

SYMPOSIUM JJ

Scientific Basis for Nuclear Waste Management XXV

November 26 – 29, 2001

Chairs

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Symposium Support

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

* Invited paper

SESSION JJ1: CONTAINER MATERIALS AND
ENGINEERED BARRIERS

Chairs: David W. Shoemsmith and Raul B. Rebak
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 1978. 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), emplaced in tunnels bored through tuffaceous rock, for adequate performance during the anticipated 10,000 years regulatory period. Present WP design uses an ~20 mm thick outer shell of Alloy 22 as a 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 deliquescent salts and other contaminants on the WP surfaces may cause liquid water to form there, even at high temperatures. Current performance projections predict that during the anticipated regulatory period localized corrosion modes will be unlikely, and that the Alloy 22 barrier 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 those 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. Gdowski, T.J. Wolery, and N.D. Rosenberg, 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 base waters 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. Oxidation-reduction couples in the natural 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

**DELIQUESCENT 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. Pabalan, Lietai Yang, Lauren Browning, Center for
Nuclear Waste Regulatory Analyses, San Antonio, TX.

Groundwater seeping into the proposed Yucca Mountain nuclear waste repository would be subjected to evaporation and salt formation processes that may enhance corrosion of metallic drip shield/waste package surfaces. Because corrosivity may increase with increasing brine concentrations, we have initiated a study to characterize the conditions associated with highly concentrated brine solutions at Yucca Mountain. In a hot repository setting, flash 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 rewetting is expected to occur after the repository temperature falls below the boiling point for the salt mixture and the equilibrium humidity, or deliquescence point, 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. 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
N06022.** Raúl B. Rebak, Tammy S. Edgcombe Summers, Todd A.
Palmer, Lawrence Livermore National Laboratory, Livermore, CA;
Paul Crook, Haynes International Inc., Kokomo, IN.

A Ni-Cr-Mo-W alloy (N06022) 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 a significant amount of welding. The phase stability of alloy N06022 gas tungsten arc welds (GTAW) was studied by aging samples at 427, 482, 538, 593, 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, degradation of the impact toughness of welded specimens begins at shorter aging times than that seen for non-welded specimens. However, Arrhenius 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. Sridhar, and G.A. Cragnolino, 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 anionic species, such as nitrate, and potentially aggressive cationic species, such as lead, were also determined in laboratory tests. In addition to the as-received material, tests were conducted on both welded and thermally aged material to evaluate the effects of waste package fabrication processes. The Alloy 22 localized corrosion susceptibility increased when temperature and chloride concentration were increased. Welding and thermal aging also decreased 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-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.

11:00 AM JJ1.7

INTEGRATED ANALYSIS FOR LONG-TERM DEGRADATION OF WASTE PACKAGE AT THE POTENTIAL YUCCA MOUNTAIN REPOSITORY FOR HIGH-LEVEL NUCLEAR WASTE DISPOSAL. J.H. Lee, Sandia National Laboratories, Las Vegas, NV; K.G. Mon, Duke Engineering & Services, Las Vegas, NV; D.E. Longine, Duke Engineering & Services, Austin, TX; B.E. Bullard, Duke Engineering & Services, Las Vegas, NV; A.M. Monib, 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 System (EBS) components. The SR waste package design has two layers: a 20-mm thick Alloy 22 outer barrier and a 50-mm thick 316NG stainless steel inner shell. The waste package is emplaced under a Titanium Grade 7 drip shield. No backfill is used. The stainless steel inner shell is to provide the structural integrity of the waste package, and 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 outer lid and one 10-mm thick inner lid. The lids are welded to the outer barrier after the waste is loaded.

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

This paper discusses the WAPDEG stochastic simulation model and the waste package degradation model results for the SR reference case. Results of the WAPDEG simulation using multiple realizations (typically 100 realizations) are presented by summary statistics for the time histories of the type (i.e., cracks by SCC, pits by localized corrosion, and large openings by general corrosion) and number of waste package and drip shield penetrations. Results show waste packages and drip shields are not subject to localized corrosion under the exposure conditions expected in the potential repository. The waste package failure in the 95th percentile confidence interval case occurs at approximately 20,000 years. Comparing the waste package failure curves to the waste package first crack failure and first patch failure curves indicates that the initial failures are due to SCC that has initiated at one or more pre-existing manufacturing flaws in the closure-lid weld regions.

11:15 AM JJ1.8

EVALUATION OF THE LONG TERM STABILITY OF PASSIVE CORROSION ON THE WASTE PACKAGE AND DRIP SHIELD UNDER YUCCA MOUNTAIN CONDITIONS. David W. Shoesmith, 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 as 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 incongruent processes; (iii) enhanced passive corrosion and increased susceptibility to localized corrosion due to materials aging; (iv) accumulation of damage and increased susceptibility to localized corrosion due to metastable localized corrosion events. Only the last of these scenarios seems capable of influencing the long term corrosion process on the waste package, but only if extremely aggressive chloride-dominated environments are produced. Under these circumstances there is a low, but finite probability that a metastable event on Alloy-22 will lead to stable crevice propagation. Providing the drip shield performs its design

function such events should be very rare. Metastable events have not been reported on titanium under oxidizing conditions.

11:30 AM JJ1.9

EFFECTS OF FLUORIDE AND CHLORINE IONS ON CORROSION OF TITANIUM GRADE 7 IN CONCENTRATED GROUNDWATERS. April L. Pulvirenti¹, Karen M. Needham¹, Mohamad A. Adel-Hadadi¹, Charles R. Marks², Jeffrey A. Gorman² and Aaron Barkatt¹. ¹Catholic University of America, Dept of Chemistry, Washington, DC. ²Dominion Engineering, Inc., McLean, VA.

Titanium Grade 7 (Ti-0.2Pd) is considered for use as a construction material for drip shields to be used to protect nuclear waste packages in a geologic repository against contact with groundwater. In sites such as Yucca Mountain, Nevada, groundwaters contain significant levels (several parts per million) of chloride and fluoride. The temperature where liquid water can first form in the vicinity of the waste package is expected to be at least around 120°C and the water in this region is expected to undergo concentration by factors exceeding 1000 due to evaporation.

Experiments have been carried out on titanium Grade 7 disks and U-bend samples at temperatures ranging between 90°C and 160°C. The solutions are based on the composition of water from the J-13 well in the vicinity of Yucca Mountain, with fluoride and chloride concentrations enhanced by factors of up to about 1000 to simulate the effect of evaporation. Optical metallography and SEM/EDS observations show that even at temperatures as low as 100-120°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, initiation of linear defects. The corrosion is particularly noticeable near the circumference of the samples, at corners, and in places where the samples have been marked using techniques such as vibroetching.

11:45 AM JJ1.10

EVOLUTION OF WATER CHEMISTRY THROUGH INTERACTIONS WITH WASTE PACKAGE. Yiming Pan, Darrell Dunn, Sean Brossia, Gustavo Cragnolino, Vijay Jain, Narasi Sridhar, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

The chemistry of water dripping into the waste packages for HLW disposal is important to the performance of engineered barriers and the subsequent release of radionuclides to the environment. A corrosion test cell that simulates the internal geometry of the waste packages has been designed to investigate changes to the in-package solution chemistry. A series of tests was conducted to evaluate solution chemistry variations as a function of applied potential, temperature, and chloride concentration using a specimen of type 316L stainless steel with a 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 micro-electrode. Preliminary measurements showed substantially high cation concentrations inside the pit due to anodic dissolution of type 316L stainless steel. The solution pH became considerably 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 JJ2: CERAMIC STRUCTURE

Chairs: Bartley B. Ebbinghaus and Martin Stuart
Monday Afternoon, November 26, 2001
Republic B (Sheraton)

1:30 PM JJ2.1

A GLASS-ENCAPSULATED CERAMIC WASTEFORM FOR THE IMMOBILIZATION OF CHLORIDE-CONTAINING ILW: FORMATION OF HALITE CRYSTALS BY REACTION BETWEEN THE GLASS ENCAPSULANT AND CERAMIC HOST. I.W. Donald, B.L. Metcalfe, R.S. Greedharee, AWE, Chemistry Research Div, Aldermaston, UNITED KINGDOM.

We have developed a calcium phosphate ceramic based on the mineral phases chlorapatite and chlorospodosite which, on the basis of evidence from non-active simulants studies, is expected to provide an extremely effective host for immobilizing the chloride constituents that result from the pyrochemical reprocessing 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 phases. In order to provide a monolithic wastefrom suitable for long term storage, the feasibility of encapsulating this product in a compatible glass is being assessed. The final wastefrom will be manufactured by a pressureless sintering route and sodium aluminophosphate based glasses 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 majority of sintering operations the Na present in the glass reacts with the chlorapatite and chlorosporodisite phases to form a dispersion of halite crystals within the final wastefrom. If the sintering temperature is high enough, some of these crystals volatilize to leave a series of well-defined voids within the wastefrom. The formation of free halite within the wastefrom 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 JJ2.2

STUDY OF NATURAL MINERALS OF PYROCHLORE TYPE STRUCTURE AS ANALOGUES OF PLUTONIUM CERAMIC WASTE FORM. Roman Bogdanov, Yuri Batrakov, Elena Puchkova, St. Petersburg Univ, Dept of Chemistry, St. Petersburg, RUSSIA; Andrey Sergeev, St. Petersburg Univ, Dept of Geology, St. Petersburg, RUSSIA; Boris Burakov, V.G. Khlopin Radium Institute, St. Petersburg, RUSSIA.

At present, crystalline ceramic based on titanate pyrochlore, $\text{Ca}(\text{Gd,Hf,Pu,U})\text{Ti}_2\text{O}_7$, is considered as US candidate waste form for the immobilization of weapons grade plutonium. Naturally occurring uranium bearing minerals with pyrochlore type structure: hatchettolite, $(\text{H}_3\text{O,Ca,U,TR,Sr})_2(\text{Nb,Ti,Ta,Si})_2(\text{O})_6(\text{OH,F})$; betafite, $(\text{U,Ca,Sr,TR,Pb})_2(\text{Ti,Nb,Ta})_2(\text{O})_6(\text{OH})$, and ellsworthite, $(\text{Ca,Sr,Pb,U})_2(\text{Nb,Ti,Ta})_2(\text{O})_6(\text{OH,F})$, containing 20, 15, 25 wt.% U respectively, were studied in order to understand the long-term behavior of actinide ceramic waste forms under conditions of geological environment. Chemical shifts (δ) of the following X-ray emission lines: $\text{U}(\text{L}\alpha_1)$ and $\text{U}(\text{L}\beta_1)$, were determined by X-ray spectrometry method. The calculations were performed on the basis of the two-dimensional $\text{L}\alpha_1$ and $\text{L}\beta_1$ correlation diagram. It was shown that 100% of uranium in hatchettolite and, probably, 95-100% of uranium in betafite are in the forms of $(\text{UO}_2)^{2+}$. The formal calculation demonstrated that ellsworthite contained only 20% uranium in the form of U^{4+} and the rest as 37% U^{5+} and 43% U^{6+} . The conversion of the initial U^{4+} ion in the structure of natural pyrochlore to $(\text{UO}_2)^{2+}$ due to metamict decay causes significant increase of uranium mobility. Data of uranium leach rate (10^{-7} g/cm²day) from hatchettolite in distilled water at 25°C for 7 days are approximately two order of magnitude higher than corresponding actinide leach rates from Synroc ceramic under the same conditions. The weak bonding of $(\text{UO}_2)^{2+}$ and as assumed, $(\text{PuO}_2)^{2+}$ and $(\text{NpO}_2)^{2+}$ in pyrochlore structure makes doubt that pyrochlore is a feasible host phase for the immobilization of actinides such as U, Pu, Np.

2:00 PM JJ2.3

THE FORMATION ENTHALPY OF 4M-ZIRCONOLITE, $\text{Ca}_{0.68}\text{Gd}_{0.60}\text{Hf}_{0.70}\text{Ti}_{2.02}\text{O}_{7.02}$. K.B. Helean, T. Lee, A. Navrotsky, Thermochemistry Facility, Dept of Chemical Engineering and Matls Sci, Univ of California-Davis, Davis, CA; J. Lian, L.M. Wang, R.C. Ewing, Dept of Radiological Sciences and Nuclear Engr, University of Michigan, Ann Arbor, MI; B. Ebbinghaus, Lawrence Livermore National Laboratory, Livermore CA.

Zirconolite, nominally ABC_2O_7 and the structurally related pyrochlore, nominally $\text{B}_2\text{C}_2\text{O}_7$ (where $\text{A}=\text{Ca, Na, REE, Th}$; $\text{B}=\text{Zr, Hf, Ce, U, REE}$; $\text{C}=\text{Zr, Ti, Fe, Al}$) are primary components of SYNROC. The pyrochlore structure becomes the only stable phase when the B-site is occupied primarily (>50 mol %) by cations substantially larger than Zr^{4+} (0.078 nm). Substituting cations such as Ce^{4+} (0.107 nm) or Gd^{3+} (0.1053 nm) stabilize the pyrochlore structure by forcing the zirconolite B-site to become 8-coordinated 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 $\text{Ca}_{0.68}\text{Gd}_{0.60}\text{Hf}_{0.70}\text{Ti}_{2.02}\text{O}_{7.02}$ lies in the pseudobinary defined by $\text{CaHfTi}_2\text{O}_7$ - $\text{Gd}_2\text{Ti}_2\text{O}_7$, 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, $(3\text{Na}_2\text{O}\bullet 4\text{MoO}_3, \text{T}=975 \text{ K}$ and $2\text{PbO}\bullet \text{B}_2\text{O}_3, \text{T}=1075 \text{ K})$ was used to measure the heats of

solution for $\text{CaCO}_3, \text{HfO}_2, \text{TiO}_2, \text{Gd}_2\text{O}_3$ and $\text{Ca}_{0.68}\text{Gd}_{0.60}\text{Hf}_{0.70}\text{Ti}_{2.02}\text{O}_{7.02}$. Applying the appropriate thermodynamic cycles to our preliminary data, the enthalpy of formation from the oxides, $\Delta H_{f-\text{ox}}$ at 298 K was calculated (kJ/mol): Pb-borate derived $\Delta H_{f-\text{ox}} = -81.4 \pm 5.3$; Na-molybdate derived $\Delta H_{f-\text{ox}} = -77.1 \pm 4.9$. 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 $(0.3\text{Gd}_2\text{Ti}_2\text{O}_7 \cdot 0.7\text{CaHfTi}_2\text{O}_7 = 4\text{M-zirconolite})$, $\Delta H_{f-\text{py}} = -89 \text{ kJ/mol}$. This suggests a small positive enthalpy of mixing (approximately $8 \pm 5 \text{ kJ/mol}$). Additional experiments are being conducted to refine these data.

2:15 PM JJ2.4

ELEMENT PARTITIONING IN A PYROCHLORE-BASED CERAMIC WASTE FORM. Reto Gieré, Carrie Hatcher, Earth & Atmospheric Sciences, Purdue University, West Lafayette, IN; Edgar Buck, Pacific Northwest National Laboratory, Richland, WA.

Titanate-based ceramic waste forms, designed for immobilization of plutonium, contain as major constituents pyrochlore [$\text{A}_2\text{Ti}_2\text{O}_7$], zirconolite [ABTi_2O_7] and brannerite [BTi_2O_6], where $\text{A} = \text{Ca, actinides, and lanthanides}$, and $\text{B} = \text{actinides, lanthanides, and Hf}$. This study reports data for a ceramic containing 0.14 wt% Al and 0.33 wt% Mo in addition to the major components present in the baseline ceramic (Ti, U, Ca, Hf, Gd and Ce oxides; Buck et al. 1999). Hafnium and Gd are added as neutron absorbers, Al and Mo represent impurities. An electron microprobe was used to generate X-ray maps in order to reveal element distributions and textural relationships between the different phases. The data demonstrate that UO_2 is strongly partitioned into brannerite (45 wt%), which is present as euhedral crystals with inclusions of unreacted UO_2 . Pyrochlore forms the groundmass and has an average UO_2 content of 28 wt%. Zirconolite contains only 15 wt% UO_2 , but is significantly more effective in accommodating Hf and Gd than both brannerite and pyrochlore, as demonstrated by the molar Hf/U and Gd/U ratios. Zirconolite accommodates U together with Hf in one structural site, whereas brannerite and pyrochlore incorporate U with Gd 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_2O_3 contents (3 wt%). The Ti and Al distribution maps reveal the presence of additional phases, a Ti-rich (rutile?) 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., U-233) might need to be considered in the future.

2:30 PM JJ2.5

THE REPLACEMENT OF TITANIUM BY ZIRCONIUM IN CERAMICS FOR PLUTONIUM IMMOBILIZATION. M.W.A. Stewart, B.D. Begg, E.R. Vance, M. Colella, K. Finnie, K.P. Hart, H. Li, G.R. Lumpkin, K.L. Smith, ANSTO, Lucas Heights, NSW, AUSTRALIA; W.J. Weber, PNNL, Richland, WA.

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: $\text{Ca}_{0.89}\text{Gd}_{0.22}\text{Hf}_{0.23}\text{Al}_{1.22}\text{A}_{2.04}(\text{Ti or Zr})_2\text{O}_7$, with $\text{A1} = \text{Ce, Th, Pu}$ and $\text{A2} = \text{Ce, U}$; plus minor excess hafnia plus rutile or zirconia. Samples of these zirconates and titanates with up to 15 wt. % of potential Pu-process wastes have also been prepared. The titanates tend to form pyrochlore as the major phase, whereas the zirconates form a fluorite. Very little of the impurities are accommodated in the fluorite with powellite, a spinel and a silicate glass appearing as extra phases. In the titanate samples the pyrochlore incorporates more impurities, with the remainder forming zirconolite, silicate glass, magnetoplumbite, perovskite and lovingite. The oxide-route zirconate required sintering temperatures of about 1550°C to produce a dense product, 200°C higher than the sintering temperature required for the titanate. Silicate impurities reduce the sintering temperatures appreciably in both titanates and zirconates. Extended annealing of all the Ti-pyrochlores and the Ce-Ce-zirconate at ~ 1100°C had no effect on the composition or microstructure. However the Th-U-zirconate sample partially transformed to pyrochlore. The results of 1 MeV Kr^{2+} and 8 MeV Au^{2+} ion irradiation experiments performed at the IVM and EMSL accelerators at ANL and PNL, respectively, will be discussed.

2:45 PM JJ2.6

IONIC SIZE LIMITS FOR A IONS IN BRANNERITE(ATi_2O_6 AND PYROCHLORE(CaATi_2O_7) TITANATE STRUCTURES (A=TETRAVALENT RARE EARTHS AND ACTINIDES). Eric Vance, Melody Carter, Martin Stewart, Arthur Day, Cliff Ball,

The lower limit of the size of the octahedral ion in the A_2O_6 brannerite structure is just smaller than that of Ce/Pu. Attempts to expand the A ion size beyond that of Th by (a) substituting a Ba ion plus two pentavalent U ions for three A ions or (b) substituting one Ba plus one hexavalent ion for two A ions did not succeed. Ge, Sn and Zr substitutions in the Ti site of brannerite do not exceed 0.2 formula units in ceramic preparations. Various attempts at single and coupled substitutions in the B site of Th-brannerite (thorutite) showed that the average site size could tolerate deviations of $<1/5\%$. Tetravalent Ce is unusually stabilised in air atmospheres at temperatures close to the melting point of 1400°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 0.100 and 0.117 nm respectively. A $BaUTi_2O_7$ stoichiometry did not produce a pyrochlore structure, and when fired in either argon or air yielded a mixture of $BaUTiO_5$, whose structure is still uncertain, plus brannerite and rutile.

SESSION JJ3: RADIATION EFFECTS

Chairs: William J. Weber and Katherine L. Smith
Monday Afternoon, November 26, 2001
Republic B (Sheraton)

3:30 PM *JJ3.1

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

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

4:00 PM JJ3.2

ION-INDUCED AMORPHIZATION OF MURATAITE. Jie Lian, University of Michigan, Ann Arbor, MI; Sergey V. Yudin, IREM RAS, Moscow, RUSSIA; Sergey V. Stefanovsky, Olga I. Kirjanova, SIA Radon, Moscow, RUSSIA; Rodney C. Ewing, University of Michigan, Ann Arbor, MI.

Murataite $A_4B_2C_7O_{22-x}$, where $A = Na^+, Ca^{2+}, REE^{3+}, An^{3+/4+}$; $B = Mn^{2+/3+}, Zn^{2+}$; $C = Ti^{4+}, Fe^{3+}, Al^{3+}$; $0 \leq x \leq 1$, is cubic fluorite-structured phase potentially suitable as phase for rare earths and actinides. Murataite varieties with three- (3C), five- (5C), and eight-fold (8C) elementary fluorite unit cells were found.

Amorphization of murataite induced by 1 MeV Kr^+ ions irradiation in three ceramic samples proposed for actinide waste immobilization was studied. The 1 MeV Kr^+ ion irradiations were performed at room temperature using IVEM interfaced with a Tandem ion accelerator at Argonne National Laboratory. Radiation damage was observed by in-situ TEM. Initially, the irradiation caused disordering of the murataite structure. Murataite was rendered fully amorphous at dose of $(1.7 \pm 1.9) \cdot 10^{18}$ ion/m² (approximately 0.2 dpa). Similar observations were obtained in the cold crucible melted sample. The susceptibility of murataite ceramics to ion irradiation induced damage increases in this order: murataite-3C \leq murataite-5C \div murataite-8C. The pyrochlore structure phase is slightly more radiation resistant to ion irradiation than the murataite structure phase with similar chemical compositions. Ce (~ 11 wt.% in murataite and ~ 28 wt.% in pyrochlore) has significant effects on the radiation resistance of pyrochlore and murataite phases and decreases the critical amorphization doses ($\times 10^{18}$ ion/m²) from ~ 2.4 to ~ 1.8 for pyrochlore and from ~ 1.8 to ~ 1.7 for murataite.

4:15 PM JJ3.3

MOLECULAR DYNAMICS SIMULATIONS OF VOID STABILITY IN AMORPHOUS Si. Maria Okuniewski, Brent J. Heuser, Yinon Ashkenazy, Robert S. Averback; University of Illinois, Urbana, IL.

We have begun a research program to investigate the effect of radiation damage and helium (He) production in simple borosilicate

glasses. As part of this program, molecular dynamics (MD) simulations of the radiation damage process in amorphous Si (a:Si) have 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 50-100 keV heavy-ion recoil, both of which can create significant damage. It is well known that He stabilizes voids against collapse in metals; a similar scenario in glass waste forms could reduce the lifetime of this storage medium. The nature of the radiation damage process in glasses is unknown, particularly the influence on the evolution of He bubbles and crack 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 with and without He and ii) temperature/pressure evolution during the displacement cascade process.

This work was funded by the DOE NEER program under grant DE-FG07-01ID14121.

4:30 PM JJ3.4

STRUCTURAL INVESTIGATION OF ION IRRADIATED SIMULATED HIGH-LEVEL WASTE GLASS. S.K. Sundaram, M.A. Haller*, Y. Su, V. Shutthanandan, J.S. Young and S. Thevuthasan, Pacific Northwest National Laboratory, Richland, WA. *ERULF summer intern 2000, University of Washington, Seattle, WA. P. Nachimuthu, R.C.C. Perera and D.K. Shuh Lawrence Berkeley National Laboratory, Berkeley, CA.

Radiation effects of HLW glass containing crystalline phases have not been extensively studied. In this study, heat-treated MS-7 glass that is a simplified version of a typical Hanford HLW glass with a TL of 1078C incorporating imbedded spinel crystals was used to investigate radiation effects. The composition of the base glass was (mass%): 8.00 Al₂O₃, 7.00 B₂O₃, 0.3 Cr₂O₃, 11.50 Fe₂O₃, 4.54 Li₂O, 0.60 MgO, 0.50 MnO, 15.30 Na₂O, 0.95 NiO, 45.31 SiO₂, and 6.00 ZrO₂. These glass samples were irradiated using 2.0 MeV Au²⁺ ions to the fluences ranging from 3.4×10^{16} to 1.25×10^{17} ions/cm² at room temperature.

After the irradiation, the samples were characterized using Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), and Raman spectroscopy at Pacific Northwest National Laboratory (PNNL) and x-ray absorption spectroscopy (XAS) using the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). Preliminary XAS results indicate that Fe occupies a tetrahedral site in a trivalent oxidation state where a larger number of non-bridging oxygen atoms exists in the base glass matrix. On ion irradiation, trivalent 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-bridging 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, Offices of Basic Energy Sciences and Biological and Environmental Research, and the Environmental Management Science Program.

4:45 PM JJ3.5

RADIATION DAMAGE IN TITANATE CERAMICS USED FOR PLUTONIUM IMMOBILIZATION. D.M. Strachan, R.D. Scheele, W.C. Buchmiller, R.L. Sell, and R.J. Elovich, 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 this material has been exposed to water. In 1999, approximately 100 specimens were made that contain approximately 10 mass% ²³⁸PuO₂ and approximately 100 sister specimens that contain about 10 mass% ²³⁹PuO₂. 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 made from the oxides and carbonates of the constituents and by sintering the mixture at 1350°C for a minimum of 4 hours. Some specimens of pyrochlore and zirconolite were sintered an additional 100 hours at 1350°C to enlarge the crystal grains. The specimens are stored at 20°C , 125°C , and 250°C with the ²³⁸Pu specimens characterized every six months to determine the effects of radiation and temperature. Characterization consists of density measurements, determining releases during a 3-day MCC-1 test, photography, and X-ray diffraction. While the XRD 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 than what was expected from the heavy ion bombardment experiments reported in the literature. The release of Pu from the ²³⁸Pu-bearing ceramics is about 100 times higher than from the ²³⁹Pu-bearing ceramics. The densities of the ceramics have been decreasing and the decrease is greater for the zirconolite-rich ceramic at 250°C than at 25°C, an unexpected result.

