

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: Materials Research Society's 'Symposium on the Scientific Basis for Nuclear Waste Management XIV'

DATE/PLACE OF TRIP: November 26-29, 1990; Boston, Massachusetts

AUTHOR: Roberto T. Pabalan

DISTRIBUTION:

CNWRA:

J. Latz
Directors
Element Managers
W. Murphy
E. Percy
D. Turner

NRC:

S. Mearse
J. Funches
S. Fortuna
B. Stiltenspole
H. Schechter
W. Ott
G. Birchard
D. Brooks
J. Bradbury
M. Silberberg

SwRI:

S. Rowe

9012190011 901219
PDR WASTE PDR
WM-11

*delete all distribution except CF, PDR 1/2
NUDOES full text 426!
WM-11
NH15 1/1*

180043

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: Materials Research Society's 'Symposium on the Scientific Basis for Nuclear Waste Management XIV'

DATE/PLACE OF TRIP: November 26-29, 1990; Boston, Massachusetts

AUTHOR: Roberto T. Pabalan

PERSONS PRESENT:

CNWRA

Roberto T. Pabalan
Narasi Sridhar

BACKGROUND:

This is the fourteenth of a series of symposia covering a wide array of topics regarding the scientific basis of nuclear waste management. Technical papers were presented regarding nuclear waste glass, radionuclide migration, grout and concrete, spent fuel, performance assessment, metals, integrated systems, and backfill materials. This conference was sponsored by the U.S. Department of Energy, U.S. Nuclear Regulatory Commission, and the Atomic Energy of Canada, Ltd. Proceedings of the symposium will be published by the Materials Research Society next year.

SCIENTIFIC ACTIVITIES:

The CNWRA's contribution at the symposium consisted of a paper presented by R. Pabalan regarding 'Nonideality Effects on Ion Exchange Behavior of the Zeolite Mineral Clinoptilolite', and a paper presented by N. Sridhar (co-authored by G. Cragnolino) regarding the 'Environmental Effects on Localized Corrosion of High Level Nuclear Waste Container Materials'. In addition, R. Pabalan co-chaired a technical session on radionuclide migration and attended symposium committee meetings. A number of Center staff (W. Murphy, D. Turner, E. Percy, R. Pabalan and N. Sridhar) were also involved prior to the meeting in the peer review of manuscripts submitted to the symposium.

A copy of the symposium schedule and abstracts are attached.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

A copy of the symposium proceedings will be obtained.

RECOMMENDATIONS:

It is important for Center technical staff to attend meetings such as these where the 'scientific basis' for nuclear waste management are discussed. These meetings provide an opportunity for the staff to be exposed to research activities being conducted in other disciplines, to be informed of recent developments in the area of high level waste research, and to interact with investigators from other organizations and countries.

SIGNATURE:

R. T. Pabalan

Roberto T. Pabalan

12/3/90

Date

CONCURRENCE SIGNATURES:

John L. Russell
John L. Russell

12-3-90

Date

Allen R. Whiting
Allen R. Whiting

12/11/90

Date

RTP/ps

Attachments

SYMPOSIUM P
SCIENTIFIC BASIS FOR NUCLEAR
-WASTE MANAGEMENT XIV



.....
November 26 - 29, 1990

Chairs

.....
T. Abrajano, Jr.
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
(708) 972-4261

Lawrence H. Johnson
Whiteshell Nuclear Research
Establishment
Pinawa, Manitoba R0E 1L0
Canada
(204) 753-2311

Symposium Support

.....
U.S. Nuclear Regulatory Commission
U.S. Department of Energy
Atomic Energy of Canada, Ltd.

.....
Proceedings published as Volume 212
of the Materials Research Society
Symposium Proceedings Series

SESSION P1. GLASS

Chair: Claude Sombret and Ned Bibler
Monday Morning, November 26
America South (W)

8:15 A.M. WELCOMING REMARKS

8:30 A.M. *P1.1

OVERVIEW OF CHEMICAL MODELING OF NUCLEAR WASTE GLASS DISSOLUTION. William L. Boursier, Lawrence Livermore National Laboratory, Livermore, CA.

9:00 A.M. P1.2

ENHANCEMENT OF BOROSILICATE GLASS DISSOLUTION BY SILICA ADSORPTION AND DIFFUSION IN COMPACTED BENTONITE: A MODEL STUDY. Erzo Curti, Paul Scherrer Institut, Villigen and Würenlingen, Switzerland; and Paul A. Smith, Paul Scherrer Institut, Villigen and Würenlingen, Switzerland.

9:15 A.M. P1.3

RARE EARTH ELEMENTS BEHAVIOUR DURING ALTERATION OF BASALTIC GLASSES: CASE OF THE WEATHERING OF ICELANDIC HYALOCLASTITES. Y. Daus, J.L. Crovisier, C.G.S., Strasbourg, France; and J.C. Petit, C.E.A., SESD/LECALT, Fontenay-aux-Roses, France.

9:30 A.M. P1.4

MINERALOGICAL, TEXTURAL AND COMPOSITIONAL DATA ON THE ALTERATION OF BASALTIC GLASS FROM KILAUEA, HAWAII TO >300°C.: INSIGHTS TO THE CORROSION OF A BOROSILICATE GLASS WASTE-FORM. David K. Smith, Lawrence Livermore National Laboratory, Livermore, CA.

9:45 A.M. P1.5

THE IMPORTANCE OF SECONDARY PHASES IN GLASS CORROSION. William L. Ebert and John K. Bates, Argonne National Laboratory, Argonne, IL.

10:00 A.M. BREAK

10:15 A.M. *P1.6

THE ROLE OF SURFACE LAYERS IN GLASS LEACHING PERFORMANCE. J.K. Bates, Argonne National Laboratory, Argonne, IL.

10:45 A.M. P1.7

MECHANISTIC EFFECTS OF DEUTERATION ON THE AQUEOUS CORROSION OF NUCLEAR WASTE GLASSES. X. Feny, L. Fu, I.L. Pegg, and P.B. Macedo, The Catholic University of America, The Vitreous State Laboratory, Washington, DC.

11:00 A.M. P1.8

HYDROLYSIS OF R7T7 NUCLEAR WASTE GLASS IN DILUTE MEDIA: MECHANISMS AND DISSOLUTION RATES AS A FUNCTION OF PH, T. Advocate, CEA-CEN/VALRHO, SDHA/SEMC, Bagnols, France; J.L. Crovisier, CGS, Institut de Géologie, Strasbourg, France; and E. Vernaz, CEA-CEN/VALRHO, SDHA/SEMC, Bagnols, France.

11:15 A.M. P1.9

TECHNICAL BASES FOR THE DWPF TESTING PROGRAM. M.J. Pindone, Westinghouse Savannah River Company, Aiken, SC.

11:30 A.M. P1.10

THE EFFECT OF SAMPLE PREPARATION METHODS ON GLASS PERFORMANCE. M.S. Oh and V.M. Oversby, Lawrence Livermore National Laboratory, Livermore, CA.

11:45 A.M. P1.11

THE USE OF PARTIAL-REPLENISHMENT TESTS IN MODELING THE LEACH BEHAVIOR OF GLASSES. Aa. Barkait, S.A. Olszowka, W. Soussanpour, T. Choudhury, y. Guo, Al. Barkait, and R. Adiga, the Catholic University of America, Washington, DC.

*Invited Paper

SESSION P2. RADIONUCLIDE MIGRATION I

Chairs: Neil Sturchio and Roberto Pabalan
Monday Afternoon, November 26
America South (W)

1:00 P.M. *P2.1

ASSESSING THE NATURAL PERFORMANCE OF FELSIC TUFFS AT YUCCA MOUNTAIN USING THE Rb-Sr AND Sm-Nd SYSTEMS. Zelj E. Peterman, Kiyoko Futa and Richard W. Spengler, U.S. Geological Survey, Denver, CO.

1:30 P.M. P2.2

NATURAL ANALOG STUDIES FOR PARTIAL VALIDATION OF CONCEPTUAL MODELS OF RADIONUCLIDE RETARDATION AT THE WIPP. D.B. Ward, D.G. Brookins, University of New Mexico, Department of Geology, Albuquerque, NM; M.D. Siegel, and S.J. Lambert, Sandia National Laboratories, Albuquerque, NM.

1:45 P.M. P2.3

RADIONUCLIDES IN HYDROTHERMAL SYSTEMS AS INDICATORS OF REPOSITORY CONDITIONS. H.A. Wollenberg and S. Flexser, Lawrence Berkeley Laboratory, Berkeley, CA.

2:00 P.M. P2.4

TEMPORAL CHANGES IN URANIUM SERIES ISOTOPE CONCENTRATION* AS A FUNCTION OF FLOW CONDITIONS IN THE SSSDP VENT, SALTON SEA, CALIFORNIA. Bret W. Leslie, Douglas E. Hammond and Teh-Lung Ku, University of Southern California, Department of Geological Sciences, Los Angeles, CA.

2:15 P.M. P2.5

THE REDISTRIBUTION OF URANIUM SERIES RADIONUCLIDES AT KOONGARRA. Robert Edis, Australian Nuclear Science and Technology Organisation, Lucas Heights Research Laboratories, Menai, Australia.

2:30 P.M. P2.6

STUDY ON ROLE OF ²³⁴TH IN URANIUM SERIES NUCLIDES MIGRATION. Toshihiko Ohnuki, Japan Atomic Energy Research Institute, Ibaraki, Japan; Shoji Watanabe, Mitsui Knowledge Industry, Tokyo, Japan; and Takashi Murakami, Japan Atomic Energy Research Institute, Ibaraki, Japan.

2:45 P.M. BREAK

3:15 P.M. *P2.7

GEOCHEMICAL CONTROLS ON URANIUM MOBILITY IN CRYSTALLINE-ROCK AQUIFERS. Richard B. Wanty, U.S. Geological Survey, Golden, CO; Donald Langmuir, Colorado of Mines, Golden, CO; Cynthia A. Rice, U.S. Geological Survey, Golden, CO; and Paul Briggs, U.S. Geological Survey, Lakewood, CO.

3:45 P.M. P2.8

FLOW PATH MINERALOGY: ITS EFFECT ON RADIONUCLIDE MIGRATION IN THE GEOSPHERE. Kenneth V. Ticknor, D. Choudari, Kamini and Tjalle T. Vandergraaf, AECL, Whiteshell Nuclear Research Establishment, Geochemistry and Applied Chemistry Department, Pinawa, Canada.

4:00 P.M. P2.9

ASSESSMENT OF RADIONUCLIDE MIGRATION IN NATURAL ANALOGUES BY RADIATION-INDUCED CENTERS IN KAOLINITES. Philippe Hildebrand, Jean-Pierre Muller, Blandine Clozel, and Georges Calas, Universités de Paris 6 et 7, Laboratoire de Minéralogie-Cristallographie, Paris, France.

4:15 P.M. P2.10

DIFFUSION POROSITY AND DIFFUSIVITY OF RADIO NUCLIDES IN GRANITIC ROCKS. PART I: DIFFUSION INTERFACES AROUND PERMEABLE FRACTURES. Veijo O. Pirhonen, Kai Frenn and Petteri Pitkänen, Technical Research Centre of Finland, Geotechnical Laboratory, Espoo, Finland.

4:30 P.M. P2.11

QUANTITATIVE INTERPRETATION OF HALOGEN POREWATER CONCENTRATION PROFILES IN LAKE SEDIMENTS, W. Eberhard Falck and Paul J. Hooker, British Geological Survey, Fluid Processes Research Group, Nottingham, United Kingdom.

4:45 P.M. P2.12

(ABSTRACT WITHDRAWN)

SESSION P3: GROUT AND CONCRETE

Chairs: Lillian Wakeley, Alan Atkinson, and P.-C. Aitcin

Tuesday Morning, November 27
America South (W)

8:30 A.M. *P3.1

RESEARCH NEEDS IN CEMENT-BASED WASTE FORMS, E.W. McDaniel, Oak Ridge National Laboratory, Oak Ridge, TN.

9:00 A.M. P3.2

PHASE RELATIONS AND SOLUBILITY MODELLING IN THE CaO- SiO₂- Al₂O₃-MgO- SO₃- H₂O SYSTEM: FOR APPLICATION TO BLENDED CEMENTS, M. Aitkin, F.P. Glasser and A. Kindness, University of Aberdeen, Department of Chemistry, Aberdeen, Scotland.

9:15 A.M. P3.3

THE EFFECTS OF CALCITE SOLID SOLUTION FORMATION ON THE TRANSIENT RELEASE OF RADIONUCLIDES FROM CONCRETE BARRIERS, Robert W. Smith and John C. Walton, Idaho National Engineering Laboratory, Idaho Falls, Idaho.

