SYMPOSIUM QQ
Scientific Basis for Nuclear Waste Management XXIII

November 29 – December 2, 1999

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*Invited paper
9:15 AM QQL.3

LONG TERM CREEP BEHAVIOR OF SPENT FUEL CLADDING FOR STORAGE AND DISPOSAL. J. Bredel, G. Cappellini, R. Limon, G. Pinte, Commissariat à l'Énergie Atomique. DRR/DMT/SEM, Saclay, Gif sur Yvette, FRANCE; P. Bouffoux, Electricité de France, Pôle Industrie, Division R&D; Dept EM; Les Renardières, Moret sur Loing, FRANCE.

In the framework of the 1991 French Law which defines the 3 major research areas to dispose of nuclear wastes, CEA is supporting a wide R&D program dealing with the 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 notion of its integrity. One of the questions being considered is 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 cladding are changed by the irradiation induced defects due to the high irradiation fluences as well as by the external zirconium layer and the hydrogen pickup resulting from the water radiocorrosion. 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 being pursued at CEA with the support of CFE and IRAMIS.

The objectives are to define and qualify the long term mechanical properties of the cladding, in particular a long term creep law and an adequate breach criterion. Long term creep properties are investigated through a stepwise approach from short term (few days) to high stress experiments (few months) to 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 QQL.4

HYDRAULICALLY-REDUCED DEGRADATION OF SPENT FUEL CLADDING UNDER REPOSITORY CONDITION. H.M. Chang, 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 subsequently 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 the presence of more inernt 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 long-term evolution of the cladding metal microstructure beneath the inner-diameter oxide layer was identified to be the key parameter presented in which the potential microstructural evolution, and in worst case, potential crack initiation at the cladding metal beneath the inner-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 QQL.5

ANALYSIS OF HYDROGEN 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

In the absence of a new temperature criterion for hydrogen storage in Zircaloy cladding, an analysis is presented for spent nuclear fuel. The analysis is based on a model that describes the behavior of Zircaloy under constant temperature and pressure conditions. The model incorporates the effects of hydrogen charging, embrittlement, and the formation of hydrides. The results of the analysis are used to determine the temperature limits for hydrogen storage in Zircaloy cladding. The temperature limits are found to be dependent on the hydrogen concentration and the oxygen content of the Zircaloy. The analysis provides a basis for evaluating the potential for hydrogen embrittlement in spent nuclear fuel.
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 allowed thermal excursion in the interim dry storage of SNF. These models are based on the Raj and ASHLY diffusion controlled cavity growth (DCCG) failure mechanism. There is a lack of experimental evidence to verify this theory for zirconium or zircaloy alloys, or any other materials, 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 DCCG 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 shape. 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 • Q11.6
SPENT FUEL DISSUSSION AN EXAMINATION OF THE IMPACTS OF OXYGEN, HYDROGEN, AND WATER ON THE PERFORMANCE OF THE MAJOR COMPARTMENTS OF DECOMMISSIONED AND SHUTDOWN REACTORS, John B. Sullivan, NRC; R. G. Buck, Energy Northwest; M. J. D. Lewis, Centre for Nuclear Technologies, University of Strathclyde; and T. J. F. James, PNNL.

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 hydrogen reduction and the presence of reductants such as Fe(II) and hydrogen arising from radionuclide corrosion. The radiolytic yield (G) of molecular oxygen, generally considered to be ~1 molecule of hydrogen peroxide per 100 eV for alpha-radiolysis, is expected to be considerably lower in the presence of reductants and this 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 iron in reducing Fe(II) release from corrosion products and the significance of alpha emitters sorbed on bentonite in producing radiolytic oxidants.

11:00 AM • Q11.7
EFFECTS OF ALTERNATION PHASE FORMATION UNDER UNSATURATED CONDITIONS IN LAIR FUELS WITH HIGH WATER CONTENT, H. C. Taylor, K. E. W. Smith, S. S. O. Smith, Safeguards Management Ltd., Hutton Build, Hope Valley, Derbyshire, ENGLAND; I. H. Johnson, Nagra, Wettengen, SWITZERLAND.

The reaction of irradiated chaf fuel segments with humid air at 175°C and with periodic injection of Surich 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 tests examine the potential for chaf 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. Dimensional measurements indicate no evidence of strain of the cladding, and simple mass balances indicate <0.5% of the fuel has been leached. The leak rate 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 developed 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 Na2SO4 solvate during the oxidative corrosion of fuel. This interaction results in the precipitation of powder mixtures of UO2 and Na2SO4 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 • Q11.8
URANIUM OXIDE MASS LOSS RATE IN WATER FOR AN INTERFACIAL UNDER ALPHA RADIATION. Catherine Corbel, Gnel Soutonney, CEA Saclay, DDEMRECAM/CMC, Gif-sur-Yvette, FRANCE; Jean-Francois Lucchini, CEA Marcoule, SCF, Bagnols-sur-Ceze, FRANCE; Marie-France Barth, CERL-CNRS, Orleans, FRANCE; Philipo Francou, François Hüet, CEA Grenoble, DRN/DEC/SECC, Grenoble, FRANCE.

Different models are describing the corrosion of spent fuel under water. However, there is room to improve the robustness of these models. One process which needs to be better understood is the effect of the radionuclides species, which are produced in water by the gamma, beta and alpha particles emitted by spent fuel, on the dissolution rate of uranium. This work presents a fundamental study by using an external alpha beam to irradiate the uranium oxide/water interface. A high energy alpha beam delivered by a cyclotron (CELI-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 that the release of uranium in irradiated water is strongly enhanced under alpha irradiation with rates depending on the alpha flux.

11:30 AM • Q11.9
RELEASE OF Tc FROM FUEL GRAIN BOUNDARIES DURING OXIDATIVE CORROSION OF SPENT UO2 FUEL IN Drippng GROUNDWATER. Robert J. Finch, Patricia A. Fin, Stephen F. Wolf, Ralph Leonard, Edgar C. Back, James C. Cunmane, 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 radionuclides-bearing solids. Most Tc in spent UO2 fuel occurs within α-fu particles, many of which decorate grain boundaries (GBs), dislocations and other defects within the fuel. Substantial dissolution can occur along defects, and α-fu 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 α-fu 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 α-fu particles accurately reflects matrix dissolution depends on the uncertainty of the proportion of Tc in α-fu particles that occur along GBs and other defects in unreacted spent fuel is unknown; however, we estimate that two percent or more of Tc may occur in α-fu particles that have reacted with groundwater along GBs in samples of AT-1, a ILM fuel of moderate burn-up (~30 MWd/kgU). Relatively rapid dissolution of α-fu particles may result in 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 through 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 (YM/SP) and part of activity D-20-43 in the YM/SP/Lawrence Livermore National Laboratory Spent Fuel Inventory Characterization Plan. This work is supported by the U.S. Department of Energy under contract W-31-109-ENG-38.

11:45 AM • Q11.10
IN SITU LONG-TERM MEASUREMENTS OF pH AND REDOX POTENTIAL DURING SPENT FUEL LEACHING UNDER STATIONARY CONDITIONS. THE METHOD AND SOME PRELIMINARY RESULTS. Kurtus Smulik, Lars Werner, SKB AB, Stockholm, SWEDEN; Jesse Low, Ulf-Britt Ekland, Stockholm Nuclear AB, Nynäsham, 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 need to be continuously measured during long term stationary leaching experiments. These data may be used together with standard chemical analytical data for modelling spent fuel corrosion, especially in more 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 developed. 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 using 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 realize in laboratory near-field conditions. An interesting case of calcite precipitation 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 untreated 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 Q2: FLOW AND TRANSPORT
Chair: Roberto T. Pabalan and Robert W. Smith
Monday Afternoon, November 29, 1999
Room 203 (H)


Reactive transport simulations are being used to evaluate the nature and extent of radionuclide contamination within an alluvial hydrogeologic environment surrounding a specific underground nuclear test at Nevada Test Site. Interest is focused on determining the abundance and chemical nature of radionuclides that are introduced into groundwater by the reactants, 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 simulation designed to assess the fate of radionuclides over longer times and larger spatial scales. Preliminary simulation results 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 Q2.2 ASSESSING EFFECTIVE REACTIVE SURFACE AREA IN HETEROGENEOUS MEDIA THROUGH THE USE 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. Schaffer, Mar. Res. Soc. Symp. Proc. 55:6 in press) the effective reactive surface area of a heterogeneous aquifer is a complex function of groundwater flow velocity and the correlation structure 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 on the use of conservative 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 that are predictive. 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 hydrosols iron oxide coated sands are being developed.

2:15 PM Q2.3 DECYA-SEAS DISEQUILIBRIUM STUDY OF IN-SITU, LONG-TERM RADIONUCLIDE TRANSPORT IN WATER-ROCK SYSTEMS. Shang Ling Liu, State Coll. of Science, L. Calif., Dept of Environ Sciences, Los Angeles, CA; Robert Roback, Michael Murrell, Los Alamos National Laboratory, Los Alamos, NM; Andris L. Meling, 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, geological and hydraulic 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 concepts was used to relate the decays-series radionuclide distributions among sorbed, and solid phases in an aquifer system to in-situ processes of water transport, sorption-desorption, dissolution-precipitation, radioactive ingrowth-decay, and a recoil. Isotopes of U (234U, 235U, 238U), Th (232Th, 233Th, 234Th, 235Th, 236Th), Ra (228Ra, 226Ra, 224Ra, 222Ra, 220Ra), Pb (210Pb), and Po (210Po) were measured in 21 groundwater samples collected from a basin area in the Idaho National Engineering and Environmental Laboratory (INEL), Idaho. The results placed constraints on the following parameters at INEL: (1) time scales of sorption [minutes for Ra and Th], description [days for Ra and years for Th], precipitation [days for Th, years for Ra, and centuries for U], (2) retardation factors due to sorption [ca. 10^4 for 234U, 10^6 for 226Ra, and 10^7 for 210Pb, and 210Po], (3) dissolution rates of rocks [ca. 70 to 800 mg/l/day], and (4) ages of groundwater (<10 to 90 years). The contours of groundwater age, as well as the spatial patterns of disequilibrium, delineated two local north-south preferential flow pathways. Large retardation factors, precipitation and dissolution rates, and a- recoil rates were found to occur mostly in the northern part of INEL near recharge areas, while the aquifer rocks appear to have more microstructures, hence larger surface areas.


Many of the Hanford tanks have leaked high level radioactive wastes (HLW) into the surrounding soil fill. The disequilibrium between the silicic rocks and highly calcic 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 (56Sr, 133Cs, 60Co, 99Tc) may be adsorbed or sequestered by alteration phases, or released in the Vadose zone for further transport by surface water. In order to predict the location and mobility of the radionuclides from leaked solutions within the Vadose zone, we are currently studying the chemical reactions between tank solution components and Hanford soil fill materials. We are investigating soil-solution reactions at: 1) elevated temperatures (90-95°C) to simulate reactive reactions which occur immediately adjacent a radiogenically heated tank; and 2) ambient temperature (25°C) to simulate reactions which take place farther from the hot tanks. Our studies show that reactions at elevated temperature result in dissolution of silicate minerals and repregnation of zeolitic phases which have the capability of sequestering Cs and Sr. At 25°C, silicate dissolution is not significant. However, CO2 uptake by the solution results in precipitation of an aluminum-oxy-hydroxide phase which has anion screening (i.e. TeO4^2-) capabilities. Formation of radionuclide-sequestering alteration phases as a function of reaction time, reaction temperature, soil composition and solution composition will be presented.

2:45 PM Q2.5 TECHNETIUM-99M 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 indicate that technetium-99 is a major contributor to dose to a hypothetical receiving group within the proposed repository system. The purpose of this presentation is to demonstrate the potential of technetium (Tc-99m) in 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 groundwater, for example at well WT #1, could lead to significantly reduced technetium solubility. Sensitivity analysis using the NRCSYSYS Performance Assessment Code were conducted to evaluate the 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 NRCSYSYS.

SESSION Q3: INTERFACIAL PROCESSES AND INTERACTIONS
Chair: Ken R. Czarwinski and George D. Redden
Monday Afternoon, November 29, 1999
Room 203 (H)

3:30 PM *Q3.1
MODELING THE BINDING OF METAL IONS TO HETEROGENEOUS ENVIRONMENTAL MATERIALS. John C. Wascall, Department of Chemistry, Oregon State University, Corvallis, OR.

Because models for speciation of metals in aqueous solutions are presented to be based on fundamental processes 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 reasonable for simple, homogeneous systems on 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 datasets (i.e., data with simultaneous variations in pH, salinity concentration, total metal concentration, etc.). An alternative to traditional surface complexes for the approach has been developed using the 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 on to a variety of field samples with systematic variations in properties. The traditional surface complexes diffuse-layer model approach, for which binding constants have been derived from study of relatively simple laboratory systems, works well over a wide range of conditions, while the affinity spectrum approach captures variations over a much wider range of data.

4:00 PM Q3.2

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 assemblies. In contrast, surface complexation models have been developed that attempt to describe sorption reactions in terms of the 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 themselves. As such, the degree of the surface complexation approach should permit estimation of sorption equilibrium where direct experimental data cannot be obtained. A number of barriers make it difficult or impractical to use surface complexation models 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 complexation 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 unexplored implication of model results that 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 Q3.3
EFFECT OF SULFATE CONCENTRATION ON THE IMPERMEABILITY OF THE BORON FRACTURE AND INLETS. R.P. Miller, A. Han, and D. Viele, National Institute of Standards and Technology, Gaithersburg, MD.

We present results of the effect of sulfate concentration on the impermeability of the BORON fracture and inlets. The BORON fracture and inlets are not expected to be completely impermeable, and the effect of sulfate concentration on permeability is of interest. We have performed a series of permeability experiments using a range of sulfate concentrations. The results of these experiments indicate that the permeability of the BORON fracture and inlets is not significantly affected by sulfate concentration.

4:30 PM Q3.4
INTERACTIONS OF URANIUM AND NEPTUNIUM WITH CEMENTOUS MATERIALS STUDIED BY XAFS. E.R. Sylvester, P.G. Allen, P. Zhao, B.E. Vinni, Lawrence Livermore National Laboratory, Livermore, CA.

We have investigated the interaction of U(VI) and Np(V) actinides with cementsitious materials that are relevant to nuclear waste repositories using X-Ray Absorption Fine Structure (XAFS) Spectroscopy. The actinide ions were individually loaded into a cement sample containing 1:1 mix of Portland cement and water. The samples were dried in air and then used as is. The samples 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 uranium 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 contrast 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$_2^{2+}$, 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 and a model 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 Q3.5
ATOMIC SIMULATION OF RADIONUCLIDE RELEASE IN A ZEOLITE WASTE FORM I: 10N EXCHANGE ISOTHERM. Tatyana Kleskova, Kenneth Czarwinski, Sidney Yi, Massachusetts Institute of Technology.
SESSION Q13: CERAMICS - CORROSION
Chair: Bernard Peter McGray and Lee Yance
Tuesday Morning, November 30, 1999
Room 203 (H)

8:30 AM Q4.1
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 filled 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 critical contact mode from a hydraulic 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 material 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 efficient 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 Nul contrast agent showed that water infiltration into a dry column is stopped at the glass/ceramic interface because the hydraulic property mismatch between the materials. This may have important implications for water percolation pathways through the waste package.

