# CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

## TRIP REPORT

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| **SUBJECT:** | Materials Science Society Annual Meeting - Symposium on the Scientific Basis for Nuclear Waste Management XVI |
| **DATE/PLACE:** | November 30-December 4, 1992; Boston, MA |
| **AUTHOR:** | David R. Turner |

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## TRIP REPORT

SUBJECT: Materials Research Society Annual Meeting - Symposium on the Scientific Basis for Nuclear Waste Management XVI

DATE/PLACE: November 30-December 4, 1992; Boston, MA

AUTHOR: David R. Turner

PERSONS PRESENT:

| CNWRA | NRC |
|---|---|
| Ross Bagtzoglou | Charles Interrante |
| Berge Gureghian | Michael McNeil |
| Bret Leslie | Tae Ahn |
| William Murphy | |
| Prasad Nair | |
| Roberto Pabalan | |
| Narasi Sridhar | |
| David Turner | |

**BACKGROUND:** This is the sixteenth in a series of symposia conducted by the Materials Research Society on nuclear waste management. The technical topics covered at the meeting are broad in scope, including papers in performance assessment, spent fuel, microbiologically influenced corrosion, glass and crystalline waste forms, radionuclide chemistry and transport, engineered barriers, and the use of natural analogues. The 1992 Symposium was supported by the U.S. Department of Energy, U.S. Nuclear Regulatory Commission, and the Atomic Energy of Canada, Ltd. The meeting was truly international in scope, with participants from Europe, Japan, Canada, The United States, and Australia. A Symposium Proceedings volume will be published in 1993.

**SCIENTIFIC ACTIVITIES:** CNWRA technical staff were heavily involved in organization both prior to and during the meeting. As co-chair of the symposium with C. Interrante of NRC, Roberto Pabalan was charged with coordinating both the meeting and the proceedings volume. William Murphy was chair for a session on Natural Analogs, and Prasad Nair co-chaired a session on Long-Term Prediction. These coordinators were responsible for selecting papers for presentation and reviewing manuscripts for inclusion in the symposium proceedings volume. In addition to logistical responsibilities, six research papers were presented by CNWRA technical staff at the symposium:

R. Pabalan, J. Prikryl, P. Muller, and T. Dietrich. 'Experimental study of uranium ($+6$) sorption on the zeolite mineral clinoptilolite.'

D. Turner, T. Griffin, and T. Dietrich. 'Radionuclide sorption modeling using the MINTEQA2 speciation code.'

B. Leslie, J. Prikryl, and E. Pearcy. 'Oxidative alteration of uraninite at Peña Blanca, Chihuahua, Mexico: Possible contaminant transport and source term constraints for the proposed repository at Yucca Mountain, Nevada.'

N. Sridhar and G. Cragnolino. 'The applicability of repassivation potentials for long-term life prediction.'

A.B. Gureghian and B. Sagar. 'Uncertainty and sensitivity analyses of groundwater travel time in a two-dimensional variably saturated fractured geologic medium.'

A. Bagtzoglou, R. Ababou, and B. Sagar. 'Effects of some common geological features on 2-D variably saturated flow.'

Abstracts of these papers are attached (See attachment A).

IMPRESSIONS/CONCLUSIONS: The breadth of topics covered in the meeting was quite impressive and covered many technical aspects of nuclear waste management. Topics included materials science, chemistry, geology, hydrology, and performance assessment (See Attachment B). It was noted that there was a general lack of DOE-sponsored research on container materials. Because of the international aspect of the meeting, it was a valuable opportunity for people involved in U.S. radioactive waste programs to hear what is being done in other countries. For example, it was reported that the conceptual framework for performance assessment activities varies between European countries due to differing regulatory requirements. In addition, research needs in Switzerland identified by scenario analysis (such as more reliable input numbers, better understanding of features and mechanisms) suggest that the Swiss HLW program may be subject to delay. However, since much of the technical work presented was specific to particular aspects of different national programs (e.g., bentonite backfill in hydrologically saturated, reducing environments), it cannot be applied directly to the Yucca Mountain site. Nevertheless, understanding gained from these studies and the refining of laboratory and field techniques, can be applied to the U.S. HLW disposal program. New data on radionuclide behavior and the properties of different elements of the Yucca Mountain system were presented by a number of U.S. scientists. New techniques such as ultracentrifugation studies to investigate partially saturated materials in the laboratory, spectroscopic work to image the solid/water interface, and microsensors for examining microbiologically-influenced environments, continue to be developed and refined, and hold promise for application in the Yucca Mountain system.

Contacts were made and renewed with participants from other nations and other elements of the U.S. waste programs. Discussions with participants at the symposium indicated that the research presented by CNWRA staff was well received and is being used to address issues in HLW research. In discussions with S. Tsujikawa, materials research on container life prediction conducted at CNWRA was found to agree well with Japanese results. Rod Ewing of the University of New Mexico suggested in a keynote address that work being performed by

CNWRA at the Peña Blanca natural analog site is one of the few successes in applying natural analog research to long term performance assessment. N. Sridhar made informal arrangements with Sandia researchers to obtain copies of public reports on spacer corrosion for comparison with predictions by CNWRA models.
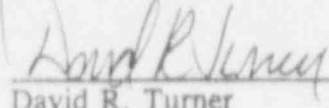
**PENDING ACTION(S):** CNWRA staff involved in organizational activities will facilitate review and revision of papers submitted to their sessions. Papers authored by CNWRA staff will be finalized and prepared in camera-ready form for publication in the proceedings volume. A copy of the proceedings volume will be obtained for the CNWRA library.

**RECOMMENDATIONS:** While it may not always be possible for CNWRA staff to participate to the high-level achieved in this particular symposium, it is important that CNWRA staff continue to be involved in international meetings of this type. They offer an excellent opportunity to disseminate research performed at CNWRA to the scientific community in general and the HLW research community in particular. In addition, CNWRA staff will continue to benefit from exposure to HLW programs in other countries and through interaction with participants from other organizations.
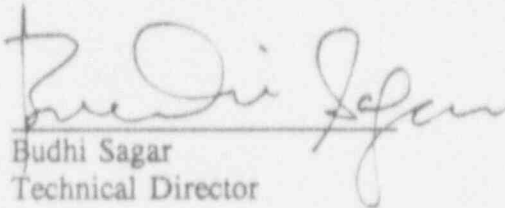
**PROBLEMS ENCOUNTERED:** None.

**REFERENCES:** None. See attachments for symposium agenda and abstracts.

SIGNATURE:

David R. Turner

12/29/92
Date

CONCURRENCE:

Budhi Sagar
Technical Director

1/9/93
Date

ATTACHMENT A

ABSTRACTS BY CNWRA TECHNICAL STAFF

# EXPERIMENTAL STUDY OF URANIUM(6+) SORPTION
# ON THE ZEOLITE MINERAL CLINOPTILOLITE

ROBERTO T. PABALAN, J. D. PRIKRYL, P. M. MULLER, AND T. B. DIETRICH

## ABSTRACT

Experiments on the sorption of uranium(6+) on clinoptilolite from solutions in equilibrium with atmospheric $CO_2(g)$ were conducted to understand the fundamental controls on uranium sorption on zeolite minerals, including the effects of pH, aqueous uranium speciation, and uranium concentration in solution. The results indicate that uranium(6+) species are strongly sorbed on the zeolite mineral clinoptilolite at near-neutral pH. The amount of uranium sorbed is strongly dependent on pH and, to some extent, on the total concentration of uranium. Uranium sorption on clinoptilolite is important in the pH range where $UO_2(OH)_2°(aq)$ is the predominant uranium aqueous species, whereas sorption is inhibited at pH's where carbonate- and hydroxy-carbonate-complexes are the primary uranyl species. Surface adsorption appears to be the main sorption mechanism, although at pH < 4 the results suggest ion exchange may occur between the $UO_2^{2+}$ ions in solution and the cations in the intracrystalline cation exchange sites of clinoptilolite.

The effectiveness of zeolite-rich horizons underneath Yucca Mountain, Nevada, as barriers to actinide transport through sorption processes will depend strongly on groundwater chemistry. Reliable predictions of radionuclide transport through these horizons will need to properly account for changes in solution chemistry.

OXIDATIVE ALTERATION OF URANINITE AT PEÑA BLANCA, CHIHUAHUA, MEXICO: POSSIBLE CONTAMINANT TRANSPORT AND SOURCE TERM CONSTRAINTS FOR THE PROPOSED REPOSITORY AT YUCCA MOUNTAIN, NEVADA. Bret W. Leslie, James D. Prikryl and English C. Pearcy, Center for Nuclear Waste Regulatory Analyses, 6220 Culebra Road, San Antonio, TX 78228-0510 USA.

Contaminant transport in nuclear waste repository performance assessments might be constrained by elucidating the mechanisms and spatial and temporal extent of uranium movement away from uraninite deposits, while the source term for nuclear waste repository performance assessments might be constrained by the solubilities of radioelement-bearing solids and/or the rates of release of radioelements from nuclear waste forms. Assessment of the mechanisms and extent of U mobility, and the solubility and rate limits for the proposed repository at Yucca Mountain, Nevada might be aided by using information from the natural analogue at Peña Blanca, Mexico. The Nopal I uranium deposit in the Peña Blanca district and the proposed repository at Yucca Mountain occur in hydrologically unsaturated tuffs located within Basin and Range horsts and have similar climates. The primary uraninite and secondary uranium mineralization at the Nopal I deposit is largely contained within a 20 x 40 x 100 m "breccia pipe", which is presently exposed at the surface. The uraninite has been largely altered to a suite of uranyl oxide hydrates and uranyl silicates. This alteration is analogous to spent fuel degradation processes expected to occur at Yucca Mountain.

Detailed petrographic analysis of uranium ore, altered and unaltered host rocks at the site combined with detailed mapping (1:25) and sampling of the exposed surface has revealed the distribution and paragenesis of alteration of the uraninite. The distribution of secondary uranium minerals appears to be constrained both spatially and temporally with uranyl oxide hydrates (ianthinite and schoepite) formation subsequent to uraninite and occurring within and very near remnant uraninite. Uranyl silicates (alpha-uranophane, weeksite, boltwoodite, soddyite, and beta-uranophane) subsequently formed and are restricted to areas away from the uraninite. Lateral redistribution of U away from the breccia pipe appears to be limited to 10 meters or less. U-series studies of mineral separates and bulk rock samples are being used to constrain the temporal and spatial distribution of U.

# REPASSIVATION POTENTIALS FOR
# LONG-TERM LIFE PREDICTION OF LOCALIZED CORROSION

N. Sridhar and G. A. Cragnolino
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute

## REVIEW SUMMARY

The U.S. Nuclear Regulatory Commission requirements for geologic disposal of high-level nuclear waste, as contained in 10 CFR 60.113, specify that the waste packages shall be designed such that containment of radionuclides will be substantially complete for a period of at least 300 - 1000 years. Pitting and crevice corrosion are two of the important failure modes to be considered in determining the performance of container materials. In computing the life-time of a container material suffering from these localized degradation events, both initiation and growth of the degradation front (pits or crevices) have to be considered. However, once a stable localized corrosion process initiates, active dissolution of a metal in the localized region can be quite high, leading to short failure times relative to the required life of the container materials. Therefore, the design of a container should involve appropriate selection of materials and fabrication technology such that, under anticipated environmental conditions, the initiation time of a localized degradation process is long relative to the overall anticipated life. It is well known that the potentials required to initiate localized corrosion processes are higher than those to propagate them. Once a growing localized corrosion front is stable, the electrode potential has to be decreased to a value lower than the initiating potential to repassivate the material. If short-term changes in the environmental conditions such as increases in redox potential and anionic concentrations lead to initiation of localized corrosion, mechanisms must be provided for the cessation of the stably growing localized corrosion front once the redox potential of the environment decreases to a stable value and the anionic species reach stable concentrations. Hence, repassivation of growing localized corrosion fronts is an important consideration in ensuring long-term performance of the container materials.

Another advantage of using repassivation potentials for long-life design of container materials is the generally lower scatter observed in the measurement of repassivation potentials compared to that of initiation potentials or initiation times. This may be related to the dominance of material surface variations on the initiation events, whereas the more aggressive environmental conditions established inside stably growing localized corrosion regions tend to minimize the effects of surface variations. Since the repassivation potential is lower than the potential for initiation of localized degradation processes, it may also form a lower bound value for selection of container materials for a given scenario of environmental evolution. A critical question in the use of repassivation potential for life prediction or material selection is whether the measured potential is truly a lower bound value or whether it decreases with the extent of prior growth of the localized corrosion front.

# EFFECTS OF SOME COMMON GEOLOGICAL FEATURES ON 2-D VARIABLY SATURATED FLOW.

A.C. Bagtzoglou; R. Ababou; and B. Sagar. Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, Texas.

This paper presents results of unsaturated flow simulations undertaken as an auxiliary analysis for the Iterative Performance Assessment (IPA) Project. The effects on flow of common geological features, such as nonhorizontal stratification and vertical or near vertical fault zones intersecting the strata, in a 2-D or "thin slice" domain are studied. The problems inherent in specifying initial and boundary conditions that are consistent with observed infiltration rates and/or measured hydrogeologic properties are discussed. A method for developing consistent initial and boundary conditions for more complex problems is applied. This method depends on steady state solutions of simpler flow problems which are assumed as init  conditions for the more complex geometry flow conditions.

The results indicate that the presence of layers and crosscutting fault zones tend to induce 3-D unstable flows in the unsaturated zone. The instability is manifested in our simulations by an oscillatory behavior of steady state, that is, at large times the solution fluctuates and does not tend to converge to a single value. This was a preliminary study, with emphasis given on process modeling rather than predictive modeling. Future work will involve a fully 3-D study that will include, as far as possible, the known properties of the Yucca Mountain site.