SESSION JJ4: PERFORMANCE ASSESSMENT (HLW)

Chairs: David W. Esh and Allan B. Hedin
Tuesday Morning, November 27, 2001
Republic B (Sheraton)

8:30 AM *JJ4.1

TOTAL-SYSTEM PERFORMANCE ASSESSMENT FOR THE YUCCA MOUNTAIN SITE. Michael L. Wilson, Peter N. Swift, Sandia National Laboratories, Albuquerque, NM; Jerry A. McNeish, 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) has been conducted over the past decade, with increasing complexity and detail in the models used for the assessments. The 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 and officially 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, Yucca Mountain 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 *JJ4.2

THE SR 97 PERFORMANCE ASSESSMENT OF A KBS 3 REPOSITORY FOR SPENT NUCLEAR FUEL - OVERVIEW, REVIEW COMMENTS AND NEW DEVELOPMENTS. Allan Hedin, Ulrik Kautsky, Lena Moren, Patrik Sellin and Jan-Olof Selroos, 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 isolating copper canisters with a high-strength cast iron insert. The canisters are surrounded by bentonite clay in individual deposition holes at a depth of 500 m in granitic bedrock. Geological data are taken from three sites in Sweden to shed light on different conditions in Swedish granitic bedrock. The future evolution of the repository system is analysed in five scenarios, treating the unperturbed evolution, initially defective canisters, climate change, earthquakes and future inadvertent human intrusion. The principal conclusion of the assessment is that the prospects of building a safe deep repository for spent nuclear fuel in Swedish granitic bedrock are good. The results of the assessment have also served as a basis for formulating requirements and preferences regarding the bedrock in site investigations, for designing a programme for site investigations and for prioritisation of research. SR 97 has been reviewed both by an international group of OECD/NEA experts and by Swedish authorities. The NEA reviewers concluded that 'SR 97 provides a

sensible illustration of the potential safety of the KBS-3 concept', and no issues were identified that need to be resolved prior to proceeding to the investigation of potential sites. The authorities conclusions 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 further developed. Also, uncertainties and lack of knowledge in different areas identified in SR 97 have strongly influenced the contents and structure of SKBs most recent research programme, RD&D-Programme 2001.

9:30 AM *JJ4.3

OVERVIEW OF THE H12 PERFORMANCE ASSESSMENT IN PERSPECTIVE. Kaname Miyahara, Hitoshi Makino, Tomoko Kato, Keiichiro Wakasugi, Atsushi Sawada, Yuji Ijiri¹, Aki Takasu², Morimasa Naito³, Hiroyuki Umeki³, Japan Nuclear Cycle Development Institute (at present: ¹Taisei Corporation, ²Nuclear Safety Research Association, ³Nuclear Waste Management Organization of JAPAN.)

The second progress report, H12, documented research and development progress for high-level waste disposal made since the publication of the earlier first progress report (H3) in 1992. The concept of geological disposal in Japan is similar to that considered in other countries, being based on a system of multiple passive barriers consisting of the geological environment and an engineered barrier system. The disposal system considered is generic, as neither host rock type nor siting area have so far been identified. The H12 performance assessment (PA) provided a test for the robustness of a system concept based on structured siting and design, taking account of a wide range of potentially suitable Japanese geological environments. The generic nature of the host rock in the H12 assessment means, however, that emphasis is placed very much on strong near field performance. The assessment included a comprehensive evaluation of uncertainty and potentially detrimental factors, including perturbations due to external events and processes. Uncertainty is addressed by a combination of alternative scenarios, alternative conceptual models and parameter variations used in deterministic calculations. This allows the significance of various types and scales of uncertainty to be investigated, leading to improved system understanding. This can, in turn, include where effort is best concentrated in order to increase the reliability of future assessments and, possibly, reduce the level of conservatism in the analysis. Despite the considerable uncertainty at the current stage of the Japanese program, a safety case that is adequate for the aims of the assessment can be made by a strategy of employing conservatism where there is uncertainty and stressing the reliability and effectiveness of the performance of the near field. The aim of this paper is to present the H12 PA in a way which makes the PA process clearer and the implications of the results more meaningful both to workers within the PA field and to a wider technical audience.

10:30 AM *JJ4.4

PERFORMANCE ASSESSMENT OF GEOLOGICAL DISPOSAL OF HIGH-LEVEL WASTE IN A PLASTIC CLAY FORMATION. Jan Marivoet, Xavier Sillen and Dirk Mallants, Belgian Nuclear Research Centre SCK-CEN, Waste & Disposal Dept., Mol, BELGIUM.

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

11:00 AM *JJ4.5

BUILDING THE SAFETY CASE FOR A DISPOSAL FACILITY

FOR SPENT FUEL, HLW AND LONG-LIVED ILW IN SWITZERLAND. L.H. Johnson, J.W. Schneider and P. Zuidema, Nagra, Wettingen, SWITZERLAND; P.A. Smith, Safety Assessment Management Ltd., UNITED KINGDOM; Peter Gribi, Vibro-Consult AG, Brugg, SWITZERLAND.

Nagra, the national co-operative for the disposal of radioactive waste, is responsible for research & development, geological investigations, design studies and safety assessment studies leading to the development of facilities for the disposal of radioactive waste in Switzerland. For disposal of spent fuel, vitrified high-level waste and long-lived intermediate-level waste, the present focus is on developing the safety case for a proposed repository sited in the Opalinus Clay in the Zürcher Weinland (northern Switzerland). The methodology to develop a safety case must include: - a 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 in safety assessment, - a procedure to process this 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 evaluation 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 *JJ4.6

GENERAL APPROACH USED IN THE PERFORMANCE ASSESSMENT FOR THE WASTE ISOLATION PILOT PLANT. Rob P. Rechard, Sandia National Laboratories, Albuquerque, NM.

In 1973, only three years before the Materials Research Society began their special sessions on nuclear waste management, the citizens in southern New Mexico invited the Atomic Energy Commission (AEC) to explore the salt beds in the Delaware Basin for a site for disposal of radioactive waste. A year later, the AEC drilled two boreholes at a potential location. By 1976, a suitable site had been found for more detailed characterization. This site eventually became the Waste Isolation Pilot Plant (WIPP), a repository for disposal of transuranic (TRU) waste that was certified by the U.S. Environmental Protection Agency (EPA) in 1998. The EPA's decision was primarily based on the technical results from a 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 PAs conducted for the WIPP that contributed to the success of the WIPP certification. For these PAs, Sandia mostly used detailed models for evaluating the performance of the repository under the stylized 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 challenging approach to PA was facilitated by the use of a database, which all codes accessed, 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 process codes, could be used directly without modification. 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 requirements (e.g., required evaluation of the effects of mining potash 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, documentation 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 PA analysis model. Fifth, the number of model 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 pedigree of parameters, since the EPA was required, by Congressional mandate, 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 JJ5: CONTAMINANT TRANSPORT I

Chairs: Roberto T. Pabalan and John A. Berry
Tuesday Afternoon, November 27, 2001
Republic B (Sheraton)

1:30 PM JJ5.1

RADIONUCLIDE INCORPORATION IN SECONDARY CRYSTALLINE MINERALS FROM CHEMICAL WEATHERING OF WASTE GLASSES. S.V. Mattigod, R.J. Serne, B.P. McGrail, and V.L. Legore, 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 unsaturated 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 interacting with the glass waste forms disposed in the immobilized low-activity waste (ILAW) facility will have moderately high ionic strengths and will be slightly alkaline. Under such conditions, several complex geochemical 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), and sequestration 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 some of the key radionuclides (Se-79, Tc-99, I-129, and U-233,235,238) in secondary crystalline minerals that form as products of chemical weathering. Weathering experiments conducted at 90°C with radionuclide-spiked Hanford Site groundwater indicated that substantial fractions of the total activities (~56% of Se-75, ~85% of Tc-99, ~49% of I-125, and ~100% of U-238) were retained by the secondary zeolitic minerals that formed during weathering of LD6-5412 glass. Tests conducted at 160°C on LD6-5412 and LAWA33 glasses indicated that ~8 - 22% of I-125, ~1 - 13% of Tc-99, and ~8 - 25% of Se-75 were incorporated into the secondary crystalline phases such as herschelite and analcime. Additionally, both glasses exhibited a greater degree of sequestration of stable isotopes (70 - 95% of I, ~58 - 100% of Re, and ~100% of Se). Implications of these data regarding the radionuclide mobilization aspects of ILAW performance assessment will be presented.

1:45 PM JJ5.2

LIQUID-SOLID PARTITION COEFFICIENTS (KD) OF ANIONIC AND CATIONIC SPECIES OF RADIONUCLIDES PRESENT IN CONTAMINATED GROUNDWATER. Francois Caron, Michael K. Haas, Edward L. Cooper, Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, ON; Dave E. Robertson, Pacific Northwest National Laboratory, Richland, WA.

Radionuclides present in contaminated groundwaters 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 (60Co, 106Ru, 137Cs, 238Pu, 239/240Pu, 241Am and 244Cm). Separate liquid-solid partitioning values for the anionic and cationic forms were measured on uncontaminated 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 uncontaminated groundwater and aquifer materials, spiked with 239/240Pu and 241Am. The dominant aqueous species of 60Co, 137Cs, 239/240Pu

and ²⁴¹Am present in the contaminated groundwater were negatively charged. The solid-liquid partitioning of these negatively charged species was lower by one to two orders of magnitude, compared to the values obtained with the tracers, ⁵⁷Co, ¹³⁴Cs, ^{239/240}Pu and ²⁴¹Am. The measurements with tracers are typical of conventional short-term laboratory K_d determinations, and they could overestimate contaminant retention, because the important 'native' 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 have a strong and apparently lasting effect on 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 JJ5.3

PREDICTION OF METAL PARTITIONING BETWEEN MINERALS AND AQUEOUS SOLUTIONS: AN IMPLICATION TO CONTAMINANT MATERIAL SELECTION FOR RADIOACTIVE WASTE DISPOSAL. Yifeng Wang, Sandia National Laboratories, Carlsbad, NM; Huifang Xu, Dept of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM; Charles Bryan, Anna C. Snider, Sandia National Laboratories, Carlsbad, NM.

Metal partitioning between authigenic minerals and aqueous solutions is an important chemical process for radioactive waste containment. In this communication, a linear free energy correlation model is developed to correlate metal partition coefficients with metal cation properties. Host minerals from an isostructural 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 isoivalent and non-isoivalent metal partitioning in carbonate minerals, and it closely fits the existing experimental data, thus demonstrating the robustness of the proposed linear free energy relationship. Using the 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. The fraction of radionuclides that can be potentially immobilized by magnesium carbonate minerals in the WIPP as a result of using MgO as a chemical backfill is evaluated. The model developed in this communication provides a useful tool for predicting unknown partition coefficients and thus helps select effective containment materials and waste forms for radioactive waste disposal.

2:15 PM JJ5.4

EFFECTS OF REACTOR DECONTAMINATION COMPLEXING AGENTS ON SOIL ADSORPTION-COLUMN STUDIES.

R. Jeff Serne, Kirk J. Cantrell, I.V. Kutnyakov, and Clark W. Lindenmeier, Applied Geology and Geochemistry Section, Pacific Northwest Laboratory, Richland, WA.

Organic complexes of radionuclides have been implicated in several instances as enhancing the mobility of radionuclides in porewaters percolating through sediments. Organic chelates have also been shown to leach from nuclear power plant decontamination wastes that end up being buried in shallow-land burial grounds.

Column adsorption experiments were conducted using two sediments, two organic complexants and two contaminants [⁶³Ni²⁺ and ²³⁹PuO₂]. The influent solutions were a simplified groundwater. The organic and metal concentrations were picolinate 10⁻⁴, EDTA 10⁻⁵, Ni 10⁻⁵, and Pu 10⁻⁷ M, respectively. The organic complexants were spiked with radiolabeled ¹⁴C, and ⁶³Ni and ²³⁹Pu. The columns were equilibrated with background electrolyte for 2 pore volumes. Then solutions containing the metal, complexant, and tracers were injected for up to 10 days. Breakthrough curves were generated from effluent 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 1.0 M nitric acid to determine mass balance.

The results show that picolinate concentrations have to be >10⁻⁴ M to significantly lower the adsorption of divalent transition metals [Ni and Co]. EDTA forms strong complexes with divalent transition metals and can stop adsorption of Ni and Co when EDTA concentrations are >10⁻⁵ M. Most other picolinate and EDTA-metal complexes appear to readily dissociate during interactions with soils. As complexes migrate from the disposal facility, dilution and interaction with competing cations and adsorption reactions will result in dissociation of all but the strongest or most kinetically recalcitrant complexes. Conditions that promote enhanced migration include high concentrations of organic ligands, low concentrations of competing

cations, alkaline pH, organic ligands with slow biodegradation rates and kinetically inert or very strong ligand-metal complexes.

At high pH values such as that created by cementitious wastes, mobilization of Ni²⁺ and Co²⁺ by EDTA becomes very significant and adsorption by sediments is essentially zero. Thus, we recommend that mixtures of metal/radionuclides and EDTA should not be co-disposed with high pH materials. For weaker organic complexants [picolinate, citrate and oxalate], co-disposal of decontamination wastes and concrete should be acceptable.

2:30 PM JJ5.5

DIFFUSION AND SORPTION OF RADIOACTIVE CESIUM AND COBALT IN REGOLITH MATERIALS OF CENTRAL AUSTRALIA. Takashi Itakura, Gordon D. McOrist, Timothy E. Payne, Australian Nuclear Science and Technology Organisation, Environment Division, Menai, NSW, AUSTRALIA; Chin Jian Leo, University of Western Nepean, School of Engineering and Industrial Design, Kingswood, NSW, AUSTRALIA.

The movement of radionuclides in geological media can be driven by advection and diffusion. Diffusion can be the dominant process in clays and under arid zone conditions where advection is not significant. Preliminary studies have been performed to describe the diffusion and sorption of ¹³⁷cesium and ⁶⁰cobalt without the influence of advection, using saturated reconstituted samples of regolith materials from an arid region in South Australia. A sample canister 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 JJ5.6

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 a key technical issue for the U.S. Nuclear Regulatory Commission (NRC). Neptunium-237 has been identified as a radionuclide of concern in analyses of performance of the proposed YM repository because of its relatively high solubility and the sensitivity of its saturated zone transport time to retardation factors used in modeling. Studies have suggested that Np-237 sorption on calcite, a mineral with widespread occurrence at YM, is enhanced relative to sorption on other common mineral phases. Nevertheless, little is known regarding the mechanism and potential for uptake of Np-237 on calcite. Batch experiments were conducted using a calcite substrate in solutions at or near saturation with respect to calcite over a pH range of 7 to 9, at 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 were also observed depending on the experimental protocol used (e.g., less sorption at pH 7-8 when calcite was added to solution after Np-237). A comparison of results from previous studies and considerations for modeling of the Np-calcite system are discussed. This work was conducted for the NRC under Contract No. NRC-02-97-009. It is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.

SESSION JJ6: CERAMICS CORROSION

Chairs: Boris E. Burakov and David B. Chamberlain

Tuesday Afternoon, November 27, 2001

Republic B (Sheraton)

3:30 PM JJ6.1

DURABILITY OF Pu-DOPED ZIRCONATE AND TITANATE CERAMICS FOR Pu DISPOSITION. Yingjie Zhang, Kaye Hart,

Bruce Begg, Zaynab Aly, Alan Brownscombe, Arthur Day, Martin Stewart, ANSTO, AUSTRALIA.

Zirconates have recently been proposed as hosts for Pu and other actinides due to their cubic (fluorite) structure, which renders them less susceptible to radiation damage than their pyrochlore/zirconolite structured titanate counterparts. Ti- and Zr- versions of the pyrochlore-rich ceramic (95wt% Ca_{0.89}Gd_{0.22}Hf_{0.23}Pu_{0.22}U_{0.44}

(Zr/Ti)₂O₇ 1 wt% HfO₂ 4 wt% (Zr/Ti)₂O₂) proposed for Pu disposition were prepared by the standard alkoxide route. The formulations were calcined in air and sintered in either air or argon atmospheres for 4 hours at temperatures between 1300 and 1500 C. An addition of 5 wt% of mixed impurities was made to some of the samples. Samples were characterized by XRD, SEM, alpha-spectrometry, and leaching at 90 C in deionized water. The titanate preparations that were free of impurities consisted of brannerite and pyrochlore whilst the zirconate formulations had formed a single-phase defect fluorite. The zirconate formulations were significantly more refractory than the titanates, and required sintering at some 150 C higher temperature to achieve equivalent level of closed porosity. SEM indicated that impurities were readily incorporated into the pyrochlore-structured titanate, which had also formed a minor amount of zirconolite. No impurities were present in the defect-fluorite structured zirconate which had formed a glassy phase along with magnetoplumbite. The presence of impurities aided sintering in both instances. Leaching results are available for the titanate and zirconate formulations containing impurities sintered at 1300 C and without impurities sintered at 1350 C. The lowest Pu leach rates were measured for the titanate formulation containing impurities. The other three formulations had similar leach rates that were higher by about a factor of 100 after 7 days of leaching than the titanate plus impurity formulation. There was no discernible effect of sintering atmosphere on the Pu leach rate. The difference in Pu leach rates appeared to be associated with the degree of consolidation in the samples. This will be discussed further along with results for zirconate batches sintered at 1400 C, with impurities, and 1500 C, without impurities.

3:45 PM JJ6.2

DISSOLUTION OF A₂Ti₂O₇ (A = Y, Gd, OR Lu) PYROCHLORE BY EXPERIMENT AT pH=2, 90°C: EVIDENCE FOR SOLUBILITY CONTROL. Jonathan P. Icenhower, B. Peter McGrail, William J. Weber, Nancy J. Hess, Elsa A. Rodriguez, Jackie L. Steele, Christopher F. Brown, Matthew J. O'Hara, Pacific Northwest National Laboratory, Richland, WA; Bruce D. Begg, ANSTO, Menai, NSW, AUSTRALIA.

Recent theories for dissolution of solids into aqueous solutions focus on analogies with ligand-exchange reactions between aqueous complexes and the solvent. Some of these theories have proven to be extremely useful in providing insights into the reactivity of solids in a homologous series containing mono- or divalent cations¹. 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 A₂Ti₂O₇, where A = Y³, Gd³⁺, or Lu³⁺ in pH = 2 solutions at 90°C. Analysis by XRD showed that all three compositions are cubic with space group Fd3m. The three compositions are chemically stoichiometric, as revealed by electron microprobe analysis. Analysis by Raman spectroscopy, however, indicates that the Y₂Ti₂O₇ specimens are more disordered compared to the other two compositions. Normalized log₁₀ dissolution rates (in g m⁻² d⁻¹) increase from Lu₂Ti₂O₇ (-3.2 to -3.3) to Gd₂Ti₂O₇ (-2.6 to -2.9), to Y₂Ti₂O₇ (-1.9 to -2.0). In contrast, ligand-exchange theory suggests that the rate of reaction should increase in inverse order of the cation field strength: Lu < Y < Gd (where the cation denotes the appropriate pyrochlore composition). Evaluation of the thermodynamic stability of the three solids was performed using a linear free-energy model and reported enthalpies and entropies of formation. The calculations indicate that reactivity should follow in the progression Lu < Gd < Y, as observed in the dissolution experiments. Although the relatively greater disorder detected in the Y₂Ti₂O₇ sample probably contributes to the faster dissolution rate observed, the relative thermodynamic stability of the samples could, by itself, explain the trend in dissolution rates. Our data indicates, therefore, that dissolution models based on ligand-exchange reactions may not be strictly applicable to simple pyrochlore minerals. (1) Casey, WH, and Westrich, HR (1992), Nature 355: 157-159.

4:00 PM JJ6.3

A STUDY OF Pu-DOPED ZIRCON ALTERATION UNDER HYDROTHERMAL CONDITIONS. Boris Burakoy, Elena Nikolaeva, Maria Yagovkina, the V.G. Khlopin Radium Institute, St. Petersburg, RUSSIA; Rodney Ewing, Michigan Univ, Ann Arbor, MI; Werner Lutze, Univ of New Mexico, Albuquerque, NM.

Plutonium doped ceramic based on zircon structure, (Zr,Pu)SiO₄, is the subject of investigation as a durable ceramic waste form for the immobilization of weapons grade plutonium and other actinides. Coprecipitated hydroxides of Zr, Si and Pu were 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 zirconia avoiding formation of silica or Pu-silicate. Then this material was dried and calcined in air at 700°C for 1 hour. The obtained powder was milled in an 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 according to X-ray powder diffraction analysis (XRD) synthesized ceramic samples were consisted of (in wt.%): zircon-95-96; monoclinic zirconia-1-3; tetragonal zirconia-3-5. Electron probe microanalysis (EPMA) has shown that zircon contained 6.1 wt.% Pu. The sizes of zirconia grains were too small (less than 2 microns) to provide precise EPMA. Single pellet of ceramic was milled in agate mortar and split off two equal parts. One part of ceramic powder was placed in special teflon vessel into water and set at 120°C for 48 days. Then the initial and altered powders were analyzed by precise XRD method including determination of zircon unit cell parameters. No differences of XRD spectra of initial and altered samples were observed. Zircon unit cell parameters were (in angstroms): a=6.619±0.004; c=5.987±0.008 and a=6.612±0.002; c=5.991±0.004 for initial and altered samples, respectively. Although the decrease of a-parameter was detected, no traces of separated Pu-oxide were found on XRD spectrum of altered sample. The results obtained confirmed the high resistance of Pu-doped zircon-based ceramic under hydrothermal conditions.

4:15 PM JJ6.4

ALTERATION OF A ZIRCONOLITE GLASS-CERAMIC MATRIX UNDER HYDROTHERMAL CONDITIONS. Christelle Martin, Isabelle Ribet, SESC/LCLT CEA Valrho, Thierry Advocat, SCDV/LMPA CEA Valrho, FRANCE.

Glass-ceramic matrices based on zirconolite (CaZrTi₂O₇) are being considered for specific conditioning of plutonium or the minor actinides. This application is contingent on a demonstration of the long-term aqueous corrosion resistance of the material. One investigative 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 material alteration is affected not only by the temperature (150°C), but also by the glass-surface-area-to-solution-volume (SA/V) ratio. Zirconolite glass-ceramics were doped with Nd (6.5 wt % Nd₂O₃ in the initial material) to simulate the actinides. Experiments were conducted at two SA/V ratios (5100 m⁻¹ in the vapor phase and 10 m⁻¹ in the liquid phase) with zirconolite glass-ceramic specimens and with reference glass specimens corresponding to the vitreous matrix of the glass-ceramic. On completion of the tests (lasting 40, 60 and 85 days) the solid specimens were observed by SEM and selected specimens were submitted to electron microprobe analysis. The liquid-phase alteration leachates were analyzed by ICP-AES. SEM observations of zirconolite glass-ceramic specimens altered for 40 or 60 days revealed that only the residual glass matrix was altered, and that an 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 crystals. The leachate analysis 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 different initial alteration rates. Tests are now in progress to verify that this different behavior affects only the initial alteration period.

4:30 PM JJ6.5

CORROSION OF GLASS-BONDED SODALITE AND ITS COMPONENTS AS A FUNCTION OF pH AND TEMPERATURE. S.-Y. Jeong, L.R. Morss, A.J. Morgan, and W.L. Ebert, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

Glass-bonded sodalite is the ceramic waste form (CWF) that is being developed to immobilize electrorefiner salt wastes from electro-metallurgical 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 20-90°C using conventional buffers. The normalized forward dissolution rates of silicon from sodalite, glass, and CWF have negative slopes in acidic solutions and positive slopes in basic solutions, with minima near neutral pH. Similar results were obtained at 70°C using recently characterized noncomplexing buffers, confirming that complexation of conventional buffers with released waste form species is not significant. The forward rates increase with increasing temperature; the temperature dependence yields the activation energy in the rate expression. 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 borosilicate glass for comparison with forward dissolution rates that were previously calculated from flow-through tests. The dissolution

rates of the five-component borosilicate glass calculated using buffered MCC-1 tests were about an order of magnitude higher than rates calculated from flow-through tests. The CWF dissolution rate parameters found in this research are similar to those calculated from data in the TSPA-VA.

4:45 PM JJ6.6

PROPERTIES OF PLUTONIUM-CONTAINING COLLOIDS RELEASED FROM GLASS-BONDED SODALITE NUCLEAR WASTE FORM. Lester R. Morss, Carol J. Mertz, A. Jeremy Kropf, Nancy L. Dietz, and Jennifer L. Holly, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

Glass-bonded sodalite, the ceramic waste form (CWF) that has been developed at Argonne National Laboratory to immobilize radioactive electrorefiner salt from spent metallic reactor fuel, has a micro-structure that consists primarily of sodalite granules surrounded by glass. Uranium and plutonium in the CWF are found as 20-50 nm particles of (U,Pu)O₂ that are encapsulated by glass near glass-sodalite phase boundaries. During tests conducted to measure the release of matrix and radioactive elements from crushed CWF samples into water, significant amounts of colloidal aluminosilicates and much smaller amounts of colloidal (U,Pu)O₂ are released into test solutions. These particles have been characterized by elemental analysis of filtrate solutions following sequential filtration, dynamic light scattering, transmission electron microscopy (TEM), surface charge measurements, and X-ray absorption spectroscopy. This paper reports the properties of these colloidal particles that are necessary to determine colloid stability and radionuclide migration: particle composition, size, agglomeration, stability in solution, and surface charge. The paper also describes the methodology that has been developed to collect and characterize the particle size by TEM. The properties of the (U,Pu)O₂ colloids will provide a significant part of the knowledge base for fundamental understanding of the processes that control colloid stability and transport and for modeling radionuclide migration in a repository.

