SYMPOSIUM QQ

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* Invited paper

8:30 AM *QQ1.1
LIMITING CHARACTERISTICS OF LWR (HIGH BURNUP) FUEL
CLADDING RELATED TO SPENT FUEL STORAGE AND
HANDLING. Carl E. Beyer, Edgar R. Gilbert, A. Burt Johnson,
Mikal A. McKinnon, Battelle, Pacific Northwest National Laboratory,
Richland, WA.

High burnup Pressurized Water Reactor (PWR) fuel is being operated
near its waterside cladding corrosion and ductility design limits. PWR
fuel is more limiting than BWR fuel in terms of cladding performance
because it leads in terms of fuel burnup and greater cladding
corrosion. Corrosion by oxidation is the primary concern because it
reduces load bearing capability, it accelerates exponentially as it
approaches 100 μm thickness, and the oxidation produces zirconium
hydride precipitates that decrease ductility. As a result, the Nuclear
Regulatory Commission has encouraged licensees to keep their
in-reactor corrosion thickness levels below 100 μm.
Mechanical tests of high burnup cladding (standard Zircaloy-4)
demonstrate that the ductile-to brittle transition temperature
increases with increasing burnup and corrosion. These tests further
demonstrate that the mechanical elongation properties degrade with
increasing burnup and decreasing temperature. This suggests that
high burnup cladding which has adequate ductility during in-reactor
operation when corrosion levels are below 100 μm may be susceptible
to brittle behavior at the lower temperatures for fuel handling and/or
shipping and possible fuel failure at low impact loads. Additional
experimental data are required over a broader range of burnup and
temperature to enable quantitative correlation and predictions of high
BU fuel during all phases of the fuel cycle.
Failure mechanisms during long term storage, i.e., cavitation and/or
crack initiation, may be affected by several hundred ppm of zirconium
hydrides in the high burnup cladding. Consequently, modeling and
predictions of allowable storage conditions and periods hypothesized
for low burnup cladding may not be conservative.
Mechanical data at high burnups are very limited for the low-Sn
Zircaloy-4 currently used for high burnup fuel and there are virtually
no data for the recently introduced Zr-1%Nb cladding alloys. A key
characteristic of the low-Sn Zircaloy is that the onset of accelerated
corrosion is extended to slightly higher burnup levels while for the
Zr-1%Nb alloys the onset of accelerated corrosion is delayed to even
higher burnup levels. The lack of mechanical data for the low-Sn
Zircaloy-4 is not of great concern because it is expected to behave
similar to the standard Zircaloy-4 at equivalent corrosion levels.
However, the mechanical behavior of standard Zircaloy-4 at high
burnups may not be directly applicable to those of Zr-1% Nb alloys.

9:00 AM QQ1.2
CLADDING EVALUATION IN THE YUCCA MOUNTAIN
PERFORMANCE ASSESSMENT. Eric R. Siegmann, Duke
Engineering and Services, Las Vegas, NV; Robert Howard, TRW
Environmental Safety Systems, Las Vegas, NV.

In the most recent Total System Performance Assessment of the
potential Yucca Mountain Repository, the 1998 Viability Assessment
(VA), the degradation of Zircaloy cladding on commercial fuel rods
and the resultant exposure of the fuel was analyzed. The degradation
mechanisms considered were: damage before emplacement, mechanical
failure from drift collapse, local corrosion, general corrosion, delayed
hydride cracking (DHC), hydride reorientation, creep rupture, and
stress corrosion cracking (SCC). The potential for further fuel
exposure from cladding degradation due to expansion by fuel
oxidation was also considered. After the Waste Package (WP) fails,
the first three mechanisms contribute to exposing fuel. These expose
from 2 percent to 47 percent of the waste form most being exposed
well after the WP offers no physical protection. The other failure
mechanisms make no significant contribution to exposing fuel because:
1) the waste package is expected to remain sealed for over 200 years
(the period of highest temperatures), or 2) the cladding temperatures
and stresses are too low for failures from these mechanisms to become
significant. In the VA design, the hottest cladding (in center of WP)
reaches temperatures in the range of 327 degrees C to 237 degrees C
and then cools to 172 degrees C to 128 degrees C after 200 years. The
hoop stresses in the fuel reach 50 MPa to 90 MPa depending on the
peak temperature and burnup. These values are too low for most
cladding failure mechanisms such as creep, SCC, or DHC to be
important. The effect of the cladding model in the VA is to limit the
amount of fuel that is exposed to water and available for dissolution.
The end result is that the doses to the affected population are reduced
by a factor of 20 to 50 from the case where no cladding is considered.

9:15 AM QQ1.3
LONG TERM CREEP BEHAVIOR OF SPENT FUEL CLADDING
FOR STORAGE AND DISPOSAL. T. Bredel, C. Cappelaere, R.
Limon, G. Pinte, Commissariat à l'Energie Atomique, DRN/DMT/
SEMI, Saclay, Gif sur Yvette, FRANCE; P. Bouffioux, Electricité de
France, Pôle Industrie, Division R&D, Dept EM, Les Renardières,
Moret sur Loing, FRANCE.

In the framework of the 1991s French Law which defines the 3 major
research axes to dispose of nuclear wastes, CEA is supporting a wide
R&D program dealing with the long term behavior of spent fuel in
various boundary conditions representative of interim storage and
geological disposal. One major issue concerns the potential evolution
with time of the mechanical properties of the irradiated cladding and
the matter of its integrity. Can the cladding be considered as a first
confinement barrier for radionuclides ? The answer to this question
will strongly influence the design and the safety analyses of the
interim storage and potentially the first stage of a geological disposal.
After irradiation, the mechanical properties of the spent fuel cladding
are changed by the irradiation induced defects due the high
irradiation fluences as well as by the external zirconia layer and the
hydrogen pickup resulting from the waterside corrosion. Furthermore,
the cladding is stressed by the relative high internal pressure due to
the production and release in the free volumes of fission gases and
helium. Since the cladding is expected to undergo a temperature in
the range of about 300 to 400°C, long term creep is expected to be a
relevant deformation mechanism which can potentially lead to a
rupture of the cladding. In order to deal with this strategic issue,
experiments on irradiated cladding samples as well as modeling work
are in progress at CEA with the support of EDF and FRAMATOME.
The ambitious objectives are to define and qualify the long term
mechanical properties of the cladding, in particular a long term creep
law and an adequate breaching criterion. Long term creep properties
are investigated through a stepwise approach from short term (few
days) and high stress experiments to long term (few years) and low
stress experiments. The validation of the extrapolation is ensured by
complete metallurgical characterizations (HRTEM, XRD, hydrogen
content). The first step of this work, medium term (about 1 month)
creep experiment on irradiated cladding will be presented.

9:30 AM QQ1.4
HYDRIDE-RELATED DEGRADATION OF SPENT FUEL
CLADDING UNDER REPOSITORY CONDITION. H.M. Chung,
Argonne National Laboratory, Argonne, IL.

Because intact cladding is a barrier that prevents release of
radionuclides in spent fuel rods, the long-term structural integrity of
fuel cladding is one of the key issues in evaluating repository system
performance. Potential degradation of spent fuel cladding by
hydride-related processes including delayed hydride cracking (DHC)
remains one of the important cladding performance issues. This paper
presents results of a critical review of literature data and an
evaluation of metallurgical processes that influence the potential for
hydride-related degradation of spent fuel cladding in the repository.
Because the key aspect of potential DHC under repository conditions
is crack initiation rather than crack propagation, the cracking
behavior of hydrogen-charged compact tension specimens, tested
under accelerated laboratory conditions at constant temperatures and
extensively reported in literature, was critically reviewed and
analyzed. It was found that DHC initiation in a CANDU pressure
tube, a proven field event, cannot be predicted based on the threshold
stress intensity factor inferred from the laboratory tests. Therefore, it
appears difficult to predict or refute the occurrence of DHC in spent
fuel cladding under repository conditions on the basis of the results
from such accelerated isothermal tests. A similar rationale indicates
that despite of the presence of more incipient flaws of relatively larger
size, DHC initiation at the inner-diameter surface of spent fuel
cladding is extremely unlikely. To understand the potential for DHC
initiation in spent fuel cladding in a repository, the potential for very
long-term evolution of the cladding metal microstructure beneath the
outer-diameter oxide layer was identified to be the key. A model is
presented in which the potential microstructural evolution, and in
worst case, potential crack initiation at the cladding metal beneath
the outer-diameter oxide, are described step by step. Results of a
review of available literature and new microstructural information are
presented to help understand the potential for these metallurgical
processes under repository conditions. *Work supported by the U.S.
Department of Energy, Office of Civilian Radioactive Waste
Management.

9:45 AM QQ1.5
ANALYSIS OF DRY STORAGE TEMPERATURE LIMITS FOR
ZIRCALOY-CLAD SPENT NUCLEAR FUEL. Troy A. Hayes, Univ
of California, San Diego, Dept of Mechanical and Aerospace
Engineering, La Jolla, CA; Robert S. Rosen, Lawrence Livermore
National Laboratory, Livermore, CA; Michael E. Kassner, Oregon
State Univ, Dept of Mechanical Engineering, Corvallis, OR; Kenneth

S. Vecchio, Univ of California, San Diego, Dept of Mechanical and Aerospace Engineering, La Jolla, CA.

Safe interim dry storage of spent nuclear fuel (SNF) must be maintained for a minimum of twenty years according to the Standard Review Plan for Dry Cask Storage Systems and the Code of Federal Regulations. The most important variable that must be regulated by dry storage licensees in order to meet current safety standards is the temperature (and temperature decay profile) of the SNF. The Nuclear Regulatory Commission has accepted two models to define the maximum allowable initial temperature for interim dry storage of SNF. These models are based on the Raj and Ashby diffusion controlled cavity growth (DCCG) failure mechanism. There is a lack of experimental evidence to verify this theory for zirconium or zirconium alloys (or other alloys), as creep tests have not been performed to failure under conditions relevant to dry storage. Current data suggest that the two accepted models may not give conservative temperature limits. Although the models are based on the same fundamental failure theory (DCCG), the researchers who developed the models have made different choices when selecting some of the most critical variables in the DCCG failure equation. These include the diffusion coefficient and the assumed cavity spacing. Small variations in these variables have a dramatic effect on the predicted failure time (or initial temperature limit). These inconsistencies are discussed together with recommended modifications to the failure models based on more recent data as well as recommended experiments.

10:30 AM *QQ1.6
SPENT FUEL DISSOLUTION: AN EXAMINATION OF THE IMPACTS OF ALPHA-RADIOLYSIS. P.A. Smith, Safety Assessment Management Ltd., Hathersage, Hope Valley, Derbyshire, ENGLAND; L.H. Johnson, Nagra, Wettingen, SWITZERLAND.

When spent fuel eventually comes into contact with groundwater, fuel matrix dissolution will be strongly influenced by redox conditions in the near field. The most significant factors influencing redox conditions on the fuel surface are alpha-radiolysis of water and the presence of reductants such as Fe(II) and hydrogen arising from canister corrosion. The radiolytic yield (G) of molecular oxidants, generally considered to be $\sim$1 molecule of hydrogen peroxide per 100 eV for alpha-radiolysis, is expected to be considerably lower in the presence of reductants but the overall effect on the rate of matrix dissolution cannot yet be reliably quantified. We have attempted to estimate the effective yield of oxidants by examining the results from various studies of spent fuel and UO2 dissolution, including alpha-radiolysis experiments. The analysis suggests that the effective yield is likely to be no greater than 0.01 in the repository environment. The implications of low G values are discussed in relation to fuel dissolution rates. Some other aspects relevant to near-field redox chemistry are also examined, including the importance of passivation of steel in reducing Fe(II) release from corrosion products and the significance of alpha emitters sorbed on bentonite in producing radiolytic oxidants.

11:00 AM QQ1.7
EFFECTS OF ALTERATION PHASE FORMATION UNDER UNSATURATED CONDITIONS IN LWR FUELS WITH BREACHED CLADDING. Stephen F. Wolf, Robert J. Finch, Rudolph A. Olson and James C. Cunnane, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

The reaction of irradiated clad fuel segments with humid air at 175°C and with periodic injection of Si-rich groundwater at 90°C is examined experimentally. The tests are designed to investigate how the secondary alteration phases that are expected to form as a result of the corrosion of the fuel may influence radionuclide release from fuel rods with breached cladding. Specific effects examined are the potential for clad splitting or unzipping due to volume expansion associated with the alteration phase formation, the role of the alteration phases in changing the effective hydraulic conductivity of the fuel and its rate of alteration and radionuclide release. The vapor tests were started June 1998. Visual examinations of vapor-reacted samples after 300-d show evidence for the formation of alteration phases. Diametrical measurements indicate no evidence of strain of the cladding, and sample mass-gains indicate <0.5% of the fuel has reacted. The leachate data from drip tests, which were initiated in February 1999, is analyzed to determine the gap inventory of Cs, I and Tc. The groundwater, which is injected under a low hydraulic head, was found to percolate through all samples at a rate >0.75-mL/3.5-d. Changes in the effective hydraulic conductivity of the fuel segments over the course of the experiment are presented. Benchtop experiments have also been designed to accelerate the formation of uranyl silicates under confined conditions. These tests facilitate investigation of the potential for wet unzipping of the cladding due to crystallization of Na-boltwoodite during the oxidative corrosion of fuel. Initial results demonstrate that the reaction of powder mixtures of UO_3 and Na-silicate glass with steam at 200°C is essentially complete within five days and results in volume expansion of the initial powders due to the reaction. The effects of the volume expansion and the associated crystallization pressures are presented.

11:15 AM QQ1.8
URANIUM OXIDE MASS LOSS RATE IN WATER FOR AN INTERFACE UNDER ALPHA IRRADIATION. Catherine Corbel, Gael Sattonnay, CEA Saclay, DSM/DRECAM/SCM, Gif-Sur-Yvette, FRANCE; Jean-Francois Lucchini, CEA Marcoule, SCD, Bagnols-sur-Ceze, FRANCE; Marie-France Barthe, CERI-CNRS, Orleans, FRANCE; Philippe Dehaudt, Francois Huet, CEA Grenoble, DRN/DEC/SECC, Grenoble, FRANCE.

Different models are describing the corrosion of spent fuel under water. However, there is room to increase the robustness of these models. One process which needs to be better understood is the effect of the radiolytic species, which are produced in water by the gamma, beta and alpha particules emitted by spent fuel, on the dissolution rate of uranium. This work proposes a fundamental approach by using an external alpha beam to irradiate the uranium oxide/water interface. A high energy alpha beam delivered by a cyclotron (CERI-CNRS, Orleans, France) is used to irradiate an uranium oxide/water interface and investigate the release of uranium in water as a function of flux, fluence and energy of the alpha beam at the interface. The alpha beam goes through the solid and penetrates in water. First results are shown that the release of uranium in aerated water is strongly enhanced under alpha irradiation with rates depending on the alpha flux.

11:30 AM QQ1.9
RELEASE OF Tc FROM FUEL-GRAIN BOUNDARIES DURING OXIDATIVE CORROSION OF SPENT UO_2 FUEL IN DRIPPING GROUNDWATER. Robert J. Finch, Patricia A. Finn, Stephen F. Wolf, Ralph Leonard, Edgar C. Buck, James C. Cunnane, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

Corrosion of spent nuclear fuel, when exposed to low volumes of groundwater, is a complex, heterogeneous process involving dissolution and precipitation of multiple radionuclide-bearing solids. Most Tc in spent UO_2 fuels occurs within ϵ-Ru particles, many of which decorate grain boundaries (GBs), dislocations and other defects within the fuel. Substantial dissolution can occur along defects, and ϵ-Ru particles along these defects may dissolve quite readily under certain conditions. Comparisons of cumulative Tc releases from small-scale batch and drip experiments suggest that a significant proportion of the Tc released after approximately five years of reaction is derived from ϵ-Ru particles along GBs and defects that intersect GBs. Because Tc has been used to monitor the volume of fuel that has dissolved under the test conditions, knowing the source of Tc is important for understanding the extent that fuel that dissolves by various means. The degree to which Tc release from GBs accurately reflects matrix dissolution along GBs is uncertain. The proportion of Tc inventory in ϵ-Ru particles that occur along GBs and defects near GBs in unreacted spent fuel is unknown; however, we estimate that two percent or more of Tc may occur in ϵ-Ru particles that have reacted with groundwater along GBs in samples of ATM-103, a LWR fuel of moderate burn-up ($\sim$30 MWd/kg-U). Relatively rapid dissolution of ϵ-Ru particles may be caused by radiolytic products, including free-radical oxidants and nitric acid, which may accumulate within thin films of water on surfaces of corroding fuel fragments in experiments conducted at low flow rates and in batch experiments with small water volumes and high surface areas. Radiolytic products may reach relatively high concentrations in water that has percolated between fuel grains, a hypothesis supported by the lack of visible U-bearing precipitates between fuel grains in drip experiments that exhibit extensive GB attack. * This task was performed under the guidance of the Yucca Mountain Site Characterization Project (YMP) and is part of activity D-20-43 in the YMP/Lawrence Livermore National Laboratory Spent Fuel Scientific Investigation Plan. This work was supported by the U.S. Department of Energy, under contract W-31-109-ENG-38.

11:45 AM QQ1.10
IN-SITU LONG TERM MEASUREMENTS OF pH AND REDOX POTENTIAL DURING SPENT FUEL LEACHING UNDER STATIONARY CONDITIONS - THE METHOD AND SOME PRELIMINARY RESULTS. Kastriot Spahiu, Lars Werme, SKB AB, Stockholm, SWEDEN; Jeanett Low, Ulla-Britt Eklund, Studsvik Nuclear AB, Nyköping, SWEDEN.

In order to get a better understanding for the spent fuel corrosion process, the variations of important intensive parameters such as pH and the redox potential (Eh) of the bulk solution have been continuously measured during long term sequential leaching experiments. These data may be used together with standard chemical analytical data for modelling spent fuel corrosion, especially in anoxic or reducing conditions. In order to overcome difficulties

caused by the strong radiation field and the long experiment times, a method for in-situ measurements of pH and Eh using a computer controlled system was worked out. The stability of the measuring system over long time periods was then tested; pH values stable within 0.05 pH units/year in buffered systems were measured. The variations of these parameters in a variety of conditions and solution compositions were followed continuously during the whole spent fuel leaching process. A discussion of the results of spent fuel leaching in anoxic conditions is presented, pointing out the difficulties to realise in laboratory near field conditions. An interesting case of calcite co-precipitation/co-dissolution is also presented. Dissolution experiments show that calcite precipitated previously during spent fuel leaching experiments in synthetic groundwater contains considerable amounts of actinides and fission products. Results from blank experiments using unirradiated UO2(s) to test the leaching in the presence of various repository near field relevant reductants as e.g. magnetite are also reported and compared to spent fuel leaching data.

SESSION QQ2: FLOW AND TRANSPORT
Chairs: Roberto T. Pabalan and Robert W. Smith
Monday Afternoon, November 29, 1999
Room 203 (H)

1:30 PM *QQ2.1
SIMULATION OF RADIONUCLIDE MIGRATION IN GROUND-WATER AWAY FROM AN UNDERGROUND NUCLEAR TEST. A.F.B. Tompson, C.J. Bruton, W.L. Bourcier, D.E. Shumaker, A.B. Kersting, D.K. Smith, S.F. Carle, G.A. Pawloski, J.A. Rard, Lawrence Livermore National Laboratory, Livermore, CA.

Reactive transport simulations are being used to evaluate the nature and extent of radionuclide contamination within an alluvial hydrologic environment surrounding a specific underground nuclear test at the Nevada Test Site. Interest is focused on determining the abundance and chemical nature of radionuclides that are introduced into groundwater as aqueous species, as well as the rate and extent of radionuclide migration and reaction in groundwater surrounding the working point of the test. This effort is being used to determine an improved hydrologic source term for use in other transport simulations designed to assess the fate of radionuclides over longer times and larger spatial scales. Preliminary transport simulations are used to illustrate the nature of radionuclide elution out of the near-field environment. The results can be particularly sensitive to the available surface area in the fractured melt glass produced by the test, reactive mineral phase distribution in the near field, and overall groundwater flow configuration, and provide a rational basis from which defensible migration assessments can proceed. This work was conducted under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract W-7405-Eng-48. This work was funded by the Underground Test Area Project, Department of Energy, U. S. Nevada Operations Office.

2:00 PM QQ2.2
ASSESSING EFFECTIVE REACTIVE SURFACE AREA IN HETEROGENEOUS MEDIA THROUGH THE USES OF CONSERVATIVE AND REACTIVE TRACERS. Robert W. Smith, Jonathan R. Ferris, Idaho National Engineering and Environmental Laboratory, Biotechnologies Dept, Idaho Falls, ID.

The characteristics and abundance of reactive surfaces in aquifer media have long been recognized as key factors controlling the migration of contaminants (e.g., metals, radionuclides, and organic ligands) and other dissolved constituents (e.g., electron donors/acceptors, nutrients required by subsurface microorganisms) in groundwater. As we have shown previously (Smith, R.W. and A.L. Schafer, Mat. Res. Soc. Symp. Proc. 556:in press) the effective reactive surface area of a heterogeneous aquifer is a complex function of groundwater advective velocity and the correlation structures of the physical and chemical heterogeneities. Although in principle, the available surface area within an aquifer could be estimated using geostatistical techniques and laboratory BET surface area determination for individual samples, this approach is fraught with difficulties associated with inadequate sample coverage and lack of appropriate methods for scaling laboratory surface area measurements. An alternative approach relies upon the uses of conservative and slightly reactive tracers to assess the integrated effective reactive surface area along flow paths. This approach sacrifices detailed understanding of the fine-scale heterogeneity but can provide integrated large-scale estimates of effective reactive surface area useful for the prediction of reactive transport. The approach is demonstrated by the analysis of the breakthrough curves for paired halide tracers (fluoride and bromide) in heterogeneous media. Through the use of numerical and laboratory experiments techniques and theory for estimating the integrated in situ effective

reactive surface area for natural hydrous iron oxide coated sands are being developed.

2:15 PM QQ2.3
DECAY-SERIES DISEQUILIBRIUM STUDY OF IN-SITU, LONG-TERM RADIONUCLIDE TRANSPORT IN WATER-ROCK SYSTEMS. Shangde Luo, Teh-Lung Ku, Univ of Southern California, Dept of Earth Sciences, Los Angeles, CA; Robert Roback, Michael Murrell, Los Alamos National Laboratory, Los Alamos, NM; Travis L. Mcling, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

Uranium and thorium-series disequilibrium in nature permits the determination of a variety of in-situ physiochemical, geologic and hydrologic variables that control the long-term migration of radionuclides in geologic systems. It also provides site-specific, natural analog information valuable to the assessment of geologic disposal of nuclear wastes. In this study, modelling based on mass balance concept was used to relate the decay-series radioisotope distributions among solution, sorbed and solid phases in an aquifer system to in-situ processes of water transport, sorption-desorption, dissolution-precipitation, radioactive ingrowth-decay, and α recoil. Isotopes of U (^{238}U, ^{234}U), Th (^{232}Th, ^{230}Th, ^{228}Th, ^{234}Th), Ra (^{226}Ra, ^{228}Ra, ^{224}Ra), Rn (^{222}Rn), Pb (^{210}Pb), and Po (^{210}Po) were measured in 23 groundwater samples collected from a basaltic aquifer at the Idaho National Engineering and Environmental Laboratory (INEEL), Idaho. The results placed constraints on the following parameters at INEEL: (1) time scales of sorption (minutes for Ra and Th), desorption (days for Ra and years for Th), and precipitation (days for Th, years for Ra, and centuries for U); (2) retardation factors due to sorption (ca. 10^6 for ^{232}Th, 10^5 for ^{210}Pb and ^{210}Po, 10^4 for ^{226}Ra, and 10^3 for ^{238}U); (3) dissolution rates of rocks (ca.70 to 800 mg/L/y); and (4) ages of groundwater (<10 to 90 years). The contours of groundwater age, as well as the spatial patterns of disequilibria, delineated two local north-south preferential flow pathways. Large retardation factors, precipitation and dissolution rates, and α-recoil rates were found to occur mostly in the northern part of INEEL near recharge areas, where the aquifer rocks appear to have more microfractures, hence larger surface areas.

2:30 PM QQ2.4
CHEMICAL EVOLUTION OF LEAKED HIGH-LEVEL LIQUID WASTES IN HANFORD SOILS. J.L. Krumhansl, M. Nyman, P. Zhang, B. Anderson, T.M. Nenoff, Sandia National Laboratories, Albuquerque, NM.

Many of the Hanford tanks have leaked high level radioactive wastes (HLW) into the surrounding soil fill. The disequilibrium between the silica-rich soils and highly caustic fluids which contain phosphate, fluoride and aluminate is a driving force for numerous reactions to take place between the soil and solution components. Hazardous solution components such as radionuclides (^{90}Sr, ^{133}Cs, ^{60}Co, ^{99}Tc) may be adsorbed or sequestered by alteration phases, or released in the Vadose zone for further transport by surface water. In order to ascertain the location and immobility of the radionuclides from leaked solutions within the Vadose zone, we are currently studying the chemical reactions between tank simulant solutions and Hanford soil fill minerals. We are investigating soil-solution reactions at: 1) elevated temperatures (60 - 90 °C) to simulate reactions which occur immediately adjacent a radiogenically heated tank; and 2) ambient temperature (25 °C) to simulate reactions which take place further from the hot tanks. Our studies show that reactions at elevated temperature result in dissolution of silicate minerals and reprecipitation of zeolitic phases which have the capability of sequestering Cs and Sr. At 25 °C, silicate dissolution is not significant. However, CO_2 uptake by the solution results in precipitation of an aluminum-oxide-hydroxide phase which has anion scavenging (i.e. $TcO_4{}^-$) capabilities. Formation of radionuclide-sequerstering alteration phases as a function of reaction time, reaction temperature, soil composition and solution composition will be presented.

2:45 PM QQ2.5
TECHNETIUM-99 CHEMISTRY IN REDUCED GROUNDWATERS: IMPLICATIONS FOR THE PERFORMANCE OF A PROPOSED HIGH-LEVEL NUCLEAR WASTE REPOSITORY AT YUCCA MOUNTAIN, NEVADA. Roberto T. Pabalan, David R. Turner, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

Performance assessment calculations by the U.S. Department of Energy and the Nuclear Regulatory Commission (NRC) indicate that technetium-99 is a major contributor to dose to a hypothetical receptor group within the first 10,000 years after permanent closure of a proposed high-level nuclear waste repository at Yucca Mountain (YM), Nevada. This result is due in large part to the high solubility and low retardation of technetium, as pertechnetate ($TcO_4{}^-$) ion, in

the YM environment. Recent site characterization data on the saturated zone groundwater chemistry at YM and surrounding areas indicate the presence of locally reducing geochemical conditions, which could reduce the solubility and enhance the sorption of technetium-99. In this study, the effects of reducing conditions on the chemical behavior of technetium-99 were evaluated. Thermodynamic calculations suggest that the redox conditions measured for some YM saturated groundwaters, for example at well WT#17, could lead to significantly reduced technetium solubility. Sensitivity analyses using the NRC Total-System Performance Assessment code were conducted to evaluate the implication of locally reducing conditions on repository performance. Results of the thermodynamic and performance assessment calculations will be discussed. 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 NRC.

SESSION QQ3: INTERFACIAL PROCESSES AND
INTERACTIONS
Chairs: Ken R. Czerwinski and George D. Redden
Monday Afternoon, November 29, 1999
Room 203 (H)

3:30 PM *QQ3.1
MODELING THE BINDING OF METAL IONS TO HETERO-
GENEOUS ENVIRONMENTAL MATERIALS. John C.Westall,
Department of Chemistry, Oregon State University, Corvallis, OR.

Because models for speciation of metals in aqueous solutions are presumed to be based on fundamental processes and inviolable laws of nature, one might conclude that predictions from such models are quite accurate; while this conclusion might be approximately correct for some well defined laboratory systems, it is not correct for most systems with complex, heterogeneous environmental sorbents, such as surfaces of rocks, soil particles, and natural organic matter. Historically, many models for the association of metals with these heterogeneous environmental sorbents have been mechanistically based, that is, one has attempted to represent basic chemistry and physics through a few classes of binding sites, regular planar/ cylindrical/spherical geometry at the scale of the electric double layer, and an electric double layer model. While these models might indeed be somewhat mechanistic for simple, homogeneous ligands and surfaces, for heterogeneous environmental sorbents, they can only be regarded as semi-empirical representations of the actual interface – of the correct mathematical form to fit the data, but not an accurate physical-chemical description. Furthermore, these models may lack the flexibility needed to represent easily multidimensional data sets (i.e., data with simultaneous variations in pH, salt concentration, total metal concentration, etc.). As an alternative to traditional surface-complexation approaches, we have advanced the use of adsorption models based on a broad distribution of binding energies described by an affinity spectrum. The merits of both modeling approaches are illustrated through consideration of experimental data for adsorption of several different metal ions onto a variety of field samples with systematic variations in properties. The traditional surface-complexation diffuse-layer model approach, for which binding constants have been derived from study of relatively simple laboratory systems, works remarkably well over a limited range of data, while the affinity spectrum approach captures variations over a much wider range of data.

4:00 PM QQ3.2
SURFACE COMPLEXATION MODELS IN SOLUTE TRANSPORT:
ISSUES OF PRACTICALITY AND APPLICABILITY FOR
TRANSPORT MODELING. George Redden, Idaho National
Engineering and Environmental Laboratory, Idaho Falls, ID; James A.
Davis, U.S. Geological Survey, Menlo Park, CA.

Empirical partitioning coefficients (Kd's) have been used to simulate solute transport in reactive porous media because they have low computational cost and are assumed to capture sorption behavior in complex mineral assemblages. In contrast, surface complexation models have been developed that attempt to describe sorption reactions in terms of distinct chemical reactions at a surface, and account for chemical speciation in solution. The power of this approach is an ability to predict sorption in systems with temporal or spatial chemical gradients, including those that result from the sorption reactions. In addition, the reductive parameterization of the surface complexation approach should permit estimating sorption equilibrium where direct experimental data cannot be obtained. A number of barriers make it difficult or impractical to utilize surface complexation in field applications. From a practical standpoint, the computational costs will be significant even in fairly simple systems. More importantly, the approaches being taken to develop complex-ation models suffer from a lack of conceptual consistency, an under-appreciation of the constraints that apply to experimentally

derived parameters as a result of different fitting protocols, the potentially large number of inaccessible parameters needed to describe complex media, and the relatively unexplored propagation of error that results from multi-component, non-linear models. System-specific, semi-empirical models that build on the functionality illustrated in complexation models offer a useful compromise approach.

4:15 PM QQ3.3
EFFECT OF CARBONATE CONCENTRATION ON THE
SORPTION OF PLUTONIUM ON GEOLOGICAL MATERIALS.
G.M.N. Baston, J.A. Berry, M. Brownsword, D.J. Ilett, C.M.
Linklater and C.J. Tweed, AEA Technology pic, Didcot, Oxfordshire,
UNITED KINGDOM; M. Yui, Japan Nuclear Cycle Development
Institute, Tokai Works, Ibaraki, JAPAN.

The sorption of radioelements onto geological materials is being studied as part of the JNC programme of generic studies to increase confidence in the performance assessment for a potential high-level radioactive waste repository in Japan. Batch sorption experiments have been performed to study the sorption of plutonium onto samples of sandstone, mudstone and basalt from equilibrated de-ionised water and seawater under reducing conditions at room temperature. Studies have been carried out with low carbonate concentrations under a nitrogen atmosphere, and further experiments are nearing completion at two higher carbonate concentrations under nitrogen atmospheres with 0.4% and 2% carbon dioxide to stabilise the increased solution carbonate levels.
Three phase separation methods are in use; (1) centrifugation at 1100g, (2) centrifugation followed by $0.45 \mu m$ filtration and (3) centrifugation followed by $0.45 \mu m$ filtration followed by 10000MWCO filtration. Rd values at low carbonate levels in equilibrated de-ionised water were in the ranges 16 - 40, 21 - 52 and 21 - 120 $m^3 kg^{-1}$ for sandstone, mudstone and basalt respectively, after filtration. For the equivalent experiments involving sorption from equilibrated seawater, Rd values were in the ranges 22 - 36, 4 - 140 and 97 - 240 $m^3 kg^{-l}$ for sandstone, mudstone and basalt respectively. Only in the case of mudstone with seawater were there significant differences between filtration through a $0.45 \mu m$ filter and through a 10000MWCO filter. There were in all cases, however, significant differences between Rd values following filtration and following centrifugation only, Rd values in the latter instances lying between 0.1 and 2.0 $m^3 kg^{-l}$. This indicates some form of particulate behaviour.
Results from the experiments at the higher carbonate concentrations are imminent and thermodynamic chemical modelling using the HARPHRQ program and HATCHES database will be carried out to help to interpret the results of this study.