ATTACHMENT B

SYMPOSIUM ABSTRACTS

# SYMPOSIUM V:

## SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT XVI

### November 30 - December 4, 1992

### Chairs

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## Symposium Support

**9:45 A.M. V1.6**

THE ROLE OF SIDEROPHORES IN THE TRANSPORT OF RADIONUCLIDES. <u>Larry E. Hersman</u>, Los Alamos National Laboratory, Los Alamos, New Mexico

Iron exists in aerobic soil and water environments most commonly as insoluble Fe(III). Siderophores are powerful, microbially produced chelating agents that are used to mobilize the insoluble Fe(III) cation. Over 80 siderophores have been isolated and characterized, with some reportedly having iron-binding constants as high as $10^{52}$. Fe(III) and Pu(IV) are similar in their charge/ionic radius ratio (4.6 and 4.2, respectively); therefore, Pu(IV) may serve as an analog to Fe(III). It is possible that some radioactive wastes could be chelated by naturally occurring siderophores, thereby altering the transport rates of those elements through the subsurface environment. This investigation was initiated to investigate that possibility. The binding of $^{239}Pu(IV)$ by four chelating agents is reported in this paper: a siderophore isolated and purified from a <u>Pseudomonas</u> sp.; desferal, a ferrioxamine siderophore commonly used for deferration therapy; EDTA, ethylenediaminetetraacetic acid; and, citrate, trisodium <u>salt</u>.

**10:15 A.M. \*V1.7**

COORDINATION CHEMISTRY IN THE MINERAL/SOLUTION INTERPHASE REGION. <u>J. O. Leckie</u>, Environmental Engineering and Science, Department of Engineering, Stanford University, Stanford, CA 94305-4020.

The formation of surface complexes in the mineral/solution interphase region has been confirmed to be of two types: outer-sphere or ion pair type and inner sphere or covalently bonded type. Analogous to solution complexes, the full range of bond types, from ionic to covalent must exist in surface complexes. Additionally, the formation of surface ring structures (organic/inorganic) is expected.

Combining macroscopic data from solution chemistry with spectroscopic studies (XAS) in situ has yielded insights into the formation of polydentate and ternary complexes as well as the ability to differentiate between surface complexes and surface precipitation.

Systematic parametric studies yield data allowing identification of system conditions promoting ternary surface complexes. Adsorbents studied include goethite, hematite, ferrihydrite, gibbsite, corundum, amorphous aluminum oxide, and quartz as well as layered and network silicates. Adsorbates include $UO_2^{2+}$, $NpO_2^+$, $Pb^{2+}$, $Cd^{2+}$, $SeO_3^{2-}$, $SeO_4^{2-}$, and others. The presence of competing ligands (e.g., $CO_3^{2-}$ and EDTA) leads to the apparent formation of ternary surface complexes for both $UO_2^{2+}$ and $NpO_2^+$ under some solution conditions and to the formation of non-adsorbing solution complexes under other system conditions.

**10:45 A.M. V1.8**

CENTRIFUGAL MODELLING INVESTIGATIONS OF IRREVERSIBLE SORPTION. <u>M Chandratillake</u>, CAPCIS MARCH LTD, UK. R G G Holmes and S Richardson, BNFL plc, UK. F R Livens, W H Craig and C M Merrifield, Manchester University, UK.

Geotechnical centrifugal modelling has been proved to be a very useful tool to study the problem of hazardous waste migration. This technique has been used to gather experimental data on the long-term flow processes in waste repositories.

Centrifuge modelling has several advantages over the classical laboratory techniques of column studies and batch equilibrium tests. Major disadvantage of the latter being that fine-grained soils, which have low permeability, require very long periods of time to conduct laboratory experiments and the results may be unrepresentative of real scenarios. In centrifugal modelling, a soil sample is spun at high rotational speeds in a centrifuge, increasing the gravitational effects which simulate in situ confining stresses. The rates at which processes occur in the centrifugal model can be related to the prototype through fundamental principles of physics. Centrifuge modelling has several advantages.

**11:00 A.M. V1.9**

EXPERIMENTAL STUDY OF URANIUM(6+) SORPTION ON THE ZEOLITE MINERAL CLINOPTILOLITE. <u>Roberto T. Pabalan</u>, James D. Prikryl, Paula M. Muller, and Todd B. Dietrich, Center for Nuclear Waste Regulatory Analyses, SwRI, 6220 Culebra Road, San Antonio, TX 78228-0510

Thick, laterally continuous zones of zeolitic (predominantly clinoptilolite) tuffs underneath the proposed high-level nuclear waste repository at Yucca Mountain, Nevada, could provide important geologic barriers to radionuclide migration from the repository to the accessible environment. To evaluate their effectiveness as barriers to radionuclide transport, experiments were conducted on the sorption of uranium(6+) on clinoptilolite. The study was designed to understand fundamental controls on uranium sorption on zeolites, including the effect of pH, aqueous uranium speciation, and total uranium concentration.

Clinoptilolite powder was reacted with $UO_2(NO_3)_2$ solutions with initial pH in the range 2.5 to 9.0. The mixtures were agitated for two weeks on gyratory shakers and maintained in equilibrium with atmospheric $CO_2(g)$. Initial and final pH and uranium concentrations were measured. The results indicate uranium sorption on clinoptilolite is strongly dependent on pH. At pH < 7, the amount of sorbed uranium increases sharply over a narrow pH range. At near neutral pH, almost complete removal (> 90%) of uranium from solution occurs. At pH > 7 where carbonate complexation of uranium becomes important, the amount of sorbed uranium sharply decreases. Reverse experiments demonstrate the sorption reaction is reversible. Also, the adsorption edge shifts to lower pH with a decrease in initial total uranium concentration. Uranium(6+) aqueous speciation calculated using EQ3 (version 3245R124) and the NEA uranium thermodynamic database (Grenthe et al., 1992) indicates that uranium sorption on clinoptilolite becomes important in the pH range where $UO_2(OH)_2^\circ$ is the predominant uranium aqueous species.

**11:15 A.M. V1.10**

RADIONUCLIDE SORPTION MODELING USING THE MINTEQA2 SPECIATION CODE. <u>D. Turner</u>, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

Storage of high-level radioactive waste in geologic repositories is likely to rely on sorption as an important mechanism in retarding radionuclide transport. Recent work indicates that many elements, including key radionuclides (e.g., U, Pu, Np, Am), exhibit complex, pH-dependent sorption behavior. To consider such behavior in a more mechanistic manner, different surface complexation models (SCM's) have been used to model sorption. Based on mathematical structures of the MINEQL speciation code the WATEQ3 data, MINTEQA2 (version 3.0) offers interactive preprocessing and seven sorption options, including three separate SCM's. These models depend on both adjustable electrostatic parameters, and on the speciation of the system of interest. For a given model and substrate, recent studies recommend values for the adjustable parameters. However, the general lack of thermodynamic data for radioelements in the MINTEQA2 database has, to date, precluded extensive application of the code to available radionuclide sorption data for the purpose of evaluating different approaches.

In the present study, radioelement thermodynamic data, mostly from the EQ3/6 code (data0.com.R7), have been adapted to MINTEQA2 format. Uranium data from EQ3/6 is based on the extensive critique and compilation of the Nuclear Energy Agency (NEA). Preliminary comparisons for the uranium system indicate that the two codes produce almost identical speciation results when using the same data.

Several recent radionuclide sorption experiments have been reinterpreted using the new MINTEQA2 database and the parameter estimation code FITEQL. Initial comparisons show that SCM's using the new database can readily simulate observed sorption results. Nonunique fits are possible, but geochemical considerations can be used to restrict the possible surface reactions for a given SCM. For the incorporation of sorption into anticipated performance assessment codes, simple models involving a minimum of species may be preferred over more complex sorption models.

## 2:30 P.M. V2.4

RADIONUCLIDE MIGRATION STUDIES ON TONALITE.
P. Hölttä, M. Siitari-Kauppi, M. Hakanen, University of Helsinki, Department of Radiochemistry, Helsinki, Finland; and A. Hautojärvi, Technical Research Centre of Finland, Nuclear Engineering Laboratory, Espoo, Finland.

To assess the safety of underground crystalline repositories the retardation characteristics of the bedrock need to be known. Water flow rate and porosity of the rock as well as migration pathways are the most important factors affecting the transport of radionuclides in fractures and in rock matrix. In this work migration of radionuclides was studied under laboratory conditions using dynamic column method and static through-diffusion method. Migration pathways in rock matrix were identified by autoradiographic method and the lateral distribution of porosity was determined using $^{14}$C-PMMA method.

In the experiments radionuclides used were tritiated water (HTO) and chloride ($^{36}$Cl) ions as non-sorbing tracers and sodium ($^{22}$Na) as slightly sorbing and strontium ($^{85}$Sr) as strongly sorbing tracers. Migration of uranium (VI) was also studied using $^{233}$U as a tracer. Transport of radionuclides was interpreted using models for dispersion and for diffusion into the rock matrix. Retardation and diffusion parameters are given and results from static and dynamic experiments are compared. Retardation properties of tonalite are discussed.

## 3:00 P.M. V2.5

RADIO-LABELLED HUMIC MATERIALS IN MIGRATION STUDIES. Lars Carlsen and Pia Lassen, National Environmental Research Institute, Roskilde, Denmark; Peter Warwick and Amanda Randall, Loughborough University of Technology, Loughborough, UK.

It is well known that humic- and fulvic acids are able to complex polyvalent metal ions, e.g. radionuclides, leading to soluble complexes of significant strength, thereby decreasing the sorption of these compounds to soils and sediments. Obviously, the interaction of humic materials with radionuclides may significantly influence the availability and transport of the latter in the environment. Typically, studies along these lines have focussed almost exclusively on the radionuclides, whereas the actual role of the humic material has been elucidated only indirectly. In order directly to study the behaviour of the naturally occurring organic macro-molecules in relation to the environmental fate of radionuclides, radio-labelled humic- and fulvic acids can advantageously be applied. Radio-labels such as carbon-14 and iodine-125 have successfully been covalently incorporated in humic- and fulvic acids. The paper discuss the labelling of humic substances as well as preliminary migration studies.

## 3:15 P.M. V2.6

COLLOID PROPERTIES IN GRANITIC GROUNDWATER SYSTEMS, WITH EMPHASIS ON THE IMPACT ON SAFETY ASSESSMENT OF A RADIOACTIVE WASTE REPOSITORY. C. Degueldre, Paul Scherrer Institut, CH-5232 Villigen, Switzerland.
Since colloids are present in all groundwater, they are studied for their potential role in the migration of relevant radionuclides in the geosphere. Colloid sampling and characterisation campaigns have been carried out in the Grimsel area, Switzerland (Grimsel Test Site, Transitgas Tunnel) and in the Northern Switzerland/Black Forest area (Leuggern, Zurzach, Bad Säckingen, Menzenschwand). On the basis of results obtain for some 24 groundwaters, the following may be concluded. The colloids in granitic systems are basically made of components of the aquifer materials (silica, clay). In deep hydrogeochemical conditions, the colloid concentrations are not expected to exceed 100 ppb,

however, in transient conditions such as those observed for physical or chemical changes, (e.g. geothermal) the colloid generation may be enhanced and reach a 10 ppm concentration, (i.e. with low calcium concentration). Nuclide sorption on colloids and transport studies have shown that the sorption behaviour given by the classical surface complexation approach should, coupled with transport, describe a non-conservative situation. Reversible attachment of the colloids onto the rock must be taken into account together with the irreversible sorption of the radionuclide onto those colloids. For the low concentrations ([Ca$^{2+}$] < 10$^{-4}$ M), and sorption capacity of the nM level, their presence in the granitic aquifer can be neglected in the safety analysis when considering the reversible surface complexation model. Risks could be larger when the sorption is followed by a complex aggregation scheme. The study shows that with the conservative size distribution in        granitic water conducting fissure that association-agglomeration scheme yielding irreversible sorption is very unlikely.

## 3:30 P.M. V2.7

THE INFLUENCE OF NON-LINEAR SORPTION ON COLLOID FACILITATED RADIONUCLIDE TRANSPORT THROUGH FRACTURED MEDIA. Paul A. Smith, Paul Scherrer Institute, Würenlingen and Villigen, Switzerland.

In the safety assessment of nuclear waste repositories, sorption of radionuclides on the surfaces of colloids may significantly modify transport behaviour where colloid concentration is sufficiently high. In the case of fractured geological media, colloids may be excluded from matrix pores, in which case radionuclides bound to them are not subject to the retarding effects of matrix diffusion and sorption onto matrix pore surfaces.

The use of a simplified transport model, with linear sorption both on pore surfaces and colloids, is desirable if it can be demonstrated to be conservative. However, it is unclear how a consistent, conservative linear model for sorption applying to both pore surfaces and colloids can be defined, since low sorption onto pore surfaces is conservative, while a high degree of sorption on colloids is also conservative.

A model is presented describing colloid facilitated transport through fractured media with non-linear sorption. A series of simulations is carried out illustrating the general behavior to be expected, and simple criteria are developed to predict when the presence of colloids will have a significant influence on transport. Additional effects (conservative or non-conservative) resulting from non-linearity of sorption are described. Finally, the question of whether the use of a simplified model, with linear sorption calculated for the highest concentration encountered along the flow path, is conservative for colloid facilitated transport is addressed.

## 3:45 P.M. V2.8

TRANSPOSRT MODELING IN A FINITE FRACTURED ROCK DOMAIN.[*] Craig F. Novak, Fluid Flow and Transport Dept. 6119, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM, 87185.