8:45 AM Q4.2
DURABILITY STUDIES ON WASTE FORM DESIGNS FOR IMMOBILIZE URANIUM AND PLUTONIUM: Kay Hart, Yingjie Zhang, Elaine R. Arthur-Deg, Michael B. Coates, Martin D. Stewart Australian Nuclear Science and Technology Organisation, Menai, AUSTRALIA; Bill Bourlier Lawrence Livermore National Laboratory, Livermore, CA.
Ceramic titanate waste forms being developed for excess weapons Pu immobilization are produced by cold-pressing and sintering. This paper reports on studies of the durability of these titanate waste forms containing Pu, U, neutrons (d/H) and nickel, and also on studies of 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 release rates of Pu, U, and other elements, and dependence of the release kinetics. Results from MC11 leaching tests at 90 °C in deionized water show that the release rates of U and Pu are less than 10−6 g m−2 d−1 after 48 days of leaching, and are not significantly affected by the presence of iron (III). Further, the release rates of neutron absorbers are low; Hf is not detected either in solution or in waste vessel strips, and Gd leach rates are at least an order of magnitude higher than those of Pu. For samples of synthetic brannerite, flow-through testing, at 70 °C, shows that the release of U is solubility limited, with the minimum occurring at about pH 8, and that this release remains at least a factor of 10 less than that of Pu. TEM examination of samples aged in sodium hydroxide for 48 days at 70°C identified the presence of small amounts of uraninite 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 granite (Finnish, 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 Q4.3
Brannerite, ideally UX4O12, 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 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 formula may deviate from the ideal stoichiometry. The U content ranges from 0.45 to 0.88 at.% per formula unit (fu). Maximum observed amounts of the other major cations on the U-site are 0.48 Ca, 0.22 Th, and 0.14 REE atoms per fu. The Ti content ranges from 1.86 to 2.10 atoms per fu. 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 per fu. Altered regions of brannerite contain significant amounts of Sb 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, 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 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 3.19 x 1019 alpha/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 Q4.4
REACTIVITY CALCULATION OF U-PYROCHLOR NUCLEAR WASTES IN YUCCA MOUNTAIN REPOSITORY ENVIRONMENT. Yifeng Wang, Sandia National Laboratories, Carlsbad, NM; Huan Xu, Department of Earth and Planetary Sciences, 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 pathways and related wastes in the waste in geological repository. Recently, Gibbs free energies of formation of pyrochlore phases with stoichiometry of CaMn4+xTi2O7 have been calculated using a linear free energy relationship (Xu and Wang, 1995). Using the obtained standard Gibbs free energies of formation for CaUTi2O7 (873.31 kcal/mole) and CaPuTi2O7 (892.42 kcal/mole), we have calculated possible reaction paths of the pyrochlore in the condition of Yucca Mountain repository environment (acidic volcanic environment). The calculation of the pyrochlore dissolution solution composition of Yucca Mountain groundwater. The solution is maintained constant at constant pCO2 = 1.0e-2.3, pH = 5.0e-30 atm, and T = 25 °C (open system). The calculated results show the U-pyrochlore will be replaced by rutile.
sodyide, halide, and carbonate. Other minerals that will also form are silicate (asbestos), nontronite, hematite, and ilite. The main difference between U-pyroclore and Pu-pyroclore alteration is that PuO2 is the only Pu-bearing phase in Pu-pyroclore alteration products. By using a dissolution rate of zirconite (Weber et al., 1986) as a first-order approximation, the real time reaction processes can be calculated.

9:30 AM QM 4.5
Dissolution Kinetics of Titanate/Pyroclore Compounds
Ceramics at 90°C by Single Particle Flow Through (SPPT)
Experiments

We have quantified the dissolution kinetics of pyroclore and zirconite ceramics at 90°C over a range of pH values (2-12) by use of single particle flow through (SPPT) experiments. Typical experimental durations are 7-10 days on powdered ceramic samples. The compositions of the ceramics are A2Ti3O7 (A = Ca2+, Ce4+, and Hf4+) with structures representing both betafite and zirconolite subgroups. In addition, the ceramics are doped with small concentrations (0.1 wt% of Mo6+) which acts as a tracer of dissolution. Concentrations of Mo6+ in the effluent solutions indicate dissolution rates of 2.53 x 10^{-4} g m^{-2} d^{-1} for both the betafite and zirconolite samples at pH = 5.7. The Mo tracer reveals an anhysteretic pH dependence of the dissolution rate with maximum 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 directly from concentrations of Ce4+ and Hf4+ at pH = 2 (3.0 x 10^{-4} g m^{-2} d^{-1}). At higher pH values of 7.5, 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 Ce4+, Hf4+, and Mo6+) of powdered samples are nearly identical to those measured on single betafite [Ce4+, Hf4+, or Y4+ Ti2O7] 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 pyroclore/ceramic waste forms can be quantitatively assessed.

9:45 AM QM 4.6

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 (multiply) SrOOC-C when exposed to D2O at 150°C for 21 days was confirmed to be ~15 nm by Elastico Recoil Detection by Rutherford Backscattering (EDRBS). Measurements of the thickness of the D-bearing surface layer (220 ± 5 nm) from EDRBS studies, the thickness of the D-bearing surface layer on zirconolite ceramics, designed for excess weapons Pu immobilization, was only ~3 nm upon exposure to D2O for 30 days at 150°C. SrOOC-C samples exposed to SrOOC-C for 7-300 days at 90°C in deoxygenated water showed no surface buildup of Sr or Ce by SIMS. Alpha spectroscopy on CeO2-polydoped SrOOC-C samples showed some surface buildup of Sr after leaching for 84 days at 70°C. In deionized water, undoped SrOOC-C also showed some weak surface adsorption of Sr, 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 heat-pressure, as shown by enhanced elemental extraction into solution and a much thinner reaction zone (20 μm vs. 1μm).

SESSION Q5: CERAMICS - STRUCTURE AND CHARACTERIZATION

Chair: Ned E. Bibler and S. V. Ramam
Tuesday Morning, November 30, 1999.
Room 203 (H)

10:50 AM QM 5.1
EXAFS and XANES Analysis of Plutonium and Cerium Edges from Titanate Ceramics for Fissile Materials Disposal.

We report X-ray absorption near edge structure (XANES) and extended x-ray fine structure analysis (EXAFS) spectra from the plutonium LII and cerium LIII edges in prototype titanate ceramic host for disposal of surplus fuel materials. The spectra are obtained using the MRCAAT beamline at the Advanced Photon Source (APS). The titanate ceramics studied are based upon the zirconium/titanium and zirconium oxide mineral structures and will serve as an immobilization host, containing as much as 10% plutonium, and 20% [natural or depleted] uranium. Formulations using cerium as a surrogate element, replacing both plutonium and uranium in the ceramic matrix, clearly indicates the III-VI coordination state for the cerium. In 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 results show a strong second-shell peak, clearly distinct from that of PuO2, 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 QM 5.2
Phase Composition and Elements Partitioning in Two-Phase Hosts for Immobilization of REE-Actinide Fraction of HLW.
Sergey V. Shchepovskoy, Maia Done, Moscow, Russia; Sergey V. Shchepovskoy, Borov S. Nikonenko, Inst of Geology of Ore Deposits, Moscow, Russia; Alexander V. Ozhkin, Natalia E. Chernyshkina, Univ of Chemical Engineering, Moscow, Russia.

Two-phase hosts bas on REEAlO3 (Zr)O2, REETiO3 (Zr,U)O2, REEOAlO3 (Zr,U)O2, and REEOAlO3 (Zr,U)O2, and REE2Ta1O10 (Zr,U)O2 assemblages were prepared by milling at 1500°C and investigated using XRD, SEM/EDS, and TEA. The in situ hosts for 40 wt% of REE-actinide fraction of HLW. In the zirconolite with nominal stoichiometry A2Ti2O7 + YTi2O7 + PuO2 actinide ions occupy VIII and VIIa f1 coordinated sites. Charge compensation is provided by incorporation of lower charge ions (A111, Fe2+74/8, Fe3+77/8) instead of Ti4+. Maximum REE O3 content (45 wt%) was observed in a Ca-free zirconolite (nominal formula REEOAlO3Ta1O2). In the pyrochlore-structured phase A2Ti2O7 + YTi2O7 + PuO2 actinide ions occupy "A" sites. Their incorporation does not require significant substitution of ions in "B" sites, for instance, Ti4+ for A111 or Fe2+74/8 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 zirconolite-based or two-phase pyrochlore-zirconolite 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 contains two pyrochlore-type phases with different U content.

11:00 AM QM 5.3
A Correlation Between Relative Cation Radius and the Phase Stability of Zirconolite.
Douglas Stremson, Poopeong Bangphasane, Dept. of Metallurgical Engineering, Michigan Technological Univ, Houghton, MI.

Geometric considerations often determine the crystal structures of ceramics. Conversely, the crystal and oxidation state of these phases in the zirconolite structure can be determined by EMX measurements. However, the exact effect of cation size on solubility remains unclear. 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 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 particular application. The present investigation was conducted to determine whether the phase stability of zirconolite (CaZrTi2O7), a common host for many actinides, 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 micro-analysis. A parameter termed the relative radius ratio, defined as the ratio of the average radius of the individual cation to the average radius of the four cations, was used to compare the relative solubilities at 1,500°C with a less than one percent standard deviation, at all solubility limit. These results suggest that the phase stability of zirconolite is governed by geometric considerations, and that chemical effects such as solubility are of secondary importance. Therefore, it should be possible to predict the stability 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 QQS.4
SYNTHESIS AND STUDY OF 239Pu-DOPED GADOLINIUM ALUMINUM GARNET. Boris E. Burakov, Eugene E. Anderson, Mirra V. Zaretskaya, Marina A. Petrenko, V.G. Khikin Radim Institute, St. Petersburg, RUSSIA.

Garnet solid solutions, Y3Al5Fe 12−xGd3Al5SiO12+2FeO (YAG-GAG), 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 0.9Gd3Al2O12.2PuO2−0.8SiO2 has already 5 wt. % 239Pu and 4.5±0.5 wt. % Ce has been synthesized through melting of oxide precursor in air in the flame of hydrogen burner. The admixtures of Sn and Sr were used to increase Pu incorporation into garnet lattice through ion charge and size compensation for Pu4+. 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 Sr provides significant incorporation (more than 2%, i.e. 3%) in the same positions into garnet structure. In other cases the behavior of U, Pu 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 Pu4+ and Np4+ for the garnet host-phase in case of using charge- and ion-compensating admixtures. Otherwise, Ce can be used as Am4+ surrogate.

11:30 AM QQS.5

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, compatibility with high thermal stability, and resistance to radiation damage, are attributed to the three-dimensional structure of Na2Zr3[PO4]6. The ability of K2Zr3[PO4]6, a member of the [NZP] structural family, to accommodate U(IV) and Pu(IV)/(III) for Zr on the octahedrally coordinated metal site has been explored. Actinide-doped [NZP] compounds were prepared from solgel derived precursors at moderate 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 Zr2+. The Zr/PoKz refined 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 random occupancy of the octahedral site in Zr/PoKz. Structures resulting from the accommodation of Pu(III)/IV on the A site in K2Zr3[PO4]6 will be discussed and compared to those resulting from U(IV) accommodation on A.

11:45 AM QQS.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. Loo, W.L. Elbert and S.G. Johnson, Argonne National Laboratory, Idaho Falls, ID and Argonne, IL.

This paper presents microscopic characterization of a glass-bonded solidified ceramic waste form (CFW) for actinide and fission product containment. The material is central to Argonne National Laboratory’s pyro-metallurgical treatment of 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 actinides, 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 isostatic pressing, the zeolite is occluded to the glass, resulting in the final glass bonded solid waste 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 H2O 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 H2O in determining the CWF microstructure. Wherein it was originally expected that actinides and rare earth contents would remain occluded in the solid waste phase, previous observations suggested that a reaction with residual H2O to form oxide was preferred over coalescence. In addition to a detailed description of the phase evolution using electron diffraction, the study will attempt to address remaining questions concerning the role of H2O to form oxide and the consequences in regard to corrosion behavior this may have.


1:30 PM QQQ.6/GG4.1
SIMULATED MICROSTRUCTURE AND TRANSPORT PROPERTIES OF ULTRA HIGH PERFORMANCE CEMENT-BASED MATERIALS. Michele Moramarco, Lab of Mechanics and Technology, ENS of Caen, FRANCE; Véronique Maste, Cécile Richet, Lab of Materials Studies, French Atomic Energy Commission, Sacy, FRANCE; Jean Michel Torrenti, National School of Roads and Bridges, Marne-la Vallee, 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 containing 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 dewatered waste. SEM observations and quantitative image analysis of cement microstructures, 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. 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 Benz and Garbozzi, 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 QQQ.2/GG4.2
PREDICTION OF THE LONG-TERM RELEASE OF HAZARDOUS SUBSTANCES FROM CEMENT-BASED MATERIALS TO WATER. Anne 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 this stage, however, the materials are demanding more research and understanding of these issues, 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 from present leaching tests and discuss whether the tests are capable of delivering consistent 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 admixtures. Substances that were focused upon were metals e.g. copper, chromium, lead, manganese and two active ingredients in admixtures thioxyurate and salt oil. Two different leaching tests have been carried out, basically adhering 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 contribution to existing models for leaching of cementitious material, such as diffusion models and models involving a shrinking dissolution front. In addition, several phenomena, that affect the leaching rate are presented. For example, leaching of portlandite caused an increasing permeability and a change of pH, and penetration of CO2 causing precipitation of CaCO3, will prevent the emission rate from correlating to Fick's law of diffusion.
2:15 PM QG6.3/ GG4.3
POROSITY AND LEACHABILITY OF CEMENT SOLIDIFIED WASTE-PART II. Take El-Kedari, Department of Civil Engineering, Worcester Polytechnic Institute, Worcester, MA; David Gross, 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 synthetic seawater and acid solution to simulate aquifer conditions. The heavy metal concentrations included calcium, lead, chromium, and arsenic. Chemical analysis included heavy metal release, pH and alkalinity. Microstructural analysis on the solidified waste and precipitates included SEM, EDAX, X-ray diffraction and mercury intrusion porosimetry. The metal leaching results are explained in terms of porosity and microstructural development during solidification and hydration of the cement and during the dynamic leaching process.

2:30 PM QG6.4/ GG4.4
MODELING THE POROSITY AND LEACHABILITY OF CEMENT SOLIDIFIED WASTE-PART II. Take El-Kedari, Department of Civil Engineering, Worcester Polytechnic Institute, Worcester, MA; David Gross, 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 calcium, 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. The results of our models were incorporated in the modeling leaching models.

3:15 PM QG6.5/ GG4.5
DIMENSIONAL ANALYSIS OF IONIC TRANSPORT MECHANISMS IN CEMENT-BASED MATERIALS. Rémi Barbarulo, Direction des études et Recherches, Electricité de France, Ménars-Lyon, FRANCE, Jacques Marchand, Centre de Recherche Interuniversitaire sur le Béton, Université Lyon1, Sainte-Croix, 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 also they 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 QG6.6/ GG4.6
INFLUENCE OF LIMESTONE ADDITION ON CALCIUM LEACHING MECHANISMS IN CEMENT-BASED MATERIALS. Sandrine Coudert, Jacques Marchand, Laval Univ, Dept of Civil Engineering, Quebec City, CANADA, Jim J. Beauchon, NRC, Materials Laboratory, Ottawa, CANADA.

In order to investigate the mechanisms of calcium leaching in cement-based materials, four different systems (CS1, CS2, CS3, As2O4H2O, CS4, CS5, As4AF, As3SO42H2O and cement) were prepared and hydrated. In addition to the mineralogical composition of the systems after inclusion of limestone, the percentage of calcium carbonate addition (0, 5, 10 and 20%) and different mixtures were blended and tested. In all cases, the water/harden ratio was fixed at 0.5. After a minimum 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 mineralogy of the various systems was also followed by length change measurements. Test results clearly indicate that the mechanism of leaching is 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 QG7.7/ GG4.7
COUPLING BETWEEN DIFFUSIVITY AND CRACKS IN CEMENT-BASED SYSTEMS. Chrie Tajmגני, LMDC, Toulouse, FRANCE; Jean Michel Torriani, ENPC, Paris, FRANCE; Jean Pierre Olivier, 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. The 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 (i.e. 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 QG8.8/ 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 porous material which changes dramatically over its lifetime. 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. This paper will present examples of concrete containing sealants, adhesives, waterproofing or corrosion chemicals are designed to release these chemical where and when they are needed. For example, brittle fibers containing additives or sealants will release the chemicals when the matrix cracks, causing the fiber to crack and release chemical. 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 work will be presented.