4:30 PM QQ3.4
INTERACTIONS OF URANIUM AND NEPTUNIUM WITH
CEMENTITIOUS MATERIALS STUDIED BY XAFS.
E.R. Sylwester, P.G. Allen, P. Zhao, B.E. Viani, Lawrence Livermore
National Laboratory, Livermore, CA.

We have investigated the interaction of U(VI) and Np(V) actinide ions with cementitious materials that are relevant to nuclear waste repositories using X-Ray Absorption Fine Structure (XAFS) Spectroscopy. The actinide ions were individually loaded onto untreated as well as hydrothermally treated cements. The mixtures were then equilibrated at varying pH's for a period of approximately 6 months. In all cases uranium was introduced in the form of aqueous uranyl ion, UO_2^{2+}, and was observed to remain in this form based on the Near Edge (XANES) spectra. The uranium samples show evidence of a strong interaction with both treated and untreated cements at all pH's, with uranyl interacting with the cement mineral phases (i.e., SiO_2) through an inner-sphere mechanism where oxygen atoms in the equatorial plane of the uranyl ion are shared with the mineral surface. In contact with the hydrothermally treated cement, the uranyl ions are also observed to form oligomeric species. Structural trends are also observed as a function of pH in both the Extended (EXAFS) and the XANES spectral regions. Neptunium was introduced as the neptunyl ion, NpO_2^+, and was observed to undergo a reduction from Np(V) to Np(IV). Two separate methods of data analysis were used to determine the extent of reduction in each sample, one utilizing component analysis of the XANES region and the other utilizing curve fitting in the EXAFS region. The comparison between the results of these methods will be discussed. Reduction occurs over a relatively slow time scale based on XAFS data collected from a fresh sample (aged for 1 month). This sample showed that ca. 15% of the Np(V) is reduced to Np(IV). In comparison, the other samples showed higher reduction rates of between 40% and 65%.

4:45 PM QQ3.5
ATOMISTIC SIMULATION OF RADIONUCLIDE RELEASE IN A
ZEOLITE WASTE FORM: I. ION EXCHANGE ISOTHERM.
Tatyana Kletskova, Kenneth Czerwinski, Sidney Yip, Massachusetts

Inst of Tech, Dept of Nuclear Engineering, Cambridge, MA; Ely Gelbard, Argonne National Lab, Reactor Analysis Division, Argonne, IL.

Ion-exchange and high adsorption properties have made zeolites extremely important for several industrial applications, including nuclear waste management. Knowledge of the radionuclide retaining properties of zeolites is necessary for their use as high-level waste forms. Atomistic simulation techniques, such as energy minimization and Monte Carlo, are particularly effective for studying these properties. An atomistic simulation was performed of a prototype zeolitic waste form, in which ion exchange was assumed to be the key leaching mechanism. The systems investigated consisted of a dehydrated zeolite (sodalite or Zeolite A), ground water, and two types of exchange cations-a radionuclide (Cs) and a natural ground-water cation (Li, K or Na). The best way to define the thermodynamic properties of the zeolite, for example the retention preference of a given cation, is to construct the corresponding ion-exchange isotherm. To determine the equilibrium states necessary for the construction of this isotherm, the free energy of the system must be defined. The interchange of different cations during the ion-exchange process causes a significant internal stress, which may lead to unreliable calculation results. Therefore, system relaxation was performed over the full range of Cs mole fractions in both sodalite and Zeolite A. Cage distortion was allowed. The free energies were first calculated as a function of the Cs mole fraction for the relaxed systems at zero temperature using the Monte Carlo method. The free energies were then calculated over the temperature range of 0 to 500 K by applying the adiabatic switching method. As a result of these calculations, new absorption sites were defined for each cation in both Zeolite A and sodalite, equilibrium constants were determined and isotherms were constructed.

SESSION QQ4: CERAMICS - CORROSION
Chairs: Bernard Peter McGrail and Lou Vance
Tuesday Morning, November 30, 1999
Room 203 (H)

8:30 AM QQ4.1
GLASS/CERAMIC INTERACTIONS IN THE can-in-CANISTER CONFIGURATION FOR DISPOSAL OF EXCESS WEAPONS PLUTONIUM. <u>B.P. McGrail</u>, P.F. Martin, H.T. Schaef, C.W. Lindenmeier and A.T. Owen, Pacific Northwest National Laboratory, Richland, WA.

A can-in-canister waste package design has been proposed for disposal of pyrochlore rich ceramics containing excess weapons plutonium. The can-in-canister configuration consists of a high-level waste (HLW) canister fitted with a rack that holds 28 minicanisters containing the ceramic. The HLW canister is then filled with glass. At some time in the distant future, water is expected to penetrate the waste containers and contact the waste forms. The most credible contact mode from a hydraulics viewpoint at the Yucca Mountain site is the slow percolation of water through the waste packages under conditions of partial hydraulic saturation. The pressurized unsaturated flow (PUF) technique was used to investigate waste form/waste form interactions that may occur under these conditions. A sandwich configuration was used where a porous bed of crushed ceramic was placed between beds of crushed glass. Flow through the materials was maintained at 1 mL/d for 17 months at a temperature of 90°C. Volumetric water content was observed to increase steadily during the test from accumulation of water mass as waters of hydration associated with alteration phases formed on the glass surface. Periodic excursions in effluent electrical conductivity and pH were monitored and correlated with secondary phases formed during the test. More than 80% of the Pu in the column effluent samples was removed upon filtration, which required both colloid formation and transport to occur under the unsaturated flow conditions of the experiment. Contact angle measurements also showed that the ceramic surface appears hydrophobic relative to the glass. X-ray tomographic measurements with a NaI contrast agent showed that water imbibition into a dry column is stopped at the glass/ceramic interface because of the hydraulic property mismatch between the materials. This may have important implications for water percolation pathways through the waste package.

8:45 AM QQ4.2
DURABILITY STUDIES ON WASTE FORMS DESIGNED TO IMMOBILISE URANIUM AND PLUTONIUM. <u>Kaye Hart</u>, Yingjie Zhang, Elaine Loi, Greg Lumpkin, R. Arthur Day, Michael Colella, Martin Stewart Australian Nuclear Science and Technology Organisation, Menai, AUSTRALIA; Bill Bourcier Lawrence Livermore National Laboratory, Livermore, CA.

Ceramic titanate waste forms being developed for excess weapons Pu

immobilisation are produced by cold-pressing and sintering. This paper reports on studies of the durability of these titanate waste forms containing Pu, U, neutron absorbers (Gd/Hf) and impurities, and also on studies on the aqueous durability of one of the phases present in the waste form, viz. brannerite. Both static and flow-through leaching tests have been carried out to allow description of the overall releases of Pu, U and other elements, and the pH-dependence of the release kinetics. Results from MCC-1 leaching tests, at 90 °C in deionised water, show that the release rates of U and Pu are low, $< 10^{-4}$ $g.m^{-2}.d^{-1}$ after 84 days of leaching, and are not significantly affected by the presence of impurity elements. Further, the release rates of neutron absorbers are low; Hf is not detected either in solution or in vessel wall strips, and Gd leach rates are about an order of magnitude higher than those of Pu. For samples of synthetic brannerite, flow-through testing, at 70 °C, shows that the releases of U are solubility limited, with the minimum occurring at about pH 8, and that Ti releases are always at least a factor of 10 less than those of U. TEM examination of powders leached in a pH 2, HCl-based solution for 84 days at 70 °C identified the presence of small amounts of anatase on the surface of the sample. Similar results from leaching monoliths of synthetic brannerite at 70 °C show that the U releases are lowest in synthetic granitic (Finnisjon, Finland) ground water having a pH of 7.7. Overall, the results show that the ceramic waste form is highly durable in aqueous media although further testing and modelling is required to qualify the waste form for repository acceptance.

9:00 AM QQ4.3
COMPOSITION, GEOCHEMICAL ALTERATION, AND ALPHA-DECAY DAMAGE EFFECTS OF NATURAL BRANNERITE. <u>G.R. Lumpkin</u>, S.H.F. Leung and M. Colella, Materials Division, Australian Nuclear Science and Technology Organisation, Menai, NSW, AUSTRALIA.

Brannerite, ideally UTi_2O_6, is an accessory phase in titanate formulations designed for the encapsulation of actinide-rich, Pu-bearing nuclear wastes. In order to investigate the long-term behavior of brannerite, we have undertaken a study of twelve natural samples from a range of geological environments. Our results indicate that seven of the samples exhibit only minor alteration, usually within veinlets or around the rim of the sample. The remaining five samples consist of variable amounts of unaltered and altered brannerite. SEM-EDX analyses of unaltered areas indicate that the chemical formulae may deviate from the ideal stoichiometry. The U content ranges from 0.45 to 0.88 atoms per formula unit (pfu). Maximum observed amounts of the other major cations on the U-site are 0.48 Ca, 0.22 Th, and 0.14 REE atoms pfu. The Ti content ranges from 1.86 to 2.10 atoms pfu. Maximum observed values of other cations on the Ti-site are 0.15 Fe, 0.14 Si, 0.09 Al, and 0.05 Nb atoms pfu. Altered regions of brannerite contain significant amounts of Si, and approximately 40-90% of the original amount of U has been lost as a result of alteration. SEM-EDX results also provide evidence for anatase or rutile, galena, and a thorite-like phase as alteration products. Electron diffraction patterns of all samples typically consist of two broad, diffuse rings which have equivalent d-spacings of 0.31 nm and 0.19 nm, indicating complete amorphization of the brannerite. Many of the grains also exhibit weak diffraction spots due to fine grained inclusions of a uranium oxide phase and galena. Using the available age data, these samples have accumulated alpha-decay doses of 3-190 x 10^{16} alphas/mg. Our results indicate that brannerite is subject to amorphization and may lose U under certain P-T-X conditions, but the overall durability of the titanate matrix remains high.

9:15 AM QQ4.4
REACTION PATH CALCULATION OF U-PYROCHIORE NUCLEAR WASTES IN YUCCA MOUNTAIN REPOSITORY ENVIRONMENT. <u>Yifeng Wang</u> , Sandia National Laboratories, Carlsbad, NM; Huifang Xu, Department of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM.

Crystalline phases of pyrochlore (CaUTi2O7, CaPuTi2O7) are durable and promising waste form for hosting radioactive U and Pu (Dosch et al., 1981; Ringwood et al., 1988; Vance et al., 1994). It is important to understand possible reaction processes and reaction rates of the waste in geological repository. Recently, Gibbs free energies of fomation of pyrochlore phases with stoichiometry of $CaM^{4+}Ti2O7$ have beed calculated using a linear free energy relationship (Xu and Wang, 1999). Using the obtained standard Gibbs free energies of formation for CaUTi2O7 (837.31 kcal/mole) and CaPuTi2O7 (830.42 kcal/mole), we have calculated possible reaction paths of the pyrochlore in the condition of Yucca Mountain repository environment (acidic volcanic rock with small amount of biotite). The calculation of the pyrochlore dissolution uses solution composition of Yucca Mountain groundwaters. The solution is maintained at constant pCO2=1E-2.3, fO2 = 1E-30 atm, and T = 25 °C (open system). The calculated results show the U-pyrochlore will be replaced by rutile,

soddyite, haiweeite, and calcite etc. Other minerals that will also form are stilbite (zeolite), nontronite, hematite, and illite. The main difference between U-pyrochlore and Pu-pyrochlore alteration is that $PuO2$ is the only Pu-bearing phase in Pu-pyrochlore alteration products. By using a dissolution rate of zirconolite (Weber et al., 1986) as a first-order approximation, the real time reaction processes can be calculated.

9:30 AM QQ4.5
DISSOLUTION KINETICS OF TITANIUM PYROCHLORE CERAMICS AT 90°C BY SINGLE-PASS FLOW-THROUGH (SPFT) EXPERIMENTS. <u>Jonathan P. Icenhower</u>, B. Peter McGrail, H. Todd Schaef, Virginia L. LeGore, Elsa A. Rodriguez, Pacific Northwest National Laboratory, Richland, WA.

We have quantified the dissolution kinetics of pyrochlore ceramics at 90°C over a range of pH values (2-12) by use of single-pass flow-through (SPFT) experiments. Typical experimental durations are >100 days on powdered ceramic samples. The compositions of the ceramics are $A_2Ti_2O_7$ ($A=Ca^{2+}$, Ce^{3+}, Gd^{3+}, and Hf^{4+}) with structures representing both betafite and zirconolite subgroups. In addition, the ceramics are doped with small concentrations (0.1 wt%)of Mo^{6+}, which acts as a tracer of dissolution. Concentrations of Mo^{6+} in the effluent solutions indicate dissolution rates of 2.5-3.5×10^{-4} (g m^{-2} d^{-1}) for both the betafite and zirconolite samples at pH = 5.7. The Mo tracer revealed an amphoteric pH dependence of the dissolution rate with minimum rates observed at moderate pH values (4-6). Mo concentrations dropped to near detection limits at pH = 2 indicating the formation of a highly insoluble compound at this pH. However, dissolution rates could be determined from concentrations of Ce^{3+} and Gd^{3+} at pH = 2 (2-4×10^{-4} g m^{-2} d^{-1}). At higher values of pH, solubility constraints were encountered for essentially every major structural component in the ceramic and so effluent concentrations of these elements do not provide reliable measures of dissolution rates. Dissolution rates (based on Ce^{3+}, Gd^{3+}, and Mo^{6+}) of powdered samples are nearly identical to those measured on simple betafite [(Gd^{3+}, Lu^{3+}, or Y^{3+})$_2Ti_2O_7$] monoliths at pH = 2, T = 90°C. Collectively, these experiments establish the baseline from which the effects of radiation damage on the dissolution rates of pyrochlore ceramic waste forms can be quantitatively assessed.

9:45 AM QQ4.6
SURFACE ALTERATION OF TITANATE CERAMICS IN AQUEOUS MEDIA. <u>E.R. Vance</u>, N. Dytlewski, K.E. Prince, K.P. Hart and E. Loi, ANSTO, Menai, AUSTRALIA.

The alteration of titanate ceramics in aqueous media has been studied by a variety of techniques. The average thickness of the surface D-bearing layer on (multiphase)Synroc-C when exposed to D_2O at 150°C for 21 days was confirmed to be ~15 nm by Elastic Recoil Detection Analysis (ERDA) of 2 MeV He ions and secondary ion mass spectrometry (SIMS). Exposure of Synroc-C to D_2O at 250°C for 21 days increased the average thickness of the D-bearing surface layer to >200 nm from ERDA measurements, and SEM revealed a ~ 1 μ-thick surface layer of anatase. Again, from ERDA studies, the thickness of the D-bearing surface layer on zirconolite-rich ceramics, designed for excess weapons Pu immobilisation, was only ~3 nm upon exposure to D_2O for 30 days at 150°C. Synroc-C samples leached for 7-336 days at 90°C in deionised water did not reveal any surface buildup of Nd or Ce by SIMS. Alpha-recoil spectroscopy on Cm/Pu-doped Synroc-C samples showed some surface buildup of Cm after leaching for 84 days at 70°C in deionised water. Undoped Synroc-C also showed some weak surface sorption of actinides in the same experiment. Admixtures of 0.001 mol/L of fluoride to a pH=2 HCl-based solution produced a strong enhancement of its reaction at 70 or 90°C with hot-pressed perovskite, as shown by enhanced elemental extraction into solution and a much thicker anatase coating (20 μ vs. 1μ).

SESSION QQ5: CERAMICS - STRUCTURE AND CHARACTERIZATION
Chairs: Ned E. Bibler and S. V. Raman
Tuesday Morning, November 30, 1999
Room 203 (H)

10:30 AM QQ5.1
EXAFS AND XANES ANALYSIS OF PLUTONIUM AND CERIUM EDGES FROM TITANATE CERAMICS FOR FISSILE MATERIALS DISPOSAL. <u>J.A. Fortner</u>, A.J. Kropf, A.J. Bakel, M.C. Hash, S.B. Aase, E.C. Buck and D.B. Chamberlain, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

We report x-ray absorption near edge structure (XANES) and extended x-ray fine structure analysis (EXAFS) spectra from the plutonium LIII and cerium LIII edges in prototype titanate ceramic hosts for disposal of surplus fissile materials. These spectra were obtained using the MRCAT beamline at the Advanced Photon Source (APS). The titanate ceramics studied are based upon the hafnium-pyrochlore and zirconolite mineral structures and will serve as an immobilization host, containing as much as 10 weight % fissile plutonium, and 20 weight % (natural or depleted) uranium. Formulations using cerium as a surrogate element, replacing both plutonium and uranium in the ceramic matrix, clearly indicate a mixed III-IV oxidation state for the cerium. In contrast, XANES analysis shows that the plutonium is present almost entirely as Pu (IV), illustrating the limitations inherent in using lanthanide surrogates to replace actinides. The EXAFS real-space structure shows a strong second-shell peak, clearly distinct from that of PuO_2, due to coordination by Hf and/or Gd. The role of these neutron-absorbing elements in the ceramic is to prevent potential criticality, so the high proximity within a single phase is important.

10:45 AM QQ5.2
PHASE COMPOSITION AND ELEMENTS PARTITIONING IN TWO-PHASE HOSTS FOR IMMOBILIZATION OF REE-ACTINIDE FRACTION OF HLW. <u>Sergey V. Stefanovsky</u>, SIA Radon, Moscow, RUSSIA; Sergey V. Yudintsev, Boris S. Nikonov, Inst of Geology of Ore Deposits, Moscow, RUSSIA; Alexander V. Ochkin, Natalia E. Chernyavskaya, Univ of Chemical Engineering, Moscow, RUSSIA.

Two-phase hosts based on REEAlO$_3$-(Zr,U)O$_2$, REE$_2$Ti$_2$O$_7$ (Zr,U)O$_2$, REEAlO$_3$-Ca(Zr,U)Ti$_2$O$_7$, and REEZrTiAlO$_7$ (Zr,U)O$_2$ assemblages were prepared by melting at 1580°C and investigated using XRD, SEM/EDS, and TEM. These hosts incorporate up to 40 wt.% of REE-actinide fraction of HLW. In the zirconolite with nominal stoichiometry $A^{VIII}B^{VII}C^{V-VI}_2O_7$ actinide ions occupy VIII and VII-fold coordinated sites. Charge compensation is provided by incorporation of lower charged ions (Al^{3+}, $Fe^{2+/3+}$, Mg^{2+}) instead of Ti^{4+}. Maximum REE$_2$O$_3$ content (45 wt.%) was observed in a Ca free zirconolite (nominal formula REEZrTiAlO$_7$). In the pyrochlore-structured phase $A^{VIII}_2B^{VI}_2O_{7-x}$ actinides and rare earths occupy "A" sites. Their incorporation doesn't require coincident substitution of ions in "B" site, for instance, Ti^{4+} for Al^{3+} or $Fe^{2+/3+}$ for charge compensation simplifying composition of the system. Pyrochlore ceramics are suitable for immobilization of high actinide wastes. At high Zr content in waste complex zirconia-based or two-phase pyrochlore-zirconia or pyrochlore-zirconolite ceramics are preferable. In the samples containing complex oxide the pyrochlore- type phase and zirconolite incorporate Ti, La, and Gd, complex oxide is enriched with Zr, Ce, and U. One of the samples contained two pyrochlore-type phases with different U content.

11:00 AM QQ5.3
A CORRELATION BETWEEN RELATIVE CATION RADIUS AND THE PHASE STABILITY OF ZIRCONOLITE. <u>Douglas Swenson</u>, Peerapong Triyacharoen, Dept of Metallurgical and Materials Engineering, Michigan Technological Univ, Houghton, MI.

Geometric considerations often determine the crystal structures of ceramic materials. Conversely, for phases of known crystal structure, it may be possible to predict phase stability based on structural arguments, e.g., by specifying ranges of relative ionic sizes over which that phase could reasonably be expected to exist. Although seldom employed, such an approach is well suited to the study of ceramic nuclear wasteforms, which are often intractable from a chemistry-oriented viewpoint. If such correlations were available, it would be possible in principle to predict the maximum solubility of an arbitrary combination of ions in a single phase wasteform based solely on its average ionic radii, greatly facilitating optimization of the wasteform for a specified application. The present investigation was conducted to determine whether the phase stability of zirconolite (CaZrTi$_2$O$_7$), a component of Synroc, could be rationalized based on geometric considerations. The maximum solubilities of several different cations (Ce, Al, Gd, Sm, Hf) in zirconolite were investigated using X-ray diffraction and electron probe microanalysis. A parameter termed the relative radius ratio, defined as the ratio of the average radius of all atoms substituting for Ca and Zr to the average radius of all atoms substituting for Ti, was calculated for each chemical system. It was found that for each chemical system studied, and for additional systems from the literature, the relative radius ratio for zirconolite is 1.590, with a less than one percent standard deviation, at its solubility limit. These results suggest that the phase stability of zirconolite is governed by geometry, and that chemical effects are of secondary importance. Therefore, it should be possible to predict the solubility limit of an arbitrary combination of cations in zirconolite, provided that it is known which lattice sites they occupy. Predicted maximum solubilities are given for several coupled substitution schemes of technological interest.

11:15 AM QQ5.4

SYNTHESIS AND STUDY OF ^{239}Pu-DOPED GADOLINIUM-ALUMINUM GARNET. Boris E. Burakov, Evgeniy E. Anderson, Maria V. Zamoryanskaya, Marina A. Petrova, V.G. Khlopin Radium Institute, St. Petersburg, RUSSIA.

Garnet solid solutions, Y3Al5O12-Gd3Al55O12-Gd3Ga5O12 (YAG-GAG-GGG), are under consideration as the prospective durable host-phases for the immobilization of actinide-containing waste of complex chemical composition. Garnet sample with simplified formula: Gd3(Ce,Ca,Sn,Ga,Pu)2Al3O12 containing approximately 5 wt.% ^{239}Pu and 4.5-5.0 wt.% Ce has been synthesized through melting of oxide precursor in air in the flame of hydrogen burner. The admixtures of Ca and Sn were used to increase Pu incorporation into garnet lattice through ion charge and size compensation for Pu^{4+}. Obtained material was studied by SEM method in comparison with other garnet samples doped with Ce and U. It was confirmed that the use of compensating admixtures such as Sn and Ca provides significant incorporation of Pu, U, Ce (not less than a few wt.%) in the same positions into garnet structure. In other cases the behavior of Pu, U and Ce is quite different. Under the same synthesis conditions without compensating elements GGG incorporates up to 6 wt.% Ce, but less than 0.1 wt.% U; and pure YAG incorporates not higher than 0.5 wt.% Ce. The preliminary conclusions have been done that garnet solid solutions can incorporate simultaneously tri- and tetravalent actinides in significant amount because they occupy different positions in the garnet structure. Ce can be considered as an acceptable simulant of Pu^{4+} and Np^{4+} for the garnet host-phase only in case of using charge- and size-compensating admixtures. Otherwise, Ce can be used as Am^{3+} surrogate.

11:30 AM QQ5.5

ACTINIDE ACCOMMODATION IN MEMBERS OF THE SODIUM DIZIRCONIUM TRIS(PHOSPHATE) STRUCTURAL FAMILY. H.T. Hawkins, D.R. Spearing, D.K. Veirs, D.M. Smith, M.P. Neu, Nuclear Materials Technology and Chemical Science and Technology Divisions, LANL, Los Alamos, NM; B.E. Scheetz, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

Members of the sodium dizirconium tris(phosphate) structural family ([NZP]) possess desirable properties that would permit their application as hosts for the actinides. These properties, which include negligible thermal expansion, compositional flexibility, high thermal stability, and resistance to radiation damage, are attributed to the three-dimensional structure of $NaZr_2(PO_4)_3$. The ability of $KZr_2(PO_4)_3$, a member of the [NZP] structural family, to accommodate U(IV) and Pu(III/IV) for Zr on the octahedrally-coordinated metal site (A) has been explored. The actinide-doped [NZP] compounds were prepared from sol-gel derived precursors at modest temperatures. The actinide oxidation state was established by comparison of the diffuse reflectance spectra of the [NZP] compounds with those of other actinide phosphates. Rietveld refined x-ray powder diffraction data confirmed a rhombohedral structure for all of the U(IV)-bearing [NZP] compounds and suggested random occupation of the A site by U/Zr; the Rietveld refined U/Zr molar ratio for each compound was in agreement with that determined by electron microprobe analysis. The Rietveld refined data showed a concomitant increase in the volume of the rhombohedral cell with an increase in the average radius of the octahedral A site occupant. Structural changes resulting from the accommodation of Pu(III/IV) on the A site in $KZr_2(PO_4)_3$ will be discussed and compared to those resulting from U(IV) accommodation on A.

11:45 AM QQ5.6

CHARACTERIZATION OF A GLASS-BONDED CERAMIC WASTE FORM LOADED WITH U AND Pu. PART II: DETAILED MICROSTRUCTURE DEVELOPMENT AND PHASE CHARACTERIZATION. Wharton Sinkler, T.P. O'Holleran, T.L. Moschetti, S.M. Frank, J.S. Luo, W.L. Ebert and S.G. Johnson, Argonne National Laboratory, Idaho Falls, ID and Argonne, IL.

This paper presents microscopic characterization of a glass-bonded sodalite ceramic waste form (CWF) for actinide and fission product containment. The material is central to Argonne National Laboratory's pyrometallurgical treatment for disposal of sodium -bonded metallic spent fuel. In an initial stage, the spent fuel is electrolytically passed through a salt bath, which separates the noble metals as well as Zr and U. Other components of the spent fuel, primarily the alkali metals, rare earths, and transuranics, remain in the process salt. The CWF is designed for disposal of process salts. The salt is first occluded into a zeolite 4A. Following this, the salt-occluded zeolite is blended with a glass frit and hot isostatically pressed. During pressing, the zeolite is transformed to sodalite, resulting in the final glass bonded sodalite composite. This study presents a detailed characterization of phase content and development in four surrogate CWF's via TEM, SEM and XRD. Both the zeolite H_2O content as well as the ratio of U to Pu content was varied in

producing the samples. A central goal of the study will be to assess the role of H_2O in determining CWF microstructure. Whereas it was originally expected that actinide and rare earth components would remain occluded in the sodalite phase, previous observations suggested that a reaction with residual H_2O to form oxide was preferred over occlusion. In addition to a detailed description of the phases present using electron diffraction, the study will attempt to address remaining questions concerning zeolite occlusion of actinides to produce an actinide host phase, and the consequences in regard to corrosion behavior this may have.

SESSION QQ6/GG4: JOINT SESSION:
CEMENT-BASED MATERIALS AND WASTE
CONTAINMENT
Chairs: Surendra P. Shah and Robert W. Smith
Tuesday Afternoon, November 30, 1999
Room 203 (H)

1:30 PM *QQ6.1/GG4.1

SIMULATED MICROSTRUCTURE AND TRANSPORT PROPERTIES OF ULTRA HIGH PERFORMANCE CEMENT BASED MATERIALS. Micheline Moranville, Lab of Mechanics and Technology, ENS of Cachan, FRANCE; Véronique Matte, Cécile Richet, Lab of Materials Studies, French Atomic Energy Commission, Saclay, FRANCE; Jean Michel Torrenti, National School of Roads and Bridges, Marne-la Vallèe, FRANCE.

Ultra-high performance cement-based materials expected to be used in nuclear waste containers were submitted to a leaching test, in order to evaluate their long-term durability. Different pastes of portland cement, portland + silica fume (10% and 30%), all with a water/cement ratio of 0.2, but two of them heat-treated like in Reactive Powder Concrete, were attacked by de-ionised water. SEM observations and quantitative image analysis of cement anhydrous phases and hydrates, porosity measurements, and calculation of the tritium diffusion coefficient using a diffusion cell, revealed two zones after leaching i.e. a sound zone underneath a degraded zone in which tricalcium and dicalcium silicates were dissolved. As the aim of the research was to determine the properties of the degraded zone, first the microstructure of the sound zone was simulated using the NIST hydration model elaborated by Bentz and Garboczi, searching for the microstructure-property relationships as the capillary pore space connectivity and diffusivity, after having determined the degree of cement hydration and tritium diffusivity. Then the cement leaching was simulated and the properties of the modeled microstructure corresponding to the degraded zone were compared to the experimental results. Porosity and tritium diffusion were particularly influential factors of the long-term durability.

2:00 PM QQ6.2/GG4.2

PREDICTION OF THE LONG-TERM RELEASE OF HAZARDOUS SUBSTANCES FROM CEMENT-BASED MATERIALS TO WATER. Ase Andersson, Chalmers Univ, Dept of Building Materials, Göteborg, SWEDEN.

The chemical content in building materials, and the environmental risk these chemicals pose, represent a fairly new field of research. At the same time, customers are demanding more information about these questions, creating a need for guidelines and regulations for the building industry. The environmental risk of a substance can only be decided if the emission behaviour is known. As diffusive emissions, emissions from products, are responsible for severe ecological effects in the water environment, there is an increasing concern being aired over building materials in contact with water, as possible sources. In this study the leaching of hazardous elements present in concrete additives are discussed. The objectives are to analyse the results of present leaching tests and discuss whether the tests are capable of delivering confident data to enable the prediction of long-term release of hazardous substances. Concrete with different additives were prepared. The concrete additives were fly ash, slag and accelerating and air entraining admixtures. Substances that were focused upon were metals e.g. copper, chromium, lead, manganese and two active ingredients in admixtures: thiocyanate and tall oil. Two different leaching tests have been carried out, basically adhered to the Dutch standards NEN 7341 (availability test) and NEN 7345 (diffusion test). A selection of the results obtained in the leaching tests are discussed with regard to their correlation to existing models for leaching of cementious materials, such as diffusional models and models involving a shrinking dissolution front. In addition, several phenomena that will affect the leaching rate are presented. For example, leaching of portlandite causing an increase of porosity and a change of pH, and penetration of CO2 causing precipitation of CaCO3, will prevent the emission rate from correlating to Ficks law of diffusion.

2:15 PM QQ6.3/GG4.3

POROSITY AND LEACHABILITY OF CEMENT SOLIDIFIED WASTE-PART I. Tahar El-Korchi, Department of Civil Engineering, Worcester Polytechnic Institute, Worcester, MA; David Gress, Department of Civil Engineering, University of New Hampshire, Durham, NH.

Cement solidification is being used as a stabilization technology for managing of heavy metal wastes prior to land disposal. In this paper, cement solidified waste was leached using sythetic seawater and acid solutions to simulate aggressive environments. The heavy metal wastes included cadmium, lead, chromium, and arsenic. Chemical analysis included heavy metal release, pH and alkalinity. Mictrostructural analysis on the solidified waste and precipitates include SEM, EDAX, X-ray diffraction and mercury intrusion porosimetry. The metal leaching results are explained in terms of porosity and microstructural developments during solidification and hydration of the cement and during the dynamic leaching process.

2:30 PM QQ6.4/GG4.4

MODELING THE POROSITY AND LEACHABILITY OF CEMENT SOLIDIFIED WASTE-PART II. Tahar El-Korchi, Department of Civil Engineering, Worcester Polytechnic Institute, Worcester, MA; David Gress, Department of Civil Engineering, University of New Hampshire, Durham, NH.

In this paper, the leaching behavior of cement solidified waste is modeled using diffusion and dissolution models. The models are developed and tested using the heavy metal release data, pH and alkalinity reported in Part I. The heavy metal wastes included cadmium, lead, chromium, and arsenic. Microstructural analysis on the solidified waste and precipitates include SEM, EDAX, X-ray diffraction and mercury intrusion porosimetry. The metal leaching models are explained in terms of porosity, permeability, and pore size distribution. Microstructural developments during solidification and cement hydration and during the dynamic leaching process are incorporated in the leaching models.

3:15 PM QQ6.5/GG4.5

DIMENSIONAL ANALYSIS OF IONIC TRANSPORT MECHANISMS IN CEMENT-BASED MATERIALS. Rèmi Barbarulo, Direction destudes et Recherches, Electricitè de France, Moret-sur-Loing, FRANCE; Jacques Marchand, Centre de Recherche Interuniversitaire sur le Bèton, Universitè Laval, Sainte-Foy, CANADA.

From an engineering point of view, the mechanisms of ion interaction are quite important. Not only do they play an important role in the development of deleterious chemical reactions but they also affect the transport of ions through the material pore structure. In most recent service-life prediction models, the influence of on-going chemical reactions on the mechanisms of transport is usually taken into account by assuming the existence of a local equilibrium, i.e. that the rate of precipitation (or dissolution) is much faster than the rate of ionic transport. In order to validate this hypothesis, a dimensional analysis of various ionic transport problems currently encountered in civil engineering has been performed. The dimensional analysis allows to compare, on a theoretical basis, the rate of ionic transport to the rate of chemical reaction. This approach has been applied to various cases involving chloride and sulfate ions. The analysis clearly shows that the local equilibrium assumption is verified in most practical cases. The results of this theoretical analysis are compared to experimental results obtained on various cement-based systems.