The Waste Isolation Pilot Plant (WIPP), a U.S. Department of Energy facility, is intended to demonstrate effective isolation of transuranic nuclear waste from the accessible environment. This demonstration includes predicting radionuclide transport rates should hypothetical human intrusion into the WIPP allow dissolved radionuclides to reach the Culebra Dolomite saline water-bearing unit overlying the WIPP. Hydrologic and geologic observations suggest the Culebra is appreciably fractured, meaning that flow occurs primarily through fractures while most solute storage occurs in the adjacent matrix. Both physical retardation (diffusion of solutes into the matrix) and chemical retardation (solute immobilization through chemical reactions) could significantly decrease radionuclide migration rates through the Culebra.
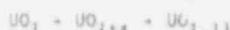
Numerical simulations with the FMT finite difference model in a finite, idealized double porosity system were performed to: 1) delineate parameter values for which a set of two coupled one-dimensional equations is insufficient to describe behavior and a fully two-dimensional representation is needed, 2) compare chemical retardation by ion exchange for fractures with and without a clay lining, and 3) compare physical and chemical retardation by ion exchange as a function of fracture velocity. The simulations differ from others in that the matrix is finite, and thus can become saturated with tracers introduced into the domain. The modeling suggests that chemical retardation caused by clay linings may not be important in this double porosity system, and that over a wide range, a single parameter group essentially determines the required complexity of the model.

## 1:30 P.M. V3.2

ELECTROCHEMICAL STUDIES OF CORROSION OF SIMFUEL: SIMULATED USED CANDU FUEL. S. Sunder, D.V. Shoesmith and N.H. Miller. Whiteshell Laboratories, AECL Research, Pinava, Manitoba, Canada ROE 1LO

The corrosion of SIMFUEL, simulated high-burnup CANDU fuel, is being investigated using electrochemical techniques and X-ray photoelectron spectroscopy. These studies are being conducted to determine the effects of the fission products in used nuclear fuel on its oxidation and dissolution. Electrodes were fabricated from SIMFUEL pellets with compositions close to that of a natural $UO_2$ fuel irradiated to 3 and 6 at.% burnups. The SIMFUEL electrodes showed higher conductivity and electrochemical reactivity than pure $UO_2$ electrodes. A comparison of the open-circuit corrosion potentials of the SIMFUEL electrodes with that of a pure $UO_2$ electrode in oxygenated solutions showed a much faster increase in the potential for the SIMFUEL electrodes at short times. This suggests that the initial stages of $UO_2$ oxidation

$$UO_2 \rightarrow UO_{2+x} \rightarrow UO_{2.33}$$

are facilitated by fission product impurities in the $UO_2$ matrix.

## 1:45 P.M. V3.3

MEASUREMENTS OF GRAIN-BOUNDARY INVENTORIES OF $^{137}Cs$, $^{90}Sr$ AND $^{99}Tc$ IN USED CANDU FUEL. S. Stroes-Gascoyne, J.C. Tait, R.J. Porth, J. McConnell and S. Watson, AECL Research, Whiteshell Laboratories, Pinava, Manitoba, Canada, ROE 1LO

The safety assessment of the geological disposal of used CANDU (CANada Deuterium Uranium) fuel requires information about the gap and grain-boundary inventories of radionuclides in used fuel. Measured gap inventories, combined with a fission gas-release code, have been used to estimate grain-boundary inventories for a number of radionuclides. This paper attempts to validate these estimates experimentally using two techniques. The first technique leached used fuels that were partially oxidized to expose grain boundaries. Only a fraction of the calculated grain-boundary inventories for $^{137}Cs$ was released, indicating that the calculations may overestimate inventories or that prior oxidation of the fuel either does not expose all grain boundaries, or renders Cs at grain-boundaries less soluble. Release of $^{90}Sr$ and $^{99}Tc$ agreed reasonably well with the estimates for these radionuclides which are, however, based on limited data and conservative assumptions. A second technique leached non-oxidized but crushed and size-fractionated used fuel in a flow-through system, to avoid any artifacts introduced by fuel oxidation or solution precipitation processes. Preliminary results for a low-power fuel indicated a gap + grain-boundary inventory for $^{137}Cs$ of 5.2%, in reasonable agreement with a calculated inventory of 4.7%.

## 2:00 P.M. V3.4

EFFECTS OF AIR OXIDATION ON THE DISSOLUTION RATE OF LWR SPENT FUEL. W. J. Gray, L. E. Thomas and R. E. Einziger, Pacific Northwest Laboratory, Richland, WA.

The long-term rate of release of soluble radionuclides from spent fuel in a geologic repository will be partially controlled by the dissolution rate of the $UO_2$ fuel matrix. Factors that could affect the dissolution rate, such as air oxidation of the fuel, must be evaluated when assessing spent fuel performance under repository conditions.

Light-water-reactor (LWR) spent fuels have been shown to oxidize along the grain boundaries, converting the $UO_2$ grains to oxygen-supersaturated $U_4O_9$. This oxidation state may persist for long times at the temperatures of interest for a repository. The oxidized fuel could dissolve at a faster rate than unoxidized fuel, either due to an increased chemical reaction rate or due to cracking along grain boundaries, resulting in increased surface area.

Dissolution tests conducted on oxidized and unoxidized fuel grains, using a flowthrough test method, have indicated that the chemical reaction rate is insensitive to the fuel's oxidation state, at least under one set of repository-relevant water chemistry conditions. Additional tests are in progress to relate the oxidation-induced change in effective surface area of the fuel to the dissolution behavior. Results of the dissolution testing as well as micro-structural characterization of the oxidized and unoxidized spent fuel specimens will be presented at the meeting.

## 2:15 P.M. V3.5

PHOTOTHERMAL DEFLECTION SPECTROSCOPY INVESTIGATIONS OF URANIUM ELECTROCHEMISTRY. James D. Rudnicki and Richard E. Russo, Lawrence Berkeley Laboratory, Berkeley, CA.

Photothermal Deflection Spectroscopy (PDS) has been applied to uranium oxide electrochemistry. The PDS technique allows the concentration gradients near the electrode surface and the optical absorption spectrum of the surface to be measured simultaneously. These measurements are performed in situ under dynamic conditions. The concentration gradients are directly related to the flux of species to and from the sample surface. The measurement of the concentration gradients detects the dissolution of species from the uranium oxide sample. The optical spectrum of the sample surface aids in the identification of the oxidation state of the surface. The literature has shown that the optical absorption of uranium oxides in the near UV changes strongly as the uranium is oxidized from $UO_2$ to higher oxides. The measurement of this absorption can discern between anodic processes that result in oxide films and processes that result in dissolution. The combination of these two measurements provides insight into the oxidation mechanism of uranium oxides.

## 2:30 P.M. V3.6

THE IMPORTANCE OF CRITICALITY IN THE SAFETY ANALYSIS OF THE SPENT FUEL WASTE CONTAINER. William G. Culbreth. and Paige Zielinski, Department of Civil and Environmental Engineering, University of Nevada, Las Vegas, NV.

The storage of high-level spent reactor fuel in the proposed national geologic repository will require the construction of containers to be placed in boreholes drilled into the host rock. Current legislation requires that the fuel be maintained subcritical. This is determined through the calculation of a neutron multiplication factor, $k_{eff}$, that must remain below 0.95 in any foreseeable situation. Criticality will play an important role in the choice of container material, the internal configuration of the fuel, and the selection of neutron poisons. An analysis of $k_{eff}$ should be a normal step in the conceptualization of new waste container designs. Unlike thermal effects in a proposed repository, criticality will remain a problem long after the 10,000 year lifetime of the facility.

In this study, nuclear criticality has been determined for the proposed spent fuel container for various situations that include varying fuel enrichment and partial air gap flooding. Results will be presented to demonstrate the impact of these variables on the design of a safe spent fuel container.

## 2:45 P.M. V3.7

KINETICALLY CONTROLLED DISSOLUTION OF $UO_2(s)$ UNDER OXIDIZING CONDITIONS. A COMBINED DISSOLUTION-OXIDATION MODEL. Ignasi Casas, Javier Giménez, Joan de Pablo, Vicenç Marti and M. Elena Torrero, Chemical Engineering Department, Universitat Politécnica Catalunya, 08028 Barcelona, Spain.

The release of uranium from three samples of $UO_2(s)$ with different particle sizes (100-300 μm, 900-1100 μm, pellet) has been studied as a function of time. In all cases, the same pH, ionic medium, temperature and oxygen partial pressure were used.

stringent; the liquid metal solvents such as copper-magnesium and zinc-magnesium, as well as molten calcium and alkaline earth halide salts, must not react excessively with containers and other components at 800°C and should have good mechanical properties and adequate thermal shock resistance. Titanium nitride is a candidate material because of its thermodynamic stability. This paper discusses the fabrication of TiN by hot pressing, effects of variables such as particle size and sintering aids on the densification process, relationships between porosity and mechanical properties, thermal shock resistance, and corrosion resistance of TiN in the molten salt and liquid metal environments.

Work supported by the U.S. Department of Energy, Nuclear Energy Research and Development Program, under Contract W-31-109-Eng-38.

### 4:30 P.M. V4.6
CRITICAL CONDITION FOR AND INITIATION LIFETIME OF LOCALIZED CORROSION OF MILD STEELS IN CONTACT WITH BENTONITE USED IN GEOLOGICAL DISPOSAL PACKAGES OF NUCLEAR WASTES. Guen Nakayama and Masatsune Akashi, Research Institute, Ishikawajima-harima Heavy Industries Co., Ltd., Tokyo Japan

The use of bentonite as an artificial barrier-cum-shock absorber is being contemplated for the use of mild steel as a material for geological package of high level radioactive nuclear wastes. For this, following critical points have been empirically clarified for mild steel, in a simulated groundwater, varying the bentonite-solution ratio (B/S ratio): 1. the relation between pH and B/S ratio, 2. effects of B/S ratio on the critical condition for initiation of localized corrosion; and 3. effects of B/S ratio and electrode potential on the initiation lifetime and subsequent rate of propagation of localized corrosion. Yet there is no escaping from the danger of the initiation of the localized corrosion occuring in weakly alkaline environments for systems containing bentonite envisaged today for geological disposal.

### 4:45 P.M. V4.7
LABORATORY STUDIES OF GAS GENERATION FOR THE WASTE ISOLATION PILOT PLANT.* L. H. Brush and M. A. Molecke, Sandia National Laboratories, Albuquerque, NM; A. J. Francis and J. B. Gillow, Brookhaven National Laboratory, Upton, NY; D. T. Reed, Argonne National Laboratory, Argonne, IL, R. H. Vreeland, West Chester University, West Chester, PA; R. E. Westerman, Battelle Pacific Northwest Laboratories, Richland, WA.

Design-basis transuranic waste to be emplaced in the Waste Isolation Pilot Plant (WIPP) may produce significant quantities of gas, which may in turn pressurize the repository to 150 atm (lithostatic pressure) and perhaps higher. Anoxic corrosion of steels produces significant quantities of $H_2$ under low-$CO_2$, brine-inundated conditions, but not under humid conditions. Under inundated conditions with initially pure $CO_2$ above brine, passivation occurs quickly. These results and thermodynamic calculations suggest microbial $CO_2$ production may shut off corrosion before it generates significant quantities of $H_2$. However, microbial activity may continue to produce significant quantities of $CO_2$ and other gases. $CO_2$ not consumed by cementitious materials in the waste and proposed backfill additives may condense to form a liquid or may form a supercritical fluid; either fluid would limit the pressurization caused by $CO_2$ production. However, microbial production of other gases may continue.

### SESSION V5: NATURAL ANALOGUES
Tuesday Morning, December 1
Theater

### 8:15 A.M. V5.1
MASS TRANSPORT MODELLING IN THE NATURAL ANALOGUE STUDY OF THE CIGAR LAKE URANIUM DEPOSIT. Ivars Neretnieks, Jinsong Liu & Jiwei Yu, Dept. Chemical Engineering, The Royal Institute of Technology, Stockholm, Sweden.

Mass transport of uranium and some other in-situ nuclear reaction products (tritium, C-14 and Cl-36) are studied in the near-field of the Cigar Lake uranium deposit in Canada. The various rock/ore matrices are modelled as porous media. Dissolution is the means by which uranium is released. Release of nuclear reaction products is dictated by the balance between mass transport, spontaneous decay and in-situ generation.

The objective of the study is to gain more confidence in the performance of final nuclear waste repositories. The hypothetical modelling is based on the natural conditions of the deposit. Because of the complex geometry of the system some idealizing assumptions are made.

The uranium transport case is solved both analytically and numerically. In the analytical approach only dissolved total uranium is addressed while in the numerical approach geochemical reactions are coupled with mass transport. Redox reactions of both minerals and aqueous species are included. In the study of nuclear reaction product transport in-situ generation in the ore, decay, dispersive and advective transport in the rock matrices are considered.

The results obtained are not in contradiction with the field observations.

### 8:30 A.M. V5.2
MODELLING IN SITU MATRIX DIFFUSION AT PALMOTTU NATURAL ANALOGUE STUDY SITE IN SW FINLAND. Kari Rasilainen, Technical Research Centre of Finland, Nuclear Engineering Laboratory, POB 208, SF-02151 Espoo, Finland; Juhani Suksi, University of Helsinki, Department of Radiochemistry, SF-00170 Helsinki, Finland

Deviations from radioactive equilibrium for the naturally occurring decay chains indicate mass flow in crystalline bedrock. Matrix diffusion theory was used to interpret the observed uranium series disequilibria around natural fractures. Profiles of easily dissolvable radionuclides from decay chains 4N+2 and 4N+3 were measured in core samples. Ammonium acetate and TAMM's oxalate were used to separate the radionuclides.

The interpretation of the profiles was based on the use of uranium series disequilibrium code URSE and migration code FTRANS. We simulated concentration profiles in time as function of depth from fracture surface into heterogeneous matrix using time-dependent boundary conditions. The system was characterized using all available experimental data, the system evolution was outlined using the available geological and geochemical history of Palmottu site.

The goals for this study were the interpretation of the observed activity profiles by matrix diffusion theory used in performance assessments, and the validation of the modelling concept.