SESSION JJ7: PERFORMANCE ASSESSMENT (LLW)

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

8:30 AM *JJ7.1

DEVELOPMENT OF A PERFORMANCE ASSESSMENT METHODOLOGY FOR DESIGN AND SITING OF A LLW REPOSITORY IN ITALY. Piero Risoluti, 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 candidatures on possible volunteer 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 Arc/View 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 *JJ7.2

DEVELOPMENT OF THE POST-CLOSURE SAFETY CASE FOR THE LOW LEVEL WASTE DISPOSAL SITE AT DRIGG, UNITED KINGDOM. Len Watts, Drigg Technical Programme Manager, Environmental Risk Assessments, Research & Technology, British Nuclear Fuels 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 assessment (PCRSA), communication activities and key factors 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 1959 to

trenches whereas current practice involves disposal to concrete vaults. Disposals are carried out under an authorisation from the UK Environment Agency (the Agency). Periodically the Agency reviews the authorisation 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 other communication activities including scientific publication, 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 review. Central to the safety case is a systematic PCRSA, which promotes transparency and traceability and demonstrates a rigorous treatment of relevant uncertainties. The approach aligns with international best practice for near-surface disposal facilities and includes the assessment of features, events and processes and the use of tools such as conceptual model uncertainty forms. This formalisation helps to identify and understand the key factors for the PCSC. Additional qualitative or simple quantitative information is used to augment the PCRSA so as to provide a wider context to inform decision-making.

9:30 AM *JJ7.3

IMMOBILIZED LOW-ACTIVITY WASTE PERFORMANCE ASSESSMENT: 2001 VERSION. Frederick M. Mann, CH2M Hill Hanford Group, Inc.; Raymond J. Puigh, S.H. Finck, R. Khaleel, Fluor Federal Services; D.H. Bacon, M.P. Bergeron, B.P. McGrail, S.K. Wurstner, Pacific Northwest National Laboratory, Richland, WA.

At the U.S. Department of Energys Hanford Site, 177 underground tanks hold over 54 million gallons of high-level radioactive, mixed waste. The current plans are to retrieve over 99% of this waste, separate it into two streams (the high-level waste stream and the low-activity waste stream), and vitrify both streams. The immobilized high-level waste will be stored at the Hanford Site until it is shipped to a federal geological repository. The immobilized low-activity waste (ILAW) will be disposed on the Hanford Site. Before the ILAW can be disposed or disposal facilities constructed, the Office of Environmental Management must issue a permit, known as a Disposal Authorization Statement (DAS). A major basis for this decision is a performance assessment (PA) that needs to show with reasonable assurance that the public health and safety and the environment will be protected. In 1998, an ILAW PA was issued based on regional information. A DAS for the entire Hanford Site was issued in 1999 and it included the disposal of ILAW. However, since 1998, important changes have occurred to the ILAW program: different facility concept (concrete vaults to trenches), different waste form (high-temperature glass to low-temperature glass), and the collection of disposal site-specific geotechnical information. Based on these new data, 16 new data packages have been released. New calculations have been performed, resulting in an estimated reduction in groundwater impacts by well over a factor of 100 since the 1998 ILAW PA. The 2001 version of ILAW PA is now undergoing review by the Low-Level Disposal Facility Federal Review Group (with a final decision promised by September 2001).

10:00 AM JJ7.4

A STOCHASTIC ASSESSMENT OF NUCLEAR WASTE MANAGEMENT PRACTICES AT THE HANFORD SITE, WASHINGTON. Charles T. Kincaid, Paul W. Eslinger, William Nichols, Robert Bryce, and Amoret Bunn, Pacific Northwest National Laboratory, Richland, WA.

Waste management and disposal decisions at the Hanford Site, Washington, depend in part on an understanding of the risks and impacts associated with alternate disposal and remedial actions. An initial proof-of-principle site-wide assessment of the risks and impacts associated with all wastes that will remain at the Hanford Site has been performed for the first time. It simulates contaminant release, migration and fate from today forward, and, thus, illustrates near-term influences on long-term risk and impact.

A stochastic simulation tool capable of addressing 1000 waste discharge and disposal sites and 10 contaminants for a period of 1000 years has been created and applied. Risk and impact are estimated in four dimensions; human health, ecological health, socio-economic impact, and cultural impact. The methodology developed is known as the System Assessment Capability (SAC).

An initial assessment based on the planning baseline of the Department of Energy (Richland Field Office and Office of River Protection) has been completed. Results of the assessment reveal the relative significance of the release, migration and fate of:
- past practices of liquid and solid waste disposals to ground,
- current and planned practices of solid waste and vitrified tank waste disposal, and

- past tank leaks, future tank losses (during waste recovery), and tank residuals.

The results also provide insight about the potential for groundwater contaminant plumes from one region of the site to impact decisions in another region of site. For example, releases from the central plateau may create groundwater plumes that pass beneath lands within the Columbia River corridor, and thus, restrict the release of land adjacent to the river for public use.

SESSION JJ8: NATURAL ANALOGS

Chairs: David A. Pickett and Regis Andre Bros
Wednesday Morning, November 28, 2001
Republic B (Sheraton)

10:30 AM JJ8.1

RADIOELEMENT TRANSPORT IN THE BANGOMBE NUCLEAR REACTOR ZONE, GABON - EVIDENCE FROM URANIUM AND SAMARIUM ISOTOPES. Regis Bros, JNC, Waste Isolation Research Div., Tokaimura, JAPAN; Toshihiko Ohnuki, JAERI, Dpt. Environmental Safety Res., Tokaimura, JAPAN; Gento Kamei, JNC, Waste Isolation Research Div., Tokaimura, JAPAN.

As a natural analogue study relevant to the safety margin of radioactive waste repository conditions, geochemical studies have been carried out on the Bangombe orebody. About two billion years ago, this U-rich zone underwent fission chain reactions leading to the production of high amounts of fission products and transuranium. The main goal is to provide insights on the mobility/retention of various radionuclides in response to the alteration of the reaction zone. Electron microprobe analyses reveal the occurrence of secondary uraninite, brannerite and coffinite which reprecipitated within a chlorite matrix. Coffinite is enriched in Zr, Ti, P and formed between chlorite sheets suggesting an initial stage of U sorption followed by mineralization by Si- and P-bearing fluids. The concentration of U and Sm isotopes was determined by ICP-MS on bulk rocks. The $^{235}\text{U}/^{238}\text{U}$ ratio displays significant deviations from the natural value in the reactor (0.00585), fractured sandstones (0.0066-0.0072) and overlying shales (0.0070-0.0072). The $^{149}\text{Sm}/^{147}\text{Sm}$ ratio also shows significant anomalies in the reactor (0.06-0.10), sandstones (0.58-0.93) and shales (0.27-0.82). These features reveal that U and REE were mobilized, the result of uraninite dissolution by groundwaters. Migrations took place laterally through conductive fractures within sandstones and vertically through shales by diffusion process. A sequential extraction was carried out to constrain the association of mobilized elements with mineral phases. In reactor samples, most of U (75-83%) and Sm (75-89%) is bound to the insoluble residue which emphasizes that the major part remained linked to irreversible sites of uraninite. Around the reactor, the insoluble fraction accounts for 60-95% of total Nd, Sm and Zr suggesting that secondary U phases played a dominant role in retarding these elements. The transfers might have been limited to the first few meters around the reactor as suggested by the absence of anomaly in farther sandstones.

10:45 AM JJ8.2

LOW-TEMPERATURE MOBILITY OF RARE EARTH ELEMENTS, U AND Th AT THE OLKILUOTO SITE, SW FINLAND. Nuria Marcos, Helsinki Univ of Tech, Espoo, FINLAND.

Rare earth element (REE), U and Th concentrations were measured in 6 groundwater samples located at depths varying between 132 and 470 m in three drill holes at the Olkiluoto site. The pH of all samples is about 8 and Eh(Pt) varies from -50 to -200 mV. Also the REE, U and Th concentrations of rock samples collected from core sections in the vicinity of water conducting fractures were measured to examine rock-water interactions. The rock samples were cut into slices parallel to the fracture surface. An aliquot of each slice was leached with 0.5 N acid nitric to examine the readily leachable REE, U and Th fraction of each slice. Loss of REE and U from fracture surface towards rock matrix is observed in samples at depths of 141, 159, and 466 m. Loss of U is also observed in a sample at about 246 m depth. Loss of Th is only observed at the depths of 159 and 246 m. The groundwater samples were normalised to shale and to each of the analysed rock samples. Either the shape of shale-normalised or rock-normalised REE patterns resembles that of the rocks the water is supposed to flow through, but certain resemblance does exist between the rock-normalised REE patterns for the groundwaters and the leachates. Loss of U (readily leachable fraction) in the rock samples seems to be linked to the hydraulic conductivity in the related water conducting fractures and to the content of sulfate in the groundwater. This work is a first intend to link hydrogeological measurements to structural modelling by using the mobility of REE, U and Th.

11:00 AM JJ8.3

THE REDOX ENVIRONMENT OF DEEP GROUNDWATERS

ASSOCIATED WITH THE TONO URANIUM DEPOSIT, JAPAN. R. Arthur, Monitor Scientific, LLC, Denver, CO; T. Iwatsuki, K. Hama, K. Amano, R. Metcalfe, K. Ota, Tono Geoscience Center, Japan Nuclear Cycle Development Institute, Toki, JAPAN.

Field investigations supporting the Tono Natural Analogue Project are aimed at characterizing hydrogeological and geochemical processes that have effectively immobilized uranium within the Tono uranium deposit in Gifu Prefecture, central Japan, for about 10 million years. An unconformity underlying the deposit represents the approximate location of a redox front separating relatively oxidizing groundwaters ($E_h \approx 0$ mV) in the weathered, fractured Toki granite from strongly reducing pore fluids ($E_h \approx -360$ mV) in sedimentary rocks of the overlying Lower Toki Lignite-bearing Formation (TL), which hosts the uranium ore body. Groundwater flow models and relative ^{14}C ages of groundwater from the granitic 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, apparent transport of uranium across the redox front, followed by reduction of U(VI) to U(IV) in the TL, may have been continuous during the past 10 million years, but there is little or no evidence of concurrent front movement into the sedimentary formation. This suggests that oxidation-reduction reactions involving pore fluids, minerals, organic matter and microbes in the TL generate an intrinsic redox-buffering intensity and redox-buffering capacity that has effectively resisted any significant change in the reducing nature of this formation for millions of years. Stable and reversible *in situ* redox potentials measured in boreholes penetrating the granite and sedimentary rocks appear to be controlled by the Fe(III)-oxyhydroxide Fe^{2+} redox couple. The crystallinity of the oxyhydroxide varies from freshly precipitated amorphous $\text{Fe}(\text{OH})_3(\text{am})$ to fine-grained goethite, or to a mixture of $\text{Fe}(\text{OH})_3(\text{am})$ plus fine-grained goethite. Equilibration of the strongly reducing groundwaters with pyrite appears to control dissolved Fe(II) concentrations in these solutions. Irreversible weathering of biotite/chlorite may control Fe(II) concentrations in the relatively oxidizing groundwaters.

11:15 AM JJ8.4

NATURAL COLLOIDS IN GROUNDWATER FROM A BENTONITE MINE - CORRELATION BETWEEN COLLOID GENERATION AND GROUNDWATER CHEMISTRY. Yoshio Kuno, Gento Kamei, JNC, Waste Isolation Research Div., JAPAN; Hiroyuki Otani, Kunimine Industries Co., Ltd., Research Lab., JAPAN.

Colloids caused by erosion of compacted bentonite by groundwater flow might enhance the transport of radionuclides from the radioactive waste repository. As a natural analogue of the colloid generation process, we investigated the groundwater dripped at the interface between bentonite bed and argillaceous rock bed (Tertiary age), cropped out at four galleries (depth range from -30 to 180m above the sea level) in the Tsukinuno bentonite mine, northern Japan. Groundwater and filtrates separated by ultrafiltration (MWCO; 10,000) were analyzed to determine the concentration of ions. The major ions in groundwater are free Na (4 - 40mM), carbonate (0 - 30mM) and sulfate (0.2 - 10mM). The colloidal particles were not detected in the groundwater sample 1 (collected at 180m above the sea level) and 4 (similarly, at -30m). On the other hand, muddy groundwater suspension was collected in case of the sample 2 (at 90m) and 3 (at 30m), whose concentrations of the suspended particles corresponded to 100 and 800 mg/L, respectively. However, most of the particles in these samples have sedimented within 2 weeks under static conditions and the concentrations of the still suspended particles were measured as 4 and 7mg/L for the sample 2 and 3, respectively. The mineral species of these particles was mainly identified as montmorillonite. The results were summarized as follows: Sample 1: pH=4.0, I=0.009, Colloid conc.=N.D. (below a few mg/L); Sample 2: pH=9.4, I=0.01, Colloid conc.=4mg/L (montmorillonite); Sample 3: pH=8.5, I=0.04, Colloid conc.=7mg/L (montmorillonite); Sample 4: pH=8.7, I=0.05, Colloid conc.= N.D. (below a few mg/L). Since few colloids were observed in these groundwaters, it is concluded that colloids generated from bentonite layer are unstable in groundwater whose ionic strength is greater than about 0.01. This is consistent with previous laboratory measurements indicating the dependence of ionic strength on the colloid stability.

11:30 AM JJ8.5

IN SITU ISOTOPIC ANALYSIS OF URANINITE MICROTEXTURES FROM THE OKLO AND OKLOBONDO NATURAL FISSION REACTORS. Mostafa Fayek, University of Tennessee, Dept of Geological Sciences, Knoxville, TN; Keld A. Jensen, National Institute of Occupational Health, DENMARK; Rodney C. Ewing, Dept of Nuclear Engineering & Radiological Sciences, University of Michigan, Ann Arbor, MI; Lee R. Riciputi, ORNL, Oak Ridge, TN.

Uranium deposits, by analogy, can provide important information on

the long-term performance of radioactive waste forms because uraninite (UO_{2-x}) is structurally and chemically similar to the UO_2 in spent nuclear fuel. The environments that host the Oklo-Okélobondo U-deposits, Gabon, 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 (nm to km). The natural fission reactors associated with the Oklo-Okélobondo U deposits occur over a range of depths (100 to 400 m) and provide a unique opportunity to study the behavior of uraninite 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 uraninite is susceptible to alteration, continuously self-anneals radiation damage, and because these processes are manifested at the mm scale. However, uranium, lead and oxygen isotopes can be used to study fluid-uraninite interaction, provided that the analyses are obtained on the micro-scale. Secondary ionization mass spectrometry (SIMS) permits in situ measurement of isotopic ratios with a spatial resolution on the scale of a few mm. Preliminary results show that uraninite from all reactor zones are highly discordant with Pb-Pb ages ranging from 40 Ma to 1680 Ma. Oxygen isotopic analyses show that uraninite from reactors that occur in near surface environments ($\delta^{18}O = -14.4\%$ to -8.5%) have reacted more extensively with groundwater relative to reactors located at greater depths ($\delta^{18}O = -10.2\%$ to -7.3%). These data show that important information can be obtained from natural analogue studies provided that high spatial resolution analysis techniques are utilized.

11:45 AM JJ8.6

APPLICATION OF SYSTEMS ANALYSIS TO A NATURAL ANALOGUE PROJECT. M.J. Stenhouse¹, R. Arthur¹, T. Iwatsuki², K. Ota² and H. Takase³. ¹ Monitor Scientific, Denver, CO. ²JNC Tono Geoscience Center, Japan Nuclear Cycle Development Institute, Toki, JAPAN. ³Quintessa Japan, Yokohama, JAPAN.

Systems 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 Tono uranium deposit (Gifu Prefecture, central Japan) was formed about 10 million years ago and available evidence suggests that this deposit has been preserved in the host sedimentary formation, i.e. uranium has not migrated significantly since then. Substantial field and modeling work is being carried out to better understand the hydrogeological and geochemical processes of uranium migration and retardation in and around the Tono uranium deposit. Systems Analysis provides a convenient framework for this project, being used to:

- develop possible scenarios for how the deposit developed,
 - link field characterization and the data gathered from these activities with predictive modeling, and
 - identify gaps in data and, hence, additional characterization needs.
- Interesting differences exist between predictions associated with this project and those obtained for repository evolution. For example, predictions for the latter are made into the future, the uncertainty in such predictions increasing with time. On the other hand, the state of the Tono uranium deposit is being investigated back from the present, the corresponding uncertainty increasing in the reverse direction. The common factor in both cases, however, is that the starting point is the present day, at which time most is known about the site. The key elements of the Systems Analysis approach, as they relate to the Tono Natural Analogue Project, are discussed in this paper, viz. - definition of the system to be studied;
- identification of features, events and processes (FEPs) associated with this system;
 - identification of external factors (EFEPs) which are likely to have influenced the area involving the Tono uranium deposit;
 - interactions between pairs of FEPs; and development of credible scenarios for site evolution.

SESSION JJ9/KK8: JOINT SESSION CEMENTS IN RADIOACTIVE WASTE IMMOBILISATION

Chair: Kenneth A. Snyder
Wednesday Afternoon, November 28, 2001
Republic B (Sheraton)

1:30 PM *JJ9.1/KK8.1

CHARACTERIZATION OF THE BARRIER PERFORMANCE OF CEMENTS. F.P. Glasser, Univ of Aberdeen, Aberdeen, Scotland, UNITED KINGDOM.

Anniversaries are a good time critically to review progress, in this instance, quantifying the barrier performance of cement materials in nuclear waste repositories. Portland cement has intrinsic advantages in this application: persistence in nature, low solubility and ease of

fabrication, either in situ or precast. Its disadvantages include inherent brittle properties and possible reactions with other types of engineered barrier materials. Research leads to the conclusion that the principal advantage of cements lies in their chemical properties: they complex and react with waste species forming solubility-limiting solids. Examples are given to show how cements can be tailored to enhance their immobilization potential for specific radionuclides. However, after 25 years it is still not possible to give a comprehensive and quantitative description of reaction sequences and their evolution with time and temperature. A wish list to address missing or inadequate data is presented. The present showdown in activity affords opportunity to research the next generation of chemical barriers and quantify their performance.

2:00 PM JJ9.2/KK8.2

PRACTICAL MODEL TO EVALUATE DURABILITY OF CEMENT-BASED MATERIALS UNDER LEACHING, COUPLING WITH INTERNATIONAL DATA BASE. Siham Kamali, Laboratory of Mechanics and Technology, Cachan, FRANCE; Bruno Gerard, Laboratory of Mechanics and Technology, Cachan, FRANCE, Electricity of France, Moret sur Loing, FRANCE; Micheline Moranville, Laboratory of Mechanics and Technology, Cachan, FRANCE.

The concrete leaching by water damages and reduces the service life of structures like radioactive waste repositories, water pipes and dams. This study develops a practical model to provide decision making in design and diagnosis of concrete structures which may be submitted to leaching. It consists on the prediction of the leaching kinetics according to material and environmental characteristics. The model assumes that the leaching kinetics follows a square root of time. Each parameter is introduced as a weight function. The model is based on international experimental published data dealing with the effect of water-to-binder ratio, silica fume content, aggressive solution pH and temperature. These data are completed by other tests in order to introduce the effect of the cement type (Portland cement, silica fume cement, fly ash cement, blast furnace slag cement) and of the interaction between the cement and water-to-binder ratio. Finally, the model is analysed and applied to practical recommendations.

2:15 PM JJ9.3/KK8.3

A SOLID SOLUTION MODEL FOR SORPTION OF RADIONUCLIDES IN CEMENT. Allan T. Emrén, Chalmers University of Technology, Dept of Nuclear Chemistry, Goteborg, SWEDEN.

Cement consists of a considerable number of phases, the two most important of which are the gel phase and a phase that is almost pure portlandite, calcium hydroxide. Both can be considered as solid solutions. This means that they are able to have a variable chemical composition. This also gives a possibility for the phases to incorporate different elements into their structure. Of these two phases, portlandite is rather compact while the gel phase has a very irregular structure, probably fractal. This suggests that sorption essentially takes place as absorption in the gel phase. Whenever this is correct, the sorption capacity could be expected to be large enough to make the contribution from other mechanisms, e.g. adsorption, negligible. In the present work, a model for multi component solid mixtures has been developed, essentially following the Guggenheim excess free enthalpy approach. Measurement of Kd for one gel composition makes it possible to calculate Kd values during the entire process of cement degradation. The main limitation is that the concentration of the radionuclide has to be low enough for all higher terms in the series expansion to be negligible. The model is mostly valid for elements forming cations and it also requires the sorbed element to form a compound of reasonably low solubility with one of the anions in cement (hydroxide or silicate). This means that it can be used essentially for metals. Kd values from the literature have been used to calculate thermodynamic properties of some solid mixtures.

2:30 PM JJ9.4/KK8.4

STABILITY OF HYDROCERAMIC WASTE FORM DURING VHT TESTING. Barry E. Scheetz, Michal W. Grutzeck, Johnson Olanrewaju, Della M. Roy, Materials Research Institute, The Pennsylvania State University, University Park, PA; D. Darryl Siemer, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

Immobilization of INEEL calcine waste by the reaction of alkali and an aluminosilicate pozzolan to form a hydroceramic waste form has been developed over the past ten years by this research team. Subsequent research has documented the rate of formation as well as the stability of the resulting waste form and its ability to sequester the hazardous radionuclides and RCRA elements contained in the calcine. Typical hydroceramic formulations were prepared and subjected to testing following the VHT protocol developed at Argonne National Laboratory - East. This test protocol maintains the test specimen in

an environment of 100% relative humidity at temperatures up to 200°C for varying time intervals. Condensation onto the test specimen then initiates surface reactions between water and the waste form at this elevated temperature. The results of the exposure of hydroceramic waste forms contrasted to EA glass will be discussed.

2:45 PM JJ9.5/KK8.5

Abstract Withdrawn.

SESSION JJ10: CONTAMINANT TRANSPORT II

Chairs: Shas V. Mattigod and JoonHong Ahn
Wednesday Afternoon, November 28, 2001
Republic B (Sheraton)

3:30 PM JJ10.1

USING LINEAR FREE ENERGY RELATIONSHIP TO PREDICT ACTINIDE PARTITIONING BETWEEN GOETHITE AND AQUEOUS SOLUTIONS. Huifang Xu, Dept. of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM; Yifeng Wang, Sandia National Laboratories, Carlsbad, NM.

Coprecipitation of trace metals and actinides in authigenic minerals of goethite, hematite and calcite will incorporate ("freeze") trace metals into stable solid phases. However, there are no such data for partitioning coefficients of actinides. It is of great interest to predict the partitioning coefficients based on theoretical model. In this paper, a linear free energy relationship developed by Wang and Xu (Geochimica et Cosmochimica 65 (2001), 1529) is extended to predict trivalent metal partitioning between goethite (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 goethite also decreases. It is predicted that the partitioning coefficients for trivalent REE and actinides increase. Similar relationship can be also derived for the metal partitioning between hematite and aqueous solution. The constrained relationship can be used to systematize the existing experimental data and to predict unknown metal partitioning coefficients.

3:45 PM JJ10.2

INFLUENCE OF HUMIC COLLOIDS ON THE CONTAMINANT TRANSPORT: APPLICABILITY OF LABORATORY RESULTS TO NATURAL SYSTEMS. Wolfram Schuessler, Robert Artinger, Bernhard Kienzler, Horst Geckeis, Thomas Rabung, Jae-Il Kim, Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, Karlsruhe, GERMANY; Dietmar Klotz, Institut für Hydrologie, GSF Forschungszentrum, Neuherberg, GERMANY.

Applicability of laboratory results to natural systems is a crucial point in safety assessment of waste disposal. The problems arising using laboratory results to predict real repository situations are discussed on the basis of the humic colloid-borne contaminant transport. As an example in this paper these questions are addressed with respect to the humic colloid-borne contaminant transport. It is shown, that a thermodynamic equilibrium approach is not suitable to describe consistent laboratory batch and migration experiments with Ca(II) and Am(III) in humic rich groundwater sand systems. In contrast, a kinetic description of the metal ion humic colloid 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 unimpeded 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 ions desorption experiments of metals bound to natural humic substances allows to define an upper limit for the worst case scenario in PA modeling. This does not solve the up scaling problem but it enables conservative PA calculations.

4:00 PM JJ10.3

RADIONUCLIDE UPTAKE AND TRANSPORT ON MICROBES IN REPOSITORY DRIFTS AT YUCCA MOUNTAIN, NEVADA. Darren M. Jolley, Duke Engineering and Services, Las Vegas, NV.

Radionuclide sorption onto microbes, microbial retention in the engineered barrier system (EBS), and their potential release from the

EBS as microbial colloids has been investigated. The microbial source term for these calculations was derived using MING V 1.0 software code (Ehrhorn and Jolley, 1998). Multiple modeling runs for different 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 (HLW) packages. These equations represent the average cumulative microbial biomass (CMB; g dry/m) generated in the EBS at time t .

$$CMB_{csnf} = 10^{(-5.7846 + 7.5541)(log t) - 2.0501(log t)^2 + 0.1891(log t)^3)}$$

$$CMB_{hlw} = 10^{(1.4824 + 0.4394(log t) + 0.4545(log t)^2 - 0.1887(log t)^3 + 0.0207(log t)^4)}$$

A distribution for uranium uptake onto microbes was applied to CMB. The distribution was derived from the data set in Suzuki and Banfield (1999) representing 45 different species of bacteria and fungus covering uranium uptake at optimum pH values of 1 to 7. The mass of uranium sorbed onto the biomass was either sequestered 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 2302 kg of uranium per meter of waste package depending on the saturation of the invert and type of waste package. Over the same time, microbial colloids may transport from 8 to 1250 kg of uranium per meter of waste package. This same model may also be used to estimate uptake and transport of plutonium and thorium by microbes.