3:30 PM QQ6.6/GG4.6

INFLUENCE OF LIMESTONE ADDITION ON CALCIUM LEACHING MECHANISMS IN CEMENT-BASED MATERIALS. Sandrine Catinaud, Jacques Marchand, Laval Univ, Dept of Civil Engineering, Quebec City, CANADA; Jim. J. Beaudoin, NRC, Materials Laboratory, Ottawa, CANADA.

In order to investigate the mechanisms of calcium leaching in cement-based materials, four different systems (C3S, C3S + C3A + CaSO4.2H2O, C3S + C4AF + CaSO4.2H2O and cement) were prepared and hydrated. In addition to the mineralogical composition of the system, test variables also included the percentage of calcium carbonate addition (0, 5, 10 and 20%). Sixteen different mixtures were blended and tested. In all cases, the water/solid ratio was fixed at 0,5. After a minimal curing period of 3 months, 1-mm thick samples of each system were cut and immersed in distilled water for a 90-day period. The kinetics of degradation were assessed by thermal and X-ray diffraction analysis after 10, 20, 40 and 90 days of immersion. The influence of calcium leaching on the volumetric stability of the various systems was also followed by length change measurements. Test results clearly indicate that the mechanisms of leaching are directly affected by the mineralogical composition of the system. The phenomenon of leaching also appears to be particularly sensitive to

the calcium carbonate content of the mixture. The mechanisms of calcium leaching are discussed from a theoretical point of view. Their implications on the long-term durability of cement-based materials are also discussed.

3:45 PM QQ6.7/GG4.7

COUPLING BETWEEN DIFFUSIVITY AND CRACKS IN CEMENT BASED SYSTEMS. Claire Tognazzi, LMDC, Toulouse, FRANCE; Jean Michel Torrenti, ENPC, Paris, FRANCE; Jean Pierre Ollivier, Myriam Carcasses, LMDC, Toulouse, FRANCE.

Cement based systems are used for radioactive waste storage. In this application, due to a very long service life, we have to consider a calcium leaching of the hardened cement paste by water. Tests have shown that this phenomenon is driven by diffusivity. This parameter depends on the microstructure of the cement paste including cracks that are often unavoidable. In this paper we present experimental results and modeling of the coupling between diffusivity and cracks. The cracks are created in our samples by means of a compression test. This is a displacement controlled test that allows us to control the crack opening. Diffusion tests on samples obtained at three different compression levels corresponding to three cracked states are then performed using tritiated water. These tests show diffusivity is affected by the existence of cracks and the main effect is observed when there is localization of the cracks (e.g. in the post-peak regime of the compression test). Finally we model the diffusion test in a simple way assuming the cracks are delimited by parallel planes. With this model we obtain an equivalent opening of the cracks which is of the same order as the opening estimated using strain measurements or image analysis.

4:00 PM QQ6.8/GG4.8

RELEASE OF INTERNAL SEALANTS, ADHESIVES, WATER-PROOFING AND ANTI-CORROSION CHEMICALS INTO CONCRETE TO REDUCE PERMEABILITY. Carolyn Dry, University of Illinois, School of Architecture, Champaign, IL.

Various types of hazardous wastes need engineered barriers to prevent outflow. Concrete is a brittle and porous material which changes dramatically over its liifetime. In order to design waste barriers using any type of concrete, the most effective intervention occurs at the time when it is needed during the life of the material and at the location undergoing distress. Internally placed encapsulators containing sealants, adhesives, waterproofing or corrosion chemicals are designed to release these chemicals where and when they are needed. For example, brittle fibers containing adheasives or sealants will release the chemicals when the matrix cracks, causing the fiber to crack and release chemicals. In the case of corrosion one design allows the fiber to be corroded, signaling the release of the chemical onto the rebar. Research from over a decade will be presented with special emphasis on permeability, cracking and corrosion data. Results from field testing and current wowk will be presented.

4:15 PM QQ6.9/GG4.9

CLAY-BASED GROUTING INTO THE EDZ FOR THE VAULT SEALING. Yutaka Sugita, Tomoo Fujita, JNC, Tokai, Ibaraki, JAPAN; Kazuhiko Masumoto, Kajima Corp, Tokyo JAPAN; Neil A. Chandler, AECL, Manitoba, CANADA.

In the Japanese concept for the disposal of the high-level radioactive wastes, the potential pathways for radioactive contaminant transport would be sealed by a combination of tunnel plug, backfilling and grouting. The material for these engineered barriers would be bentonite or a bentonite-based mixture under consideration of long-term stability of the seals. It is anticipated that an excavation damaged zone (EDZ) will exist in the rock immediately adjacent to the tunnel, and that this EDZ will have a high hydraulic conductivity as a consequence of the development of fractures during excavation. It will be necessary to design the engineered barriers to interrupt the migration of nuclides through the EDZ, and one element of the design will be grouting of the EDZ. Two tests of bentonite grouting for sealing the EDZ were conducted in the granitic rock at Atomic Energy of Canada Limited's Underground Research Laboratory. One test was the trial for the development of grouting procedure and the evaluation of grouting effectiveness, and the second test was a demonstration of the grouting around the clay bulkhead of the Tunnel Sealing Experiment (TSX). In the trial, grout was injected from a diluted slurry (0.2% bentonite by weight) to a concentrated one (8.0%) and the injection proportion of 4.0% was the most efficient. The result of the seepage test around the zone of grouted EDZ showed that grouting resulted in a reduction of permeability of the EDZ in the floor of the tunnel. In the TSX, a bentonite-based grout was injected into the EDZ adjacent to the clay bulkhead using the same procedure as in the trial. Although the hydraulic pulse test didn't indicate that the grouting greatly reduced the rock permeability, the

test was useful site-scale demonstration of bentonite grout injection for the purpose of EDZ sealing around a tunnel bulkhead.

4:30 PM QQ6.10/GG4.10
STUDY ON EFFECTS OF HYDRAULIC TRANSPORT OF GROUNDWATER IN CEMENT. <u>Masumitsu Toyohara</u>, Masaaki Kaneko, Nuclear Engineering Laboratory, Toshiba Corporation; Fumiyo Matsumura, Norimasa Mitsutsuka, Advanced Energy Design & Engineering Dept., Toshiba Corporation; Yasutoshi Kobayashi and Mitsutaka Imamura, Planning Dept., Japan Nuclear Fuel Limited.

This paper discusses the effects of solution velocity thorough the cementitious materials on formation of secondary hydrates. These hydrates are produced by the reaction of hydrates in cement and chemical compounds in groundwater. In Japan, the ground water velocity is presumed to be high, and so its decrease in disposal facilities for radioactive waste is very important in order to reduce the release of radio-elements to the environment. Cement is used for the materials of disposal facilities due to its attractive properties. But cement structures are not considered to decrease the groundwater velocity because of the existence of voids or microfractures in it. Thus the retention of the radio-elements which have poor sorption on engineering barrier and natural one is current problem. In recent years, the studies reported by PSI, a research institute in Switzerland, showed that the groundwater velocity in cementitious materials was decreased by filling the voids and microfractures due to the hydrates (secondary hydrates) produced by the reaction of cement hydrates and the compounds in groundwater. If the same reactions occur under our disposal condition, the migration of the radio-elements with poor sorption will be estimated to decrease. Therefore, their results encouraged us to study on the relation between the solution velocity and formation of secondary hydrates. The column experiments were carried out to measure the amounts of solutions through the cementitious materials filled in a column. Hardened ordinary Portland cement was ground into particles. After that, they were filled in the column (2cm diameter, 5cm long) and then the column allowed in nitrogen atmosphere. The solutions were poured into the column and the amount of solutions passed through the column was measured periodically. The compounds in solutions were Na2CO3 or Na2SO4, which were considered to be main ones of groundwater in Japan. Both these compounds and their concentrations were selected as parameters. The hydrates formed in the column were also measured by XRD experiments. The experimental results showed that the solution flow was terminated by formation of calcite (CaCO3), in the case of 1.8E-2 mol/L CO32- of solution. At less than this concentration, solution flows were decreased and eventually became constant but were not terminated. From these results, the relation between formation of secondary hydrates and dissolution of original ones in materials determined the degree of solution velocity. In the case of restricted concentration of compositions in groundwater, the formation of secondary hydrates was expected to decrease the groundwater velocity in cement structures in disposal facilities.

4:45 PM QQ6.11/GG4.11
IS AND XRD STUDY OF CEMENT-BASED MATERIALS CONTAINING ORGANIC POLLUTANTS. <u>Giovanni Dotelli</u>, Donatella Botta, Politecnico di Milano, Dept. of Industrial Chemistry and Chemical Engineering, Milano, ITALY; Isabella Natali Sora, Universita di Brescia, INFM and Dept. of Mechanical Engineering, ITALY; Claudio M. Mari, Universita di Milano Bicocca, Dept. of Materials Science, ITALY.

Some kinds of hazardous organic pollutants, specifically the aromatic amines, were immobilised by means of a cement-based S/S process. The aromatic amines were pre-sorbed in organophilic clays before solidification in the cement matrix. Monoliths with different types and amounts of clays were prepared as well as, for comparison, virgin cement samples and samples containing clays non wetted with aromatic amines. The phase composition and the possible structural alterations in the solid matrix introduced by the presence of the organic material were studied from XRD data. Moreover the morfology and the size distribution of the various phases were studied by SEM technique. Impedance spectroscopy (IS) measurements were performed in order to gain information about the variations of diffusivity, through the Nernst equation, induced by the presence of the organic pollutant.

SESSION QQ7: POSTER SESSION: SPECIATION, SORPTION, AND TRANSPORT
Chair: Larry C. Hull
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ7.1
THERMODYNAMIC INTERPRETATIONS OF CHEMICAL ANALYSES OF WATER FROM YUCCA MOUNTAIN, NEVADA. <u>Lauren Browning</u>, William M. Murphy, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX; William L. Dam and Bret W. Leslie, U.S. Nuclear Regulatory Commission, Washington, DC.

Groundwater chemistry is used in performance assessments of systems proposed for geologic disposal of nuclear waste. Ironically, geologic systems with low water/rock ratios, which are desirable for geologic waste isolation, also lead to ambiguous characterization of water chemistry. Difficulties in obtaining accurate geochemical data in the unsaturated zone result from air drilling of core samples, pore water evaporation, and compression techniques that alter pore water chemistry [1,2]. Thermodynamic interpretations of analytical data for unsaturated zone pore water from Yucca Mountain, Nevada, [1,2] indicate CO_3^{2-}/HCO_3^- ratios are incompatible with reported pHs. Significant ionic charge imbalances demonstrate data errors. Furthermore, large differences in reported pH over small distances seem unlikely in the ambient system. Analytical results were reinterpreted using equilibrium aqueous speciation calculations by introducing measured CO_2 gas pressure as a constraint and by imposing charge balancing by adjustment of pH. The reinterpreted, thermodynamically consistent data reveal new chemical trends, and indicate that some trends previously identified may be artifacts of water extraction processes. Data reinterpretations reduce pH variations from $7.3 < pH < 9.2$ to $8.0 < pH < 8.6$. Reinterpreted water chemistry data can be used to evaluate and interpret vertical and lateral variations in water chemistry and differences between unsaturated zone pore and perched water compositions. Characteristics of flow patterns and mineralogic control of groundwater chemistry at Yucca Mountain may also be inferred from patterns in thermodynamic aqueous activity ratios. This work does not represent the views or regulatory position of the U.S. Nuclear Regulatory Commission. References: 1. U.S.G.S. WRIR 96-4058; 2. U.S.G.S. WRIR 98-4132.

QQ7.2
RESEARCH INTO EFFECTS OF REPOSITORY HETERO-GENEITY. Mehdi Askarieh, United Kingdom Nirex Limited, Harwell, UNITED KINGDOM; <u>Adam Chambers</u> and Louise Gould, AEA Technology plc, Harwell, UNITED KINGDOM.

Calculations of the radiological consequences of deep waste disposal require models that apply a simplified description of the evolution of a repository. In work carried out to date for United Kingdom Nirex Limited (Nirex), models of repository performance have assumed that the contents of the repository are homogeneous. No account is taken, for example, of the fact that all the waste will be contained initially within waste packages, with the backfill surrounding the packages. It is important that the assumption of a homogeneous repository is demonstrated to be cautious (i.e. such that the model should not significantly underestimate the release of radionuclides). This paper describes models that describe the impact of specific heterogeneities on radionuclide release. These have been constructed and applied, in order to assess the appropriateness of the assumption of homogeneity. Calculations using the NAMMU computer program have examined the release of radionuclides from within waste packaging. These calculations suggest that recent performance assessments overestimate the release of short-lived radionuclides. Calculations, including the use of the INHOMOG computer program, have examined the relative placement of different categories of waste packages within repository vaults (for the Nirex disposal concept). It is concluded from the calculations that, for a few radionuclides, consideration of the distribution of some waste packages may be appropriate in future performance assessments.

QQ7.3
Abstract Withdrawn.

QQ7.4
SURFACE CHARGE AND ELECTROPHORETIC PROPERTIES OF COLLOIDS OBTAINED FROM HOMOIONIC AND NATURAL BENTONITE. <u>Tiziana Missana</u>, Maria J. Turrero, Andres Adell, CIEMAT, Departamento de Impacto Ambiental de la Energia, Madrid, SPAIN.

It has been recently shown that bentonite colloids can be generated at the near/field far field interface of a radioactive waste repository and can therefore affect the transport of contaminants to the biosphere. The study of the surface characteristics of such colloids is necessary to improve the understanding of the mechanisms that lead to retention and to the formation of pseudo-colloids at the repository/geosphere interface, as well as to determine their stability. Colloids were obtained for this study from samples of FEBEX bentonite. Tests were performed with the material previously purified and Na-homoionised,

and with the as-received material. Acid/base titrations and electrophoretic mobility measurements were carried out on both systems for comparison and for determining the effect on the surface properties of the colloids, due to the interactions of colloids with the impurities present in the water. The z potential of the colloids is always negative over the whole range of pH studied (3-11) and a clear iso - electric point or dependence from the ionic strength cannot be observed in any case. The generation of positive charge at edge sites at pH lower than the PZSE (6.5 for homoinised/purified and 8.3 for as received material) is less in absolute value than the structural permanent negative charge developed in the layers and the net charge of the particles remains negative. Experimental data obtained by acid/base titration were interpreted according the EDL theory. The model prediction agrees satisfactorily with the experimental data only in the alkaline pH range. Protonation / deprotonation reactions of surface functional groups (SOH) can be then considered the main charge - determining surface mechanism only in the alkaline pH range whereas ion - exchange type reactions have to be taken into account over the acidic pH range. Part of this work has been funded within the frame of the European Commission's Nuclear Fission Safety Research and Training Programme (1994-1998) under contract F14-Ct96-0021 and by the Spanish Ciemat Enresa.

QQ7.5
DIFFUSION OF PLUTONIUM IN COMPACTED BENTONITES IN THE REDUCING CONDITION WITH CORROSION PRODUCTS OF IRON. <u>Kazuya Idemitsu</u>, Xiaobin Xia, Tsuneo Ichishima, Hirotaka Furuya, Yaohiro Inagaki, Tatsumi Arima, Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, JAPAN; Toshiaki Mitsugashira, Mitsuo Hara, Yoshimitsu Suzuki, The Oarai Branch, Institute for Materials Research, Tohoku University, JAPAN.

In high-level waste repository, a carbon steel overpack will be corroded after closure. This will create a reducing environment in the vicinity of the repository. Reducing conditions are expected to retard the migration of redox-sensitive radionuclides such as plutonium. The apparent diffusion coefficients of plutonium were measured in compacted bentonites (Kunigel V1 and Kunipia F, JAPAN) in contact with carbon steel and its corrosion products under a reducing condition or without carbon steel under an oxidizing condition for comparison. Gas bubbles were observed in some bentonite specimens which had low dry densities after contact with carbon steels for approximately 2 years. This observation suggests hydrogen generation during corrosion of the carbon steel. The apparent diffusion coefficients measured were approximately 10^{-14} m^2/s under the reducing condition and less than 10^{-15} m^2/s under the oxidizing condition. There was a significant effect of redox conditions on the apparent diffusion coefficients. The effects of dry density (0.8 to 2.0 Mg/m^3) and montmorillonite contents (50% for Kunigel V1 or 100% for Kunipia F), however, were not observed clearly. The chemical species of plutonium were expected as PuOH^{2+} for the reducing condition and Pu(OH)$_4$ for the oxidizing condition, respectively.

QQ7.6
EFFECT OF IONIC CHARGE ON EFFECTIVE DIFFUSION COEFFICIENT IN COMPACTED SODIUM BENTONITE. <u>Haruo Sato</u>, Japan Nuclear Cycle Development Institute, Tokai-mura, Naka-gun, Ibaraki, JAPAN.

In performance assessment of the geological disposal of high-level radioactive waste, effective diffusion coefficient (De) is one of the important parameters. In this study, De values in compacted bentonite were measured as a function of ionic charge to evaluate the degree of surface diffusion and anion exclusion. The De measurements for Ni2+, Sm3+ and SeO32- were carried out with a dry density of 1.8 Mg/m3 by through-diffusion method. Sodium bentonite, Kunigel-V1, which is a crude bentonite, was used in this study. The measurements for only Se were carried out in an Ar atmospheric glove-box (O2 concentration ¡ 1ppm). The order of obtained De values was Sm3+ ¿ Ni2+ ¿ SeO32-. These De values were compared with that reported to date for the same bentonite. Consequently, the order of De values was Cs+ ¿ Sm3+ ¿ HTO (tritiated water) ¿ Ni2+ ¿ anions (I-, Cl-, CO32-, SeO32-, TcO4-, NpO2CO3-, UO2(CO3)34-), showing a tendency of cations ¿ neutral species ¿ anions. The reason that the De of Ni2+ was lower than that of HTO is because the ionic diffusion coefficient of Ni2+ in free water (Do) is about 1/3 of that of self-diffusion coefficient of water. The formation factors (FF), which were calculated normalizing De values by Do values showed a tendency of Sm3+ ¿ Cs+ ¿ Ni2+ ¿ HTO ¿ anions, indicating a possibility of surface diffusion in cations. In this case, the FF of Sm3+ was approximately 4 times greater than that of HTO. However, since the Do of Sm3+ is originally about 1/3 of self-diffusion coefficient of water, the actually measured De of Sm3+ is a little higher than that of HTO. Based on this, it is presumed that the effect of surface diffusion on De in compacted bentonite is insignificant.

QQ7.7
MODEL FOR SORPTION OF U(VI) ONTO BENTONITE. <u>Ursula Alonso</u>, Tiziana Missana, Miguel Garcia Gutierrez.

Bentonite has been considered as a candidate buffer material for high level radioactive waste repository because of its very high sorption capability and low permeability. Predictive modelling performance needs the development of the analysis onto different steps, the first one including the study of the sorption properties of the material and the second one the determination of the chemical mechanisms involved in the radionuclide/ clay / water interactions. The determination of the sorption capability of bentonite for U(VI) has been studied under a wide range of experimental parameters including concentration of sorbent and sorbate, ionic strength and pH by means of batch experiments. All the sorption experiments have been carried out using the as received material without performing any type of washing or purification. The chemistry of the water interacted with the clay, at the different experimental conditions used in batch experiments, was analysed in parallel, in terms of mayor ions and trace metals. The comparison of both sets of data allowed to develop a model for U(VI) sorption which includes a physicochemical approach with surface complexation and ion-exchange mechanisms coupled with geochemical processes. The model has been also tested with sorption and diffusion data obtained from experiments in compacted bentonite.

QQ7.8
ADSORPTION PARAMETERS FOR RADIOACTIVE LIQUID WASTE MIGRATION. <u>Larry Hull</u>, George Redden and Molly Pace, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

At the Idaho National Engineering and Environmental Laboratory, radioactive liquid waste from reprocessing spent nuclear fuel is one molar nitric acid with mg/L levels of uranium and plutonium. Past spills of the liquid waste to the soil were rapidly neutralized by calcite with concurrent large pH changes, generation of carbon dioxide gas, strong chemical gradients, and adsorption onto soil minerals. More mechanisms than can be addressed by an empirical Kd are needed to understand the migration potential of this waste. Apparent equilibrium constants for surface complexation reactions are measured on individual soil minerals (goethite, illite, smectite) and on whole-soil samples. Additive adsorption models for the individual minerals based on soil characterization data are compared to adsorption onto composite soil material. Geochemical computer models are used to compare the performance of a mechanistic approach based on surface complexation to an empirical Kd approach for fate and transport modeling.

QQ7.9
EFFECTS OF SURFACTANT-MODIFICATION ON THE SORPTION BEHAVIOR OF NATURAL ZEOLITES FOR STRONTIUM(2+) AND URANIUM(6+). James D. Prikryl, F. Paul Bertetti and <u>Roberto T. Pabalan</u>, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

Natural zeolite minerals have a strong ion exchange selectivity for alkali and alkaline earth radionuclides, such as strontium and cesium, but only limited sorption affinity for actinides such as uranium. In a previous study, surfactant-modification of the zeolite surface was shown to enhance uranium(6+) sorption at solution pHs greater than about 5.5. In this study, experiments were conducted to evaluate the ability of surfactant-modified zeolite to sorb both strontium(2+) and uranium(6+). A surfactant-modified zeolite was prepared by treating specimens composed mainly of clinoptilolite with the cationic surfactant hexadecyltrimethylammonium-bromide (HDTMA). The surfactant-modified clinoptilolite was reacted with strontium solutions having a range of strontium concentration, and with a mixture of strontium and uranium. Experiments were conducted as a function of pH and in equilibrium with atmospheric CO2(g). Results indicate that surfactant-modification of clinoptilolite decreases the ion exchange selectivity of clinoptilolite for strontium at acidic to near-neutral pH. Strontium exchange data were compared to previously developed model predictions of strontium ion exchange behavior on clinoptilolite. The presence of both uranium and strontium in solution had little effect on either the ion exchange selectivity of the surfactant-modified clinoptilolite for strontium or on the enhanced sorption of uranium at pH greater than 5.5. A surface complexation/ion exchange approach was used to model uranium and strontium sorption behavior.

QQ7.10
METAL ION STABILIZATION IN GEOMEDIA BY IN-SITU PHOSPHATE MINERALIZATION. Kenneth L. Nash, Mark P. Jensen, <u>Andrew H. Bond</u>, Chemistry Division, Argonne National Laboratory, Argonne, IL.

At the former nuclear weapons production facilities, transport of hazardous and radioactive materials through the vadose zone to

underlying aquifers or surface water recharge zones is a problem of potentially enormous impact to the biosphere. Because the vadose zone is unsaturated, a remediation method like pump-and-treat decontamination of subsurface waters may not be feasible for cleanup. This leaves excavation/soil washing or in-situ immobilization as the most reasonable methods of sequestering the contaminants from the biosphere. Previous results have indicated the potential of an in-situ immobilization method for actinide ions using a combination of cation exchange and phosphate mineralization. The conversion of potentially mobile cations to thermodynamically stable phosphate phases reduces the solubility of the target metal ions in the mobile solution phase. The calcium salt of the natural product phytic acid (myo-inositol-hexakisphosphoric acid), a simple sugar derivative containing six doubly-ionizable phosphate groups, has been demonstrated to function as an effective cation exchange medium for actinides in the tri- and hexavalent oxidation states. Its subsequent decomposition generates phosphate, which forms stable mineral phases with many polyvalent metal ions. After initial investigations of the conversion of actinide phytates into stable phosphate minerals, studies of the capacity of calcium phytates to remove actinides from simulated groundwater in the presence of soils from the Fernald and INEEL sites were conducted. Work performed under the auspices of the U. S. Department of Energy, Office of Science and Technology, Efficient Separations and Processes Crosscutting Program under contract number W-31-109-ENG-38.

QQ7.11
EXPERIMENTAL STUDY OF THE NICKEL SOLUBILITY IN SULPHIDIC GRONDWATER UNDER ANOXIC CONDITIONS. T. Carlsson, U. Vuorinen, T. Kekki, H. Aalto, VTT Chemical Technology, Industrial Physics, Espoo, FINLAND.

Recent literature recognizes a lack of proper chemical data that is necessary for the calculation of realistic values of the nickel solubility in sulphidic groundwaters. The literature also states that the published solubility constants for, e.g., NiS vary by many orders of magnitude, and that there is a lack of data for reactions involving nickel coprecipitation with iron compounds, and nickel complexation with sulphides. Consequently, in order for the performance assessment of radioactive waste repositories to be conservative, it is necessary to use solubility values that clearly exceed those obtained from modelling and experiments. The safety analysis of waste from the Olkiluoto NPP indicates that Ni-59, together with Nb-94, will dominate the dose rates in the waste after about 65 000 years. However, the estimated solubility limit of nickel is uncertain, and more studies are needed. This paper presents the results from a study of the nickel solubility in sulphidic groundwater under anoxic conditions. The waters used were natural groundwater from Olkiluoto and synthetic saline water, to which sodium sulphide had been added. The sulphidic concentrations were varied between 0.1 and 3 mg/L. In short, the nickel solubility in the waters was studied by adding nickel chloride spiked with Ni-63 to the samples and comparing the initial and final nickel activities using liquid scintillation counting. The initial nickel concentrations were 10^{-6} M and 10^{-3} M. All the experiments were carried out in carbon-dioxide free nitrogen atmosphere at room temperature. The duration of the experiments varied between 1 week and 3 months. The waters were analyzed with regard to their chemical compositions as well as colloid contents. The nickel solubility is discussed in terms of the analytically determined water chemistries, and the measured nickel solubilities are compared with those obtained from modelling using the geochemical code EQ3/6.

SESSION QQ8: POSTER SESSION:
RADIATION EFFECTS
Chairs: Ned E. Bibler and Donald T. Reed
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ8.1
ACCELERATED ALPHA RADIATION DAMAGE IN A CERAMIC WASTE FORM, INTERIM RESULTS. Steven M. Frank, Stephen G. Johnson, Tanya L. Moschetti, Thomas P. O'Holleran, Wharton Sinkler, David W. Esh, Argonne National Laboratory-West, Idaho Falls, ID.

Interim results are presented on the accelerated alpha decay damage study of a 238-Pu loaded ceramic waste form. Results include x-ray diffraction (XRD) observations of unit cell expansion of major phases in the waste form, microstructure characterization performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy and wavelength dispersive spectroscopy (EDS/WDS) and electron diffraction. In addition, bulk density measurements and waste form durability, performed by a product consistency test (PCT), are presented. The data presented concludes the first year of a four-year study for an accumulated alpha decay dose of approximately 5E17 alpha decays/gram of material. The waste form is a salt-occluded sodalite material with 25-weight percent glass binder. The ceramic waste form (CWF) is produced to immobilize fission products and actinide materials accumulated during the electrometallurgical treatment of spent nuclear fuel at Argonne National Laboratory in Idaho. In this accelerated radiation damage study, the CWF is loaded to approximately 2.5 wt% 238-Pu. This Pu loading is roughly 10 to 20 times the actual Pu (elemental) loading of the CWF produced during the fuel treatment process. The microstructure of the CWF consists of several-micron diameter sodalite grains surrounded by the glass binder. Plutonium is found primarily as PuO2 in the glass intergranular boundaries between sodalite grains. A second Pu containing phase has been identified as a tetragonal silicate material. Unit cell expansion of the PuO2 phase has reached saturation with, to date, an overall expansion of 0.6%. The sodalite phase also shows possible unit cell expansion, but this is questioned considering the small quantity of Pu in the phase. The bulk density has remained relatively constant. To date the durability of the 238-Pu material has performed very similar to the reference CWF, which is comparable or better than typical high level waste glass.

QQ8.2
FORMATION OF PEROVSKITE AND "CALZIRTITE" DURING ZIRCONOLITE ALTERATION. Jan Malmström, Eric Reusser, Mineralogy and Petrography, ETH-Zürich, SWITZERLAND; Detlef Günther, Institute for Inorganic Chemistry, ETH-Zürich, SWITZERLAND; Reto Gierë, Earth and Atmospheric Sciences, Purdue University; Gregory R. Lumpkin, Materials Division, ANSTO, AUSTRALIA; Richard Guggenheim, Marcel Düggelin, Daniel Mathys, SEM-Laboratory, University of Basle, SWITZERLAND.

Zirconolite is a major constituent of Synroc-type nuclear waste forms and a principal host for actinides and certain fission products. Preliminary leaching experiments showed that zirconolite is corroded by various aqueous fluids at 50 MPa and at temperatures above $250°C$, and the extent of reaction is strongly related to temperature, molality of the fluid, and time. The aim of this study is to investigate the stability of zirconolite in 0.1 M NaOH at the specific conditions of $550°C$ and 50 MPa. The leaching experiments were made with a single phase, polycrystalline Nd-doped zirconolite-2M ($Ca_{0.8}Nd_{0.2}$-$ZrTi_{1.8}Al_{0.2}O_7$, Nd as actinide analogue) which was loaded together with 25 μl fluid in small sealed gold capsules (SA/V = 4-6 cm^{-1}) to obtain a closed system. All experiments were carried out in externally heated pressure vessels and performed over several different run times (one hour up to 21 days) to determine the kinetics. Fluid run products together with the solid reaction products indicate a time-dependent element fractionation between fluid and solid secondary phases (perovskite and "calzirtite"). Crystallization of perovskite starts almost immediately (after one hour run time), and is accompanied by a decreasing Na concentration in the fluid. Crystallization of "calzirtite" begins at a later stage (after 12-24 hours). During the first few days the change in concentration of all elements in the fluid reflects the dissolution-precipitation process, which reaches a steady state after seven days under closed system conditions. The observed decreasing zirconolite corrosion rate is accompanied by an increasing degree of armoring. Our data can be used to assess the long-term behavior of zirconolite-based nuclear waste forms in final disposal sites by providing information on the mechanism underlying releases of waste elements from these matrices thereby giving confidence to the long-term extrapolation of laboratory data.

QQ8.3
MOLECULAR DYNAMICS STUDY OF THE INFLUENCE OF A SURFACE ON A SIMPLIFIED NUCLEAR GLASS STRUCTURE AND ON DISPLACEMENT CASCADES. Abdalkarim Abbas, CE Saclay, DTA/DECM/SRMP, FRANCE; Jean-Marc Delaye, Dominique Ghaleb, CEA Valrho-Marcoule, DCC/DRRV/SCD, FRANCE.

Resistance to radiation of nuclear glasses are generally based on external irradiation experiments. It is then important to determine the surface effect in order to validate these experiments. Molecular dynamics simulations of displacement cascades, by allowing analysis at the atomic scale, can be a very useful technique to enlighten the surface. The composition studied is a simplified nuclear glass composed by 6 oxides (SiO2 + B2O3 + Na2O + Al2O3 + ZrO2 + CaO). The simulated structure is prepared first by forming a liquid at 5000K, then by cooling until ambient temperature. The equilibrium volume is measured using a constant pressure algorithm (NPH system). Tridimensional periodic boundary conditions are applied at each stage of the preparation. A system with a surface is prepared by removing the periodic conditions along one direction (two parallel surfaces are created) and by further relaxing at ambient temperature. The two structures, with and without surface, are close one to another, so the surface influence can be precisely determined on the glassy structure and on a displacement cascade. Images of the

simulated surface show an accumulation of Na. This observation is confirmed by the plot of the chemical concentration profiles. Parally, we observe a decrease of the Si coordination near the surface, and an enlargement of the first neighbor distance distribution around Si. However, these effects are limited to the very proximity of the surface, due to the short duration of the simulations (few picoseconds) which prevent from observing these changes on a larger scale. We compared the evolution of displacement cascades performed in the structure with and without a surface. For this, an oxygen or zirconium atom is accelerated with an energy comprised between 300eV and 700eV. We observe that when a surface is present, the number of displaced atoms increases. The level of polymerization during the cascade always begins to decrease (a depolymerization peak appears), then the structure progressively repolymerizes. The surface induces an increase of the depolymerization peak but also an acceleration of the repolymerization rate.

QQ8.4
TEMPERATURE DEPENDENCE OF ION IRRADIATION INDUCED AMORPHISATION OF ZIRCONOLITE.

Katherine L. Smith, Mark G. Blackford, Gregory R. Lumpkin, Australian Nuclear Science and Technology Organisation, Materials Division, Menai, AUSTRALIA; Nestor J. Zaluzec, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Zirconolite is one of the host phases for actinides in various titanate wasteforms for immobilising high level radioactive waste. The critical dose for amorphisation, D_c, of zirconolite ($CaZrTi_2O_7$) was measured as a function of irradiation temperature using the HVEM-Tandem Facility at Argonne National Laboratory. Two samples were studied: one sample was hot pressed at 1473 K for 2 hours (1200 sample) and the other was sintered at 1723 K for 1 week (1450 sample). The 1450 sample has the zirconolite-2M polytype structure with a high level of crystallographic perfection. The 1200 sample also predominantly has the zirconolite-2M polytype structure but this sample contains many stacking faults and twins on the scale of the unit cell. Specimens of each sample were irradiated with 1.5 MeV Kr^+ ions at various temperatures from 20 K to 773 K and observed in situ in the HVEM. The temperature dependence of the critical dose for amorphisation is similar for both samples and shows single stage dependence of D_c on temperature. D_c is almost constant up to temperatures near the critical temperature for amorphisation, T_c, (above which recrystallisation is complete over the entire cascade volume), then it rises rapidly. Least squares fitting of the data according to current models shows that a) that the activation energy for self annealing E_a of the 1200 and 1450 samples are 0.14 ± 0.04 and 0.15 ± 0.06 eV respectively and b) the T_c values of the 1200 and 1450 samples are 637 ± 22 and 680 ± 27 K respectively. Previous authors investigating end-member zirconolite saw a two stage dependence of D_c on temperature for which they calculated E_a values of 0.1 and 0.32 eV and T_c values of 373 and 640 K. Similarities and disparities between our data and that of previous authors will be discussed in the paper.