### 8:45 A.M. V5.3
URANIUM-MINERAL — GROUNDWATER EQUILIBRIATION AT PALMOTTU NATURAL ANALOGUE STUDY SITE, FINLAND. Lasse Ahonen, Timo Ruskeeniemi, Runar Blomqvist, Geological Survey of Finland; and Riitta Pilvio, University of Helsinki, Department of Radiochemistry.

The behaviour of natural uranium in and around a small Precambrian U-Th mineralization hosted by pegmatites and migmatized gneisses is being studied as a natural analogue of radionuclides possibly released from a HLW-repository. The most important primary U-mineral of the mineralization is uraninite, which is partially altered to uranium silicate. The composition of groundwater in the bedrock fractures varies from fresh to slightly saline (TDS about 1.5 g/l). Uranium concentrations in the groundwaters vary from about 100 ppb to values below 1 ppb. The

the smectites should be regarded as true solid solutions rather than stoichiometric minerals or thermodynamically ill-defined substances capable of only simple ion exchange. Moreover, compositional variability apparently exists even at the dimensions of the unit cell in smectite, suggesting that measurements of smectite's thermodynamic properties must account for compositional differences among multiple cells in individual crystals. This introduces an extraordinary level of virtually irreducible complexity, and hence uncertainty, into models of bentonite-water interactions.

Thermodynamic models accounting for smectite's solid-solution behavior can nevertheless unequivocally bound ranges in aqueous solution compositions that are an explicit function of the uncertainty in smectite composition. In one approach, we quantify uncertainty in terms of ranges in concentrations of octahedral and tetrahedral Al, and exchange-site cations and vacancies. Mass transfer in bentonite-water systems is then modeled using conventional mass-action relations and standard Gibbs energies for stoichiometric minerals, and the site-occupancy constraints combined with site-mixing relations for smectite. The resultant bounding conditions in aqueous solution compositions predicted in the model may be large or small depending on which aqueous species are considered, but they are valid irrespective of equilibrium/disequilibrium in smectite-water reactions.

## 10:30 A.M. V6.2

AQUEOUS DIFFUSION IN REPOSITORY AND BACKFILL ENVIRONMENTS. James L. Conca, WSU Tri-Cities, Richland, WA 99352; Michael J. Apted and Randy Arthur, INTERA Sciences, Denver, CO 80235.

Aqueous diffusion coefficients have been determined in a variety of porous media using transient and steady-state, direct and indirect methods. For performance assessments, the simple diffusion coefficient, $D$, must be separated from retardation effects, e.g., sorption. $D$ is only a function of volumetric water content, $\theta$, and not material characteristics. At high water contents, $D$ gradually declines as water content decreases, from $10^{-5}$ cm$^2$/sec at $\theta$ ~ 50% to $10^{-7}$ cm$^2$/sec at $\theta$ ~ 5%, followed by a sharp decline to $10^{-10}$ cm$^2$/sec at $\theta$ ~ 0.5%. For example, a saturated fractured whole rock with a total porosity of 10%, and an unsaturated gravel with a total porosity of 40% that is only 25% saturated, have the same water content, $\theta$ ~ 10%, and the same $D$ of 3 x $10^{-7}$ cm$^2$/sec. Natural materials have highly tortuous diffusion paths, and log-normal distributions of fracture aperture widths or pore volume/throat distributions that are similarly affected by changes in the water content. Although surface diffusion has a strong experimental basis in the transport of gases along metal surfaces, and a strong theoretical basis in clay systems, experimental evidence conclusively indicates that surface diffusion is not important in aqueous geologic/backfill systems, even in compacted bentonite, because of the extremely poor connectivity among electric double-layers and the extremely low diffusivities and high $\partial C/\partial x$ at small area/point contacts which more than negate the increased flux along individual grain surfaces.

## 10:45 A.M. V6.3

STUDY ON RETARDATION MECHANISM OF ³H, ⁹⁹Tc, ¹³⁷Cs, ⁹⁵Nb AND ²⁴¹Am IN COMPACTED SODIUM BENTONITE. Haruo SATO, Takashi ASHIDA, Yukitoshi KOHARA and Mikazu YUI, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, 319-11, JAPAN.

The apparent diffusion coefficients were measured at room temperature (about 23 °C) under atmospheric condition by one-dimensional non-steady state diffusion for ³H, ⁹⁹Tc, ¹³⁷Cs, ⁹⁵Nb and ²⁴¹Am in water-saturated compacted sodium bentonite. Japanese commercially available sodium-bentonite, Kunigel¹ [1], was used for this study and its montmorillonite content is 50 ~55wt%. The bentonite was dried at 110°C and was compacted in a half cell with the size of 20mm in diameter and 20mm in height with the density of $0.4 - 2.0 (\times 10^3$ kg/m³). Compacted bentonite in the cell was prepared to be saturated with distilled water. The apparent diffusion coefficient decreases with increasing dry density of bentonite. ³H has the largest apparent diffusion coefficient of these radionuclides. The results that the apparent diffusion coefficient of ³H decreased as a function of dry density of bentonite would be the effect of the change of porous structure with dry density of bentonite because ³H has no sorption behavior on bentonite. ⁹⁹Tc may be retarded by anion exclusion because dominant diffusion species of ⁹⁹Tc is pertechnetate ion under atmospheric

condition. Retardation for ¹³⁷Cs may be caused by ion-exchange on bentonite. The sorption, anion exclusion and molecular filtration are considered as retardation mechanism for ⁹⁵Nb and ²⁴¹Am because those dominant species have negatively charge and large ionic size.

[1]: Kunigel¹ ® is a product of the Kunimine Industries Co., Ltd.

## 11:00 A.M. V6.4

DIFFUSION OF URANIUM IN COMPACTED SODIUM BENTONITE. Arto Muurinen, Technical Research Centre of Finland, Reactor Laboratory, P.O. Box 200, SF-02151, Espoo, Finland.

The major factor controlling the mobilization of most fission products and actinides from spent fuel under disposal conditions is the rate of dissolution of the UO$_2$ matrix. The progress of the dissolution process is controlled by the diffusion of the dissolved uranium through buffer to groundwater.

In this study, diffusion of uranium dissolved from uranium oxide fuel was studied experimentally in compacted sodium bentonite. The diffusivities were determined by the steady-state method. The parameters varied in the study were the density of bentonite, salt content of the solution and redox conditions.

The solubility of uranium in the non-saline (300 ppm) water was about 25 ppm in aerobic conditions, and uranium stayed well in the solution both in aerobic and anaerobic diffusion tests. The effective diffusivities of uranium depended considerably on the density of bentonite, probably as a result of anion exclusion.

The solubility of uranium in the saline (35000 ppm) water was about 11 ppm in aerobic conditions. In anaerobic conditions uranium, however, tended to precipitate, uranium diffusion through the samples being controlled by the low solubility.

## 11:15 A.M. V6.5

TEMPERATURE AND MOISTURE DISTRIBTIONS IN A CLAY BUFFER MATERIAL DUE TO THERMAL GRADIENTS, Mohamed, A.M.O., Yong, R.N., Geotechnical Research Centre, McGill University, Montreal, Canada; Kjartanson, B., AECL Reserach, Whiteshell Laboratories, Pinawa, Manitoba, Canada.

This paper addresses the experimental study and evaluation of the material parameters governing the process of coupled heat and mass flow in the buffer material. A one-dimensional test configuration was used to examine the transient temperature and moisture flow in a buffer material. Several series of one-dimensional tests were used to investigate the nature of the temperature and moisture movement under different externally imposed temperature gradients. The measured temperature and moisture gradients were used to calculate the diffusion parameters governing heat and moisture movement in the buffer material. An identification technique was then used to calculate the diffusion parameters. The empirical relationships of the diffusion parameters are presented. These relationships will be used to assess the time dependent moisture and temperature profiles of the buffer to analyze its thermal performance before it becomes saturated with water.

## 11:30 A.M. V6.6

MOISTURE ADSORPTION AND VOLUME CHANGE OF PARTIALLY SATURATED BENTONITE BUFFER MATERIALS. Takeshi Kanno and Hisao Wakamatsu, Ishikawajima-Harima Heavy Industries Co., Ltd., Yokonama, Japan.

Water vapor adsorption characteristics of buffer materials to be used for the geologic disposal of high-level radioactive waste are investigated. Highly compacted blocks of Japanese Na bentonite and a bentonite-sand mixture are used as the buffer material. Initial dry density of the blocks

### 3:30 P.M. *V7.5

THE USE OF IMAGE ANALYSIS IN LONG-TERM NONDESTRUCTIVE CORROSION MONITORING OF NUCLEAR ALLOYS, P. J. R. Scott, CARIAD Consultants, 397 Parkview Ave., North York, Ontario, Canada M2N 3Z7, S. Sandloenken, Ontario Hydro Research, 800 Kipling Ave., Toronto, Ont., and G. Guérin, Centre de Caracterisation Microscopique des Materiaux, Ecole Polytechnique, Montreal, P.Q.

Direct examination of materials suspected of damage is always desirable, but not always feasible. For example, it may be impractical to cut specimens from reactors or high integrity waste containers. In these cases, replication of areas of interest using a combination of image analysis and replicating tape can provide a rapid, inexpensive, and nondestructive alternative. It also results in an easily stored permanent record of the damaged area. This technique may be of particular use in analyzing microbiological corrosion effects, but biofilm effects may be significant.
To test the reliability of the results using replicating techniques in combination with the image analyzer a "standard" sample and one sample from a real pitting problem were examined by direct examination combined with image analysis, by image analysis of an untreated peel, and by image analysis of peels from samples treated with penetrants. The results of these analyses indicated that image analysis with replicating technique having an adherent penetrant was best for localized corrosion. Different penetrant options are discussed, and the potential for applying this type of technique to analysis of microbiological degradation of buried objects such as waste containers is considered.

### 4:00 P.M. V7.6

ANALYSES OF CORROSION PRODUCTS AND DEPOSITS ON THE SURFACE OF AUSTENITIC ALLOYS EXPOSED TO FRESH WATER, A.M. Brennenstuhl, Ontario Hydro Research, 800 Kipling Avenue, Toronto, Ontario, Canada, M8Z 5S4; R.D. Davidson, Surface Science Laboratory, University of Western Ontario, London, Ontario, Canada, N6A 5B7; and T.S. Gendron, Chalk River Laboratories, Chalk River, Ontario, Canada, K0J 1J0.

Corrosion product and deposit analyses are a necessary part of corrosion mechanism determination. When corrosion has resulted in an environment in which microbiological factors have had an important role, such characterization takes on an even greater importance. This is because the chemistry of the natural environment is generally difficult to define.

Bulk analysis techniques such as ICP, ICP-MS and XRD will yield elemental and chemical information from deposits. Microprobe techniques which include SEM/EDS, XPS and SIMS are better suited for extracting elemental and chemical information from corrosion products. This paper discusses the application of these techniques and how they can help in mechanism elucidation.

### 4:15 P.M. V7.7

EFFECTS OF MICROORGANISMS GROWTH ON THE LONG TERM STABILITY OF CEMENT AND BITUMEN - M.F. Libert, Nuclear Research Center of Cadarache, 13108 St Paul Lez Durance Cedex, FRANCE, R. Sellier, G. Jouquet, M. Trescinski and H. Spor.

Cement are used as a coating matrix for nuclear wastes or as engineered barrier of wastes repositories situated in geological formations.

The effect of mineral acids excreted by bacteria (Thiobacillus) or organic acids produced by fungi, on the biodegradation of three kinds of cement is discussed. Organic acids are quantitatively and qualitatively determined during growth of fungi over a two year period. Anaerobic conditions promote the organic acid production. Even with high pH conditions, pH of the cement = 11, growth of microorganisms occurs.

Biodeterioration of cement is expressed in terms of bioleaching velocity of calcium and modifications of physical properties.

Bitumen is commonly used as a matrix for the long term storage of radioactive wastes. Long term biodegrability of bitumen is discussed as a function of its chemical composition and of various studied microorganisms.

### 4:30 P.M. V7.8

CHARACTERIZATION OF SPUTTER-DEPOSITED 316L-STAINLESS STEEL ULTRATHIN FILMS FOR USE IN MIC STUDIES, A.J. Pedraza, M.J. Godbole, University of Tennessee, Knoxville, TN and P. Suci and G. Geesey, Montana State University, Bozeman, MT.

Thin films ranging in thickness from 6-12 nm were deposited on germanium internal reflection elements but sputter deposition. The chemical composition of the films differed by no more than 10% of the bulk stainless steel target. Films 6-12 nm in thickness were found to be continuous and contained amorphous and base center cubic (BCC) phases. A face centered cubic (FCC austenitic) phase could be produced after heating to 873 K but this produced eruptions and depressions in the film. Corrosion rates of films composed of amorphous and BCC phases were similar to that of the bulk material although the passivating current was higher for thin films than the bulk material. Films exposed to flowing sterile bacterial culture medium were stable for at least 1000 h as were films challenged with a consortium of bacteria when evaluated by attenuated total reflectance Fourier transform infrared spectroscopy. The results suggest that thin films of stainless steel may be used in conjunction with infrared spectroscopy to evaluate corrosion reactions promoted by bacterial biofilms.

### 4:45 P.M. V7.9

MICROBIAL INFLUENCE ON ENVIRONMENTAL CRACKING OF HIGH STRENGTH STEELS. Tim Ford and Ralph Mitchell, Harvard University, Cambridge MA; and Marianne Walch, Naval Surface Warfare Center, Silver Spring, Md.

Failure of hardened steels used in ocean engineering systems is often due to embrittlement of the material. Although hydrogen adsorbed in manufacture may be partially responsible, marine bacteria rapidly colonize grain boundaries and include species that produce hydrogen, acids and sulfides, all of which can be important in accelerating embrittlement.