4:15 PM QG6.9/ GG4.9
CLAY-BASED GROUTING INTO THE EDZ FOR THE VAULT SUBDRAIN. Yuriko Sugita, Tamco Fuji, JNC, Tokai, Ibaraki, JAPAN; Kazuhiko Maemoto, Kajima Corp, Tokyo JAPAN; Neil A. Chandler, AECI, Minoh, JAPAN.

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 bentonite-based mixture under consideration of long-term stability of the seal. 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 and bedding planes. It will be necessary to design the engineered barriers to interrupt the migration of nuclides through the EDZ, and one of the element of the design will be granular grouting. Two tests of bentonite grouting for sealing the EDZ were conducted in the granite 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 performance. A dilution test has been done successfully with a total of 0.2% bentonite by weight to a concentrated one. The injection proportion of 4.0% was the most efficient. The rock 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 test, a bentonite-based grout was injected into the EDZ above the tunnel head. The test was conducted using the same procedure as in the trial. Although the hydraulic pulse test did indicate that the grouting greatly reduced the rock permeability, the
test was useful site-scale demonstration of bentonite grout injection for the purpose of ID2 sealing around a tunnel bulkhead.

4:30 P.M. Q06.10/GG4.10

STUDY ON EFFECTS OF HYDRAULIC TRANSPORT OF GROUNDWATER IN CEMENT. Masatomi Tachibana, Masaki Koyama, Municipal Engineering Laboratory, Tochigi Corporation; Fumiyo Matsuura, Norimasa Masuoka, Advanced Energy Design & Engineering Dept., Toshiba Corporation; Yasuichi Kobayashi and Masutaka Inamura, Planning Dept., Japan Nuclear Fuel Limited.

This paper discusses the effects of solution velocity through the cementitious materials on formation of secondary hydrates. These hydrates are produced by reaction of hydrates in cement and chemical compounds with groundwater. The formation of secondary hydrates is expected to decrease the groundwater velocity since the components in ground water are very important in order to reduce the release of radionuclides 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 radionuclides 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 radionuclides with poor sorption will be estimated to decrease. Therefore, their effects were investigated through the relations 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 (2m 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 experiments 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 1.8-2 mol/L, CaCO3 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 P.M. Q06.11/GG4.11

IS AND XRD STUDY OF CEMENT-BASED MATERIALS CONTAINING ORGANIC POLLUTANTS. Giovanni Dotelli, Donatella Botta, Politecnico di Milano, Dept. of Industrial Chemistry and Chemical Engineering, Milano, ITALY; Isabella Nasti Sora, University of Milano D.M.I., Metallurgical Engineering, Milano, ITALY; Claudio M. Masi, Universita’ di Milano Bicocca, Dept. of Materials Science, ITALY.

Some kinds of hazardous organic pollutants, specifically the aromatic amine, were immobilized by means of a cement-based S/S process. The aromatic amine were proscribed in organicphlic clay 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 by XRD and DTA analyses, and by means of a thermogravimetric technique. The clay samples and the mixture with aromatic amines were analyzed by XRD and DTA techniques. Moreover, the morphology 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 Q07: POSTER SESSION

SPECIFICATION, SORPTION, AND TRANSPORT

Chair: Larry C. Hull

Tuesday Evening, November 30, 1999
8:00 P.M.

Exhibition Hall D (H)
and with the received material. Acid-base titrations and electrophoretic mobility measurements were carried out on both systems and for determining the effects of the surface properties of the colloid, due to the interactions of colloids with the impurities present in the water. The zeta 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 PZEC (15 for humic-like/purified and 8.3 for as received material) is less in absolute value than the structural change that have been developed in the negative surface charge of the particles remains negative. Experimental data obtained by acid/base titration were interpreted according the EDL theory. The model predictions were satisfactorily consistent with experimental data only in the alkaline pH range. Protassociation/deprotassociation reactions of surface functional groups (SOH) can be then considered the main changes determining surface mechanism only in the alkaline pH range whereas in acid conditions the reaction 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 Fusion Safety Research and Training Programme (1994-1998) under contract FI-b-Ct96-0192 and by the Spanish Ciemat Enterprise.

Q7.5 DIFFUSION OF PLUTONIUM IN COMPACTED BENTONITES IN THE NUCLEAR INDUSTRY UNDER CONFINED CONDITIONS. PRODUCTS OF IRON. Kunyuya Ida, Masahisa Kimura, Masayoshi Cabras, Hiroshi Moriyuki, Yujiro Inagaki, Tsuomi Aizuma, Department of Applied Quantum Physics and Nuclear Engineering, Kogakuen University, JAPAN; Toshihiko Mitsuihara, Misaio Hara, Yoshitomo Suzuki, The Okura 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 (Kunigai V1 and Kunigai 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 been kept in contact with carbon steel for approximately 7 years. This observation suggests hydrogen generation during corrosion of the carbon steel. The apparent diffusion coefficients measured were approximately $10^{-15}$ m²/s under the reducing condition and less than $10^{-16}$ m²/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/m³) and montmorillonite contents (50% for Kunigai V1 and 100% for Kunigai F), however, were not observed clearly. The chemical species of plutonium were expected to be PuOH²⁻ for the reducing condition and PuO²⁺ for the oxidizing condition, respectively.

Q7.6 EFFECT OF IONIC CHARGE ON EFFECTIVE DIFFUSION COEFFICIENT IN COMPACTED SODIUM BENTONITE. Haruo Sato, Japan Nuclear Cycle Development Institute, Tokai-mura, Naka-gun, Ibaraki, Japan, JAPAN.

In performance assessment of the geological disposal of high-level radioactive waste, effective diffusion coefficient ($D_e$) is one of the important parameters. In this study, $D_e$ values in compacted bentonite were measured as a function of ionic charge to evaluate the degree of surface diffusion and mineral exclusion. The $D_e$ measurements for Na₂4+, Sm₃⁺ and SeO₃²⁻ were carried out with a dry density of 1.8 Mg/m³ by fluid through-diffusion method. Sodium bentonite, Kunigai V1, which is a compacted bentonite, was used in this study. The measurements for only Se₂⁻ were carried out in an Ar atmosphere glove-box (2% O₂ concentration, 1 ppm H₂O). The order of $D_e$ values was $\text{Na}_2^+$ > $\text{Sm}_3^+$ > $\text{SeO}_3^{2-}$, which corresponds to the same tendency of the same bentonite. Consequently, the order of apparent diffusion coefficients was $\text{Na}_2^+$ > $\text{Sm}_3^+$ > $\text{SeO}_3^{2-}$. These $D_e$ values were compared with those reported in the literature for the same bentonite. The tendency of $D_e$ values was $\text{Na}_2^+$ > $\text{Sm}_3^+$ > $\text{SeO}_3^{2-}$ and the results indicate a possibility of surface diffusion in cations. This conclusion is supported by the fact that the FF of Sm₃⁺ was approximately 4 times greater than that of HTO. However, the diffusion of Na₂⁺ in HTO is about 1/3 of that of self-diffusion coefficient of water. The formation factor (FF), which were calculated normalizing diffusion by $D_e$ values, showed a tendency of $\text{Na}_2^+$ > $\text{Sm}_3^+$ > $\text{SeO}_3^{2-}$, indicating a possibility of surface diffusion in cations in this case. This FF of Sm₃⁺ was about 4 times greater than that of HTO. However, since the $D_e$ Sm₃⁺ is greater than about 1/3 of the self-diffusion coefficient of water, the actual measured $D_e$ of Sm₃⁺ is a little higher than that of HTO. Based on this, it is presumed that the effect of surface diffusion on Sm in compacted bentonite is insignificant.

Q7.7 MODEL FOR SORPTION OF U(VI) ONTO BENTONITE. Ursula Almeida, Tinuviel Misawa, Miguel García-Gutierrez.

Bentonite has been considered as a candidate buffer material for high level radioactive waste repository because of its high sorption capacity and low permeability. Predictive modeling performance needs the development of the methodology on 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 interaction/micelle/clay behavior. The model for the sorption capability of bentonite for U(VI) has been studied under a wide range of experimental parameters including concentration of sorbate and surfactant, 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 analyzed in parallel, in terms of major ions and trace elements. 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.

Q7.8 ADSORPTION PARAMETERS FOR RADIOACTIVE LIQUID WASTE MIGRATION. Larry Hall, George Redden and Molly Papp, 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 mol% nitric acid with mg/L levels of uranium and plutonium. Post-spent nuclear fuel will be rapidly neutralized and decontaminated 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. Adsorption models for the individual minerals based on soil characterization data are compared to sorption 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.

Q7.9 EFFECTS OF SURFACANT-MODIFICATION ON THE SORPTION BEHAVIOR OF NATURAL ZEOLITES FOR STRONTIUM(M²⁺) AND URANIUM(M⁶⁺). James D. Priekel, F. Paul Bertetti and Roberto P. Palburn, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

Natural zeolite minerals have a strong ion exchange selectivity for alkali and earth lanthanide cations, such as strontium and cesium, but only limited sorption affinity for actinides such as uranium. In a previous study, surfactant-modified the ability of surfactant-modified zeolite to sorb both strontium(M²⁺) and uranium(M⁶⁺). The 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 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 ion exchange behavior.

Q7.10 METALLION STABILIZATION IN GEOEMEDIA BY IN-SITU PHOSPHATE MINERALIZATION. Kenneth L. Nash, Mark P. Jensen, Andrew H. Bower, 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 unconsolidated, a remediation strategy analogous to pump-and-treat decontamination of subsurface waters may not be feasible for cleanup. This leaves excavation/solvent washing or in-situ immobilization as the most reasonable methods of sequestering the contaminants in 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-inositolhexakisphosphoric 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. Further initial measurements 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 INEL 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.

Q9.1 EXPERIMENTAL STUDY OF THE NICKEL SOLUBILITY IN SULPHIDIC GROUNDWATER UNDER ANOXIC CONDITIONS. T. Carlson, U. Vaisanen, T. Kekki, H. Anko, VTT Chemical Technology, Industrial Physics, Espoo, FINLAND.

Recent literature recognizes a lack of proper chemical data that is necessary for the calculation of solubility values of the nickel solubility in sulfidic groundwater. These literature values deviates from 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 precipitation with iron compounds, and nickel complexation with sulfides. Consequently, in order for the performance assessment of radioactive waste repositories to be conservative, it is necessary to use solubility values that closely exceed those obtained from modeling their reactions. The safety analysis of waste from the Olkiluoto NPP indicates that NiSo, together with NiS, will dominate the dose rates in the water 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 sulfidic groundwater under anoxic conditions. The waters used were natural groundwater from Olkiluoto and synthetic saline water, to which sodium sulfide had been added. The sulfide 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 NiSo to the samples and comparing the initial and final nickel activities using liquid scintillation counting. The initial nickel concentrations were 10^-10^-7 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 nickel composition, Ni, Mn. The nickel solubility is discussed in terms of the analytically determined water chemistries, and the measured nickel solubilities are compared with those obtained from modeling using the geochemical code EQ9.1.
simulated surface show an accumulation of Na. This observation is confirmed by the plot of the chemical concentration profiles. Parally, we observe a decrease in 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 them changing the changes on a longer scale. The evolution of the 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 300 keV and 700 keV. 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 progresses to depolymerization. The surface induces an increase of the depolymerization peak but also an acceleration of the depolymerization rate.

**Q5.8** TEMPERATURE DEPENDENCE OF ION IRRADIATION INDUCED AMORPHIZATION OF ZIRCONOLITE

Katherine L. Smith, Mark G. Blackford, Gregory R. Lampkin, Australian Nuclear Science and Technology Organization, Materials Science Division, Menara, Australia; Nestor J. Zhuzec, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Zirconolite is one of the host phases for actinides in various vitrification wasteforms for immobilising high level radioactive waste. The critical dose for amorphization, Dc, of zirconolite (CaZrTi2O7) was measured as a function of irradiation temperature using the HVEM/TEM-Tandem Facility at Argonne National Laboratory, Argonne, IL. Two samples were irradiated: 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 predominately 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 723 K and observed in situ in the HVEM. The temperature dependence of the critical dose for amorphization is similar for both samples and shows a single stage dependence of Dc on temperature. Dc is almost constant up to temperatures near the critical temperature for amorphization, Tc (above which recrystallization is complete over the entire cascade volume), then it rises rapidly. Least squares fitting of the data according to current models shows that a) the activation energy for self annealing Ea of the 1200 and 1450 samples are 0.14 ± 0.04 and 0.15 ± 0.06 eV respectively and b) the Tc 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 Dc on temperature for which they calculated Ea values of 0.1 and 0.32 eV and Tc values of 373 and 640 K. Similarities and disparities between our data and that of previous authors will be discussed in the paper.

**Q5.5** COMPUTER SIMULATION OF COLLISION CASCADES IN ZIRCONOLITE

Byungjung Park, L. Reno 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 among 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 Ei, which could be responsible for the morphological features of damage. 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 employed has been modified to implement irradiation process in the material. 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 calculated by Ewald method. The total number of atoms in the system was 134,400 (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 of ions. A number of histories for 10 keV ions were observed for about 10 ps. Details of the simulation results will be presented.

**Q5.6** RADIATION AND THERMAL EFFECTS IN ZIRCONOLITE-NAY

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

Zirconolite-NAy is susceptible to radiation- and thermally-induced amorphization. Both zirconolite-NAy and the Ca-exchanged zirconolite-NAy undergoes a crystalline-to-amorphous transition when irradiated with 200 keV electron beam. At room temperature, complete amorphization was achieved at a dose of 4.0 (1018) e+ cm⁻² and 5.0 (1018) e+ cm⁻² for zirconolite-NAy and the Ca-exchanged zirconolite-NAy, respectively. The amorphization of zirconolite-NAy and the Ca-exchanged zirconolite-NAy was also achieved by thermal treatment. Zirconolite-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 found during the ion exchange reaction. The Ca-exchanged zirconolite-NAy phase has a slightly higher thermal stability than the unexchanged zirconolite-NAy, i.e. complete amorphization was achieved when the Ca-exchanged zirconolite-NAy was heated at 1000°C. The Ca-exchanged zirconolite-NAy, obtained by thermal treatment, lost approximately 95 percent of its ion exchange capacity for cesium, as compared with the crystalline zirconolite-NAy. The reduction in ion exchange capacity is attributed to the loss of exchangeable cation species and to the blockage of access to exchangeable cation sites. A description study indicated that the amorphization of cesium-loaded zirconolite-NAy enhances the retention capacity of exchangeable C ions due to the closure of structural channels.

**Q5.7** RADIATION EFFECTS IN CHLORIDE MOLTEN SALT COMPOSITION

Svante Bodin Ignatius, Dmitry Pankratov and Eugene 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 NaC1 (70% mol) and Pr6C2 (30% mol) 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 were also analyzed under irradiation by secondary neutrons of different flow density and hardness, that appear in the target and surrounding blanket. For the LANSE (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 MARS10 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 ~12.9 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. Effective flux 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 1.5 times less than low energy contamination for energies two times higher than 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 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 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.

**Q5.8** ELECTRON IRRADIATION EFFECTS ON BUBBLE FORMATION AND GROWTH IN NBS-1 GLASS

Xiaolong Chen, Robert Bither, Materials Science Division, Argonne National Laboratory, Argonne, IL.

We studied electron irradiation effects on bubble growth in sodium borosilicate glass (NBS-1) during electron beam irradiation. Xe ion implantation. The 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 the 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 behavior of this shrinkage are studied. These results provide insights on this ionization enhanced diffusion.