QQ8.5
COMPUTER SIMULATION OF COLLISION CASCADES IN ZIRCON. Byeongwon Park, L. Rene Corrales, William J. Weber, Pacific Northwest National Laboratory, Richland, WA; Ramaswami Devanathan, Department of Metallurgical Engineering, Indian Institute of Technology Madras, Chennai, INDIA.

Collision cascades in zircon, which is candidate host phase for the immobilization of plutonium and other high-actinide wastes, have been studied using molecular dynamics (MD) simulation methods. Though there have been many experimental studies on irradiation damage in zircon, computer simulation of irradiation effects has been rather limited. We have developed a viable potential model for zircon and obtained displacement threshold energies for Zr, Si and O along several directions by molecular dynamics. As expected, the threshold displacement energies for cation and anion sublattices are quite different and there was a strong directional dependence in Ed, which could be explained by anisotropic structural features of zircon. In the current study, we investigated a 10 keV collision cascade in zircon by MD as an extension of the displacement threshold energy calculations. The MD code used is DLPOLY, which has been modified to implement irradiation process in the materials. The short-range interactions are represented by Buckingham type potentials with Ziegler-Biersack-Littmark (ZBL) form of the repulsive potential at shorter distances. The long-range Coulomb interactions are evaluated by Ewald method. The total number of atoms in the system was 194,400 (18x18x25 unit cell) and 10 keV kinetic energy was rendered to an atom at the top of cell to high index direction to avoid possible channeling. The evolution of lattice damage in a 10 keV cascade was observed for about 10 ps. Details of the simulation results will be presented.

QQ8.6
RADIATION AND THERMAL EFFECTS IN ZEOLITE-NAY.

Binxi Gu, Lumin Wang and Rod C. Ewing, Department of Nuclear Engineering and Radiological Science, University of Michigan, Ann Arbor, MI.

Zeolite-NaY is susceptible to irradiation- and thermally-induced amorphization. Both zeolite-NaY and the Cs-exchanged zeolite-NaY undergo a crystalline-to-amorphous transformation when irradiated with 200 keV electron beam. At room temperature, complete amorphization was achieved at the doses of 4.0×10^{19} e^-/cm^2 and 5.0×10^{19} e^-/cm^2 for zeolite-NaY and the Cs-exchanged zeolite-NaY, respectively. The amorphization of zeolite-NaY and the Cs-exchanged zeolite-NaY was also achieved by thermal treatment. Zeolite-NaY became fully amorphized after thermally treated at 900°C in air for 30 min. Based on x-ray diffraction analysis, a secondary phase was formed during the ion exchange reaction with cesium. The Cs-exchanged zeolite-NaY phase has a slightly higher thermal stability than the unexchanged zeolite-NaY, i.e. complete amorphization was achieved when the Cs-exchanged zeoite-NaY was heated at 1000°C. The amorphized zeolite-NaY, obtained by thermal treatment, lost approximately 95 percent of its ion exchange capacity for cesium, as compared with the crystalline zeolite-NaY. The reduction in ion exchange capacity is attributed to the loss of exchangeable cation species and/or the blockage of access to exchangeable cation sites. A desorption study indicated that the amorphization of cesium-loaded zeolite-NaY enhances the retention capacity of exchangeable Cs ions due to the closure of structural channels.

QQ8.7
RADIATION EFFECTS IN CHLORIDE MOLTEN SALT COMPOSITION. Sviatoslav Ignatiev, Dmitry Pankratov and Evgeny Yefimov, Inst of Physics and Power Engineering, Dept of Special Nuclear Power Units, Obninsk, RUSSIA.

At present the assembly of tungsten neutron generating target along with molten salt subcritical blanket cooled by molten salt of actinides are studying as a variant of accelerator driven transmutation system for nuclear waste incineration. The system where molten chloride of actinides are directly irradiated by high energy protons are also considering. The purpose of this work was to study radiation effects in the composition of NaCl (70% mole) and PbCl2 (30% mole) salts irradiated by high energy proton beam. This target was formed as cylinder of 20 cm in diameter and 200 cm in length. The isotopic percentage and radiation parameters versus target thickness were analyzed under irradiation by secondary neutrons of different flow density and hardness, that appear in the target and surrounding blanket. For the LANSCE (LANL) accelerator conditions (proton energy 800 MeV, current 1 mA) the secondary neutron flux densities, as well as spectra of protons and secondary neutrons, were calculated using MARS-10 code. Total energy deposition in the target proved to be as much as ~437 kW, i.e. ~54% of beam power, while average specific energy deposition was ~12.63 W per cubic cm. The effect of high-energy neutrons on change of molten salt isotope composition and radiation parameters was studied. Due to inelastic neutron scattering on lead nuclides a comparatively high radioactivity is accumulated in the target. It average value for flux power ~1 MW at the switch-off moment after 1 year operation is as much as ~1000 millions becquerels per cubic cm. After 1 year cooling the contribution of activity induced by high energy neutrons proved to be 1.6 and 15 times less than low energy contribution for «bare» target and target-blanket system correspondingly. The analysis of radiation decomposition and recombination effects in the molten salt components was done. Radiation strength was analyzed from the viewpoint of the following key problems: -radiolysis of the system and a possibility to appear of a new phases; chloride compounds strength relative to lead compounds; radiolysis products influence on the process of structure material corrosion; radiolysis due to residual irradiation. In the whole, in the temperature interval from ~50 C to ~1200 C the chloride fuel composition in question can be considered as radiation-resistant material, that permits to recommend its use as a perspective fuel of high-temperature molten salt reactor.

QQ8.8
ELECTRON IRRADIATION EFFECTS ON BUBBLE FORMATION AND GROWTH IN NBS-1 GLASS. Xidong Chen, Robert Birtcher, Materials Science Division, Argonne National Laboratory, Argonne, IL.

We studied electron irradiation effects on bubble growth in sodium borosilicate glass (NBS-1) during Xe ion implantation at 200 °C. EDAX spectrums confirmed that Xe bubbles formed as a result of Xe implantation. Contrary to previous claims, we have found no evidence of oxygen bubble formation under electron irradiation, with or without Xe implantation. It was found that electron irradiation increases the average Xe bubble size in the glass. Quantitative measurements of this enhancement are made through measuring the bubble size. Ionization enhanced diffusion is responsible for this size increase. A mechanism based on excitons is suggested. The same mechanism is also shown by

the shrinkage of Xe bubbles under electron irradiation after the Xe implantation. Dynamic behaviors of this shrinkage are studied. These results provide insights on this ionization enhanced diffusion.

QQ8.9
HYDROGEN GAS EVOLUTION FROM WATER DISPERSING NANOPARTICLES IRRADIATED WITH GAMMA RAY. Satoshi Seino, Ryosuke Fujimoto, Takao A Yamamoto, Masahiro Katsura, Osaka Univ, Dept of Nuclear Engineering, Osaka, JAPAN; Shuichi Okuda, Osaka Univ, Institute of Scientific and Industrial Research, Osaka, JAPAN; Kenji Okitsu, Nagasaki Univ, Dept of Science and Engineering, Nagasaki, JAPAN; Ryuichiro Osima, Osaka Prefecture Univ, Research Institute for Advanced Science and Technology, Osaka, JAPAN.

Hydrogen gas evolution induced by ^{60}Co γ-ray irradiation of nanoparticles dispersed in aqueous solution was investigated under various conditions by measuring hydrogen yields by a gas chromatograph. Nanoparticles of TiO_2, Al_2O_3, ZnO, ZrO_2 and CeO_2 were examined. Their average sizes were from 21 nm to 700 nm. Some particles supporting Pd, Pt, or Au were also examined. Some of the nanoparticles showed hydrogen yields much larger than that caused by the water radiolysis, about 14 times at most. These hydrogen yields seemed to depend on size and shape rather than chemical species of the particles. The yield increased with increasing dose rate almost linearly, and increased and saturated with increasing amount of particles dispersed in water. These two facts indicate that hydrogen evolution is a synergistic effect of radiation and particles dispersed in water. Supporting noble metals had large effects on the yield, which indicates particle surface plays an important role in the hydrogen evolution. Observed hydrogen yields are discussed taking account of miscellaneous active species generated by the water radiolysis.

QQ8.10
DIAMOND DETECTORS FOR ALPHA MONITORING IN CORROSIVE MEDIA FOR NUCLEAR FUEL ASSEMBLY REPROCESSING. P. Bergonzo, F. Foulon, A. Brambilla, D. Tromson, C. Mer, B. Guizard, S. Haan, LETI (CEA-Technologies Avances)/DEIN/SPE, CEA/Saclay, Gif-sur-Yvette, FRANCE.

Applications within the environmental monitoring, as well as control and nuclear waste recycling in nuclear industries have been identified which require a detector element capable of monitoring the nuclear activity in liquid solutions. Such detectors must withstand immersion in corrosive media, and particularly in nitric acid solutions. Diamond is the unique candidate for such detectors. It is naturally inert to corrosion and can sustain high integrated levels of ionising radiations. The recent advances in diamond synthesis techniques using chemical vapour deposition methods (CVD) enabled its use for the monitoring of alpha particles on an industrial basis. Thin layers of diamond have been grown, processed, and used for the fabrication of corrosion hard alpha detectors. The device geometry enables the sensor to be directly immerged in the corrosive solution, thus limiting any significant absorption that would be induced with a protective coating. The devices have been tested using Plutonium 239 isotope dissolved in nitric acid. They appeared extremely reliable and measurements of the solution activity were achieved across 3 decades. The response was stable under continuous immersion over 100 hours, and prevision would suggest they could be stable during months of continuous use. One inherent problem that rises when devices are immersed in nuclear liquid solutions is their inherent contamination. Due to the high surface tension of CVD diamond, we found that the devices are hardly contaminated after use, and that they can be completely cleaned using a simple acid rinsing procedure. These promising detectors now open the market of CVD diamond towards nuclear waste monitoring.

SESSION QQ9: POSTER SESSION:
NATURAL ANALOGS
Chair: William M. Murphy
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ9.1
AN ARCHEOLOGICAL SITE AT AKROTIRI, GREECE, AS A NATURAL ANALOG FOR RADIONUCLIDE TRANSPORT: IMPLICATIONS FOR VALIDITY OF PERFORMANCE ASSESSMENTS. D.L. Hughson, L. Browning, W.M. Murphy, R. Green, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

Natural analog studies provide a means to test assumptions in performance assessment models. Data on the spatial distribution of metals derived from an archeological site at Akrotiri, Greece, were used to evaluate performance assessment model assumptions of

radionuclide transport through unsaturated volcanic tuffs hosting the proposed HLW repository at Yucca Mountain, Nevada. Performance assessment abstractions of radionuclide transport through the unsaturated zone to the water table range from simple 1-D advective transport models to 3-D dual continuum flow and transport models incorporating sorption, dispersion, matrix diffusion, perched water zones, colloidal transport, and solute advection. Processes controlling transport of trace elements from 3,600 year old artifacts at Akrotiri are analogous to processes controlling radionuclide transport at Yucca Mountain. Archeological information temporally and spatially constrains the source and chemistry of these trace elements, providing a comparison basis for model validation efforts. Despite these constraints and characterization of the Akrotiri site, the data are open to different interpretations as the extent of the plume emanating from the Minoan artifacts, transport pathways, heterogeneities in parameters, and boundary conditions are uncertain. Various conceptual models of flow and transport predict substantially different trace element distributions. Model results of plume migration are presented illustrating these uncertainties. Rather than validating a conceptual model of flow and transport, the Akrotiri site data indicate that 1-D models of aqueous phase transport in the unsaturated zone may be unrealistically overconservative. The data also indicate that more complex models may neglect important transport mechanisms. This study suggests that site characterization and predictive modeling alone are insufficient to adequately assess natural processes occurring over thousands of years. Natural analog sites provide a valuable source of data for improving and increasing confidence in predictive models. This work is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the U.S. Nuclear Regulatory Commission.

QQ9.2
BEHAVIOR OF URANIUM-RICH MICROLITE DURING ARGILLITIC ALTERATION. Reto Gieré, Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN; Edgar Buck, Chemical Technology Division, Argonne National Laboratory, Argonne, IL; Richard Guggenheim, Daniel Mathys, SEM Laboratory, University of Basel, Basel, SWITZERLAND; Eric Reusser, Institute of Mineralogy and Petrography, ETH Zentrum, Zürich, SWITZERLAND.

Pyrochlore-based ceramic waste forms are currently under development for the immobilization of excess weapons plutonium. These ceramics are polyphase crystalline waste forms consisting of mainly pyrochlore and subordinate amounts of brannerite, zirconolite, and rutile. Minerals of the pyrochlore group conform to the general formula $A_2B_2O_7$, where actinides and certain fission products are accommodated in the A site. On the basis of the B-site cations, three subgroups are distinguished: pyrochlore ss. (Nb-rich); microlite (Ta-rich); and betafite (Ti-rich). Pyrochlore-group minerals are excellent natural analogues for pyrochlore-based nuclear waste forms, because samples of variable age and with high actinide contents are available. Microlite occurs primarily in granitic pegmatites. It is a characteristic phase in the old (approximately 600 Ma) lithium pegmatites of the Mozambique Belt in East Africa, where large euhedral microlite occurs in association with albite, spodumene and lithian mica. We have examined a sample from a strongly altered pegmatite in Mozambique. This microlite exhibits a pronounced growth zoning, with a U-free core surrounded by a U-rich rim (UO_2 up to 13 wt.%). The microlite core exhibits a conjugate set of straight fractures formed prior to the U-rich rim. These fractures provided a pathway for the late-stage U-enriched pegmatitic fluid. The fluid interacted with the U-free microlite to produce a distinct U enrichment along the fractures and also caused the U enrichment in the rim. The latter is characterized by a large number of irregular cracks which, as indicated by radiation damage microstructures observed by TEM, are the result of metamictization. After the incorporation of U into the rim and along the fractures in the core, the pegmatite was subjected to intense argillitic alteration. There is no evidence of U loss and therefore, this example documents that microlite is able to retain U over geologic time scales even after low-temperature alteration of its host rock.

QQ9.3
CRANDALLITES AND COFFINITE: RETARDATION OF NUCLEAR REACTION PRODUCTS AT THE BANGOMB NATURAL FISSION REACTOR. Keld A. Jensen, University of Aarhus, Department of Earth Sciences, Aarhus, DENMARK; Janusz Janeczek, University of Silesia, Faculty of Earth Sciences, Sosnoweic, POLAND; Rodney C. Ewing, University of Michigan, Department of Nuclear Engineering and Radiological Sciences, Department of Geological Sciences, MI; Peter Stille, Francois Gauthier-Lafaye, Centre National de la Recherche Scientifique, Centre de Geochimie de la Surface, Strasbourg, FRANCE.

Crandallite group minerals incorporate significant amounts of Sr and lanthanide elements (Ln's) in the end-members goyazite and florencite,

respectively. Relatively high concentrations of Ln's can also substitute for U in coffinite. Both Ln-rich crandallites and coffinite have recently been reported to occur in the weathered zone of the near-surface ($\sim$12 m depth) natural fission reactor at Bangombe [RZB], SE-Gabon. Florencite-(Nd), $(La_{0.38}Ce_{0.35}Nd_{0.06}Sm_{0.01},Ca_{0.03},Sr_{0.17})(Al_{2.98}Fe_{0.02})(PO_4)[PO_{3.80}(OH)_{0.20}](OH)_6$ was reported to contain up to 30% and 71% fissiogenic Nd and Sm, respectively. Analytical transmission electron microscopy has revealed that the Ln-Sr-crandallites frequently occur in the < 2 μm clay fraction from the supergene weathering zone and hydrothermal clay halo above RZB. Uranyl phosphates and uranyl sulfates, among which francoisite-Nd, torbernite and uranopelite have been identified, were observed in fractures down to $\sim$ 12.5 m depth. The francoisite-Nd is rare and the only uranyl phase reported to contain notable amounts of Ln's. Hence, Ln-rich crandallites appear to be the primary host of the fissiogenic Ln's whereas U is mainly retained in the various uranyl phases above the core of RZB (11.60 to 12.00 m depth). In and below the reactor core, uraninite and phosphatian coffinite, with elevated contents of Zr, Th, Ce, and Nd, are the main source of the actinides and Ln's. The groundwater in RZB (pH = 5.96; Eh = 143 mV) contains low concentrations of dissolved U (3.09 ppt) and Lns (10.11 ppt). This suggests that the observed mineral assemblage effectively retards the majority of the fissiogenic Zr, Th, U, and Lns in the supergene weathering horizon at Bangombe. Consequently, the retardation of nuclear reaction products in the geosphere is likely to be facilitated by incorporation into multiple phases. The conditions of formation and the implications for the retardation of fissiogenic elements by crandallite and coffinite during migration in the geosphere are discussed.

SESSION QQ10: POSTER SESSION:
PERFORMANCE ASSESSMENT
Chair: Osvaldo Pensado
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ10.1
CHEMICAL INTERACTIONS IN THE NEAR-FIELD OF A REPOSITORY FOR SPENT NUCLEAR FUEL - A MODELLING STUDY. Heikki Kumpulainen, Jarmo Lehikoinen and Arto Muurinen, VTT Chemical Technology, VTT, FINLAND.

In this work, the evolution of the near-field chemistry affecting radionuclide release from a repository for spent nuclear fuel was studied by applying equilibrium modelling (EQ3/6 and HYDRAQL/ CE). The chemical interactions of a water simulating Finnish fresh granitic groundwater and the three successive near-field components of the repository (bentonite clay, canister and fuel), taken to be closed systems in the modelling, were calculated using a sequential solution scheme. In the first step, groundwater was allowed to equilibrate with bentonite. The resulting bentonite water was then assumed to react with the canister. Finally, this canister-equilibrated water was let to react with the spent fuel under oxidizing conditions caused by water radiolysis. The results from the modelling of bentonite-groundwater interaction are compared with experimental data from a bentonite equilibration study. The implications of the modelling exercise for radionuclide solubilities for the spent fuel are discussed.

QQ10.2
RESULTS OF AN AQUEOUS SOURCE TERM MODEL FOR A RADIOLOGICAL RISK ASSESSMENT OF THE DRIGG LLW SITE, UK. J.S. Small, P.N. Humphreys, T.L. Johnstone, R. Plant, M. Randall and D.P. Trivedi, BNFL Research and Technology, Risley, UNITED KINGDOM.

Disposals to the UK low level radioactive waste (LLW) site at Drigg, owned and operated by BNFL, are authorised by the Environment Agency under the terms of the Radioactive Substances Act 1993. The DRINK mechanistic source term model has, in support of the associated safety case, been used to simulate and understand better the characteristics of the biogeochemical evolution of the site, and provides a numerical input to a risk assessment model. DRINK models the release from earlier disposals in trenches excavated into clay-bearing glacial sediments as well as the current emplacement of compacted waste into engineered cementitious vaults. Drigg LLW contains a large proportion of cellulosic waste together with disposed steel and contaminated soil; the DRINK model simulates the chemical evolution of this complex trench and vault system over periods up to 10,000 years. The chemical interaction of groundwater with soil and cement minerals and aqueous and solid radionuclides is modelled using an equilibrium chemical module based on the PHREEQE code. The redox potential at which speciation calculations are performed is determined by a microbial kinetic model which considers the hydrolysis of cellulose and the mediation of redox reactions between

cellulose degradation products, and other microbial substrates such as Fe(III) present in soil, sulphate in groundwater and hydrogen produced by corrosion of steel. The evolving chemistry simulated by the DRINK model is used to calculate the partitioning of solubility controlled radionuclides between the aqueous phase and discrete solid phases. The chemical evolution is also used as a basis to select appropriate retardation coefficients (Kd's) which effectively control the release of non-solubility controlled radionuclides. Results of the DRINK aqueous source term model will be presented, which illustrate the simulated microbial, corrosion, and pe-pH evolution of the Drigg trenches and vaults. Examples will be provided of the simulated varying aqueous concentration of radionuclides, which are influenced by solubility control, sorption and radioactive decay and ingrowth.

QQ10.3
RADIONUCLIDE RELEASE RATES AT THE RECEPTOR LOCATION FOR THE PROPOSED HIGH-LEVEL RADIOACTIVE WASTE DISPOSAL SITE AT YUCCA MOUNTAIN. Sitakanta Mohanty, Robert Rice, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

One of the primary goals of the Department of Energy program for the proposed repository at Yucca Mountain is the near-complete containment of radionuclides in the natural barrier for several thousand years. To assess the repository performance, Nuclear Regulatory Commission (NRC) has developed a Total-system Performance Assessment (TPA) code that models processes such as the dissolution of spent fuel (SF) and subsequent transport through the natural barriers (unsaturated and saturated zones) to the hypothetical receptor location. The TPA code utilizes fast and slow dissolution rate models, simulates time-dependent flow velocities in the unsaturated zone, calculates the transport of radionuclides through the porous rock matrix or fractures in the unsaturated zone based on the hydraulic properties of each major hydro-stratigraphic unit at Yucca Mountain, and accounts for retardation by chemical sorption in the unsaturated and saturated zone rock matrix. The release rates at the receptor location computed using the fast dissolution rate models show a sinusoidal nature, while at slow dissolution rates, this behavior vanishes. This paper identifies the reasons for these trends in the release rates as attributable to the effects of the repository spatial discretization, waste package failure time, inventory depletion and radioactive decay including ingrowth, SF alteration rate, radionuclide solubility limits, and transport properties of the unsaturated and saturated zones. Calculations also suggest that at a slow dissolution rate, only 0.005 percent of the SF would be transported to the receptor location in 50,000 yr. [ACKNOWLEDGMENTS: The paper was prepared to document work performed by the Center for Nuclear waste Regulatory Analyses (CNWRA) for the Nuclear Regulatory Commission (NRC) under contract No. NRC-02-97-009. The activity reported here was performed on behalf of the Office of Nuclear Material Safety and Safeguards. The paper is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.]

QQ10.4
SAFETY ASSESSMENT OF BORE-HOLE REPOSITORIES FOR SEALED RADIATION SOURCES DISPOSAL. Andrew V. Gouskov, Michael I. Ojovan, Lev B. Prozorov, Arthur E. Arustamov, Pavel P. Poluektov, Boris B. Serebriakov, SIA Radon, Moscow, RUSSIA.

Bore-hole repositories (BHR) are considered as very promising for disposal of HLW and spent sealed radiation sources (SRS). For a long time they are used for storage and disposal of SRS in new independent states - former republics of USSR. A typical shallow ground BHR with a 200 l stainless steel underground vessel in a concrete steel enforced well as SRS reservoir was designed for disposal of sources with total radioactivity up to 50 kg-eqv. of radium. Initial disposal technology was corrected in the middle of 80-s by addition of a supplementary SRS immobilization. Immobilization procedure is carried out directly in underground vessel by applying metal matrices (mainly lead). SRS with total radioactivity higher than one million Ci are disposed off in Russian Federation, being immobilized in metal matrices [1]. Safety assessment of used BHR was carried out on the basis of geological environment analysis as well as overall available parameters on BHR and SRS design and radionuclides inventory. MASCOT and MOP computer codes were used for BHR safety assessment. Probabilistic calculations taken into account some data uncertainties and variability. They showed that practically there is no any release of short lived radionuclides into environment during about 1000 years. This is completely due to very low corrosion rate of lead matrix. Various models were applied for more detail numeric simulation of temperature and radiation fields, migration of radionuclides in geosphere. Super-conservative scenarios were chosen for these models. The worst case comprises both breaching of all engineer barriers and flooding of disposal site plus eventual non-qualitative immobilization of sources with some sources partly

out of matrix. Maximum dose was found to be not higher in this case than 55 - 75 microSv/year for population. Even this super-conservative estimation is much below safety criterion 10 mSv/year in Russian Federation. Reference: Sobolev I.A. et al., Mat. Res. Soc. Symp. Proc., Vol.506, 1998, p.1003-1008.

QQ10.5
PREDICTION OF WASTE PACKAGE LIFE FOR HIGH-LEVEL RADIOACTIVE WASTE DISPOSAL AT YUCCA MOUNTAIN. Osvaldo Pensado and Sitakanta Mohanty, Center for Nuclear Waste Regulatory Analyses (CNWRA), San Antonio, TX.

In December 1998, the Department of Energy (DOE) released a viability assessment (VA) for the proposed high-level radioactive waste repository at Yucca Mountain (YM) [1]. A major current objective of the DOE YM program is to show the feasibility of near-complete containment of radionuclides within the waste packages (WPs) for several thousand years [2]. The US Nuclear Regulatory Commission (NRC), with the technical support of the CNWRA, conducted a review of the DOE WP degradation models and supporting data (described in the DOE VA [1]) to understand their relative importance in the overall repository performance. The objective of this paper is to independently evaluate the WP lifetime and comment on the overall performance of the proposed repository in terms of the total dose rate affecting an idealized receptor group. In particular, results are presented from a study using the NRC WP degradation model [3] and the degradation parameters published in the DOE VA. The corrosion rate of the inner overpack WP material is a key factor controlling the WP lifetime. Alloy 22 corrosion rates reported in the DOE VA span five orders of magnitude, implying a wide range in the computed WP lifetimes from the order of a thousand to millions of years, for a 2-cm thick wall of Alloy 22. On the other hand, the NRC base case predicts an expected WP lifetime between ten and one hundred thousand years. Because of this difference in the extent of the importance assigned to corrosion-induced failure, relevant variations are noted between the two approaches. However, the Alloy 22 corrosion rates disclosed in the VA are the result of an expert elicitation consensus, supported by limited experimental data. The study indicates that juvenile failure plays a major role in the total dose predicted on the basis of DOE data and the NRC models. Therefore, a strong technical basis is needed to assess the probability of the presence of juvenile failure for WPs. Other relevant comparisons between the results obtained from the NRC base case and the NRC models utilizing the DOE VA data are discussed in this paper. ACKNOWLEDGMENTS: The paper was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the Nuclear Regulatory Commission (NRC) under contract No. NRC-02-93-005. The activity reported here was performed on behalf of the Office of Nuclear Material Safety and Safeguards. The paper is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC. REFERENCES: 1. Viability Assessment of a Repository at Yucca Mountain. December 1998. DOE/RW-0508. 2. TRW Environmental Safety Systems, Inc. 1996. Mined Geologic Disposal System Advanced Conceptual Design Report. Engineered Barrier Segment/waste Package. B00000000-01717-5705-00027. Rev. 00. Las Vegas, NV: TRW Environmental Safety Systems, Inc. Vol. III. 3. Mohanty, S. and T.J. McCartin. 1998. Total-system Performance Assessment (TPA) Version 3.2 Code: Module Description and User's Guide. CNWRA Report. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.

QQ10.6
THERMOHYDROCHEMICAL COUPLING AND THE REDISTRIBUTION OF CHLORIDE IN THE NEAR-FIELD ENVIRONMENT. David W. Esh, Argonne National Laboratory, Idaho Falls, ID; Barry E. Scheetz, The Pennsylvania State University, University Park, PA.

Thermohydrochemical (T-H-C) processes result from the placement of heat-generating radioactive materials in unsaturated, fractured geologic materials. The placement of materials in the proposed Yucca Mountain repository will result in complex environmental conditions. Models are developed linking thermohydrological effects simulated with TOUGH2 to system chemistry, with an example presented for chloride. Various conceptual models to represent fractures are utilized in TOUGH2 simulations of thermohydrological processes (ECM, DK, MINC). The simulated moisture redistribution is then coupled to simple chemical models to demonstrate the complexity and potential magnitude of T-H-C processes. The concentration of chloride in solution (returning to the engineered barrier system) is demonstrated, in extreme cases, to exceed 100,000 mg/L. The implications of the T-H-C modeling are numerous and potentially important to overall system performance. Perturbations to near-field chemistry may have a significant impact on the migration of actinides and fission products in geologic materials. The chemical composition of fluids that interact with the engineered barrier system (after waste emplacement) may be significantly different from ambient chemical composition. In addition,

the complexity of the coupling process is demonstrated to induce error when assessing which process metrics are important to system performance. An important parameter in determining the magnitude of the perturbation of ambient chemistry (for chloride) is the initial rewetting processes in the fractures. For T-H coupling, the initial rewetting processes are unimportant to system performance. However, for T-H-C coupling the initial rewetting processes are of primary importance for an assessment of chloride redistribution.

QQ10.7
THERMOHYDROLOGIC ANALYSIS OF REPOSITORY DESIGN ALTERNATIVES AT YUCCA MOUNTAIN. Thomas A. Buscheck, James Gansemer, Nina D. Rosenberg, Lawrence Livermore National Laboratory, Livermore, CA; Yunwei Sun, Weiss Associates, LLNL, Livermore, CA.

Depending on the design, heat from the decay of radioactive waste can have a dominant influence on the hydrologic system that develops around the potential repository at Yucca Mountain, effecting critical system performance variables such as temperature, relative humidity, and seepage flux on waste packages. The combination of two characteristics of the Yucca Mountain repository, a vadose zone location and waste packages with a high heat-generation rate, allows thermal management to be utilized as a design tool to help optimize repository performance. The Yucca Mountain Site Characterization Project (YMP) has undertaken a major effort to improve the conceptual engineering design for a repository at Yucca Mountain. This effort, termed the License Application Design Selection (LADS) project, was intended to develop the design concept to be used during the Site Recommendation and License Application phase of the YMP. This paper describes the thermohydrologic-model calculations supporting Phase 2 of the LADS project, which considered seven enhanced design alternatives (EDAs). The EDAs cover a wide range of heat-driven thermohydrologic behavior. In some, sub-boiling temperatures persist throughout the repository. In others, the boiling zone can extend more than 200 m from the repository and last up to 10,000 years. A combination of end-to-end waste package spacing in widely spaced drifts, ventilation, and backfilling the drifts results in a design which promotes better drainage pathways around drifts, reduced likelihood of moisture contact on waste packages, and reduced in-drift and rock temperatures (with much less variability along the drift axis), relative to alternative designs. Backfilling drifts with a granular material with coarse, well-sorted, nonporous grains (e.g., a coarse quartz sand) results in a large, persistent reduction in relative humidity on waste packages. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No.W-7405-Eng-48.

SESSION QQ11: POSTER SESSION:
WASTE FORMS
Chair: Michele A. Lewis
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ11.1
GRAPHITE PROCESSING WITH CARBON RETENTION IN A WASTE FORM. Michael I. Ojovan, Olga K. Karlina, Vsevolod L. Klimov, Galina Yu. Pavlova, SIA Radon, Moscow, RUSSIA.

Waste graphite containing fragments of nuclear fuel and fission products is produced mainly as a result of operation of uranium-graphite reactors. Retention of radionuclides including carbon-14 is an important goal of treatment procedure. Conversion of waste graphite into a stable waste form acceptable for long term storage and disposal was considered both theoretically and experimentally. Self-sustaining transformation process of graphite in composition with suitable precursors was studied. Powder precursors were applied: Al+SiO2 (1), Al+TiO2 (2) and Ti+SiO2 (3). Numeric thermodynamic simulation was performed. Equilibrium temperatures and chemical compositions of reaction products were determined for a wide range of component ratios in source mixtures. The highest temperatures up to 2300 K were observed for precursor type (2). Precursor type (3) demonstrated minimal rise of temperature up to 1900 K. Equilibrium phase composition diagrams were created for every precursor type. Regions of compositions with complete binding of all chemical elements as well as production of stable final products were found to be rather narrows. Gas phase of reaction products was studied to minimize carry over of radionuclides. Carbon oxide was shown to be main component of gaseous phase. Behavior of radionuclides was studied in possible processing areas. Optimal processing regions were determined for every precursor type providing complete carbon binding and minimum volatilization of radionuclides. About 10 - 15 wt.% of carbon can be processed in composition with given precursors. Experiments on waste forms processing were carried

out. Self-sustaining synthesis process was conducted in ceramic crucibles at ambient pressure in air atmosphere. Masses of used batches ranged between 0.1 - 1 kg. Best results were obtained for the processing of graphite in composition with Al and TiO2. XRD analysis has shown titanium carbide and corundum in the waste form produced. Experiments confirmed that carbon can be converted completely into a stable waste form.