9:30 A.M. P3.4

HIGH-PERFORMANCE CEMENT-BASED MATERIALS FOR NUCLEAR FUEL WASTE DISPOSAL, Pierre-Claude Aitcin, University of Sherbrooke, Sherbrooke, Canada; Maria Onofrei and Malcolm N. Gray, Atomic Energy of Canada Limited, Pinawa, Canada.

9:45 A.M. P3.5

MODELING GEOCHEMICAL STABILITY OF CEMENT FORMULATIONS FOR USE AS SHAFT LINER AND SEALING COMPONENTS AT YUCCA MOUNTAIN, Mark A. Gardiner, IT Corporation, Albuquerque, NM; Thomas J. Hinklebein, Sandia National Laboratories, Albuquerque, NM; and Jonathan Myers, IT Corporation, Albuquerque, NP

10:00 A.M. BREAK

10:30 A.M. *P3.6

THE LONG-TERM PROPERTIES OF CEMENT AND CONCRETES, M. Aitkin, J. Cowie, F.P. Glasser, A. Kindness, and L.P. Moroni, University of Aberdeen, Old Aberdeen, Scotland.

11:00 A.M. P3.7

EVALUATION OF DRY-SOLIDS-BLEND MATERIAL SOURCE ON A CEMENTITIOUS WASTE FORM, T.M. Gilliam, R.D. Spence, S.C. Osborne, and C.L. Francis, Oak Ridge National Laboratory, Chemical Technology Division, Oak Ridge, TN.

11:15 A.M. P3.8

THE ROLE OF ADVECTION AND DIFFUSION IN THE DEGRADATION OF PORTLAND CEMENT GROUT SEAL MATERIALS IN REPOSITORY ENVIRONMENTS, S.R. Alcorn, T.L. Christian-Frear, and M.G. Wallace, RE/SPEC Inc., Albuquerque, NM.

11:30 A.M. P3.9

KEY PARAMETERS OF GLASS DISSOLUTION IN INTEGRATED SYSTEMS, Etienne Y. Vernaz and Nicole Godon, CEA-VALRHU, Bagnols, France.

11:45 A.M. P3.10

THE EFFECT OF LEACHING ON THE PORE STRUCTURE OF CEMENT-BASED GROUTS FOR USE IN A NUCLEAR FUEL WASTE DISPOSAL VAULT, M. Onofrei, M.N. Gray, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Canada; D. Breton and G. Ballivy, Sherbrooke University, Sherbrooke, Canada.

SESSION P4: RADIONUCLIDE MIGRATION II

Chair: Robert Silva

Tuesday Afternoon, November 27
America South (W)

1:00 P.M. *P4.1

BASIC RESEARCH FOR ASSESSMENT OF GEOLOGIC NUCLEAR WASTE REPOSITORIES: WHAT SOLUBILITY AND SPECIATION STUDIES OF TRANSURANIUM ELEMENTS CAN TELL US, Heino Nitsche, Lawrence Berkeley Laboratory, Earth Sciences Division, Berkeley, CA.

1:30 P.M. P4.2

MASS RELATIONSHIPS AND TRANSPORT POTENTIAL OF VOLATILE NUCLIDE SPECIES IN SUBSURFACE ENVIRONMENT, Abraham Lerman, Northwestern University, Department of Geological Sciences, Evanston, IL.

1:45 P.M. P4.3

ACTINIDE SPECIATION BY PHOTOTHERMAL SPECTROSCOPIC INSTRUMENTATION DEVELOPMENT, John M. Berg, C. Drew Tail, David E. Morris and William H. Woodruff, Los Alamos National Laboratory, Isotope and Nuclear Chemistry Division, Los Alamos, NM.

2:00 P.M. P4.4

REMOTE MEASUREMENTS OF ACTINIDE SPECIES USING AN OPTICAL FIBER AND PHOTOACOUSTIC SPECTROSCOPY, R.E. Russo, Lawrence Berkeley Laboratory, Applied Science Division, Berkeley, CA; and P. Robouch and R.J. Silva, Lawrence Livermore National Laboratory, Nuclear Chemistry Division, Livermore, CA.

2:15 P.M. P4.5

(ABSTRACT WITHDRAWN)

2:15 P.M. P4.6

THE APPLICATION OF POSITRON EMISSION TOMOGRAPHY TO THE STUDY OF MASS TRANSFER IN FRACTURED ROCKS, D. Gilling, N.L. Jefferies, Harwell Laboratory, AEA Decommissioning and Radwaste, Oxon, United Kingdom; M.R. Hawkesworth and D. Parker, University of Birmingham, Birmingham, United Kingdom.

2:30 P.M. BREAK

3:00 P.M. P4.7

MIGRATION OF RADIONUCLIDES IN GEOLOGIC MEDIA: FUNDAMENTAL RESEARCH NEEDS, D.T. Reed, Argonne National Laboratory, Argonne, IL; F.J. Wobber, U.S. Department of Energy, Office of Health and Environmental Research, Washington, DC; and J.M. Zachara, Pacific Northwest Laboratory, Richland, WA.

3:15 P.M. P4.8

THE EFFECT OF EXPERIMENTAL CONDITIONS OF THE MODIFIED LANGMUIR ISOTHERM ADSORPTION PARAMETERS, Wilfred L. Polzer, Los Alamos National Laboratory, Environmental Science Group, Los Alamos, NM; M. Gopala Rao, Howard University, Washington, DC; and Hector R. Fuentes, University of Texas at El Paso, El Paso, TX.

3:30 P.M. P4.9

NONIDEALTY EFFECTS ON ION EXCHANGE BEHAVIOR OF THE ZEOLITE MINERAL CLINOPTILOLITE, Roberto T. Pabalan, Southwest Research Institute, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

3:45 P.M. P4.10

EFFECTS OF MINERALOGY ON SORPTION OF Sr AND Cs ONTO CALICO HILLS TUFF, R.E. Meyer, W.D. Arnold, F.I. Case, G.D. O'Kelley, and J.F. Land, Oak Ridge National Laboratory, Oak Ridge, TN.

4:00 P.M. P4.11

ESTIMATION OF THE MIGRATION PARAMETERS FOR THE BOOM CLAY FORMATION BY PERCOLATION EXPERIMENTS ON UNDISTURBED CLAY CORES, M.J. Put, M. Monsecour, A. Fonteyne, SCK/CEN Mol, Mol, Belgium; and H. Yoshida, PNC, Tokyo, Japan.

4:15 P.M. P4.12

MIGRATION OF RADIONUCLIDES IN FRACTURE COLUMNS, Pirkko Hölttä, Martti Hakonen, University of Helsinki, Department of Radiochemistry, Helsinki, Finland; and Aimo Hautajärvi, Technical Research Centre of Finland, Nuclear Engineering Laboratory, Helsinki, Finland.

4:30 P.M. P4.13

(ABSTRACT WITHDRAWN)

4:30 P.M. P4.14

THE INFLUENCE OF TRACE ELEMENTS IN CONSOLIDATED SEDIMENTARY ROCKS ON THE MIGRATION BEHAVIOUR OF RADIONUCLIDES, W. Bode, GSF - Institut für Tief Lagerung, Braunschweig, West Germany; and B. Bode, Lahstedt, West Germany.

SESSION P5: POSTER SESSION

Tuesday Evening, November 27

7:30 P.M. - 10:30 P.M.

America Ballroom (W)

P5.1 EFFECTS OF HEAT TREATMENT ON THE MICROSTRUCTURE OF A FULLY SIMULATED NUCLEAR WASTE GLASS, Terese V. Palmiter, I. Joseph, and L. David Pye, NYS College of Ceramics at Alfred University, Institute of Glass Science and Engineering, Alfred, NY.

P5.2 EFFECTS OF HIPING TIME, TEMPERATURE, AND PRESSURE ON ICPP EXPERIMENTAL WASTE FORM PROPERTIES, B.A. Staples, Westinghouse Idaho Nuclear Company, Idaho Falls, ID; and D.V. Miley, EG&G Idaho Company, Idaho Falls, ID.

P5.3 LEACH RATE EXCURSIONS IN BOROSILICATE GLASSES: EFFECTS OF GLASS AND LEACHANT COMPOSITION, Aaron Barkati, S.A. Olszowska, W. Sousanpour, M.A. Adel-Eladadi, R. Adiga, Al. Barkati, G.S. Marbury, S. Li, The Catholic University of America, Washington, DC.

P5.4 R7T7 GLASS INITIAL DISSOLUTION RATE MEASUREMENTS USING A HIGH TEMPERATURE SOXHLET DEVICE, F. Delage, J.L. Dussauxoy, CEN-Vairrhé, SDHA/SEMC, Bagnols-sur-Cèze, France.

P5.5 APPLICATION OF THE GRAMBOW MODEL TO LEACH TEST DATA ON WEST VALLEY GLASSES, X. Feng, I.S. Muller, Hsing-yie Ting, I.L. Pegg and P.B. Macedo, The Catholic University of America, Vitreous State Laboratory, Washington, DC.

P5.6 EFFECTS OF COMPOSITION VARIATIONS ON MICROSTRUCTURE AND CHEMICAL DURABILITY OF WEST VALLEY REFERENCE GLASS, A.C. Buechele, X. Feng, H. Gu, I.S. Muller and I.L. Pegg, The Catholic University of America, The Vitreous State Laboratory, Washington, DC.

P5.7 (ABSTRACT WITHDRAWN)

P5.8 MEASUREMENTS OF RADON EMISSIONS FROM NUCLEAR WASTE, G. Espinosa, H. Hu and V.M. Castaño, Instituto de Física UNAM, México, México.

P5.9 CHARACTERISTICS OF MIGRATION OF ⁸⁷Sr AND ¹³⁷Cs IN ALKALINE SOLUTION THROUGH SANDY SOIL, Toshihiko Ohnuki, Japan Atomic Energy Research Institute, Department of Environmental Safety Research, Tokai, Japan.

P5.10 STUDIES OF THE EFFECTS OF DEGRADATION PRODUCTS ON THE SORPTION OF TIN AND RADIUM, J.A. Berry, G.M.N. Baston, K.A. Bond, C.M. Linklater and N.J. Pilkington, Harwell Laboratory, AEA Decommissioning and Radwaste, Oxfordshire, United Kingdom

P5.11 DEVELOPMENT OF HIGH-TEMPERATURE UV-VIS-NIR SPECTROSCOPY FOR THE MEASUREMENT OF FREE ENERGIES OF COMPLEXATION AT ELEVATED TEMPERATURES, P. Rohoush, P. Grant, R. Torres, and R. Silva, Livermore National Laboratory, Nuclear Chemistry Division, Livermore, CA.

P5.12 APPLICATIONS OF SPHAGNUM PEAT FOR IMMOBILIZING RADIOACTIVE AND HAZARDOUS CONTAMINANTS IN THE SUBSURFACE, P.A. Longmire, D.G. Brookins, B. Thomson, University of New Mexico, Albuquerque, NM; and P.O. Eller, Los Alamos National Laboratories, Los Alamos, NM.

P5.13 DIFFUSION MEASUREMENTS OF RADIONUCLIDES IN SITE-SPECIFIC SEDIMENT/GROUNDWATER-SYSTEMS, Hans Meier, Erwin Zimmerhackl, Günter Zeitler, and Pius Menge, Staatl. Forschungsinstitut für Geochemie/Außenstelle des Geologischen Landesamtes, Bamberg, West Germany.

P5.14 IMMOBILIZATION OF RADIOACTIVE STRONTIUM IN CONTAMINATED SOILS BY PHOSPHATE TREATMENT, K.H. Kim, University of Tennessee, Knoxville, TN; and S.Y. Lee, Oak Ridge National Laboratory, Environmental Sciences Division, Oak Ridge, TN.

P5.15 INFLUENCE ON THE TRANSPORT PROPERTIES OF REDOX-SENSITIVE ELEMENTS (E.G. TECHNETIUM) BY MICRO-ENVIRONMENTS AND MICROORGANISMS, Hansjörg Brühl, Asaf Pekdeger and Andreas Winkler, Freie Universität Berlin, Berlin, West Germany.

P5.16 THERMODYNAMIC MODELLING AND AQUEOUS CHEMISTRY IN THE CaO-Al₂O₃-SiO₂-H₂O SYSTEM, Alan Aikinsoo, John A. Hearne and Clive F. Knights, Harwell Laboratory, AEA Technology, Didcot, United Kingdom.