This paper will describe our joint research program on embrittlement of hardened steels. We have previously measured hydrogen concentrations under biofilms of sufficient magnitude to damage susceptible steels. We have also found that stressed high tensile strength steel rods are susceptible to stress cracking in the presence of a hydrogen- and acid-producing bacterium.

Our current research focuses on two areas: (1) We are investigating hydrogen permeation rates through thin films of steels used in ocean engineering systems. These materials are being exposed to pure and mixed cultures of organisms of different metabolic types. In addition, we are exposing stressed samples to flowing and stagnant seawater to test the effect of microbial colonization on rates of crack formation. We will describe our methodological approach to examining susceptibility of hardened steels to microbial attack, and present preliminary results on materials failure.

## 9:45 A.M. V8.6

URANIUM AND RARE EARTH PARTITIONING IN SYNROC.
Katherine L. Smith, Gregory R. Lumpkin, Mark G. Blackford and
R Arthur Day, Australian Nuclear Science and Technology Organisation,
P.M.B. 1, Menai N.S.W. 2234, Australia.

Synroc is a dense titanate ceramic designed to encapsulate high level
nuclear waste (HLW). Approximately 75 vol. % of Synroc consists of
zirconolite, perovskite and hollandite. These three phases are the major
hosts for Sr, Ca, rare earth elements (REEs) and actinides (ACTs) in the
HLW. Other phases include: rutile/Magneli phases (~20 vol.%),
intermetallic alloys (consisting of noble metals and P) and several Ca-Al-
titanate phases (which in combination generally constitute < 5 vol.%).
REEs and ACTs predominantly partition between zirconolite and
perovskite, with a small percentages being incorporated in one of the
minor phases (CAT).

This study was initiated to determine the partitioning of ACTs and REEs
between zirconolite, perovskite and CAT in Synrocs containing different
amounts of simulated waste (10 and 30 wt.%) and different processing
impurities (Fe₂O₃ and Na₂O). U was used to simulate tetravalent
actinides, and Ce, Nd and Gd were used to simulate trivalent actinides.

It was found that regardless of waste loading or the presence of processing
impurities, partitioning ratios for zirconolite : perovskite were
approximately 2 : 1, 1 : 4, 1 : 10, and 1 : 1 for U, Ce, Nd and Gd,
respectively. Comparisons will be drawn between the results of this study
and the results of previous authors.

## 10:00 A.M. V8.7

THE INTERACTION OF SYNROC-C WITH BOOM CLAY. Pierre Van
Iseghem, SCK/CEN, Mol, B.; and K. Hart, ANSTO, Lucas Heights,
NSW

The dissolution behaviour of Synroc-C in contact with Boom
clay has been investigated. Inactive Synroc-C samples with
a waste loading of 10 % were exposed at 90 °C or 150 °C in
natural Boom clay or a diluted clay slurry, for durations up
to two years. Synroc-C appears to dissolve much slower than
high-level waste glass. The dissolution behaviour of Synroc-
C is controlled both by the very low solubility of its
constituent phases. Leached species sorb onto the clay
further reducing solution concentrations. The experiments
are interpreted in terms of mass loss, solution analysis and
surface analysis.

## SESSION V9: GLASS LEACHING
Wednesday Morning, December 2
Theater

## 10:30 A.M. V9.1

THE LEACHING OF Pu, Am, Np, AND Tc FROM HIGH-LEVEL WASTE
GLASS IN CLAY MEDIA. P. Van Iseghem ; K. Lemmens ; W. Lian,
SCK/CEN, Mol, B

The leaching behaviour of Pu, Am, Np and Tc from the high-
level waste glasses of interest to Belgium has been studied.
The corrosion tests were carried out on inactive glasses (the
Cogema R7T7 glass SON68 and the DWK Pamela glasses SM513 and
SM527) traced with the radionuclides. Nuclide leaching was
studied in contact with a Boom clay slurry (clay diluted with
claywater), eventually loaded with metal corrosion products,
at 90 °C and 40 °C, for durations up to three years. Nuclide
concentration in mobile form (smaller than 10⁵ MWU) was found
to be rather independent on duration, and was about 10⁻⁹
Mol/l (Pu, Np) or less (Am, Tc). This value was decreasing
in the presence of metal corrosion products. Largest part of
the activity leached is sorbed onto the clay in an immobile
form. The mobile concentrations leached do not fit with
solubility limits, meaning that other phenomena such as
complexation would control the mobile concentration.

## 10:45 A.M. V9.2

ENHANCEMENT OF THE GLASS CORROSION IN THE PRESENCE OF CLAY
MINERALS: TESTING EXPERIMENTAL RESULTS WITH AN INTEGRATED
GLASS DISSOLUTION MODEL. Enzo Curti, Paul Scherrer Institut, 5232 Villigen
PSI, Switzerland; Nicole Godon, and Etienne Vernaz, CEN-VALRHO,B.P. 171,
30205 Bagnois-sur-Cèze Cedex, France.

ABSTRACT

Recent glass dissolution experiments, in which borosilicate glass specimens were
leached at 90°C with various environment materials, indicate remarkably faster glass
corrosion in the presence of clay, compared to tests with glass alone or with other
backfill materials. This effect correlates with the clay content in the backfill, and was
attributed to the removal of silica from solution. Sorption, or dissolution with repre-
cipitation of a silica-rich clay, were proposed as possible mechanisms for the silica con-
sumption.

The results of some experiments have been tested against a glass dissolution model, in
which a widely used kinetic equation for glass corrosion is coupled with diffusive silica
transport through a simple porosity, linearly sorbing medium. Because the kinetic equa-
tion imposes glass corrosion rates, which are inversely proportional to the silicic acid
concentration in the leachant contacting the glass, the model predicts an enhancement of
the corrosion kinetics when silica is sorbed by the porous medium.

The experimental data proved to be fully consistent with the predicted acceleration of
the glass dissolution. Moreover, the model-estimated distribution coefficients for silica
sorption ($K_d$) fall within the range of values extracted from available literature data,
thus supporting the hypothesis that the observed high corrosion rates are due to sorption
of silica on the clay mineral surfaces.

## 11:00 A.M. V9.3

DISSOLUTION OF R7T7 GLASS IN STATIC AND FLOWING
CONDITIONS : INFLUENCE OF Si DIFFUSION MECHANISM IN
THE LEACHED LAYER. F. Delage, CEA-CEN
Valrho/SCD/SDMC, BP171, 30205 Bagnois sur Cèze Cedex,
France; F. Larché, University of Montpellier II, GDPC, F34090
Montpellier, France; and E. Vernaz, CEA-CEN
Valrho/SCD/SDMC, BP171, 30205 Bagnois sur Cèze Cedex,
France.

Leach tests of the R7T7 nuclear waste glass in distilled water, are
conducted at 50 and 90°C, under static and slow flowing
conditions, with a glass-surface-area-to-solution-volume of 0.5
cm⁻¹. A computer model for glass dissolution (LIXIVER) is used to
interpret the data.
The mechanistic model is based on the combination of the first
order law governing surface reactions, the equation of silicon
mass transport in the interstitial solution of the alteration film, and
an empirical law of partial silicon retention in the alteration layer.
The LIXIVER model satisfactorily accounts for the experimental
results. The importance of Si diffusion mechanism, in the leached
layer, is stressed. Silicon apparent diffusion coefficient are
pointed out : $DS_i$ values are ranged between $10^{-16}$ and $10^{-14}$
m²/s at 50°C, and between $10^{-14}$ and $10^{-13}$ m²/s at 90°C.

## 11:15 A.M. V9.4

EFFECTS OF MgO ON SHORT AND LONG TERM STABILITIES IN
WATER OF R7T7 AND M7 NUCLEAR WASTE GLASSES.
T. Advocat, CEA-CEN/VALRHO, Marcoule BP171, 30207 Bagnois/Cèze-
France; E. Vernaz (idem); J. L. Crovisier, CGS-CNRS, 1 rue Blessig, 67000
Strasbourg-France; J. Dussossoy, CEA-CEN-VALRHO.

Magnesium oxide was added to the standard R7T7 and M7 glass
compositions developed for containment of fission product solutions. M7
differs from the R7T7 reference glass mainly by a larger proportion of
network modifier elements and a correspondingly lower proportion of
glass network forming elements. The percentage of fission products,
simulated in this study by inactive elements, was the same in both cases.
Increasing the MgO content of the glass compositions by 2 to 5 wt%
resulted in significant variations in the aqueous leaching resistance at 90
and 100°C.

## 2:30 P.M. V10.3
### Modeling SA/V effects in borosilicate glass dissolution

W. L. Bourcier, Lawrence Livermore National Laboratory, Livermore, CA 94550
J. Gerl and I. Feng, Argonne National Laboratory, Argonne, IL 60439

Experimental data for borosilicate glass dissolution show that above a certain surface area to volume ratio (SA/V), closed system test results do not scale according to (SA/V)$^*$t where t is time. Following suggestions of others, we have evaluated the role of ion exchange in understanding SA/V$^*$T scaling in chemical modeling of glass. At high SA/V, the mass of the alteration layer in the glass-water system is significant and must be accounted for in the simulation. Stoichiometric dissolution cannot be assumed. We can use modeling results to estimate the thickness of this exchange zone and determine whether this mechanism can explain the lack of SA/V$^*$t scaling in high SA/V tests. In our model, non-stoichiometric release is combined with data for the increase in rate coefficient with increasing pH obtained in flow-through glass dissolution tests. Model calculations for distilled water interacting with typical borosilicate waste glasses predict the lack of scaling results even if the exchanging layer is less than 10 nanometers thick. The model also predicts that glass dissolution in J-13 water or other waters better buffered in pH than distilled water should scale according to SA/V$^*$t to higher SA/V values. The lack of SA/V$^*$t scaling in high SA/V tests therefore does not indicate any fundamental deficiency in our current understanding of glass dissolution as embodied in glass dissolution models. It is a simple consequence of ion exchange which must be accounted for in elemental mass balances in the chemical model. Work performed under the auspices of the U.S. Department of Energy Office of Civilian Waste Management, Yucca Mountain Project Office, by Lawrence Livermore National Laboratory under contract W-7404-ENG-48.

## 2:45 P.M. V10.4
### EFFECTS OF CRACKING ON THE KINETICS OF THE INTERACTION OF SILICATE GLASSES WITH WATER.

Jing C. Sang and Aaron Barkatt, The Catholic University of America, Washington, DC; and Inna G. Talmy and Marriner K. Norr, Naval Surface Warfare Center, Silver Spring, MD.

Comparative studies of two multi-component silicate glasses have confirmed the observation that glasses with a relatively low $SiO_2 + AlO_{3/2}$ content may exhibit temporary increase in leach rates during the initial stages of their exposure to water. SEM studies of the leached glass surfaces strongly support the assumption that this phenomenon is due to cracking of the leached glass and a consequent increase of the exposed surface area.

## 3:00 P.M. *V10.5
### NON-LINEARITIES IN LONG-TERM LEACH TESTS ON NUCLEAR WASTE GLASSES.

Pedro B. Macedo and Andrew C. Buechele, Vitreous State Laboratory, The Catholic University of America, Washington, D.C.

Long term tests on the durability of nuclear waste glasses, both under laboratory conditions and in actual burial environments, have shown that after periods of several months or years the rates of glass corrosion can show unexpected increases. In burial tests in brine environments the growth of the thickness of the surface layer during years 3-5 was found to be faster than expected on the basis of findings during the first 2 years. Lab tests under repository-relevant environments have shown the delayed formation of colloids. Pulsed flow tests indicate that sudden increases in leach rate may occur after 3-20 months. These findings show that is it important to extend durability tests to long periods in order to establish a reliable basis for predictive modeling of long-term glass durability.

## 3:15 P.M. V10.6 (ABSTRACT NOT AVAILABLE)

## 3:30 P.M. V10.7
### ANCIENT METALLURGY AND NUCLEAR WASTE CONTAINMENT.

Martha Goodway, Smithsonian Institution, Washington DC 20560

Archaeological artifacts of metal, usually of bronze, are examples of very long term corrosion resistance and as such have been evaluated by the nuclear agencies of several countries as a guide to materials choices for the containment of nuclear waste. Complete evaluation is thwarted by the loss of some objects to the corrosion process, and by uncertainty as to the environmental history under which others survived.

It is suggested that instead of metal, an impermeable ceramic composite used in ancient metals processing installations should be reproduced and tested for its resistance to radiation damage. Though this material was synthesized twenty five centuries ago, these installations are intact and still hold water.

## 3:45 P.M. *V10.8
### LONG TERM PREDICTIONS RELATING TO ENVIRONMENT SENSITIVE CRACKING (ESC).

R.N.Parkins, University of Newcastle upon Tyne, Newcastle NE1 7RU, England.

In the great majority of instances of ESC that occur with operating structures, such a mode of failure is not anticipated at the design stage. This is usually because the environment that results in cracking was not identified as potent or it was locally generated from the bulk environment and that had not been anticipated. There are many examples of such, but buried pipelines may be used to illustrate the problem, since the environments involved have similarities to those that may be encountered with any buried structure. While understanding of the mechanisms of ESC in buried pipelines has evolved following the advent of such failures, the experimental methods used in arriving at that understanding and its reproduction in laboratory tests are more generally applicable and may be employed in considering the potency of any feasible environment to which a structure is likely to be exposed. However, demonstration of the potency of a particular environment to promote ESC in a particular metal in laboratory tests does not mean that such will occur in an operating structure and there is a need to recognise the variability of the incidence of ESC in service.

## 4:15 P.M. *V10.9
### The Assessment of the Long-Term Effects of Localised Corrosion of Carbon and Stainless Steel Containers for Radioactive Waste.

C.C.Naish, S.M.Sharland, A.C.Smith and K.J.Taylor.
AEA Technology, Harwell Laboratory, Oxfordshire, OX11 0RA, U.K.