QQ11.2
LONG TERM BEHAVIOUR OF BITUMEN WASTE FORM. Igor A. Sobolev, Alexander S. Barinov, Michael I. Ojovan, Natalya V. Ojovan, Irene V. Startceva, Zinaide V. Golubeva, Scientifc and Industrial Association Radon, Moscow, RUSSIA.

Three principal types of waste forms for low and intermediate level waste (LILW) immobilisation are under investigation at SIA 'Radon' for about three decades. Cemented, bituminized and vitrified waste blocks are produced at industrial and pilot scale facilities and disposed of at the testing area consisting of an open testing site and experimental shallow-ground repositories. Bitumen has been used for solidification of wet wastes (sludges from evaporation or precipitation) since 1965. Three types of bitumen were used in the laboratory and nature experiments. Bitumized waste blocks were prepared on base of NPP-operational and other LILW and tested under laboratory and near-surface disposal conditions. Leaching of radionuclides as well as of chemical species were studied in laboratory conditions. Irradiation of bituminized waste up to doses 10 Gy had no effect on leach resistance of samples. Long term tests on open testing area as well as in experimental shallow-ground repositories are carried out about 27 years continuously. Waste form behaviour is assessed mainly through the contamination of contact water. Water samples are routinely collected, usually twice a month, for chemical, radiochemical and radiometric analyses. Open site conditions allow regular visual observations of waste sample alteration. Data generated from the experiments are used for database compilation. On the basis of radiometric data, the parameters of radionuclide releases are calculated: leach rate (R), leached mass (M), leach factor (L), diffusion coefficient (D), and leached radioactivity fraction (f). Leach rates of non radioactive waste components and depth of radionuclide penetration into the host loamy soil were estimated also. Bituminized waste seems to occupy a middle position between cemented and vitrified waste forms concerning radionuclide retention ability. However, some properties of bitumen as a waste matrix are not fully understood for modelling the waste form behaviour on time periods of several hundreds years.

QQ11.3
CORROSION BEHAVIORS OF SODALITE, GLASS AND THE COMPOSITE GLASS-BONDED SODALITE CERAMIC WASTE FORM. M.A. Lewis, M.L. Stanley and W.L. Ebert, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

A ceramic waste form (CWF) of glass-bonded sodalite is being developed for the long-term immobilization of waste salts generated during conditioning of spent sodium-bonded fuel from the DOE EBR-II reactor. The waste is generated during electrometallurgical treatment of spent nuclear fuel and consists of the electrolyte salt, LiCl-KCl and the accumulated fission products and transuranics, which exist as chlorides. The CWF consists of two major phases, about 75 mass% sodalite, 25 mass% glass and small amounts of other phases such as halides, oxides, and oxychlorides. A mechanistic model of the corrosion processes is being developed to support qualification of the CWF for disposal. The initial set of characterization tests included two standard tests that have been used extensively to characterize the corrosion behavior of high-level waste glasses: the Material Characterization Center-1 (MCC-1) Test and the Product Consistency Test (PCT). We have completed PCT and MCC-1 tests of the CWF, and with the individual sodalite and glass phases in demineralized water at 90°C for durations up to one year. Dissolution mechanisms, such as free salt and occluded salt dissolution, hydrolysis of the silicate networks for the sodalite and glass, and ion exchange of the glass, were identified in tests with the sodalite and glass. Synergies were identified by comparing the results of the tests with the single phases to those with the CWF composite. Synergies associated with the CWF included formation of a Cs-containing alteration phase, less free salt released, and smaller amounts of glass corroded.

QQ11.4
LONG-TERM BEHAVIOUR OF BITUMINIZED WASTE: MODELLING AUTO-IRRADIATION AND LEACHING. Pascal Chaix, CEA Saclay, FRANCE; Sylvie Camaro, Beatrice Simondi-Teisseire, CEA Cadarache, FRANCE; Veronique Blanc, Cogema, Saint Quentin en Yvelines, FRANCE.

The chemical compatibility of bitumen matrix with most of reagents used to decontaminate the radioactive liquid effluents, its binding capacity, its waterproofing and its easy implementation at low temperatures, have led to the choice of this material in France for the conditioning of low and medium activity waste resulting from effluents treatment.
The French Atomic Energy Commission CEA and Cogema conduct research programs on the long term behaviour of bituminized waste, both in long period storage and deep geological disposal, which are the two ways of long-term management for medium activity waste that are currently under consideration.
During storage, and before radioactive decrease, the main evolution factor is radiolysis, while in the deep disposal scenario, after radioactive decrease site resaturation with water and container corrosion, water leaching is the main factor of evolution.
This paper presents two models, designed to describe respectively radiolytic gas evacuation, and bituminized waste degradation under leaching.
The first model is based on the integration of simple descriptions of gas production by radiolysis, gas diffusive transport, bubble nucleation and ripening, and bubble transport under buoyancy and viscosity.
The second model is based on the following processes: water adsorption and solubilization at the surface, water diffusion into the matrix, water uptake by the most soluble salts, salt grain swelling and degradation of matrix waterproofing, diffusive transport of salts out of the waste.

QQ11.5
CHARACTERIZATION OF A CERAMIC WASTE FORM INCORPORATING RADIOACTIVE ELECTROREFINER SALT. T.L. Moschetti, W. Sinkler, T. DiSanto, M.H. Noy, A.R. Warren, S.G. Johnson, K.M. Goff and K.J. Bateman, Argonne National Laboratory-West, Idaho Falls, ID.

Argonne National Laboratory has developed a ceramic waste form to immobilize high-level radioactive waste salt produced during the electrometallurgical treatment of spent fuel. This study presents the first results from electron microscopy and durability testing of a ceramic waste form produced from radioactive electrorefiner salt. The waste form consists of two primary phases: sodalite and glass. The sodalite phase appears to incorporate most of the alkali and alkaline earth fission products. Other fission products (rare earths and yttrium) tend to form a separate phase and are frequently associated with the actinides. Leach test results will also be presented. In addition, results of previous work on waste forms, which incorporated surrogate fission product or plutonium loaded salt, correspond well with the results of this study.

QQ11.6
Abstract Withdrawn.

QQ11.7
TEM CHARACTERIZATION OF CORROSION PRODUCTS FORMED ON A SS-15ZR ALLOY. J.S. Luo and D.P. Abraham, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

Stainless steel-zirconium alloys are being developed for the disposal of metallic waste generated by the electrometallurgical treatment of spent nuclear fuel. The baseline waste form is a stainless steel-15 wt% zirconium (SS-15Zr) alloy, which contains a eutectic microstructure of a stainless steel phase, ferrite, and a $ZrFe_2$-type Laves intermetallic. In this article, we present the characterization of corrosion layers formed on the SS-15Zr alloy using energy-filtered transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). Specimens of SS-15Zr alloy, crushed to 75 to 150 μm size, were reacted in 90°C deionized water for a period of two years. The stainless steel particles were found to exhibit little reaction presumably due to the formation of a protective layer, which retards alloy corrosion. On the other hand, corrosion layers were frequently observed on the Zr-intermetallic, with thickness ranging from less than 10 nm to more than 0.1 μm. The layers were well adherent and the interface between the layer and the Zr-intermetallic was sharp and uniform. Careful examination of electron diffraction patterns suggested that the corrosion products were amorphous in nature. We also examined an area that contained adjacent particles of stainless steel and the Zr-intermetallic. Our observation suggests that the stainless steel phase in the SS-15Zr alloy is more resistant to corrosion than the Zr-based Laves intermetallic. This finding is significant because the Zr-intermetallics contain many of the fission products and all the actinide elements present in the SS-15Zr waste form.

QQ11.8
LEACHING CHARACTERISTICS OF THE METAL WASTE FORM FROM THE ELECTROMETALLURGICAL TREATMENT PROCESS: PRODUCT CONSISTENCY TESTING. S.G. Johnson, D.D. Keiser, S.M. Frank, T. DiSanto and M. Noy, 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 /1-2 wt % U. The behavior of technetium is of particular importance from a disposal point of view for this waste form due to its long half life, 2.14E5 years, and its mobility in groundwater. Leaching results will be presented from several tests and sample types: 1) 2 week monolithic immersion tests on actual metal waste forms produced from irradiated cladding hulls, 2) long term (>2 years) pulsed flow tests on samples containing technetium and uranium and 3) crushed sample immersion tests on cold simulated metal waste form samples. The test results will be compared and their relevance for waste form product consistency testing discussed.

SESSION QQ12: POSTER SESSION:
CERAMICS
Chair: David B. Chamberlain
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ12.1
DEVELOPMENT AND CHARACTERIZATION OF CERAMIC WASTE FORMS FROM Cs-LOADED CRYSTALLINE SILICOTITANATES. Y. Su, M.L. Balmer, E. Bitten, Pacific Northwest National Lab., Richland, WA; H. Xu and A. Navrotsky, University of California-Davis, Davis, CA; M.D. Nyman and T.M. Nenoff, Sandia National Lab, Albuquerque, NM; R.S. Roth, National Institute of Standards and Technology, Gaithersburg, MD.

A thermally treated crystalline silicotitanate ion exchanger, which selectively removes Cs from Na-rich radioactive wastes, is being evaluated as a waste form. This metastable ion exchanger structure undergoes a series of phase transformations with increasing heat treatment temperature. It ultimately becomes chemically durable ceramic with a stable mixed phase. The Cs leach rate first increases then decreases as a function of heat treatment temperature. A comparison of Cs leach rates shows that the release rate of thermally treated CSTs is several orders of magnitude lower than that of borosilcate glass compositions. The relationship among the Cs release rate, the phase selection and local Cs environment has been identified. Results indicate that Cs is likely to be contained in crystalline phase $Cs_2XSi_3O_9$. Correlations between chemical durability and crystal structure of component oxides will be presented.

QQ12.2
MICROSTRUCTURE AND CRYSTALLIZATION SEQUENCE OF SYNROC SAMPLES CRYSTALLIZED FROM $CaCeTi_2O_7$ CHEMICAL SYSTEM: HRTEM/AEM INVESTIGATION. Huifang Xu, Department of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM; Yifeng Wang, Sandia National Laboratories, Carlsbad, NM; Robert L. Putnam, Jose Gutierriez and Alex Navrosky, Dept. of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA.

Pyrochlore phase has been considered as a durable crystalline waste form for hosting weapon-usable Pu. $CaCeTi_2O_7$, pyrochlore phase is a chemical analogue for the real waste form $CaPuTi_2O_7$. Ce-pyrochlore was synthesized by annealing oxide mixture of CeO_2, TiO_2, and CaO with stoichiometry of CaCeTi2O7. The annealed products contain Ce-pyrochlore, Ce-bearing perovskite, CeO_2, and minor other Ca-bearing phases. The mixture annealed in air at lower temperature of 1140 °C contains more pyrochlore phase than that annealed at higher temperature of 1300 °C. The Ca/Ce ratio is slightly lower than the ideal ratio (one). Electron energy-loss spectroscopy results show there are small proportion of Ce^{3+} in the pyrochlore. Ce in perovskite is dominated by Ce^{3+}. High-resolution TEM images show the boundary between pyrochlore and perovskite is coherently bonded. The orientation relationship between the neighboring pyrochlore and perovskite is not random. There are no glassy phases at the grain boundary between pyrochlore and perovskite, and the boundary between CeO_2 and pyrochlore. The $CeTiO_4$ phase does not form in the $CaCeTi_2O_7$ chemical system. However, the $ZrTiO_4$ phase forms in the $CaZrTi_2O_7$ chemical system. A pseudo-binary phase diagram for the $CaPuTi_2O_7$ system is also proposed.

QQ12.3
THE CORROSION BEHAVOIR OF TITANATE CERAMICS FOR PU DISPOSITION; RATE-CONTROLLING PROCESSES. Allen J. Bakel, C.J. Mertz and D.C. Chamberlain, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

The Plutonium Immobilization Project of the Fissile Materials Disposition Program is developing and testing a titanate ceramic material for the immobilization of Pu. The goal of this paper is to describe the rate-controlling corrosion mechanism for a zirconolite-rich ceramic. Short-term MCC-1 (up to 35 days) tests were conducted in DIW at 90°C. These data indicate that the NL(Ca) increases rapidly for up to 3 days, and changes little after 3 days. This rate is 0.7 g/(m^2 d) based on Ca release and about 10^{-5} g/(m^2 d) based on Ti or Pu. This suggests that the release of Ca is controlled by a different process than the release of either Ti or Pu. The PCT-B tests were conducted with crushed ceramic in DIW at 90°C for up to two years. The normalized mass losses based on Ca, Zr, Gd and Pu continue to increase from 98 to 728 days, showing that corrosion continues for up to two years in these tests. The release rates based on Pu and Gd are on the order of 10^{-5} g/(m^2 d). Results from MCC-1 and PCT-B tests show that the release rate of Ca from a zirconolite-rich titanate ceramic is high in short-term tests and lower in long-term tests. The release rates of Ti and Pu are constant. Controlling factors might include solubility limits, high initial surface area, and formation of a protective layer. Each of these possibilities will be discussed in the full paper.

QQ12.4
POROSITY AND STRUCTURE OF NANOPARTICLE AGG-REGATES IN SPRAY-DRIED MICROSPHERES. S. Lyonnard, O. Spalla and Th. Zemb, SCM, CEA-Saclay, FRANCE; J.R Bartlett, E. Sizgek, K.S Finnie and J.L. Woolfrey, ANSTO, MaterialsDivision, Lucas Heights, AUSTRALIA.

Precursor nanopowders for producing advanced ceramics are often prepared by spray-drying concentrated sols, to produce aggregated particles for ease of handling during subsequent processing. The spray-drying process involves drying atomised droplets of the sol (typically < 50 microns diameter) under controlled conditions in hot air, to produce mesoporous, gel microspheres. In the Synroc process for nuclear waste disposal, such titania-based powders, with controlled pore structures, readily sorb up to 20 wt% concentrated waste solutions, before thermal processing. A series of spray-dried titania powders was produced by varying the solids content and electrolyte strength (aluminium nitrate) in the precursor sols. The resultant powders were characterised by SEM, nitrogen sorption, SANS, SAXS and USAXS. The USAXS and conventional SAXS of the dried powders was measured over threedecades of q, between 2 micron and 0.5 nm, real space. Absolute scaled measurements in this range show two exponential regimes and a transition region. For this type of signal, we propose a general method of data evaluation for samples with two length scales to obtain: - the surface area of the nanometer sized, connected pores available for adsorption of ions per macroscopic powder grain (from the Porod region); - the total porosity of the dried grains without any assumptions (from the transition regime); - the average size of the microspheres (from the low-q regime). The precursor sols were also analysed by SANS and the interaction potential, as well as the size of initial nanoparticles, was determined. The relationship between the interaction potential in the sol and the porosity of the resulting spray-dried powders will be discussed.

QQ12.5
SOLID SOLUBILITIES OF Pu,U,Hf AND Gd IN CANDIDATE CERAMIC PHASES FOR ACTINIDE WASTE IMMOBILISATION. E.R. Vance, M.L. Carter, B.D. Begg and S.H.F. Leung, ANSTO, Menai, AUSTRALIA.

Solid solubility limits of Pu, U, and the neutron absorbers Hf and Gd have been measured for zircon, monazite, titanite, perovskite, apatite and whitlockite in almost all cases where these limits were not known beforehand. The method used was to oversaturate the host phase with the dopant, using a nominated substitutional scheme, and then establish the dopant content of the host phase by microanalysis/ scanning electron microscopy. Tetravalent U had limited (<0.1 formula units(f.u.)) solid solubilities in $CaTiO_3$, apatite, whitlockite and titanite, and data on trivalent and tetravalent Pu solubilities will be reported. X-ray absorption near-edge and diffuse reflectance spectroscopies were used to show that U was tetravalent in U-doped $CaTiO_3$ prepared in both argon and hydrogen/nitrogen atmospheres, with different charge compensation schemes. 0.5 and <0.1 f.u. of Hf are soluble in titanite and monazite respectively; Hf solubilities in apatite will be reported. Approximately 0.3 and <0.1 f.u. of Gd are soluble in titanite and zircon respectively.

QQ12.6
CATHODOLUMINESCENCE OF THE GARNET HOST PHASE, ACTIVETED BY Ce, U AND Pu. Maria V. Zamoryanskaya, Boris E. Burakov, Khlopin Radium Institute, St. Petersburg, RUSSIA.

The garnet $(Y,Gd,An)_3(Al,Ga,An)_5O_{12}$ has been suggested for the immobilisation of the military actinide-wastes. This crystalline phase is chemically and mechanically durable and desirable for the

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incorporation of Pu, Am and other elements in the form of solid solutions. However the lattice capacity of garnet depends on the valence state of accommodating ions. The ions of Ce^{4+} and U^{4+} are good imitators of the Pu^{4+} and Np^{4+}. And at the same time the military actinid-wastes contain these elements. Ions Ce^{3+} and U^{6+} have characteristic cathodoluminescence (CL) lines too in blue-green region of the CL spectrum. However, there is no CL emission of the ions of Ce^{4+} and U^{4+} CL emission in visible region. The garnets of different composition and oxides have characteristic CL band. That is why the method of cathodoluminescence was suggest for the effective control of valence state of such ions as Ce and U and for phase diagnostics. The samples of garnet were synthesised by a method that uses melting (at T=1300-2000°C). For successful incorporation of Ce^{4+}, U^{4+}, Pu^{4+} ions in garnet the charge and radius-compensating elements (Sn, Ca) were used. All samples were studied by local methods simultaneously: cathodoluminescence and microprobe analysis. The use of two local methods gives the information on the composition and CL emission in the same microvolume (d=3μ) of samples. The experiment shows the difference between U^{6+} and U^{4+} accommodation in the garnet: smaller than 0.05%wt and about 4%wt respectively. The same result was obtained for garnet doped by Ce. The characteristics of CL emission of garnets, doped by Pu (0.5-5%wt) were studied. For such garnets the correlation between accommodation of Ce^{4+} and Pu was found. The simultaneous use of local methods: CL and microprobe are very effective for studing the different kinds of ceramic, for examples, CL emission: ZrO_2:Pu and $ZrSiO_2$:Pu.

QQ12.7
ALMINA-DOPED TITANIA CERAMIC WASTE FORMS PRODUCED BY MELTING METHOD. Masayoshi Uno, Hajime Kinoshita, Shinsuke Yamanaka, Osaka University, Department of Nuclear Engineering, Osaka, JAPAN.

It is of great interest to investigate the material in which nuclear waste can be contained stably by a simple procedure. We found that some rare earth elements (RE)-Ti complex oxides with a ideal composition $RE_2Ti_3O_9$ melt up to 1673 K by doping alumina. We firstly studied the phase stability and melting temperature of alumina-doped RE-Ti-O system with the composition variation. Secondly, some TiO_2 based waste forms containing RE and alkaline earth elements for immobilization were prepared: (1) with alumina-doping by a simple melting method at 1673 K in 1 hour; (2) without almina-doping by pressing starting mixture at 60 MPa and sintering the green pellets at 1673 K for 5 hours, and some properties were investigated. Melting of the mixture of Nd_2O_3, CeO_2, SrO, TiO_2 and Al_2O_3 at 1673 K in 1 hour produced $RE_2Ti_3O_9$ phase, and the chemical formula of the oxide was assumed to be $(CeNdSr)_2(TiAl)_3O9$. A Differential Scanning Calorimetry (DSC) measurement showed that the melting temperature of this compound was 1646 K. Density of the alumina-doped oxide was higher than that of the oxide obtained by the pressing and sintering without alumina. Vickers hardness of the oxide obtained by the pressing and sintering was 5.3 GPa and nearly the same as that of glass waste. That of the alumina-doped oxide was around 7 GPa. A 3-day Soxhlet leach test (MCC-5) followed by an Inductively Coupled Plasma Spectrometry (ICP) showed that normalized reaching rates of Ti for the oxide obtained by the pressing and sintering was 5.54x10-3 kg/m2 and that for the alumina-doped oxide was 2.24x10-3 kg/m2. The value of Sr for the pressed and sintered sample was 0.034x10-3 kg/m2 but that for alumina-doped sample was below the detection limit (0.01x10-3 kg/m2). Alminium was not detected from the leachate of the alumina-doped sample.

QQ12.8
MELTING SIMULATED HIGH-LEVEL LIQUID WASTE WITH ADDITION OF TITANIUM AND ALMINIUM NITRIDES. Masayoshi Uno, Hajime Kinoshita, Shinsuke Yamanaka, Osaka University, Department of Nuclear Engineering, Osaka, JAPAN.

Calcined simulated high level liquid waste (HLLW) with a small amount of reducing agents, TiN and AlN was heat-treated at 1673-1873 K. In this treatment, depending on the value of their standard free energy of oxide formation, elements are to be separated into two groups: alloy phase and oxide phase. Elements with higher value (platinum metals and other transition metals) are reduced and form the alloy phase. Elements with lower value (alkaline earth elements, rare earth elements, Zr and the metal elements of the reducing agents) form the oxide phase. The alloy phase will be recovered, and the oxide phase will be stored as a waste form. It has been confirmed that the alloy phase melts up to 1673 K by alloying the refractory platinum metals or Mo with corrosion products (Fe, Cr, Ni), and that the oxide phase melts up to 1873 K by forming complex oxides of fission products and the metal elements of the reducing agents. In the present work, it was revealed that the mixture of TiN and AlN (the atomic ratio of Al to Ti is 1:9) caused the melting of both phases at 1673 K. The product contained the alloy phase in the

center surrounded by the oxide phase. The X-ray diffraction for the oxide phase revealed that almost all alkaline earth and rare earth elements formed the complex oxides with Ti. The density and hardness for the oxide phase were 4.91 g/cm3 and 8.75 Gpa, respectively. A 7-day Soxhlet leach test showed that the concentration of any elements in the leachate was below the detection limit of the Inductively Coupled Plasma Spectroscopy (ICP-ES) method. Thus, there is a possibility that the ceramic waste form is obtained by a simple melting method at 1673K with the recovery of useful metals.

QQ12.9
ISOMORPHIC CAPACITY OF SYNTHETIC SPHENE WITH RESPECT TO Gd AND U. Sergey V. Stefanovsky, SIA Radon, Moscow, RUSSIA; Sergey V. Yudintsev, Boris S. Nikonov, Boris I. Omelianenko, Inst of Geology of Ore Deposits, Moscow, RUSSIA.

Phase relations in the system: $CaO-TiO_2-SiO_2-(Na_2O,Al_2O_3,Gd_2O_3,UO_2)$ were studied. This system is of interest due to formation of sphene, perovskite, and other phases potentially suitable for immobilization of high level waste (HLW) elements. Within the series $Ca_{1-x}Na_{0.5x}Gd_{0.5x}TiSiO_5$ sphene is still present at x=0.3 whereas within the series $Ca_{1-x}U_{0.5x}TiSiO_5$ limiting x value is 0.1. In the melted samples of the system $CaO-TiO_2-SiO_2-(Na_2O,Al_2O_3,Gd_2O_3,UO_2)$ along with sphene, the other phases in the samples: rutile, chevkinite, anortite, crystobalite, and pyrochlore-structured phases were found. Sphene is able to incorporate up to 21.5 wt.% Gd_2O_3 and 9.3 wt.% UO_2 or, in formula units: 0.25 Gd^{3+} and 0.07 U^{4+}. Minimum concentrations providing to reveal the pyrochlore-structured phase are 8.9 wt.% Gd_2O_3 and 6.6 wt.% UO_2 in the Gd- and U-containing systems, respectively. Chevkinite-pierrierite is present in the sample Gd-2 with 8.9 wt.% Gd_2O_3 but it is absent at higher Gd concentrations. Maximum Gd_2O_3 concentration in chevkinite and pyrochlore-type phase reached 43.0 and 52.8 wt.% respectively. Maximum UO_2 content in the pyrochlore-structured phase was found to be 45.8 wt.%.

QQ12.10
CHEMICAL DURABILITY OF YTTRIA-STABILIZED ZIRCONIA FOR HIGHLY CONCENTRATED TRU WASTES. Hajime Kinoshita, Masayoshi Uno, Shinsuke Yamanaka, Osaka University, Dept of Nuclear Engineering, Osaka, JAPAN; Ken-ichi Kuramoto, Japan Atomic Energy Research Institute, Dept of Nuclear Energy System, Ibaraki, JAPAN; Hisayoshi Mitamura, Tsunetaka Banba, Japan Atomic Energy Research Institute, Dept of Environmental Sciences, Ibaraki, JAPAN.

Isolation of hazardous radionuclides is one of the most important issues in nuclear waste management. In particular, TRU elements should be conditioned with special concern since they have extremely long half-lives. The general purpose of this work is to study the applicability of Yttria-Stabilized Zirconia (YSZ) as a host matrix for the waste form of highly concentrated TRU. YSZ with fluorite structure is able to contain TRU elements as a part of that structure. Possible advantages from the YSZ waste form are, therefore: (1) the accommodation of TRU elements in high concentration; and (2) the production of very stable waste forms. The resultant high quality waste form could then be utilized in other applications, such as TRU burning. In the present study, YSZ samples doped with Np-237 in high concentration (20, 30, 40 mol%) were fabricated (sintered in Air or Ar, at 1773 K, for 80 hours), and their leaching test (in deionized water, at 363 K, for 90 days) was carried out. The leaching rate is one of the most important indicators of the chemical durability of the waste form. The results indicated that the obtained leaching rates were much smaller than those of the Synroc and glass waste form, and that the increase in Np content did not cause any drastic changes in the leaching rates of Zr, Y, or Np. They were also compared to previously obtained results of YSZ doped with Ce and/or Nd. Overall, the work showed that YSZ doped with Np in high concentration has an excellent chemical durability.

SESSION QQ13: POSTER SESSION:
GLASS WASTE FORMS
Chair: John D. Vienna
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ13.1
RAMAN AND HIGH RESOLUTION ELECTRON MICROSCOPY STUDIES OF NEPHELINE (NaAlSiO4) CRYSTALLIZATION IN SIMULATED HIGH-LEVEL WASTE GLASSES. Hong Li, Yali Su, Maoxu Qian, John D. Vienna, and Pavel Hrma, Pacific Northwest National Laboratory, Richland, WA.

Nepheline crystallization was previously studied over the composition

region (wt%): Al2O3 (6.3 - 19.3), B2O3 (0 - 20), Na2O (13.3 - 14.8), and SiO2 (38.4 - 47.3) for the simulated high-level waste glasses. In this study, results of an on-going Raman spectroscopy and high resolution electron microscopy (HREM) studies are presented over the same composition region. We observed a characteristic Raman scattering band near 850 cm-1 in glasses that were quenched from melting temperature and did not contain any crystals. The intensity of the 850 cm-1 band, in terms of the normalized peak area, was dependent on glass composition and linearly correlated with liquidus temperature (for nepheline crystallization) of the glasses. The 850 cm-1 band was considered to be related to the formation of distorted structure units of [NaAlSiO4] as reported in literature for ternary silicate glasses. To further elucidate the nature of the 850 cm-1 band, HREM was performed using the baseline glasses that were equilibrated over the vicinity of its liquidus temperature (920C) at 910 and 938C for 24 hours, respectively. The Raman results will be discussed in conjunction with the data from the HREM.

QQ13.2
THE EFFECT OF ADDING CRYSTALLINE SILICOTITANATE ON THE DURABILITY, LIQUIDUS, AND VISCOSITY OF SIMULATED HIGH-LEVEL WASTE GLASSES AT SAVANNAH RIVER SITE. John R. Harbour, Thomas B. Edwards and Rhonda J. Workman, Savannah River Technology Center, Aiken, SC.

One alternative that is being considered for removal of Cs-137 from HLW salt supernate at SRS is the ion exchange sorbent, crystalline silicotitanate (CST). As part of that effort, it is essential to demonstrate that the Cs-137 loaded CST can be incorporated, along with HLW sludge, into a borosilicate glass. The glass waste form must meet waste acceptance criteria for HLW and be processible in the Defense Waste Processing Facility melter. Therefore, a preliminary variability study was conducted to determine the feasibility of incorporating CST into the glass waste form. For this study, a simulated sludge and a frit having a composition determined from previous efforts were used. In the variability study, the sludge loading was tested at 22, 26 and 30 weight% (oxide basis) and the CST at 3, 6, and 9 weight %. Measurements of glass durability were accomplished using the ASTM PCT test. For the processing parameters, the melt viscosity at 1150°C and the liquidus temperature were determined. These data were compared to the predictions obtained from models currently used at DWPF for process control. X-ray diffraction and scanning electron microscopy were used to determine the microstructure of the glasses. Results indicate that a suitable glass can be prepared at the center point of 26 wt% sludge and 6 wt% CST. This paper summarizes results at all waste loadings.

QQ13.3
HIGH TEMPERATURE ELECTRICAL CONDUCTIVITY IN IRON PHOSPHATE MELTS. Chen Fuyi, State Key Laboratory of Solidification Process, Northwestern Polytechnic University, Xian, PR CHINA; Delbert E. Day, Department of Ceramic Engineering, University of Missouri-Rolla, Rolla, MO.

The electrical resistivity of iron phosphate melts containing simulated industry wastes was investigated as a function of temperature and composition. An irreversibility was found in the temperature dependent electrical resistivity during the first heating and cooling cycle when the sodium content was low. The irreversibility was reduced with increasing sodium content. The electrical resistivity tended to decreased slightly with time. The temperature dependent electrical resistivity and activation energy of these melts was discussed using the Mott theory and was correlated to the Fe(II) content in the melts.

QQ13.4
CONDUCTIVITY - CHEMISTRY RELATIONSHIP IN SIMULATED NUCLEAR WASTE GLASS MELTS. S.K. Sundaram, Pacific Northwest National Laboratory, Richland, WA; Elvis Q. Le, Department of Mechanical Engineering, Washington State University, Tri-Cities Campus, Richland, WA.

Electrical conductivity of glass melts is one of the most important processing parameters in the Joule-heated melters used for vitrification of nuclear wastes. Operating specification requires electrical conductivity of glass melt should be in the acceptance range 10 - 100 S/m. A low electrical conductivity at the melting temperature would require a higher voltage across the electrodes resulting in conduction within the melter refractory. A low electrical conductivity could also cause melter start-up difficulties unless undesirably large electrical power system are supplied. If the electrical conductivity were too high, the current required to melt glasses would exceed the recommended maximum density for the melter electrodes. A high-accuracy, calibration-free coaxial cylinders technique was selected because accurate electrical conductivity measurements can be made in high temperature, relative conductive, highly corrosive melts like molten oxides in radioactive waste glass melts. Glass chemistries

representing both low-level and high-active wastes at Hanford and Savannah River sites were used in this study. Conductivity was measured for a wide range of temperatures. Based on these results, a preliminary conductivity-chemistry relationship will be presented.

QQ13.5
LIQUIDUS TEMPERATURE OF HIGH-LEVEL WASTE BOROSILICATE GLASSES WITH SPINEL PRIMARY PHASE. Pavel Hrma, John Vienna, Jarrod Crum and Greg Piepel, Pacific Northwest National Laboratory, Richland, WA; Martin Mika, Institute of Chemical Technology, Prague, CZECH REPUBLIC.

We measured liquidus temperature (T_L) for high-level waste (HLW) borosilicate glasses that cover a Savannah River composition region. All glasses had a high concentration of RuO_2 (0.09 mass%). The primary crystallization phase for most glasses was spinel, a solid solution of trevorite with other oxides (mainly FeO, MnO, and Cr_2O_3). We resolved several major experimental difficulties, such as dealing with a large quantity of insoluble RuO_2 and reaching equilibrium of glass samples with atmospheric oxygen while minimizing volatilization losses (the strong effect of p_{O_2} on spinel formation made T_L sensitive to the temperature history of the specimen). The T_L values ranged from 859 to 1310°C. T_L increases per 1 mass% component additions to a baseline composition were Cr_2O_3 260°C, NiO 85°C, TiO_2 42°C, MgO 33°C, Al_2O_3 18°C, and Fe_2O_3 18°C. T_L decreases per 1 mass% component additions were Na_2O 29°C, Li_2O 28°C, K_2O 20°C, and B_2O_3 8°C. Other oxides (MnO, SiO_2, and U_3O_8) had little effect. The role of RuO_2 in spinel formation remains unclear (other data suggest that RuO_2 increases T_L by 300°C per 1 mass%).

QQ13.6
EFFECT OF RARE EARTH CONCENTRATIONS ON THE LIQUIDUS TEMPERATURE OF RARE EARTH-ALUMINO-BOROSILICATE GLASSES. Brian J. Riley, John D. Vienna, Michael J. Schweiger, Pacific Northwest National Laboratory, Richland, WA; David K. Peeler and Irene A. Reamer, Savannah River Technology Center, Aiken, SC.