P5.17 MIGRATION OF CESIUM, STRONTIUM AND COBALT IN WATER-SATURATED CONCRETES, Kazuwa Idemitsu, Hirotsuka Furiya, Ryuji Tsutsumi, Sigeaki Yonezawa, Yoshiro Inagaki, Kyushu University, Fukuoka, Japan; and Seichi Sato, Hokkaido University, Sapporo, Japan.

P5.18 THE EFFECT OF SILICA FUME AND WATER-TO CEMENT RATIO ON THE HYDRAULIC CONDUCTIVITY OF CEMENT-BASED GROUT, A.A. Al-Manasser, M. Onofrei, M.N. Gray and B. Shenton, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Canada.

P5.19 SENSITIVITY OF A CEMENTITIOUS GEOCHEMICAL MODEL TO CHANGES IN THE GIBB'S FREE ENERGY OF THE COMPONENTS, Mark A. Gardiner and Craig A. Givens, IT Corporation, Albuquerque, NM.

P5.20 EFFECTS OF CHLORITE ALTERATION ON URANIUM REDISTRIBUTION IN KOONGARRA, AUSTRALIA, Takashi Murakami, Hiroshi Isobe, Japan Atomic Energy Research Institute, Ibaraki, Japan; and Robert Edis, Australian Nuclear Science and Technology Organisation, Menai, Australia.

P5.21 COMPARISON OF TUFF, GRANITE, AND BASALT AS HIGH-LEVEL REPOSITORY HOST ROCKS: LITHOLOGIC FACTORS INFLUENCING FLUID COMPOSITIONS, G.C. Ulmer, V.J. Grassi, A. Lee, D. E. Grandstaff, Temple University, Geology Department, Philadelphia, PA.

P5.22 HIGH-TEMPERATURE ANNEALING OF NATURAL UO₂, Janusz Janeczek and Rodney C. Ewing, University of New Mexico, Department of Geology, Albuquerque, NM.

P5.23 ON THE COMPARISON OF THE EFFECT OF pH ON THE SOLUBILITY OF AN UNIRRADIATED UO₂ IN BOTH PER CHLORATE AND CHLORIDE TEST SOLUTIONS. INFLUENCE OF THE SOLID MORPHOLOGY, E. Torrente, I. Casas, M. Aguilar, J. de Pablo, J. Giménez, UPC, Department of Chemical Engineering, Barcelona, Spain; and J. Bruno, KTH, Department of Inorganic Chemicals, Stockholm, Sweden.

P5.24 DIRECT ANALYSIS OF TIME DEPENDENT FUNDAMENTAL SOLUTION IN THREE-DIMENSIONAL TRANSIENT ADVECTION DIFFUSION BY BOUNDARY ELEMENT METHOD, Ryuji Kawamura and Akira Isono, Information and Mathematical Science Laboratory Inc., Tokyo, Japan.

PS 25 THREE-DIMENSIONAL VISUALIZATION: A MEANS OF OPTIMIZING ANALYSIS OF TECHNICAL INFORMATION FOR A GEOLOGIC REPOSITORY FOR HIGH-LEVEL NUCLEAR WASTE. Donald H. Alexander, U.S. Dept. of Energy, Washington, DC; E. Richard Hill, John L. Smoot, Pacific Northwest Laboratory, Richland, WA; Dennis R. Smith, Kareo Waldo, Dynamic Graphics, Inc., Bethesda, MD; Kenneth G. Eggert, Los Alamos National Laboratory, Los Alamos, NM; and Kenneth M. Krupka, Pacific Northwest Laboratory, Richland, WA.

PS 26 MODELLING THE CHEMICAL BEHAVIOUR OF RADIONUCLIDES IN WASTE DISPOSAL IN GRANITE. R. Fabriol, BRGM Department of Geochemistry, Orléans, France; G. Ouzounian, Andra, Fontenay-aux-Roses, France.

PS 27 DIFFUSION POROSITY AND DIFFUSIVITY OF RADIONUCLIDES IN GRANITE ROCKS. PART II: DIFFUSIVITY AND ELECTRICAL RESISTIVITY MEASUREMENTS IN ROCK MATRIX AROUND FRACTURES. Heikki Kumpulainen, Ano Muurinen and Kari Uusheimo, Technical Research Centre of Finland, Reactor Laboratory, Espoo, Finland.

PS 28 RADIOACTIVE TRACER STUDY PERFORMED IN A DIPOLE GEOMETRY IN A HIGHLY CONDUCTIVE FRACTURE ZONE. Johan Byegård, Gunnar Skarnemark, Mats Skälberg, Chalmers University of Technology, Department of Nuclear Chemistry, Gothenburg, Sweden.

PS 29 TEMPERATURE INDUCED REDOX FRONT IN THE NEAR FIELD OF A REPOSITORY FOR SPENT FUEL. Allan T. Emrén, Chalmers University of Technology, Department of Nuclear Chemistry, Göteborg, Sweden.

PS 30 CRITICAL CHLORIDE CONCENTRATIONS FOR PITTING OF AUSTENITIC AND HIGH-NICKEL ALLOYS. B. Daniel McGrath, Joseph C. Farmer, and Dennis L. Fleming, Lawrence Livermore National Laboratory, Livermore, CA.

PS 31 STATISTICALLY DESIGNED LEAD CORROSION EXPERIMENTS FOR NUCLEAR WASTE DISPOSAL. P. Mani Mathew and P.A. Krueger, Atomic Energy of Canada Limited, Containment Analysis Branch, Pinawa, Canada.

PS 32 UNCERTAINTIES IN CONTAINER FAILURE TIME PREDICTIONS. R.E. Williford, Pacific Northwest Laboratory, Richland, WA.

PS 33 AN ADVANCED COLD PROCESS CANISTER DESIGN FOR NUCLEAR WASTE DISPOSAL. Heikki Raiko, Technical Research Centre of Finland, Nuclear Engineering Laboratory, Helsinki, Finland; and Jukka-Pekka Salo, Teollisuuden Voima Oy, Nuclear Waste Office, Helsinki, Finland.

PS 34 EVALUATION OF THERMAL CONDUCTIVITY OF BACKFILL MATERIAL VIA A TRIAL FUNCTION TECHNIQUE. J.M. Xu, R.N. Yong and A.M.O. Mohamed, McGill University, Geotechnical Research Centre, McGill University, Montreal, Canada.

PS 35 MODELLING STUDIES OF SORPTION OF URANIUM AND PLUTONIUM IN THE FAR-FIELD OF A NUCLEAR WASTE REPOSITORY. A. Haworth, S.M. Sharland and C.J. Toward, Harwell Laboratory, Radwaste Disposal R&D Division, AEA Decommissioning and Radwaste, AEA Technology, Didcot, United Kingdom.

PS 36 DESIGN AND TENTATIVE RESULTS OF REDOX CAPACITY MEASUREMENTS OF GRANITIC ROCKS AND MINERALS. Ylevo O. Pirhonen, Technical Research Centre of Finland, Geotechnical Laboratory, Espoo, Finland.

PS 37 THE WIPP BIN-SCALE CH TRU WASTE TEST PROGRAM INITIATION. Marin A. Molevks, Sandia National Laboratories, Albuquerque, NM.

PS 38 COUPLED THERMO-HYDRAULIC BEHAVIOR AROUND ACCESS SHAFT SEALED WITH BACKFILL MATERIAL. J. Okamoto, Kajima Corporation, Nuclear Power Department, Tokyo, Japan; K. Ishihara, Y. Sawauchi, Kajima Corporation, Civil Engineering Design Division, Tokyo, Japan; K. Hara, N. Sasaki, Power Reactor and Nuclear Fuel Development Corporation, Geological Isolation Technology Section, Ibaraki-ken, Japan.

PS 39 BENTONITE-GROUNDWATER INTERACTION IN INERT NITROGEN ATMOSPHERE. Anna Nystrom, Irene Lundén, Chalmers University of Technology, Department of Nuclear Chemistry, Göteborg, Sweden.

PS 40 CHARACTERISTICS OF BOOM CLAY AS SEALING AND BACKFILLING MATERIAL. Geert T.C. Voickens and Frank T.L. Vandervoort, SCK/CEN, Department of Geo-Technology, Mol, Belgium.

PS 41 A REVIEW PROCESS AND A DATABASE FOR WASTE-PACKAGE DOCUMENTS. Charles G. Inerente, U.S. Nuclear Regulatory Commission, Division of High-Level Waste Management, Office of Nuclear Materials Safety and Safeguards, Washington, DC; Carla A. Messina, Consultant, Bethesda, MD; and Anna C. Fraker, National Institute of Standards and Technology, Gaithersburg, MD.

PS 42 EFFECT OF OXYGEN TRANSPORT AND RESISTIVITY OF THE ENVIRONMENT ON THE CORROSION OF STEEL. E. Escalante, U. Bertocci, National Institute of Standards and Technology, Gaithersburg, MD; and T. Oka, Nippon Steel Corporation, Japan.

SESSION P6: SPENT FUEL

Chair: Lawrence Johnson
Wednesday Morning, November 28
America South (W)

8:30 A.M. ***P6.1**
SPENT FUEL DEGRADATION. Roy S. Forsyth, Studsvik Energiteknik AB, Nyköping, Sweden.

9:00 A.M. **P6.2**
PHASE RELATIONS OF THE URANYL OXIDE HYDRATES AND THEIR SIGNIFICANCE TO THE DISPOSAL OF SPENT FUEL. R.J. Elnsh and R.C. Ewing, University of New Mexico, Geology Department, Albuquerque, NM.

9:15 A.M. **P6.3**
DISSOLUTION BEHAVIOUR OF USED CANDU FUEL UNDER REDUCING CONDITIONS. J.C. Taji, S. Stroes-Gascoyne, W.H. Hocking, A.M. Duclos, R.J. Poth and D.L. Wilkin, AECL, Whiteshell Nuclear Research Establishment, Pinawa, Canada.

9:45 A.M. BREAK

10:15 A.M. **P6.4**
RESULTS FROM LONG-TERM DISSOLUTION TESTS USING OXIDIZED SPENT FUEL. Charles N. Wilson, Pacific Northwest Laboratory, Richland, WA.

10:30 A.M. **P6.5**
RADIATION INDUCED DISSOLUTION OF UO₂. Hilbert Christensen, Studsvik Nuclear, Nyköping, Sweden.

10:45 A.M. **P6.6**
UO₂ MATRIX DISSOLUTION RATES AND GRAIN BOUNDARY INVENTORIES OF Cs, Sr, AND Tc IN SPENT LWR FUEL. W.J. Gray and D.M. Strachan, Pacific Northwest Laboratory, Richland, WA.

11:00 A.M. **P6.7**
SIMFUEL DISSOLUTION STUDIES IN GRANITIC GROUNDWATER UNDER OXIC CONDITIONS AT 25°C. Jordi Bruno and Amalia Sendino, Royal Institute of Technology, Department of Inorganic Chemistry, Stockholm, Sweden.

11:15 A.M. **P6.8**
A DESCRIPTION OF THE KINETICS AND MECHANISMS WHICH CONTROL THE RELEASE OF HLW ELEMENTS FROM SYNROC. K.L. Smith, K.P. Hart, G.R. Lumpkin, P. McGlinn, J. Bartlett, P. Lam and M.G. Blackford, Australian Nuclear Science and Technology Organisation, Lucas Heights Research Laboratories, Sydney, Australia.

KEYNOTE SPEAKER

1:00 P.M. *P7.1

RETHINKING HIGH LEVEL NUCLEAR WASTE MANAGEMENT, Frank L. Parker, Vanderbilt University, Department of Civil and Environmental Engineering, Nashville, TN.

SESSION P7: PERFORMANCE ASSESSMENT

Chair: Jun Abraham and Hans Wanner
Wednesday Afternoon, November 28
America South (W)

2:00 P.M. P7.2

HEAT-PIPE EFFECT ON THE TRANSPORT OF GASEOUS RADIONUCLIDES RELEASED FROM A NUCLEAR WASTE CONTAINER, W. Zhou, P.L. Chambré, T.H. Pigford, and W.W.-L. Lee, University of California, Berkeley, Department of Nuclear Engineering, University of California and Lawrence Berkeley Laboratory, Berkeley, CA.

2:15 P.M. P7.3

RELEASE AND TRANSPORT OF GASEOUS C-14 FROM A NUCLEAR WASTE REPOSITORY IN AN UNSATURATED MEDIUM, W.B. Light, E.D. Zwhlen, T.H. Pigford, P.L. Chambré and W.W.-L. Lee, University of California and Lawrence Berkeley Laboratory, University of California, Berkeley, Department of Nuclear Engineering, Berkeley, CA.