4:15 PM JJ10.4

SOLUBILITY EVALUATION FOR YUCCA MOUNTAIN TSPA-SR. Yueting Chen, Amy Loch, Duke Engineering & Services; Terry Steinborn, 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 Commission (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 geochemical model calculations were used to estimate radionuclide solubilities. The study uses the computer code EQ3NR as the major geochemical 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, Tc, I, C, Ra, Cs, Pb, and Sr) and their solubilities are 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 JJ10.5

A QUANTITATIVE KINETIC MODEL FOR PLUTONIUM OXIDE SOLUBILITY. John M. Haschke, Actinide Science Consulting, Waco, TX; Virginia M. Oversby, VMO 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 spontaneously reacts with water to form a fluorite-related higher oxide solid solution, PuO_{2+x} , with O:Pu ratios approaching or exceeding 2.3 and on extensive literature data for dissolution of plutonium dioxide and tetrahydroxide. Results suggest that dependencies of Pu concentration on pH, time, Eh, and other parameters, as well as consistent appearance of Pu(V) and Pu(VI) as the dominant steady-state species over the pH 1-9 range, are most consistent with kinetic control of dissolution, not with equilibrium control. Involvement of the higher oxide is implied by diffraction data showing that lattice parameters of the face-centered-cubic solid formed by both dioxide and hydroxide at steady state correspond with those of higher oxide and by coincidence of the observed oxide dissolution rate with the measured rate of Pu(V) formation in the

higher oxide. According to the conceptual model, Pu(V) and Pu(VI) accumulate in solution and a steady state is established when their rates of formation and disproportionation become equal. Pu(IV) formed by disproportionation accumulates until the concentration is fixed by tetrahydroxide precipitation. Pu(V) and Pu(VI) concentrations are a function of the ratio of 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 JJ10.6

IODINE RELEASE FROM SILVER IODIDE UNDER REDUCING CONDITION WITH IRON-BEARING MINERALS. X. Xia, Y. Inagaki, A. Hattori, K. Idemitsu, T. Arima, Department of Nuclear Engineering, Kyushu University, Fukuoka, JAPAN.

During reprocessing of spent fuel in Japan, radioiodine(I-129) is collected as a form of silver iodide (AgI) in adsorbents to be one of the major wastes. The waste form is planned to be incorporated into more durable forms for geological disposal. Evaluation of iodine release from the waste form is essential for long-term safety assessment of the disposal because of its long half-life and weak adsorption on many geological materials. 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. Dissolution tests were performed on AgI in the presence of iron-bearing minerals, goethite(FeOOH), magnetite (Fe₃O₄) and wustite(FeO), in a glove box purged with gas mixture (Ar 5%H₂), and concentrations of I⁻ and Ag⁺ in the solutions were measured as a function of time by using ICP-MS. The saturated concentrations of I⁻ were 4.0×10^{-8} , 4.3×10^{-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 5.4×10^{-3} 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 Ag(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-SMECTITE BY MOLECULAR DYNAMICS SIMULATIONS. Satoru Suzuki, Japan Nuclear Cycle Development Institute, Waste Isolation Research Division, Tokai-mura, Ibaraki-ken, JAPAN; Katsuyuki Kawamura, Tokyo Institute of Technology, Tokyo, JAPAN.

Interactions between water and clay are of scientific and practical interest for the modeling of physical or chemical properties of compacted bentonite as an engineered barrier for the HLW disposal. A vibrational feature of water is a good probe for the microscopic interactions with smectite, the major constituent of bentonite. We studied correlation between a vibrational spectrum and molecular structure simultaneously obtained by the molecular dynamics simulations. The simulated results were in good agreement with IR spectroscopic observations. A stretching vibrational spectrum of interlayer water consisted of a broad band with a peak top at around 3400 cm^{-1} and a sharp peak around 3650 to 3700 cm^{-1} . The former broad band was assigned to O-H vibrations between water molecules as bulk water, while the latter band was attributed to O-H ones oriented to siloxane 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 siloxane surface ($O_{H2O}-O_{clay} > 3.0 \text{ \AA}$) was larger than that between water molecules ($O_{H2O}-O_{H2O} = \text{ca. } 2.8 \text{ \AA}$). These results suggest that interaction between water molecule and siloxane 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. Aalto,

T. Carlsson, H. Kumpulainen, J. Lehtikoinen, A. Muurinen, VTT Chemical Technology, Industrial Physics, Espoo, FINLAND.

It has been planned to dispose of spent nuclear fuel in Finland in a repository at a depth of about 500 m in crystalline bedrock. The near-field barriers in the excavated space of the repository comprise a compacted bentonite clay buffer, a copper-lined iron canister, and the spent fuel matrix. The barriers mutually interact via the groundwater and tend towards a thermodynamic equilibrium with each other and with their geochemical environment. In order to study experimentally the interactions between the groundwater, bentonite and the canister, 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, focussing on the state-of-the-art concerning relevant aspects of the post-closure repository chemistry, and on b) the results from modelling of the chemical interactions using the thermodynamic computer codes HYDRAQL/CE and EQ3/6. In short, the experimental set-up consists of 12 vessels, each of which contains a copper cylinder submerged in a solution that is initially either distilled water or an 0.5 M NaCl solution. The copper cylinder contains water-saturated MX-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 30°C). The parameters that are determined during the course of the experiment are the water chemistry, the extent to which surface corrosion occur 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. Narasi Sridhar, G. Douglas Gute, Andrew Grohmann, Brittain E. Hill, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

The proposed Yucca Mountain repository site has a 1:1000 to 1:10,000 probability of disruption by basaltic magma during the next 10,000 years. Basaltic magmas have temperatures of approximately 1100°C, a density of 2600 kg/m³, fluid pressures on order 0.1-10 MPa, and flow velocities on order 1-100 m/s. Integrity of HLW containers likely 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 alloy 22 and type 316 NG stainless steel will be used along with preliminary calculations of stress levels and temperatures of the container wall to determine the potential for creep and stress rupture. Exposure to high temperatures (600 to 1100°C) for days to months also will precipitate secondary phase particles in the alloy (carbides, nitrides, and intermetallics) that can cause loss of ductility upon cooling to ambient temperatures. Secondary phases may then adversely affect corrosion performance and mechanical integrity of containers during seismically induced loading. Finally, acidic gases produced from basaltic magma can cause high temperature corrosion. Depending upon gas chemistry, high temperature corrosion can be in the form of oxidation, sulfidation, and molten salt corrosion. The rate of corrosion for container materials in hot gases will be estimated based on effects of gas chemistry and temperature on alloy compositions similar to the proposed container materials. Reported experience with magma-metal interactions will be used as an additional source of information in this evaluation.

This work, supported by U.S. Nuclear Regulatory Commission (Contract NRC-02-97-009), is an independent product of CNWRA that does not necessarily reflect NRC views or regulatory positions.

JJ11.4

EXPERIMENTAL DETERMINATION OF THE CONDUCTIVITY BEHAVIOR OF MULTICOMPONENT SALT DEPOSITS AS A FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY. Lietai Yang, Roberto T. Pabalan, Lauren Browning, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

Evaporation and aerosol deposition may lead to the accumulation of hygroscopic salts on drip shield (DS)/waste package (WP) surfaces. These hygroscopic salts will absorb moisture from the atmosphere, potentially causing aqueous corrosion of the DS and WP. The U.S. Department of Energy (DOE) performance assessment abstraction 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 deliquescence point of pure 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 salts. Because of the increase in conductivity, the initiation of DS or WP aqueous corrosion 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.

JJ11.5

EFFECTS OF HEAVY METAL IONS ON CORROSION OF TITANIUM GRADE 7 IN CONCENTRATED GROUNDWATERS. April L. Pulvirenti¹, Karen M. Needham¹, Mohamad A. Adel-Hadidi¹, Charles R. Marks², Jeffrey A. Gorman¹ and Aaron Barkatt¹.

¹Catholic University of America, Dept of Chemistry, Washington, DC. ²Dominion 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 surfaces of the canisters containing nuclear waste. It is therefore expected that the drip shield will be in contact, intermittently or continuously, with water of various concentrations of mineralogical species.

Among the species that may be expected to be present in the water contacting the drip shield are heavy metals, which may accelerate the corrosion of titanium. This paper presents the results of an investigation into the effects of three species, 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 fastest.

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.

JJ11.6

EFFECTS OF LEAD AND MERCURY ON CORROSION OF C-22 IN CONCENTRATED GROUNDWATERS AS A FUNCTION OF pH AND TEMPERATURE. April L. Pulvirenti¹, Karen M. Needham¹, Mohamad A. Adel-Hadidi¹, Charles R. Marks², Jeffrey A. Gorman² and Aaron Barkatt¹. ¹Catholic Univ of America, Dept of Chemistry, Washington, DC. ²Dominion Engineering, Inc., McLean, VA.

Corrosion tests have been carried out on Alloy C-22 in environments contaminated by lead or mercury. The tests explore how the presence of lead and mercury contaminants 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 longer-term service conditions. The test methods used included dissolution tests of disks at temperatures up to 160°C and U-bend tests at temperatures up to 250°C. The water used in the tests approximated the chemistry of thermally concentrated J-13 well water. Room temperature pH values ranged from 1 to 14. Various aggressive species were added. Several potentially aggressive species tested, including lead and mercury, affected the extent of corrosion of the C-22 specimens. Results of the tests for both dissolution and SCC were extrapolated to waste repository service conditions using trends developed from the technical literature for alloys 600 and 690 with regard to temperature and pH. Thus, it has been observed that in the presence of lead the onset of pitting is slowed down when the pH is raised for 1 to 3 to 5 or when the temperature is lowered from 250°C to 230°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.

JJ11.7

CREEP ANALYSES OF TITANIUM DRIP SHIELD SUBJECTED TO ROCKFALL STATIC LOADS IN THE PROPOSED GEOLOGIC REPOSITORY AT YUCCA MOUNTAIN. Brett W. Neuberger, Charles A. Greene, U.S. Nuclear Regulatory Commission, Washington

DC; G. Douglas Gute, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

The U.S. Department of Energy (DOE) has included a Titanium drip shield as a principle component of the post closure safety case for the proposed high-level nuclear waste repository at Yucca Mountain. As currently designed by DOE, the titanium drip shields will be fabricated from Titanium grade 7 (Ti Gr 7) 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 rockfall. Because the repository tunnels are expected to gradually collapse over time, NRC's evaluation of the drip shield includes an examination of the effects of rockfall under both dynamic and static load conditions. For the purpose of this study, the finite element method has been used to approximate the residual static loads and concomitant stress levels remaining in the drip shield after dynamic rock block impacts. These static loads and stress levels, when expressed as a fraction of the Ti alloy yield strength (YS), can be used to assess the potential effects of creep on drip shield performance in terms of the impacting rock block size. It has been shown in the literature that alpha and near-alpha 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.

JJ11.8

CORROSION BEHAVIOR OF CARBON STEEL IN BICARBONATE SOLUTIONS. J.H. Dong, T. Nishimura, T. Kodama, Natl Inst of Materials Science, Tsukuba, Ibaraki, JAPAN.

Carbon steel is one of the candidate materials for overpacks for high-level radioactive waste disposal. Effects of bicarbonate solutions on the corrosion behavior and corrosion products of carbon 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 out layer film formation of carbon steel, whereas it inhibits pitting at a nobler potential. The FT-IR and XRD spectral analysis of the anodized film showed that siderite (FeCO₃) was formed in 0.5 ~ 1.0mol/L bicarbonate solution, Fe₂(OH)₂CO₃ was formed in 0.1 ~ 0.2mol/L bicarbonate solution, while Fe₆(OH)₁₂CO₃ was formed in 0.02~ 0.05mol/L bicarbonate solution. In all cases the pH value was around 8.3. The stability of these chemical compositions was discussed using a potential - pH diagram.

JJ11.9

DIFFUSION BEHAVIOR OF IRON CORROSION PRODUCTS IN BUFFER MATERIALS. Kazuya Idemitsu, Seiji Yano, Xia Xiaobin, Yaohiro Inagaki, Tatsumi Arima, Kyushu Univ, Dept of Applied Quantum Physics and Nuclear Engineering, Fukuoka, JAPAN; Toshiaki Mitsugashira, Mitsuo Hara and Yoshimitsu Suzuki, Tohoku Univ, Institute for Materials Research, Ibaraki, JAPAN.

Carbon steel is one of the candidate overpack materials for high-level waste disposal and is expected to assure complete containment of vitrified waste glass during an initial period of 1000 years in Japan. 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 consuming oxygen introduced by repository construction after closure of repository and then will keep the reducing environment in the vicinity of repository. The reducing condition will be expected to retard the migration of redox-sensitive radionuclides by lowering their solubilities. Therefore, the diffusion of corrosion products of iron in buffer material is important to discuss the corrosion rate of overpack, migration of redox-sensitive radionuclides and properties of buffer material. The purpose of this paper is to study diffusion behavior of a corrosion product of iron in compacted bentonites under a reducing condition with a carbon steel. The diffusion mechanism of iron in the compacted bentonites were discussed by estimation of iron species in the bentonite pore water. It seems that there are two diffusion paths of iron in the compacted bentonites used in this study; the fast path has low capacity of iron, ca. 1 wt%, and large apparent diffusion coefficient, ca. 10⁻¹² m²/s and the slow path has high capacity of iron, ca. 10 wt%, and small apparent diffusion coefficient, ca. 10⁻¹⁴ m²/s.

JJ11.10

Transferred to JJ11.10

JJ11.11
EFFECTS OF TEMPERATURE ON THE BEHAVIOR OF Cs AND I IN YSZ-BASED INERT MATRIX FUEL AND WASTE FORM. S. Zhu, L.M. Wang, S.X. Wang and R.C. Ewing, Department of Nuclear Engineering and Radiological Sciences, The University of Michigan, Ann Arbor, MI.

Since the concept of inert matrix fuel has been proposed for disposition of excess plutonium from the dismantlement of nuclear weapons and the reprocessing of commercial nuclear fuel, various kinds of materials have been studied for this purpose. Among them, yttria stabilized zirconia (YSZ) is a promising candidate material for both inert matrix fuel and waste form based on its high solubility for actinides, high chemical durability and its reported exceptional stability under radiation. In this study, the temperature effects of long-lived fission product cesium and iodine incorporation on YSZ were investigated to learn the behavior of these radionuclides in YSZ as a waste form. Implantations of 400 keV Cs⁺ and 200 keV I⁺ were conducted in room temperature with fluences up to 1×10^{21} ions/m². Subsequent annealing was completed at 800°C and 1000°C for 2 hours, respectively. Cross-sectional TEM was performed after implantation of the bulk sample to reveal the depth; dependent microstructure induced by ion implantation and annealing. In the Cs⁺-implantation sample, an amorphous band was shown in a depth range where Cs concentration is greater than 8 at. % (300 dpa). After annealing at 1000°C, a high density of bubbles (2×10^{16} bubbles/cm³) with diameters from 6 to 60 nm occurred in the whole range of implantation. The amorphous area re-crystallized again because Cs⁺ precipitated out and formed bubbles at high temperature. No amorphization was observed after 200 keV I⁺ implantation though the damage level also reached 300 dpa. After annealing at 800°C and 1000°C, I⁺ bubbles formed in the I⁺-implantation samples and the density reached 8×10^{16} bubbles/cm³ at 1000°C. The diameters of bubbles range from 3 to 18 nanometers. For both samples, the bubble size is increased as the temperature increasing. The swelling due to the formation of bubble were estimated. The distribution and migration of implantation ions after annealing are also studied.

JJ11.12
SYNTHESIS AND STUDY OF CUBIC ZIRCONIA, (Zr,Gd,Pu)O₂, DOPED WITH ²³⁸Pu. Boris Burakov, Evgeniy Anderson, Maria Zamoryanskaya, Maria Yagovkina, Elena Nikolaeva, the V.G. Khlopin Radium Institute, St. Petersburg, RUSSIA.

Crystalline ceramic based on cubic zirconia has been proposed as a candidate waste form for the immobilization of weapons grade Pu and other actinides. In order to investigate the resistance of this actinide host phase to radiation damage for long term storage the polycrystalline samples of cubic zirconia, (Zr,Gd,Pu)O₂, doped with ²³⁸Pu were obtained and studied. The isotope composition of Pu was (in wt.%): ²³⁸Pu-81.3; ²³⁹Pu-15.2 and other Pu isotopes -3.5. Oxalates of Zr-Pu-Gd were co-precipitated at 60-70°C by ammonia-oxalate from the water solution of zirconyl-nitrate, Gd-nitrate and Pu-nitrate. The obtained powder was calcined in air at 600°C for one hour. After calcination the precursor was milled in an agate mortar and then cold pressed into pellets of 10 mm in diameter and of 3.0-3.5 mm in height. Ceramic synthesis was done by sintering in air at 1500°C for 4 hours. Synthesized samples were studied by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The zirconia composition measured by EPMA was (in wt.%): Zr-50.1; Gd-15.4 and Pu-12.2. Ceramic density measured was 5.8 g/cm³. No changes were observed in zirconia XRD spectra which were obtained immediately after ceramic synthesis and then 88 and 201 days later. The MCC-1 leach tests were performed on ceramic specimens in deionized water at 90°C for 28 days. It was found that without correction on ceramic porosity the initial Pu mass loss (NL) was 0.043 g/m². It was increased to 0.35 g/m² six months later. Results obtained allow us to confirm that actinide-doped cubic zirconia is a highly resistant to radiation damage and therefore, it is an efficient material for actinide immobilization in deep geological formations.

JJ11.13
SYNTHESIS AND EXAMINATION OF NEW ACTINIDE PYROCHLORES. Sergey V. Yudinsev, Institute of Geology of Ore Deposits, Moscow, RUSSIA; Sergey V. Stefanovsky, SIA Radon, Moscow, RUSSIA; Y.N. Jang, Korea Institute of Geology, Taejon, KOREA.

Pyrochlore A₂B₂O_{7-x} (0 ≤ x < 0.5) is cubic phase with two-fold fluorite unit cell, which is capable to incorporate actinides and rare earths. Pyrochlore-based ceramics are promising forms for long-lived actinides immobilization due to high radiation stability and chemical durability. We studied new pyrochlore-based actinide waste forms in the systems: CaO - ThO₂ - SnO₂, SrO - UO₂ (ThO₂) - SnO₂, CaO - UO₂ (ThO₂) - ZrO₂, and CaO - UO₂ (ThO₂) - Gd₂O₃ - TiO₂ - ZrO₂.

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 Sr-bearing ceramics and ceramics with CaUZr₂O₇ and (Ca_{0.5}GdU_{0.5})Zr₂O₇ specified compositions pyrochlore was not formed. In the other ceramics (with bulk compositions CaThZr₂O₇, (Ca_{0.5}GdTh_{0.5})(ZrTi)O₇, (Ca_{0.5}GdU_{0.5})(ZrTi)O₇, CaThSn₂O₇) pyrochlore was found to be a major phase, but minor fluorite-structured oxide was also present. Crystal-chemical reasons for appearance of the phase assemblages in the samples are discussed.

JJ11.14
XRD, SEM AND TEM STUDY OF THE Gd-DOPED ZIRCONOLITES. Sergey V. Stefanovsky, Albert Y. Troole, SIA "Radon", Moscow, RUSSIA; Maria I. Lapina, B.S. Nokonov, Anatoly V. Sintsov, IGEM RAS, Moscow, RUSSIA.

Ceramic samples with formulations Ca_{1-x}Gd_xZrTi_{2-x}Al_x (0 ≤ x ≤ 1) were prepared by cold pressing in pellets at 200 MPa followed by sintering at either 1400 or 1500°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 Al contents (x = 0.9 and 1.0). The samples produced at 1500°C were higher homogeneous and less porous than the samples sintered at 1400°C. From SEM/EDS data average compositions of zirconolite in the samples are very close to specified formulation (within experimental error), for example, zirconolite formula in the ceramic with x = 1 was found to be GdZrTi_{1.2}Al_{0.8}O₇ (probably GdZrTi⁴⁺Ti³⁺_{0.2}Al_{0.8}O₇). XRD and TEM patterns showed monoclinic (2M) structure for zirconolites within 0 ≤ x ≤ 0.5 compositional range. Zirconolites with x ≥ 0.5 forms two varieties. One of them is monoclinic (2M), the other has higher symmetry, supposedly orthorhombic or tetragonal.

JJ11.15
CHARACTERIZATION AND DISSOLUTION OF ZrTh₃UO₁₀ AND Th₃UO₈ CERAMICS. V. Curran, Y. Sevestre, W. Rattray, P.G. Allen*, K. Czerwinski, Nuclear Engineering Department, Massachusetts Institute of Technology, Cambridge, MA. *Seaborg Institute, Lawrence Livermore National Laboratory, Livermore, CA.

Thoria-uranium-zirconia ceramics were studied in order to investigate the long-term behavior of potential thorium fuels in a repository environment. The ceramics were prepared by coprecipitation. Zirconia was added to determine if further stabilization of the thorium-uranium system could be achieved. In addition, 0.5 wt% MgO was added to some samples to increase stability and density. The ceramics with the inclusion of Zr were shown not to dramatically enhance the stability of the matrix. Comparison with ceramics of higher Zr stoichiometry, up to a metal ratio of Zr₆Th₃U, also showed no enhanced stability against dissolution.

Material properties of the ceramic 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-based x-ray absorption studies including EXAFS and XANES were also used to reveal elements of the phase structure and chemistry of the ceramics. XRD and EDX show that these ceramics separate into a zirconium-based phase and an actinide-based phase with low mutual affinity of thorium and zirconium, as well as partial solubilization of uranium in zirconium. The comparison of EELS spectra collected for the ceramics with spectra collected for UO₂ and UO₃ reference materials also allow 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.

JJ11.16
INSTABILITY MODEL OF THE NZP STRUCTURE. Albert Troole, Sergey Stefanovsky, SIA "Radon", Moscow, RUSSIA.

Incorporation of paramagnetic species in NaZr₂(PO₄)₃ (NZP) single crystal made possible to investigate local distortion of the NZP structure from EPR data. Cr³⁺ and Fe³⁺ ions were used as paramagnetic probes. We mapped invariant sum of cubic component of the fourth rank tensor of crystal field, the indicative surface of the B₀₄ element of this tensor as well as 2nd, 3rd, and 4th orders axes of the cubic component of the same tensor. From these data the coordination polyhedron of the ion-probe has been modeled and direction to charge compensator has been determined. Based on the coordination polyhedron model obtained it has been shown how would the local symmetry be lowered from C₃ (initial symmetry of the Zr-polyhedron) to C₁ (Zr substitute ion-probe). A comparison of dynamics of the structure occurring at lowering the symmetry with allowed dynamics of the NZP structure (Roy-Alamo-Agrawal model) makes easily explainable why the dynamics observed results in an instability of the NZP structure and breaking the symmetry from R 3c to C2/c.

JJ11.17

MICROSTRUCTURE AND DISSOLUTION OF U- AND HF-BEARING PYROCHLORE AND ZIRCONOLITE: HRTEM AND AEM INVESTIGATION. Huifang Xu, Transmission Electron Microscopy Lab, Department of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM; Yifeng Wang, Sandia National Laboratory, Carlsbad, NM; Pihong Zhao, Lawrence Livermore National Laboratory, Livermore, CA.

Transmission electron microscopy results from a sintered ceramics with stoichiometry of $\text{Ca}(\text{U}_{0.5}\text{Ce}_{0.25}\text{Hf}_{0.25})\text{Ti}_2\text{O}_7$ show the material contains both pyrochlore and zirconolite phases and structural intergrowth of zirconolite lamellae within pyrochlore. (001) plane of zirconolite 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+Hf) ratios for the coexisting pyrochlore and zirconolite at 1350°C are 0.72 and 0.28, respectively. Dissolution experiments show that the dissolution rate decreases as dissolution time increases. High-resolution TEM results show that a Hf- 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 that was leached for 1.5 year 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).

JJ11.18

INVESTIGATION OF Pu-DOPED CERAMICS USING MCC-1 LEACH TEST. Elena Nikolaeva, Boris Burakov, 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, $(\text{Zr,Gd,Pu})\text{O}_2$, doped with 10 wt.% ^{239}Pu , zircon, $(\text{Zr,Pu})\text{SiO}_4$, doped with separately 5-6 and 10 wt.% ^{239}Pu , pyrochlore, $(\text{Ca,Pu,Gd,Hf,U})\text{Ti}_2\text{O}_7$, doped with 10 wt.% ^{239}Pu , 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/m^2) after 14 and 28 days were: - for the zirconia ceramic - 2E-2/4E-2 - at 90°C and 8E-3/9E-3 - at 25°C; - for zircon doped with 5-6 wt.% Pu - 7.0E-3/8.2E-3 - at 90°C and 1.0E-3/1.2E-3 - at 25°C; - for zircon doped with 10 wt.% Pu - 0.2/0.2 - at 90°C and 3.0E-2/4.0E-2 - at 25°C; - for pyrochlore - 1.0E-3/1.0E-3 - at 90°C and 2.0E-3/3.0E-3 - at 25°C. It was shown that the high leach rate for zircon based ceramic doped with 10 wt.% Pu was caused by the presence of the separated inclusions of PuO_2 phases observed in ceramic matrix. The results obtained so far allow us to conclude that ceramics based on zircon, zirconia and pyrochlore are characterized by similar chemical resistance to leaching in deionized water. Based on its low porosity, zircon may be most durable ceramic host phase for Pu.