The liquidus temperature (TL) of mixed rare earth-alumino-borosilicate glasses was studied. The concentration of total rare earth oxides was systematically varied between 38 and 54 mass percent in glass. The composition of the rare-earth oxide mix was also varied in this study. Thirty-two glasses were melted in covered platinum-rhodium crucibles at 1350°C and quenched on a steel plate. The liquidus temperatures of the glasses were measured by 24 h uniform temperature heat-treatments in covered platinum-rhodium crucibles. Two primary crystalline phases were found to precipitate from these glasses, mullite with TL values ranging from 1164°C to 1265°C and a rare-earth silicate (RES) with TL values ranging from 1163°C to 1298°C. For rare earth oxide concentrations less than 43 mass percent mullite was found to be the primary phase, glasses with higher rare earth oxide concentrations were in the RES primary phase. A strong correlation was found between TL and the rare earth oxide concentration and average ionic radius for glasses in both primary phase fields. A minimum in TL is found at roughly 44 mass percent rare earth oxide concentration with increasing TL at both higher and lower concentrations.

QQ13.7
GADOLINIUM AND HAFNIUM ALUMINO-BOROSILICATE GLASSES: DIRECT MEASUREMENTS OF THE COMPOSITIONS AND THEIR EFFECTS ON Gd AND Hf SOLUBILITIES IN THE GLASSES. Donggao Zhao, L.M. Wang, R.C. Ewing, Department of Nuclear Engineering and Radiological Sciences and Department of Geological Sciences, The University of Michigan, Ann Arbor, MI; Liyu Li, L.L. Davis, D.M. Strachan, Pacific Northwest National Laboratory, Richland, WA.

The aim of this study is to understand the solubility of actinides in glasses. Hafnium and gadolinium are used as surrogates for Pu(IV) and Pu(III), respectively, but they are also used as neutron absorbers to prevent criticality. A series of sodium alumino-borosilicate glasses were used as the basis with which to collect data on the dependence of solubility on glass composition. Initially, solubility was determined by examining the glasses under an optical microscope to determine if crystals had formed and by using the target glass composition. To be more precise in the determination of the solubility, a more sensitive determination of the glass compositions was needed. The compositions of a representative number of glasses were obtained with an electron microprobe. One of these glass samples was known to have micrometer-size Gd-rich silicate crystals with an apatite structure. The precipitated crystals contained more gadolinium (about 80 mass% Gd_2O_3) than the bulk glass. The glass composition near the precipitated crystals was depleted in Gd and richer in the other glass components. The measured compositions of the remaining glass samples were close to the target compositions. However, for Hf-

containing glasses, the difference between the measured and target compositions were up to 2 mass% for SiO_2 and for HfO_2. The electron microprobe data also show that Na was lost during the preparation of the high Na_2O (30 mole %) glasses. The direct measurements of the glasses and crystals with an electron microprobe confirmed that glass compositions have, in some instances, changed during preparation and that Gd-rich crystals contain boron as well as Si.

QQ13.8
JOINT VITRIFICATION OF VARIOUS MIXED WASTES. Olga I. Kiryanova, Tatiana N. Lashtchenova, Fedor A. Lifanov, Sergey V. Stefanovsky, Olga V. Tolstova, SIA Radon, Moscow, RUSSIA.

Mixed wastes involve radioactive constituent and hazardous components and must be conditioned to be disposed. Joint vitrification of low and intermediate level radioactive wastes (LILW) of NPPs, spent catalysts, sorbents, and cathode ray tube (CRT) glass is suggested. Preliminary experiments on vitrification in crucibles in a laboratory resistive furnace were carried out. A possibility of 40 wt.% of LILW salts loading in a batch has been demonstrated. Homogeneous silicate- and borosilicate-based glasses have been obtained and characterized. Phase separation problem at high sulfates and chlorides content with "yellow phase" formation occurred. To prevent it sulfates and chlorides must be separated from LILW. The most promising method of mixed waste vitrification is inductive melting in a cold crucible (IMCC) due to high productivity, high temperature availability, and long lifetime. Bench-scale tests have been carried out. Preliminary testing of IMCC of spent CRT glass and a batch from this glass and LILW salts (surrogate) was also conducted. LILW salts loading in the batch reached 30 wt.%. A starting melt was formed by heating of electric conductive silicon carbide rod in high frequency electromagnetic field. CRT glassmelt has low electric conductivity and high viscosity at temperatures about 1200°C not allowing to form the starting melt. Addition to the batch up to 30 wt.% of surrogate of RW salts increases electric conductivity and reduces viscosity of the melt to values providing IMCC. The batch is preferably fed as calcine.

SESSION QQ14: POSTER SESSION:
REPOSITORY, CONTAINERS, SPENT FUEL, AND
CLADDING
Chairs: Brian M. Ikeda and Lawrence H. Johnson
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ14.1
BEHAVIOR OF MgO AS A CO_2 SCAVENGER AT THE WASTE ISOLATION PILOT PLANT (WIPP), CARLSBAD, NEW MEXICO. Pengchu Zhang, Howard Anderson, Hans Papenguth and Jim Krumhansl, Sandia National Laboratories, Albuquerque, NM.

The WIPP, a repository for defense-related transuranic nuclear wastes, is located about 2150 feet underground in the bedded rock salt of the Salado Formation 26 miles southeast of Carlsbad, New Mexico. A MgO backfill was included in the repository design to scavenge CO_2 produced by decaying organic components in the waste and buffer pH to decrease actinide solubility. However, it has been suggested that early-formed precipitates may isolate MgO pellets, thus preventing complete reaction with CO_2. However, recent data suggest otherwise. To address this concern, hard-burned MgO pellets 2-4 mm in diameter were immersed in WIPP brines and exposed to CO_2. At CO_2 partial pressures near 1 atm. nesquehonite $MgCO_3.3H_2O]$ formed, but partial pressures near 0.05 atm. produced hydromagnesite $[(4- 3)MgCO_3.Mg(OH)_2.(3-4)H_2O]$. Nesquehonite was more effective at slowing CO_2 uptake rates, but should not form in the WIPP where the excess MgO will maintain a low CO_2 partial pressure. The difference in behavior occurs because nesquehonite forms dense mats of needle-like crystals whereas hydromagnesite initially forms loose aggregates of plate-like crystals. Hydromagnesite ultimately will react further producing magnesite $[MgCO_3]$, though rates were unknown. Hydrothermal studies (to 200° C) demonstrated that the coexisting fluid strongly affects the transformation rate. Increasing the ionic strength of NaCl brines increases the conversion rates but adding ppt levels of Mg greatly slows the rate even in nearly saturated NaCl brines. At room temperature hydromagnesite should persist for many decades, and possibly centuries, in the Mg-rich brines indigenous to the Salado. This resistance agrees with field observations regarding the very slow transition of hydromagnesite to magnesite in present-day evaporitic environments. 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.

QQ14.2
VADOSE ZONE MONITORING SYSTEM FOR SITE CHARACTERIZATION AND TRANSPORT MODELING. J.B. Sisson, J.M. Hubbell, A.N. Schafer, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

Estimating the rate of contaminate transport through thick vadose zones typically requires a major characterization effort followed by an equally intensive modeling effort. One possibility for reducing the total effort is to provide a monitoring system that is capable of collecting the vadose zone state variables: water content, water potential and contaminate concentrations. The Vadose Zone Monitoring System (VZMS) developed at the Idaho National Engineering and Environmental Laboratory (INEEL) was designed to collect these state variables. The VZMS when operated over extended periods of time provides an early detection system prior to aquifer contamination in addition to providing data needed for model calibration and direct estimates of unsaturated hydraulic properties. This paper presents a description of a working VZMS, examples of data collected to date and operational requirements for continuous data collection. The importance of episodic hydrologic events are discussed.

QQ14.3
PITTING CORROSION OF COPPER. EQUILIBRIUM - MASS TRANSPORT LIMITATIONS. Claes Taxen, Swedish Corrosion Institute, Stockholm, SWEDEN.

Predictions from a mathematical model of the propagation of a corrosion pit in copper are reported. The model uses equilibrium data for solid and aqueous species to calculate local chemical and electrochemical equilibria in small volume elements. Mass transport between elements under local internal equilibrium is calculated using aqueous diffusion coefficients with the constraint of electrical neutrality. Propagation of a corrosion pit is deemed possible when the fraction of the oxidised copper that forms solid corrosion products, at the copper metal, is insufficient to completely cover the underlying metal. Calculations have been made for a large number of water compositions. The effects of pH, and salt concentrations of the bulk water have been studied as well as the effect of temperature. Results are presented in the form of E-log C diagrams where E is the corrosion potential and C is the total bulk concentration of a particular ion e.g. chloride. When the concentration of chloride is varied, the E-log C diagram shows two separate areas where pitting is found to be possible. One region at low chloride concentration and high potential and one region at high chloride concentration and low potential. Increased sulphate concentrations are found to be detrimental with respect to pitting corrosion, particularly in the high potential region. Increased carbonate concentrations are found to be beneficial, particularly in the low potential region. Pitting corrosion of copper can be described as a case of galvanic corrosion where cuprous oxide at a pH similar to that of the bulk is the cathode material for oxygen reduction and copper metal at the local, lower pH in a corrosion pit may behave as the anode.

QQ14.4
CORROSION PERFORMANCE OF C-22 ALLOY AGED AT 260°C TO 800°C FOR 1 H TO 40,000 H. Raúl B. Rebak, Natalie E. Koon, John P. Cotner, Haynes International Inc., Kokomo, IN; Ricardo M. Carranza, Silvia A. Fernández, Comisión Nacional de Energía Atómica, Buenos Aires, ARGENTINA.

C-22 alloy (Ni-22Cr-13Mo-3W) is resistant to localized corrosion such as pitting corrosion, crevice corrosion and stress corrosion cracking. The purpose of the present study was to characterize the changes in the microstructure and corrosion behavior of C-22 alloy after aging in the temperature range 260°C to 800°C for 1 h to 40,000 h. This information could be relevant to the design and life prediction of high level nuclear waste containers that will be buried at the Yucca Mountain site. The corrosion resistance and anodic behavior of aged C-22 alloy were determined using standard immersion tests and electrochemical techniques. Immersion tests included ASTM G 28 A, ASTM G 28 B, boiling 2.5% HCl and 10% HCl solutions with and without ferric ions, boiling 10% NaOH solution with and without chloride ions. Electrochemical tests included polarization resistance (ASTM G 59), cyclic potentiodynamic polarization (ASTM G 61) and impedance measurements (ASTM G 106). The electrochemical tests were carried out in deaerated and aerated simulated J-13 water at 95°C and in deaerated 1 M HCl solution at 66°C.

QQ14.5
THEORETICAL STUDY OF BULK AND SURFACE PROPERTIES OF DIGENITE $Cu_{2-\delta}S$. P.A. Korzhavyi, I.A. Abrikosov and B. Johansson, Uppsala Univ, Dept of Physics, Uppsala, SWEDEN.

In relation with the problems of mid-temperature embrittlement and sulfide corrosion of copper, we perform an *ab initio* study of intrinsic properties of copper(I) sulfide in the antifluorite crystalstructure

(digenite). The energies of the (111) and (110) non-polar surfaces of Cu_2S are calculated using the interface Green's function technique. The (111) surface was found to have the lowest energy, in agreement with the cleavage pattern of digenite mineral. The low value of the surface energy (of about 1/3 of the surface energy of pure Cu) suggests that a precipitation of Cu_2S may be responsible for the embrittlement of Cu at intermediate temperatures. Locally self-consistent Green's function method is used to obtain the formation and interaction energies of native point defects in the bulk digenite. The results show that digenite exists as a non-stoichiometric compound $Cu_{2-\delta}S$ with stable (constitutional) cation vacancies, in agreement with experiment. The presence of cation vacancies combined with the calculated low value of the formation energy of Frenkel defects implies a high cation mobility in $Cu_{2-\delta}S$, which is consistent with the superionic behavior of the high digenite. This work is funded by SKB AB, the Swedish Nuclear Fuel and Waste Management Company.

QQ14.6
SIMFUEL LEACHING EXPERIMENTES IN PRESENCE OF γ EXTERNAL SOURCES (^{60}Co). Joaquin A. Serrano, Javier Quinones, Paloma Diaz-Arocas, Jose L. Rodriguez-Almazan, Joaquin Cobos, Dept. de Fision Nuclear, CIEMAT, Madrid, SPAIN; Jose A. Esteban, Aurora Martinez-Esparza, ENRESA, Madrid, SPAIN.

One of the factors considered within the studies of performance assessment on spent fuel under final repository conditions is the effect of the radiation on its leaching behaviour. Radiation from spent fuel can modify some properties of both solid phase and leachant and therefore it would alter the chemical behaviour of the near field. Particularising in the effect of the radiation on the leachant, it will cause generation of radiolytic species that could change the redox potential of the environment and therefore may bring on variations in the leaching process. In this work, the chemical analogue utilized was SIMFUEL (natural UO_2 doped with non radioactive elements simulating fission products) and the leachants selected were saline and granite bentonite waters both under initial anoxic conditions. To emulate γ radiation field of a spent fuel, leaching experiments with external ^{60}Co sources in a CIEMAT irradiation facility (Nayade) were performed. Initial dose rate used was 0.014 Gy/s. Preliminary results indicate that radiation produces an increase of dissolution rate, being the latest concentrations observed close to those in oxic atmosphere without radiation field. On the other hand, a tentative approach to modelling the role of γ radiolysis in the experimental data obtained has been carried out as well. First estimations show the importance of taking into account the composition of leachants due to the generation of specifics radyolitics species such us $CO_4^=$, CO_3^-, Cl_-, $ClOH_-$, etc. These studies are being carried out in the Dept. de Fision Nuclear (CIEMAT) within the agreement CIEMAT ENRESA in the frame of the final disposal of nuclear irradiated fuel.

QQ14.7
OXIDATIVE ALTERATION OF SPENT FUEL IN YUCCA MOUNTAIN REPOSITORY ENVIRONMENT: SEM/AEM INVESTIGATION AND GEOCHEMICAL MODELING. Yifeng Wang, Sandia National Laboratories, Carlsbad, NM; Huifang Xu, Department of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM.

Spent fuel (UO_2) will be directly deposited in geological repository in Yucca Mountain. Because UO_2 is very reactive in oxidized environment, it will be altered into uranyl (UO_2^{2+})-bearing phases and dissolved uranyl species in fluid phase. It is essential to understand long-term behavior of spent fuel in the geological repository. Naturally weathered uraninite and its reaction products can provide useful information about possible oxidative reactions of spent fuel in repository environment. Scanning electron microscopy (SEM) and analytical electron microscopy (AEM) investigation of a weathered uraninite from Shinkolobwe of Congo show that the main alteration products are soddyite and uranophane. Other U-bearing phases are sklodowskite, rutherfordine, schoepite, and kasolite. Silica-free U6+-bearing minerals (such as schoepite) are reaction products of uraninite and silica-depleted water during late stage reaction. Electron energy-loss spectroscopy results show the U^{6+}/U^{4+} ratio of the uraninite is about 1/1. We have calculated possible reaction paths of spent fuel in the condition of Yucca Mountain repository environment. The calculation of spent fuel alteration uses solution composition of Yucca Mountain groundwaters. The solution is maintained at constant pCO2=1E-2.3, fO2 = 1E-30 atm, and T = 25 ^{circ}C (open system). The calculated results show spent fuel will be replaced by U^{6+}-bearing phases of haiweeite and soddyite. Silica-free U^{6+}-phases (e.g., schoepite) will not occur in the studied environment. If phosphate is used as a component of backfill materials, the dissolved uranium will form less soluble phosphate phase, autunite. Based on predicted Gibbs free energies of formation for the phases with autunite structure, Ca-autunite is able to incorporate NpO_2^+, but not Cs^+. Other minerals that will also form are stilbite (zeolite), nontronite, hematite, and illite. By using

reaction rates from laboratory measurement and naturally weathered uraninite as up-limit and low-limit respectively, the real time oxidative reaction processes can be calculated.

QQ14.8
RELEASE OF RADIOTOXIC ELEMENTS FROM DEFECTIVE HIGH BURN-UP UO_2 AND MOX FUEL IN A REROSITORY. Jean-Paul Glatz, Javier Gimenez, Achileas Stalios, Detlef Wegen, European Commission, Directorate-General JRC, Institute for Transuranium Elements, Karlsruhe, GERMANY.

The processes responsible for the release of radiotoxic radionuclides from a spent fuel repository are dissolution and transport as a result of the groundwater flow. The cladding will be the last of all natural and man-made barriers before the water comes into contact with the fuel, namely with the interface between the outer rim of the pellet and the inner surface of the cladding. In order to simulate this realistic case of groundwater coming into contact with a spent nuclear fuel repository, the leaching of irradiated UO_2 (up to 60 GWd/tU) and MOX (up to 40 GWd/tU) fuel rods with pre-set cladding defects has been studied. The leaching experiments at 100 $^\circ$C under anoxic or reducing conditions for a duration of 2 years have shown, that the release of the matrix elements uranium and plutonium are limited by the low solubility product of the actinide-bearing solids. On the other hand especially high initial release rates were found for caesium and iodine, due to an heterogeneous distribution of these radionuclides within the fuel as a consequence of migration to the grain boundaries and to the pellet during irradiation. For all main radionuclides the release process can be described considering a two-step dissolution mechanism that includes the initial dissolution of an oxidised layer present on the fuel surface and a long-term oxidative matrix dissolution. The latter will be of course significantly influenced by radiolysis effects. The relative importance of α-radiolysis is increased due to an increased inventory of α-emitters and also due to large S/V ratios. In comparison to UO_2 the release of some major fission products is about two orders of magnitude higher for MOX fuels. Electrochemical techniques are used to investigate the complex corrosion behavior of the heterogeneous MOX fuel materials.

QQ14.9
CORROSION OF UNIRRADIATED N-REACTOR FUEL IN UNSATURATED TEST CONDITIONS. M.M. Goldberg, D.L. Bowers, S.F. Wolf, Y. Tsai, R.J. Finch and J.A. Fortner, Chemical Technology Division; T.S.Bray, ET Division, Argonne National Laboratory, Argonne IL.

The U.S. Department of Energy (DOE) currently owns approximately 2100 metric tons of spent metallic uranium fuel, primarily from the N-Reactor at Hanford, that it intends to dispose in the Mined Geological Disposal System at Yucca Mountain, NV. In order to document and enable development of a realistic model of the corrosion behavior of the fuel in a wet, oxidizing environment that is possibly representative of the repository at a future time, Argonne National Laboratory (ANL) is conducting corrosion tests on N-Reactor fuel specimens. Both unirradiated and irradiated fuel segments are being characterized and tested. To date, results are available from the unirradiated fuel tests. These tests were conducted prior to tests on the spent fuel in order to optimize test parameters and apparatus design, provide an estimate of corrosion rate of the metallic fuel, test hypotheses regarding corrosion mechanisms, and provide a basis for comparison of corrosion results in the presence and absence of a radiation field. Unsaturated corrosion tests were conducted in an air atmosphere at 90°C, with a small quantity (0.75 mL) of simulated groundwater (EJ-13) injected twice weekly. Results will be presented indicating that the fuel begins to oxidize immediately, forms a series of uranium oxides, generates H_2, and alters the pH of both the leachate solution and solution in longer contact with the fuel. The rate of fuel corrosion was monitored by periodically weighing the fuel coupons, measuring the coupons dimensions, determining dissolved uranium content in the leachate solution and adsorbed uranium on the vessel walls, and estimating uranium content of spalled corrosion products. The corrosion products exhibit several interesting properties of significance to repository performance: significant quantities of corrosion products spall from the coupon surface; the spalled products form films and aggregate in loosely consolidated clumps; and in the presence of excess water, the products exhibit characteristics of hydrophobic films, moving with and aggregating at the leading edge of the solution.

QQ14.10
POTENTIAL INCORPORATION OF TRANSURANICS INTO URANIUM ALTERATION PHASES. Cheol-Woon Kim, David J. Wronkiewicz, University of Missouri-Rolla, Department of Geology and Geophysics, Rolla, MO; Edgar C. Buck, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

Alteration of spent nuclear fuel may be expected under unsaturated

moist oxidizing conditions such as those which exist at the proposed nuclear waste repository at Yucca Mountain, Nevada. Experimental studies examining the alteration of UO_2 and spent nuclear fuel under such conditions have shown that the alteration products are primarily U^{6+} phases. The incorporation of radionuclides contained in spent fuel into the structure of U^{6+} phases will effect their mobility. A series of precipitation tests were conducted at either 150 or $90°C$ to determine the potential incorporation of Ce^{4+} and Nd^{3+} (surrogates for Pu^{4+} and Am^{3+}, respectively) into uranium alteration phases. Ianthinite ($U^{4+}U^{6+}{}_5O_{17}\cdot10H_2O$) was produced by dissolving uranyl oxyacetate in a solution containing copper acetate monohydrate as a reductant. The leachant solutions used in these tests were doped with either 2.1 ppm cerium or 399 ppm neodymium. The ICP-MS results indicate that about 306 ppm Ce was present in the ianthinite after seven days, while neodymium contents were much higher, being approximately 24,800 ppm. Solid phase examinations using SEM/EDS indicate a uniform distribution of Nd, while Ce contents were too low to be detected. The more sensitive AEM/EELS technique will be used to characterize Ce distributions in the future. Becquerelite ($Ca[(UO_2)_6O_4(OH)_6]\cdot8H_2O$) was produced by dissolving uranyl oxyacetate in a solution containing calcium acetate. The leachant solutions in these tests were doped with either 4.6 ppm cerium or 277 ppm neodymium. The cerium concentration in the solid phase from the 190-day test was 103 ppm, whereas Nd contents were 1310 ppm after seven days and 680 ppm after 35 days. Both the Ce and Nd contents in the solid were below the limits of detection using SEM/EDS. The more sensitive AEM/EELS technique will also be used to examine for becquerelite phase heterogeneities in the future.

QQ14.11
PIT INITIATION AND EVOLUTION ON STAINLESS STEELS AND Ni-BASED ALLOYS. Peter J. Bedrossian and Joseph C. Farmer, Lawrence Livermore National Laboratory, Livermore, CA.

The development of realistic models for the prediction of long-term material degradation under corrosion requires a scientifically sound basis for scaling in both space and time, from atomic-level processes to macroscopic containers, and from experimental to geological time scales. To this end, we have initiated a study of the spatial scaling of surface roughness caused by corrosion, spanning length scales from nanometers to millimeters. By applying Atomic Force Microscopy (AFM) in fluid in an electrochemical cell, we have observed the surface morphological evolution of Type 304 and 316 stainless steels exposed to brine and acidic chloride environments on the nanometer scale. Pit formation occurs only after an induction time period during which no corrosion is detected. Once localized attack begins, pits grow and coalesce rapidly. We observe that pit initiation occurs preferentially at triple junctions, where three random grain boundaries meet. The observations of corrosion of stainless steels stand in contrast to tests on the corrosion-resistant, Ni-based Alloy 22, which do not reveal similar pit growth processes. The authors are grateful to David Fix for technical assistance. Research was performed at Lawrence Livermore National Laboratory under the auspices of the US Dept. of Energy under Contract W-7405-Eng-48 and was supported by the Yucca Mountain Project.

SESSION QQ15: POSTER SESSION:
WASTE PROCESSING
Chair: Andrew H. Bond
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

QQ15.1
ATTRACTIVE INTERACTIONS BETWEEN REVERSE AGGREGATES AND PHASE SEPARATION IN CONCENTRATED MALONAMIDE EXTRACTANT SOLUTIONS. Laurence Martinet, Corinne Erlinger, L. Belloni, Thomas Zemb, Laurence Berthon and Charles Madic, CEA Saclay and Marcoule, FRANCE.

We investigate the supramolecular chemistry associated with the liquid-luiquid selective extraction using reverse micelles in equilibrium with excess brine. Using SAXS, conductivity and phase behaviour determination, we show that concentrated solutions of molanamide extractants, dimethyldibutyltetradecylmalonamide (DMDBTDMA), are organised in reverse oligomeric aggregates which have many features in common with reverse micelles. The aggregation numbers of these reverse globular aggregates as well as their interaction potential are determined from absolute scattering curves. An attractive interaction is responsible for the demixing of the oil phase when in equilibrium with excess oil. Prediction of conductivity as well as the formation conditions for the third phase is possible using standard liquid theory applied to the extractant aggregates. The interactions, modelled with the sticky sphere model proposed by Baxter, are shown to be due to steric interactions resulting form the hydrophobic tails of

the extractant molecule and van der Waals forces between the highly polarisable water core of the reverse micelles. The attractive interaction in the oil phase, equilibrated with water, is determined as a fonction of temperature, extractant molecule concentration, as well as proton and neodynium (III) cation concentration. It is shown that van der Waals interactions, with an effective Hamaker constant of 3 kT, quantitatively explains the behaviour of DMDBTDMA in n-dodecane in terms of scattering as well as phase stability limits.

QQ15.2
BEHAVIOR OF ACTINIDE IONS DURING SLUDGE WASHING OF ALKALINE RADIOACTIVE WASTES. Andrew H. Bond, Kenneth L. Nash, Mark P. Jensen, James C. Sullivan, Chemistry Division, Argonne National Laboratory, Argonne, IL; Linfeng Rao, Lawrence Berkeley National Laboratory, Berkeley, CA.

The bismuth phosphate, Redox, and PUREX separations processes were used at Hanford for the large-scale purification of plutonium for defense purposes. The residual wastes from these processes were made alkaline, producing sludge materials that, over time, have settled into stratified layers in the tanks. In order to minimize the volume of waste and to simplify the feed stream directed to the vitrification facility, Hanfords current baseline strategy for treating alkaline radioactive wastes involves removal of the supernatant and saltcake prior to sluicing and washing of the remaining sludge materials. Based on the available experimental data, it has been assumed that the actinides will remain in the sludge during these transfer and leaching procedures. Unfortunately, this model does not account for the diverse chemistry and conditions that have evolved in these wastes over the past fifty years. Because sludge washing operations will encounter a heterogeneous mixture of solids whose thermodynamic and kinetic behavior may differ with respect to actinide mobilization, the present work aims to characterize the solution and solid state actinide species from representative sludge simulants from the three plutonium purification flowsheets. With this information, predictive capabilities will be developed that permit the identification of those tanks having a high probability of actinide solubilization during sludge pretreatment. The influences of thermal and radiolytic aging of sludges on actinide speciation and preliminary results from sludge washing operations using a series of increasingly aggressive leachants is discussed. This work is funded by the Environmental Management Sciences Program of the Offices of Energy Research and Environmental Management, United States Department of Energy, under contract number W-31-109-ENG-38.

QQ15.3
NOVEL Sr-SELECTIVE INORGANIC ION EXCHANGERS. M. Nyman and T.M. Nenoff; Sandia National Labs, Albuquerque, NM; M.L. Balmer and Y. Su, Pacific Northwest National Laboratory, Richland, WA; A. Navrotsky and H. Xu, Dept. of Chemical Engineering and Material Science, University of California-Davis, Davis, CA.

Radionuclides of Sr and Cs account for > 99% of the radioactive inventory of the Hanford waste tanks. We are currently researching novel materials for sequestration (ion exchanger materials) and disposal/storage (waste form materials) of radionuclides such as ^{137}Cs and ^{90}Sr. We have developed a class of niobate-based inorganic ion exchanger materials which are selective for bivalent cations including strontium. Additionally, thermal treatment of the Sr-loaded material results in conversion to perovskite, which is an extremely durable waste form material. Substitutions of heteroatoms can be made into the niobate framework , and functional properties (i.e. ion exchange) vary with concentration of the heteroatom. Thus, these materials are tunable in their functionality. Synthesis, characterization, ion exchange and thermal conversion of the new phases will be presented. Additionally, exchange properties will be discussed in terms of heteroatom concentration. This work was supported by the U.S. DOE under contract DE-AC04-94AL85000.

QQ15.4
DEMONSTRATION OF CESIUM REMOVAL FROM THE FUEL STORAGE WATER AT THE SAVANNAH RIVER SITE R-BUILDING DISASSEMBLY BASIN USING 3M EMPORE-MEMBRANE FILTER TECHNOLOGY. Lawrence N. Oji, M. C. Thompson, Kurt Peterson, Westinghouse Savannah River Company, Savannah River Site, Aiken, SC; Thomas M. Kafka, 3M Center, 3M Company, St. Paul, MN.

This papper describes results from a seven-day demonstration of the use of 3M EMPORE-membrane filter loaded with ion exchange material (potassium cobalt hexacynoferrate (CoHex)) for cesium uptake from the R-Disassembly Basin (irradiated nuclear fuel storage pool) at the Savannah River Site. The goal of the demonstration was to evaluate the ability of the Process Absorber Development unit (PADU), a water pre-filtration/CoHex configuration on a skid, to remove cesium from R-Disassembly Basin at a linear processing flow

rate of 22.7 liters per minute. Over 210,000 liters of R-Disassembly Basin water was processed through the PADU without a cesium breakthrough, that is, the effluent after treatment with CoHex, contained less than detectable amounts of radioactive cesium. Some of the observed advantages of the EMPORE-membrane filter technology over conventional packed column ion exchange systems includes rapid flow rates without channeling effects, low volume secondary waste and fast extraction or rapid kinetics per unit of flow.

QQ15.5
SOLVENT EXTRACTION OF TC-99 FROM INTERMEDIATE LIQUID WASTE BY DIBENZO-18-CROWN-6. <u>Patricia Paviet-Hartmann</u>, Los Alamos National Laboratory, Chemical Science and Technology Division, Los Alamos, NM; Alain Raymond, Centre d'Etudes de Cadarache, Direction du Cycle du Combustible, Saint Paul Lez Durance, FRANCE.

Technetium is one of the most prominent problems since its most stable specie in the environment, the pertechnetate ion, is highly mobile and considered as a long-term hazard in nuclear waste disposal. Because of the small activities of Tc-99 relative to other fission products Cs-137 or Sr-90, and its long half-life time ($t_{1/2} = 2.1 \times 10^5$ yrs), Tc-99 is one of the key isotopes that should always be analyzed in the radioactive liquid waste streams from the reprocessing industry where the largest concentrations are to be expected. Furthermore, Tc-99 is a high-yield fission product of uranium and as a pure beta-emitter, it has to be isolated from the intermediate level waste (ILW) stream prior to any measurement in such complex media. We have developed a method for Tc-99 extraction providing recommendations that will be useful for extracting it from acid and basic ILW. The extraction of Tc-99 from ILW by Dibenzo-18-Crown-6 (DB18C6) has been investigated and a simplex optimization of key parameters involved in the procedure has allowed us to set up their best values. Experiments have been carried out on synthetic and real effluents from La Hague reprocessing plant, France, and results show that DB18C6 is highly selective towards Tc-99. Through the process, with only one single extraction step, 85 to 95% of Tc-99 has been extracted. The total preparation time of the chemical separation takes only 20 minutes for a batch of 8 samples. The application of this procedure has been successfully demonstrated through the analysis of actual waste streams coming from the two reprocessing plants at La Hague and Marcoule, France.

QQ15.6
ANALYSIS OF WASTE FROM A DRY RECYCLE PROCESS. <u>Michael P. Reynard</u>, Mujid Kazimi, K.R. Czerwinski, Massachusetts Institute of Technology, Nuclear Engineering Department, Cambridge, MA; Jerry Christian, Idaho National Engineering and Environmental Laboratory, National SNF Program, Idaho Falls, ID.

AIROX is a dry process involving irradiated fuel oxidation by O_2 and reduction under H2 between 400-600°C. The oxidation transforms UO_2 to U_3O_8 with a volume increase on the order of 30%, allowing the removal of the volatile and semi-volatile fission products. Remaining fuel is mixed with UO_2 or PuO_2, then resintered at 1700°C and refabricated. Potentially, AIROX can reduce the amount of spent fuel which needs to be placed in a repository. An assessment of AIROX fission product removal and the consequence of isotope removal is made. The examined elements are chosen based on neutronic and dose considerations. Elemental removal based on chemical properties and tendencies are estimated. High removal rates are expected for Cd, Cs, Se, Tc, and Te. Using removal estimates, the fraction of neutron absorption removed by the AIROX for different fuel cooling times is found. Over the cooling time of 1 year to 200 years, there is a slight decreae in fraction removed absorptions, going from 0.175 (1 year) down to 0.150 (200 years). In the limiting case of long cooling times before spent fuel undergoes AIROX, the amount of neutron absorptions AIROX should remove is 15%. The isotopes which contribute most to the total neutron absorptions removed by AIROX, throughout the time span of 1 year to 200 years, are ^{131}Xe and ^{133}Cs. Lanthanides, which have high neutron capture cross sections, are not effectively removed by AIROX AIROX also effects the gamma dose from spent fuel. In the limiting case of long cooling times before spent fuel undergoes AIROX, the amount of gamma dose AIROX should remove approaches 95%. From 10 years on, ^{137}Cs is the isotope which contributes the most gamma dose from spent fuel, explaining the effective dose removal by AIROX.