Q9.5 HYDROGEN GAS EVOLUTION FROM WATER DISPERSING NANOPARTICLES IRRADIATED WITH GAMMA RAY
Satoshi Sato, Ryoasuke Fujimoto, Takao A Yamamoto, Masahiro Kasum, Etsuko Oshiki, Osaka Univ, Dept of Nuclear Engineering, Osaka, JAPAN; Shigeki Ikeda, Osaka Univ, Institute of Scientific and Industrial Research, Osaka; Kenji Ouchi, Osaka Univ, Institute of Science and Engineering, Nagasaki, JAPAN; Riyo Oyama, Osaka Prefecture Univ, Research Institute for Advanced Science and Technology, Osaka, JAPAN.

Hydrogen gas evolution induced by 60Co γ-ray irradiation of nanoparticles dispersed in aqueous solution was investigated under various conditions by measuring hydrogen yields by a gas chromatography. Particle sizes of TiO2, ZrO2, ZrO2 and CO2 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 particularly Au plays an important role in the hydrogen evolution. Observed hydrogen yields are discussed taking account of miscellaneous active species generated by the water radiolysis.

Q9.6 DIAMOND DETECTORS FOR ALPHA MONITORING IN CORROSION MEDIA FOR NUCLEAR FUEL ASSEMBLY REPROCESSING.
P. Bergamo, F. Fouquet, A. Brimbal, D. Thomsen, C. Mer, H. Guizard, S. Huon, LETI | CEA-Technologies Avances/DEI/SPE, CEA/French, Grenoble, 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 ionizing irradiations. 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. This layer of diamond has been grown, processed, and used for the fabrication of hard alpha detectors. The detector geometry enables the sensor to be directly immersed in the corrosive solution, thus limiting any significant absorption that would be induced with a protective coating. The devices have been successfully operated using Platinum 238 isotope dispersed 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 1000 hours, and previous would suggest they could be stable during months of continuous use. One inherent problem that arises 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 Q9: POSTER SESSION: NATURAL ANALOGS
Chair: William M Murphy, Tuesday Evening, October 31, 998
8:00 PM
Exhibition Hall D (H)

Q9.1 AN ARCHAEOLOGICAL SITE AT AKROTRI, GREECE, AS A NATURAL ANALOG FOR RADONUCLEIDE TRANSPORT: IMPLICATIONS FOR NUCLEAR WASTE PERFORMANCE ASSESSMENTS.
D.L. Higdon, L. Browning, W.M. Murphy, R. Green, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

Natural analogy studies provide a means to test assumptions in performance assessment models. Data on the spatial distribution of metal derived from an archeological site at Akrotiri, Greece, were used to evaluate performance assessment model assumptions of radionuclide transport through unconsolidated volcanic tuffs hosting the proposed HLW repository at Yucca Mountain, Nevada. Performance assessment abstractions of radionuclide transport through the unconsolidated zone to the water table range from simple 1-D advective transport models to 3-D continuum flow and transport models incorporating sorption, dispersion, matrix diffusion, perched water zones, and colloidal transport, and solute advection. Processes controlling radionuclide transport of trace elements from 3,000 year old artifacts at Akrotiri are analogous to processes controlling radionuclide transport at Yucca Mountain. Archeological information temporarily and spatially constrain the source and pathway of these radionuclides, providing a comparison basis for model validation efforts. Despite these constraints and characteristics of the Akrotiri site, the data are open to different interpretations as to the extent of the planar emanating from the Minosian artifacts, transport pathways, heterogeneities in parameters, and boundary conditions are uncertain. Various conceptual models of flow and transport predict substantially different transport distributions. Model results of plume transport 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 conservative. 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.

Q9.2 BEHAVIOR OF URANIUM-rich MICA FlATES DURING ARCHEOLOGICAL ALTERATION.
Peter Gifford, Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN; Edgar Beck, Chemical Technology Division, Argonne National Laboratory, Argonne, IL; Richard Guggisberg, Daniel Mahy, SEM Laboratory, University of Basel, Basel, SWITZERLAND; Eric Reuss, Institute of Mineralogy and Petrology, ETH Zurich, 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 A2B2O7, where A and B are cations and certain fluorine products are accommodated in the A site. On the basis of the B-site cations, three subgroups are distinguished: pyrochlore (Na- rich); pyrochlore (Ti-rich); and bixbyte (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. Microtext occurs primarily in granitic pegmatites. It is a characteristic feature of the alkali granitoids (approximately 60%) and pegmatites of the Mozambique Belt in East Africa, where large euhedral microtext occurs in association with biotite, spodumene, and lithium mica. We have examined a sample from a strongly altered pegmatite in Mozambique. This pegmatite exhibits a pronounced growth zoning, with a U-free core surrounded by a U-rich rim (UO2 up to 13 wt %). The microtextite exhibits a conjugate set of straight fractures formed prior to the U-rich rim. These fractures provided a pathway for the intergrowth bixbyte-U-bearing fluid, which interacted with the U-free microtextite to produce a distinct 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 metasomatism. After the incorporation of U into the rim and along the fractures in the core, the pegmatite was subjected to intense argillic alteration. There is no evidence of U loss and therefore, this example document that this microtextite is able to retain U over geologic time scales even after low-temperature alteration of its host rock.

Q9.3 CRANDALLITES AND COFFINITE: RETARDATION OF NUCLEAR REACTION PRODUCTS AT THE BANGOMB NATURAL FISSION REACTOR.
Keld A. Jensen, University of Aarhus, Department of Earth Sciences, AUSTRALIA; Przemyslaw Janeczko, University of Silesia, Faculty of Earth Sciences, Silesia, POLAND; Rodney C. Ewing, University of Michigan, Department of Nuclear Engineering and Radiological Sciences, Department of Geological Sciences, MI; Peter Stale, Francis 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 garnet and florencite,
respectively. Relatively high concentrations of Ln's can also substitute for U in caffeine. Both Ln-rich claddings and coffee have recently been reported to contain the weathered zone of the neuseaface (>12 m depth) natural fission reactor at Bungmore [RBZ], SE-Gabon. Florencite (Nd), Lrso, Cernb, and Sr0.1(Fe,Fe)2PO4.75SrSO4 and Sr0.1(Fe,Fe)2PO4.75SrSO4 were reported to contain up to 3% and 2% Sr0.1(Fe,Fe)2PO4.75SrSO4 and Sr0.1(Fe,Fe)2PO4.75SrSO4. Chemical transmission electron microscopy has revealed that the Le-Sn-Orannalities frequently occur in the < 2 μm clay fraction from the superfine weathering zone and hydrothermal clay halos above RBZ. U runphil phosphates and uranyl sulfates, among which francnios-Nd, torbernite and uranopite have been identified, were observed in fractures down to ~ 12.5 m depth. The francnios-Nd is rare and the only uranyl phase reported to contain notable amounts of Ln's. Hence, Ln-rich claddings appear to be the primary host of the fssicnic Ln's whereas U is mainly retained in the various uranyl phases above the core of RBZ [11.60 to 12.98 m depth]. In and below the reactor core, the Ln's are finite, with elevated contents of Zr, Th, Ce, and Nd, are the main source of the actinides and Ln's. The groundwater in RBZ (pH = 5.96; Eh = 143 mV) contains low concentrations of dissolved U [3.09 ppb] and Lns [1.11 ppb]. This suggests that the observed mineral assemblage effectively retransports the majority of the fssicnic Zr, Th, U, and Ln in the superfine weathering horizon at Bungmore. 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 fssicnic elements by cladding and coffee during migration in the geosphere are discussed.

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

QQ10.1 CHEMICAL INTERACTIONS IN THE NEAR-FIELD OF A REPOSITORY FOR SPENT NUCLEAR FUEL - A MODELING STUDY
H. Hellman, U. Kogelmann, A. Masuhr, A. Muennion, VTT Chemical Technology, VTT, FINLAND

In this work, the evolution of the near-field chemistry affecting radicamide release from a repository for spent fuel was studied by applying equilibrium modelling [EQS/II 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, casing 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 casing. Finally, this caser-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 radicamide solubilities for the spent fuel are discussed.

QQ10.2 RESULTS OF AN AQUEOUS SOURCE TERM MODEL FOR A RADIOACTIVE RISK ASSESSMENT OF THE DRIGG LLW SITE, UK
J. S. Small, P. N. Humphreys, T. L. Johnstone, R. Phnt, M. Randall and D. P. Trivedi, BNFL Research and Technology, Raley, 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 DRIGG LLW repository is modelled as a large spatially distributed source term. Calculations are carried out using the sequential solution scheme of HYDRAQL/CE. 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 matrix and various and solid radionuclides is modelled using an equilibrium chemical model 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 reduction of redox reactions between cellulose degradation products, and other microbial substances such as Fe(III) present in soil, sulfate in groundwater and hydrogen produced by corrosion of stainless steel. The evolving chemical speciation computed by the DRING model is used to calculate the partitioning of soluble radionuclides between the aqueous phase and discrete solid phases. The chemical evolution is also used as a basis to select appropriate fate and transport models. An initial estimate of the release of non-soluble radionuclides. Results of the DRING aqueous source term model will be presented, which illustrate the integrated microbial, chemical, and peph evolution of the Drigg trenches and vaults. The model provides the 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, Nevada
Mohamed, 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 independent 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, and the transport 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 model 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 degradation rate, radionuclide solubility limits, and the hydraulic properties of the unsaturated and saturated zones. Calculations also suggest that at a slow dissolution rate, only 0.0005 percent of the SF would be transported to the receptor location in 50,000 yr.

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QQ10.4 SAFETY ASSESSMENT OF BORE-HOLE REPOSITORIES FOR SEALED RADIATION SOURCES DISPOSAL.
Andrew V. Gourevich, Michael I. Ogban, Lev B. Freiman, Arthur F. Pudnko, P. Pulkov, Boris B. Serebrinok, SIA Radon, Moscow, RUSSIA.

Bore-hole repositories (BHR) are considered very promising for disposal of HLW and spent sealed radiation sources (SHS). For a long time they are used for storage and disposal of SRS in independent states - former republics of USSR. A typical shallow ground BHR with a 200 l stainless steel underground vessel in a concrete cell with water as SRS reservoir was designed for disposal of sources with total radioactivity up to 50 kg-equiv. 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 calculation of source 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 detailed numerical simulation of evolution fields, migration and immobilization of radionuclides in geosphere. Super-conservative scenarios were chosen for these models. The worst case comprises both breakdown of all engine barriers and flooding of disposal site plus eventual non-qualitative immobilization of sources with some sources partly

QQ10.5
PREDICTION OF WASTE PACKAGE LIFE FOR HIGH-LEVEL RADIOACTIVE WASTE DISPOSAL AT YUCCA MOUNTAIN.
Osvaldo Perando and Stanislaw 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). A major current objective of the DOE YM program is to show the feasibility of non-competitive containment of radionuclides within the waste packages [WPs] for several thousand years [2]. The US Nuclear Regulatory Commission (NRC), with input from the Yucca Mountain Site Characterization Project (YM SP), 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 Characterization and Demonstration phase of the YMP. This paper presents the hydrogeologic-analysis results for the proposed repository project. The Yucca Mountain Site Characterization Project (YM) has undertaken a major effort to improve the conceptual engineering design for a repository at Yucca Mountain.

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. The hydrologic 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 high heat generation rates, allow thermal management to be utilized as a design tool to help optimize repository performance. The Yucca Mountain Site Characterization Project (YMMP) has undertaken a major effort to improve the conceptual engineering design for a repository at Yucca Mountain.

SESSION QQ11: POSTER SESSION
WASTE FORMS
Chair: Michele A. Lewis
Tuesday Evening, November 30, 1999
8:10 P.M.
Exhibition Hall D (H)

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

Waste graphite containing fragments of nuclear fuel and fissile 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 experimentally. Self-sustaining transformation process of graphite in composition with suitable precursors was studied. Powder precursors were applied: Al₂SiO₄ [2], Al₂TiO₃ [3] and Ti₃SiO₃ [3]. Numerical 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 the chemical elements as well as undetermined phase compositions and final products were found to be rather narrow. Gas phase reaction products was studied to minimize carbon oxygen. Carbon oxide was shown to be main component of gaseous phase. Behavior of radionuclides was studied in possible processing areas. Thermal processing regions were determined for every precursor type providing complete carbon binding and minimum volatilisation of radionuclides. About 0.1 - 0.5 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 batch were ranging between 0.1 - 1 kg. Best results were obtained for the processing of graphite in combination 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.

**Q11.2**

**LONG-TERM BEHAVIOUR OF BITUMEN WASTE FORM**

Igor A. Scholze, Alexander S. Barinov, Michael I. Ovyan, Natalya V. Ovyan, Irene V. Staraceva, Zinade V. Golubeva, Scientific and Industrial Association Radon, Moscow, RUSSIA.

Three principal types of waste forms for low and intermediate level waste [LLW] 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 in a near-surface non-clayey, open testing mine 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 near-surface experimental bitumen waste blocks were prepared on base of NPP operational and other LLW and tested under laboratory and near-surface disposal conditions. Leaching of radionuclides as well as 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 the 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 important data on a waste matrix are not fully understood for modelling the waste form behaviour on time periods of several hundreds years.

**Q11.3**

**CORROSION BEHAVIOURS 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 immobilisation of waste salt generated during conditioning of spent sodium fluoride 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 make up about 90% of the CWF content. The waste matrix contains about 75 mass% sodalite, 25 mass% glass and small amounts of other phases such as halides, oxides, and oxochlorides. 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-I (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 ionic leach salt dissolution, hydration 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 Ca-containing alteration phase, less free salt released, and smaller amounts of glass corroded.

**Q11.4**

**LONG-TERM BEHAVIOUR OF BITUMINIZED WASTE: MODELLING AUTO-IRRADIATION AND LEACHING**

Pascal Chay, CEA Saclay, FRANCE; Sylvie Camaro, Benoist Simond-Tesserre, CEA Cadarache, FRANCE; Veronique Blanc, Cogemins, 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 CEAN and Cogemins 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 radioactivity, while in the deep disposal scenario, after radioactive decrease site reutilisation with water and container corrosion, water leaching is the main factor of evolution.

This paper presents two models, designed to describe respectively radioactive gas evaporation, and bituminized waste degradation under leaching.

The first model is based on the integration of simple descriptions of gas production by radioactivity, gas diffusive transport, bubble nucleation and pinning, 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.

**Q11.5**

**CHARACTERIZATION OF A CERAMIC WASTE FORM INCORPORATING RADIOACTIVE ELECTROREFINERY SALTS**


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 electrolyte 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 fusion products. Other fusion products (pure 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 fusion product or plutonium loaded salt, correspond well with the results of this study.

**Q11.6**

**Abstract Withdrawn.**

**Q11.7**

**TEM CHARACTERIZATION OF CORROSION PRODUCTS FORMED ON A SS-152R 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 152r) alloy, which contains a eutectic microstructure of a zirconium rich phase and a Zr-Fe metallic phase. In this article, we present the characterization of corrosion layers formed on the SS-152r alloy using energy-filtered transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). Specimens of SS-152r alloy, crushed to 78 to 150 gm size, were reacted in 900°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-152r alloy is more resistant to corrosion through that the Zr-based Intermetallic. This finding is significant because the Zr-Intermetallics contain many of the fusion products and all the actinide elements present in the SS-152r waste form.