This paper describes a general methodology that has been developed to predict the long-term corrosion behaviour of radioactive waste containers under repository conditions. In particular, the studies described consider localised corrosion, which is the process most likely to affect container integrity in the short-term. The assessment of the

most in any period of the weathering except for the early stage, and that the uranium fractionation between minerals varies with time until the end of the weathering. The present study suggests that the uranium fractionation between minerals is affected by rock alteration, which should be therefore included in models to predict uranium migration over long, geologic timescales.

## V11.5

### A MODELLING STUDY OF THE EFFECT OF ROCK ALTERATION ON THE REDISTRIBUTION OF URANIUM.

Takashi Murakami and Hideo Kimura, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan.

A modelling study was carried out to understand the effect of rock alteration on uranium radionuclide concentrations in rocks, in the vicinity of the Koongarra ore deposit, Australia. The one-dimensional, advection-dispersion-sorption model considers two important factors resulting from the process, mechanism and rate of chlorite weathering, one of the rock alterations over a million year period, (a) the change in time of the distribution coefficients of uranium and thorium and (b) that of rock porosity. The distribution coefficient and rock porosity at a given time, are expressed as average values of those of the coexisting minerals.

By assuming a Darcy velocity and an initial concentration of uranium in the groundwater, 0.9 m/y and 0.5 ppm, respectively, similar to present-day values, we were able to derive from the finite element modelling, uranium concentrations in the rock which are in good agreement with measured values. The calculated values of Th-230/U-234 activity ratios show a similar trend to those observed, although more experimental data are necessary to confirm the similarity. However, in the absence of the rock alteration, the calculated results did not agree with those observed. The present study suggests that rock alteration should be included in models used to predict uranium migration over long, geologic timescales.

## V11.6

### PILOT AND FIELD SCALE URANIUM LYSIMETER STUDIES AT THE OAK RIDGE Y-12 PLANT.

D. D. Cates, C. W. Francis, Oak Ridge National Laboratory, Oak Ridge, TN; L. M. Lasher, R. R. Kimmralf, Y-12 Plant, Oak Ridge, TN.

Field and pilot scale uranium leaching facilities (lysimeters) have been constructed at the Oak Ridge Y-12 Plant to investigate the rate of uranium (U) leaching and the residual U concentration that can be expected when low level radioactive waste (LLW) is buried in landfills. Current plans are to load two 8 ft diameter, 10 ft deep standard column lysimeters with compacted production trash (blotter, waste wipes, paper ect) and apply groundwater to the surface of the lysimeters at a rate equal to 5 times the natural annual rainfall at the Y-12 site.

Several issues had to be addressed before the field lysimeters could be loaded with the LLW. Predominate among these concerns was how to adequately characterize the waste placed in the lysimeters ( ~ 300 ft³ waste per lysimeter) and how to effectively collect in-situ leachate samples from compacted wasteforms in the absence of soil. Pilot scale studies revealed that monitoring individual bags (30 gal) of LLW with a waste curie monitor containing 6 large scintillation detectors would be sufficient to determine the initial U loading. Additional studies revealed that conventional suction candles would perform adequately within the compacted waste for extended time periods ( > 194 days) provided sufficient silica flour is packed around the candles.

In the pilot leaching studies, the highest U concentrations (approx. 0.2 mg/l) in the leachate was observed during the first month of leaching before active biological decomposition processes became dominant making the lysimeter anoxic. After the initial toxic flushing, U concentrations in the leachate became very low (avg = 0.021 mg/l). Leaching data obtained from the pilot leaching study revealed U transfer coefficients from the solid phase of the U contaminated waste to the solution phase to range between 0.001 and 0.0001 kg/l. Data of this type will be used in the development of leaching and transport models and pathways analyses of U moving off landfill sites.

## V11.7

### LATTICE BOLTZMAN MODELS FOR COUPLED HETEROGENEOUS FLOW AND MULTICOMPONENT SORPTION IN PORE NETWORKS

D.R. Janecky, S. Chen, W.P. Myers, and I. Triay, Los Alamos National Laboratory, Los Alamos, NM.

Lattice automata models allow explicit examination of processes involved in coupling between solute transport within heterogeneous pore networks and chemical reactions at mineral surfaces. Multicomponent solute transport and diffusion has been coupled with lattice Boltzman approaches for solution of Navier-Stokes equations, resulting in efficient, parallel calculations. Chemical reactions at solid surfaces, including multicomponet sorption/desorption/site competition, can be examined with the model because heterogeneous pore network structures, hydrodynamic transport, solute diffusion and mineral surface processes are all treated explicitly with space and time. The simplicity and flexibility of the approach provides the ability to study the interrelationship between fluid flow and chemical reactions in porous materials, at a level of complexity that has not previously been computationally possible. Of particular importance to investigations of radionuclide transport in the environment is the opportunity to examine interactions and integration of surface processes as a function of spatial scale and heterogeneity.

## V11.8

### DISSOLUTION OF $UO_2(S)$ IN $MgCl_2$-BRINES UNDER DIFFERENT REDOX CONDITIONS.

Ignasi Casas, Javier Giménez, Joan de Pablo and M. Elena Torrero, Chemical Engineering Department, Universitat Politècnica Catalunya, 08028 Barcelona, Spain.

The dissolution of unirradiated $UO_2(s)$, with a particle size of 1 mm, has been studied in $MgCl_2$ brines at 298 K under both reducing and oxidizing conditions.

Results obtained under reducing conditions ($H_2$ atmosphere in the presence of a palladium catalyst) show an initial increase of the total uranium concentration in solution and a subsequent decrease until equilibrium (or steady state) values are reached. The whole process takes about three weeks.

Results obtained under oxidizing conditions (nominal oxygen partial pressures of 0.05 and 1 atm) show two different trends. A relatively fast initial dissolution rate which is found to be first-order dependent on the oxygen partial pressure. After approximately 1-2 weeks, a slower dissolution rate is obtained.

X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM), are applied to ascertain possible changes on the solid surface.

## V11.9

### THE ALTERATION OF URANINITE TO CLARKEITE.

R. J. Finch and R. C. Ewing, Department of Geology, University of New Mexico, Albuquerque, New Mexico 87131.

The hydrothermal (200 - 400°C) alteration of uraninite by alkali-bearing solutions commonly results in the formation of clarkeite $(Na,Ca,Pb)U_2O_7 \cdot nH_2O$ (n~1). The structure of clarkeite has not been refined, but it is essentially isostructural with $Ca(UO_2)O_2$ and $Na_2U_2O_7$. Clarkeite can accommodate Th, Zr and rare earth elements (REE) (1-3 wt. %), but concentrations vary considerably, depending on locality. Mole percent Na equals or exceeds Ca; Pb is highly variable but is less than

## VII.15

ANALYTIC SOLUTIONS FOR CONTAMINANT GAS DISCHARGE FROM A NUCLEAR WASTE CONTAINER. E.D. Zwahlen, P. L. Chambre, W. W.-L. Lee and T. H. Pigford, Departments of Nuclear Engineering, University of California, Berkeley, CA 94720-0001 and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720-0001

We derive analytic solutions for the migration of radioactive gases through a penetration of a nuclear waste container in unsaturated rock, for penetrations occurring in the first 1000 years after emplacement. The velocity of the bulk gas is calculated using Poiseuille flow, which has been experimentally validated for holes with radii of 2.5 μm and an analytic approximation of the temperature profile in the repository. Using the bulk gas velocity we solve the advective-diffusion equation for $^{14}CO_2$ in the combined system of the container and the hole. We calculate the profile of the bulk gas velocity as a function of hole size. We then calculate the release rates of $^{14}CO_2$ from the combined effects of bulk gas advection and diffusion.

For illustration we calculate the bulk gas velocity and $^{14}CO_2$ release rate for holes occurring at 300 years, for sealing temperatures of 298 K and 558 K. For sealing temperature of 298 K, there is a pulse release for holes larger than 10 μm, followed by essentially pure diffusive release because the direction of flow is reversed shortly thereafter. The USNRC release rate limit is exceeded for only a short time. For the 5 μm hole, however, there is no pulse release, and there is advective outflow of $^{14}CO_2$ for several hundred years because flow reversal does not occur until 900 years after penetration. For containers sealed at 558 K, there is only flow of air into the container, and release of $^{14}CO_2$ is only by counter-diffusion. Without the pulse release of $^{14}CO_2$, the diffusive gradient is higher for the same hole size.

Further analysis of gas flows awaits definition of hole formation, timing and penetration geometry.

## VII.16

### EVALUATION OF THE RETENTION CAPABILITY OF THE DIFFERENT BARRIERS AND THEIR CONTRIBUTION TO REPOSITORY PERFORMANCE.

N.K.Ghattas, K.A.El Adham, S.B.Eskander, N.S.Mahmoud Atomic Energy Authority, Egypt.

The work reported is part of a comprehensive research program including comparative studies on the retention capability of the different barriers in a simulating disposal environment. The different engineering barriers were evaluated on basis of minimal release of radionuclides to the environment. The aim was to study their possible efficiency for the confinement of radioactive waste to the disposal site and their contribution to repository performance. The interest is also directed to study the chemistry and microstructure of cement based materials.

The present study focused on the retention capability of the different local BACKFILL materials and on horizontal and vertical radionuclides migration in simulating repository conditions of saturated static humid environment using single or combined components of the near-field. The aim was to keep radioactive waste processing as low as reasonably achievable by improving nonradioactive engineering barriers which may lead to avoid partially or perhaps totally the processes of improvement of waste forms.

## VII.17

DIFFUSION OF CORROSION PRODUCT OF IRON IN COMPACTED BENTONITE. 
Kazuya Idemitsu, Hirotaka Furuya and Yaohiro Inagaki, Kyushu Univ., 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812, JAPAN.

Carbon steel is one of the candidate overpack materials for high-level waste disposal. The corrosion rate of carbon steel is restricted by the presence of buffer material such as bentonite and seems to be affected by the diffusion of corrosive materials and corrosion products through the buffer material.

The apparent diffusivities of corrosion product of iron were measured in some bentonite specimens with bulk of carbon steel. The apparent diffusivities of iron ion were also measured without bulk of carbon steel for comparison. The apparent diffusivities of corrosion product were in the order of $10^{-12}$ m$^2$/s and showed a tendency to decrease with increasing density of bentonite specimen. There was no significant effect of silica sand on the apparent diffusivities. While the apparent diffusivities of iron

ion were in the range of $10^{-14}$ to $10^{-15}$ m$^2$/s and showed a tendency to increase with increasing silica sand content. The difference of the diffusivities between corrosion product and ion of iron seems to be due to the difference of diffusion species. The color of the corrosion product was dark-green during contact with bentonite specimens and became red on exposure to air in a few minutes. Gas bubbles were also observed in the corrosion product. This suggests hydrogen generation during corrosion of the carbon steel. Thus the diffusion species of corrosion product seems to be in a reduced state, possibly ferrous hydroxide. On the other hand, the diffusion species of iron ion without bulk steel was probably ferric complex. This suggests that ferrous complex could be adsorbed on bentonite 2 or 3 order of magnitude smaller than ferric one.

## VII.18

### REDOX REACTIONS IN A MIXED-LAYER KAOLINITE/SMECTITE: IMPLICATIONS FOR RADIOACTIVE WASTE DISPOSAL.

G. Bruno and A. Decarreau, University of Poitiers, France; and J. W. Stucki, University of Illinois, Urbana, IL.

The effect of iron oxidation state of a mixed-layer Kaolinite\Smectite on its chemical and physical properties were studied. The material was reduced with sodium dithionite in a buffer solution for different lengths of time at 70°C. The results showed an increase in the $Fe^{2+}$/total Fe ratio with time, to a maximum of 0.45. However, the reduction of structural iron apparently is affected by the presence of Fe oxides in the system. On the other hand, different phases with variable $Fe^{2+}$ content were observed in the reduced material. Hence, the $Fe^{2+}$ content measured could have been an average value. The mass ratio of water to clay, $m_w/m_c$, was determined at different values of the swelling pressure using a special inert-atmosphere apparatus. The values of $m_w/m_c$ decreased with increasing $Fe^{2+}$ at each value of the swelling pressure. Further investigations revealed an increase in both layer charge and cation fixation with increasing $Fe^{2+}$, which is of great interest for using the material as an engineered barrier. Electron microscopy and Mössbauer spectroscopy as a function of the oxidation state are currently being performed in order to follow the structural organization of the material.

## VII.19

Study on the performance of sealing system for access shaft in a HLW repository. 
A. Sasaoka, K. Hara, J. Okamoto, Power Reactor & Nuclear Fuel Development Co., Tokai-mura, Ibaraki 319-11, Japan.

The roles of shafts sealing in HLW disposal system are to minimize water flow passage and to retard radionuclide transport from the repository to the accessible environment.

It is important to estimate radionuclide migration along the sealed shafts from the viewpoint of design and performance assessment of the sealing system.

This study presents the results of sensitivity analyses on radionuclide migration in the vicinity of access shafts of a repository to evaluate effects of the thickness of plug, number of plugs and curtain grouts.

In this study, the upward hydraulic gradient of groundwater flow along the shafts was used based on transient coupled thermo-hydraulic analyses around a repository. Hydraulic conductivities of backfill material and disturbed zone around shaft tunnel were also assumed one order and two order of magnitude higher than that of host rock, respectively.

The results show that the velocity of the groundwater within the shaft and disturbed zone is reduced by a factor of 1/3 by installing a few plugs into the shaft filled with backfill material. The curtain grouts have the effect of retardation of the radionuclides migration rates from the repository to the ground surface about a factor of 5 and a few plugs installation have the same effect. The sealing system properly assorted with backfill, plugs and grouts can provide the same performance as original host rock.