2:30 P.M. P7.4

WASTE STORAGE IN THE VADOSE ZONE AFFECTED BY WATER VAPOR CONDENSATION AND LEACHING, J.W. Cary, G.W. Gee, Battelle-Pacific Northwest Laboratory, Geosciences Department, G.A. Whyatt, Battelle Memorial Institute, Waste Technology Center, Richland, WA.

2:45 P.M. P7.5

AQUEOUS DIFFUSION IN UNSATURATED MATERIALS, James L. Conger, Washington State University Tri-Cities, Environmental Sciences, Richland, WA; Judith Wright, Pacific Northwest Laboratory, Richland, WA.

3:00 P.M. BREAK

3:30 P.M. *P7.6

DEMONSTRATION OF A SYSTEM PERFORMANCE ASSESSMENT PROCESS, K.W. Dormuth, AECL Research, Whiteshell Laboratories, Manitoba, Canada.

4:00 P.M. P7.7

PRELIMINARY MODEL OF REPOSITORY CHEMISTRY FOR THE WASTE ISOLATION PILOT PLANT, L.H. Brugh, Sandia National Laboratories, Albuquerque, NM; D. Orlic-Galic, Stanford University, Stanford, CA; D.T. Reed, Argonne National Laboratory, Argonne, IL; X. Tong, Stanford University, Stanford, CA; R.H. Vreeland, West Chester University, West Chester, PA; and R.E. Westerman, Pacific Northwest Laboratory, Richland, WA.

4:15 P.M. P7.8

ON THE PROBLEM OF CONSISTENCY OF CHEMICAL THERMODYNAMIC DATA BASES, Hans Wanner, OECD Nuclear Energy Agency, Data Bank, Gif-sur-Yvette, France.

4:30 P.M. P7.9

QUANTIFYING THE EFFECTS OF UNCERTAINTY IN THERMODYNAMIC MODELLING, J.M. Bealby, A. Dawes and D. Read, W.S. Atkins Engineering Sciences, Fluids Department, Epsom, United Kingdom.

4:45 P.M. P7.10

A NOVEL CONCEPTUAL MODEL FOR THE FLOW AND TRANSPORT IN FRACTURED ROCK, Aimo Hautajärvi, Veikko Taivassalo and Seppo Vuori, Nuclear Engineering Laboratory, Technical Research Centre of Finland, Helsinki, Finland.

SESSION P8: METAL

Chair: Lars Werme
Thursday Morning, November 29
America South (W)

8:30 A.M. *P8.1

CONTAINER MATERIALS FOR HIGH-LEVEL NUCLEAR WASTE AT THE PROPOSED YUCCA MOUNTAIN SITE, R. Daniel McCright, Lawrence Livermore National Laboratory, Livermore, CA.

9:00 A.M. P8.2

REPASSIVATION METHOD TO PREDICT LONG TERM INTEGRITY OF LOW ALLOY TITANIUM USED FOR NUCLEAR WASTE PACKAGE, Shigeo Tsujikawa and Yoichi Koizumi, The University of Tokyo, Materials Science Department, Tokyo, Japan.

9:15 A.M. P8.3

HYDROGEN EVOLUTION FROM CORROSION OF IRON AND STEEL IN INTERMEDIATE LEVEL WASTE REPOSITORIES, R. Greuer, Paul Scherrer Institute, Villigen, Switzerland; B. Knecht, NAGRA, Nuclear Technology Department, Baden, Switzerland; P. Kreis and J.P. Simpson, Sulzer Innotec Ltd., Winterthur, Switzerland.

9:45 A.M. BREAK

10:15 A.M. P8.4

ENVIRONMENTAL EFFECTS ON LOCALIZED CORROSION OF HIGH LEVEL NUCLEAR WASTE CONTAINER MATERIALS, Gustavo Cregolinio, Narasi Sridhar, Southwest Research Institute, Center for Nuclear Waste Regulatory Analysis, San Antonio, TX; and Walter J. Machowski, Southwest Research Institute, San Antonio, TX.

10:30 A.M. P8.5

THE CRITICAL CONDITION FOR THE INITIATION OF LOCALIZED CORROSION OF MILD STEEL USED FOR NUCLEAR WASTE PACKAGE, Gen Nakayama and Masatsune Akaishi, Ishikawajima-Harima Heavy Industries Company, Ltd., Research Institute, Tokyo, Japan.

10:45 A.M. P8.6

CORROSION PRODUCTS AND MECHANISMS IN LONG-TERM CORROSION OF COPPER ALLOYS, M.B. McNeill, Naval Coastal Systems, Systems Center, Panama City, FL, and B.J. Little, Naval Oceanographic and Atmospheric Research Laboratory, NSTL, MS.

11:00 A.M. P8.7

EFFECT OF COMPACTED BENTONITE ON THE CORROSION BEHAVIOR OF CARBON STEEL AS A GEOLOGICAL ISOLATION OVERPACK MATERIAL, A. Honda, T. Teshima, K. Tsurudome, H. Ishikawa, Y. Yusa and N. Sasaki, Power Reactor and Nuclear Fuel Development Corporation, Ibaraki, Japan.

11:15 A.M. P8.8

CORROSION OF COPPER-BASED MATERIALS IN IRRADIATED HIGH-HUMIDITY AIR SYSTEMS, D.T. Reed, Argonne National Laboratory, Chemical Technology Division, Argonne, IL; and R.A. Van Konyenburg, Lawrence Livermore National Laboratory, Livermore, CA.

11:30 A.M. P8.9

STAINLESS STEEL WELDS IN CONTAINERS OF NUCLEAR WASTE, T.M. Deving, University of California, Berkeley, Department of Materials Science and Mineral Engineering, Berkeley, CA

SESSION P9: INTEGRATED SYSTEMS

Chair: John Bates
Thursday Afternoon, November 29
America South (W)

1:00 P.M. *P9.1

KEY PARAMETERS OF GLASS DISSOLUTION IN INTEGRATED SYSTEMS, Erienne Y. Vernez and Nicole Godon, CEA-VALRHO, Department DPR/SCD, Bagnols-sur-Cèze, France.

1:30 P.M. P9.2

NEAR-FIELD PERFORMANCE OF THE ADVANCED COLD PROCESS CANISTER, L.O. Werme, SKB, Stockholm, Sweden; and J-P. Salo, TVO, Helsinki, Finland.

1:45 P.M. P9.3

THE ROLE OF LABORATORY ANALOG EXPERIMENTS IN ASSESSING THE PERFORMANCE OF WASTE PACKAGE MATERIALS, J.C. Cunniff and J.K. Bates, Argonne National Laboratory, Argonne, IL.

2:00 P.M. P9.4

ACTINIDE TRANSPORT IN TOPOPAH SPRING TUFF: PORE SIZE, PARTICLE SIZE, AND DIFFUSION, Marilyn Buchholz ten Brink, Lawrence Livermore National Laboratory, Earth Sciences Department, Livermore, CA; Douglas L. Phinney, Lawrence Livermore National Laboratory, Nuclear Chemistry Department, Livermore, CA; and David K. Smith, Lawrence Livermore National Laboratory, Earth Sciences Department, Livermore, CA.

2:15 P.M. P9.5

GAS FORMATION IN A HLW DEPOSITORY. EVALUATION AND MODELLING OF THE PRODUCTION RATES AND CONSEQUENCES ON THE SAFETY OF THE REPOSITORY, Francois Beaus, CEA/IPSN/DAS, Fontenay-aux-Roses, France; and Sylvie Voisin, CEA/ANDRA, Fontenay-aux-Roses, France.

2:30 P.M. P9.6

PARAMETRIC SIMULATION OF ROCK SALT BEHAVIOUR RESULTING FROM DISPOSAL OF HIGH LEVEL RADIOACTIVE WASTE, D. Caramelle, M. Gaudez CEA, Saclay, France; J. Monig, GSF Braunschweig, Germany; G. Ouzounian, Andra/Desa, Fontenay Aux Roses, France, and G. Simonet, CEA Fer IPSN/DSMN, Fontenay Aux Roses, France.

2:45 P.M. P9.7

EFFECTS OF ALPHA AND GAMMA RADIATION ON UNSATURATED REPOSITORY ENVIRONMENT, John E. Young and John K. Bates, Argonne National Laboratory, Argonne, IL.

3:00 P.M. BREAK

SESSION P10: BACKFILL

Chair: P.C. Altin

Thursday Afternoon, November 29

America South (W)

3:30 P.M. P10.1

THE EFFECTS OF MOISTURE REDISTRIBUTION AND TEMPERATURE ON THE LOAD-BEARING CAPABILITY OF A CLAY-BASED BACKFILL, S.C.H. Cheung, M.N. Gray, Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Canada; R.N. Yong and A.M.O. Mohamed, McGill University, Geotechnical Research Centre, Montreal, Canada.

3:45 P.M. P10.2

COMPRESSIVE BEHAVIOUR OF CLAY-BASED BACKFILL UNDER LARGE HYDRAULIC LOADING, H.T. Chan and K.C. Lau, Ontario Hydro, Civil Research Department, Toronto, Canada.

4:00 P.M. P10.3

APPLICATION OF ELASTO-PLASTIC MODEL TO MECHANICAL AND HYDRAULIC BEHAVIOR OF BUFFER MATERIAL UNDER WATER UPTAKE IN A REPOSITORY, T. Fujita, K. Hara, Y. Yusa, N. Sasaki, Power Reactor and Nuclear Fuel Development Corporation, Ibaraki, Japan.

4:15 P.M. P10.4

HYDRO-THERMAL PERFORMANCE OF AN ENGINEERED CLAY BARRIER, A.P.S. Selvadurai, Carleton University, Department of Civil Engineering, Ontario, Canada.

4:30 P.M. P10.5

DEVELOPMENTS FOR IN SITU TESTS ON COMPACTED BENTONITE-BASED BUFFER MATERIALS, B.H. Kjartanson and M.N. Gray, AECL Research, Manitoba, Canada; and B. Pulles, EBA Consultants, Alberta, Canada.

Overview of Chemical Modeling of Nuclear Waste Glass Dissolution William L. Bourcier, Lawrence Livermore National Laboratory, P 219, Livermore, CA 94550

The various mechanisms proposed to be rate-limiting for borosilicate glass dissolution fall into three broad categories: (1) armoring and diffusion-limited transport of constituents through a surface precipitate; (2) surface reaction rate control due to dissolution affinity of the glass or an altered layer on the glass surface; and (3) diffusion through a leached layer. Recent experimental results including NMR spectroscopy of hydrated surface layers, dissolution rate measurements in D_2O solutions, and as well as closed-system and flow-through glass dissolution tests are consistent with surface reaction control.

Models of glass dissolution incorporating surface reaction rate control have been successfully applied to glass dissolution experimental results, in particular, the work of Grambow. Model refinements are aimed at using experimental results to provide model parameters rather than obtaining the parameters through regression of glass dissolution results. Future experimental and modeling work should be aimed at providing definitive proof of the surface reaction rate control mechanism. Simple experiments should be performed that isolate specific effects such as glass composition, pH, and solution composition, while holding all other parameters constant. Confidence in our ability to make long-term predictions of glass performance in a nuclear waste repository critically depends on accurate knowledge of rate-limiting dissolution mechanisms.

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-7405-ENG-48.

P1.2

ENHANCEMENT OF BOROSILICATE GLASS DISSOLUTION BY SILICA SORPTION AND DIFFUSION IN COMPACTED BENTONITE: A MODEL STUDY. Enzo Curti, Paul Scherrer Institut, Villigen and Würenlingen, Switzerland; and Paul A. Smith, Paul Scherrer Institut, Villigen and Würenlingen, Switzerland.

Experimental evidence indicates that glass corrosion rates decrease proportionally with the increase of silicic acid concentration in the solution contacting the glass surface. A minimum corrosion rate (L_{33}) is reached when the solution becomes saturated with respect to amorphous SiO_2 . In a repository where the vitrified waste form is surrounded by compacted bentonite, the silica dissolved from the glass will diffuse into the pore solution and concentration gradients will be established throughout the backfill material. The silicic acid concentration at the glass-bentonite interface, and thus the glass corrosion rate, will then be diffusion controlled. Moreover, experimental work suggests that significant sorption of silica by clay minerals in bentonite may accelerate glass corrosion.