**Q11.8**

**LEACHING CHARACTERISTICS OF THE METAL WASTE FORM FROM THE ELECTROMETALLURGICAL TREATMENT PROCESS: PRODUCT CONSISTENCY TESTING**


Argonne National Laboratory is developing an electrometallurgical waste form.
treatment for spent fuel from the experimental breeder reactor H. A product of this treatment process is a metal waste form that incorporates the stainless steel clad chalcogenide from the fuel and the fission products that are noble to the process, i.e., Tc, Ru, Pd, Rh, Ag. The nominal composition of this waste form is stainless steel/15 wt % zirconium/1-4 wt % noble metal fission products/<1 wt % U. The behavior of technetium is of particular importance from a dispositional point of view for this waste form due to its long half life, 2.14±5 years, and its mobility in groundwater. Leaching results will be presented from several tests and sample types. 1) 2 week microwave-leaching tests with synthetic waste form produced from irradiated chalcopyrite blank, 2) long-term (>2 years) pulsed flow tests on samples containing technetium and uranium and 3) crushed spallation reaction test on cold simulated metal waste form samples. The test results will be compared and their relevance for waste form product consistency testing discussed.

SESSION Q12 POSTER SESSION: CERAMICS
Chair: David H. Chamberlain
Tuesday, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

Q12.1 DEVELOPMENT AND CHARACTERIZATION OF CERAMIC WASTE FORMS FROM Cu-LOADED CRITICAL SILICOTITANATES: Y. Su, M.L. Balmer, E. Bitten, Pacific Northwest National Laboratory, Richland, WA, and A. Narowski, University of California-Davis, Davis, CA, M.D. Nyman and T.M. Nencoff, 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 waste, is being evaluated as a waste form. This metastable ion exchanger structure undergoes a series of phase transformations with increasing leach treatment temperature. It ultimately becomes chemically durable crystal with a stable mixed phase. The Cs leach rate first increases then decreases as a function of better 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 borosilicate glass compositions. The relationship among the Cs release rates, the phase selection and local Cs environment has been identified. Results indicate that Cs is likely to be contained in crystalline phosphate Cs2X2SiO4. Correlations between chemical durability and crystal structure of component oxides will be presented.

Q12.2 MICROSTRUCTURE AND CRYSTALLIZATION SEQUENCE OF SYNROC SAMPLES CRISTALIZED FROM CuCeTi2O7 CHEMICAL SYSTEM: H.RITEMAN, AIRMS/CEM. Investigating the physical and chemical properties of the waste form produced by varying the solid content and electrolyte strength (aluminum nitrate) in the precursors.

Pyrochlore phase has been considered as a durable crystalline waste form for holding weapon-grade Pu. CuCeTi2O7 pyrochlore phase is a chemical analogue for the real waste form. CePuTi2O7 pyrochlore was synthesized by annealing oxide mixture of Ce2O3, Ti2O3, and CuO with stoichiometry of CuCeTi2O7. The annealed products contain Cu-oxo-pyrochlore phase, Ce-bearing perovskite, CeO2, and minor other Ce-bearing phases. There are no glassy phases in the grain boundary between pyrochlore and perovskite. The orientation relationship between the neighboring pyrochlore and perovskite is not random. There are no glassy phases in the grain boundary between pyrochlore and perovskite. The CeTiO3 phase does not form in the CePuTi2O7 chemical system. Heat-treatment of pyrochlore in the CuCeTi2O7 chemical system. A pseudo-binary phase diagram for the CuPuTi2O7 system is also presented.

Q12.3 THE CORROSION BEHAVIOR OF TITANATE CERAMICS FOR PU DISPOSAL, RATE-CONTROLLING PROCESSES: Allen J. Binko, C.J. Mertz and D.C. Chamberlin, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

The Plutonium Immobilization Project of the Fissile Materials Disposition Project is a project to develop a material for the immobilization of Pu. The goal of this paper is to describe the rate-controlling corrosion mechanism for a zirconate-titane-oxide ceramic. Short-term MCC-1 (up to 35 days) tests were conducted in DW at 80°C. These data indicate that the N2/Ca increases rapidly for up to 3 days, and changes little after that. This rate is 0.7 g/m² d based on Ca release and about 10^-5 g/m² 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 synthetic waste form produced in DW at 80°C for up to two years. The normalized mass losses based on Ca, Zr, Gd and Pu continue to increase from 150 to 728 days, showing that corrosion continues for these tests. The release rates based on Pu and Gd are on the order of 10^-5 g/m² d. Results from MCC-1 and PCT-B tests show that the release rate of Ca from a zirconate-titane-oxide ceramic is in short-term tests and lower in long-term tests. The release rates of the other elements are controlled. Factors affecting the rate-controlling corrosion mechanism will be discussed in the full paper.

Q12.4 POROSITY AND STRUCTURE OF PARTICLE AGG. REGATES IN SPRAY-DRIED MICROSPHERES: S. Lynnard, O. Spalla and T. Zeeb, SCM, CEA, Sacyk, FRANCE; J.R. Birtel, E. Singel, R. F. Ferri and J.L. Woldfleie, ANSTO, Materials Division, Lucas Heights, AUSTRALIA.

Precursor powders for producing advanced ceramics are often prepared by spray-drying sols, to produce primary particles of ease handling during subsequent processing. The spray-drying process involves drying atomized droplets of the sol (typically <50 micron diameter) under controlled conditions in hot air to produce mesoscopic, gel microspheres. In the Synroc process for nuclear waste disposal, such titanium-based powders, with controlled pore structures, react sinter to form 90 wt % dense waste solutions, before thermal processing. A series of spray-dried titanium powders was produced by varying the solid content and electrolyte strength (aluminum nitrate) in the precursors. The resultant powders were characterized by SEM, nitrogen sorption, SANS, SAXS and USAXS. The USAXS and conventional SAXS of the dried powders was measured over three decades of q from 2 micron and 0.5 nm, real space. Absolute scaled measurements in this range show two exponential regimes and a transition regime. 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 microscopic powder grain (from the Porod regime); - the total porosity of the dried grain 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 is the sol and the porosity of the resulting spray-dried powders will be discussed.

Q12.5 SOLID SOLUBILITIES OF Pu, U, Hf AND Gd IN CANDIDATE CERAMIC PHASES FOR ACTINIDE WASTE IMMOLATION: E.R. Vance, ML. Carter, B.D. Begg and S.P. Leung, ANSTO, Menai, AUSTRALIA.

Solid solubility limits of Pu, U, and the neutron absorbers Hf and Gd have been measured for zircon, monazite, titane, perovskite, apatite and whitlockite in almost all cases where these limits were not known beforehand. The method used was to over-saturate the host phase with the dopant, using a non-stoichiometric substitutional scheme, and then to allow the dopant content of the host phase to be determined by liquid scintillation or mass spectrometry. Ternary U + Hf + Gd solubility was measured in both synthetic and reactor derived materials, and tetradentate Pu solubilities will be reported. X-ray absorption near-edge and diffuse reflectance spectroscopies were used to show that U was tetradentate in Udensed CeTiO3 and monazite, and apatite, and can be present in solid phase. Hf, in the synthetic and reactor derived materials, was found to be soluble in both titane and monazite respectively. Hf solubility in apatite was reported. Approximately 0.3 and 0.01 % of Gd and of Hf are found in titane and monazite respectively.

Q12.6 CATHODOLUMINESCENCE OF THE GARNET HOST PHASE, ACTIVATED BY Ce, U AND Pu: Maria V. Zamorskyak, Boris E. Burakov, Kholopov Institute, St. Petersburg, RUSSIA.

The garnet (Y, Gd, An)3(Al, Ga, An)5O12 has been suggested for the immobilization of the military actinide-wastes. This crystalline phase is chemically and mechanically durable and desirable for the
incorporation of Pu, Am and other elements in the form of solid solutions. However, the lattice parameter of garnet depends on the valence state of the actinide ions. The ions of Ce IV and U VI are good imitators of the Pu IV and Np IV. And at the same time the military actinide-wastes contain these elements. Ions Ce IV and U VI have characteristic cathodoluminescence (CL) lines in clear-blue green region of the spectrum. However, in our case the ions of Ce IV and U VI CL emission in visible region. The garnets of different composition and oxides have characteristic CL bands. That is why the method of cathodoluminescence was suggested for the effective control of state of actinides in Ceramics and for phase identification. The samples of garnet were synthesized by a method that uses melting (at T=1300-2000°C). For successful incorporation of Ce IV, U IV, Pu IV ions in garnet the charge and radii-compensating elements (Sn IV) were used. All samples were studied by low methods: cathodoluminescence analysis and microprobe analysis. The use of two local methods gives the information on the composition and CL emission in the same microvolume (3x3µm2) of samples. The experiment shows the difference between Ce IV and U VI and U IV 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% wt) were studied. For such garnets the correlation between accommodation of Ce IV and Pu IV was found. The simultaneous use of local methods: CL and microprobe are very effective for studying the different kind of ceramics, for examples, CL emission: ZrO2-Pu and Zr2O3-Pu.

Q11.2
ALUMINA-DOPED TITANIA CERAMIC WASTE FORMS PRODUCED BY MELTING METHOD: Masayoshi Uno, Hajime Kinoshita, Shinsuke Yamamura, Osaka University, Department of Nuclear Engineering, Osaka, JAPAN.

It is of great interest to investigate the material in which nuclear waste can be emplaced for a long period by a simple procedure. We found that rare earth elements (RE)-Ti complex oxides with a ideal composition RE2Ti2O7 melt up to 1672 K by using aluminia. We firstly studied the phase stability and melting temperature of aluminium-doped RE2Ti2O7 system with the composition variation. Secondly, some TiO2-based waste forms containing RE and alkali earth elements for immobilization were prepared: 1) with aluminium-doping by a simple melting method at 1673 K in 1 hour, 2) without aluminium-doping by pressing at 298 MPa up to 1673 K for 5 hours, and some properties were investigated. Melting of the mixture of Nd2O3, CeO2, TiO2 and Al2O3 at 1673 K in 1 hour produced RE2Ti2O7 phase, and the chemical formula of the oxide was assumed to be (Ce0.5Nd0.5)2Ti2O7. A Differential Scanning Calorimetry (DSC) measurement showed that the melting temperature of this compound was 1646 K. Density of the aluminium-doped oxide was higher than that of the oxide obtained by the pressing and sintering without aluminium. 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 aluminium-doped oxide was around 7 GPa. A 3-day Sochet leach test (Masayoshi Uno) showed an Inductive Coupled Plasma Spectrometer (ICP) showed that normalized reaching rates of Ti for the oxide obtained by the pressing and sintering was 5.5 ± 1.3 kg/m2 and that for the aluminium-doped oxide was 2.5 ± 1.3 kg/m2. The value of Sr for the pressed and sintered sample was 1.0 ± 0.3 kg/m2, but that for aluminium-doped sample was below the detection limit (0.01 ± 0.1 kg/m2). Alumina was not detected from the leachate of the aluminium-doped sample.

Q11.2.8
MELTING SIMULATED HIGH-LEVEL LIQUID WASTE WITH ADDITION OF TITANIUM AND ALUMINUM NITRIDES: Masayoshi Uno, Hajime Kinoshita, Shinsuke Yamamura, Osaka University, Department of Nuclear Engineering, Osaka, JAPAN.

Calculated simulated high level liquid waste (HLW) 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 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 this alloy phase melts up to 1673 K by alloying the refractory platinum metals or Np with corrosion products (Fe, Cr, Ni), and that the oxide phase melts up to 1823 K by forming complex oxides of fission products and the metal elements of the reducing agents. In the present study, 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 Sochet leach test showed that the concentration of any elements in the leachate was below the detection limit of the Inductively Coupled Plasma Spectrometer (ICP-MS) 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.

Q11.2.9
ISOMORPHIC CAPACITY OF SYNTHETIC SPHENE WITH RESPECT TO Gd AND U: Sergey V. Stebnowsk, SL Rusak, Moscow, RUSSIA; Sergey V. Vasilyev, Boris S. Nikonorov, Boris I. Omelintsev, Inst. of Geology of Ore Deposits, Moscow, RUSSIA.

Phase relations in the system CeO2-TiO2-SiO2 (N2O5-Al2O3-Gd2O3-U3O8) 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 Ce1-x-Nax-Gd2O3-TiO2-SiO2 sphere is still present at x≤0.3 whereas within the series Ce1-x-Ux-Gd2O3-TiO2-SiO2 limiting x value is 0.1. In the melted samples of the system CeO2-TiO2-SiO2 (N2O5-Al2O3-Gd2O3-U3O8) along with sphere, the other phases in the samples: rutile, chevkinite, moritite, crystobalite, and pyrochlore-structured phases were found. Sphere is able to incorporate up to 21.5 wt % Gd2O3 and 9.5 wt % U3O8 or, in formula units: 0.25 Gd2O3 and 0.07 UO2. Minimum concentrations providing to reveal the pyrochlore-structured phase are 8.9 wt % Gd2O3 and 6.6 wt % U3O8 in the Gd and U-containing systems, respectively. Chevkinite-perovskite is present in the sample with Gd2O3 and 8.9 wt % Gd2O3 but it absent at higher Gd concentrations. Maximum Gd2O3 concentration in chevkinite and pyrochlore-type phase reached 45.4 and 35 wt % respectively. Maximum U3O8 content in the pyrochlore-structured phase was found to be 45.8 wt %.

Q11.10
CHEMICAL DURABILITY OF YTTRIA-STABILIZED ZIRCONIA FOR HIGHLY CONCENTRATED TRU WASTES: Hajime Kinoshita, Masayoshi Uno, Shinsuke Yamamura, Osaka University, Department of Nuclear Engineering, Osaka, JAPAN; Kenichi Kurokumo, Japan Atomic Energy Research Institute, Dept of Nuclear Energy System, Ibaraki, JAPAN; Hidemi Yamamura, Tetsujiro Banno, 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 host matrix for the immobilization of highly concentrated TRU wastes. YSZ structure is able to contain TRU elements as a part of that structure. Possible advantages from the YSZ waste form are: 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 (30, 30, 40 wt %) were fabricated (sintered in Air or Ar, at 1725 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 Q11: POSTER SESSION: GLASS WASTE FORMS
Chair: John D. Vieni
Tuesday Evening, November 30, 1999
8:00 P.M.-9:00 P.M.
Exhibition Hall D (H)

Q13.1
RAMAN AND HIGH-RESOLUTION ELECTRON MICROSCOPY STUDIES OF NAPHELINE NaAlSiO4 CRYSTALLIZATION IN SIMULATED HIGH-LEVEL WASTE GLASSES: Hong Li, Yuh Su, Meow Qie, John D. Vieni, and Pavel Harm, Pacific Northwest National Laboratory, Richland, WA.

Nepheline crystallization was previously studied over the composition
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.

**Q13.5** LIQUIDUS TEMPERATURE OF HIGH-LEVEL WASTE BOROSILICATE GLASSES WITH SPINEL PRIMARY PHASE

Pavel Hrona, John Vienna, Jarrod Crum and Greg Piepel, Pacific Northwest National Laboratory, Richland, WA.

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 $\text{UO}_2$ (0.09 mass%). The primary crystallization phase for most glasses was spinel, a solid solution of trioctet with other oxides (mainly $\text{FeO}$, $\text{MnO}$, and $\text{Cr}_2\text{O}_3$). We resolved several major experimental difficulties, such as dealing with a large quantity of insoluble $\text{UO}_2$ and establishing equilibrium of glass samples with atmospheric oxygen while minimizing volatility losses (the strong effect of $p\text{O}_2$ on spinel formation made $T_L$ sensitive to the temperature history of the specimen). The $T_L$ values ranged from 850 to $1310^\circ\text{C}$; $T_L$ increases per 1 mass% component additions to a baseline composition were $\text{Cr}_2\text{O}_3$ $260^\circ\text{C}$, $\text{NiO}$ $85^\circ\text{C}$, $\text{TiO}_2$ $42^\circ\text{C}$, $\text{MnO}$ $32^\circ\text{C}$, $\text{Al}_2\text{O}_3$ $18^\circ\text{C}$, and $\text{Fe}_2\text{O}_3$ $50^\circ\text{C}$. $T_L$ decreases per 1 mass% component additions were $\text{Na}_2\text{O}$ $25^\circ\text{C}$, $\text{Li}_2\text{O}$ $28^\circ\text{C}$, $\text{K}_2\text{O}$ $20^\circ\text{C}$, and $\text{BaO}$ $8^\circ\text{C}$.