## FUNDAMENTAL STUDY ON THE SOLIDIFICATION OF $Cs^+$ AND $Sr^{2+}$ WITH HYDROUS $Ti^{IV}$ OXIDE MODIFIED WITH Si AND Zr.

Y. Inoue, H. Yamazaki and R. Erza, Tohoku University, Sendai, Japan.

Hydrous $Ti^{IV}$ oxides modified with either Si or Zr have larger ion-exchange capacity than a simple hydrous $Ti^{IV}$ oxide. They are promising for use as solidification materials of radionuclides in a huge volume of liquid wastes, since they have high sorption capacity for cations and can be transformed into stable solid forms by heat treatment.

The purpose of the present study is to provide fundamental data for the potential use of hydrous $Si-Ti^{IV}$ oxide (the TS exchanger) and hydrous $Zr-Ti^{IV}$ oxide (the TZ exchanger) as the solidification media of radioactive $Cs^+$ and $Sr^{2+}$. The sorption capacity for $Cs^+$ and $Sr^{2+}$ at various conditions, and the structure and composition of the exchangers in these ionic forms at high temperature were investigated, followed by measuring the leaching rate from calcined exchangers into water at room temperature.

Based on these results, the TS exchanger was considered to be superior to the TZ exchanger in the sorption capacity and the fixation capability of $Cs^+$ and $Sr^{2+}$ on the exchanger matrix.

## V11.26

### THE REACTION OF SRL 202 GLASS IN J-13 AND DIW.

W. L. Ebert, J. K. Bates, and E. C. Buck, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

Glasses produced from WSRC frit 202 were reacted in tuff groundwater and in DIW in steel and Teflon reaction vessels at SA/V values of 340, 2000, and 20,000 $m^{-1}$. Both the leachate solutions and the reacted solids were analyzed to characterize the extent of glass reaction. Reaction was similar in steel and Teflon vessels, but the release of silicon was less in tuff groundwater than in DIW in tests at 340 and 2000 $m^{-1}$. Tests at 20,000 $m^{-1}$ showed highly concentrated solutions to be generated in all tests which overwhelmed the differences in initial leachant compositions. Two effects of Teflon, namely the permeability of Teflon to $CO_2$ and the release of hydrofluoric acid from the Teflon, did not affect the glass reaction. The latter effect was minimized by performing a rigorous cleaning procedure prior to vessel use. These results indicate that either steel or Teflon vessels can be used to perform static leach tests for times up to one year and that while the test results may be affected by the leachant composition at short reaction times, the glass reaction will eventually dominate the solution chemistry.

## V11.27

### ANALYTICAL ELECTRON MICROSCOPY STUDY OF COLLOIDS FROM NUCLEAR WASTE GLASS REACTION.

E. C. Buck, J. K. Bates, J. C. Cunnane, W. L. Ebert, X. Feng, and D. J. Wronkiewicz, Argonne National Lab, 9700 South Cass Avenue, Argonne, IL 60439-4837.

There is great interest in the potential role of colloids in radionuclide transport from high level nuclear waste repositories. Colloidal particles have the potential to increase greatly the release rate of radionuclides into the environment. Most previous studies have concentrated on colloids present in groundwater (pseudocolloids) as the likely vector for radionuclide transport, or the formation of real colloids by the hydrolysis of actinide elements.

Analytical Electron Microscopy (AEM) has been used to identify small (<100 nm in diameter) colloidal phases using electron diffraction, energy dispersive spectroscopy and high resolution images. Clay colloids can be identified by the production of oblique textured electron diffraction patterns. Most of the phases have been found to be clays, usually smectites, however other phases are often observed, such as calcite and rutile.

The results of examining colloids from a number of different waste glasses reacted under different conditions will be presented. Characterization of phases present in the leachate has shown that both precipitated and spalled clay layers may be present in solution. Concentrating of hazardous elements such as uranium was also found within colloidal particles of the leachate.

## V11.28

### EFFECTS OF RADIATION EXPOSURE ON GLASS ALTERATION IN A STEAM ENVIRONMENT.

D. J. Wronkiewicz,[1] L. M. Wang,[2] J. K. Bates,[1] and B. S. Tani.[1] [1]Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439; [2]University of New Mexico, Albuquerque, NM 87131.

Several glass compositions were reacted in steam at temperatures of 150°C to 200°C. Half of the tests utilized actinide-doped monoliths and were exposed to an external ionizing gamma source, while the remainder were doped with U and reacted without radiation exposure. The glass reacted to form surface precipitates and an in situ leached surface layer within the first week of testing. Adularia, analcime, herschelite, illite, phillipsite, tobermorite, weeksite, and a Ca-Si phase formed on most samples. Uranophane was also detected in irradiated tests with SRL 202 glasses. The in situ layer in the nonirradiated tests was composed of nontronite, with an overlying layer of illite that was precipitated from solution. In the irradiated tests, up to three clay-rich layers covered a rounded and sometimes fractured glass core. By 35 to 65 days, the remnant glass cores were replaced by a massive to banded textured Fe- and Si-rich core. The reaction layer developed at a rate of 2.3 to 32 μm/day for the nonirradiated and irradiated 202 glasses, respectively, indicating that layer development is accelerated by ~15X due to radiation exposure at high SA/V conditions.

## V11.29

### PLUTONIUM AND NEPTUNIUM LEACHING FROM SIMULATED HLW GLASSES IN SYNTHETIC INTERSTITIAL CLAYWATER.

Lian Wang, SCK/CEN, Mol, B ; Pierre Van Iseghem, SCK/CEN, Mol, B ; and A. Maes, KUL, Leuven, B

Solubility and colloid generation of key actinides during dissolution of HLW glasses will define or influence the source term for the transport process of the actinides to the geosphere. The equilibrium concentrations of Plutonium and Neptunium-237 were determined from leaching tests of simulated HLW glasses (PWG124 for Pu and SM527 for Np-237) in synthetic Interstitial Claywater (SIC) at 90 °C, pH = 9, in inert ($N_2$) atmosphere. The solubility of $PuO_2.xH_2O$ (am) has been measured in the same solution at 25 °C. The results were then compared with the Pu solubility calculation by using published complex stability constants and $PuO_2.xH_2O$ (am) as the solubility controlling phase. The measured Pu solubilities of both Pu-doped glass powder and $PuO_2.xH_2O$ (am) were higher than the value calculated for SIC solution using known solubility product of $PuO_2.xH_2O$ (am). The influence of Humic Acid (HA) on the leaching behaviour of the two actinides was investigated by using leaching solutions with and without HA and ultrafiltration technique. The results indicate that HA enhances the total Np-237 but not Pu release from glass forms and that a large amount of HA-actinide colloid is generated. The colloid formed is filterable by

with glass frit in an induction melting pot.
In 1994 it was suggested by Utaxe et al. to use
Sol-Gel technique to decrease the calcination
temperature of NaNO₃.
In this work we used Thermal-Analysis technique
to forward the catalitic effect of some glass
network former like SiO₂,B₂O₃,and some
intermidiate oxides like Al₂O₃,Fe₂O₃,MgO,TiO₂,ZnO.
The best effect was achieved by adding 37%
Diatomaceous Earth(Kiselguhr). In that case the
calcingtion temperature onset decreased from 780°C
to 644°C.   The advantages of this process are:
1. The additive is a glass network former that has
   to be added anyway in the next process step.
2. There is no additional sodium to the final
   product(i.e. the leachability will not increase)
3. There is no problem to add the additive(very
   porousive SiO₂) since it is flowable powder.

## SESSION V12: PERFORMANCE ASSESSMENT OF GEOLOGICAL SYSTEMS
Thursday Morning, December 3
Salon G (M)

### 8:30 A.M.  *V12.1
APPROACHES TO LONG-TERM PERFORMANCE ASSESSMENT OF
DEEP UNDERGROUND DISPOSAL OF RADIOACTIVE WASTES A
EUROPEAN PERSPECTIVE. Trevor J. Sumerling* and David Read**
*Intera Information Technologies. Henley-on-Thames, UK.
**WS Atkins Science and Technology, Epsom, UK.

The aim of long-term performance assessment is generally to develop
confidence that the disposal system will perform within certain
bounds or give rise to acceptably low impacts or risks.  The
performance assessment procedure must be able to deal with
uncertainty due to limited or incomplete understanding of the
relevant processes; uncertainty due to variability and limited
sampling of the structures and characteristics of the system and
especially the geological media; uncertainty about future conditions
and processes leading to changes in the disposal system or affecting
radionuclide release, transport and exposure pathways.

Different approaches have been taken to dealing with such
uncertainties.  The differences can be traced to differences in national
regulatory guidance, differences in the rôle of the implementor and
the regulator.  This paper will differentiate roles of regulator and
implementor, and illustrate alternative assessment approaches for
dealing with uncertainty that lie at extremes of the range of possible
approaches based on examples from Nagra (Switzerland) and HMIP
(United Kindom) assessment programmes.

### 9:00 A.M.  *V12.2
IS IT POSSIBLE TO DEMONSTRATE COMPLIANCE WITH THE
REGULATIONS FOR HIGH-LEVEL WASTE REPOSITORIES? Felton
W. Bingham, Sandia National Laboratories, Albuquerque, NM.

The regulations that currently govern repositories for spent fuel and high-
level waste require demonstrations that are sometimes described as
impossible to make. To make them will require an understanding of the
current and the future phenomena at repository sites; it will also require
credible estimates of the probabilities that the phenomena will occur in the
distant future. Experts in many fields — earth science, statistics, numerical
modeling, and the law — have questioned whether any amount of data
collection can allow modelers to meet these requirements with enough
confidence to satisfy the regulators. In recent years some performance
assessments have begun to shed light on this question. They have used the
results of actual site investigations, along with expert opinion, to make
preliminary demonstrations of compliance. Although these studies do not
settle the question definitively, a review of their results suggests that

compliance may not be impossible to demonstrate. The review also suggests,
however, that the demonstrations can be only at the "reasonable" levels of
assurance mentioned, but not defined, in the regulations. The final decisions
about compliance are likely to turn on the regulators' final decisions about
reasonableness.

### 9:30 A.M.  *V12.3
CONCEPTUAL STRUCTURE OF PERFORMANCE
ASSESSMENTS CONDUCTED FOR THE WASTE ISOLATION
PILOT PLANT.  Jon C. Helton, Arizona State University, Tempe,
AZ;  Mel G. Marietta and Rob P. Rechard, Sandia National
Laboratories, Albuquerque, NM.

The Waste Isolation Pilot Plant (WIPP) in southeastern New Mexico
is being developed by the U.S. Department of Energy as a disposal
facility for transuranic waste.  In support of this project, Sandia
National Laboratories is conducting an ongoing performance
assessment for the WIPP.  The ordered triple representation for risk
proposed by Kaplan and Garrick is used to provide a clear
conceptual structure for this performance assessment.  This
presentation describes how the preceding representation provides a
basis in the WIPP performance assessment for (1) the definition of
scenarios and the calculation of scenario probabilities and
consequences, (2) the separation of subjective and stochastic
uncertainties, (3) construction of the complementary cumulative
distribution functions required in comparisons with the U.S.
Environmental Protection Agency's standard for the geologic disposal
of radioactive waste (i.e., 40 CFR Part 191, Subpart B), and (4) the
performance of uncertainty and sensitivity studies.  Results obtained
in a preliminary performance assessment for the WIPP completed in
December of 1991 are used for illustration.

### 10:00 A.M.  *V12.4
ACCOUNTING  FOR  UNCERTAINTY  IN  PERFORMANCE
ASSESSMENTS.  Professor Milton E. Harr, School of Civil
Engineering, Purdue University, West Lafayette, Indiana 47907.

The ways in which natural systems of, on, or in the ground perform
demonstrate considerable differences between hypothetical models
and actual performance.  All such systems are subject to complex
interrelationships of voids and solids, particle irregularities, ambient
effects, differing concentrations of fluids and, hence, to varying
degrees of randomness (uncertainty).  Various analytical methods
have been offered in the past to accommodate uncertainties.  The
most common procedure is the Monte Carlo method.  The method
requires that the probability distribution functions of all component
variables be known completely and "a priori." The procedure selects a
single random sample for the assumed probability distributions of each
entering parameter.  These are then combined deterministically, to
provide one realization (trial) of the dependent output.  For all but a
very few random variables, numerous trials are required to attain
tolerable levels of accuracy.  For performance assessment of real
systems, which by their very nature require very many variables and
complete probability density functions, Monte Carlo simulations are of
questionable value.  Even greater doubt surrounds this methodology if
the variables are correlated.

The present paper presents a simple methodology for extracting
stochastic information for the parameters from laboratory results or
from in situ measurements.  It then demonstrates how this information
can be used to make predictions of anticipated performance.  A
number of worked examples are presented to illustrate the
methodology.

### 10:45 A.M.  V12.5
MODEL VALIDATION AND DECISION MAKING. Natalie E. Olague, Paul
A. Davis, Sandia National Laboratories, Albuquerque, NM 87185-5800.

Results from ground-water flow and transport models are often used to make
decisions about the safety of potential waste disposal sites. Consequently, the
validity of these models has to be defended. This is usually done by comparing
results from the models to experimental data, which is thought to provide
evidence that the models represent reality. Typically, these exercises consist of
calibrating a model and visually comparing the model results to the experimental
data. A subjective conclusion about the validity of the model is made, unrelated

protection of long-term public health and safety. A repository project cannot be successful if reliable and acceptable criteria are not established. The U.S. program is particularly vulnerable.

Waste-container issues include establishing what constitutes failure, predicting the time-distribution of container failures throughout the repository, and analyzing the benefit from tortuous penetrations and corrosion products in reducing radionuclide release rates. Predicting release rates requires better definition of the diffusive/convective pathways for ingress of liquid and oxidants and for release of gases and dissolved species. Better data and theories are needed on rates of chemical reaction of waste solids with liquids. key phenomena affecting release of soluble species. Better knowledge of the chemical environment within a failed waste package, affected by container material, possible air ingress, and radiolysis, is needed to predict releases of low-solubility species. Experiments are needed to confirm the theories of colloid transport from waste packages, including filtration by porous materials in and around a failed package. The rate that water drips penetrate a failed container in an unsaturated-rock repository has not been sufficiently analysed. Gaseous releases are particularly important in an unsaturated-rock repository. In a salt repository flow of brine into a borehole before salt consolidation and subsequent flow and diffusion of contaminants outward through consolidated salt and porous materials should be considered.