A model describing glass corrosion coupled with diffusive transport and sorption of silica in bentonite has been developed and incorporated in a FORTRAN computer code (GLADIS). The model assumes: (a) a linear isotherm for the sorption of silica (K_D), (b) time and space invariant pH, temperature and ionic strength, (c) proportionality between the quantity of silica precipitated and the amount of glass dissolved and (d) cylindrical geometry. Preliminary calculations for unfractured glass, assuming no silica sorption on the bentonite, indicate that a stationary state is rapidly reached in which the silica concentration at the glass-bentonite interface is lower than the saturation concentration. This implies that the glass corrodes at a more rapid rate than L_{33} ($L_{33} \sim 6 \cdot L_{33}$). If moderate silica sorption is assumed ($K_D = 0.5 \text{ m}^3 \text{ kg}^{-1}$), the attainment of stationary conditions is delayed by the removal of silicic acid from solution, and the average corrosion rate is further increased by a factor ~ 2 .

P1.3

RARE EARTH ELEMENTS BEHAVIOR DURING ALTERATION OF BASALTIC GLASSES: CASE OF THE WEATHERING OF ICELANDIC HYALOCLASTITES. Roux V.L., Crovisier J.L., C.G.S., Strasbourg, FR; and Petit J.C., C.E.A., SESO/LECALY, Fontenay-aux-Roses, FR.

The studied samples are basaltic hyaloclastites with ages ranging from 1800 years to 2.4 My, collected in the Hengill and Huseafell areas, Iceland. They were altered in subglacial or meteoric conditions at temperatures close to 0°C . Initial solutions were very diluted, neutral to weakly acid and oxidizing. The hyaloclastites are made of millimetric grains of glass surrounded by an alteration rim (palagonite) and cemented by intergranular materials.

1- Palagonites, often appearing amorphous by X-ray diffraction, are in fact made up of small smectitic particles limited to few layers while intergranular materials which appear crystallized by X-ray diffraction are composed of well expanded trioctahedral smectites.

2- In a same sample the REE contents of palagonites are generally higher than the intergranular material ones.

3- Assuming a constant iron content we calculated an absolute REE enrichment of the amorphous secondary products in contrast with an absolute REE depletion of the corresponding crystallized ones. Knowing that solution contributions can be neglected, we may conclude that the enrichment in REE in amorphous material is in fact relative, when considering the whole reaction products.

Numerous studies of borosilicate glasses altered in water have shown that actinides (the analogs of which are the REE) are trapped by amorphous alteration rims. An increase of the crystallinity of these rims with time would be penalizing for the confinement of radionuclides in the near field insofar as REE retention capacity of amorphous alteration products is far better than crystallized products one.

P1.4

MINERALOGICAL, TEXTURAL AND COMPOSITIONAL DATA ON THE ALTERATION OF BASALTIC GLASS FROM KILAUEA, HAWAII TO $>300^\circ\text{C}$: INSIGHTS TO THE CORROSION OF A BOROSILICATE GLASS WASTE-FORM. David K. Smith, Lawrence Livermore National Laboratory, Livermore, CA 94550

Studies of the hydrothermal alteration of porphyritic basalt (61 wt% SiO_2) by hot ($> 300^\circ\text{C}$) brines circulating at depth through the East Rift Zone, Kilauea, Hawaii may be indicative of alteration mineralogies expected during surface reaction of a borosilicate glass waste-form. This investigation documents the sequence of secondary phases produced by the alteration of basalt, the textures of these constituents and compositional data. The 1967m deep HGP-A geothermal well penetrates a sequence of glassy basalts altered by vapor and fluids of variable salinity (FDS: 3-20 mg/ml). Optical, SEM, XRD and electron probe analyses of core and pump samples confirm the down-hole progression of the alteration sequence from 1) intermittent prehnite to 2) smectite (montmorillonite to saponite) to 3) mixed chlorite-smectite - chlorite to 4) actinolitic hornblende - actinolite, epidote and anhydrite at total depth. Texturally, alteration sequences are best developed in fractures and vesicles where secondary minerals grow in rinds in excess of 100 microns thick; representative reaction surfaces exhibit the inward growth of an alteration front within the glass matrix; palagonite superceded by Fe-rich clays; clays at high temperature, amphibole fractures or water-filled vesicles control fluid circulation, and alteration throughout the HGP-A surface alteration layers mimic that of a SHL-165 glass produced during a sixty day static leaching test at 150°C . Substitution of the surface alteration layer reveals the presence of an amorphous SiO_2 depleted (relative to the fresh glass) front preceding the secondary alteration rind during growth into the glass matrix. The high temperature and saline chemistry of fluids and vapor variably acting on an anisotropic partially crystalline basalt detract from HGP-A as a constrained analog; however, documentation of alteration phases and their consurvent texture and composition may be of utility in assessing models of borosilicate glass corrosion.

P1.5

THE IMPORTANCE OF SECONDARY PHASES IN GLASS CORROSION. William L. Ebert and John K. Bates, Argonne National Laboratory, Argonne, IL 60439.

The durability of borosilicate glasses in the hydrologically unsaturated environment anticipated at the proposed Yucca Mountain repository site must be sufficiently well understood to project possible radionuclide release rates over very long time periods. Such an environment is not well represented by typical

leaching tests using large volumes of water. Experiments in a steam environment wherein the volume of water available for reaction is restricted to a small amount of condensed water have shown the rate of glass reaction to accelerate upon formation of secondary phases. The influence of the secondary phases is through a decrease in the solution concentrations of major glass species which increases the affinity for glass dissolution. The solubility products of the secondary phases which form control the solution chemistry and so the glass dissolution rate, and identification of these phases is necessary to project the behavior of glass waste forms over long times using computer simulations. An experimental technique is described which accelerates the glass reaction such that secondary phases are produced after only a few days of reaction, and associated solution concentrations are measured. A correlation between the experimental results and the glass modeling effort underway by the Yucca Mountain Project is shown.

Work supported by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project under subcontract to Lawrence Livermore National Laboratory, SANL 910-005.

PI.6

THE ROLE OF SURFACE LAYERS IN GLASS LEACHING PERFORMANCE.
J. K. Bates, Argonne National Laboratory, Argonne, IL 60439.

The mechanistic assessment of glass reaction processes with water requires the assimilation of data regarding elements released to solution plus the structure of reacted layers that remain on the glass. Recent advances in analytical electron microscopy provide new insight into the role of surface layers in glass reaction. Examples are given where layers, consisting of individual bands, form, remain attached to the glass, and restructure into crystalline phases. These crystalline phases may include actinide elements and thus the layer acts as a barrier for release of selected elements. Other examples are given where the layers form only loosely attached to the glass, with a solution gap forming between the layer and the glass. In this case, the layer can be detached from the glass during the leaching process which affects elemental transport through a repository environment, plus further reaction of glass. The effects of layer formation are discussed in the context of varying SA/V and for conditions of vapor and standard leaching reactions.

PI.7

MECHANISTIC EFFECTS OF DEUTERATION ON THE AQUEOUS CORROSION OF NUCLEAR WASTE GLASSES. X. Fang, L. Fu, I. L. Pegg and P. B. Macedo, The Vitreous State Laboratory, The Catholic University of America, Washington, D. C. 20064.

Isotopically labeled water has been utilized by several researchers to help elucidate the glass dissolution mechanism in aqueous media. However, most of the results have been obtained with simple silicate glasses and have utilized low surface to volume (S/V) ratios and relatively short time scales. In this paper we report the results of an extensive study of the leach behavior of the preliminary West Valley nuclear waste glass composition, WV205, in deuterium oxide using multiple S/V ratios at both short and long times. The WV205 glass was leached in parallel in both ordinary deionized water and in deuterated water at five S/V ratios (20, 100, 200, 2000 and 10000/m) at 90°C under PCT (the SRL-modified MCC3 procedure) conditions with sampling at 1, 3, 7, 28, 56, 120 days, and four times annually thereafter; the tests will continue for several years. Initial rates were isolated by measurements at shorter times with

polished monoliths. A significant isotope effect, as measured by the ratio of leach rates, R_{D2O}/R_{H2O} , was found at all S/V ratios and reached values as large as 360%. Our data yield different values for R_{D2O}/R_{H2O} in the diffusion, matrix dissolution, and saturation dominated regimes with the largest effect in the middle stage. Large values of R_{D2O}/R_{H2O} would be characteristic of primary or secondary kinetic isotope effects suggestive of a bond breakage involving hydrogen being involved in the rate determining step.

PI.8

HYDROLYSIS OF R7T7 NUCLEAR WASTE GLASS IN DILUTE MEDIA: MECHANISMS AND DISSOLUTION RATES AS A FUNCTION OF PH.

T. ADVOCAT (*), J. L. CROVISIER (**), and E. VERNAZ (*).
(*)CEA/CEN VALRHU. SDMA/SEMC. Marcoule 30205 BAGNOLS/CEZ FRANCE
(**)CGS. Institut de Geologie. 1 rue Blessig 67000 STRASBOURG FRANCE

Long term modelling of nuclear waste glass corrosion first requires mechanisms and dissolution rate determinations. An experimental study was carried out using R7T7 nuclear waste glass and distilled water on the one hand, and buffer solutions with fixed pH values from 4.8 to 10 on the other hand. All experiments were conducted at 90°C, in dilute media (SA/V = 10 m⁻¹) and far from saturation with respect to the glass, in order to neglect the affinity term of the following general kinetic relation:

$$v = dc/dt = k' \cdot s \cdot a_p^n \cdot (1 - a^{RT})$$

where k' is the kinetic constant, s the glass surface area, a_p the proton activity and n the reaction coefficient; A is the affinity term, R the gas constant and T the temperature.

Our experimental design, consisting in regular solution sampling on the same leaching cell allows to determine the k' and n values. We also demonstrate that glass dissolution mechanism varies with the solution pH:

- In distilled water, glass dissolution is selective over 40 hours. Then, a stoichiometric dissolution occurs when the pH of the solution evolves toward alkaline values (> 6.2 at 90°C)

- In acidic media, glass dissolution remains selective over at least 22 days, the further incongruity being the result of the saturation product formations. From pH 4.8 to 7, the dissolution rate is quite pH-independent.

- In basic media, glass dissolution is stoichiometric from the outset of the experiments. The glass dissolution rate varies by a factor 15 between pH 7 and 10.

These experiments allow to refine the kinetic part of the geochemical codes, such as D155OL, used for long term modelling of nuclear waste glass and water interactions.

PI.9

TECHNICAL BASES FOR THE DWPF TESTING PROGRAM.
M. J. Plodinec, Westinghouse Savannah River Co., Aiken, SC.

The Defense Waste Processing Facility (DWPF) will be the first production facility in the United States for the immobilization of high-level nuclear waste. Production of DWPF canistered waste forms will begin prior to repository licensing, so that decisions on facility startup will have to be made before repository licensing. The Department of Energy's Office of Civilian Radioactive Waste Management (RW) has addressed this discrepancy by defining a Waste Acceptance Process to provide reasonable assurance that the waste glass produced in the DWPF will be acceptable for permanent storage in a federal repository. As part of this process, detailed technical specifications have been developed for the DWPF product.

SRS has developed detailed strategies for demonstrating compliance with each of the specifications. An important part of compliance is the testing which will be carried out in the DWPF. In this paper, the bases for each of the tests to be performed in the DWPF to establish compliance with the specifications are described. The initial tests, those relating to characterization of canister closure welds, have been used to define an operating window for weld closure parameters. In addition, product control tests using actual radi-

gactive waste in small-scale equipment, and using simulated waste in engineering scale equipment give confidence that the testing program will achieve its goals.

P1.10

THE EFFECT OF SAMPLE PREPARATION METHODS ON GLASS PERFORMANCE. M. S. Oh and V. M. Oversby, Lawrence Livermore National Laboratory, Livermore, CA 94550

The composition of aqueous solutions used in waste glass testing has been shown to have a strong influence on the leaching behavior of the glasses in short term tests. Data have also suggested that sample preparation methods, because of the resulting variability in glass surface area, influence the results of short term tests; however, this phenomenon has not been studied in a controlled manner. It is also possible that both surface preparation methods and chemical composition of leaching solutions could affect the nature of the alteration layers that develop on the glasses. If different assemblages of metastable reaction products form on the glass surfaces in leachants of different chemical composition, the influence of the solution composition might be long-lasting.

We conducted a controlled experiment to investigate the effects of sample preparation method and leaching solution composition on

1. The release rate and total release of glass constituents to the leaching solution; 2. The morphology of the surface layer development on the altered glasses; and 3. The chemical and phase composition of the alteration layers.

This report will focus on the first two topics. Results of surface layer characterization will be reported in a separate communication.

P1.11

THE USE OF PARTIAL-REPLENISHMENT TESTS IN MODELING THE LEACH BEHAVIOR OF GLASSES. Aa. Barkatt, S. A. Olszowka, W. Sousanpour, T. Choudhury, Y. Guo, Al. Barkatt, and R. Adiga, The Catholic University of America, Washington, D.C.