Other oxides ($\text{MnO}$, $\text{SO}_2$, and $\text{U}_2\text{O}_3$) had little effect. The role of $\text{UO}_2$ in spinel formation remains unclear (other data suggest that $\text{UO}_2$ increases $T_L$ by $300^\circ\text{C}$ per 1 mass%).

**Q13.6** EFFECT OF RARE EARTH CONCENTRATIONS ON THE LIQUIDUS TEMPERATURE OF RARE EARTH-ALUMINO-BOROSILICATE GLASSES

Michael J. Schweiger, Pacific Northwest National Laboratory, Richland, WA.

David K. Feeder and Irene A. Remmer, Savannah River Technology Center, Aiken, SC.

The liquidus temperature ($T_L$) of mixed rare earth-alumino-borate glasses was studied. The concentration of total rare earth oxides was systematically varied between 38 and 54 mass percent in glass. The composition with the rare earth oxide mix was also varied in this study. Thirty-two glasses were melted in covered platinum-rhodium crucibles at $1350^\circ\text{C}$ and quenched on a steel plate. The temperatures of the glasses were measured by 24 h uniform temperature heat treatments in a covered platinum-rhodium crucibles. Two primary crystalline phases were found to precipitate from these glasses, mullite with $T_L$ values ranging from 1164 to $1263^\circ\text{C}$ and rare-earth silicate (RES) with $T_L$ values ranging from 1163 to $1298^\circ\text{C}$. 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 $T_L$ and the rare earth oxide concentration and average ionic radius for glass in both primary phase fields. A minimum in $T_L$ is found at roughly 44 mass percent rare earth oxide concentration with increasing $T_L$ at both higher and lower concentrations.

**Q13.7** GADOLINIUM AND HAFNIUM ALUMINO-BOROSILICATE GLASSES: DIRECT MEASUREMENTS OF THE COMPOSITIONS AND THEIR EFFECTS ON Cd AND Hg SOLUBILITIES IN THE GLASSES

Denguo 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, M.M. Struchman, 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 in the batch 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 glasses was conducted. The compositions of a representative number of glasses were obtained with an electron microprobe. One of these glasses was known to have micron-sized Gd-rich silicate crystals with an igneous structure. The precipitated crystals were about gadolinium (about 80 mass% $\text{Gd}_2\text{O}_3$) than the bulk glass. The glass composition near the precipitated crystals was depleted in Gd and richer in the other glass compositions. 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\textsubscript{2} and for H\textsubscript{2}O. The electron microprobe data shown that Na\textsubscript{3}C\textsubscript{2}O\textsubscript{4}, Mg\textsubscript{2}C\textsubscript{2}O\textsubscript{4}, and Mg\textsubscript{2}SiO\textsubscript{4} were not present in the preparation of the high Na\textsubscript{2}O (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. Oka I. Krymskaya, Tert-1, N. Lashkov, Fiodor A. Lifachev, Sergey V. Stefanovsky, Oka V. Tolostov, 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 (LLW) of NPPs, spent catalytic, sorbents, and cathode ray tube (CRT) glass is suggested. Preliminary experiments on vitrification in crucibles in a laboratory resistant furnace were carried out. A possibility of 40 wt. % of LLW 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 LLW.

The most promising method of mixed waste vitrification is inductive melting in a crucible crucible (IMCC) due to high productivity, high temperature and energy. Bench-scale tests have been carried out. Preliminary testing of IMCC of spent CRT glass and a batch from this glass and LLW salts (surrogate) was also conducted. LLW 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 glass made 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 calcium fluoride (CaF\textsubscript{2}) in silicate lead to increase electric conductivity and reduces viscosity of the melt to values provided IMCC. The batch is preferably fed as calcite.

**SESSION QQ14**

**POSTER SESSION - REPOSITORY, CONTAINERS, SPENT FUEL, AND CLADDING**

**Chairs:** Brian M. Redd and Lawrence H. Johnson

Tuesday Evening, November 30, 1999

8:00 PM

Exhibition Hall D (H)

**QQ14.1**

**BEHAVIOR OF MgO AS A CO\textsubscript{2} SCAVENGER AT THE WASTE ISOLATION PILOT PLANT (WIPP), CARLSBAD, NEW MEXICO. Pengzhao Zha, Zheng, and Jin Krumholz, Sandia National Laboratories, Albuquerque, NM.**

The WIPP, a repository for defense-related transuranic nuclear wastes, is located at about 1,500 feet underground in the bedded rock salt of the Salado Formation 26 miles southeast of Carlsbad, New Mexico. MgO backfill was included in the repository design to scavenge CO\textsubscript{2} produced by decaying organic components in the waste and buffer pH. However, it has been suggested that early-formed precipitates include Mg\textsubscript{2}O pellets, thus preventing complete reaction with CO\textsubscript{2}. However, recent data suggest otherwise. To address this concern, hard-formed MgO pellets 2.4 mm in diameter were immersed in WIPP brines and exposed to CO\textsubscript{2} at CO\textsubscript{2} partial pressures near 1 atm. no-precipitate MgCO\textsubscript{3}\textsubscript{2}H\textsubscript{2}O\textsubscript{2} formed, but partial pressures near 0.05 atm. produced hydromagnesite [4-3 MgCO\textsubscript{3}Mg(OH)\textsubscript{2}3-4 H\textsubscript{2}O]. No-precipitate was more effective in preventing Mg\textsubscript{2}O precipitation. It should not form in the WIPP where the excess Mg\textsubscript{2}O will maintain a low CO\textsubscript{2} partial pressure. The difference in behavior occurs because no-precipitate forms dense mats of needle-like crystals whereas hydromagnesite, initially forms sparse aggregates of plate-like crystals. Hydromagnesite ultimately will react further producing magnetite (MgCO\textsubscript{3}), though rates were unknown. Hydrothermal studies (to 200°C) demonstrated that the existing fluids strongly affects the transformation rates.

Increasing the ionic strength of NaCl brines increases the conversion rates but adding pF 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 Gd-rich brines indigenous to the Salado. This resistance agrees with field observations regarding the very slow transition of hydromagnesite to magnetite in present-day evaporitic environments. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, on behalf of the United States Department of Energy under Contract DE-AC04-94AL85000.
(diginite). The energies of the (111) and (110) non-polar surfaces of CaS are calculated using the interface Green’s function technique. The (111) surface is the least energetic, in agreement with the cleavage pattern of diginite mineral. The low value of the surface energy (of about 1/3 of the surface energy of pure Ca) suggests that a precipitation of CaS may be responsible for the embrittlement of Cu at intermediate temperatures. Locally semi-conducting Green’s function method is used to obtain the formation and interaction energies of native point defects in the bulk diginite. The results show that diginite exists as a non-stoichiometric compound Ca$_2$S$_2$ with stable stoichiometric 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 degree of radiation response of Ca$_2$S$_2$, which is consistent with the superionic behavior of the high diginite. This work is funded by SKB AB, the Swedish Nuclear Fuel and Waste Management Company.

Q14.6

**SIMULATING LEACHING EXPERIMENTS IN THE PRESENCE OF $\gamma$ EXTERNAL SOURCES ($^{60}$Co).** Joaquín A. Serrano, Javier Quiñones, Paloma Díaz-Aroca, Jose L. Rodríguez-Alvarez, Joaquín Cobas, Dept de Físic Nuclear, CIEMAT, Madrid, SPAIN; Jose A. Esteban, Aurora Martínez-España, 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. Particularizing in the effect of the radiation on the leachant, it cause generation of anionic 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 SIMULFUEL (natural UO$_2$ doped with non-radioactive elements simulating fuel, transuranic elements and fission products) and the incidence of some saline and granite bentonite waters both under initial anoxic conditions. To emulate $\gamma$ radiation field of a spent fuel, leaching experiments with external $^{60}$Co sources in a CIEZAT irradiation facility (Nagoya) were performed. The $\gamma$-ray dose rate used was 0.014 Gy/s. Preliminary results indicate that radiation produces an increase of dissolution rate, being the highest concentrations observed close to those in our atmospheric environment without radiation field. On the other hand, a tentative approach to modelize the radiation-induced leaching in the environment 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 radionuclides such as CO$_2^-$, CO$_3^{2-}$, Cl$^-$, ClO$_4^{-}$, etc. These studies are being carried out in the Dept. de Física Nuclear (CIEMAT) within the agreement CIEMAT-ENRESA in the frame of the final disposal of nuclear irradiated fuel.

Q14.7

**OXIDATIVE ALTERATION OF SPENT FUEL IN YUCCA MOUNTAIN REPOSITORY ENVIRONMENT - SEM/AFM INVESTIGATION AND GEOCHEMICAL MODELING.** Yifei Wang, Michael R. Winningham, H. M. Hufnagel, X.D. 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 kantoberite, rutheniferite, scheelite, and kimotite. Silicate-free U-bearing minerals (such as fero-uraninite) and some products of uraninite and silica-depleted water during late stage reaction. Electron energy-loss spectroscopy results show the $E_{1}$ and $2E_{1}$ 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 pH 2.2, TOC = 10 ppm, and T = 25 $^\circ$C. These calculated results show spent fuel will be replaced by U$^{4+}$-bearing phases of haiselite and soddyite. Silicate-free U$^{4+}$-phases (e.g., scheelite) will not occur in the studied environment. If phosphate is used as a component of backfill materials, the dissolved uraninite will form less soluble phosphate phase, patinate. Based on predicted Gibbs free energies of formation for the phases with some structure, Ca$_2$-uraninite is able to incorporate Na$_2$O$_4$, but not Ca$_2$. Other minerals that will also form are stellite (molybdate), neotrite, hemimorphite, and blite. 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.

**Q14.8**

**RELEASE OF RADIONUCLIDES FROM DEFECTIVE HIGH-BURNUP UO$_2$ AND MOX FUEL IN A HEAT-FOUNDATION.** Jean-Paul Gérard, Javier Gimenez, Achim S. Stekas, Detlef Wegen. European Commission, Directorate-General JRC, Institute for Transuranium Elements, Karlsruhe, GERMANY.

The processes responsible for the release of radionuclides from spent fuel repository are dissolution and transport as result of the groundwater flow. The cladding will be the last of natural and man-made barriers before 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 fuel, 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 major elements uranium and plutonium is 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 a 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 $\alpha$-radiolysis is due to an increased inventory of $\alpha$-emitters and also due to large S/N ratio. In comparison to UO$_2$ the release rate of some major fission products is about two orders of magnitude higher for MOX fuel. Electrochemical techniques are used to investigate the complex corrosion behavior of the heterogeneous MOX fuel materials.

Q14.9

**CORROSION OF UNIRRADIATED N-REACTOR FUEL IN UNSATURATED TEST CONDITIONS.** M. Goldberg, D. L. Beauchesne, S.F. Wolf, Y. Tuan. Canadian Nuclear Safety, Chemical Technology Division; T.S. Berg, 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 Mixed Geothermal 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 samples. Both unirradiated fuel samples and irradiated fuel samples, both unirradiated and irradiated fuel samples, 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. We provide an estimate of corrosion rate of the various test hypotheses regarding corrosion mechanisms, and provide a basis for comparison of corrosion results in the presence and absence of a radiation field. Unirradiated corrosion tests were conducted in an air atmosphere at 60 $^\circ$C, with a small quantity (0.76 mL) of simulated groundwater (EL-13) injected twice weekly. Results will be presented indicating that the fuel begins to oxidize immediately, forms a series of uranium oxides, generates $\text{H}_2$, 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 absorbed uranium on the vessel walls, and estimating uranium content of the corrosion products. The corrosion products exhibit several interesting properties of significance to repository performance: significant quantities of corrosion products per surface from a coupon; the corrosion products form films and aggregate in loosely consolidated clumps; and in the presence of excess water, the products exhibit characteristics of hydrophilic films, moving with and aggregating at the leading edge of the solution.

Q14.10

**POSSIBILITY INCORPORATION OF TRANSURANICS INTO URANIUM ALTERATION PHASES.** Cheol-Won Kim, David J. Wrotniak, 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 $U^{4+}$ phases. The incorporation of radionuclides contained in spent fuel into the structure of $U^{4+}$ phases will effect their mobility. A series of precipitation experiments was conducted to determine the potential incorporation of $Ce^{3+}$, $Nd^{3+}$, and $Am^{3+}$ into uranium alteration phases. Immersion of $UO_2$ in $1\ M\ H_2O_2$ was produced by dissolving uranyl oxalate in a solution containing sodium oxalate. The leachate solutions used in these tests were doped with either 2.1 ppm cerium or 399 ppm neodymium. The ICP-MS results indicate that about 308 ppm Ce was present in the leachate 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. The resorption (Ce)$_2$($UO_2$)$_3$ oxalate in a solution containing calcium oxalate. The leachate solutions used in these tests were doped with either 4.6 ppm cerium or 277 ppm neodymium. The cerium concentration in the solid phase from the 198-day test was 183 ppm, whereas Nd contents were 1310 ppm after seven days and 688 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.

Q11.4.11
FIT INITIATION AND EVOLUTION ON STAINLESS STEELS AND Ni-BASED ALLOYS. Peter J. Bedrossian and Joseph C. Farber, 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 developed a model of the spatial and temporal evolution of surface roughness caused by corrosion, spanning length scales from nanometers to millimeters. By applying Atomic Force Microscopy (AFM) in vacuum, we have observed the surface topological 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 observed 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 622, which do not reveal similar pit growth processes. The authors are grateful to Dave Fick for technical assistance. Research was performed at Lawrence Livermore National Laboratory under the auspices of the US Dept. of Energy under Contract W-7405ENG-36 and was supported by the Yucca Mountain Project.

SESSION Q15. POSTER SESSION
WASTE PROCESSING
Chair: Andrew H. Bond
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

Q15.1
ATTRACTIVE INTERACTIONS BETWEEN REVERSE AGGREGATES AND PHASE SEPARATION IN CONCENTRATED MALONAVIDEXTRACTANT SOLUTIONS. Laurence Martineau, Corinne Erdinger, L. Belloni, Thomas Zemb, Laurence Berthon and Charles Madic, CEA Sarlcy and Marcoule, FRANCE.

We investigate the supramolecular chemistry associated with the liquid-liquid selective extraction using reverse micelles in equilibrium with excess brine. Using SAXS, conductivity and phase behaviour determinations, we show that concentrated solutions of microemulsion extractants, dimethylbisdithiobutylyltracnedithiolamine (DMDDBTMA), are organized in reverse micellar aggregates which have many features in common with reverse micelles: aggregate microstructure of these reverse globular aggregates as well as their interaction potential are determined from absolute scattering curves. An attractive interaction responsible for the demixing of the oil phase when in equilibrium with aqueous oil and water are relative to the destructive 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 polarizable water core of the reverse micelles. The attractive interaction in the oil phase, equilibrated with water, is determined as a function of temperature, extractant molecule concentration, as well as proton and neodymium (III) ion concentration. It is shown that van der Waals interactions, with an effective Hamaker constant of 3.1 kcal/mol, quantitatively explain the behavior of DMDDBTMA in n-dodecane in terms of scattering as well as phase stability limits.

Q15.2
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; Liming R. Zou, 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-related purposes. The residual wastes from these processes include 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, Hanford's current baseline strategy for treating alkaline radioactive wastes involves removal of the supernatant and sludge prior to sludging 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 40 years. Because sludge washing operations will separate an inhomogeneous 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 materials from the PUREX, PUF, and PACE purification flowsheets. With this information, practical capabilities will be developed that permit the identification of those factors having a high probability of actinide solidification during sludge pretreatment. The influences of apparent oxidation state on actinide behavior are discussed. This work is funded by the Environmental Management Science Program of the Office of Energy Research, Environmental Management, United States Department of Energy, under contract number W-31-109-ENG-38.