QQ15.7
CHARACTERIZATION OF AND WASTE ACCEPTANCE RADIONUCLIDES TO BE REPORTED FOR THE SECOND MACRO-BATCH OF HIGH-LEVEL WASTE SLUDGE BEING VITRIFIED IN THE DWPF MELTER. <u>Terri L. Fellinger</u> and Ned E. Bibler, Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC.

The Defense Waste Processing Facility (DWPF), at the Savannah River Site (SRS), is currently processing the second million gallon batch (Macro-Batch 2) of radioactive sludge slurry into a durable borosilicate glass for permanent geological disposal. To meet the reporting requirements as specified in the Department of Energy's Waste Acceptance Product Specifications (WAPS), for the final glass product, the nonradioactive and radioactive elemental compositions must be provided for a Macro-Batch of material. In order to meet this requirement, sludge slurry samples from Macro-Batch 2 were analyzed in the Shielded Cells Facility of the Savannah River Technology Center. This information is used to complete the necessary Production Records at DWPF so that the final glass product, resulting from Macro Batch 2, may be disposed of at a Federal Repository. This paper describes the results obtained from the analyses of the sludge slurry samples taken from Macro-Batch 2 to meet the reporting requirements of the WAPS. The sludge slurry samples were analyzed for nonradioactive elemental composition by Inductively Coupled Plasma- Emission Spectroscopy (ICP-ES). The ICP-ES results identified twenty-eight nonradioactive elements for Macro-Batch 2. Determination of the radioactive elemental composition for the sludge slurry was completed by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) and counting techniques. Special separation techniques were used to detect C-14, I-129, Cm-246 and Cm-247 in the sludge slurry. This is the first time these radionuclides have been detected and measured in radioactive sludge slurry at the SRS. The radioisotopes from these analyses that met the WAPS criteria of having a half life longer than 10 years were decayed by a computer program from time zero (May 1999) to 2000 years (May 3999). This was completed in order to determine the radioactivity of the glass 1100 years after production in the DWPF as required by the WAPS. Thirty-one radioisotopes were identified as reportable for Macro Batch 2.

QQ15.8
MATRIX-ASSISTED LASER DESORPTION-IONIZATION MASS SPECTROMETRY OF ORGANIC MOLECULES ON SODIUM NITRATE. David R. Ermer, Michelle Baltz-Knorr, Michael R. Papantonakis, <u>Richard F. Haglund, Jr.</u>, Vanderbilt University, Dept of Physics and Astronomy, Nashville, TN.

Quantitative identification of organic molecules embedded in or adsorbed on sodium nitrate is an important part of characterizing the salt cake in mixed high-level radioactive waste-storage tanks. In conventional matrix-assisted laser desorption-ionization (MALDI) mass spectrometry using uv lasers, the salt cake incorporating organic molecules would be dispersed in a matrix chosen for optimal laser absorption. However, we find that electronic transitions induced in sodium nitrate by a KrF laser (248 nm) can produce some organic-ion signal. This signal can be enhanced by adding DHB (dihydroxybenzoic acid) to the sample. On the other hand, organic molecules such as benzene, toluene and various crown ethers can also be detected with high sensitivity by tuning an infrared laser into the mid-infrared stretching modes of the sodium nitrate. Interestingly, addition of either HCCA (hydroxy-cyano-cinnamic acid) or succinic acid as matrix material fails to increase the organic-ion yield in ir-MALDI. We compare the relative sensitivities of the two techniques, and consider the differences in mechanisms which underly the differing uv- and ir-MALDI responses to the addition of exogenous matrix materials to the organic-doped sodium-nitrate samples. Supported by the U. S. Department of Energy under contract DE-FG07-98ER62710. The W. M. Keck Foundation Free-Electron Laser Center at Vanderbilt University is supported by the Office of Naval Research under the Medical Free-Electron Laser Program, contract N00014-94-1-0123.

QQ15.9
SUPERCRITICAL CO_2 TREATMENT OF RADIOACTIVE GYPSUM-BASED WASTE-FORMS. <u>Thomas Hartmann</u>, Patricia Paviet-Hartmann, James Rubin, Kirk Hollis, Craig Taylor, Los Alamos National Laboratory, Chemical Science and Technology Division, Los Alamos, NM.

A traditional practice at the Rocky Flats DOE site (Colorado) to immobilize weapon generated oil-solvents was to slurry these transuranic (TRU) waste mixtures with water and emulsifiers and stabilize them in a gypsum-based matrix. A polymerization agent, melamine-formaldehyde was employed in order to increase leach resistance as well as to solidify the water immiscible organic inventory. Today, some of the so-generated waste-forms do not fulfill both: (a) DOT requirement for free liquid using TRUPACT-II transportation container, and (b) waste acceptance criteria (WAC) to be stored at the Waste Isolation Pilot Plant (WIPP). Waste drums sampled for volatile organic compounds (VOCs) in the headspace are containing high tetrachloride carbon contents, up to 180,000 ppmv (part per millions by volume). The administrative limit is 7510 ppmv. Flammable organics can also be measured in high concentrations with 100,000 ppmv versus a limit of 500 ppmv. These high amounts of TOC (total organic carbon) as well as the free liquid content requires

a highly efficient and fast method for extracting the diluents from the sludge without repackaging. In this study, we demonstrate that organic solvents as well as oil-water emulsions can be selectively and quantitatively extracted by applying a supercritical CO^2 (SCCO2) treatment. The effect of SCCO2 treatment applying different CO^2 pressure and temperature conditions (8.4 MPa$<$p$<$28 MPa, 35°C$<$T$<$62°C) on the efficiency of the solvent extraction progress and on the leach resistance will be presented. SCCO2 treatment of gypsum-based legacy waste-forms is proven to be a suitable technique to satisfy the DOT requirements pertaining the free liquid content and the WAC for VOCs and TOC at the WIPP. The deployment of this technology will contribute to the massive cleanup effort at Rocky Flats and will provide a highly improved waste-form and furthermore trustworthy risk assessment for the repository regarding the migration of the radionuclides.

SESSION QQ16: CONTAINERS AND REPOSITORY
Chairs: Darrell S. Dunn, David W. Shoesmith, and
Lars O. Werme
Wednesday Morning, December 1, 1999
Room 203 (H)

8:30 AM *QQ16.1
FABRICATION AND TESTING OF COPPER CANISTER FOR LONG TERM ISOLATION OF SPENT NUCLEAR FUEL. Lars O. Werme, Swedish Nuclear Fuel and Waste Management Co.(SKB), Stockholm, SWEDEN.

In 1993 SKB launched its Encapsulation Plant Project. Within this project, SKB has: a) designed a facility for encapsulation of nuclear fuel b) laid down the design premises for a canister for disposal of nuclear fuel c) tested and developed fabrication methods for copper canisters d) evaluated the long term chemical and mechanical behavior of the canister e) made preliminary plans for a factory for the production of copper canister f) constructed a canister laboratory for full scale testing of the key operations in an encapsulation plant. The conclusions of this project were that a canister consisting of an outer layer of 50 mm copper over an insert of cast nodular iron would provide sufficient corrosion protection and would have sufficient mechanical strength. This canister can be produced by several methods such as forming from rolled plates, hot extrusion, and pierce and draw. These methods have been tested at full scale and the results from these manufacturing tests will be presented and discussed. The canister will be sealed by electron beam welding in the encapsulation plant and the integrity of the weld will be verified by ultrasonic testing and high-energy radiography. The final development work in this area will be performed in the Canister Laboratory in Oskarshamn, Sweden. The laboratory is now in operation and is equipped with a 100 kW EB-welding unit, a 9 MV digital X-ray unit and a state-of-the-art phased array ultrasonic testing unit. The status of the work in the laboratory will also be discussed.

9:00 AM QQ16.2
PASSIVE DISSOLUTION AND LOCALIZED CORROSION OF ALLOY 22 HLW CONTAINER WELDMENTS. Darrell S. Dunn, Gustavo Cragnolino, Narasi Sridhar, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

The lifetime of Alloy 22 high level nuclear waste (HLW) containers in a repository environment will likely be determined by the localized corrosion resistance and passive dissolution rate of the container material. Numerous tests conducted with non-welded specimens have shown that Alloy 22 has excellent corrosion resistance characterized by a low passive dissolution rate and high repassivation potentials in chloride solutions at temperatures up to 95°C. The performance of welded Alloy 22 has been investigated and compared to the as-received material. Tests were also conducted with thermally aged Alloy 22 specimens to determine the effect of exposure to elevated temperatures during welding on the corrosion resistance of the material. Repassivation potential measurements for welded Alloy 22, conducted over a wide range of chloride concentrations (0.02 to 11 molar) and temperatures (25 to 150°C), indicate that welding decreased the corrosion resistance of the alloy. Compared to the as-received material, lower repassivation potentials were observed with welded specimens as well as an increased susceptibility to localized corrosion at lower chloride concentrations. Passive corrosion rate measurements with thermally aged (870°C) Alloy 22 indicate that material exposed to elevated temperatures had a greater dissolution rate than the as-received material and was prone to intergranular attack under oxidizing conditions. Overall performance of the Alloy 22 containers, as indicated by container lifetimes, was calculated as a function of alloy condition and environmental variations.

9:15 AM QQ16.3
STRESS CORROSION CRACK GROWTH IN COPPER FOR WASTE CANISTER APPLICATION. Kjell Pettersson, Magnus Oskarsson, KTH, Dept. of Materials Science and Engineering, Stockholm, SWEDEN.

Stress corrosion crack growth in pure copper has been studied with the aim of determining data which may be used in extrapolations to conditions of interest for use of copper as a canister material for long term storage of spent nuclear fuel. The canister should retain its integrity for a time of 100 000 years and the ultimate aim of the project is to show that stress corrosion cracking is not a threat to the canister integrity. The crack growth is studied as a function of applied stress intensity factor and environmental factors such as solute concentration and electrochemical potential. The approach used is to determine crack growth rates under conditions which give low but measurable rates which can then be extrapolated to times and conditions of relevance to canister integrity. The most accurate method of on-line crack growth monitoring, DC potential drop, is unfortunately in conflict with the low resistivity of copper. However useful results have been obtained which on extrapolation to long times indicate that even pre-existing cracks in the canister can not grow appreciably during the canister life time. Additional data will be needed to improve the credibility of the extrapolation.

10:00 AM QQ16.4
NUMERICAL SIMULATION OF BENTONITE EXTRUSION IN A HORIZONTAL PLANAR FRACTURE. Joonhong Ahn, Paul L. Chambré, and Jerome Verbeke, Department of Nuclear Engineering, University of California, Berkeley, CA.

This paper presents results of a numerical analysis for bentonite expansion in a planar fracture. The bentonite expands in a radial direction through a horizontal planar gap, which intersects the cylinder filled with water- saturated bentonite. The gap has a constant width and is filled up originally with stagnant water. This simulation has been motivated by an experiment performed previously and reported elsewhere. A mathematical model has been developed based on Terzaghi's theory for clay deformation due to water intrusion. The permeability and the compressibility of the bentonite, which are two key parameters for bentonite expansion, are assumed functions of its void ratio. The resulting governing equation is a non-linear diffusion-like equation with void-ratio-dependent coefficients. Numerical solutions for the space-time-dependent void ratio in the expanding bentonite are obtained by applying the Finite Element Method. The finite element solution is combined with a predictor-corrector scheme for evaluations of the void ratio distribution and the location of the moving bentonite- tip boundary. A computer code has been developed for the numerical solutions. The numerical scheme is supported by comparing the results with an analytical solution with constant coefficients for early times. We have utilized the void ratio dependencies of the permeability and the compressibility of bentonite, which are experimentally measured, and are reported elsewhere. The location of the expanding tip was also experimentally observed as a function of time. Numerical simulations by the code give a good agreement with the experimental results conducted for a time period of 100 hours by assuming that the void ratio at the tip has a prescribed value.

10:15 AM QQ16.5
THERMAL STUDIES FOR RADIOACTIVE WASTE MANAGE-MENT. Dominique Manzoni, Sabine Le Bonhomme, EDF, Dept of Heat Transfer and Aerodynamics, Chatou, FRANCE; Bruno Soulier, Ecole Nationale Supérieure, Cachan, FRANCE; Yves Guilloux, ANDRA, Châtenay-Malabry, FRANCE.

A radioactive waste disposal is characterized by an arrangement of various essential factors: repository concept, number of waste packages by tunnel, rock characteristics, bentonite characteristics, distance between waste packages and tunnels, initial cooling time for containers before storage... This arrangement must verify some thermal criteria, in particular in the bentonite, so that the degradation of the clay and the canister corrosion will be moderated. In order to confirm and optimize the Initial Option of Storage, ANDRA (National Radioactive Waste Management Agency) asked EDF/HTA to realize a parametric study with the objective to evaluate the temperature level in the repository as a function of the different factors. All the calculations have been performed with a 3D conduction and radiation code called SYRTHES and developed at EDF. As the number of calculations is very important, an Experiment Design Method has been used to evaluate the influence of each of the eight parameters. The maximum of the bentonite temperature has been approached by a polynomial model of second order for all the factors and of first order for the interactions between factors. In this way, it has been developed on Excel a simple model of the maximum of temperature in the bentonite

for different repository concepts as a function of the eight parameters. The average error is about 5°C in the boundary of the domain.

10:30 AM QQ16.6
LONG TERM TEST OF BUFFER MATERIAL AT ASPO HARD ROCK LABORATORY SWEDEN. Ola Karnland, Torbjörn Sanden, Clay Technology AB, Lund, SWEDEN.

Bentonite clay has been proposed as buffer material in several concepts for HLW repositories. The Long Term Test of Buffer Material series aims at validating models and hypotheses concerning physical properties in a bentonite buffer material and of related processes regarding mineralogy, microbiology, radionuclide transport, copper corrosion and gas transport under conditions similar to those in a the Swedish KBS3 repository. The test series comprises 6 test parcels which will be run for 1, 5 and 20 years. The testing principle is to emplace parcels containing heater, central copper tube, precompacted clay buffer, instruments, and parameter controlling equipment in vertical boreholes in granitic rock. The parcels are equipped with heaters in order to simulate the decay power from spent nuclear fuel at standard KBS3 conditions (90°C) and adverse condition (130°C). Adverse conditions in this context refer also to high temperature gradients over the buffer, and additional accessory minerals leading to i.a. high pH and high potassium concentration in clay pore water. Temperature, total pressure, water pressure and water content, are measured during the heating period. At test termination water content are determined and subsequent well-defined chemical, mineralogical analyses and physical testing are made. The two pilot tests (1 year tests) have been completed and results are at hand.

10:45 AM QQ16.7
O_2 CONSUMPTION IN A GRANITIC ENVIRONMENT. I. Puigdomenech, Royal Institute of Technology, Inorg Chem, Stockholm, SWEDEN; S. Kotelnikova, K. Pedersen, Univ of Gothenburg, Dept of Cell and Molecular Biology, Gothenburg, SWEDEN; E. Gustafsson, Geosigma AB, Uppsala, SWEDEN; E.-L. Tullborg, Terralogica AB , Gråbo, SWEDEN; L. Griffault, ANDRA, Chatenay-Malabry, FRANCE; L. Trotignon, V. Michaud, CEA, Cadarache, FRANCE; J.-E Lartigue, CNRS, Aix-en-Provence, FRANCE; S.A. Banwart, University of Sheffield, Dept of Civil & Structural Engineering, Sheffield, UNITED KINGDOM; J. Rivas Perez, University of Bradford, Dept Civil & Environmental Engineering, Bradford, UNITED KINGDOM; K. Bateman, A.E. Milodowski, J.M. West, BGS, Fluid Processes Group, Keyworth, UNITED KINGDOM; K. Hama, H. Yoshida, JNC, Tono Geoscience Center, Gifu, JAPAN.

Molecular oxygen entrapped in a granite repository after closure may affect the corrosion of metal canisters. Similarly, future intrusions of oxygen-rich melt waters during a glacial event may affect the integrity of the canisters, as well as the migration of radionuclides.
The fate of O_2 in a granite repository has been addressed by an international project: The redox experiment in detailed scale (REX). The emphasis of the project is on a field experiment involving groundwater in contact with a fracture surface. To this aim a borehole, ≈ 20 cm in diameter, has been drilled at 380 m depth in the tunnel of the Äspö Hard Rock Laboratory, Sweden. O_2 injection pulses have been performed at *in situ* temperature and pressure. Several microbial and chemical parameters have been studied: microbial counts, pH and O_2-concentration as a function of time, etc. The field study has been supported by laboratory experiments to determine O_2 reaction rates and mechanisms with Äspö samples (both for inorganic and microbially mediated processes). A replica experiment has been perfomed at CEA, France, with the other half of the fracture surface obtained in the drilling procedure of the field experiment. The aim of the replica experiment has been to duplicate as far as possible the conditions of the REX *in situ* experiment, for example by using groundwater sampled at the REX site in Sweden, shipped in special containers to France.
The data that has been collected from the O_2 injection pulses in the REX field and replica experiments are compared with the rates of molecular oxygen consumption determined in the laboratory experiments. These data allow to estimate life-times for oxygen consumption in granitic fractures, which is of consequence for performance assessment calculations.

11:00 AM QQ16.8
THE LONG-TERM BEHAVIOUR OF STEEL REDOX BARRIERS IN NUCLEAR FUEL WASTE CONTAINERS. Simcha Stroes-Gascoyne and Miroslav Kolar, Atomic Energy of Canada Limited, Whiteshell Laboratories, Pinawa, Manitoba, CANADA; Fraser King, Integrity Corrosion Consulting, Calgary, Alberta, CANADA; David W. Shoesmith, University of Western Ontario, London, Ontario, CANADA.

Steel components of nuclear fuel waste containers may act as the principal corrosion barrier or provide mechanical strength for

less-robust corrosion-resistant overpacks. In addition, the presence of steel may form a significant redox barrier to the release of radionuclides. Radiolysis species may react on Fe surfaces instead of supporting oxidative dissolution of used fuel. Dissolved U(VI) and other radionuclides may undergo interfacial or homogeneous reactions, producing less-mobile reduced species. Sorption of radionuclides on Fe oxides may retard their migration. The long-term effectiveness of such a redox barrier, however, requires that either the surface continues to release Fe(II) to solution or that electroactive species reach the underlying Fe surface or semi-conducting Fe oxide film. A conceptual model was developed to predict the long-term effects of Fe-based redox processes on the oxidative dissolution of used fuel and the subsequent transport of dissolved U(VI) and other radionuclides. The model is based in part on a literature survey of the corrosion and electrochemical behaviour of C-steel and Fe oxides. In this model, C-steel surfaces are covered by a porous Fe(II)-containing oxide film. Bare C-steel is exposed at the base of the pores at the film/metal interface. Oxidized species diffuse through the film and react at the underlying Fe surface. The oxide film dissolves and releases Fe(II) to solution, which then reacts with U(VI) and other oxidized species. The Fe(II) release rate is potential dependent, with the potential determined by the relative rates of redox processes occurring on the Fe(II) oxide and underlying Fe surface. This model has been incorporated into a used fuel oxidative dissolution Mixed-Potential Model (MPM). This conceptual model will be described and results from MPM simulations presented. Additionally, results from experiments to confirm the porosity of oxide films on C-steel will be discussed. This work was funded by Ontario Power Generation.

1:30 PM *QQ17.1
NATURAL ANALOGS AND PERFORMANCE ASSESSMENT. William M. Murphy, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

Natural analog studies can build confidence in the scientific basis for nuclear waste management by strengthening performance assessments for proposed repositories. The conceptual basis for geologic disposal of nuclear waste and for performance assessments relies on scientific expertise regarding the stability of geologic environments, the potential stability of waste containment structures and waste forms in geologic media, and the migration of radionuclides in geologic systems. Studies of features, events, and processes that may contribute to alteration of waste containers and waste forms and transport of radionuclides in geologic settings analogous to nuclear waste repository sites permit evaluations of their inclusion in performance assessments. Analog data have been used widely in supporting performance assessments. Most applications qualitatively address conceptual models and contribute to confidence building for the legitimacy of experimental and model results and applications. Quantitative uses of natural analog data in support of performance assessments are challenging because of imperfect analogies and uncertain geologic histories. Nevertheless, existing uses of analog data in performance assessments include quantifying parameters describing the role of matrix diffusion in retarding radionuclide migration, calculation of alternate source term radionuclide release rates, and testing models quantifying the probability and consequences of certain geologic events. As performance assessments are conducted, natural analog data can be used to test or screen model hypotheses, evaluate experimental data, and judge data approximations. This work is a product of the Center for Nuclear Waste Regulatory Analyses and does not represent the views or regulatory position of the U.S. Nuclear Regulatory Commission.

2:00 PM QQ17.2
USING INFORMATION FROM NATURAL ANALOGS IN REPOSITORY PERFORMANCE ANALYSIS: EXAMPLES FROM OKLO. V.M. Oversby, VMO Konsult, Stockholm, SWEDEN.

Repositories designed for the long term disposal of nuclear waste will contain engineered materials for which predictions must be made concerning their long-term behavior. Some of these materials have chemical compositions and physical properties that are closely similar to naturally occurring materials. In these cases, the natural materials can be studied as analogs of the engineered materials. The Oklo, Gabon, ore deposits are a special example of a natural analog for spent fuel, since portions of the ore achieved a critical condition and sustained nuclear reactions about 2000 million years ago. Studies of the Oklo deposits will be reviewed for their potential for providing

information that can be used in the performance assessment of waste repositories. Particular attention will be focussed on the issues of criticality in a natural setting, the stability or dissolution of spent fuel, and the retardation of radionuclide transport through the processes of secondary phase formation, sorption, and dispersion. The difficulties with finding a natural analog for spent fuel dissolution arise because of the need for determining the hydrologic conditions, including water chemistry, redox state, and flow rate over the geologic history of the ore deposits. Finding natural analogs for spent fuel that show stability of the ore over geologic time is much easier, and occurs in several of the Oklo natural reactor sites. In addition, south of Oklo, there is a natural reactor site at Bangomb, which can be used to study the processes associated with such a deposit during weathering under near-surface tropical conditions.

2:15 PM QQ17.3
NATURAL SYSTEMS CONSTRAINTS ON MODELS OF THE LONG-TERM CHEMICAL EVOLUTION OF BUFFER PORE-WATERS. Randy Arthur, Monitor Scientific, LLC, Denver, CO; Ju Wang, Beijing Research Institute of Geology, Beijing, PR CHINA.

The solubilities of radioelements that constrain the source term in performance assessments of disposal concepts for HLW [e.g., Sweden (SITE-94; SR-97); Finland (TVO-92); Japan (H-12)] are calculated based on the chemistry of porewaters in the buffer (i.e., the bentonite component of the EBS). Ion-exchange (1), surface-chemical (2) and ideal site-mixing (3) models that have been proposed to predict the chemistry of these solutions are based on the results of short-term experiments (1, 2) or semi-empirical observations of activity-composition relations among smectite clays and illite (3). To evaluate the accuracy of these models over time scales considered in performance assessments, we use Models 1 and 2 to predict the pH of porewaters in natural claystones that are similar to aged (i.e., illitized) buffer materials. Model 3 is used to correlate porewater compositions with possible equilibrium mineral assemblages in these rocks. Predictions are compared with chemical analyses reported in the literature of porewaters squeezed from claystones using a compression-rig apparatus. All three models fail to accurately simulate respective conditions in the claystones. The pH calculated using Model 1 is consistently lower (by as much as 3 pH units) than measured values. Model 2 generally overpredicts the pH of these solutions (by as much as 3 pH units), but better agreement is obtained at higher pH values. Solution compositions corresponding to the stable coexistence of kaolinite plus smectite and illite solid solutions (Model 3) are inconsistent with observed porewater compositions, yet these minerals exist in the claystones. We speculate that the models fail because they do not account for long-term effects on porewater compositions of metastability and slow reaction rates, but note that the concept of a representative porewater composition, adopted in all the models, is ambiguous because the chemistry of solutions squeezed from claystones is observed to vary with increasing applied load.

2:30 PM QQ17.4
NATURAL ANALOG CONSTRAINTS IN TOTAL SYSTEM PERFORMANCE ASSESSMENT OF A POTENTIAL REPOSITORY AT YUCCA MOUNTAIN, NEVADA. David C. Sassani, Darren M. Jolley, Duke Engineering and Services Inc., CRWMS M&O, Las Vegas, NV, Robert Howard, TRW Environmental Safety Systems, CRWMS M&O, Las Vegas, NV.

In the recent viability assessment (VA) of a potential geologic repository for high-level nuclear waste at Yucca Mountain, NV, the total system performance assessment (TSPA) integrates models of the major engineered and geologic components of the site. In a number of areas, the models of the system include constraints from natural analogs. Such constraints were utilized in the TSPA-VA in two main ways. First, natural analogs were used in some cases to formulate or refine conceptual models of the major processes occurring in the system. Second, natural analogs were used to constrain parameter values that are input to the computational models. In some cases, this latter aspect allowed development of functional dependencies on other system parameters. One example of the first type of natural analog usage is the conceptual model that compositions of ambient water flowing through fractures at Yucca Mountain should be more like the saturated-zone fluids than those found in pores in the unsaturated zone. This conclusion was based on the observed water compositions from fractures at Ranier Mesa, NV, and their relation to the unsaturated-zone fluids (both pore water and perched water) and the saturated-zone fluid compositions there. Such natural analog conceptual constraints were also used for models of spent fuel alteration, microbial growth, and salt precipitation in TSPA-VA sensitivity studies. An example of the second type of natural analog is the data on colloid concentrations in various fluid compositions from around the world. These data were used to quantify the stable colloid concentration as a function of ionic strength. Additional examples of this type of natural analog include constraints on values used within models of climate change and geosphere transport.

2:45 PM QQ17.5
NATURAL ANALOGUES: WHY ARE THEY NOT USED IN PERFORMANCE ASSESSMENTS? R.C. Ewing, Department of Nuclear Engineering & Radiological Sciences, University of Michigan, Ann Arbor, MI.

During the previous two decades, studies of natural systems have provided a tremendous amount of data on waste form durability, backfill and canister performance, and the geochemical and hydrologic aspects of radionuclide release, migration and retardation. These studies have also focused on specific sites with high concentrations of uranium and daughter products, such as Alligator Rivers, Cigar Lake, Palottu, Pena Blaca, Pocos de Caldes and Oklo, and have provided a test-bed for studying radionuclide behavior in different geologic environments. Proposed regulations inevitably make some mention of natural analogues in the context of comparison of simulations with observations drawn from an integrated program of laboratory tests, field tests, and analogue studies. However, in spite of the abundant data base provided by these studies and the extraordinary need to confirm long-term extrapolations of repository performance, natural analogue studies seldom find explicit inclusion in probabilistic performance assessments of long-term repository behavior. This paper explores some of the reasons for the limited use of natural analogue data and suggests appropriate and useful applications of data obtained from studies of natural systems. Special mention will be made of the use of natural systems to estimate the uncertainty in extrapolated performance estimates.

SESSION QQ18: MICROBIAL PROCESSES IN
WASTE MANAGEMENT
Chairs: Melinda A. Hamilton and Donald T. Reed
Wednesday Afternoon, December 1, 1999
Room 203 (H)

3:30 PM *QQ18.1
EFFECTS OF MICROBIALLY INFLUENCED DEGRADATION ON MATERIALS USED FOR THE ENCAPSULATION OF LOW-LEVEL RADIOACTIVE WASTE. Robert D. Rogers, Idaho National Engineering and Enviromental Laboratory, Biotechnology Department, Idaho Falls, ID; Michael Idachaba, Kafui Nyavor, Nosa O. Egiebor, Tuskegee Univ, Dept of Chemical Engineering, Tuskegee, AL; Jonathan Knight, Chris Cheeseman, Imperial College, Centre for Environmental Control and Waste Management, London, ENGLAND.

Naturally occurring microorganisms have been shown to affect the integrity of cements used for the solidification of Class B and C low-level radioactive waste (LLW). The valuation of other inorganic, ceramic, binding agents is not well documented. Technical Position on Waste Form, Revision 1(U.S. Nuclear Regulatory Commission [NRC]) states that microbially influenced degradation (MID) on waste form integrity must be addressed. At the request of the NRC, the Idaho National Engineering and Environmental Laboratory (INEEL) developed a testing procedure for evaluation of MID of cement waste forms. Results from this initial effort have been reported previously. This paper reports on (1) the further development of the MIC testing procedure so that data on the effects of microbial growth on a waste form surface can be better monitored and (2) the testing of new ceramic material which have been suggested as possible binding or surface protection products. Information will be provided on the inoculation and sustained growth of the sulfuric acid producing bacterium Thiobacilus thiooxidans on the surface of cement, cement enriched with manginess tailings, phosphate bonded ceramics, and ceramic coated carbon steel. Results to be discussed include the physical appearance, microscopic examination of waste form cross sections, and the elements leached from various simulated waste forms.

4:00 PM QQ18.2
MICROBIAL ANALYSIS OF THE ISOTHERMAL TEST AT AECL'S UNDERGROUND RESEARCH LABORATORY. Simcha Stroes-Gascoyne and Connie J. Hamon, Atomic Energy of Canada Limited, Pinawa, Manitoba, CANADA.

The behaviour (including the microbial characteristics) of Reference Buffer Material (RBM) in a simulated nuclear fuel waste disposal vault environment, in the absence of thermal gradients, was studied in the Isothermal Test (ITT) conducted at AECLs Underground Research Laboratory (URL). The ITT was installed at the 240m level of the URL in 1992, when 2 m of compacted RBM (50/50 bentonite/ sand, 18% moisture) was placed in a 5 m deep borehole, topped with a 1.25 m thick concrete cap. This assembly was left undisturbed until decommissioning in 1999. This paper describes the microbial sampling and analyses carried out (i) to determine if a viable, active microbial population was present, (ii) to determine its composition, and (iii) to determine how far the buffer environment had evolved from aerobic to

more anaerobic conditions as evident from the microbial population. The buffer was sampled in 7 locations at the concrete/buffer and the buffer/rock interface and in 8 locations inside the buffer. Enumerations were completed for aerobic and anaerobic heterotrophs, sulphate-reducing bacteria (SRB) and methanogens. Results indicated that the anaerobic population survived better than the anaerobic population, suggesting a partial evolution towards lower redox potentials in the buffer. SRB populations ranged from 50 to 200 SRB/g. Buffer samples were analyzed for sulphide as an indication of in situ SRB activity, because of the implications for Cu container corrosion. Results suggested very localized and low rate SRB activity; the maximum amount of sulphide found was 6.83 microgram/g, whereas buffer contained about 1400 microgram total S/g, (as sulphate). Buffer samples were analyzed for methane, and buffer was incubated to determine a methane production rate, to assess if in situ methane production could be larger than methane diffusion in buffer, possibly causing the formation of a gas phase. This work was funded by Ontario Power Generation.

4:15 PM QQ18.3
IMAGING MICROBIOLOGICALLY-INFLUENCED PITTING CORROSION OF SPENT NUCLEAR FUEL CLADDING MATERIAL WITH A SCANNING REFERENCE ELECTRODE TECHNIQUE (SRET). Patrick J. Pinhero and Carolyn S. Watkins, INEEL, Idaho Falls, ID.

Recently we demonstrated that bacteria isolated from spent nuclear fuel (SNF) storage pools at the Idaho National Engineering and Environmental Laboratory (INEEL) show little or no sensitivity to gamma irradiation.[1] We utilize this knowledge to examine the effects of these bacteria on three cladding materials: Al-6061, SS-304, and Zr/4. This talk focuses on one facet of our studies, the dynamic imaging of pitting corrosion on these various material surfaces. In this study we polish the surfaces of the materials to 0.5 μm. We then use aseptic techniques to remove all bacterial contamination and insure sterile conditions until each specimen is introduced into its final (a)biotic environment. Many different bacteria are studied: individually, in combination, and collectively. Some of these are known to form biofilms, e.g. the *Pseudomonads*, while others, such as the sulfate-reducing bacteria, have been implicated as corrosive agents. We have used a scanning reference electrode technique (SRET) to obtain images of the electrochemical activity on the surfaces sampled once a week over the course of one month. By coupling the SRET with potentiodynamic electrochemical techniques, we are able to acquire images at various applied potentials. This allows us to examine pit initiation and evolution. Using these techniques we have been able to determine the effects of microbiological environments upon the corrosion process for a range of different systems.
1. Bruhn, D.F., et al. Irradiation of Microbes from Spent Nuclear Fuel Storage Pool Environments. in Global'99: International Conference on Future Nuclear Systems. 1999. Jackson Hole, WY.

4:30 PM QQ18.4
Se- AND U-BEARING COLLOIDAL PARTICLES PRODUCED BY SULFATE-REDUCING BACTERIA: TEM/AEM STUDY. Huifang Xu, Department of Earth and Planetary Sciences, and Larry L. Barton, Department of Biology, The University of New Mexico, Albuquerque, NM.