Experiments intended to characterize the effects of the parameters of partial-replenishment tests on the test results show that the effect of the magnitude of the exchange volume of fraction, for fractions of up to 0.25, on leachate concentrations becomes limited within a few months to ~10%. The results also show that leachate concentrations recover within one week after each exchange at 90%. These results facilitate the use of partial-exchange test data in quantitative leach modeling.

P2.1

ASSESSING THE NATURAL PERFORMANCE OF FELSIC TUFFS AT YUCCA MOUNTAIN USING THE Rb-Sr and Sm-Nd SYSTEMS. Zell E. Peterman, Kiyoto Futa, and Richard W. Spengler, U.S. Geological Survey, MS 963, Box 25046 DFC, Denver, CO 80225

If Yucca Mountain, Nevada, is selected for development as a nuclear waste site, felsic welded tuff of the Topopah Spring Member of the Miocene Paintbrush Tuff will host the repository. Because the geologic system is the final barrier to the release of radionuclides to the environment, understanding past element mobility in the host rock and underlying units is essential for predicting the future performance of the rock mass. The distribution of depth-dependent zones of diagenetic alteration in the tuffs, described by Broxton and others (1987), provide the alteration framework for ongoing isotopic and trace element studies of the Topopah Spring Member and older volcanic units at Yucca Mountain.

Geochronologists have known for more than two decades that the whole-rock Rb-Sr system in felsic tuffs commonly fails to yield accurate crystallization ages. This open-system behavior is primed by diagenetic hydration of volcanic glass and formation of secondary minerals such as zeolites and clays. Subsequent loss or redistribution of radiogenic ⁸⁷Sr is facilitated by recrystallization, new mineral growth, and dewatering of the volcanic pile all of which may accompany increasing temperature and pressure during prograde metamorphism. Because of its sensitivity to hydration/dehydration and mineralogical reactions, the Rb-Sr system will be of particular value for assessing the timing and extent of past open-system behavior in the felsic tuffs at Yucca Mountain at both the mineralogic and bulk rock scales. In contrast, the Sm-Nd system is currently considered more robust during alteration events and will aid in differentiating primary and secondary isotopic variations in these felsic tuffs. These data will be helpful in predicting the performance of the rock mass and in assessing the potential for near-field element mobility induced on underlying zeolitic zones by the expected thermal loading of the repository.

P2.2

NATURAL-ANALOG STUDIES FOR PARTIAL VALIDATION OF CONCEPTUAL MODELS OF RADIONUCLIDE RETARDATION AT THE WIPP

D. B. Ward and D. G. Brookins, University of New Mexico, and M. D. Siegel and S. J. Lambert, Sandia National Laboratories, all in Albuquerque, NM

Transport by groundwater within the Culebra Dolomite, an aquifer above the Waste Isolation Pilot Plant (WIPP), is the most probable mechanism for long-term release of radionuclides to the accessible environment. Radionuclides could be retarded by sorption if the groundwater is exposed to sufficient amounts of fracture-lining clays. In this natural-analog study, distributions of U and trace metals have been examined to constrain the strength of clay/solute interactions within the Culebra.

Factor analysis and mass balance calculations suggest that Mg-rich clays dissolve in Pleistocene-age groundwaters and/or are converted to Na-rich smectites, and that B and Li are taken up from the water by the clays. Rb/Sr ages, however, imply long-term stability of the clays, with resetting occurring >250 Ma ago. Apparently, the solution chemistry reflects gradual equilibration of clays with groundwater, but thus far the bulk of the clays remain structurally intact.

Uranium solid/liquid distribution ratios, calculated from U concentrations of groundwaters and consanguineous fracture-filling clays, range from ~80 to 800 ml/g. The distribution of U in the Culebra can be used as a natural analog for actinide behavior only if the inert and exchangeable components of the U content of the clays can be quantified; these are being determined by selective extraction techniques combined with detailed mineralogical studies.

Sponsored by the U.S. Dept. of Energy under Contract No. DE-AC04-76-DP00789.

P2.3

RADIONUCLIDES IN HYDROTHERMAL SYSTEMS AS INDICATORS OF REPOSITORY CONDITIONS. H.A. Wollenberg and S. Flexser, Lawrence Berkeley Laboratory, 1 Cyclotron Rd., Berkeley CA, 94720.

Hydro-geochemical processes must be understood if the movement of radionuclides away from a breached radioactive waste canister is to be modeled and predicted. Hydrothermal systems in tuffaceous and older sedimentary rocks contain evidence of the interaction of radionuclides in fluids with materials lining fractures, in settings that are somewhat analogous to the candidate repository site at Yucca Mountain, NV. Earlier studies encompassed the occurrences of U and Th in a "fossil" hydrothermal system in tuffaceous rock of the San Juan Mountains volcanic field, CO. More recent and ongoing studies examine active hydrothermal systems at the Long Valley caldera, CA and the Valles caldera, NM. The occurrences of U and Th in fractured and unfractured rhyolitic tuff that was heated to simulate the introduction of radioactive waste are also under

investigation. In these studies high-resolution gamma spectrometry and fission-track radiography are coupled with observations of alteration mineralogy, stable-isotope ratio measurements, and thermal profiles to deduce the evidence of, or propensity for movement of U and Th in response to the thermal regimes.

Observations to date suggest that U is mobile in hydrothermal systems, but that localized reducing environments provided by Fe-rich minerals and/or carbonaceous material concentrate U and thus attenuate its migration.

P2.4

TEMPORAL CHANGES IN URANIUM SERIES ISOTOPE CONCENTRATIONS AS A FUNCTION OF FLOW CONDITIONS IN THE SSSDP WELL, SALTON SEA, CALIFORNIA. Bret W. Leslie, Douglas E. Hammond, and Teh-Lung Ku, University of Southern California, Los Angeles, CA.

Naturally occurring radionuclides produced in the ^{238}U , ^{235}U and ^{232}Th decay series have been measured in 300 °C brines from several flow tests, spanning three years, of the Salton Sea Scientific Drilling Project (SSSDP) well. Activities (pCi/kg) at the initial flow test of the well were ^{222}Rn (960), ^{226}Ra (990), ^{228}Ra (505), ^{224}Ra (455), ^{223}Ra (3), ^{210}Pb (1470), and ^{212}Pb (1015). Alpha recoil, mineral dissolution, and the high solubility of radium and lead in these chloride rich brines (130,000 ppm Cl) all play a role in maintaining these high concentrations. In contrast, isotopes of U and Th are 2-3 orders of magnitude lower in concentration, reflecting the lower solubility of phases containing these isotopes, the rapid sorption of these elements from solution to solid phases, and absence of ligands capable of complexing appreciable amounts of these elements. Models have been developed to quantitatively calculate rates of exchange between brine and rock.

Following the first flow test (12/85), the well was deepened and sampled during a short flow test (3/86). Radium and uranium concentrations were lower by a factor of two during the second flow test, while other elements were similar. During a subsequent 20 day flow test of the well (6/88), well-head pressure was regulated to change total flow rates, and radium concentrations were inversely correlated to the flow rate. The concentrations varied by a factor of four, roughly the variation in total flow rate, while well-head pressure varied only by 25%. Ratios of short-lived daughters to longer-lived parents increased in the both these flow tests. Differences in the characteristics (surface area/volume) of fractures that contribute to flow under different well-head pressures appear to control radium concentrations, while scaling influences the isotope ratios.

P2.5

THE REDISTRIBUTION OF URANIUM SERIES RADIONUCLIDES AT KOONGARRA. Robert Edghill, Australian Nuclear Science and Technology Organisation, Lucas Heights Research Laboratories, PMB 1, MENAI NSW 2234, AUSTRALIA.

The distribution of ^{238}U , ^{234}U , ^{230}Th and ^{226}Ra in rocks from the Koongarra uranium deposit has been examined. A two-phase extraction scheme was used to estimate elements in 'accessible' and 'inaccessible' phases, using α -spectrometry and ICP-MS; bulk analyses of visibly distinct zones were made using PIXE-PIGME, DNAA and XRF.

The secondary U dispersion fan of the Koongarra site is characterised by $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$ activity ratios below unity in the extractable (accessible) phases, and above unity in the non-extractable (inaccessible) phases. The proposed process for this partitioning involves an α -recoil emplacement of daughter nuclei into inaccessible phases. The patterns of the activity ratios suggest zones of different U deposition and leaching rates with the most rapid accumulation at the base of weathering, especially at the extremities of the dispersion fan.

The elemental analyses show U concentrated in zones rich in iron and/or manganese oxides, while areas showing

gleying contain much less uranium. Mossbauer spectrometry suggests these iron oxides are mixtures of goethite and ferrihydrite. The extractable iron was from 5 to 30% of the total iron. Uranium in bulk samples was significantly correlated to Li, Na, K, Ca, Ti, Mn, Ni, Cu, Zn and Rb, at the 1% level of significance, using 28 weathered rock samples. Iron and uranium were not significantly correlative at this level, possibly due to heterogeneous accessibility of U to iron oxides.

P2.6

STUDY ON ROLE OF ^{234}Th IN URANIUM SERIES NUCLIDES MIGRATION. Toshihiko Ohnuki, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan; Shoji Watanabe, Mitsui Knowledge Industry, Tokyo, Japan; and Takashi Murakami, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan.

The role of ^{234}Th , a daughter nuclide of ^{238}U having a half life of 24 days, in migration of uranium series nuclides has been studied by using a mathematical model. In order to understand the mechanisms giving a faster velocity to ^{238}U than to ^{234}U . In the model, we assumed that ^{234}Th was adsorbed at two different adsorption sites, a loosely adsorbed site and a tightly adsorbed site.

The calculations for up to one million years after the discharge gave a positive relationship between activity ratios of $^{234}\text{U}/^{238}\text{U}$ and those of $^{230}\text{Th}/^{238}\text{U}$, when ^{234}Th was assumed to be fixed to a rock, indicating that the migration velocity of ^{238}U was larger than that of ^{234}U . A large rate constant of the ^{234}Th fixation to a rock gave a large difference in mobility between ^{238}U and ^{234}U . Therefore, the ^{234}Th fixation can introduce the apparent delay of the migration velocity of ^{234}U , and different rate constants of the ^{234}Th fixation can control the difference in mobility between ^{238}U and ^{234}U . The calculations assuming the only one loosely adsorbed site for the ^{234}Th adsorption gave the same migration velocity for ^{238}U and ^{234}U .

P2.7

GEOCHEMICAL CONTROLS ON URANIUM MOBILITY IN CRYSTALLINE-ROCK AQUIFERS. Richard B. Werry, US Geological Survey, Golden, CO; Donald Langmuir, Colorado School of Mines, Golden, CO; Cynthia A. Rice, US Geological Survey, Golden, CO; and Paul Briggs, US Geological Survey, Lakewood, CO.

Approximately 140 ground-water wells in crystalline-rock aquifers from PA, NJ, MD, and CO were analyzed for all major cations and anions, as well as uranium, to evaluate the mobility of natural uranium in ground waters. Field-measured pH values ranged from 4.4 to 9.4; estimated Eh values ranged from -0.13 to +0.83 volts. Modelling with PHREEQE revealed that uraninite or coffinite may be near saturation in reducing waters, which limits U concentrations to <1 ppb (detection limit is 0.05 ppb). However, uranium minerals are below saturation in all oxidizing ground waters. Uranyl carbonate complexes are the dominant U species in the oxidizing waters. Autoradioluxographs of rock samples from these areas show that uranium is concentrated along fracture boundaries and ferric oxide grain coatings. Because uranium minerals are undersaturated, uranium mobility probably is limited by adsorption onto ferric oxides and lesser amounts of manganese oxides. Uranium concentrations in the ground waters (<0.05 to 1200 ppb) are comparable to the results of published experimental studies of uranium adsorption onto various ferric oxides in the pH range of the water samples. Consistent with the experimental studies, higher dissolved uranium occurs in alkaline carbonate-rich waters, suggesting that as expected, the formation of uranyl-carbonate complexes inhibits adsorption. Preliminary calculations of uranyl adsorption onto goethite using MINTEQA2 show that in low-carbonate waters (<50 ppm ΣCO_3), the ratio of adsorbed:dissolved U is greater than 10:1. In alkaline waters, adsorption is less, and higher aqueous uranium concentrations are predicted. These results are important to understand the migration of uranium from radioactive waste repositories in oxidizing ground water systems where the uranium minerals rarely attain saturation. In oxidized water-rock systems, the slow escape of uranium from a breached repository may be compensated for by its continual adsorption onto mineral surfaces in the rock.