Q15.3
NOVEL Sr. SELECTIVE INORGANIC ION EXCHANGERS. Cyrille Nyman and T.M. Nenoff, Sandia National Labs, Albuquerque, NM; M.L. Balmer and Y. Su, Pacific Northwest National Laboratory, Richland, WA; A. Novoskys and H. Xu, Dept. of Chemical Engineering and Material Science, University of California-Davis, CA.

Radionuclides of Sr and Cs account for > 99% of the radioactive inventory of the Hanford waste tanks. We are currently synthesizing novel materials for sequestration (ion exchange 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 exchange materials which are selective for linear and branched 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 heterotrons can be made into the niobate framework, and functional properties (i.e. ion exchange) vary with concentration of the heterotrons. 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 heterotrons concentration. This work was supported by the U.S. DOE under contract DE-AC04-94AL85000.

Q15.4
DEMONSTRATION OF CESIUM REMOVAL FROM THE FUEL STORAGE WATER AT THE SAVANNAH RIVER SITE AU-BUILDING DISASSEMBLY BASIN USING 3M EPM EMBLEB disposable filter technology. Lawrence N. Qii, 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 paper describes results from a seven-day demonstration of the use of 3M EPM disposable filter loaded with ion exchange material (potassium cobalt hexacyanoferrate (Colix)) for cesium uptake from the R-Disassembly (radioactive 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-treatment/Colix configuration on a scale, to remove cesium from R-Disassembly Basin in a linear processing flow.
rate of 22.7 liters per minute. Over 210,000 liters of R-Diasmblon Basin water was processed through the PADD without a cessation breakthrough. The 200 MCR (Macro-Batch 2) of radioactive sludge slurry into a durable borosilicate glass for permanent geopolitical disposal. To meet the reporting requirements as specified in the Department of Energy's Waste Acceptance Product Specifications (WAPS), for the final glass product, mass effects, radioactive elements, and the secondary waste and fast extraction or rapid kinetics per unit of flow.

**QQ15.5**

**SOFTEN EXTRACTION OF TC-99 FROM INTERMEDIATE LIQUID WASTE BY DIBENZO-18-CROWN-6.** Patricia Paceit-Hartmann, Los Alamos National Laboratory, Chemical Science and Technology Division, Los Alamos, NM; Alan Raymond, Centre d'Etudes de l'Eau et des Terres, 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 (t1/2 = 2.1 x 107 yrs), TC-99 is one of the key isotope that should always be analyzed in the radioactive liquid waste streams from the reprocessing industry where the largest concentrations are to be expected.

Furthermore, To-99 is a high-yield fission product of uranium and as a pure 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 To-99 extraction providing recommendations that will be useful for extracting it from acid and basic ILW streams. To-99 from To-99, by Dibenzo-18-Crown-6 (DB18C6) has been investigated and a simple 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 the reprocessing plant, France, and results show that DB18C6 is highly selective towards To-99. Through the process, with only one single extraction step, 85 to 95% of To-99 has been extracted. The total preparation time of the chemical separation takes only 20-30 minutes. 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.** Michael P. Reynolds, Mujd Arzumi, K.R. Czerniawski, Massachusetts Institute of Technology, Nuclear Engineering Department, Cambridge, MA; Jennifer Choe and Environmental Laboratory, National SfE Program, Idaho Falls, ID.

AIROX is a dry process involving irradiated fuel oxidation by O2 and reduction under H2 between 400-600 °C. The oxidation transforms UO2 to U3O8 with a volume increase on the order of 30%, allowing the removal of the volatile and semi-volatile fission products. Remaining fuel, with UO2, that is formed 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 neutron and electron transport reactions. Removal based on chemical properties and tendencies are estimated. High removal rates are expected for Cs, Sr, Te, 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 to 200 years, there is a slight decrease in fraction removal absorbed, 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 absorption AIROX should remove approaches 90%. On 10 years on, 115% is the isotope which contributes most to the total neutron absorptions removed by AIROX, throughout the time span of 1 to 200 years, are 133Xe and 133Cs. Lanthanides, which have high neutron capture cross-sections, are not effectively removed by AIROX AIROX also affects 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%. On 10 years on, 115% is the isotope which contributes most the 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.** Tori L. Fejinger 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 of [Macro-Batch 2] of radioactive sludge slurry into a durable borosilicate glass for permanent geopolitical disposal. To meet the reporting requirements as specified in the Department of Energy’s Waste Acceptance Product Specifications (WAPS), for the final glass product, mass effects, radioactive elements, and the secondary waste and fast extraction or rapid kinetics per unit of flow.

**QQ15.8**

**MATRIX-ASSISTED LASER DESORPTION-IONIZATION MASS SPECTROMETRY OF ORGANIC MOLECULES ON SODIUM NITRATE.** David R. Ermer, Michelle Baiz-Knorr, Michael R. Papoutsakis, Richard F. Hughson, Jr., 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 solution in mixed high-level radioactive waste, the key low-level radioactive waste storage form. In conventional matrix-assisted laser desorption-ionization (MALDI) mass spectrometry using UV lasers, the salt coating organic molecules would be dispersed in a matrix chosen for optimal laser absorption. However, we find that the organic molecules adsorbed in sodium nitrate by a KrF laser (248 nm) can produce 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 our laser into the mid-infrared stretching modes of the sodium nitrate. Interestingly, addition of ethylalcohol (ECAH; hydroxy-cyclo-aliphatic acid) to the matrix material fails to increase the organic-iod yield in its MALDI. We compare the two sensitivities, and we consider the differences in mechanisms which underly the differing abilities.

**QQ15.9**

**SPECTROSCOPIC CO2 TREATMENT OF RADIOACTIVE GLASS.** Thomas Hartmann, Patricia Paceit-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 oilsolvent was to slur them in a commercial (TRU) waste mixtures with water and emulsifiers and to utilize them in a gaseous mixed. A polymerization agent, methyl-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 TRUACT-H II transport container; and (b) waste acceptance criteria (WAC) to be stored at the Waste Isolation Pilot Plant (WIIPP). Waste drums stored for volatile organic compounds (VOCs) which are containing high tetrahydrochloroform carbon contents, with up to 180,000 ppm (part per millions by volume). The administrative limit is 7510 ppm. Flammable organics can also be measured in high concentrations with 1000 ppm (mass) versus a limit of 50 ppm. These high numbers of TCO (total organic carbon) as well as the free liquid content requires
a highly efficient and fast method for extracting the diols from the sludge without repackaging. In this study, we demonstrate that organic solvents can be effectively used to remove organics from the sludge and quantitatively extracted by applying a supercritical CO$_2$ (SCCO$_2$) treatment. The effect of SCCO$_2$ treatment applying different CO$_2$ pressure and temperature conditions (84 MPa, 38°C; 90 MPa, 55°C; 100 MPa, 70°C) on the recovery of solubilized organics is presented in the free liquid content and the impurities in the WAC and VOC and TOC in the WPP. The developed 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 STOREROY
Chair: Darrell S. Dunn, David W. Scharnow, and Lars O. Werme
Wednesday, December 1, 1999
Room 203 [H]

8:30 AM *QQ16.1 FABRICATION AND TESTING OF COPPER CANISTER FOR LONG TERM STORAGE OF SPENT NUCLEAR FUEL Lars O. Werme, Swedish Nuclear Fuel and Waste Management Co (SKB), Stockholm, SWEDEN.
In 1990, 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) developed testing and fabrication methods for copper canisters d) evaluated the long-term chemical and mechanical behavior of the canister e) conducted preliminary designs for a factory for the production of copper canisters 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 inner layer of tantalum would provide sufficient corrosion protection and would have a sufficient mechanical strength. This canister can be produced by several methods, such as casting from molten metal, hot extrusion, and drawing and rolling. These methods have been evaluated at full-scale and the results of 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 capable of welding with a 100 kW electron beam welding unit, a 2 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 Grindrod, Namul Sehur, 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 specimen 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 75°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 potentials 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 concentrations of passive dissolution rate measurements with thermally aged (750°C) Alloy 22 indicate that the 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 WHITE CANISTER APPLICATION. Kjell Peterson, 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 at a time of 1000 yr and the ultimate objective 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 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 PLANE FRACTURE. Joosok Ahn, Paul L. Chambrel, 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 plane 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 to the governing equations, the non-dimensional 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 the 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 fair agreement with the experimental results conducted for a time period of 1000 hr by assuming that the void ratio at the tip has a prescribed value.

10:15 AM QQ16.5 THERMAL STUDIES FOR RADIOACTIVE WASTE MANAGEMENT. Demiriecz Marconzi, Sabine Le Bonhomme, EDF, Dept. of Heat Transfer and Aerodynamics, Chassieu, FRANCE, Bruno Soulier, Ecole Nationale Superieure, Cachan, FRANCE, Yves Guilloux, ANDRA, Chizéney-Maillot, FRANCE.
A radioactive waste disposal is characterized by an arrangement of various essential factors: repository concept, number of 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, the temperature should be such that 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/HIT 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 Experimental Point 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° in the boundary of the domain.

10:30 AM QQ16.6
LONG TERM TEST OF BUFFER MATERIAL AT ASPO HARD ROCK LABORATORY SWEDEN. Ola Karlsson, Torbjorn 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 of experiments describes mechanical 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 the Swedish KB33 test series. Six test parcels which will be run for 1, 5 and 20 years. The testing principle is to expose each containing bentonite, central copper tube, precompressed clay buffer, instruments, and parameter controlling equipment in a vertical borehole. The boreholes are equipped with heaters in order to simulate the decay power from spent nuclear fuel at standard KB33 conditions (90°C) and adverse condition (130°C). Adverse conditions in this context refer also to high temperature gradients over the buffer, and additional necessary minerals leading to i.e., 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

Molecular oxygen entrapped in a granite repository after closure may affect the corrosion of metallic 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 O₂ in a granite repository has been addressed by an international project: The redox experiment in detailed scale (RED). 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 Aspo Hard Rock Laboratory, Sweden. O₂ injection pulses have been performed at its site temperature and pressure. Several microbial and chemical parameters have been studied: microbial counts, pH and O₂-concentration as a function of time, etc. The field study has been supported by laboratory experiments to determine O₂ reaction rates and mechanisms with Aspo samples (both for inorganic and microbially mediated processes). A redox experiment has been performed at CEA, France, with the other half of the fracture surface obtained in the drilling procedure of the field experiment. The aim of the redox experiment has been to duplicate as far as possible the conditions at the RED in situ experiment, for example by using groundwater sampled at the RED site in Sweden, shipped in special containers to France. The data that has been collected from the O₂ injection pulses in the RED field and redox experiments are compared with predictions for the role of molecular oxygen consumption determined in the laboratory experiments. These data allow to estimate times for oxygen consumption in granite fractures, which is of consequence for performance assessment calculations.

SESSION QQ17: USE OF NATURAL ANALOG INFORMATION IN PERFORMANCE ASSESSMENT

Chairs: Rodney C. Evans and William M. Murphy
Wednesday Afternoon, December 1, 1999
Room 208 (H)

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 repositories can permit evaluations of their inclusion in performance assessments. Analog data can be 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 biology and uncertain geologic histories. Nevertheless, existing uses of analog data in performance assessments include quantifying parameters describing the role of matrix diffusion in describing 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 ASSESSMENTS: EXAMPLES FROM OKLO. V.M. Overcash, YMO 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 core deposits are a specific example of the natural analog for spent fuel, since portions of the core achieved a critical condition and sustained nuclear reactions about 2.7 billion 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 focused on the issues of
criticality in nuclide transport, the stability 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 geologic time is much easier, and occurs
in several natural local ore 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 Q17.3
NATURAL SYSTEMS CONSTRAINTS ON MODELS OF THE LONG-TERM CHEMICAL EVOLUTION OF BUTTER PORTE.
WITORS, Radiation Monitor for Transport, Radioactivity
Ju Wang, Beijing Research Institute of Geology, Beijing, PR CHINA.
The solubilities of radionuclides that contain the source term in
performance assessments of conceptual models 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 amosite clays and ilite (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 chloystones that are similar to aged (i.e.,
illuminated) buffer materials. Model 3 is used to correlate porewater
compositions with possible equilibrium reactions in these rocks. Predictions are compared with chemical analyses reported in
the literature of porewaters squeezed from chloystones using a compression-rig apparatus. All three models fail to
accurately simulate respective conditions in the chloystones. 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. Reaction path simulation results for the stable coexistence of kaolinite plus amosite and ilite solids solutions
(Model 3) are inconsistent with observed porewater compositions, yet
these minerals exist in the chloystones. We suspect that the model
fails 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 chloystones is observed to vary with increasing applied load.

2:30 PM Q17.4
NATURAL ANALOGUES CONSTRAINT IN TOTAL SYSTEM PERFORMANCE ASSESSMENT OF A POTENTIAL
REPOSITORY AT YUCCA MOUNTAIN, NEVADA.
David C. Shanks, Darren M. Jolley, Duke Engineering and Services
Inc., CHIMSS MD-0, Las Vegas, NV; Robert Howard, TRW
Environmental Safety Systems, CHIMSS MD-0, Las Vegas, NV.
In the recent visibility 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 output 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 Rimer Mead, NV, and their relation to the
unsaturated-zone pore 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 ion strength. Additional examples of
this type of natural analog include constraints on values used within models of climate change and gas-phase transport.

2:45 PM Q17.5
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 past 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
natures 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, Penn Bluffs, Pocos de Caldes and Oklo, and have provided a
tool for studying radionuclide behavior in waste form 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,
declives, and analogue site observations. However, in spite of the
large 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 Q18: MICROBIAL PROCESSES IN WASTE MANAGEMENT
Chair: Melinda A. Hamilton and Donald T. Reed
Wednesday afternoon, November 1, 1995
Room 203 (H)

3:30 PM Q18.1
EFFECTS OF MICROBIAL INFLUENCED DEGRADATION ON MATERIALS USED FOR THE ENCAPSULATION OF LOW-
LEVEL RADIOACTIVE WASTE. Robert D. Rogers, Idaho National
Engineering and Environmental Laboratory, Biotchnology
Department, Idaho Falls, ID; Michael Ichikawa, Kofu Nymon, Noun.
O. Egiebor, Tuskagee Univ, Dept of Chemical Engineering, Tuskagee,
AL; Jonathan Knight, Chris Chessman, 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 evaluation of other
inorganic and 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 MID testing procedures 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 Thiothrix thiooxanisa on the surface of cement, cement
enriched with manganese tellurides, phosphate bonded ceramics, and
ceramic coated carbon steel. Results to be discuss include the
physical appearance, microscopic examination of waste form cross
sections, and the elements leached from various simulated waste forms.

4:00 PM Q18.2
MICROBIAL ANALYSIS OF THE ISOTHERMAL TEST AT AECL’S UNDERGROUND RESEARCH LABORATORY.
Simcha Stros-Gascogne 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 AECL’s 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
dehumidification 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

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more anaerobic conditions as evident from the microbial population. The buffer was sampled in 7 locations at the composite/buffer and the buffer/pore water in 9 and at 8 locations the SBD buffer. Enumerations were completed for aerobic and anaerobic heterotrophs, sulphide-reducing bacterium (SRB) and methanogens. Results indicated that the anaerobic population survived better than the anaerobic population, suggesting a partial evolution towards lower reducing potentials in the buffer. SRB populations ranged from 50 to 200 SRB/g. Buffer samples were analyzed for sulphide as an indication of its SRH activity, because of the implications for Cu container corrosion. Results showed very low levels of SRH activity; the maximum amount of sulphide found was 6.83 microgram/g, whereas buffer contained about 1400 microgram total S/g, as sulphide. 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 greater 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. Pinheiro and Carolyn S. Watkins, INEL, Idaho Falls, ID.