## 1:45 P.M. *V13.2
PROGRESS IN WASTE PACKAGE AND ENGINEERED BARRIER SYSTEM PERFORMANCE ASSESSMENT AND DESIGN. Abraham E. Van Luik, M&O/Intera, Inc., Las Vegas, NV; David Stahl, M&O/B&W Fuels Corp., Las Vegas, NV; Diane Harrison-Giesler, U.S. Department of Energy, Las Vegas, NV

As part of the Yucca Mountain Project Office's evaluation of site suitability, long-term interactions between the engineered barrier system and the site must be determined. This requires a waste-package/engineered-system design, a description of the environment around the emplacement zone, and models that simulate operative processes describing these engineered/natural system interactions. The M&O is evaluating candidate designs, including a more robust multi-barrier waste package, and a drift emplacement mode. Design and emplacement mode options are described.

Tools for evaluating designs and emplacement mode are the currently available waste-package/engineered-system performance assessment codes developed for the project. For assessments that support site-suitability, environmental-impact, or licensing decisions, more capable codes are needed. The M&O is drawing up code capability requirements, and will evaluate existing codes against those requirements. Recommendations will be made to narrow waste-package/engineered-system code development to prepare one code that is fully capable. Preliminary M&O code evaluations are discussed.

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Civilian Radioactive Waste Management Systems, Management & Operations (M&O) Contractor

## 2:00 P.M. *V13.3
Some important mechanisms and processes in the near-field of the Swedish HLW repository.

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ABSTRACT

In the proposed design of the Swedish high-level waste repository the spent fuel is contained in thick walled copper canisters. They are embedded in compacted bentonite and emplaced in holes in the bottom of drifts deep down in granitic rock. The naturally reducing conditions in the rock ensures that the corrosion rate of copper is extremely low. It is expected that only a few canisters will be damaged, and then by small holes, for a very long time. The nuclides may escape out through the damage into the bentonite by diffusion. The rate of escape will be governed by geometrical factors as well as by chemical and physical factors. The paper discusses the main factors which influence the release rate and where the major uncertainties are deemed to be. They include the presence of a disturbed zone around the drift, our understanding of and means to describe the system of fractures which conduct water in the near field, diffusion in the backfill and rock and radiolysis which potentially might cause a locally oxidizing environment to develop.

Some special very flexible modelling tools have been developed and are used to assess where the major resistances to the release are. These tools are also used to elucidate which release pathways and mechanisms are better known and quantified than others.

## 2:15 P.M. *V13.4
PERFORMANCE ASSESSMENT OF ENGINEERED BARRIERS USING THE VAULT MODEL. L.H. Johnson and D.M. LeNeveu, AECL Research, Whiteshell Laboratories, Pinawa, Manitoba, Canada ROE 1L0.

A model for assessing engineered barrier performance has been developed as part of the preparation of an Environmental Impact Statement to be presented to a Federal Environmental Assessment Review Panel reviewing the Canadian nuclear fuel waste disposal concept. The model describes the lifetime of titanium containers, radionuclide release from used fuel and migration of radionuclides through buffer and backfill materials and into the surrounding geosphere. The basic models for all of these processes will be outlined, with particular emphasis on key performance issues that arose in their development. The basic assumptions in the models will be described and conservatism and the treatment of uncertainties will be discussed. The relative importance of the various barriers will be illustrated through presentation of results from system simulations and sensitivity analyses. Finally, some areas of research that are focusing on validating key aspects of the model and reducing uncertainties will be discussed.

## 2:30 P.M. *V13.5
KEY ISSUES INFLUENCING THE PERFORMANCE OF NEAR-FIELD BARRIERS. Philip W. Tasker, Simon J. Wisbey and Charles B. Boyle, AEA Technology, Harwell Laboratory, UK.

In developing a national strategy for the disposal of radioactive wastes, each country will consider isolation options that are appropriate to the types of waste produced. The options are developed in response to specific national regulatory requirements and therefore will focus on different aspects of performance. However, there are a number of technical concerns that are common to all programmes.

The major issues concerning the behaviour of the chemical and physical barriers in the near-field of a radioactive waste repository are discussed in this paper. In describing these issues, they have been divided into the following categories: barrier design, barrier evolution, scientific understanding through modelling, and validation of performance.

The near-field barriers are selected and designed to provide appropriate radionuclide containment and control. The evolution of these barriers, such as container degradation and gas generation, affects the subsequent release of radionuclides to the human environment. Modelling repository evolution is therefore an integral feature of performance assessments and issues such as the treatment of inhomogeneities, non-equilibrium chemistry and timescales must be addressed. However, the use of mathematical and computer models carries a requirement for validation. The use of demonstration experiments and natural analogues builds confidence in the predictions of repository performance models and provides a degree of validation for otherwise inaccessible timescales.

## 2:45 P.M. *V13.6
RESEARCH NEEDS IN HLW DISPOSAL PROGRAMMES. Jörg Hadermann, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland; and Charles McCombie, National Cooperative for the Disposal of Radioactive Waste, CH-5430 Wettingen, Switzerland.

A repository for high-level radioactive waste will not be in operation in Switzerland (or elsewhere) before the turn of the next century. However, extensive investigations for disposal in specific regions or sites are ongoing and formal safety analyses have been performed in many countries. Broadly speaking these analyses show the feasibility of the chosen disposal options. At the present stage, before a licensing application, performance assessments have a further important application: to identify further needs to improve system understanding, and to guide the necessary research activities. Performance assessments are thus indispensable tools for focussing in on research requirements and discriminating between necessary and merely desirable or interesting research projects.

Based on experience from the forthcoming assessment of HLW disposal in the crystalline of Northern Switzerland ("KRISTALLIN I") we consider in detail the chain of models resulting from a scenario analysis. For each model block, such as e.g. engineered barriers performance, hydrology, and radionuclide transport, the adequacy in understanding is addressed and the necessary research needs pointed out. These needs cover a wide span from the requirement for more reliable input numbers (example: long-term corrosion rate of glass) to a better understanding of important features (example: excavation damaged zone) and key mechanisms (example: sorption).

## 9:00 A.M. V14.3

**THE ROLE OF OXYGEN DIFFUSION IN THE RELEASE OF TECHNETIUM FROM REDUCING CEMENTITIOUS WASTE FORMS.** Robert W. Smith, Idaho National Engineering Laboratory, P. O. Box 1625, Idaho Falls, ID 83415-2110; and John C. Walton, CNWRA, Southwest Research Institute, 6220 Culebra Rd., San Antonio, TX 78228-0510

Cementitious materials provide an ideal geochemical environment for the immobilization of nuclear waste (e.g., high pH pore fluids and large surface areas for sorption). The inclusion of reducing agents, such as blast-furnace slags (BFS) can result in the immobilization of radionuclides by the formation of solid sulfide phases. Thermodynamic calculations using the MINTEQ geochemical computer code indicate that elemental sulfur present in the BFS reacts with the highly mobile $TcO_4^-$ anion to form insoluble $Tc_2S_{7(s)}$. Initially, the waste form very effectively immobilizes technetium. However, as oxygen diffuses into the waste form, an outer zone of oxidized concrete and a shrinking core of reduced intact concrete will develop. Oxidation of sulfur in the outer zone results in increased technetium concentrations in the pore fluid because $Tc_2S_{7(s)}$ oxidizes to the mobile $TcO_4^-$ anion. The $TcO_4^-$ anion can then diffuse from the waste form into the environment.

A mathematical model that accounts for diffusion of oxygen into concrete coupled with oxidation of sulfur and sulfide to sulfate has been developed. This model assumes the existence of an oxidized outer layer of concrete surrounding a shrinking core of reducing intact concrete. A sharp boundary between the two zones moves slowly inward resulting in oxidation of $Tc_2S_{7(s)}$ and subsequent release of $TcO_4^-$ via aqueous diffusion in the concrete pore fluids. This model is used to calculate the consequences of oxygen diffusion on the release of technetium from a BFS cementitious waste forms.

## 9:15 A.M. V14.4

**ALKALI-ACTIVATED FLY ASH-SLAG CEMENT BASED NUCLEAR WASTE FORMS.** W. Jiang, X. Wu and D.M. Roy, Materials Research Laboratory(MRL), The Pennsylvania State University, University Park, PA 16802, USA

This paper is based on the results of an on the way R&D Project about alkali-activated cement system at MRL. The objective of this research is to establish the potential for large use fly ash and slag as main components of the cement system. Alkali-activated fly ash-slag cement (AAFSC) was studied as a matrix for immobilization of nuclear wastes. AAFSC is characterized by high early strength, high ultimate strength, low porosity, lower solubilities of the hydrates and high resistance to chemical corrosion as well as the freezing and heating. All these advanced properties are particularly favorable to the immobilization the nuclear wastes.

In the experiments, 92-87% raw materials are fly ash and slag, cement or lime is 5-10% used as stabilizer, the alkali is 3% (By $R_2O$) used as activator. The result is promising. For immobilization of nuclear wastes, AAFSC is better than ordinary Portland cement. Hardened AAFSC paste has good performances. AAFSC-based nuclear waste forms exhibit lower cesium leachability, especially in the case of higher temperture.

## 9:30 A.M. *V14.5

**MICROBIAL DEGRADATION OF CEMENT SOLIDIFIED LOW-LEVEL RADIOACTIVE WASTE FORMS.** Robert D. Rogers, Melinda A. Hamilton, and John W. McConnell, Idaho National Engineering Laboratory, Idaho Falls, ID 83415-2203.

Researchers familiar with the NRC Technical Position on Waste Form biodegradation tests have found them unapplicable for use with cement solidified LLW. Concerns over the tests included lack of demonstrable evidence that microorganisms required by the standard tests promote degradation of cement waste forms under any test conditions.

The NRC's Advisory Committee on Nuclear Waste has raised concerns about biodegradation testing of LLW. They recommend that biodegradation testing for cementitious waste matrices use bacteria that are likely to affect cement as well as the organic component of the waste.

Information will be presented outlining procedures for the development of a new testing protocol for cement solidified waste forms. Included will be a discussion of mechanisms and microbes involved in the microbial degradation of cement materials. Initial testing data will also be presented.

## 10:15 A.M. V14.6

**BORATE SUBSTITUTED ETTRINGITES.** Laszlo J. Csetenyi and Fred P. Glasser, Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland.

The setting of cement is adversely affected by soluble borates. To reduce interference, the extent to which borate can be insolubilized has been investigated. One specific mechanism of insolubilization is by inclusion into ettringite. Ettringite is a normal and stable constituent of Portland cement. It has an open but non-zeolitic framework. Borate can substitute partially or fully for sulfate.

Formation conditions, solubility and stability of borate ettringites ($Ca_6Al_2(BO_4)_{2-4}(OH,O)_{12-26}H_2O$) are characterised using XRD, IR, DTA, DSC, and SEM.

Durability of borate ettringites in a repository environment have been assessed by exposing to Na-sulfate and Na-carbonate attack at different concentrations. Back substitution by sulfate is incomplete; high carbonate concentrations can, however, decompose borate ettringite.

On heat treatment up to 85°C the crystallite morphology and the OH arrangement of the structure are altered, but the X-ray pattern and hence its structural framework are not affected.

It is concluded that ettringite has potential to reduce the solubility of borate.

## 10:30 A.M. V14.7

**MOBILITY OF CHELATED RADIONUCLIDES IN ENGINEERED CONCRETE BARRIERS.** Craig A. Dicke and Robert W. Smith, Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2110.

Concrete is a major component in many low-level waste disposal facilities (LLW). The use of concrete is widespread because of its physical and structural properties and also to provide geochemical control on metal and radionuclide releases. Organic compounds are often codisposed with radionuclides in LLW disposal facilities. Interactions between radionuclides and chelating agents must be evaluated to estimate the mobility of radionuclides in concrete vaults.

Citrate and ethylenediaminetetraacetic acid (EDTA) are common organic components in mixed waste solutions in LLW facilities. Radionuclides such as Co, Sr, Ni, Am and $UO_2$ react with citrate and EDTA to form stable chelated-radionuclide complexes. Equilibrium speciation calculations are used to determine the response of these complexes to highly alkaline concrete pore fluids.

Equilibrium speciation calculations indicate that radionuclides are chelated in 'natural' groundwater (pH=7), but are destabilized in the highly alkaline (pH>13) concrete pore fluids. Most of the radionuclides complexed by EDTA are replaced by $Ca^{2+}$ in the concrete pore fluids. Calcium also replaces nuclides in the citrate complex. In addition, the citrate nuclide complex reacts to form uncomplexed citrate in concrete pore fluids. Performance of concrete LLW disposal facilities should not be compromised by small amounts of chelating agents codisposed with radionuclides.

## 10:45 A.M. V14.8

**THE RADIATION STABILITY OF GROUND GRANULATED BLASTFURNACE SLAG/ORDINARY PORTLAND CEMENT GROUTS CONTAINING ORGANIC ADMIXTURE.** John D Palmer & Graham A Fairhall, British Nuclear Fuels plc, Sellafield, Seascale, Cumbria, UK.

Organic admixtures are extensively used in the cement and construction industries to modify the properties of grouts and concretes. The advantages of using admixtures can include improved grout fluidity making placement easier; alteration in setting times to compensate for seasonal temperature variations; or improved durability to freeze/thaw cycling. These properties can also be of benefit in the nuclear industry where cement grouts are used to immobilise radioactive wastes.