JJ11.19

Transferred to JJ6.4

JJ11.20

THERMODYNAMIC FUNCTIONS OF ZIRCONOLITE AND THEIR USE IN COMPUTER THERMODYNAMIC SIMULATION OF EXOTHERMIC REACTIONS FOR MINERAL-LIKE MATRIX SYNTHESIS. George A. Bergman, Michael I. Ojovan, Vsevolod L. Klimov, Olga K. Karlina, SIA RADON, Moscow, RUSSIA.

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 to thermodynamic analysis of this reaction. A. Navrotsky with 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 \pm 20 kJ/mol and 350 \pm 50 J/(mol·K) respectively. Using these data and results of A. Navrotsky et. al, thermodynamic functions of solid and liquid zirconolite are calculated. The data obtained are introduced in the database on thermodynamic properties of the thermodynamic calculation code. 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 us. It is demonstrated that synthesis of zirconolite-like matrix materials is possible using the self-sustaining exothermic reaction. Some preliminary experimental results indicate the same.

JJ11.21

PRELIMINARY STUDIES OF THE DISPOSITION OF CESIUM IN A CERAMIC WASTE FORM. Marsha J. Lambregts, 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 nuclear fuel. This process produces a LiCl/KCl eutectic salt contaminated with fission products 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 of particular interest because of its high mobility within the environment. The amount of cesium found in the waste form is approximately 0.1 wt%. Because of the small amount of cesium present, it was unaccounted for in previous studies and thought to be uniformly distributed throughout the waste form. This paper presents preliminary XRD, SEM-WDS/EDS, and NMR data exploring the disposition of the cesium in cesium doped ceramic waste forms similar to the actual ceramic waste form.

JJ11.22

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

A baseline formulation based upon a target mineralogy of 95 wt.% pyrochlore ($\text{Ca}_{0.89}\text{Gd}_{0.22}\text{Hf}_{0.23}\text{Pu}_{0.22}\text{U}_{0.44}\text{Ti}_2\text{O}_7$); plus 5 wt.% Hf-doped rutile (approximately $\text{Ti}_{10.9}\text{Hf}_{0.1}\text{O}_2$) has been developed for the disposition of excess weapons plutonium. In experimental work Ce and Th have been used as an analogue for Pu and Ce as an analogue for U. Zr can also replace Hf for testing purposes. We discuss the effect of sintering atmosphere (air, argon and 3.7 % hydrogen in argon) and temperature on the mineralogy of Pu/U, Th/U, Ce/U and Ce/Ce-baseline compositions. The pyrochlore ceramics produced proved to be extremely flexible with charge compensation mechanisms allowing the production of a desirable mineralogy under a variety of processing conditions. The redox state of U has been examined using diffuse reflectance spectroscopy. The limitations of each analogue and the effects of processing impurities will also be discussed.

JJ11.23

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

We have evaluated the possible use of the Product Consistency Test (PCT), that was developed to monitor the product consistency of borosilicate 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 multiphase waste form comprised of about 70% sodalite, 25% borosilicate glass binder, and small amounts of halite and oxide inclusions. It must be qualified 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 borosilicate HLW glasses and the sodalite and glass binder phases of the CWF. Tests have been conducted to measure the within-laboratory and between-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 consistency test that can be used during CWF 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.

JJ11.24

THE ENERGETICS OF FORMATION OF ZIRCONOLITE, $\text{CaZrTi}_2\text{O}_7$ AND HF-ZIRCONOLITE, $\text{CaHfTi}_2\text{O}_7$ REVISITED. K.B. Helean, T. Lee, A. Navrotsky, Thermochemistry Facility, Department of Chemical Engineering and Materials Science, The University of California at Davis, Davis, CA; R.L. Putnam, Los Alamos National Laboratory, Los Alamos, NM; B. Ebbinghaus, Lawrence Livermore National Laboratory, Livermore, CA.

Zirconolite, nominally $\text{CaM}_x\text{Ti}_{3-x}\text{O}_7$, $0.8 < x < 1.37$ and $M = \text{Zr, Hf, Ce, U, REE}$, is a primary component of SYNROC. As such zirconolite has been the subject of numerous studies. Despite the interest in zirconolite, its fundamental thermodynamic properties were unknown

until recently. Previous calorimetric investigations of zirconolite and Hf-zirconolite used Pb-borate ($2\text{PbO}\cdot\text{B}_2\text{O}_3$) near 973 K as a solvent. As was noted in these studies, dissolution of these refractory oxides was slow. Calorimetric experiments for the Hf-bearing compounds were conducted by mixing the materials with powdered solvent to aid in the dissolution. This introduces additional uncertainty in the data and does not necessarily ensure that dissolution is complete. Therefore, a second calorimetric investigation was undertaken using an alternative molten oxide solvent in which the samples appear to dissolve more readily. High temperature oxide melt solution calorimetry at 975 K using sodium molybdate ($3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$) solvent was used to measure the heats of solution for CaCO_3 , ZrO_2 , HfO_2 , TiO_2 , Gd_2O_3 , $\text{CaZrTi}_2\text{O}_7$, $\text{CaHfTi}_2\text{O}_7$, and $\text{Ca}_{0.68}\text{Gd}_{0.60}\text{Hf}_{0.70}\text{Ti}_{2.02}\text{O}_{7.02}$. Applying the appropriate thermodynamic cycles to our preliminary data, the enthalpies of formation from the oxides, $\Delta H_{f-\text{ox}}^0$, at 298 K were calculated (kJ/mol): $\text{CaZrTi}_2\text{O}_7$ (-89.8 ± 3.5 kJ/mol) and $\text{CaHfTi}_2\text{O}_7$ (-77.7 ± 2.7). The enthalpy of formation derived from dissolution in the $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ solvent for $\text{CaZrTi}_2\text{O}_7$, within error equal to the previously published value derived from $2\text{PbO}\cdot\text{B}_2\text{O}_3$ solution data. However, the preliminary results for $\text{CaHfTi}_2\text{O}_7$, indicate that its $\Delta H_{f-\text{ox}}^0$ is as much as 34 kJ/mol more endothermic than previously reported.

JJ11.25

ENERGETIC TRENDS IN REE-TITANATE AND ZIRCONATE PYROCHLORES. K.B. Helean, S.V. Ushakov, A. Navrotsky, Thermochemistry Facility, Department of Chemical Engineering and Materials Science, The University of California at Davis, Davis, CA; J. Lian, L.M. Wang, R.C. Ewing, Department of Radiological Sciences and Nuclear Engineering, The University of Michigan, Ann Arbor, MI; L.A. Boatner and J.M. Farmer, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Rare-earth-element-bearing titanate and zirconate pyrochlores, nominally, $\text{REE}_2\text{M}_2\text{O}_7$, where REE = lanthanides plus Y and M = Ti, Zr, are used as solid ionic conductors and oxygen sensors in numerous industrial applications. In addition, $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$ 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 REE-titanate and zirconate pyrochlore samples. High-temperature oxide melt solution calorimetry was used to measure heats of drop solution, ΔH_{ds} , using $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ solvent at 975 K for REE_2O_3 (REE = Y, La, Nd, Sm, Eu, Gd, Ho, Er, Tm), $\text{REE}_2\text{Ti}_2\text{O}_7$ (REE = Y, Tm, Er, Ho, Gd, Eu, Sm) and $\text{REE}_2\text{Zr}_2\text{O}_7$ (REE = La, Nd, Eu, Gd). These data were used to calculate enthalpies of formation from the oxides, $\Delta H_{f-\text{ox}}$, at 298 K (kJ/mol), for example: $\text{Gd}_2\text{Zr}_2\text{O}_7$ (-52.8 ± 4.8), $\text{Nd}_2\text{Zr}_2\text{O}_7$ (-66.8 ± 4.0), $\text{Y}_2\text{Ti}_2\text{O}_7$ (-86.0 ± 1.5) and $\text{Sm}_2\text{Ti}_2\text{O}_7$ (-115.4 ± 5.0). These data, when plotted against the radius ratio $R(\text{REE})/R(\text{M})$, define a linear trend with $\Delta H_{f-\text{ox}} = -186.84[R(\text{REE})/R(\text{M})] + 221.06$. Approximately 94% of the variation in the data is defined by this trend. As $R(\text{REE})/R(\text{M})$ decreases, the pyrochlore phases become less stable. Structural details plus the complete calorimetric data set will be presented.

JJ11.26

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

Cerium-actinide bearing natural minerals which demonstrate their physico-chemical durability for long time ($>10^5$ years) would be considered as the analogues of actinide ceramic waste forms. Radiation damage of crystalline materials causes oxidation of cerium from initial Ce^{3+} to Ce^{4+} . Therefore, cerium valence state in actinide-cerium bearing natural minerals reflects in some cases the resistant of such minerals to radiation damage. Cerium valence state was determined in the following natural minerals of similar age and similar U-Th-contents: - monazite, $(\text{Ce},\text{TR},\text{Th},\text{U})\text{PO}_4$ (4 samples); - britholite $(\text{Ce},\text{TR},\text{Ca},\text{Th},\text{U})_5(\text{SiO}_4)_3(\text{OH},\text{F})_2$ (2 samples); - aeschynite, $(\text{Ce},\text{TR},\text{Th},\text{U},\text{Ca})(\text{Nb},\text{Ti})_2(\text{O},\text{OH})_6$ (1 sample). The method of chemical shifts of X-ray emission (Ce $\text{K}\alpha_1$ line) was used. The $\text{Ce}(\text{NO}_3)_3$ and CeO_2 were used as standards of Ce^{3+} and Ce^{4+} , respectively. The following contents of Ce^{4+} were observed: - more than 30% in britholite; - 11% in aeschynite; - 0% in monazite. The results obtained allow us to conclude that durability of these actinide host phases decreases in the raw "monazite-aeschynite-britholite".

JJ11.27

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

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

Zircon (ZrSiO_4) has been proposed as a potential waste form for actinides, particularly "excess" plutonium. The chemical and physical durability of zircon is well established because of its use in geologic age-dating. Radiation damage due to alpha decay events is known to decrease the chemical durability of zircon; however, the mechanism of damage accumulation and the structure of metamict zircon are still under active investigation. In this work, an oscillatory-zoned single crystal of zircon from Sri Lanka (570 Ma) has been studied using a variety of microanalytical techniques in order to relate the accumulation of radiation damage to atomic-scale structural changes. An electron microprobe traverse across optical zones shows that variations in birefringence reflect changes in the U and Th content ($0.10 < \text{UO}_2 + \text{ThO}_2 < 0.62$ wt-%). Based on these concentrations, a cumulative alpha decay dose can be calculated for each zone. The calculated doses, 1.9×10^{15} to 1.1×10^{16} alpha-decay events/mg, suggest that zones within the crystal represent crystalline, transitional and amorphous regions. A traverse across these zones using micro-Raman spectroscopy confirmed that a structural change occurs between zones of varying radiation damage. The decrease in phonon frequencies and peak intensities with increasing dose for both internal and external modes implies a rotation of the SiO_4 tetrahedra and/or an increase in bond lengths. 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 amorphous domains with some suggestion of the formation of ZrO_2 nano-particles.

JJ11.28

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

From crystal-chemical 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 $\text{A}^{\text{VIII}}_3\text{B}^{\text{VI}}_2[\text{XO}_4]_3$. In order to evaluate feasibility of usage of the garnets for actinide waste immobilization research of synthetic phases formed in the system: $\text{CaO} - \text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{ZrO}_2 - \text{Gd}_2\text{O}_3 - \text{UO}_2$ was carried out. Experiments were performed in air medium at 1400-1500°C and 1 atm. All of the garnets produced have high capacity in respect of Gd and Zr, while incorporation of U in the structure was found to be greatly dependent on the phase overall composition. Solubility of uranium varied from 16-18 wt.% to 0.6-0.8 wt.%. The highest U content was observed in Ca-Zr-Fe garnet, the lowest - in Si-containing phases. In the Gd-rich garnets the element content ranged from 3 to 6 wt.%. Analysis of garnets formula calculated from their compositions allow to conclude that U enters both the $[\text{A}]^{\text{VIII}}$ and $[\text{B}]^{\text{VI}}$ sites of the structure, Gd occupies the $[\text{A}]$ -sites, while Zr fills the $[\text{B}]$ structural positions only. Ion irradiation (1.0 MeV Kr^+) experiments were completed on the garnet phase with composition: $(\text{Ca}_{1.5}\text{Gd}_{1.5})^{\text{VIII}}(\text{U}_{0.1}\text{Zr}_{1.5}\text{Fe}_{0.4})^{\text{VI}}(\text{Al}_{1.1}\text{Fe}_{1.9})^{\text{IV}}\text{O}_{12}$. Amorphization does of the phase at room temperature was 1.5×10^{14} (ions/cm²), that is close to many other actinide host, for example titanate-based pyrochlores. The other actinide-bearing phase observed in sample (fluorite-structured oxide) did not become amorphous even at a dose of three times higher of critical fluency for garnet. The critical amorphization temperature above which the garnet structure could not be amorphized was determined to be 1104K.

JJ11.29

A CATHODOLUMINESCENCE INVESTIGATION OF PYROCHLORE, $(\text{Ca},\text{Gd},\text{Hf},\text{U},\text{Pu})_2\text{Ti}_2\text{O}_7$, DOPED WITH ^{238}Pu AND ^{239}Pu . Maria Zamoryanskaya, Boris Burakov, The V.G. Khlopin Radium Institute, St. Petersburg, RUSSIA; Roman Bogdanov, Dept of Chemistry, Saint-Petersburg Univ, St. Petersburg, RUSSIA; Andrey Sergeev, Dept of Geology, Saint-Petersburg Univ, St. Petersburg, RUSSIA.

Crystalline ceramic based on the pyrochlore structure $(\text{Ca},\text{Gd},\text{Hf},\text{U},\text{Pu})_2\text{Ti}_2\text{O}_7$ has been proposed in the U.S. as a waste form for the immobilization of weapons grade plutonium. Several samples of polycrystalline pyrochlore doped separately with ^{238}Pu and ^{239}Pu 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 wt.% Pu and 20.9 wt.% U. The Pu and U contents determined by electron probe microanalysis

(EPMA) in single pyrochlore grains, however, were variable. Pyrochlore doped with ^{239}Pu contained (in wt.% El): Pu \sim 9.0-10.7 and U \sim 23.1. The EPMA data obtained after 245 days after sample synthesis revealed that pyrochlore doped with ^{238}Pu became inhomogeneous and contained (in wt.% El): Pu \sim 3.4-26.8 and U \sim 32.9-13.2. The CL spectra of pyrochlore doped with ^{239}Pu and ^{238}Pu obtained immediately after synthesis were the same and characterized a typical broad band emission with a maximum peak centered at 2.5 eV. New CL peaks with maximum intensities at 2.5, 2.4 and 2.3 eV in the emission spectra of ^{238}Pu -doped pyrochlore were observed 175, 245, 405 days later, although no significant changes of CL spectra of ^{239}Pu -doped sample were identified over the same period of time. It was determined that these newly formed CL peaks are similar to ones in CL spectrum of artificial standard glass doped with the uranyl ion (UO_2) $^{2+}$. 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 pyrochlore-based ceramic waste form is accompanied with conversion of uranium incorporated into pyrochlore structure to the mobile uranyl ion.

JJ11.30

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 accumulated from electrometallurgical treatment of spent DOE fuel has been studied. This involved the preparation of a surrogate ceramic waste form containing two-weight percent plutonium-238 and monitoring changes to the waste form resulting from alpha-decay damage. The phase assembly of the ceramic waste form consists of glass-bonded sodalite granules with small quantities of nepheline, halite and plutonium oxide. The surrogate waste form has been monitored for four years and has acquired an internal alpha-decay dose of approximately $1\text{e}18$ disintegrations per gram of material. Methods used to monitor the material include: density determination to measure possible macroscopic swelling, chemical durability measured by leach testing, microstructure analysis by scanning and transmission electron microscopy and phase composition by powder x-ray diffraction. The investigation has, to date, found little alteration to the waste form due to alpha-decay damage. X-ray diffraction analysis has detected a unit cell volume increase of 0.6 percent of the Pu bearing phase. Furthermore, possible He bubble formation has been observed by transmission electron microscopy in the sodalite phase; however, these findings remain inconclusive.

JJ11.31

ION IRRADIATION EFFECTS IN THE GARNET-BASED WASTE FORM. Satoshi Utsunomiya, LuMin Wang, Rodney C. Ewing, University of Michigan, College of Engineering, Ann Arbor, MI; Sergey Yudinsev, Russian Academy of Sciences, Inst. of Geology of Ore Deposits, Moscow, RUSSIA.

Garnet is an orthosilicate, ideally $\text{A}_3\text{B}_2(\text{XO}_4)_3$. The isometric structure consists of a corner-sharing framework of XO_4 -tetrahedra, AO_8 -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 study, we investigate radiation susceptibility of several synthetic garnet compositions as candidates for waste forms. The compositions of the synthetic garnets are (cations normalized by 24 oxygen): N56: $\text{Ca}_{4.62}\text{Ce}_{0.41}\text{Fe}_{5.20}\text{Gd}_{0.75}\text{Si}_{4.81}\text{O}_{24}$ N77: $\text{Ca}_{3.45}\text{La}_{0.36}\text{Ce}_{0.31}\text{Zr}_{0.44}\text{Fe}_{1.49}\text{Nd}_{0.31}\text{Eu}_{0.05}\text{Si}_{7.87}\text{O}_{24}$ G2: $\text{Ca}_{2.87}\text{U}_{0.18}\text{Zr}_{2.55}\text{Gd}_{3.17}\text{Al}_{3.29}\text{Fe}_{4.00}\text{O}_{24}$ G3: $\text{Ca}_{2.73}\text{U}_{0.13}\text{Zr}_{2.42}\text{Gd}_{3.30}\text{Al}_{2.34}\text{Fe}_{5.13}\text{O}_{24}$ G4: $\text{Ca}_{6.08}\text{U}_{1.11}\text{Zr}_{3.16}\text{Al}_{2.44}\text{Fe}_{3.81}\text{O}_{24}$ N56 and N77 are silicate garnet, while G2, G3 and G4 are aluminate-ferrate garnet. Ion irradiation experiments (1.0 MeV Kr) have been completed in those synthetic garnets and natural garnet (andradite: $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$). The critical amorphization temperature (T_c), 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 1030 K for andradite, respectively. T_c increased as the total molecular weight in the formula increased. Although the garnet structure has different cation-sites, the relationship between T_c and atomic mass is consistent with previously reported T_c -mass relationships for A-site cations in zircon-structure phosphates. At high temperature, nano-crystals formed with d-spacings consistent with a unit cell in which the lattice parameter is one-half of that of the original garnet. This suggests that the nano-crystals are cation-disordered garnets.

JJ11.32

COMPUTER STUDY OF THE EFFECT OF POINT DEFECTS ON X-RAY DIFFRACTION SPECTRA OF IRRADIATED

MATERIALS. Stephan Grigull, European Synchrotron Radiation Facility, Grenoble, FRANCE.

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 information can only be obtained if the static lattice 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 Rietveld codes. The K-dependence of this factor is determined by details of the spatial rearrangement of the lattice atoms surrounding the defects which to date cannot be calculated with sufficient accuracy by analytical methods. In the present work the Molecular Dynamics simulation technique is used to generate defective crystal structures in the computer for which X-ray diffraction spectra can be easily calculated. Intensity correction factors are evaluated for different defect types and concentrations in a fcc metal, and it is discussed under what conditions the K-dependence of the factor may be sufficiently simple for use in practical structure refinement.

JJ11.33

Abstract Withdrawn.

JJ11.34

THE STRUCTURAL CHANGE OF TITANATE PYROCHLORES INDUCED BY ION IRRADIATION: XPS INTERPRETATION.

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Titanate pyrochlores are expected to use for the disposition of excess weapons plutonium; they also have potential in solid electrolytes and oxygen gas sensor. The radiation-induced microstructure evolutions of titanate pyrochlore have been characterized using transmission electron spectroscopy (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 fluence of $1.7\text{times}10^{14}$ Xe^+/cm^2 , a 300 nm-thick amorphous layer was formed at the specimen surface by cross-sectional TEM. XPS analysis of Ti 2p and O 1s binding energy shifts of $\text{Gd}_2\text{Ti}_2\text{O}_7$ surface layer 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 titanate 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.

JJ11.35

HEAVY 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^+ and a 500 keV Au^+ irradiation were performed for different $\text{Ln}_2\text{Zr}_2\text{O}_7$ pyrochlore compositions (A=La, 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_c for $\text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$ series increase with the cascade size resulting from different incident ion sources, and the increasing radiation resistance with the increasing Zr content was further evidenced. Only partial amorphization was observed in $\text{Gd}_2\text{Ti}_{0.5}\text{Zr}_{1.5}\text{O}_7$ irradiated by 1.5 MeV Xe to 34 dpa at 25 K. $\text{La}_2\text{Zr}_2\text{O}_7$ is the only zirconate pyrochlore that can be amorphized with a critical amorphization temperature of \sim 310 K. The susceptibility to amorphization of $\text{La}_2\text{Zr}_2\text{O}_7$ is related to the fact that it has the largest structure deviation from the ideal fluorite structure, and the highest energy barrier for ion-irradiation enhanced recrystallization.

JJ11.36

ATOMISTIC SIMULATION OF DISPLACEMENT CASCADES IN ZIRCON. R. Devanathan, Department of Metallurgical Engineering, Indian Institute of Technology Madras, Chennai, INDIA;

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Zircon ($ZrSiO_4$) 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 and aqueous corrosion of glass waste forms. Previous experimental studies have shed light on radiation effects, thermal decomposition, and recrystallization of $ZrSiO_4$, but such studies have not yielded much-needed information on the atomistic details of defect production processes in energetic alpha-decay events and subsequent defect migration. These processes play a vital role in determining the radiation response of $ZrSiO_4$ and can be elucidated by realistic computer simulations of displacement cascades. However, very few simulations of cascades in $ZrSiO_4$ 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 $ZrSiO_4$ have been investigated by molecular dynamic simulations using a Coulombic model for long-range interactions, Buckingham potentials for short range interactions, and Ziegler-Biersack Littmark potentials for close-pair interactions. The statistics of defect production and evolution of the primary damage state will be presented to shed light on displacement damage produced by energetic Zr recoils in $ZrSiO_4$. Polymerization of Si, and distributions of bond length and bond angles in the cascade will be compared with those in amorphous zircon.

JJ11.37
RADIOGENIC TRANSMUTATION EFFECTS IN A CRYSTALLINE ALUMINOSILICATE CERAMIC: A TEM STUDY. Jeffrey Fortner, Scott Aase, and Don Reed, Argonne National Laboratory, Argonne, IL.

We demonstrate the use of TEM to study the effects of the radioactive (β -decay) of ^{137}Cs to ^{137}Ba in crystalline pollucite ($CsAlSi_2O_6$). Most prior work on radiation effects in materials has focused on structural damage from alpha radiation. Beta radiation, on the other hand, causes little atomic displacement but the decay transmutation results in progeny with different valence and ionic radius. Cesium-137 is a fission product of uranium and is a major contaminant at U.S. Department of Energy production facilities. Pollucite is an aluminosilicate ceramic being considered for long-term storage of ^{137}Cs . We focused on one of several available ^{137}Cs sources originally fabricated in the 1970s and 1980s for tumor treatment. These sources were small, sealed, stainless steel capsules containing pollucite in which varying amounts of the natural Cs had been replaced by radioactive ^{137}Cs ($t_{1/2} = 30.13$ years). The sample chosen for TEM examination had aged for nearly 20 years and contained the most radiogenic barium nearly 16% of the total cesium and was expected to show the largest radiation effects. Bright field transmission images revealed a homogeneous, crystalline matrix, with no evidence of distinct Ba phases or ex-solution phenomena resulting from the ^{137}Cs transmutation. Electron diffraction patterns were obtained from several portions of the sample and were consistent with literature values for pollucite. These data suggest that no substantial damage was done to the crystal structure of this sample, despite the transmutation of nearly 16% of the cesium to barium over the elapsed 20 years. Although our observations are limited, these are, to our knowledge, the only available data in which transmutation effects have been isolated from other radiation damage phenomena.

JJ11.38
EXPERIMENTAL DETERMINATION OF THE DISSOLUTION KINETICS OF PLUTONIUM- AND URANIUM BEARING CERAMICS AT 90°. J.P. Icenhower, B.P. McGrail, D.M. Strachan, R.D. Scheele, V.L. Legore, E.A. Rodriguez, J.L. Steele, C.F. Brown, and M.J. OHara. Pacific Northwest National Laboratory, Richland, WA.