Recently we demonstrated that bacteria isolated from spent nuclear fuel (SNF) storage pools at the Idaho National Engineering and Environmental Laboratory (INEL) show little or no sensitivity to gamma irradiation. We seek to evaluate the surface composition and topography 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 scanning technique to remove all bacterial contamination and instigate sterile conditions until each specimen is introduced into its final (in)hibitory environment. Many different bacteria are studied: individually, in colonies, and collectively. Some of these are known to form biofilms, e.g. the Pseudomonads, while others, such as the sulfates-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 samples surfaces once a week over the course of one month. By coupling the SRET with potential-change electrochemical techniques, we are able to acquire images at various applied potentials. This allows us to examine pitting initiation and corrosion. Using these techniques we have been able to determine the effects of microbiological environments upon the corrosion process for a range of different systems.


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

Selenium (79Se) is a fissile product of nuclear fuel with a half-life time of 65,000 years. Oxidative liberation of spent nuclear fuel will result in the formation of selenium (SeO2-) and selenium (SeO4^{2-}) cationic together with uranium exsolution in solution. Sorption of the oxides on clays and other minerals are extremely low. Because they are chemically and radiologically toxic, it is important to immobilize the aqueous selenium and uranium species. Sulfate-reducing bacteria are able to reduce sulfate and other oxidized cations such as selenium, selenite, and uranium (UO2^{2+}) etc. In general, the reduction potentials of oxidized pairs (at pH 7) utilized by bacteria are within the range of -0.7 to +1.35 eV. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) from the selenite and selenium with a sulfate-reducing bacteria of Desulfovibrio desulfuricans show that yellow spherical (Se,S) sub-micro crystals precipitated outside the cells of the bacterial particles may also inside the bacterial cell. It is proposed that the Sr-rich particles are at the periplasmic region between membrane and plasma membrane [Tomei et al., 1995]. The bacteria is more active in the solution containing selenite than in the solution containing selenium. Further reduction results in Sr-rich particle (orange color), as the bacteria use S as electron acceptor. Similar features [U-oxide nano-crystals] also occur in the Desulfovibrio desulfuricans bacteria that have reduced the radioactive materials from the Savannah River Site. The Bacillus subtilis and selenium bacteria may also 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 Motamed, Ola Karlund, Torbjörn Sandén, and Karsten Pedersen, Göteborg University; Department of Biocell and Molecular Microbiology, Microbiology, Göteborg, SWEDEN; 2, Clay Technology AB, Ileon Research Center, Lund, SWEDEN.

The potential toxicity and persistence of high level nuclear waste material (HLW) makes it important to find safe methods for its disposal. One concept for the disposal of HLW is to encapsulate it in copper containers and deposit them in boreholes in a depth of 500 m. The containers are 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 38 weeks viable cells of most bacterial genera studied could not be detected in the Bentonite clay. One possible negative effect bacteria in a repository buffer material 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 containers. It was found that SRB were active and could colonize the interface between compacted bentonite and copper discs using a silica foil method. In addition, the activity of SRB was confirmed by production of inorganic sulfides and turnover of radioactive sulfite to radioactive sulfide. The activity of the SRB depended on the water content of compacted bentonite. The highest sulfide reduction activity observed was compacted bentonite with a water activity (a_w) of 0.999 corresponding to a density of 1.5 g cm^-3.

SESSION QQ19: GLASS - PROCESSING AND CHARACTERIZATION

8:30 AM QQ19.1

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 frits, melting the mixture in a 22-barrel electric melting furnace at 1150°C, and then pouring the molten glass into stainless steel containers for final disposal. During melting, volatilization can occur of radionuclides such as Te-99 and Cs-137. This paper presents an estimate of the fraction of Te-99 and Cs-137 that may have volatilized from the melt during the processing of the first microbatch of sludge slurry in the DWPF. The first microbatch consisted of approximately 400,000 gallons of sludge slurry and produced 497 containers each containing ~3800 pounds of glass. During processing the first microbatch, 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 melting using a special sampler while molten glass was being poured into containers 50, 40, 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-radiative isotopes. Te-99 and Cs-137 were measured in both the feed and the glass samples by inductively coupled 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, etc., and the concentrations of Te-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 Te-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

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 in a nitric acid solution in an SRS 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 mole nitric acid feed material is precipitated with 8 wt% acetic acid, decanted, washed with one-tenth mole acetic acid, and decanted again. The washed, deionized nitrate oxide slurry is then gravity drained and the melter vessel. The vitrification stage grinds and calcines the precipitated solids and then incorporates the oxides into an alumina-borosilicate glass matrix to a product loading ranging from 30-40%. The molten glass is then gravity drained to a crucible. 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 33% preliminary design that was completed with formal approval in May of this year. The paper provides a brief chronology leading to the proposed batch process. The paper will also describe the details of the demonstration process and presents a pathway for the design, testing and installation of the tanks 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 BOHO-SILICATE GLASSES. Trevor Plaisted, Ryan Plaisted, Pavel Hrma, John Vissnia, and Antonin Jirick, 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 wt% ZrO_2. The glass compositions studied included: 4Li_2O-1Al_2O_3-19SiO_2-76ZrO_2 (z), 4Li_2O-1Al_2O_3-19SiO_2-76ZrO_2 (b), and 4Li_2O-1Al_2O_3-19SiO_2-76ZrO_2-10Na_2O (n). These compositions represent members of the 4Li_2O-1Al_2O_3-19SiO_2-76ZrO_2 glass system. From these and previously published data, we have computed T_L for glass compositions that are of interest for use in High-Level Wastes. The maximum reaction temperature (T_R) for glass compositions that are of interest for use in High-Level Wastes is 1350°C to 1400°C.

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

A thermochromatographic representation of the Na-Al-Si-O system relevant for nuclear waste glass has been developed based on the associative species approach for the glass solution phase. Thermochromatographic data were measured and associated species data determined for binary and ternary glasses containing various amounts of Na_2O, Al_2O_3, and SiO_2. The computed correlation coefficients (R^2) for 12 glass compositions are 0.9998 for Na_2O, 0.9999 for Al_2O_3, and 0.9998 for SiO_2. These data have been used to evaluate the performance of the thermochromatic model for predicting glass composition.

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

Inorganic metal oxide clusters known as polyoxoanions (POAs) are good complements of rare-earth (RE) elements. A diverse array of polyoxoanions, [M_4O_9]^11+, and heteropolyoxoanions, [X_4Mo_12O_40]^2−, comprised of M = Mo, W and X = Si, P polyhedra are being investigated for their potential applications. The behavior of RE-POA complexes under vitrification conditions can be used to form a borosilicate glass that is largely unexplored. We have prepared RE complexes of two well-known series of heteropolyoxoanions: the Prewitt-Wu-O_4^15− and Wells-Dawson [α-2P_2W_12O_40]^3−, 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 forms and solution precursor complexes. The results and implications for the use of POAs as RE ion complexes in technology will be discussed. This environment management of high-level radioactive waste will be noted. This work is supported by the U.S. DOE 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 CHARACTERIZATION AND RADIATION RESISTANCE OF A MIXED-KALKI BOROSILICATE GLASS FOR HLW VITRIFICATION. Jonathan M. Roderick, Diane Holland, Warwick Univ., Dept of Physics, Coventry, UNITED KINGDOM; Charles R. Scales, BNL Ltd, Sellafield, Sellafield, Cumbria, UNITED KINGDOM.

Glasses to be used for 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 thermal and structural characteristics of these glasses, we measured a range of boron oxide contents. Furthermore, several glass series have been prepared for a range of alkali oxide to boron oxide ratios, R, 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 used to exhibit a maximum density at a minimum in the fraction of four-coordinated borons at 22mole% and 29mole% boron oxide, respectively. Initial results on the effect of increasing R indicate an increase in T_L to a maximum before a sharp decrease and subsequent leveling off at a density larger than that of the glass. However, density measurements exhibited a maximum at the same value of R and then remained constant within experimental error. The glasses doped with sodium lithium borosilicates were destroyed by high temperatures above 1550°C. The physical properties of the glasses, such as density, yield strength, and thermal conductivity, were measured to determine the fraction of four-coordinated borons present. This change in T_L is consistent with work done on the sodium-lithium-silicate system and can be attributed to a combination of sodium cations with [LaO_4] coordination and removal of nonbridging oxygens. Initial a-particle irradiation tests have also been carried out on several base glass samples and show evidence of B(a, n) reactions, the occurrence of which could have important consequences for future use of the wasteform.

SESSION QQ19: GLASS - CORROSION AND CHARACTERIZATION

Chairs: William L. Elbert and David J. Wrackmeyer
Thursday Morning, December 2, 1999
Room 268 (H)


Using energy-loss filtered transmission electron microscopy (EFTEM), we observed the formation of silicon-rich zones on the corroded surface of a West Valley (WW) glass. This layer is approximately 1.0-2.0 nm thick and is directly underneath a precipitated smectic 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 Grammow 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 and boron depleted zones have not been found on corroded Savannah River Laboratory (SRL) borosilicate glasses, including SRL-65 and SRL-61, although they possessed similar looking clay layers. At this time it is not possible to quantify differences in the dissolution characteristics of WW6 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. Mora, Mary Stanley, Chad Torko, and William L. Elbert, 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 sandstone, which is a ceramic composite consisting of 75 mass% glass binder, is the ceramic waste form (CFW) that has been selected to immobilize the radioactive electrofilter salt from the electrofilter.

In order to model the durability of glass-bonded sandstone in a nuclear waste repository, the dependence of the corrosion rate on temperature and pH must be known. We have carried out corrosion tests with monoliths of sandstone, binder glass, and glass-bonded sandstone (CFW) in deionized water at temperatures in the range 25°C, 70°C, and 120°C. The pH and temperature dependence of the corrosion behavior of the sandstone and sandstone components of the CFW. 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 sandstone component of the CFW dissolution rate is similar to that of natural sandstone, and all have 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 dependencies 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 Q20.3
VAPOUR IONIZATION OF BOROSILICATE WASTE GLASS.
Ralph A. Olson, Jeffrey A. Fortner, William L. Ebert, Shin-Wing Tam, Stephen F. Wolf, and James C. Cummans, 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. Unstressed drop experiments performed on mock and vapor-hydration shielded glasses from the Seabed Recycling River (SLR) waste forms show that the alteration of the glass by vapor hydration reactions 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 the behavior with time corresponding to t + 1/2 or t + 1/2, consistent with diffusion transport through clay alteration layers 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 minimized when the amount of water in the vessel was close to that required to just saturate the vessel, and increased 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 Q20.3
PLUTONIUM-CONTAINING ALTERATION PHASES PRODUCED BY AQUEOUS CORROSION OF BOROSILICATE GLASS. J.A. Fortner, C.J. Mertz, A.J. Bikel, 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/lanthane silicate alteration phases upon aqueous corrosion under a range of conditions. Microscopic plutonium/lanthane silicate crystallites formed on the surface of the glass at 20°C and 100% humidity, while an intermediate layer of crystalline platinum/lanthane silicate formed in situ within the altered glass beneath the surface. The phases observed were generally rich in lanthanide (La) elements, and were related to the lanthanide orthosilicate phases of the monoclinic Ln2O3 type. The composition of the phases was variable regarding [La]/[Pb], depending upon type of corrosion test and on the location within the alteration layer. The 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 Q20.5
THE ROLE OF ALTERATION PHASES IN INFLUENCING THE KINETICS OF GLASS DISSOLUTION. David J. Wnekiewicz, University 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 stability of 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 glass in a waste package is being examined in a series of Product Consistency Tests (PCTs). The PCTs used an Na2O-CaO-K2O-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 120°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-montmorillonite, Na-amorphite, and Na-chlorite) were added to the individual tests to assess their potential role in glass corrosion. These results have been noted to occur following the reaction of both natural volcanic and simulated borosilicate waste glasses. Boron release was generally higher from tests with Na-montmorillonite or Na-amorphite 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 Na-chlorite 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 sodium did not correlate closely with boron, suggesting that factors other than the activity of silicate acid may be involved in the controlling the kinetics of glass dissolution.

11:45 AM Q20.6
ESTIMATING MODEL FOR METER VALUES FOR HIGH LEVEL WASTE GLASSES FOR TOTAL SYSTEM PERFORMANCE ASSESSMENT. William L. Ebert, Shin-Wing Tam, and James C. Cummans, 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 (TSAP) calculations. We are developing methods that can be used to estimate or constrain 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, i.e., 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 Q21: WASTE PROCESSING
Chairs: Randy Arthur and Dieter A. Kneck
Thursday Afternoon, December 2, 1999
Room 268 (H)

1:30 PM Q21.1
CONCEPTS FOR DRY PROCESSING OF SPENT NUCLEAR FUEL FOR RECYCLING TO LIGHT-WATER REACTORS. Jerry Christian, James Serbertz, David Abbott, Idaho National Engineering and Environmental Laboratory, National SNF Program; Kenneth Cierniak, Massachusetts Institute of Technology, Dept of Nuclear Engineering, Cambridge, MA; Richard Capc Pasti, 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 100°C. In addition to permanent gases and fission products that are vaporized during pellet sintering, this can remove Ti, Mo, and some Ru and improve the neutronics. A number of experiments are being evaluated for efficient sintering and rhodium, initially by thermodynamic modeling and review of literature. The lanthanides exist in solid solution with UO2, so separations methods will require conversion to fine powder; rhodium
is present as a metallic inclusion in the epsilon phase. Chlorination of finely powdered titanates, at 1100-1200°C, would vaporize substantial portions of TiO, and Bi. A fraction of the uranium should 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 be applicable for recovering 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 QQ21.4
FLOWSHEET DEVELOPMENT FOR THE SEPARATION AND IMMOLIZATION OF PERCETINATE FROM ALKALINE RADIOACTIVE WASTES. Andrew H. Bond, Chemistry Division, Argonne National Laboratory, Argonne, Ill; Robert D. Rogers, Department of Chemistry, The University of Alabama, Tuscaloosa, AL; Michael J. Gula, E. Philip Horvitz, James T. Harvey, Echelon Industries, Inc., Durbin, Ill; Jack L. Collins, Oak Ridge National Laboratory, Oak Ridge, TN.

A flowsheet for the selective removal of the perctenate 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 described. The flowsheet comprises the steps of selective extraction of the perctenate anion by ABEC\textsuperscript{TM} resins, secondary concentration of perctenate from water by nonselective silica-based union-exchange resin, and encapsulation of the radionuclide-loaded union-exchange resin in hydrous titanium oxide microspheres. Each of the extraction, secondary concentration, and encapsulation stages has been independently tested using similar solutions. The final encapsulated waste form has been contacted with the Toxicity Characteristic Leach Procedure (TCLP) and simulated Waste Isolation Pilot Plant (WIPP) brine leaches. Of the initially loaded perctenate, less than 0.3\% and less than 0.6\% was released to the TCLP and simulated WIPP brine leaches, respectively, over a 188 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 by less than 0.06\% by a perctenate leach of 1 Cu.

Accounting for a 55 gallon drum shipping/storage container and the standard engineering barriers of the repository, the perctenate anion can be effectively immobilized and shielded for long-term waste storage by this flowsheet. This work was sponsored by the U. S. Department of Energy Magnox Energy Technology Center under contract number DE-AC21-97MC30137 to Echelon, 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. Don Cigloto, David Vincenzi, and Natalia M. Rusakov. 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 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 measurement of non-destructive information related to 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 generating linewidths. 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 the 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 MILTS IN THE MELT-DILUTE TREATMENT TECHNOLOGY DEVELOPMENT FOR AL-BASED DOE SPENT NUCLEAR FUELS. Thad M. Adkins, Andrew J. Duncan, Harold B. Peacock, Jr., Washington Nuclear, 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 AlBase 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 reprocessing reactors. The melt-dilute treatment technology will meet the
fuel assemblies to reduce their volume and alloy them with depleted uranium to isotope 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 SRRC 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. Finally, validation of this offgas concept will occur during full-scale irradiated testing in FY2000.