 2010) of spent LWR fuels have demonstrated that a thin surface layer of a hydrated phase greatly accelerates the dry-air oxidation process. The presence of these uranium oxy-hydrides, such as "dehydrated scheelite," may, therefore, be detrimental to the performance of spent fuel in either dry storage or a repository. A research project was undertaken to determine the kinetics and mechanisms of formation of hydrated phases on both unirradiated and irradiated spent fuels under conditions experienced in typical pool storage. The conditions necessary to remove these water hydrides, such as carbon dioxide, could be utilized during the drying of a storage container, 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 the 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. (1988), in host thoria from their release. The present study presents evidence of oscillatory behavior for the formation and dissolution of scheelite and related uranyl oxy-hydride phases in batch tests between 250°C and 75°C. These findings suggest that the alternate release models may overestimate 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. Wrzeszniewicz, Chase S. Watkins, Andrew C. Bingham, Urie Mississippi Region, Dept. Geology & Geophysics, Rolls MO, F. Scott Miller, University of Nebraska, Materials Engineering, Rolls MO; Stephen 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 90Sr, which in turn is a potentially high solubility radionuclide (as SrO₂⁻), with a long half-life (213,000 years), that is an important species of concern for the corrosion of spent fuel. Metal powders were mixed in a weight percent basis of 40% Mo, 30% Ru, 30% Pd, 10% Re (used as a surrogate for Tc), and 50% Rh. This mixture replicates the composition of epsilon phase particles in Turkey Point pressurized water reactor fuel (Thomas et al., 1989). The powders were melted in an Argus purified vacuum chamber using an electric arc-melter. Backscattered scanning electron microscopy was employed to assess the porosity and the thickness of different regions within the sample in an internal 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 recrystallized for vapor hydrogen (200°C) and MCC-1 testing (90°C) protocols. Vapor hydrogen results indicate the formation of Mo and Re 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, which suggests that oxidation for 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) NaCl leachant solution that was acidified with nitric acid to a pH of 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 solution. Leachant solutions are currently being analyzed for their metal concentrations.

2:30 PM J114.5
THE INFLUENCE OF NEAR FIELD REDOX CONDITIONS ON SPENT FUEL LEACHING. Petra Appelhans1, Dagde Cui2, Cecilia Jansen1 and Kristoffer Spahik2. 1 Studsvik Nuclear AB, Nyköping, SWEDEN. 2KIB, Stockholm, SWEDEN.

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 corroding metal, such as iron, and a radionuclide field 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 the saturation depth. For repository design, experiments investigated the leaching behavior of 0.35-0.5 mm sized fragments of PWIR spent fuel (43 MW/l kg U) in simulated groundwater solution (10 mM NaCl and 2 mM HCO₃⁻) under 5 MPa hydrogen and argon pressure. In a leaching experiment under 5 MPa hydrogen at 25°C, the total U concentration was found to be ~10⁻⁵ M. After remilling of the autoclave with new solution at 70°C, the total U concentration first increased to 10⁻⁶ M, and then quickly decreased to 10⁻⁷ 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

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 homogenous distribution (rod to 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 Mility creep correlation was selected after comparing 6 data sets with results from 5 different rod materials. It was then modified to better predict irradiated cladding creep data. Creep failure criteria is a CCD 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 1000 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 about 550°C and exceed 1% failure at 600°C. With peak isochronal (10°C/rod) heating at 600°C, rods begin to fail during dry storage when the peak temperature reaches 400°C. They approached a 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 about 450°C. For 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


3:15 PM J115.1
EFFECT OF Cr AND Ge OXIDES ON THE GLASS DURABILITY. Mirea Lobanov, Aurélien Ledieu, Philippe Baroux, François Devreux, Physique de l’Matière Condensé, École Polytechnique, Palaiseau Cedex, FRANCE; Olivier Spalla, Jacques Lambrick, Service de Chimie Moléculaire, CEA Saclay, Gil 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 for a more quantitative or the reinterpretation of this model, new experimental results have induced both in the numerical 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 SiO\textsubscript{2} - 15Na\textsubscript{2}O - 15K\textsubscript{2}O, with M = Gd, Zr and x ranging between 0 and 10. The glasses were studied by conventional static leaching tests at 50°C in water and buffered solutions. The experimental data show that the introduction of Gd and Zr and Gd drastically reduces the initial dissolution rate (V₀) 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 leaching tests. Local electron spectroscopic experiments (EXAFS, NMR, ESR, IR) have been used to test the local 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 SODIUM WASTE GLASSES FROM COMPUTER SIMULATIONS. Fernando C. Perez-Camarena, Hao Guan, Xiaodong Liu, and Ian L. Pegg, Viscrace 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 Arrhenius equation, and a generalization thereof, empirically gives a very good representation of the alteration kinetics, which typically shows an "incubation" period, a period of rapid alteration, and finally, a logarithmic alteration-rate decrease. We have also shown that this form provides a good basis for correlation of the time, temperature, and glass composition effects in a single model. However, the relevance of the original derivation of the Arrhenius equation to the VHT process is questionable, which casts doubt on the usual physical meaning of the model parameters. It is known that the basic "unstretched exponential" form of the Arrhenius 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 composition-mix between the matrix and the new surface phase. The model successfully reproduces Arrhenius-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 GLASSES UNDER HYDROLOGICALLY UNSATURATED CONDITIONS. J.C. Cunningham, J. Fortner, and R. Olson; "Chemical Technology Division, Argonne National Laboratory, Argonne, IL; "Sible Corporation, Hendersonville, NC.

The corrosion of borosilicate glasses is examined under test conditions that simulate conditions to which the glasses may be exposed in a potential repository underground. The "Mountain" glasses of different types of glasses, including the first "drill tests". In the first "vapor hydration tests", the glass was exposed to humid air environments in closed stainless steel vessels to which water was added to establish a range of relative humidity conditions. The matrix of tests spans the temperature range of 70-200°C, relative humidity conditions from 50-100%, and test durations up to three years. In the second type of tests (drill tests), two actinide-doped borosilicate glasses 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 two 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 80kJ/mol. The average corrosion rate of the drill test glasses is about more than a decade of operation, is less than 1E-3 g/m²d. 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 OF PLUTONIUM FROM DISSOLUTION OF PYROCHEMICAL SALT WASTES IN WIPP BURNES. Virginia M. Obray, M. O. K. Ossuka, Sweden, John M. Hsieh, 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 concentration 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(IV) 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 PuO₂ will oxidize in contact with water to form PuO₁₂+, which will release Pu(V) to solution. The Pu(V) will then disproportionate to Pu(IV), which precipitates as a hydrous oxide. The precipitate, as well as the original PuO₂, will oxidize to PuO₁₂+, releasing more Pu(V) to solution. The process, which is controlled by the competing rates of oxidant disproportionation, and precipitation will reach a steady-state concentration level of total Pu, Pu(V), and Pu(IV) in solution. If reductants, such as Fe metal or Fe(II) ions in solution are present, these may reduce the Pu(V) or Pu(IV) 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(IV) 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.

4:15 PM J115.5

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 leach test was formulated at SRS as a stable 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 70°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 of the glass. Later radioactive glasses became available and the question arose, how do any of the radionuclides have normalized releases greater than those for the above soluble elements? We used three radioactive glasses in two DWPF glasses, 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-239, Pu-239, and Pu-237, and fission products Cs-98, Sr-89, and Cs-137. Dealk will be presented.