Titanate-based ceramics have emerged as the leading candidate for a matrix for disposal of excess weapons-grade plutonium in a deep geologic repository. Concern persists, however, that accumulation of radiation damage will compromise the chemical durability of the titanate matrix. As a first step toward understanding the effects of radiation damage on element release rates, we performed single-pass flow-through (SPFT) experiments with ^{239}Pu - and ^{238}U -bearing ceramics over a solution pH-interval of 2 to 10 at 90°C. The ceramics tested include chemically complex zirconolite ($CaBTi_2O_7$), betafite (Ti -rich pyrochlore, $ABTi_2O_7$) ($A = Ca^{2+}$, Gd^{3+} , $B = Gd^{3+}$, Hf^{4+} , Pu^{4+} , $U^{4+/6+}$), and betafite-rich samples. The ^{239}Pu -bearing specimens contained 7.4 to 12.4 mass% PuO_2 and 15.4 to 23.7 mass% UO_2 . In addition, a ^{238}Pu -bearing (11.8 and 23.9 mass% PuO_2 and UO_2 , respectively) betafite-rich specimen was tested at pH = 2, 90°C. The experiment with the ^{238}Pu -bearing ceramic utilized a platinum-lined Teflon reactor to eliminate radiation damage to the Teflon from direct contact with the ceramic powder. The ^{239}Pu -bearing specimens slowly released Pu to solution (rate =

$8.3 \times 10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$), even at pH = 2. At higher pH values, the dissolution rate decreased by a factor of 10 and then increased near pH = 10. Rates based upon release of calcium are typically >10X faster and are inconsistent with rates based on other elements. Compared to results from the ^{238}Pu -bearing materials, the ^{238}Pu -bearing specimen released Pu nearly 400X faster (rate = $3.2 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$). Release rates of U, Gd, and Hf are also faster from the ^{238}Pu -bearing ceramic compared to the specimen containing ^{239}Pu . Although preliminary, the data can be interpreted to indicate that accumulation of radiation damage may result in faster release of Pu and U to solution than previously suspected.

JJ11.39
A THERMAL PARAMETRIC STUDY FOR IN-FLOOR TYPE NUCLEAR WASTE REPOSITORY FOR SYNROC. Devlet Sizgek, Australian Nuclear Science and Technology Organisation, Materials Division, Sydney, AUSTRALIA.

A study of temperature distribution for an in-floor type nuclear waste repository in granitic rock for high level nuclear waste (HLW) bearing synroc is presented. Transient calculations for a 3-D model has been carried out for both 20 weight percent and 10 weight percent HLW bearing synroc, 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 vertical planes of the investigated domain are assumed to be insulated (zero heat flux). This implies that the canister is in the centre of the repository and surrounded by the canisters of equal output. Thus it accounts for the effect of all canisters contained within in the repository. The temperatures in the repository were found to be sensitive to interim surface cooling period as well as the amount of waste loaded. For the base geometry (tunnel spacing 30 m and canister spacing 6 m), the maximum temperature reached at the waste centreline was calculated to be 200 C, for 10 weight percent HLW bearing synroc, with 5-year interim cooling period. On the other hand for similar centerline temperatures interim cooling period for 20 weight percent HLW containing synroc was predicted to be about 20 years. In comparison to the base geometry, decreasing the spacing between the canisters was found to have a more pronounced effect on the temperature field than decreasing the space between the adjacent tunnels.

JJ11.40
SUCCESSFUL RADIOACTIVE WASTE MANAGEMENT APPROACHES AND METHODS AT THE WASTE ISOLATION PLANT. Ines Triay, Mark Matthews, P.E., US DOE, Carlsbad, NM; Leif Eriksson, GRAM, Albuquerque, NM.

On March 26, 1999, the U.S. Department of Energy (DOE), supported by its local contractors, achieved a global milestone by opening the world's first, specially constructed, independently certified, deep-geological disposal system (repository) for long-lived radioactive wastes/materials (LLRMs) at the Waste Isolation Pilot Plant (WIPP) site in New Mexico. The WIPP repository is situated approximately 650 meters (m) below the ground surface in a 250-million-year-old, 600-m-thick, undisturbed, virtually impermeable salt bed, known as the Salado Formation. A 24-year-long site selection, site characterization, and repository-development process preceded the opening of the WIPP repository. During the last seven years of this process, the DOE had to overcome considerable challenges posed by evolving laws, regulations, and legal actions. The establishment of the DOE Carlsbad Field Office, and its successful development and implementation of the WIPP Disposal Decision Plan, the Systems Prioritization Method, and the performance assessment studies and development of an effective safety case, were instrumental to the successful resolution of these challenges. They were also instrumental in establishing a broad-based national acceptance and, ultimately, the certification of WIPP by virtue of the strength of the WIPP Safety Case. At the end of May 2001, 245 shipments of LLRMs had been safely received and disposed at the WIPP site. When filled to its current statutory capacity, the WIPP repository will safely contain and isolate up to 175,586 cubic meters of long-lived, transuranic radioactive waste (TRUW). The TRUW will contain between 12 and 17 metric tons of radioactive isotopes with half-lives in excess of 24,000 years, and TRUW containers with surface dose rates up to 10 sieverts per hour. However, several additional challenges remain to be overcome before WIPP has accomplished its current statutory mission. The 'filling of the pipeline to WIPP', i.e., increasing the current waste characterization and shipping capacities, the successful re-certification of WIPP by March 26, 2004, and the safe continued operation of WIPP are foremost among current challenges and priorities. This paper will focus upon the approaches, methods, key findings, and successes in the establishment and future directions of WIPP.

JJ11.41

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

Depleted uranium dioxide (DUO₂) waste packages (WPs) for spent nuclear fuel (SNF) are being investigated to (1) reduce radionuclide releases from WPs, (2) decrease the potential for repository nuclear criticality events, and (3) provide a means to beneficially use excess DU. Conceptually, the DUO₂ WP with SNF is similar to a small (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) a fill for all void spaces in the WP-including SNF coolant channels-and (2) as a component of a DUO₂-steel cermet. Cermets are a mechanism to create a ductile form of DUO₂. The cermet, containing 40 to 65 vol % DUO₂ embedded in steel, substitutes for the steel components (shell and basket) of the WP. The WP includes an outer non-cermet layer of a more corrosion-resistant alloy such as C-22. The same mechanisms that have preserved ore bodies containing UO₂ in some areas of oxidizing groundwater are expected to help preserve UO₂ in SNF and thus delay the release of those radionuclides trapped in the fuel pellets. The WP materials 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 resistant metal layer, diffusion barriers, etc.), maintenance of chemically reducing conditions within the WP by preferential oxidation of DUO₂ and steel, saturation of fluids in the WP with 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 DU oxides, and long-term buildup of uranium silicate surfaces.

JJ11.42

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

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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 Multiphases (STORM) code was used to evaluate the impacts of design modifications on the performance of two shallow subsurface disposal systems for low-level radioactive waste. The first site located at Hanford is for disposal of 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 gave a slightly lower (15%) normalized Tc 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 backfill, where the SiO₂(aq) concentration goes through a sharp transition because of mineralogical and transport property differences across the interface. Since the glass saturation index is significantly lower at these interfaces (higher corrosion rate), having one less interface with the 3-layer design offsets the effect of the slightly 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 LLW disposal facility under design in Italy that contains radioactive waste mixed with concrete. The effect of locating 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 compete for precipitation of calcite (the reaction product with portlandite), the simulations suggested that locating the graphite packages in portions of the facility with lower partial pressures of atmospheric CO₂ would lower overall C-14 release rates.

JJ11.43

RADIOISOTOPE FRACTIONATION AND SECULAR DISEQUILIBRIUM IN PERFORMANCE ASSESSMENT. William M. Murphy, Dept of Geosciences, California State Univ, Chico, CA; David A. Pickett, CNWRA, Southwest Research Institute, San Antonio, TX.

Radioisotopes of actinides and their decay products are fractionated in natural geochemical systems and in chemical processes associated

with geologic disposal of nuclear waste. Two potential applications of isotope fractionation and decay-series disequilibrium in performance assessment for geologic repositories for nuclear waste are preferential radionuclide release and characterization of system closure. Systems that are closed on time scales that are long relative to the half-lives of decay chain nuclides achieve secular equilibrium, characterized by unit activity ratios among nuclides. Natural systems are commonly out of secular equilibrium. For example, U-234/U-238 activity ratios in groundwaters reach values of 5 to 10. A primary mechanism is selective release and mobility of alpha decay products because of nuclear recoil effects. Preferential release of radioisotopes from nuclear waste forms or solubility limiting solid phases could affect repository performance; however, consequences of differential radioisotope release have not been regarded previously in performance assessments. For example, in DOE TSPA-SR performance assessment calculation 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 could be affected. Another possible application arises from the usefulness of decay-series disequilibrium to characterize open-system behavior in natural systems. For geologic disposal of nuclear waste, a criterion focused on chemical system closure could capture the essential performance feature of the natural system with respect to radionuclide transport and could be based quantitatively on uranium and thorium decay series isotope equilibria/disequilibria. This work is supported in part by the U.S. Nuclear Regulatory Commission (NRC) under contract number NRC-02-97-009. This is an independent product and does not necessarily represent the views or regulatory position of the NRC.

JJ11.44

MASS-BASED MEASURES FOR IMPACTS OF GEOLOGIC DISPOSAL. Joonhong Ahn, Paul L. Chambré, University of California, Berkeley, Dept of Nuclear Engineering, Berkeley, CA.

In previous performance assessments, radionuclide mass released from an independent waste canister was first obtained, and then used as the inlet boundary condition for the radionuclide transport into the far-field. 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. Masses of a radionuclide in the repository and in 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 ²³⁷Np in two extreme configurations. In configuration (A), *N* 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, *N* canisters are lined up in the direction perpendicular to the water flow, and are assumed to act independently 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 water stream, 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 canisters on the repository performance are clearly observed if the mass-based measures are applied.

JJ11.45

Abstract Withdrawn.

JJ11.46

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

This paper presents the latest results from part of the JNC programme of generic studies for the performance assessment of a potential high-level radioactive waste repository in Japan. The sorption of plutonium onto basalt and sandstone was studied as a function of redox conditions ranging from strongly reducing to oxidising. Initial thermodynamic modelling indicated that at pH 8, strongly-reducing conditions (using sodium dithionite, Eh ~-500mV) would provide predominantly Pu(III) in solution and that Pu(IV) would dominate between 100mV and +150mV (e.g. using hydroxy ammonium chloride). Hydrogen peroxide was selected as an oxidising agent that would give a high redox potential without causing experimental difficulties.

Batch sorption experiments were carried out at a liquid solid ratio of

5:1 for a 3-month equilibration period. Pu-238 was added to synthetic rock-equilibrated water as solutions of Pu(III), Pu(IV) and Pu(VI). Phase separation was a centrifugation, 0.45 μm filtration and 10000MWC0 filtration. Results were as follows. Under strongly-reducing conditions ($E_h \sim -500\text{mV}$), the distribution ratios (R_D values after filtration were similar for both rock types, values being $\sim 20\text{m}^3\text{kg}^{-1}$. Under intermediate conditions ($E_h = -40 - +40\text{mV}$), R_D values were generally between 20 and $360\text{m}^3\text{kg}^{-1}$, sorption being stronger onto basalt. Under oxidising conditions, ($E_h = \sim +360\text{mV}$), R_D values were in the range $1-70\text{m}^3\text{kg}^{-1}$ for basalt with some variation with phase separation method, and $\sim 5\text{m}^3\text{kg}^{-1}$ 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 underpredict the sorption of plutonium onto basalt under intermediate and oxidising conditions.

JJ11.47

SOFTWARE FOR THERMODYNAMIC SIMULATION OF HIGH-TEMPERATURE CHEMICAL EQUILIBRIUM. Boris G. Trusov, Vsevolod L. Klimov, Michael I. Ojovan, Olga K. Karlina, SIA RADON, Moscow, RUSSIA.

Thermodynamic computer-based simulation is an effective tool for chemical engineers and scientists engaged in thermochemical treatment of radioactive wastes. It allows investigation the systems with an arbitrary chemical composition using only reference data on thermochemical and 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 poorly investigated systems, especially containing high-level wastes. The goal of this 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 TERRA coupled with database on thermodynamic properties of about 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 most simplify specification 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, a set of 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 has been developed for IBM-compatible PC operating under the control of Windows 95/98/NT/2000. Examples of software TERRA application for a number of problems relating to the radioactive waste thermochemical treatment are demonstrated.

JJ11.48

GAS CONTAMINANT MOBILITY AT SUBSURFACE DISPOSAL AREA. Chang Oh, Todd Housley, Jeff Sondrup, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID; Sheldon Smith, Wayne Downs, Brigham Young Univ, Dept of Civil Engineering, Provo, UT; Vance Wilding, 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 903 Storage Area in July of 1959, and to RFP Building 774 for processing beginning in January, 1967. Processing included the mixing of the VOCs and miscellaneous oils 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 setups or "743 Series Waste" was double or triple bagged and placed in 55 gallon drums. Following processing and containerization, 743 Series

Waste drums were shipped to the SDA for burial located at the Idaho National Engineering and Environmental Laboratory (INEEL). From October 7, 1966 through November 3, 1968 approximately 9,691 743 Series Waste drums were buried in the Subsurface Disposal Area (SDA). Note that beginning in November 1970, transuranic waste received at the RWMC was placed in retrievable, surface-storage in compliance with direction to discontinue subsurface disposal of transuranic wastes. In order to understand the phenomena controlling the transport of volatile organic compounds (VOCs) from the burial site at the INEEL, we studied potential contaminant transport scenarios and evaluated the equilibrium relationships that exist 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.

JJ11.49

RESULTS OF MODELING VADOSE ZONE FLOW AND TRANSPORT AT THE 241-S-SX TANK FARMS, HANFORD SITE. A.J. Knepp, CH2M Hill Hanford Group, Richland, WA; R. Khaleel, Fluor Federal Services, Richland, WA; M.D. White, Pacific Northwest National Laboratory, Richland, WA.

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-S-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 presently within the vadose zone, contaminant movement through the vadose zone to groundwater, and contaminant movement in the groundwater to points of compliance. The two-dimensional models consider the accelerated movement of water around and beneath single-shell tanks that is attributed to bare, gravel surfaces and thus enhancing net infiltration of meteoric water (from winter precipitation and snowmelt). Water influx further amplified in the tank farm because of the umbrella effect (i.e., the effect of percolating water being diverted by an impermeable, sloping surface), created by large, 24-m diameter, buried tank domes. A principal objective of the investigation was to evaluate the effectiveness of interim barriers to the infiltration of meteoric water on the migration of contaminants from previous leak sources. The reference suite of simulations (Base Case) considered the migration of contaminants from field estimates of concentration distributions through the vadose zone and groundwater to the SSX 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 at the WMA boundary was delayed by 15 to 18 years with the interim barrier, the peak concentrations were reduced by 70%, 90%, and 57% for Te99, Cr, and NO₃, 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.

JJ11.50

INFLUENCE OF SALINITY ON THE HYDRAULIC CONDUCTIVITY OF COMPACTED BENTONITE. Won-Jin Cho, Jae-Owan 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 buffer material for the underground repository. The hydraulic conductivities in the compacted bentonites with dry densities of 1.0 Mg/m^3 to 1.8 Mg/m^3 were measured. Permeants were demineralized water, 0.4 M and 0.04 M NaCl solutions. 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/m^3 and 1.2 Mg/m^3 , 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 densities higher than 1.4 Mg/m^3 , the salinity has an insignificant 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 bentonite platelets and the thickness of diffuse double layer. For the dry densities of 1.0 Mg/m^3 to 1.8 Mg/m^3 , the half distance between bentonite platelets varies from 1.81 nm to 0.53 nm. In the

case of 0.04 M and 0.4 M NaCl solution, the thickness of the diffuse double layer are 1.64 nm and 0.48 nm respectively. Therefore, if the dry density of bentonite is over 1.4 Mg/m³, the distance between the platelets is so small that the contracted diffuse double layers are still overlapped resulting in the nearly constant hydraulic conductivity

JJ11.51

THERMODYNAMIC MODELING OF BINARY AND TERNARY ION-EXCHANGE EQUILIBRIA BETWEEN AQUEOUS SOLUTIONS AND THE ZEOLITE MINERAL CLINOPTILOLITE. Roberto T. Pabalan, F. Paul Bertetti, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

Because of their high cation-exchange capacity, zeolite minerals are potentially useful in the treatment of nuclear, municipal, and industrial wastewaters and 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 Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, are used to derive parameters for a solid solution model based on the Wilson equation, in addition to equilibrium constants for binary ion-exchange reactions. Where experimental data are not available, equilibrium constants are derived using a correlation method. The results indicate that, for the systems studied, the correlation method is successful in predicting ion-exchange equilibrium constants. The Wilson model, using parameters derived from binary systems, is applied to predictions of ternary ion-exchange equilibria.

JJ11.52

Abstract Withdrawn.

JJ11.53

Abstract Withdrawn.

JJ11.54

Transferred to JJ15.5

JJ11.55

MINERAL PHASE FORMATION FROM R7T7 WASTE GLASS ALTERATION AND ASSOCIATED CESIUM RELEASE. Y. Inagaki, K. Idemitsu, T. Arima, Kyushu Univ., Dept. of Nucl. Eng., Fukuoka, JAPAN; T. Maeda, H. Ogawa, F. Itonaga, Japan Atomic Energy Research Institute, Tokai Research Establishment, Ibaraki, JAPAN.

A large number of studies on HLW glass corrosion have shown that the glass reacts with water to form more stable mineral phases (alteration phases) during the long-term geological disposal. The potential phases have been evaluated by use of thermodynamic calculations to be SiO₂(am), gibbsite, zeolite, smectite and etc, depending on the conditions. Recent studies have suggested that the formation of zeolite can accelerate the glass corrosion. On the other hand, the formed phases such as zeolite and smectite are expected to have a retention capacity for some radionuclides. Therefore, the phase 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 R7T7 glass in alkaline solutions at elevated temperatures to accelerate the reaction, and mineral phases formed were analyzed by XRD. The results showed that analcime (zeolite) is formed as the dominant phase coexisting with SiO₂(am), and beidellite (smectite) or gibbsite coexists depending on the conditions. The solution analysis indicated that most of the cesium is retained in the phases of beidellite and analcime by sorption.

JJ11.56

Abstract Withdrawn.

JJ11.57

EFFECTS OF THE URANIUM CONTENT ON THE STRUCTURE OF IRON-PHOSPHATE GLASS WASTEFORMS. Diego O. Russo, Diego Rodríguez, Mario E. Sterba, Nuclear Materials Group, National Atomic Energy Commission, ARGENTINA; José Ma. Rincón López, Instituto E. Torroja, 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% Fe₂O₃, 50 to 74 wt% P₂O₅, 0 to 15 wt% UO₂). We have performed DTA/TG analysis so as to find the glass transition temperature, crystallization temperature and melting point. We also did dilatometric experiences to confirm the data obtained in the DTA/TG experiments and to get the softening point and thermal expansion coefficients. Additional data obtained from X-Ray diffraction, infrared spectrometry and Raman spectrometry, helped us to understand the role played by the polyvalent uranium in the vitreous structure of the glass. Finally, chemical durability of the glass was evaluated by water corrosion experiments (PCT Test and MCC-1 Test).

JJ11.58

SURFACE AND NEAR SURFACE REACTIONS IN SODIUM AND BORO SILICATE GLASSES EXPOSED TO AQUEOUS SOLUTION. V. Shutthanandan, S. Thevuthasan, D.R. Baer, J.P. Icenhower, and B.P. McGrail, Pacific Northwest National Laboratory, Richland, WA; S. Maheswaran, University of Western Sydney, Kingswood, AUSTRALIA; N. Dytlewski, Australian Nuclear Science and Technology Organization, Menai, AUSTRALIA; A.A. Saleh, 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 Na 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 D₂¹⁸O solution to understand the process that lead to ion exchange and sodium release. Solution compositions were used to determine the overall ion exchange rates. Our objective has been to relate the overall ion exchange rates to Na loss and reaction layer formation that occurs near the glass surface. A combination of Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), heavy ion elastic recoil detection (heavy ion ERD) and secondary ion mass spectrometry (Dynamic SIMS) techniques along with SIMNRA simulations were used to measure the sodium removal and the deuterium and oxygen uptake in the surface and near surface regions of the reacted glass 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 matrix dissolution rate. Although the sodium concentration is decreased in the near surface region, it is not completely removed from the outer surface. In the same region, there is also significant amount of ¹⁸O incorporated demonstrating considerable interactions between the water and the glass. On the basis of the depth distributions of Na, D and ¹⁸O, different regions including reaction and diffusion regions were identified in the glass samples. Work was supported by the U.S Department of Energy (DOE) Environmental Management Science Program, the Office of Biological and Environmental Research and Australian Institute of Nuclear Science and Engineering.

JJ11.59

SENSITIVITY STUDIES OF THE EFFECT OF CLADDING DEGRADATION ON TSPA RESULTS. Eric Siegmann, 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 - Viability Assessment (TSPA-VA) and have evolved to the recently released TSPA-SR (Sight 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 represents improvements in the waste form 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 dissolution (cladding not perforated). If all the cladding is perforated but unzipping is considered, the peak dose is within 4% of that of bare fuel. The unzipping model and UO₂ dissolution rate is sufficiently rapid so that an instant unzipping increases the dose by only 12% from the base case. Overall, the current cladding degradation model reduces the dose for the first 100,000 years by a factor of 16 when compared with bare fuel. This is because of the low initial cladding failure rate (2.1% including SSC and creep) and few failures from localized corrosion (late WP patch opening and little water entering the WPs). Rock overburden starts to fail the cladding after about 100,500 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.

JJ11.60

PRECIPITATION OF CRYSTALLINE NpO₂ DURING OXIDATIVE CORROSION OF NEPTUNIUM-BEARING URANIUM OXIDES.

Robert J. Finch, Argonne National Laboratory, Argonne, IL.

Neptunium-237 is a radioisotope that is of special concern, because of its potential mobility in Yucca Mountain groundwaters and its long half-life (2.14×10^6 yr). Current thermodynamic data indicate that crystalline Np(IV) dioxide NpO₂ is the stable Np solid in YM-like groundwaters; however, NpO₂ may be kinetically inhibited from precipitating from homogeneous Np(V)-containing solutions at near-ambient temperatures (~ 25 - 30°C) [1]. Here we report precipitation of crystalline NpO₂ during the corrosion of Np-doped U₃O₈ (Np:U approximately 1:8) in humid air at 90°C and 150°C . The Np-doped U₃O₈ was reacted for several weeks in 22 mL sealed stainless-steel vessels to which 0.3 mL of water and a few drops of H₂O₂ were added. X-ray powder diffraction (XRD) of unreacted solids confirmed U₃O₈ as the only crystalline solid present. Reacted solids were examined by scanning electron microscopy with energy-dispersive x-ray emission spectroscopy (SEM/EDS), and bladed crystals of a uranium (hydr)oxide comprise the predominant corrosion product; spherical, Np-bearing particles (~ 1 - 2 micrometer diameter) were also found. The XRD powder pattern from the reacted solids indicates that the bladed crystals correspond to 'dehydrated schoepite'. In addition to a small amount of unreacted U₃O₈, a cubic phase is also apparent, with a diffraction pattern identical to that of NpO₂. A full-pattern Rietveld refinement was performed, with alpha-U₃O₈, alpha-UO₂(OH)₂, and NpO₂ used as starting structural models for the three compounds. Refined unit-cell parameters for the cubic phase (NpO₂) are consistent with literature values for NpO₂. The refinement indicates that the reacted solids consist of approximately 79 mass % dehydrated schoepite, 9 mass % NpO₂, and 12 mass % U₃O₈. [1] Roberts et al. (1999). Abstracts volume for Migration 99. Program # A1-02.

JJ11.61

ASSESSMENT OF SPENT FUEL OF ALPHA CLASS NUCLEAR SUBMARINES.

Mikhail Bugreev, Evgueni Efimov, Sviatoslav Ignatiev, Dmitri Pankratov, Ludmila Riabya, Vladimir Tchitaykin, Institute of Physics and Power Engineering, Obninsk, RUSSIA.

The purpose of this work was to assess and analyze the radiation parameters of the spent nuclear fuel unloaded from the Alpha class Nuclear Submarines (NS) of Project 705K, determine its radioactivity composition and set the problems on its treatment as a radwaste. During 1960-1990 the Institute of Physics and Power Engineering has developed a unique reactor technology that has been realized in the building of the nuclear reactors (NR) cooled by lead-bismuth eutectic alloy in the primary circuit. Such NR were used in high-speed and maneuverable Alfa class NS. In order to support the coolant technology mastering a couple of land-based lead-bismuth test facilities have been created and operated as a prototype of such NS. All of the operated NR in question belonged to the intermediate neutron reactor type. The reactor fuel composition included the inter-metallic compound of uranium-beryllium with 90 percent of U-235 enrichment and dispersed into the beryllium matrix. At present all Alfa class NS are decommissioned. Opposite to water-cooled reactors the refueling of these NR was implemented through the unloading of a single removable blocks, including reactor core with dropped control rods, reflector (moderator), and upper closure fitting of biological shielding. So, in fact it was the unloading of a sub-critical reactor. The unloaded and non-unloaded spent removable blocks (SRB) have been allocated for a temporal storage at the coastal repository and inside the cut reactor modules at Kola Peninsula. However, the permanent storage of the SRB has not been assumed originally. In order to assess the problems of treatment of these SRB during its long-term unplanned storage the radiation parameters of that unloaded from the NS of the Project 705K are determined. Based on that determination the reasonable cost-effective project of step-by-step solution of these problems is proposed and the technological and other challenges that the project faces in its realization are considered. Our expertise has showed that: a) a rather high-level radioactivity is accumulated in the single SRB and even after 100 years of cooling it belongs to the HLW form; b) the stored SRB have a relatively low sub-criticality that is sensitive to the exposure of an external adverse conditions; c) the technology of SRB storage preparation does not exclude a possibility of water penetration into the SRB volume. Thus, the SRB stored are the source of a potential nuclear and radiation danger and must be undoubtedly removed from the reactors and coastal temporary repositories, dismantled and then finally reprocessed.