Selenium (^{79}Se) is a fission product of nuclear fuel with a half-life time of 65000 years. Oxidative alteration of spent nuclear fuel will result in the formation of selenate ($SeO_4{}^{2-}$) and selenite ($SeO_3{}^{2-}$) oxy-anions together with uranyl oxy-cation in solution. Sorption of the anions on clays and other minerals are extremely low. Because they are chemically and radiologically toxic, it is important to immobilize the aqueous selenium and uranyl species. Sulfate-reducing bacteria are able to reduce sulfate and other oxidized oxy-anions such as selenate, selenite, and uranyl ($UO_2{}^{2+}$) etc. In general, the reduction potentials of redox pairs (at pH 7) utilized by bacteria are within the range of -0.7 eV to +1.36 eV. Transmission electron microscopy (TEM) results from the systems containing selenate and selenite with a sulfate-reducing bacteria of Desulfovibrio deslfuricans show that yellow spherical (Se,S) sub-micro crystals precipitated outside the cell. Amorphous-like Se-rich spherical particles may also occur inside the bacteria cell. It is proposed that the Se-rich particles are at the periplasmic region between out membrane and plasma membrane (Tomei et al., 1995). The bacteria is more active in the solution containing selenite than in the solution containing selenate. Further reduction results in Se-rich particle (orange color), as the bacteria use S as electron acceptor. Similar features (U-oxide nano-crystals) also occur in the Desulfovibrio deslfuricans bacteria that have reduced uranyl ions. The rod-like U-oxide nano-crystals distribute at the area between out membrane and plasma membrane.

4:45 PM QQ18.5
PENETRATION AND ACTIVITY OF BACTERIA IN A COMPACTED BENTONITE CLAY SYSTEM RELEVANT TO NUCLEAR FUEL WASTE DISPOSAL. Mehrdad Motamedi[1], Ola Karland[2], Torbjörn Sandén[2], and Karsten Pedersen[1]. [1]Göteborg University, Department of Cell and Molecular Biology, Microbiology, Göteborg, SWEDEN; [2]Clay Technology AB, Ideon Research Center, Lund, SWEDEN.

The potential toxicity and persistence of high level nuclear waste material (HLW) makes it is important to find safe methods for its disposal. One concept for the disposal of HLW is to encapsulate it in copper canisters and deposit them in boreholes in tunnels at a depth of 500 m. The canisters will be surrounded by a clay buffer material. Microorganisms may contaminate such a repository e.g. via migration from groundwater into the buffer. Laboratory simulated system experiments suggest that bacteria are able to penetrate of least 6 mm into the buffer as it swells. The relation between survival of the penetrating bacteria and the water content in clay was also studied. After a period of 28 weeks viable cells of most bacterial genera studied could not be detected in the bentonite clay. One possibly negative effect of bacteria in a repository is microbiologically induced corrosion (MIC). Sulfate reducing bacteria (SRB) can induce corrosion by their production of hydrogen sulfide if they colonize and make biofilms on the surface of copper canisters. It was found that SRB were active and could colonize the interface between compacted bentonite and copper discs using a silver foil method. In addition, the activity of SRB was confirmed by production of inorganic sulfides and turnover of radioactive sulfate to radioactive sulfide. The activity of the SRB depended on the water content of compacted bentonite. The highest sulfate reduction activity was observed in compacted bentonite with a water activity (a_w) of 0.999 corresponding to a density of 1.5 g cm^{-3}.

8:30 AM QQ19.1
TECHNETIUM AND CESIUM VOLATILITY FROM THE PRODUCTION MELTER DURING VITRIFICATION OF THE FIRST MACROBATCH OF HLW SLUDGE AT THE SAVANNAH RIVER SITE. N.E. Bibler, T.L. Fellinger, S.L. Marra and J.W. Ray, Savannah River Technology Center, Westinghouse Savannah River Co., Aiken, SC.

The Defense Waste Processing Facility (DWPF) at Savannah River Site (SRS) is currently processing and immobilizing the high level waste sludge slurries at SRS into a borosilicate glass for geologic disposal. This glass is prepared at the DWPF by mixing the sludge with glass formers, melting the mixture in a Joule heated melter at 1150°C, and then pouring the molten glass into stainless steel canisters for final disposal. During melting, volatilization can occur of radionuclides such as Tc-99 and Cs-137. This paper presents an estimate of the fraction of Tc-99 and Cs-137 that may have volatilized from the melter during the processing of the first macrobatch of sludge slurry in the DWPF. The first macrobatch consisted of approximately 400,000 gallons of sludge slurry and produced 497 canisters each containing ~3800 pounds of glass. During processing the first macrobatch, which took ~30 months, the chemical and radionuclide composition of the feed remained essentially constant. Glass samples were obtained from the pour stream of the melter using a special sampler while molten glass was being poured into canisters 50, 61, and 409. The sludge slurry feed and the three glass samples were fully characterized including the determination of the concentrations of 27 nonradioactive elements and 56 individual radioactive and non-radioactive isotopes. Tc-99 and Cs-137 were measured in both the feed and the glass samples by inductively couple mass spectroscopy and gamma counting, respectively. By knowing the concentrations of the major non- radioactive waste elements in the sludge and glass such as Fe, Al, Mn, and Ca, the concentrations of Tc-99 and Cs-137 can be predicted presuming the above elements are not volatized during the melting process. When this is done, the measured concentrations of Tc-99 in the three glass samples, agree within ~10% of the predicted values. For Cs-137 the agreement was better than 10%.

8:45 AM QQ19.2
AMERICIUM/CURIUM VITRIFICATION PROCESS DEVELOP-MENT PART II. A.P. Fellinger, M.A. Baich, B.J. Hardy, T.M. Jones, J.E. Marra, C.B. Miller, D.H. Miller, T.K. Snyder, M.E. Stone and D.C. Witt, Westinghouse Savannah River Company, Aiken, SC.

Isotopes of americium and curium were produced at the Savannah River Site (SRS) for radiological, medical and research applications. These highly radioactive isotopes have been stored as a nitric acid solution in an SRS canyon facility for several years. Stabilization of these isotopes as a glass form will allow the material to be safely

stored until it can be transported to a facility at the DOE Oak Ridge Complex where the americium and curium could be recovered and used in research and medical applications. In December of 1997, the Savannah River Technology Center (SRTC) officially proposed a two-stage batch process to stabilize the material. The process incorporated a feed precipitation / washing stage and a vitrification stage using a Cylindrical Induction Melter (CIM). The one molar nitric acid feed material is precipitated with 8 wt% oxalic acid, decanted, washed with one-tenth molar oxalic acid, and decanted again. The washed, de-nitrated rare-earth oxalate slurry is then gravity drained to the melter vessel. The vitrification stage dries and calcines the precipitated solids and then incorporates the oxides into an alumina-borosilicate glass matrix to a product loading ranging from 30-47%. The molten glass is then gravity drained to a canister. The full-scale precipitation and batch vitrification process and associated equipment were successfully demonstrated in December of 1998. The successful process demonstration provided the basis for a 35% preliminary design that was completed and formally reviewed May of this year. This paper provides a brief chronology leading to the proposed batch process. The paper will also describe the details of the demonstrated process and presents a pathforward for the design, testing and installation of the racks for stabilizing the highly radioactive Am-Cm solution.

9:00 AM QQ19.3
LIQUIDUS TEMPERATURE AND PRIMARY CRYSTALLIZATION PHASES IN HIGH-ZIRCONIA HIGH-LEVEL WASTE BORO-SILICATE GLASSES. Trevor Plaisted, Ryan Plaisted, Pavel Hrma, John Vienna, and Antonin Jiricka, Pacific Northwest National Laboratory, Richland, WA.

Liquidus temperature (T_L) was measured and the primary crystallization phases were determined for high-level waste (HLW) borosilicate glasses containing up to 16.5 mass% ZrO_2. Three main primary phases were identified: baddelyite (ZrO_2), zircon ($ZrSiO_4$), and alkali-zirconium silicates, such as parakeldyshite ($Na_2ZrSi_2O_7$). From these and previously published data, we have computed T_L component coefficients for up to 12 glass components for zircon primary phase and 6 glass components for baddelyite and parakeldyshite. In the Na_2O-SiO_2-ZrO_2 submixture, we have determined approximate positions of the boundaries between the three major Zr-containing phases. 16.5 mass% ZrO_2 appears to be the maximum that can dissolve at 1150°C in a borosilicate HLW glass subjected to common processability and acceptability constraints.

9:15 AM QQ19.4
ASSESSMENT OF NEPHELINE PRECIPITATION IN NUCLEAR WASTE GLASS VIA THERMOCHEMICAL MODELING. Theodore M. Besmann, Edward C. Beahm, Oak Ridge National Laboratory, Oak Ridge, TN; Karl E. Spear, Materials Science and Engineering Department, Pennsylvania State University, University Park, PA.

A thermochemical representation of the Na-Al-Si-B-O system relevant for nuclear waste glass has been developed based on the associate species approach for the glass solution phase. Thermochemical data were assessed and associate species data determined for binary and ternary subsystems in the Na_2O-Al_2O_3-SiO_2-B_2O_3 oxide system. Computed binary and ternary phase diagrams were compared to published diagrams during this process, with adjustments in data made as necessary to obtain consistent thermodynamic values. The resulting representation for the four oxide system was used to help understand the problem of nepheline precipitation in certain waste glass formulations. Research sponsored by the U. S. Department of Energy, Office of Environmental Management, Office of Science and Technology, Environmental Management Science Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

9:30 AM QQ19.5
POLYOXOANIONS IN GLASS. Mark R. Antonio, Soenke Seifert, Clayton W. Williams, L. Soderholm, Chemistry Division, Argonne National Laboratory, Argonne, IL.

Inorganic metal oxide clusters known as polyoxoanions (POAs) are good complexants of rare-earth (RE) elements. A diverse array of rugged isopolyoxoanions, $[M_xO_y]^{z-}$, and heteropolyoxoanions, $[X_aM_bO_c]^{d-}$, comprised of M = Mo, W and X = Si, P polyhedra are being investigated for their ability to bind RE ions. The behavior of RE-POA complexes under vitrification conditions germane to the formation of borosilicate glass is largely unexplored. We have prepared RE complexes of two well-known series of heteropolyo-xoanions-the Preyssler $[P_5W_{30}O_{110}]^{15-}$ and Wells-Dawson $[\alpha$-2-$P_2W_{17}O_{61}]^{10-}$-and have examined their solubility and immobilization as discrete clusters in glasses. X-ray diffraction and small-angle X-ray scattering experiments were used to characterize

the solid glass forms and solution precursor complexes. The results and implications for the use of POAs as RE ion complexants in technology of significance to the environmental management of high level radioactive waste will be noted. This work is supported by the U.S. D.O.E. Environmental Management Science Program, Office of Science and Technology, Office of Environmental Management under contract W-31-109-ENG-38.

9:45 AM QQ19.6
CHARACTERISATION AND RADIATION RESISTANCE OF A MIXED-ALKALI BOROSILICATE GLASS FOR HLW VITRI-FICATION. Jonathan M. Roderick, Diane Holland, Warwick Univ, Dept of Physics, Coventry, UNITED KINGDOM; Charles R. Scales, BNFL Ltd, Sellafield, Seascale, Cumbria, UNITED KINGDOM.

Glasses to be used for the vitrification of radioactive high-level waste have been produced from the sodium-lithium-borosilicate system. In order to improve the state of knowledge and, as a result, improve the suitability of the current system for HLW vitrification, the thermal and structural characteristics of these glasses were measured for a wide range of boron oxide contents. Furthermore, several glass series have been prepared for a range of alkali oxide to boron oxide ratios, R, and for several fixed silica to boron oxide ratios, K. A series of glasses using the base borosilicate composition, doped with increasing amounts of lanthanum oxide, was also prepared and analysed by the same methods. The mixed alkali borosilicate was seen to exhibit a maximum in T_g and a minimum in the fraction of four coordinated borons at 22mol% and 29mol% boron oxide, respectively. Initial results on the effect of increasing R indicate an increase in T_g to a maximum before a sharp decrease and subsequent levelling off at larger R. However, density measurements exhibited a maximum at the same value of R and then remained constant within experimental error. The lanthanum-doped sodium-lithium borosilicate glasses displayed very clear trends, with continuous increases in T_g and density, alongside a steady decrease in the fraction of four coordinated borons present. This change in T_g is consistent with work done on the sodium-lanthanum-silicate system and can be attributed to association of sodium ions with $[LaO_4]^-$ tetrahedra and removal of nonbridging oxygens. Initial α-particle irradiation tests have also been carried out on several base glass samples and show evidence of B(α, n) reactions, the occurrence of which could have important consequences for future use of the wasteform.

SESSION QQ20: GLASS - CORROSION AND CHARACTERIZATION
Chairs: William L. Ebert and David J. Wronkiewicz
Thursday Morning, December 2, 1999
Room 203 (H)

10:30 AM QQ20.1
THE BEHAVIOR OF SILICON AND BORON AT THE SURFACE OF CORRODED NUCLEAR WASTE GLASSES: AN ENERGY-FILTERED TRANSMISSION ELECTRON MICROSCOPY STUDY. Edgar Buck, Argonne National Laboratory, Argonne, IL; Katherine Smith, Australian Nuclear Science and Technology Organization, Sydney, AUSTRALIA.

Using energy-loss filtered transmission electron microscopy (EFTEM), we observed the formation of silicon-rich zones on the corroded surface of a West Valley (WV6) glass. This layer is approximately 100-200 nm thick and is directly underneath a precipitated smectite clay layer. Under conventional TEM illumination, this feature is invisible; indeed, more commonly used analytical techniques, such as x-ray energy dispersive spectroscopy, have failed to describe fully the localized changes in the boron and silicon contents across this region. The silicon layer may be described as a gel layer, following the Grambow model for glass dissolution. We will discuss whether this layer may be a barrier to the movement of boron and silicon through comparison with solution analysis. To date, similar silicon-rich and boron depleted zones have not been found on corroded Savannah River Laboratory (SRL) borosilicate glasses, including SRL-EA and SRL-51, although they possessed similar looking clay layers. At this time it is not possible to quantify differences in the dissolution characteristics of WV6 and SRL glasses with EFTEM; however, this study demonstrates a new method of examining the corroded surfaces of materials.

10:45 AM QQ20.2
CORROSION OF GLASS-BONDED SODALITE AS A FUNCTION OF pH AND TEMPERATURE. Lester R. Morss, Mary Stanley, Chad Tatko, and William L. Ebert, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

The Electrometallurgical Treatment Program for spent nuclear fuel that has been developed at Argonne National Laboratory accumulates

sodium, fission products, and transuranic elements in a (Li,K)Cl electrolyte. Glass-bonded sodalite, which is a ceramic composite consisting of approximately 75 mass % sodalite and 25 mass % glass binder, is the ceramic waste form (CWF) that has been selected to immobilize the radioactive electrorefiner salt from the electrorefiner. In order to model the durability of glass-bonded sodalite in a nuclear waste repository, the dependence of the forward dissolution rate upon temperature and pH must be known. We have carried out corrosion tests with monoliths of sodalite, binder glass, and glass-bonded sodalite (CWF) in dilute pH-buffered solutions in the range pH 4-11 at three temperatures, 40, 70, and 90°C. This paper describes the pH and temperature dependence of the corrosion behavior of the glass and sodalite components of the CWF. The pH dependence of the binder glass dissolution rate is similar to that of borosilicate nuclear waste glasses, with a negative pH dependence in the acid region and a positive pH dependence in the basic region. The pH dependence of the sodalite component of the CWF dissolution rate is similar to that of natural sodalite, also having a negative pH dependence in the acid region and a positive pH dependence in the basic region. Our results on the forward dissolution rates and their temperature and pH dependecies will be used as components of a waste form degradation model to predict the long-term behavior of the CWF in a nuclear waste repository.

11:00 AM QQ20.3
VAPOR HYDRATION OF BOROSILICATE WASTE GLASS. Rudolph A. Olson, Jeffrey A. Fortner, William L. Ebert, Shiu-Wing Tam, Stephen F. Wolf, and James C. Cunnane, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

Tests are being conducted to support the development of a model to include vapor hydration in Total System Performance Assessment calculations for the Yucca Mountain disposal system. Unsaturated drip experiments performed on as-cast and vapor-hydrated sludge-based Savannah River (SRL) waste glasses show that pre-alteration of the glass by vapor hydration results in a more rapid release of most soluble elements and actinides from the alteration layer when the glass is subsequently exposed to dripping water. The release of soluble elements follows a power-law behavior with time corresponding to t^x with $1/4 < x < 1/2$, consistent with diffusion transport through clay alteration phases on the glass surface. The alteration of borosilicate glass in humid air was investigated with respect to time, temperature, and humidity. Experiments were performed in stainless-steel vessels at temperatures ranging from 90 to 200°C and times between 0.2 and 182 days. Humidity was varied using amounts of water above and below that required to saturate the vessel volume. The alteration rate initially decreased with an inverse square root of time dependence, then increased with time. The effective activation energy for the initial stage was consistent with values that have been reported for glass network hydrolysis, while that for the second stage was significantly lower. The thickness of the alteration layer on glass hydrated for 21 days was maximized when the amount of water in the vessel was close to that required to just saturate the volume of the vessel, and decreased sharply when the amount was increased or decreased from this critical volume. Increasing the amount of water above that required to saturate the vessel volume is believed to induce a condensation/drip mechanism that acts to reduce the alkalinity of the film of water on the glass and slow the alteration rate.

11:15 AM QQ20.4
PLUTONIUM SILICATE ALTERATION PHASES PRODUCED BY AQUEOUS CORROSION OF BOROSILICATE GLASS. J.A. Fortner, C.J. Mertz, A.J. Bakel, R.J. Finch, and D.B. Chamberlain, Argonne National Laboratory, Chemical Technology Division, Argonne, IL.

Borosilicate glasses loaded with 10 mass percent plutonium were found to produce plutonium/lanthanide silicate alteration phases upon aqueous corrosion under a range of conditions. Macroscopic plutonium/lanthanide silicate crystallites formed on the surface of the glass at 200°C and 100% humidity, while an imbedded layer of cryptocrystalline plutonium/lanthanide silicate formed in situ within the altered glass beneath the surface. The phases observed were generally rich in lanthanide (Ln) elements, and were related to the lanthanide orthosilicate phases of the monoclinic Ln_2SiO_5 type. The composition of the phases was variable regarding [Ln]/[Pu], depending upon type of corrosion test and on the location within the alteration layer. These observations suggest that incorporation of plutonium into silicate alteration phases may be an important process within the silicate-rich environment of the proposed Yucca Mountain Repository for waste forms in general.

11:30 AM QQ20.5
THE ROLE OF ALTERATION PHASES IN INFLUENCING THE KINETICS OF GLASS DISSOLUTION. David J. Wronkiewicz, Univ of Missouri-Rolla, Dept of Geology and Geophysics, Rolla, MO.

Alteration phases may influence the kinetics of nuclear waste glass corrosion by controlling the aqueous solubility of important glass forming elements. The long-term dissolution rate of borosilicate glass, and the release of contained radionuclides, may therefore be influenced by the nucleation of these phases. The potential effect of alteration phases on the corrosion of glass is being examined in a series of Product Consistency Tests (90°C; 7, 35, and 91 days) with a Na-Ca-K-Al-borosilicate glass being reacted in the presence of a high-ionic strength fluid. This leachant solution was prepared by reacting a boron-free mixture of the powdered glass components in deionized water at 90°C for nine months. The release of boron relative to other glass-forming components was subsequently used to monitor dissolution rates. "Seed-crystals" of various alteration phases (Na-smectite, analcime, adularia, and chabazite) were added to the individual tests to assess their potential role on glass corrosion. These phases have been noted to occur following the reaction of both natural volcanic and simulated borosilicate waste glasses. Boron release was generally the highest from tests with either analcime or adularia present, however, concentrations were only slightly above those recorded from control tests where the glass was reacted without any seed-crystals being added. Boron release from tests where chabazite or Na-montmorillonite was added was slightly lower than that of the control tests. The pH values for the tests remained relatively constant, ranging from 10.14 to 10.29. The release of silicon did not correlate closely with boron, suggesting that factors other than the activity of silicic acid may be involved in the controlling the kinetics of glass dissolution.

11:45 AM QQ20.6
ESTIMATING MODEL PARAMETER VALUES FOR HIGH-LEVEL WASTE GLASSES FOR TOTAL SYSTEM PERFORMANCE ASSESSMENT. William L. Ebert, Shiu-Wing Tam, and James C. Cunnane, Argonne National Laboratory, Argonne, IL.

Model parameter values are needed to account for glass dissolution and the release of radionuclides from high-level waste glasses in total system performance assessment (TSPA) calculations. We are developing methods that can be used to estimate or bound the parameter values that may depend on glass composition, which include the intrinsic dissolution rate, the equilibrium constant, and the long-term rate constant. Methods to estimate the values of these parameters are being developed and evaluated using the results of MCC-1, Product Consistency Test Method A (PCT), and vapor hydration tests conducted with eight reference glasses. We are also evaluating whether values can be adequately estimated using only information that is to be provided for waste acceptance, primarily the glass composition and response in the PCT. This capability will be important in evaluating waste glasses that will be formulated in the future. The glasses used in testing are representative of anticipated waste forms for high-level waste streams and provide a wide range of compositions. Results available to date indicate that the value of the intrinsic dissolution rate varies only slightly with the glass composition and is not correlated with the concentrations of Al, B, Na, or Si in the glass.

SESSION QQ21: WASTE PROCESSING
Chairs: Randy Arthur and Dieter A. Knecht
Thursday Afternoon, December 2, 1999
Room 203 (H)

1:30 PM QQ21.1
CONCEPTS FOR DRY PROCESSING OF SPENT NUCLEAR FUEL FOR RECYCLING TO LIGHT-WATER REACTORS. Jerry Christian, James Sterbentz, David Abbott, Idaho National Engineering and Environmental Laboratory, National SNF Program; Kenneth Czerwinski, Massachusetts Institute of Technology, Dept of Nuclear Engineering, Cambridge, MA; Richard Cacciapouti, Duke Engineering Services, Marlborough, MA.

We have initiated study of improved methods for implementing dry (AIROX) processing of commercial spent nuclear fuels for recycling back into light-water reactors. In this proliferation-resistant recycle, the spent fuel is converted to a powder, blended with fresh medium-enriched uranium powder, and refabricated into fuel elements. Evaluations of neutronic characteristics show that it will be necessary to remove a substantial portion of the neutron-absorbing fission products in the spent fuel, especially lanthanides and rhodium, in order to achieve efficient utilization of the spent fuel. We have already modeled oxidative vaporization of selected fission products from the powder at 1000°C. In addition to permanent gases and fission products that are vaporized during pellet sintering, this can remove Tc, Mo, and some Ru and improve the neutronics. A number of approaches are being evaluated for removing lanthanides and rhodium, initially by thermodynamic modeling and review of literature. The lanthanides exist in solid solution with UO_2, so separations methods will require conversion to fine powder; rhodium

is present as a metallic inclusion in the epsilon phase. Chlorination of finely powdered oxide at 1100-1200°C would vaporize substantial portions of Nd, Eu, Gd, and Rh. A fraction of the uranium would also vaporize; if significant, it could be recovered for recycle. A promising approach is to reduce the lanthanides with thorium metal. This may lend the lanthanides to magnetic separation. Magnetic separation techniques may also be applicable for removing rhodium in the fine powder metallic inclusions. Another is to determine whether the lanthanide oxides can be selectively leached from the fuel matrix by exposing the powder to dilute nitric acid. These technical considerations provide the basis for a suggested experimental program.

1:45 PM QQ21.2
POWERFUL GELS FOR POWER PLANT DECONTAMINATION. David Cheung, Jean-Louis Pascal, Fred Favier, Univ Montpellier 2, Laboratoire des Agregats Moleculaires et Materiaux Inorganiques, Montpellier, FRANCE; Stephane Bargues, Societe des Techniques en Milieux Ionisants (STMI), Gif-sur-Yvette, FRANCE.

Most chemical decontamination processes of nuclear plants operate either by the immersion of components in concentrated and aggressive solutions, electrodecontamination or using foaming agents. These techniques present several drawbacks such as huge infrastructures, hazard risks in dismantling, worker exposure, prohibitive volumes of waste generated, high costs. To avoid these major disadvantages while keeping the high efficiency of chemical methods, we have developed a process using corrosive gels. The gels are projected directly onto the plant components or all types of surfaces to be decontaminated (stainless steels, alloys, painted surfaces). Thus plant pieces do not require dismantling. The gels adhere to any surface (reverse, vertical or complex) and operate by dissolving the radioactive deposit and also a thin layer of the support, so that the radioactivity trapped at the surface can be removed. No consequent damage is observed from the materials treated, and decontamination factors can exceed 2000. The main interest lies in the thixotropic property of the gels : liquid during projection, and solid when stationary to permit strong adhesion. The other important aspect of the gels is the use of small quantities (0.5-1 kg/m2 surface area treated). Furthermore, the easy cleaning of the plant components (under high water pressure) allows limitation of generated waste. The process is also suitable for the decontamination of complex systems such as reactors, heat exchangers, glove bags. The dissolving agent is a corrosive solution constituted of a strong oxidizing reagent, stabilized in a concentrated acidic medium. In the same way, other types of gels can be formulated such as basic or reducing gels, suitable for degreasing plant items. Different decontamination processes by gels can also be combined to improve decontamination results.

2:00 PM QQ21.3
DEVELOPMENT AND TESTING OF A NEW POROUS CRYSTALLINE MATRIX (GUBKA) FOR STABILIZING ACTINIDE SOLUTIONS. Albert S. Aloy, Khlopin Radium Institute, St. Petersburg, RUSSIA; A.S. Anshits, Institute of Chemistry and Chemical Technology, Krasnoyarsk, RUSSIA; D.A. Knecht and T.J. Tranter, INEEL, Idaho Falls, ID; A. Tretyakov, Minining and Chemical Combine, Zheleznogorsk, RUSSIA; J. Macheret, DOE-ID, Idaho Falls, ID.

Actinide solutions requiring stabilization under Defense Nuclear Facilities Safety Board (DNFSB) 94-1 exist in various compositions at the Savannah River Site (SRS) and the Hanford site. A solution stabilization technology using a new matrix (Gubka) has recently been identified. The materials used for this technology will adsorb components such as plutonium, americium, curium and HLW from the waste solution at ambient to moderate, below boiling, temperatures. The Gubka material, consisting of glass-ceramic microspheres at various chemical compositions, has been developed by the Institute of Chemistry and Chemical Technology from fly ashes formed from coal burning. Preliminary studies have shown the feasibility of using the Gubka matrices to immobilize rare earth elements as actinide surrogates as well as long-lived radionuclides as technicium-99, zirconium-95, neptunium and plutonium. The trapped isotopes can be recovered by dissolution in acid. This paper will describe the results of a joint research program with Russian institutes at St. Petersburg, Krasyonarsk, and Zheleznogorsk. The preparation and properties of the porous silicate Gubka material from Siberian coal fly ashes will be described. Surrogate solutions were tested for trapping by the Gubka matrix, which contained cerium nitrate and lanthanide mixtures in nitric acid as actinide surrogates and, in some cases, contained tracer americium-241. These tests resulted in maximum loading measured as mass percent (100 x cerium mass divided by sample mass) ranging from about 20 % to 80 % up to 39 saturation-drying cycles. The rates of actinide and lanthanide recovery were measured in nitric acid up to 60°C using simulated lanthanide solutions spiked by Am-241. Similar Gubka behavior was observed using samples with a 20-fold difference in size. Hot pressing densification tests that resulted in a 60 % volume reduction were also run.

2:15 PM QQ21.4
FLOWSHEET DEVELOPMENT FOR THE SEPARATION AND IMMOBILIZATION OF PERTECHNETATE FROM ALKALINE RADIOACTIVE WASTES. Andrew H. Bond, Chemistry Division, Argonne National Laboratory, Argonne, IL; Robin D. Rogers, Department of Chemistry, The University of Alabama, Tuscaloosa, AL; Michael J. Gula, E. Philip Horwitz, James T. Harvey, Eichrom Industries, Inc., Darien, IL; Jack L. Collins, Oak Ridge National Laboratory, Oak Ridge, TN.

A flowsheet for the selective removal of the pertechnetate anion from alkaline radioactive tank wastes, vitrification off-gas scrubber solutions, and solvent wash stages from the treatment of acidic high-level liquid wastes is discussed. The three-stage flowsheet comprises the steps of selective extraction of the pertechnetate anion by $ABEC^{TM}$ resins, secondary concentration of pertechnetate from water by a nonselective silica-based anion-exchange resin, and encapsulation of the radionuclide-loaded anion-exchange resin in hydrous titanium oxide microspheres. Each of the extraction, secondary concentration, and encapsulation stages has been independently tested using simulant solutions. The final encapsulated waste form has been contacted with the Toxicity Characteristic Leach Procedure (TCLP) and simulated Waste Isolation Pilot Plant (WIPP) brine leachants. Of the initially loaded pertechnetate, less than 0.3% and less than 0.6% was released to the TCLP and simulated WIPP brine leachants, respectively, over a 168 hour period. Dose rate and heating calculations have been performed and show that the final encapsulated waste form effectively reduces the technetium-99 dose rate to less than 0.06 μrem/hr at a pertechnetate loading of 1 mCi. Accounting for a 55 gallon drum shipping/storage container and the standard engineering barriers of the repository, the pertechnetate anion can be effectively immobilized and shielded for long-term near-surface storage by this flowsheet. This work was funded by the U. S. Department of Energy Morgantown Energy Technology Center under contract number DE-AC21-97MC33137 to Eichrom, Industries, Inc.

2:30 PM QQ21.5
CHARACTERIZING TRANSPORT AND SORPTION OF ION-SPECIFIC RESIN COLUMNS USING NUCLEAR MAGNETIC RESONANCE (NMR) IMAGING AND A LANTHANIDE TRACER. Dan Caputo, David Cory and Ken Czerwinski, Massachusetts Institute of Technology, Department of Nuclear Engineering, Cambridge, MA.

Ion-specific resins have been developed to partition similar inorganic chemical species, such as lanthanides and actinides, from waste streams in radioactive waste reprocessing operations. This work examines the behavior of the resins under flow conditions using nuclear magnetic resonance NMR imaging. Many analytical methods exist to provide information on the bulk characteristics of a packed resin column, however, few methods exist to extract real-time spatial information from the columns. NMR imaging provides a powerful means to non-destructively extract spatial information from complex systems on a near real-time basis. The lanthanide tracer, trivalent Gd, was selected based on its chemical similarity to typical high-level waste constituents (i.e. Am-241 and Cm-244) and its ability to provide contrast in an NMR experiment by paramagnetism. The goal of this work is to assess the physical transport properties of the lanthanide through the column while determining the sorption properties of the resin. The transport and some sorption properties can be extracted from the NMR imaging data, and in addition, the effluent is batch collected and analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). NMR imaging results of various flow experiments are provided showing a variety of transport phenomena and resin column loading profiles. ICP-AES data is provided to show resin proton exchange capacities (PECs) and to breakthrough curves. The use of NMR imaging with a lanthanide tracer will lead to a better understanding of the transport and sorption properties of these ion-specific resins and other complex porous systems.

2:45 PM QQ21.6
VOLATILIZATION OF FISSION PRODUCTS FROM METALLIC MELTS IN THE MELT-DILUTE TREATMENT TECHNOLOGY DEVELOPMENT FOR Al-BASED DOE SPENT NUCLEAR FUELS. Thad M. Adams, Andrew J. Duncan, Harold B. Peacock, Jr., Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, SC.

The melt-dilute treatment technology is being developed to facilitate the ultimate disposition of highly enriched Al-Base DOE spent nuclear fuels in a geologic repository such as that proposed for Yucca Mountain. Currently, approximately 28 MTHM is expected to be returned to the Savannah River Site from domestic and foreign research reactors. The melt-dilute treatment technology will melt the

fuel assemblies to reduce their volume and alloys them with depleted uranium to isotopically dilute the 235U concentration and reduce the potential for criticality and proliferation concerns. A critical technology element in the development of the melt-dilute process is the development of offgas system requirements. The volatilization of radioactive species during the melting stage of the process primarily constitutes the offgas in this process. Several of the species present following irradiation of a fuel assembly have previously been shown to be volatile or semi-volatile under reactor core melt-down conditions. Some of the key species that have previously been studied are krypton, iodine, and cesium. All of these species have been shown to volatilize during melting experiments however, the degree to which they are released is highly dependent upon atmosphere, fuel burnup, temperature, and fuel composition. With this in mind a modeling and experimental program has been undertaken to assess the volatility and capture of species under the melt-dilute operating conditions. The modeling and experimental tests conducted at both SRTC and ANL, has identified cesium as the melt constituent of most concern with respect to volatilization. Experimental tests using both cesium surrogates and radioactive cesium have shown that zeolite 4A is an effective gaseous cesium trap and as a result a preliminary offgas system concept has been developed employing dry zeolite 4A absorber beds as the primary cesium trapping medium. Final, validation of this offgas concept will occur during full-scale irradiated testing in FY2000.