FLOW PATH MINERALOGY: ITS EFFECT ON RADIONUCLIDE MIGRATION IN THE GEOSPHERE. Kenneth V. Ticknor, D. Choudari Kamineni, and Tjalle T. Vandergraaf, ABCL, Whiteshell Nuclear Research Establishment, Pinawa, MB.

The geological formation surrounding a nuclear fuel waste disposal vault is an important barrier to the migration of radionuclides to the biosphere. Field geological investigations in the Canadian Shield have shown that open, water-bearing fractures form the main paths for potential migration of radionuclides through the geosphere. Any interaction between the radionuclides in solution and the materials in these fractures will retard radionuclide movement towards the biosphere. The minerals lining these open fractures have been subject to varying degrees of alteration over time, and, in general, are quite different from the bulk mineralogy of the intact host rock.

The variability of radionuclide sorption with mineralogy was examined by laboratory sorption studies, using static batch techniques and petrography/autoradiography. The radionuclides studied included fission products, rare earth elements and actinides. It was found that clay alteration minerals such as illite and kaolinite have a high sorption capacity for the radionuclides studied. Other fracture-infilling minerals such as hematite, goethite, chlorite, epidote, gypsum and muscovite show preferential sorption for certain radionuclides. Calcite removes some rare earth and actinide elements from solution, while quartz shows the least affinity for the radionuclides studied.

It is concluded that variations in fracture infilling mineralogy must be considered in the assessment of the suitability of any geological formation as a radioactive wastes disposal site.

P2.9

ASSESSMENT OF RADIONUCLIDE MIGRATION IN NATURAL ANALOGUES BY RADIATION-INDUCED CENTERS IN KAOLINITES

Philippe ILDEFONSE, Jean-Pierre MULLER, Blandine CLOZEL, and Georges CALAS

Laboratoire de Minéralogie-Cristallographie, UA CNRS 09, Universités de Paris 6 et 7, 4 Place Jussieu, 75252 Paris cedex 05, France

U-deposit hosted in hydrothermally altered tuffs in Mexico, together with two weathering systems in tropical areas (latites from Brazil and Cameroon) were studied as natural analogues of radionuclide release and migration in the geosphere (HLNWR and LLNWR). In these alteration systems, kaolinite is the main secondary phyllosilicate associated with more or less iron oxy-hydroxides. With petrological analysis, at all scales from that of field to that of micrometer, we have distinguished distinct kaolinites by their location, parolite morphology, structural order and substitutional iron content. Defect centers are demonstrated in natural kaolinites by means of electron paramagnetic resonance. The irradiation origin of these paramagnetic defect centers (PDC) is evidenced by artificial irradiation (four types have been used: X-rays, γ -rays, He^+ and Pb^{2+} ion beam implantation) of kaolinites representing different formation conditions (hydrothermal, weathering, synthesis). Several types of PDC (designated A, A' and B-centers) are clearly identified and can be separated with respect to their relative stability. One (A-center) is stable over geological periods. Moreover, it is shown that defect centers in kaolinites effectively reflect the cumulative radiation dose.

The potential use of tracing radionuclide migration through PDC in kaolinite has been tested on the three low-temperature alteration systems studied. The kaolinites investigated show a significant concentration of PDC which corresponds to background natural irradiation. The different types of PDC detected may form a record of successive irradiations of kaolinite directly linked to geochemical conditions prevailing during and after kaolinite growth. Because of their different thermal stability, these different centers can be considered as formed at different periods. This makes a unique tool for tracing the dynamics of the transfer of radionuclides and allows the use of kaolinite as a very sensitive *in-situ* dosimeter. Because some of the geological settings chosen for nuclear wastes are located in environments containing kaolinites, PDC dosimetry could be directly useful to a safety assessment of these wastes.

P2.10

DIFFUSION POROSITY AND DIFFUSIVITY OF RADIO NUCLEIDES IN GRANITIC ROCKS. PART I: DIFFUSION INTERFACES AROUND PERMEABLE FRACTURES. Veijo O. Pirhonen, Kai Front and Petteri Pitkänen. Technical Research Centre of Finland, Geotechnical Laboratory, Betonimiehenukuja 1, SF-02150 Espoo, Finland

This paper addresses the problem of evaluation of retardation of radionuclides in fractured rocks. The diffusion interfaces around permeable fractures were examined by means of porosity and chemical profiling technique.

Scanning electron micrographs show that the examined interfaces contain microfractures and tube-like diffusion channels. These are most common within 2 - 4 cm from a fracture surface depending on a type of the fracture. Behind the interface, the porosity and the chemical contents of rock reach the background level, where the diffusivity of radionuclides is in the minimum.

It is inferred that permeable fractures govern the dispersion of radionuclides in crystalline rocks. Diffusion into the rock matrix is restricted to few centimeters from the fracture surface where the microscopic diffusion pathways are most common. In this zone, adsorption on mineral surfaces and diffusion into mineral interspace are the most important retardation factors. Diffusion deeper into the rock matrix is slow and less important compared to dispersion and diffusion in the major fractures and diffusion interfaces.

P2.11

QUANTITATIVE INTERPRETATION OF HALOGEN FOREWATER CONCENTRATION PROFILES IN LAKE SEDIMENTS.

W. Eberhard Falck and Paul J. Hooker, Fluid Processes Research Group, British Geological Survey, Nottingham, U.K.

A natural analogue example of halogen migration through clay-rich sediments is particularly well documented in cores from Loch Lomond, Scotland, where distinct distribution patterns for Cl, Br and I have been observed. The sediments consist of a sequence of marine and freshwater silts and clays which cover glacial deposits. A transgression 6900 y B.P. to 5400 y B.P. resulted in a marine horizon which now acts as a source for the halogens diffusing into the older and younger sediments.

A 1-D conceptual model and FORTRAN code has been developed taking into account variations in the concentration boundary conditions and the accumulation of sediments, i.e. movement of the upper boundary with time. The model has been calibrated using Cl concentration distributions for which boundary conditions can be estimated readily.

The model has been applied to Br and I profiles using reasonable assumptions for boundary and initial conditions. Deviations between measured and calculated profiles were attributed to reactive processes. Release rates from the marine horizon for Br (zero order: $4 \text{ mg m}^{-2} \text{ y}^{-1}$) and I (1st order: $2.5 \cdot 10^{-7} \text{ y}^{-1}$) are deduced. Their sensitivity with respect to system properties, assumptions over boundary and initial conditions and reaction mechanisms is discussed.

P3.1

RESEARCH NEEDS IN CEMENT-BASED WASTE FORMS. E. W. McDaniel, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

This paper, which serves as the session pacesetter, will discuss R&D needs in the use of cement and cement-based materials in waste immobilization. Cement-based materials are the oldest, most commonly used and least understood materials in waste immobilization/solidification. Past approaches, coupled with future needs in a changing environment, are discussed.

P3.2

PHASE RELATIONS AND SOLUBILITY MODELLING IN THE $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{MgO}-\text{SO}_3-\text{H}_2\text{O}$ SYSTEM: FOR APPLICATION TO BLENDED CEMENTS. M. Atkins, F.P. Glasser and A. Kindness, Department of Chemistry, University of Aberdeen, Scotland.

Cement blends are likely to form a large fraction of the materials in the near field of planned radioactive repositories. Being chemically reactive (slightly soluble), their effect on near field chemistry will be very marked. Predictions of nuclide migration in this zone will therefore depend on accurate modelling of cement chemistry.

The modelling approach, described previously, requires the establishment of correct phase relations in the $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{MgO}-\text{SO}_3-\text{H}_2\text{O}$ system (the major cement components). More than 40 compatibility experiments were carried out, to determine these relationships. Purified cement hydrates were shaken continuously in CO_2 -free water, for up to 6 months. The results from these, with data from the literature, enabled us to construct a more complete phase relations scheme than has hitherto been possible.

Interpretational problems were encountered, particularly with the calcium aluminate (sulphate) hydrates in the presence of excess $\text{Ca}(\text{OH})_2$. Special dissolution/precipitation equilibria obtaining at early age allowed 'AF_m' type phases to form, where C_3AH_6 and AF_t were thermodynamically favoured.

P3.3

THE EFFECTS OF CALCITE SOLID SOLUTION FORMATION ON THE TRANSIENT RELEASE OF RADIONUCLIDES FROM CONCRETE BARRIERS. Robert W. Smith and John C. Walton, Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, Idaho 83415-2107

Concrete barriers are an important component of designs for disposal of radioactive waste in the subsurface. Effective design of a concrete vault requires an understanding of chemical processes affecting the performance of concrete barriers. One important chemical process is carbonation; the reaction of concrete with carbon dioxide or carbonate to form calcium carbonate (calcite). This process is significant to radionuclide retardation because the formation of a solid carbonate phase in the concrete provides a sink for ^{14}C and many radionuclides (e.g. ^{90}Sr and ^{60}Co) can coprecipitate with calcite to form solid solutions.

A predictive model has been developed to describe solid solution behavior of cations in calcite. Coupling of this solid solution model with transient mass transport calculations allows evaluation of solid solution effects on the migration of radionuclides through concrete barriers. The coupled model considers carbonation of concrete by ingress of CO_2 and reaction with portlandite, solid solution effects in the precipitated calcite, and mass transport of dissolved radionuclides through the carbonation zone. Because the model focuses on the behavior of weathered, carbonated concrete rather than new intact materials, the resulting calculations may represent the long term chemical performance of concrete better than similar calculations that assume time-independent concrete properties.

P3.4

HIGH-PERFORMANCE CEMENT-BASED MATERIALS FOR NUCLEAR FUEL WASTE DISPOSAL. Pierre-Claude Aitcin, University of Sherbrooke, Quebec, Canada; Maria Jnofrei and Malcolm N. Gray, Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada.

Cement-based materials are being considered as engineered components of seals for underground vaults in which nuclear fuel wastes will be isolated. Formulating these materials to provide for the specific characteristics required by the host geology and to meet the workability requirements of the engineering application depends on a full understanding of the processes and complexities of cement-phase hydration.

Industrial-grade portland cements can be considered to consist of five major unhydrated calcium-alumina-silica phases that interact and react with water to produce a hardened hydrated mass. However, the specifications for industrial-grade cements allow for ranges of impurities within any one cement type. Minor differences in the quantity and nature of these impurities change the microstructure of the cement and, thus, may influence performance in the vault. Moreover, admixtures may be used to change the hydration reactions or otherwise alter engineering properties. Similarly, supplementary cementitious materials may be used to enhance the long-term performance of the hydrated product.

This paper presents a discussion of those aspects of cement hydration that are affected by the specific pozzolans and admixtures that allow for the production of high-performance materials. The effects on microstructure and performance are emphasized. Data are presented to show that, despite natural and man-made variations in cement quality, products that are likely to perform effectively in a vault environment can be developed. Specific reference is made to data on materials developed for grouting experiments in Atomic Energy of Canada Limited's Underground Research Laboratory and in the OECD/NEA Stripa Mine.

P3.5

MODELING GEOCHEMICAL STABILITY OF CEMENT FORMULATIONS FOR USE AS SHAFT LINER AND SEALING COMPONENTS AT YUCCA MOUNTAIN. Mark A. Gardiner, IT Corporation, Albuquerque, NM; Thomas E. Hinkebein, Sandia National Laboratory, Albuquerque, NM; and Jonathan Myers, IT Corporation, Albuquerque, NM.

Interaction of water with a cementitious material will result in dissolution of certain cement phases and changes in the water chemistry. These changes in the water chemistry may further lead to the precipitation of minerals either in the concrete or, at the Yucca Mountain site (YMS), in the surrounding tuff. These changes were examined along five specific water-flow paths which are representative of many possible flow paths for water movement in the shafts and boreholes at the YMS. In each path the geochemical speciation/solubility/reaction path code EQ3NR/EQ6 (EQ3/6) was used to model the interaction of cementitious materials and water and the interactions of tuff phases and altered water. Two initial water compositions (representative of meteoric and J-13 waters), three different temperatures (25° to 76°C), two hydrogeologic scenarios ("open" and "closed" systems) and four different cement formulations were used in the simulations. Only the cementitious material/J-13 water reactions at 25°C are discussed in this paper.

Results of the modeling suggest the following conclusions: (1) solution composition is controlled by equilibrium between the dissolving cement phases (primarily C-S-H, C-A-H and ettringite) and precipitating secondary minerals (dominantly zeolites, secondary C-S-H, gypsum, calcite and minor clay); (2) solution pH generally stabilized at approximately 12; (3) concretes with excess silica behave similarly to concrete with excess portlandite, with respect to the overall water chemistry; (4) a small number of reactions are required to account for the majority of the dissolution/precipitation predicted by EQ3/6; (5) cement reactivity is increased by the presence of portlandite, ettringite and reactive silica which react with other C-S-H and C-A-H phases.