JJ11.62

THERMOTRANSPORT OF HYDROGEN IN MODIFIED ZIRCALOY-4 AS A FUNCTION OF HYDROGEN AND OXYGEN CONCENTRATIONS.

Hyun Sook Kim, Kyung Sub Lee and Seon jin

Kim, Hanyang Univ, Dept of Material and Science Engineering, Seoul, KOREA.

The hydrogen redistribution induced by the thermotransport in modified Zircaloy-4 at temperatures likely to be encountered in nuclear power reactors (300 - 340°C) was investigated by means of steady state techniques. The modified Zircaloy-4 was prepared by changing the chemical compositions of Zircaloy-4, which is used widely as a nuclear fuel cladding material in pressurized water reactors. Under the influence of a temperature gradient, hydrogen in modified Zircaloy-4 moved towards the colder regions until a steady state is reached. Zirconium hydride was precipitated at the cold end of the specimen due to the low solubility of hydrogen in Zircaloy-4 and it was confirmed by XRD, OM, SEM. In addition, the change of Q^* for hydrogen, which describes the sign and magnitude of the thermotransport, with increasing hydrogen and oxygen concentration was also investigated in modified Zircaloy-4. The values for Q^* for hydrogen in modified Zircaloy-4 alloys were found to be about 7 kcal/mole and the value of Q^* for hydrogen was not affected by hydrogen concentration. While the value of Q^* for hydrogen decreased with increasing oxygen concentration and it was considered to be due to the trapping of hydrogen by oxygen. Keywords: hydrogen, modified Zircaloy-4, thermotransport, oxygen, heat of transport

JJ11.63

NEPTUNIUM INCORPORATION IN URANIUM(VI) COMPOUNDS FORMED DURING THE AQUEOUS CORROSION OF

NEPTUNIUM-BEARING URANIUM OXIDES. Robert J. Finch, Edgar C. Buck, and Stephen F. Wolf, Argonne National Laboratory, Argonne, IL, Battelle Pacific Northwest National Laboratory, Richland, WA.

Neptunium-237 (^{237}Np) is an isotope relevant to evaluating the long-term performance of a geologic repository for high-level nuclear waste, because of its potential mobility in Yucca Mountain groundwaters and its long half-life (2.14×10^6 yr). We report on the first experimental studies of Np behavior during the aqueous corrosion of unirradiated Np-bearing uranium oxides. In the experimental studies described here, Np-doped uranium oxides were reacted in humid air within sealed stainless-steel vessels, to which H₂O₂ was added. The starting solids were reacted at 90°C and 150°C for several weeks. The reacted solids are being examined by scanning and transmission electron microscopies (SEM and TEM) 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 schoepite is the predominant uranium(VI) compound formed in these tests. Crystalline NpO₂ also precipitated during these experiments. Dehydrated schoepite may be expected to incorporate some Np into its structure, and coexistence of NpO₂ and dehydrated schoepite may help define the miscibility of Np in dehydrated schoepite in the presence of NpO₂ under these conditions. The Np concentration in dehydrated schoepite 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.

JJ11.64

A HIGH SURFACE AREA-TO-SOLUTION VOLUME, STATIC TEST OF EBR-II IRRADIATED MIXED-OXIDE FUEL.

J. A. Fortner, P.A. Finn, and M.M. Goldberg, Argonne National Laboratory, Argonne, IL; and Colleen Shelton-Davis, Idaho National Environmental Engineering Laboratory, Idaho Falls, ID.

The Department of Energy National Spent Nuclear Fuel Program (NSNFP) is evaluating the long-term corrosion behavior of DOE-owned spent nuclear fuel (DOE-SNF). Permanent disposal of the spent fuel is proposed in a repository to be located in the volcanic tuff beds near Yucca Mountain, Nevada. It is the responsibility of the NSNFP to determine the release of fission products from the DOE spent fuel and the release and redistribution of fissile material resulting from spent fuel corrosion. We describe batch tests on irradiated mixed oxide (MOX) fuel from the Idaho Experimental Breeder Reactor (EBR-II) in Yucca Mountain groundwater. The static batch tests feature very high surface area (fuel grains) to small groundwater volume (high S/V). The objectives of the static batch tests are to examine the composition of the thin film of water that contacts irradiated MOX fuel, to evaluate the alteration-phase formation and paragenesis under conditions that maintain a high S/V, and to compare results of these tests to others performed at low S/V conditions and/or at different solution replacement rates. Under conditions of frequent replacement of the batch test solution and high S/V, the fuel released radionuclides at a rate consistent, to within an order of magnitude, with that in unsaturated (drip) tests of EBR-II MOX which are conducted with much more frequent solution

replacement and at much lower S/V. 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 unsaturated tests. These results suggest an approach to solution saturation of a dissolving species or solution depletion of a groundwater species. Thus, spent oxide fuel corrosion does not experience a strong acceleration from increased fuel surface area to solution volume (S/V) effects. This is contrary to other systems where the S/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.

JJ11.65

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

According to Fujino 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 Orlander suggest that uranium should be oxidized to U₅ in spent UO₂. Compounds containing U₅ are rare and usually unstable. Known examples include, U₂MoO₈, U₅BO₃, UVO₅, and U₅O₁₂Cl. Burns and Finch found crystallographic evidence for U₅ in a natural mineral, wyartite, [CaU₅(UO₂)₂(CO₃)O₄(OH)(H₂O)₇]; however, this orthorhombic phase is extremely unstable. The existence of U₅ in a solid phase cannot be determined directly but must be deduced 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 certainty, U₅ from a mixture of U₄ and U₆. In this study, the nature of the U-O bond was investigated with Electron Energy-Loss Spectroscopy (EELS) on the Transmission Electron Microscopy (TEM). Through measurement of the covalent contribution 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 covalency in the M-O bond in the spent fuel, as expected, given the major substitutions are rare earths and actinides. In contrast, the O-K edge from (VI) uranophane shows only covalent M-O bonding. The M-O covalency shifts the O-K edge to around 540 eV.

JJ11.66

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

The near-field migration behavior of radionuclides in a nuclear-waste repository will be influenced, in part, by their equilibrium solubilities and/or adsorption affinities as trace components onto the 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 following their release from the spent fuel matrix. The potential for incorporating rare earth elements (REE) into crystalline compounds has been evaluated by precipitating uranyl phases from aqueous solutions containing 2.1 ppm Ce⁴⁺, at a temperature of 90°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 (UO₂(OH)₂; cf. JCPDS card #30-1403) and several uranyl carbonate phases. An analysis of the leachant, leachate, and solid phase reaction products (the latter, after dissolution in a nitric 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 20, and finally 11 ppm for crystals produced in 7, 35, and 190 day tests, respectively. This trend correlates with a coarsening of the crystals over the same time interval, suggesting a lowering of the potential for Ce incorporation as the overall surface area/volume ratio of the crystals decreases. This correlation indicates that surface adsorption is playing a key role in the immobilization of cerium by the solid phase in these experiments.

JJ11.67

SORPTION-REAGENT METHOD IN LIQUID RADIOACTIVE WASTE MANAGEMENT. Valentin Avramenko, Veniamin Zhelezov, Elena Kaplun, Dmitri Marinin, Tatiana Sokolnitskaya, Anna Yukhkam, Inst of Chemistry FEDRAS, Vladivostok, 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 management technologies. 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 cobalt-60. It was shown by comparative analysis of radionuclide removal efficiency by traditional selective sorbents and developed sorption-reagent materials that the latter have the highest distribution coefficients in systems too complex for pure sorption/ion-exchange decontamination. For example, the sorption-reagent materials 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 formed whether as a result of ion-exchanger filters regeneration in LRW management systems 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 (SRW) 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 deactivation waste. The decontaminated LRW met all the national (and international) safety standards. Total volume of SRW sent for final disposal was 0.6 cubic meters.

JJ11.68

POROUS CRYSTALLINE SILICA (GUBKA) AS A INORGANIC SUPPORT MATRIX FOR NOVEL SORBENTS. T.J. Tranter, Idaho National Engineering and Environmental Laboratory (INEEL), Idaho Falls, ID; A.S. Aloy, N.V. Sapozhnikova, Khlopin Radium Institute, St. Petersburg, RUSSIA; A.A. Tretyakov, Mining and Chemical Combine, Zheleznogorsk, RUSSIA; A.G. Anshits, Institute of Chemistry and Chemical Technology, Krasnoyarsk, RUSSIA; D.A. Knecht, T.A. Todd, and J. Macheret, INEEL, Idaho Falls, ID.

Inorganic ion exchange media typically exist as fine powders, making large-scale use impractical, unless the media can be affixed 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, that 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 (Gubka) matrix. This approach allows for target radionuclides to be adsorbed into a porous micro-crystalline glass matrix which encapsulates the contaminant and becomes the final waste form. Subsequent to adsorption of the radionuclides, the Gubka matrix can be compressed in a hot uniaxial press, resulting in an overall volume reduction (vol. liquid/vol. final waste form) of 1400. The porous glass matrix is produced in Russia using fly ash residue from coal combustion power generating plants. It consists of consolidated arrays of hollow glass cenospheres and is termed Gubka which is the Russian word for sponge. This paper describes results of a collaborative research program between the Khlopin Radium Institute (KRII), 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 molybdophosphate (AMP) for the removal of cesium from acidic liquid waste and Octyl(phenyl)-N-N-diisobutyl-carbamoylmethylphosphine oxide (CMPO), for the removal of lanthanides and actinides from acidic liquid) have been successfully incorporated into Gubka matrices. Test results for cesium and americium removal, using AMP-Gubka and CMPO-Gubka, respectively, will be discussed.

JJ11.69

DEMONSTRATION OF THE FEASIBILITY OF RECOVERING AMERICIUM AND CURIUM ISOTOPES FROM A LANTHANIDE BOROSILICATE GLASS. Tracy S. Rudisill, David K. Peeler, and Thomas B. Edwards, Westinghouse Savannah River Company, Aiken, SC.

A solution containing kilogram quantities of highly radioactive isotopes of americium and curium (Am/Cm) is currently stored in a process tank at the Department of Energy's (DOE's) Savannah River Site. This tank and its vital support systems are old, subject to deterioration, and prone to possible leakage. For this reason, a decision was made to vitrify the material and store the glass until

programmatic decisions on use or disposal are made by the DOE. Potentially, the glass could be shipped to the isotope production and distribution programs at the Oak Ridge National Laboratory for californium-252 production and use by the transplutonium research community. To facilitate subsequent recovery of the Am/Cm, a lanthanide borosilicate glass was selected for the vitrification process since the lanthanides are highly soluble in strong acid solutions. 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 elements as surrogates for Am/Cm due to 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 particle size, and dissolved in 8M nitric acid at 110°C. Under these conditions, at least 98% of the lanthanide oxides in the glass dissolved in less than 2 h meeting a recoverability criterion established for the vitrification process and imposing no limitations on the acceptable glass composition region.

JJ11.70

SYNTHESIS, CRYSTAL CHEMISTRY AND ENERGETICS OF MICROPOROUS SILICOTITANATES IN THE $(K_{1-x}Cs_x)_3Ti_4Si_3O_{15}(OH) \cdot nH_2O$ SYSTEM. H. Xu, A. Navrotsky, 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, M.L. Balmer, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA.

Crystalline silicotitanate (CST) ion exchangers are of considerable interest because of their high selectivity for radioactive ^{137}Cs and thus their potential application in the separation of ^{137}Cs from aqueous nuclear wastes. In this study, we synthesized a suite of microporous phases with the compositions $(K_{1-x}Cs_x)_3Ti_4Si_3O_{15}(OH) \cdot nH_2O$ ($n = 4$ to 6 , $0 \leq x \leq 1$) using the hydrothermal methods. Rietveld analysis of synchrotron XRD data indicates that these phases are isostructural with the mineral pharmacosiderite (space group $P43m$) and that the lattice parameter a increases linearly with increasing Cs content. The enthalpies of formation from the oxides and from the elements were determined by drop solution calorimetry with $2PbO \cdot B_2O_3$ being the solvent at 974 K. Our results show that the formation enthalpies become more exothermic with increasing Cs/K ratio. Thus the Cs uptake in this solid solution series is largely thermodynamically driven.

JJ11.71

A-Nb-Ti-Si (A = Na, K, Rb, Cs, Sr, Ba) OXIDE FRAMEWORK CONDENSED AND MICROPOROUS PHASES AND THEIR APPLICATION TO RADIONUCLIDE SEQUESTRATION AND IMMOBILIZATION. May Nyman, Tina M. Nenoff, Sandia National Laboratories, Albuquerque, NM; Robert S. Maxwell, Lawrence Livermore National Laboratory, Livermore, CA; Akhilesh Tripathi and John B. Parise, Department of Chemistry and Department of Geosciences, State University of New York, Stony Brook, NY; Alexandra Navrotsky and Hongwu Xu, Dept. of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA.

Crystalline silicotitanate (CST) is a microporous ion exchanger that has undergone extensive and advanced testing for the application of selective removal of radioactive Cs from DOE defense wastes. Substitution of small amounts of Nb^V into the Ti^{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 protons; 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 A-Nb-Ti-Si (A = Na, K, Rb, Cs, Sr, Ba) oxide framework materials, geared toward the application of radionuclide sequestration and immobilization, where condensed phases are optimized toward stability, and microporous phases are optimized toward selective, high capacity or rapid ion exchange. We report here two new families of niobate-based ion exchangers in which heterovalent substitutions are made. Ion exchange and stability properties are investigated as a function of framework substitution, particularly with regard to selective exchange of divalent cations. We also report a series of extremely stable titanosilicate-based 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.

JJ11.72

Transferred to JJ12.5

JJ11.73

RELEASE BEHAVIOR OF NEPTUNIUM, PLUTONIUM, URANIUM AND TECHNETIUM FROM THE METALLIC WASTE FORM FROM THE ELECTROMETALLURGICAL TREATMENT PROCESS. S.G. Johnson, M. Noy, T. DiSanto and T.L. Moschetti Argonne National Laboratory-West, Idaho Falls, ID.

Argonne National Laboratory is developing an electrometallurgical treatment for spent fuel from the experimental breeder reactor II. A product of this treatment process is a metal waste form that incorporates the stainless steel cladding hulls, zirconium from the fuel and the fission products that are noble to the process, i.e., Tc, Ru, Pd, Rh, Ag. The nominal composition of this waste form is stainless steel/ 15 wt% zirconium/ 1-4 wt% noble metal fission products / < 1 wt % U. The process used to produce the metal waste form ingots from the cladding hulls is straightforward. The hulls after being removed from the electrorefiner are introduced to a furnace where the adhering salt from the electrorefiner is distilled off. The hulls are then placed into a crucible and, if necessary, small amounts of zirconium 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, U, Pu, and Np, and Tc is evaluated using a standardized leach test modeled after ASTM C1220. Alloys of the base composition stainless steel with 15 wt% zirconium were produced that were doped with U, Np, Pu and Tc. 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 leachant was 40 m⁻¹. The leachant used was simulated ground water, SJ-13. The surface finish of each monolithic sample was prepared to, as nearly as possible, an identical state. The tests were performed in triplicate to provide for adequate gauge of the precision. The tests were terminated at 14, 34 or 91 days and the samples removed from solution, dried and weighed. The test solutions were acidified to 2 vol.% acidity using high purity nitric acid. The test vessels were subjected to an 18 hour 90 C acid strip using a 2 vol.% nitric solution. This acid strip solution was also analyzed. The test and the acid strip solutions were analyzed for Fe, Cr, Ni, Mo, Mn, Zr, Pu, U, Np and Tc using inductive coupled plasma mass spectrometry (ICP-MS). The intent of these tests was to determine which, if any, of the various 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 the 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.

JJ11.74

THERMAL BEHAVIOR OF POLYMERIC MATRICES FOR NUCLEAR WASTE IMMOBILIZATION BY DSC AND TG. Edésia 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 polyethylene, in pellets form, was tested as component of the matrices. Vanadium pentoxide catalyst and ion exchange resins with inactive cesium were used as the dangerous waste. The polymeric matrices, pure and with waste, obtained by the solubilization of polyethylene recycled in isoparaffin oil and kerosene oil, were macroscopically homogeneous. The thermal behavior of all the matrices was evaluated by Differential Scanning Calorimetry (DSC) and Thermogravimetry - TG. With the DSC curves it was possible to verify the melting and degradation temperatures of the polyethylene and matrices. From the TG curves it was possible to determine the mass variations during the heating of the samples. These curves evidenced that the processing of the polymeric matrices do not alter the thermal behavior of the polymeric matrices. Use of the recycled polyethylene indicates a great potential for immobilization of dangerous waste.

JJ11.75

AGEING OF BITUMEN WASTE FORM IN WET REPOSITORY CONDITION. Michael I. Ojovan, Natalya V. Ojovan, Zoya I. Golubeva, Irene V. Startceva, Alexander S. Barinov, SIA Radon, Moscow, RUSSIA.

Bitumen waste form for low and intermediate level waste (LILW) immobilisation is under investigation at SIA 'Radon' for about three decades. Bituminized waste blocks were prepared at industrial plant on base of NPP-operational waste. Physical and chemical parameters of bitumen waste form containing 31 wt.% salts were investigated

after its long-term storage in an experimental shallow-ground repository during 12 years. Leaching behaviour of bituminized waste form was studied: 0.002% of initial radioactivity inventory was released from the block during 12 years of storage. Non-homogeneous distribution was determined for both salts and radionuclides along vertical axis. Fraction composition of bitumen host matrix was studied. Three main components of bitumen: asphaltenes, saturated and aromatic hydrocarbons were separated for different parts of bituminized waste block. The bitumen fractions were distributed vertically non-homogeneously as well as the radioactivity of bitumen host matrix. The radioactivity of bitumen was maximal in the middle part of block. Ageing of bitumen waste form during 12 years is characterised mainly by the increase of asphaltenes fraction content (about 4%). The changes in the bitumen waste form will be used for modelling its long-term behaviour in the repository conditions.

SESSION JJ12: WASTE PROCESSING

Chairs: Bill Holtzscheiter and Frederick M. Mann
Thursday Morning, November 29, 2001
Republic B (Sheraton)

8:30 AM JJ12.1

WASHING SRS HLW SLUDGES IN PREPARATION FOR VITRIFICATION - FULL SCALE RESULTS AND BEHAVIOR OF ACTINIDES AND U-235 FISSION PRODUCTS. T.L. Fellingner, N.E. Bibler, R.F. Swingle, M.S. Hay, and D.C. Bumgardner, Westinghouse Savannah River Co., Aiken, SC.

Radioactive high level waste (HLW) sludges at Savannah River Site are stored as caustic slurries in million gallon tanks. These slurries are being processed and immobilized into borosilicate glass in the Defense Waste Processing Facility (DWPF) for geologic disposal. A batch of feed for the DWPF is approximately 500,000 gallons of washed slurry and is obtained by combining slurries from different tanks into a single million gallon feed tank. Washing occurs in this tank. This paper discusses the washing of the next batch of feed for the DWPF. Results of a laboratory scale test with actual radioactive slurry and of 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, nitrite, and nitrate concentrations in the slurry. In unwashed slurry, these concentrations are too high. They are reduced by washing the slurry several times with inhibited water (IW) (0.01 M NaOH and NaNO₂). Reduction of these is necessary because sodium affects glass quality and nitrate and nitrite affects NO_x 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 Jantzen and James Laurinat, Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC.

A nitrated aluminosilicate in the sodalite/cancrinite mineral family (Na₈Al₆Si₆O₂₄(NO₃)₂) and sodium diuranate (Na₂U₂O₇) formed intermittently in the Savannah River Site (SRS) 2H High Level Waste (HLW) Evaporator during operations between 1996-1999. Eventually, the aluminosilicate scale deposits caused the SRS 2H Evaporator to become completely inoperable. Accumulation of the sodium diuranate phase, which appears to have co-precipitated with the aluminosilicate phase, has caused criticality 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 supersaturation, 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 caustic solutions to form a sodium aluminosilicate (NAS) hydrogel at ambient temperature. The hydrogel converts to Zeolite-A (Na₁₂Al₁₂Si₁₂O₄₈•27H₂O) under hydrothermal conditions at elevated temperature, e.g. the conditions existing in the SRS evaporators. The complete set of sequential densification (aging) transformations is: NAS gel ⇒ Zeolite-A(cubic) ⇒ sodalite(cubic) ⇒ cancrinite (hexagonal). The initial step is the saturation of the evaporator feed tank solutions with respect to the parent NAS gel

phase, the primary phase from which all the others are derived. The NAS gel phase formation is also the kinetically most rapid step in the formation sequence. Therefore, the thermodynamic modeling was performed on the NAS gel. While thermodynamically derived activity diagrams, also known as stability diagrams, are commonly used to represent equilibria between mineral species and aqueous solutions on geologic time scales, activity diagram representation is appropriate since the formation of the NAS gel and the sodium diuranate are kinetically very rapid compared to the evaporator residence times (2-3 hours).

9:00 AM JJ12.3

PROOF-OF-CONCEPT FLOWSHEET TESTS FOR CESIUM REMOVAL FROM TANK WASTE BY CAUSTIC-SIDE SOLVENT EXTRACTION. David B. Chamberlain, Scott Aase, Hassan A. Arafat, Cliff Conner, Ralph A. Leonard, Monica C. Regalbuto, and George F. 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 BOBCalixC6; a modifier, 0.50 M Cs-7SB; and a suppressant, 0.001 M trioctyl amine in a branched paraffinic hydrocarbon diluent, IsoparL. 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 2-cm centrifugal contactor at ANL. Three short-term (3-4 hours) tests were completed to demonstrate various aspects of the flowsheet. These tests were followed by a 71-h 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 with a decontamination factor greater than 40,000, (2) concentration of cesium in the aqueous strip effluent by a factor of 15 using dilute nitric acid, and (3) stripping the solvent sufficiently to allow it to be recycled many times. The results from these tests, and the improvements that were made to the 2-cm centrifugal contactors to improve extraction efficiency, will be discussed.

9:15 AM JJ12.4

CHEMICAL INTERACTIONS OF UOP INSiV[®] IE-911 (CST) WITH SRS WASTE SIMULANTS. May Nyman, James L. Krumhansl, Carlos Jove-Colon Pengchu Zhang, Tina M. Nenoff, Thomas J. Headley, Sandia National Laboratories, Albuquerque, NM; Yali Su and Liyu Li, Pacific Northwest National Laboratory, Richland, WA.

UOP IONSIVNSIV[®] IE-911 IE-911 is a bound form of crystalline silicotitanate (CST) for use in ion exchange columns that was extensively tested for removing Cs-137 from the Savannah River Site (SRS) tank wastes. In some simulant tests, column plugging incidents were observed, which led to thorough investigations to determine the causes and to develop protocols to avoid future plugging incidents. A related problem was the apparent decrease in Cs scavenging capacity in some long-term tests. Our studies revealed that two column plugging precipitates could form as a result of the interaction of IE-911 with the highly basic, high ionic strength, average salt simulant (simulant of averaged SRS waste tank compositions). One type of precipitate is a poorly crystalline, hydrous sodium niobate and the second is crystalline aluminosilicate zeolite, or cancrinite. The source for the hydrous sodium niobate precipitate was determined to be a minor impurity phase that is a byproduct of CST manufacturing. The mechanisms of dissolution and re-precipitation of this phase in column pretreatment fluid (2N NaOH) was investigated, and a pretreatment protocol to rid IE-911 of this impurity was devised. Further, the IE-911 manufacturing company (UOP) modified its production procedure in a similar manner to rid IE-911 of this impurity. On the other hand, the source material for the aluminosilicate zeolite precipitate was determined to be predominantly from the waste solution rather than the IE-911. Solubility experiments coupled with a thermodynamic analysis provided a protocol to predict when aluminosilicate precipitation will and will not occur. This, in turn, suggested that dilution may be used to prevent in-service column plugging by aluminosilicate precipitation. Finally, it was also established that aluminosilicate precipitation on the surfaces of the IE-911 granules could also account for an apparent decrease in equilibrium K_d as well as decreasing the kinetics of Cs sorption.

9:30 AM JJ12.5

INVESTIGATION OF CHEMICAL AND THERMAL STABILITIES OF Cs-LOADED CRYSTALLINE SILICOTITANATE. Yali Su, Liyu Li, James S. Young, Pacific Northwest National Laboratory, Richland, WA; M. Lou Balmer, Caterpillar Inc., Peoria, IL.

An inorganic ion exchanger based on crystalline silicotitanate (CST),

IONSIV IE-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. While 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-911 was exposed to waste simulant at 55°C and 80°C for durations of 1 to 60 days to determine if irreversible desorption of Cs from IE-911 occurs and the cause of desorption, as well as the time/temperature profiles over which desorption occurs. The Cs-loaded ion exchangers were analyzed by XRD, Raman spectroscopy, and SEM/EDS. High Cs loading, high simulant/IE-911 ratio, and high-temperature heat treatment could cause irreversible Cs desorption. SEM results showed that a crystalline sodium aluminosilicate (nitrate cancrinite) phase precipitated on the surface of IE-911 shortly after exposure to simulant both at 55°C and at 80°C. The morphology of the coating depends on the heat-treatment temperature, heat-treatment time, IE-911-to-simulant ratio, and simulant composition. IE-911 is not the major Si source for the aluminosilicate precipitation. The coating should not be the major reason for the irreversible Cs desorption because it was found on the surface of almost all the heat-treated IE-911 samples. Cancrinite-type aluminosilicate has large size openings in its structure so that Cs should be able to diffuse through these pores to IE-911 when the temperature was lowered. The mechanism for irreversible Cs desorption is under investigation and will be presented in the meeting.

9:45 AM JJ12.6

SYNTHESIS AND EVALUATION OF URANIUM- AND THORIUM-IMPRINTED RESINS. K.L. Noyes, M. Draye *, A. Favre-Rguillon**, J. Foos **, A. Guy **, and K.R. Czerwinski, Nuclear Engineering Department, Massachusetts Institute of Technology, Cambridge, MA. *Ecole Nationale Supérieure de Chimie de Paris, Paris, FRANCE. **Conservatoire National Des Arts Et Metiers, Laboratoire Des Sciences Nucleaires, Paris, FRANCE.

Organic based ion selective resins have a desirable properties as materials for the separation and treatment of nuclear waste: ease of synthesis, high metal ion complexation ability, and flexibility for different nuclear waste management applications. For most chelating polymers, the ligand is deemed to be of primary importance for the interaction with the targeted 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 target metal ion.

Ion exchange resins were created to selectively complex either uranium or thorium ions. The target metal ion, either UO₂²⁺ or Th⁴⁺, was dissolved in the solvent, CCl₂H₂, while the resin was created around the ions to provide a unique structure based upon each metal. These resins were synthesized by a radical polymerization method, producing a reusable organic solid. The resins were qualified by obtaining values for their proton exchange capacities and data to define their complexation kinetics. Proton exchange capacities were determined using an indirect titration and were found to be 6.40 meq/g for the uranium-based resin and 4.61 meq/g for the thorium-based resin. Data for the resins kinetics were obtained at pH 1.0, 2.5, 4.0, and 5.5. Results show that the templated resin removed the target actinides 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 JJ13: GLASS STRUCTURE AND CORROSION

Chairs: Ned E. Bibler and Olivier Spalla
Thursday Morning, November 29, 2001
Republic B (Sheraton)

10:30 AM JJ13.1

ORIGINS OF DISCREPANCIES BETWEEN KINETIC RATE LAW THEORY AND EXPERIMENTS IN THE Na₂O-Al₂O₃-B₂O₃-SiO₂ SYSTEM. B.P. McGrail, J.P. Icenhower, M.H. Engelhard, D.R. Baer, and J.G. Darab. Pacific Northwest National Laboratory, Richland, WA.

Single-pass flow through (SPFT) experiments were performed with a series of simple mineral analog glasses along the albite-reedmergnerite join [(2.5-y)Na₂O·xAl₂O₃·(0.5-x+y)B₂O₃·7SiO₂, 0 ≤ y ≤ 1] and with a high-level waste analog glass (1.47Na₂O·1.86B₂O₃·7SiO₂) that has been tested extensively in France. Dissolution rates for these glasses were determined at fixed solution pH as a function of SiO₂(aq) activity up to amorphous silica saturation. At early times in the experiments (non-steady state conditions), there is no correlation between SiO₂(aq) 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 B/Na ratio is >1 of 3-coordinate boron (determined from ¹¹B MAS-NMR) into borate units that are much more reactive than the bulk glass matrix. These factors dominate the early time behavior in static experiments, and so explain the reported strong deviation from expected behavior based on the transition state theory (TST) of chemical kinetics. In contrast, once steady state is obtained, the dissolution rates vary linearly with respect to a finite range of SiO₂(aq) activities that depends on glass composition. For glasses with few NBO sites, steady-state dissolution rates vary linearly with respect to SiO₂(aq) activity all the way to SiO₂(am) saturation, which is in direct accord with expectations from TST rate laws. In contrast, glasses with a significant population density of NBO sites are susceptible to alkali ion exchange reactions that cause enhanced rates of glass dissolution in silica-saturated solutions. Consequently, the behavior of these glasses deviates strongly from TST. By doping the aqueous phase with Si-30 and tracking its penetration profile in the glass surface layers, it was also possible to quantitatively evaluate alternative models that consider the gel layer as a significant mass transport barrier. In general, the results were more consistent with secondary reaction mechanisms as the source of deviations from TST. Consideration of these important secondary effects is critical to developing an improved kinetic theory for dissolution of silicate glasses and minerals.

10:45 AM JJ13.2

X-RAY ABSORPTION STUDIES OF VANADIUM VALENCE AND LOCAL ENVIRONMENT IN BOROSILICATE WASTE GLASSES. David A. McKeown, Isabelle S. Muller, Keith S. Matlack, and Ian 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 sulfur-bearing radioactive wastes 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-load-limiting constituent in this process, because of its low solubility in silicate melts. Recent investigations have suggested that adding vanadium to borosilicate formulations improves sulfur solubility in the melt. It is therefore of interest to determine if vanadium has any 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 9 wt.%. The data for all glasses investigated indicate that most, if not all, vanadium is 5 valent and is tetrahedrally coordinated by four oxygen atoms. There is no evidence from the data of V-S bonds in any of the glasses investigated. Both XANES and EXAFS also show that melter glasses synthesized under reducing conditions can have small amounts of V⁴O₅ up to approximately 20 to 25% of all vanadium present in the glass with the remainder being V⁵O₄. Increasing concentrations of penta-coordinated V⁴ in the melter glasses can be correlated with amounts of reductant 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 additional sulfur bonding sites in the glass structure; however, vanadium bonding to SO₄ sulfate tetrahedra cannot be completely ruled out.

11:00 AM JJ13.3

STRUCTURAL ENVIRONMENT OF HAFNIUM IN BOROSILICATE GLASSES WITH VARYING SODIUM ALUMINUM RATIOS. Dana L. Caulder, Galileo Laboratories, San Jose, CA; Linda L. Davis, Department of Geology, Northern Arizona University, Flagstaff, AZ; John G. Darab, Battelle, Pacific Northwest National Laboratory, Richland, WA; David K. Shuh, Corwin H. Booth, Jerry J. Bucher, Ernest O. Lawrence Berkeley National Laboratory, Berkeley, CA; Denis M. Strachan, Battelle, Pacific Northwest National Laboratory, Richland, WA.

Hafnium-bearing glass series were made in crucibles at temperatures between 1450 and 1560°C. The manner in which the Hf is incorporated into the crystal-free glasses was the object of an X-ray absorption spectroscopic study. Data for glasses with peraluminous to peralkaline compositions are presented here. We note an unusual feature at the white line maximum at the Hf L₃ absorption edge: 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 noted in the L₃ XANES of Er and Lu. This split peak is best observed in the second derivative spectrum of the XANES as a double well. The double well is indicative of crystal field splitting of the vacant d-manifold of Hf(IV), and is characteristic of Hf in an octahedral coordination environment. As the composition in a glass series changes from peralkaline (where for these compositions, Na>Al) to peraluminous (Al>Na), the double well disappears, indicating a

change in the coordination environment from octahedral to perhaps 7- or 8-fold coordination. Analysis of Hf L₁ XANES corroborates that of the Hf L₃ XANES. Our EXAFS studies at the Hf L₃ edge reveal that all the peralkaline glasses are essentially structurally identical to each other, and similar to a Hf siloxane standard in which Hf is in octahedral coordination. The Hf-O bond distances are near 2.06 Å, typical of 6-coordinate Hf, and bond distances for the second shell Si (or Na, B, or Al) and O are consistent with the six-membered ring structural motif observed in the Hf siloxane. The data for the peraluminous glasses is consistent with the presence of two different Hf environments: one similar to that in the Hf in peralkaline glasses and, additionally a structural motif distinct from the siloxane.

11:15 AM JJ13.4

INFLUENCE OF THE ALTERATION LAYER ON A NUCLEAR WASTE GLASS DISSOLUTION. Arnaud Gauthier, GRECI Faculte des Sciences, Reims, FRANCE; Philippe Le Coustumer, Jean-Hugues Thomassin, ESIP, Faculte des Sciences, Poitiers, FRANCE.

In order to determine the influence of the alteration layer on the R7T7 nuclear waste glass dissolution, some experiments were conducted. Alteration tests were performed in different aqueous media (pure water, siliceous and silico-phosphatic solutions) at 90°C. The S/V ratio is closed 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, traducing a stabilization of the alteration rate. In fact, by comparison to other studies in static condition, the glass alteration rate r_0 diminishes in a constant way during the four tests. The surface solid analysis shows the development of microscopic crystals at the external part of the glass during the alteration in pure water and siliceous media. 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 studies show crystallization 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 Lyonnard, Jacques Lambard, Antoine Thill, CEA Saclay, Service de Chimie Moleculaire, Saclay, FRANCE; Philippe Barboux, Ecole Polytechnique, Laboratoire de Physique de La Matiere Condensee, 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, without drying the morphology of the porous layer at the mesoscopic scale (1-100nm). In the presentation we will 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 present the effect of the initial Zr content on the morphology of the gel layer. The glass grains (32-50microns) 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 examined through Small Angle X-ray Scattering (SAXS) and Anomalous Small Angle X-ray Scattering (ASAXS) at the K-edge of the hardener element Zr. The results shows that the layer is nanoporous. Furthermore, the size of the pores and the porous 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 remains very small (1nm), then the thickness of the layer remains constant but the pores 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 Pirlet, Karel Lemmens, Pierre Van Iseghem, SCK.CEN, Waste and Disposal Department, Mol, BELGIUM.

Boom Clay is the candidate geological formation in Belgium for disposal of vitrified high level waste for which Np-237 and Tc-99 are some of the main critical radionuclides. The results of corrosion tests

involving glasses doped with Np and Tc depend strongly on the redox conditions of the media contacting the glass. Tests with the R7T7 glass and the PAMELA glass doped with Np and Tc were performed in two clay media that may interact with the glass during the geological disposal. The first test medium consisted of FoCa-clay which is an oxidised clay and the second was a mixture of backfill material with metal corrosion products and Boom Clay. Lower Np and Tc concentrations were found in Boom Clay compared to the FoCa-clay. In FoCa-clay, Np and Tc were mostly in their oxidised form. If Tc is clearly present in the soluble pertechnetate form, the Np concentrations are smaller than expected for the chemistry of Np(V) in the medium. Different mechanisms can be invoked to explain these Np concentrations. In Boom Clay, the presence of pyrite and iron corrosion products facilitates the reduction of these elements to their sparingly soluble forms. If the measured Np concentrations are close to the solubility limit, the Tc concentrations are slightly higher than those calculated in Boom Clay at thermodynamic equilibrium. The kinetic aspects of reduction have to be taken into account in the system. Furthermore, the glass composition and the initial specific activity of the radionuclide in the glass were found to influence the soluble concentration. Np and Tc were not found to be retained in the glass reaction layer for both media although glass SON68 is known to form gel layers at the surface. This is probably due to the dissolution of the gel in the presence of concentrated clay.

SESSION JJ14: SPENT FUEL AND TRANSURANIC CHEMISTRY

Chairs: Edgar Buck and Christophe Poinssot
Thursday Afternoon, November 29, 2001
Republic B (Sheraton)

1:30 PM JJ14.1

COMPARISON OF NUCLIDE RELEASE UNDER UNSATURATED TEST CONDITIONS FROM LWR FUELS WITH A RANGE OF BURNUPS. Patricia A. Finn, Y. Tsai, S. Wolf and J.C. Cunnane, 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/kgM) and two PWR fuels (burnup of 30 and 45 MWd/kgM) were exposed to humid air and dripping groundwater. Differences in the fuels included burnup, geometric surface area (two times larger for the BWR fuels), and Gd content (2% Gd in the 64 MWd/kgM BWR fuel (Gd BWR)). The release rates of ²³⁸U, ²³⁹Pu, ²³⁷Np, ²⁴⁴Cm, ²⁴¹Am, ⁹⁹Tc, ⁹⁰Sr, ⁹⁷Mo, ¹²⁹I, and ¹³⁷Cs were compared at each test interval for the first two years of reaction. The release rates for all four fuels were within an order of magnitude of each other except for ¹²⁹I and ²³⁹Pu. For ¹²⁹I, 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 ²³⁸U, ²³⁹Pu, and ²³⁷Np in the leachate were also examined. The ²³⁸U concentrations (2 to 6 x 10⁻⁶ M) were similar for the PWR and BWR fuels. This agreement was consistent with the formation of similar uranyl alteration phases in both sets of tests. The Pu concentration was between 10⁻⁷ and 10⁻¹⁰ M for the four fuels. Most of the Pu was sorbed on the stainless-steel vessel for all four tests. Up to 5% of the released Pu was associated with colloidal material. The Np concentration was about 10⁻⁹ M for the BWR fuels and 10⁻¹⁰ to 10⁻¹¹ M for the PWR fuels. The Np/U mass fraction ratio was examined to determine if Np and U were released congruently; i.e., a ratio of one. At the two-year test interval, the Np/U ratio was in the range of 0.1 to 0.8 for the four fuels. At longer test intervals, the Np/U ratio for the PWR fuels was 0.8.

1:45 PM JJ14.2

ASSESSMENT OF THE EVOLUTION WITH TIME OF THE INSTANT RELEASE FRACTION OF SPENT NUCLEAR FUEL IN GEOLOGICAL DISPOSAL CONDITIONS. Christophe Poinssot, Patrick Lovera, Marie-Helene Faure, Commissariat a 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 cedex, 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 instantaneously 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 rim zone 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

burnup. The global RN inventory located in the rim zone represents hence 20% of the total inventory. The part of radionuclides in the gap, grain boundaries and fractures is assumed to be 5% of the total inventory. - the inner part of the pellet is composed of 8µm diameter grains with a regular RN distribution. Diffusion process is a combination of both a Fickian diffusion and also an irradiation-enhanced diffusion (diffusion coefficient $D \approx 1 \cdot 10^{-25} \text{ m}^2 \cdot \text{s}^{-1}$). - the concentrations at the grain boundary are zero, which corresponds to an instantaneous release of the labile activity. In this model, the IRF inventory strongly increases with time reaching for example $\approx 60\%$ of the total inventory in 10 000 years for the expected D value. Results will be presented. They enlighten (i) the significance of the irradiation-enhanced diffusion which may lead to a significant evolution of the RN locations within the rods, (ii) the necessity for a good knowledge of representative values for diffusion coefficients D and (iii) the significant evolution of IRF inventory with time, to be accounted for in RN source term calculations.

2:00 PM JJ14.3

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

Recent studies (Kansa et al. 1998, CRWMS M&O 2000) 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-hydroxides, such as "dehydrated schoepite", may, therefore, be detrimental to the performance of spent fuel in either dry storage or a geologic repository. This study was undertaken to determine the kinetics and mechanisms of formation of hydrated phases on both unirradiated and spent fuels under conditions experienced in typical pool storage. The conditions necessary to remove these waters of hydration, such as could be utilized during the drying of a storage canister, were examined. These studies appear to have implications for the models being developed for the geologic disposal of spent fuel. Alternate radionuclide release models for the proposed Yucca Mountain repository are based on the co-precipitation and solubility of secondary U(VI) mineral phases, such as schoepite (Chen 2000, Murphy 2000). Other release models rely on the incorporation of radionuclides, Np in particular as reported by Buck et al. (1998), in the secondary phases to limit their release. The present study presents evidence of oscillatory behavior for the formation and dissolution of schoepite and related uranyl oxy-hydroxide phases in batch tests between 25°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 JJ14.4

CORROSION TESTING OF A SIMULATED FIVE-METAL EPSILON PHASE IN SPENT NUCLEAR FUEL.

David J. Wronkiewicz, Chase S. Watkins, Andrew C. Baughman, Univ. Missouri-Rolla, Dept. Geology & Geophysics, Rolla MO; F. Scott Miller, Univ. Missouri-Rolla, Dept. Metallurgical Engineering, Rolla MO; Stephan F. Wolf, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

The five-metal epsilon phase represents an important component with respect to the corrosion of spent nuclear fuel. This importance is emphasized in its being a host for ^{99}Tc ; which in turn is a potentially high solubility radionuclide (as TcO_4^-), with a long half-life (213,000 years), that is utilized as a monitor for the corrosion of spent fuel. Metal powders were mixed in a weight percent basis of 40% Mo, 30% Ru, 15% Pd, 10% Re (used as a surrogate for Tc), and 5% Rh. This mixture replicates the composition of epsilon phase particles in Turkey Point pressurized-water spent reactor fuel (Thomas et al., 1989). The powders were melted in an Ar-gas purged vacuum chamber using an electric arc-melter. Backscattered - scanning electron microscopy images of the as-cast samples denote two separate regions with an inner zone enriched in Ru, Re, and Rh relative to the outer zone. Each zone is composed of a mixture of micron-sized crystals. Sample wafers of the simulated epsilon phase were reacted using vapor hydration (200°C) and MCC-1 testing (90°C) protocols. Vapor hydration 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 mode. This difference suggests that oxide and/or 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) an aqueous solution 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. Leachate solutions are currently being analyzed for their metal concentrations.

2:30 PM JJ14.5

THE INFLUENCE OF NEAR FIELD REDOX CONDITIONS ON SPENT FUEL LEACHING. Petra Appelblad¹, Daqing Cui¹, Cecilia Janzon¹ and Kastriot Spahi². ¹Studsvik Nuclear AB, Nyköping, SWEDEN. ²SKB, 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 radiation field present at the same time. In an anaerobic 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 hydrostatic pressure at the repository depth. For this reason, we investigated the leaching behavior of 0.25-0.5 mm sized fragments of PWR spent fuel (43 MWd/Kg U) in simulated groundwater solution (10 mM NaCl and 2 mM HCO_3^-) under 5 MPa hydrogen and argon pressure. In a leaching experiment under 5 MPa hydrogen at 25°C, the total U concentration was found to be $\sim 10^{-8}\text{M}$. After refilling of the autoclave with new solution at 70°C, the total U concentration first increased to $10^{-6.3}\text{M}$, and then quickly decreased to 10^{-8}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 by argon 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 JJ14.6

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

Creep strain has been identified as the dominant failure mode for dry storage, including the vacuum drying phase. It could also be important during the early period of repository closure. A statistical analysis of creep failure during these three phases was performed. Starting with an assumed burnup distribution (rod average = 44 MWd/kgU, range = 2 to 75 MWd/kgU), a distribution of rod properties, and finally a conservative stress distribution was developed. The Murty creep correlation was selected after comparing 6 different correlations with results from 5 different experimenters. It was then modified to better predict irradiated cladding creep data. Creep failure criteria is a CCDF 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 vacuum drying temperature of 430°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 430°C. In the current 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 fuel behavior and the distributions can be modified for specific applications.

SESSION JJ15: GLASS AND ALTERNATIVE WASTE FORMS

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

3:15 PM JJ15.1

EFFECT OF Zr AND Gd OXIDES ON THE GLASS DURABILITY. Marie Lobanova, Aurélien Ledieu, Philippe Barboux, François Devreux, Physique de la Matière Condensée, Ecole Polytechnique, Palaiseau Cedex, FRANCE; Olivier Spalla, Jacques Lambard, Service de Chimie Moléculaire, CEA Saclay, Gif sur Yvette, FRANCE.

We have analysed the experimental data on the dissolution of ternary sodium borosilicate glasses in the framework of a numerical model based on percolation concepts and Monte-Carlo simulations. This simplified model accounts qualitatively well for the effect of soluble species (Na, B) on the dissolution kinetics, on the saturation concentrations of silica in static conditions as well as on the porous morphology of the alteration layers. The comparison with the

experimental data allows to introduce realistic dissolution parameters for the numerical calculations. In the process of searching a more quantitative application of this model to more realistic glasses we have introduced 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 $70 \text{ SiO}_2 - 15 \text{ Na}_2\text{O} - 15 \text{ B}_2\text{O}_3 - x \text{ MO}_n$ with $M = \text{Gd, Zr}$ and x ranging between 0 and 10. The glasses were studied by conventional static leach tests at 90°C in water and buffered solutions. The experimental data show that the introduction of Zr and Gd drastically reduces the initial dissolution rate (V_0) of the glass. It also decreases the final silica solubility which is predicted by the numerical model but in a larger amount. The porous layer morphology is strongly modified in good agreement with the calculations. Local spectroscopic experiments (EXAFS, NMR, ESR, IR) have been used to assess 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 JJ15.2

MECHANISM OF VAPOR PHASE HYDRATION IN HIGH-SODIUM WASTE GLASSES FROM COMPUTER SIMULATIONS. Fernando C. Perez-Cardenas, Hao Gan, Xiaodong Lu, and Ian L. Pegg, Vitreous 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 alteration of waste glasses and has recently been adopted as a product-quality requirement for Hanford Low Activity Waste (LAW) glasses. However, the mechanism of the vapor phase hydration of LAW glasses is complex and relatively poorly understood. We have recently shown that the Avrami equation, and a generalization thereof, empirically gives a very good representation of the alteration kinetics, which typically shows an "incubation" period, a period of rapid alteration, and finally, a late-stage 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 Avrami 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 "stretched exponential" form of the Avrami equation can arise in many ways. In this paper we present results from computer simulations with a cell model of the VHT process in which the key parameters are the water diffusion rate; the hydration reaction rate and stoichiometry; and the compositional mismatch between the matrix and the new surface phase. The model successfully reproduces Avrami-like behavior over most of progress to reaction completion. Furthermore, by introducing site-site cooperative effects, the reaction front can be made either planar or dendritic, reproducing the "fingering fronts" in alteration layers that are experimentally observed for some LAW glasses.

3:45 PM JJ15.3

LONG-TERM CORROSION OF BOROSILICATE GLASS UNDER HYDROLOGICALLY UNSATURATED CONDITIONS. J.C. Cunnane^a, J. Fortner^a, and R. Olson^b; ^aChemical Technology Division, Argonne National Laboratory, Argonne, IL; ^bSelec Corporation, Hendersonville, NC.

The corrosion of borosilicate glass is examined under test conditions that simulate conditions to which the glass may be exposed in a potential repository at Yucca Mountain. Two types of tests were conducted. In the first ('vapor hydration tests'), the glass was exposed to humid air environments in closed stainless steel vessels to which enough water was added to establish a range of relative humidity conditions. The matrix of tests span the temperature range of 70 -200°C, relative humidity conditions from 50-100% and test durations up to three years. In the second type of tests ('drip tests'), two actinide-doped borosilicate glass compositions were exposed to humid air and twice weekly injections of a 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 glass corrosion rate observed in the drip tests, after more than a decade of operation, is less than $1\text{E-}3 \text{ g/m}^2\text{d}$. 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 glass.

4:00 PM JJ15.4

THE OXIDATION STATE OF PLUTONIUM FROM DISSOLUTION OF PYROCHEMICAL SALT WASTES IN WIPP BRINES. Virginia M. Oversby, VMO Konsult, SWEDEN; John M. Haschke,

Actinide Science Consulting, Waco, TX; Matthew K. Silva, Environmental Evaluation Group, Albuquerque, NM.

Pyrochemical salt wastes from the Rocky Flats plant in Colorado contain about 1 tonne of plutonium in the form of metal and/or oxide. The concentrations of Pu in the salts can be up to 10%. Tests of similar pyrochemical salt wastes in brines at Los Alamos National Laboratory gave very high solution concentrations of Pu. Pu(V) and Pu(VI) were identified by spectroscopy in some of the solutions with high concentrations of total Pu. We have developed a model to explain the presence of higher oxidation states of Pu in brines in contact with pyrochemical salts. The model predicts that PuO₂ will oxidize in contact with water to form PuO_{2+x}, which will release Pu(V) to solution. The Pu(V) will then disproportionate to Pu(VI), which remains in solution, and Pu(IV), which precipitates as a hydrous oxide. The precipitate, as well as the original PuO₂, will oxidize to PuO_{2+x}, releasing more Pu(V) to solution. This process, which is controlled by the competing rates of oxidation, disproportionation, and precipitation will reach a steady-state concentration level of total Pu, Pu(IV), Pu(V), and Pu(VI) in solution. If reductants, such as Fe metal or Fe(II) ions in solution are present, these may reduce the Pu(V) or Pu(VI) to Pu(IV), which will precipitate as the hydrous oxide. Once precipitation occurs, however, the process of oxidation by water will continue, generating more Pu(V) and Pu(VI) in solution. The rate of reduction will then be a factor in the final steady-state 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.

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LEACHING ACTINIDES AND U-235 FISSION PRODUCTS FROM HLW GLASSES IN THE STANDARD ASTM 1285 TEST. N.E. Bibler, T.L. Fellingner, C.L. Crawford and R.F. Schumacher, Savannah River Technology Center, Westinghouse Savannah River Co., Aiken, SC.

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 reliable test that could be performed remotely to demonstrate the consistency of the durability of the radioactive glass produced during the lifetime of the DWPF; hence, the name Product Consistency Test (PCT) was adopted. After refinement, the PCT was approved by the ASTM and became a consensus standard test for measuring the durability of HLW glasses. In the PCT the glass is crushed, sieved to a uniform size distribution, washed, dried, and then leached in deionized water (10 grams water per gram glass) at 90°C for seven days. The leachate is analyzed to measure concentrations of elements that were leached from the glass. Normalized releases are calculated in terms of grams of glass dissolved based on these elements and their concentrations in the glass. In the DWPF developmental program when radioactive glasses were not available, the elements B, Li, and Na in the glass were chosen as indicators of glass durability because of their solubilities in the leachate. These elements indicated the largest normalized releases compared to those based on other elements in the glass. Later radioactive glasses became available and the question arose, do any of the radionuclides have normalized releases greater than those for the above soluble elements? We used three radioactive glasses (two DWPF glasses and a glass containing Hanford HLW) to answer this question. Some had releases equal to those for B, Li, or Na, but none had higher. Examples of the radionuclides are actinides U-238, Pu-239, and Np-237, and fission products Tc-99, Sr-90, and Cs-137. Details will be presented.