P3.6

THE LONG-TERM PROPERTIES OF CEMENT AND CONCRETES M. Atkins, J. Cowie, F.P. Glasser, A. Kindness and L.P. Moroni, University of Aberdeen, Old Aberdeen, AB9 2UE, Scotland.

It is essential to use mathematical models in order

to predict the long-term behaviour and properties of cements. Appropriate models require an extensive, validated data base for their implementation. The authors' perceptions of the problems associated with the data base and its application are discussed. More data are needed on the hydration kinetics of the components of blended cement systems, of the steady-state conditions on higher-temperature isotherms $>20^{\circ}\text{C}$ and on specific radwaste incorporation mechanisms as well as on the impact of dissolved components, both organic and inorganic, on cement performance. Overall progress towards achieving these goals is assessed.

P3.7

EVALUATION OF DRY-SOLIDS-BLEND MATERIAL SOURCE ON A CEMENTITIOUS WASTE FORM.

T. M. Gilliam, R. D. Spence, S. C. Osborne, and C. L. Francis, Oak Ridge National Laboratory, Oak Ridge, TN.

This paper presents the evaluation of dry-solids-blend material source and the subsequent impact on waste-form performance criteria. The evaluation includes characterization of the individual dry materials, as well as the synergistic effect of the dry materials on grout properties.

P3.8

THE ROLE OF ADVECTION AND DIFFUSION IN THE DEGRADATION OF PORTLAND CEMENT GROUT SEAL MATERIALS IN REPOSITORY ENVIRONMENTS

S. R. Akorn, T. L. Christian-Frear, and M. G. Wallace, RF/SPEC Inc, Albuquerque, NM 87111, USA

The sealing of openings in underground repositories and the assessment of the potential for seal materials to perform acceptably for long periods of time are concerns of decision makers considering the deep disposal of nuclear waste as part of their waste management programs. Two grouting materials, bentonite and portland cement, have been identified by many programs as likely candidate seal materials. An ongoing investigation of both of these materials is being conducted as a part of Phase III of the Stripa Project. To date a number of coordinated laboratory, modeling, and field studies have been completed or are underway. Long-term performance has been recognized as an important issue particularly for cement, since most solid phases in cement are metastable, and therefore it is likely that cement seal performance would degrade with time. In previous investigations by the first author, geochemical and permeability modeling have been used together to estimate how long cement seals would perform acceptably in hydrologic regimes where some flow (advection) might be expected to occur. In this investigation diffusion processes in cementitious grout have been analyzed to enable the evaluation of low- and no-flow hydrologic scenarios in which diffusion is likely to be the dominant mass transport process. Actual granitic terrain groundwater compositions ranging from fresh to saline have been used to calculate cement-groundwater interactions. A literature search has been conducted to determine coefficients of diffusion of water and ions in cements and to determine relationships among factors affecting diffusion constants, such as material properties including porosity, and permeability. Changes in performance with time may have been predicted by conservatively estimating diffusion rates of water and aqueous ions as a function of changes in cement properties due to degradation. But the conditions considered, preliminary results indicate that in low flow conditions where diffusion is dominant, the conversion of low molar volume phases such as portlandite to higher volume calcium silicate hydrate (CSH) phases, clays, and zeolites may serve to increase diffusion times of both water and aqueous ions due to the clogging of pore spaces and increasing tortuosity. Based on this investigation, cement grout performance may be acceptable for very long periods of time (tens of thousands to millions of years), provided that hydrologic gradients are low and cement and groundwater chemistries promote moderate grout dissolution and precipitation of high molar volume secondary phases.

P3.9

KEY PARAMETERS OF GLASS DISSOLUTION IN INTEGRATED SYSTEMS. Etienne Y. Vernaz and Nicole Godon, CEA, CEN VALRHU, BP 171, 30205 Bagnols-sur-Cèze Cedex, France

Numerous leaching studies have been conducted during the last ten years to identify the basic mechanisms of glass corrosion in order to develop long-term behavior models. Considering the multiple parameters affecting a geological repository, however, integrated experiments simulating all the actual disposal conditions are necessary to check that all the key parameters are taken into account, to detect possible synergy effects and to qualify the model under realistic conditions.

Integral test mockups referred to as "TAV" experiments have been used in France to simulate several storage scenarios at 90°C under a pressure of 10 MPa. Simulated geological water is allowed to reach equilibrium with the test medium in a conditioning vessel before leaching the glass with a pseudo flow rate corresponding to samples of

a few cm^3 taken at 2-month intervals. The principal findings have been the following:

- Glass alteration is similar in French granite or salt, but much greater in clay.
- The backfilling material has a significant effect. Most clays constitute silica sinks and maintain a high long-term alteration rate. However, some highly siliceous bentonites do not accelerate glass alteration.
- In a granite medium at 90°C , the canister materials (NS 24, Hastelloy or AZS ceramic) are only slightly altered and have a minor effect on glass corrosion.
- The effects of fracturation of the glass block depend on the environmental conditions. In a granite medium where saturation conditions are quickly reached, the dissolved glass quantity increases by only a factor of 1.4 when the exchange surface area is multiplied by 10.
- Radioactive experiments with doped glass specimens have shown that a radiolysis does not modify the bulk glass dissolution rate, but that environmental materials do affect the actinide retention factor in the surface gel layer.
- Finally, an experiment has been in progress for over 7 years in a granite medium. After 3 years the corrosion rate dropped to about $2 \times 10^{-3} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and depends only on the flow rate imposed by the sampling intervals.

P3.10

THE EFFECT OF LEACHING ON THE PORE STRUCTURE OF CEMENT-BASED GROUTS FOR USE IN A NUCLEAR FUEL WASTE DISPOSAL VAULT. M. Onofrei and M.N. Gray, AECL, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, ROE 1LO, Canada; D. Breton and G. Ballivy Sherbrooke University, Sherbrooke, Quebec, J1K 2R1, Canada.

Research on the longevity of cement-based grout materials for sealing a deep geological disposal vault is an important aspect of both the Canadian and other nuclear fuel waste management programs. These studies include assessments on the chemical durability of cement grouts and the effects of leaching and phase transformation on the long-term hydraulic and diffusion characteristics of grouts.

This paper presents the results of laboratory studies carried out to assess the effects of leaching of cement phases on the pore structure of hardened grouts. Measurements of mercury intrusion, and scanning electron microscopy with energy dispersive x-ray analysis, have been used to investigate the changes in pore structure of the reference grout (90% Type 50 cement, 10% silica fume, water-to-cement (w/c) ratio between 0.4 and 0.7) as a function of leaching time and groundwater composition.

Preliminary analyses show that the pore radius, the volume of pores and the effective porosity (capillary porosity) of the grout decreases with leaching time. The decrease in the effective porosity was found to be more pronounced in the reference grout with low w/c ratio than in the same grout with high w/c ratio. The decrease in the porosity was attributed to the changes in the volume of solids caused by continuous hydration, precipitation and associated reactions.

It is commonly assumed in the durability models used to predict the longevity of grout that grouts degrade through pore water exchange and associated leaching. The observed changes in the pore structure strongly indicate that these assumptions may not be appropriate.

P4.1

BASIC RESEARCH FOR ASSESSMENT OF GEOLOGIC NUCLEAR WASTE REPOSITORIES: WHAT SOLUBILITY AND SPECIATION STUDIES OF TRANSURANIC ELEMENTS CAN TELL US. Hans-Nikung, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Mail Stop 70A-1174, Berkeley, CA 94720.

To understand the migration behavior of radioactive elements from geologic repositories to the accessible environment, fundamental knowledge is required of the underlying basic principles. The migration behavior of transuranic elements depends strongly on their chemical behavior (chemistry, solubility, sorption-desorption behavior and complexation) and on the oxidation state, the degree of complexation, and the hydrolytic behavior. Solubility provides information on the chemical form (soluble, colloidal, pseudocolloidal, etc.) and on the concentrations of the radionuclide.

There is a great need for experimental data on the solubility and speciation of transuranic elements under a wide range of varying conditions for

example, pH, the temperature and composition of groundwaters. Additionally, the influence of alpha radiation and the radiolysis of the inorganic compounds must be studied.

Generic solubility and speciation data can be adapted to the conditions of a specific site. They can be used to validate geochemical modules of predictive multicomponent transport models for performance assessment.

This paper will discuss the state of solubility and speciation studies of radionuclide elements and areas of future research.

This work is supported by the Yucca Mountain Project Office as part of the Civilian Radioactive Waste Management Program. This project is managed by the U.S. Department of Energy, Nevada Operations Office, Lawrence Berkeley Laboratory is operated by the University of California for the U.S. Department of Energy under contract DE-AC03-76SF00098.

P4.2

MASS RELATIONSHIPS AND TRANSPORT POTENTIAL OF VOLATILE NUCLIDE SPECIES IN SUBSURFACE ENVIRONMENT. Abraham Lerman, Department of Geological Sciences, Northwestern University, Evanston, IL.

Among the metal and heavier nuclides in a uranium-oxide spent fuel, the following may form volatile species: ^{79}Se , ^{93}Zr , ^{99}Tc , ^{126}Sn , ^{129}I , and ^{135}Cs . These six nuclides collectively represent a mole fraction of about 9×10^{-3} of the total nuclide mass in a model fuel at 1,000 years after disposal. Depending on the conditions, nuclide metal-oxides, metal-selenides and iodides, or elemental states may occur either as pure solids or as minor components of solid solutions with the matrix phases. For a limiting case of an ideal solid solution, the mole fractions of the six individual nuclides (or of their compounds), 10^{-5} to 10^{-3} , indicate a measure of possible reduction of the partial pressures relative to the pure phases.

For a number of oxide, iodide, selenide, and elemental species of the six radionuclides, taken as their stable chemical analogs, relatively high vapor pressures are indicated for pure solid-gas equilibrium systems: 10^0 to 10^4 Pa (10^{-5} to 10^{-1} atm), at 200° - 100°C and lower. Among the metal iodides and selenides, higher vapor pressures are associated with the higher metal oxidation state +4, as in the following series:



In a limiting case of the entire spent-fuel inventory of I and Se taken up in iodides and selenides of Zr, Sn and Cs, large fractions of the metal nuclide inventories would occur in other chemical forms: for ^{135}Cs , about 68% left over; for ^{93}Zr , 97%; and for ^{126}Sn , $73 \pm 8\%$. The p-T relationships for the various volatile nuclide species make it possible to assess their upper limit concentrations in a dry rock pore space at different temperatures, and to estimate their partitioning between the gaseous and aqueous phases at different levels of water saturation.

P4.3

ACTINIDE SPECIATION BY PHOTOTHERMAL SPECTROSCOPIC INSTRUMENTATION DEVELOPMENT. John M. Berg, C. Drew Tait, David E. Morris, and William H. Woodruff; Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 USA

An understanding actinide speciation in aqueous solution is necessary for the evaluation of the suitability of nuclear waste storage sites and for the development of strategies for waste site remediation. Photoacoustic spectroscopy using pulsed laser excitation is being developed by a number of research groups as one of the most promising methods for studying speciation of actinides in solution at environmentally relevant concentrations. We will present details of a number of hardware and software techniques which we have implemented which we believe improve the sensitivity

limits of the method. We will illustrate the capabilities of our current system by presenting spectra of Pu(IV) at nanomolar concentrations, as well as discussing other ongoing work.

P4.4

REMOTE MEASUREMENTS OF ACTINIDE SPECIES USING AN OPTICAL FIBER AND PHOTOACOUSTIC SPECTROSCOPY

P.L. Russo, Applied Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, P. Robinson and R.J. Silva, Nuclear Chemistry Division, Lawrence Livermore National Laboratory, Livermore, California 94550.

The measurement of actinide species at sub-micromolar concentrations in aqueous solutions has become increasingly important for the determination of thermodynamic properties, for research in high-level nuclear waste management, and for environmental monitoring and characterization. The oxidation states of actinide species in solution can be determined directly from an optical absorption spectrum. Photoacoustic spectroscopy (PAS) is a sensitive optical absorption technique capable of determining oxidation states and studying complexation at high sensitivity levels. We developed a photoacoustic spectrometer for remote measurements of rare earth and actinide species using an optical fiber to transmit the excitation laser light to a sample solution in a glove box located in a separate laboratory, 85 meters from the laser and detection electronics. The system is ideally suited for conducting actinide research on highly radioactive species in a protected enclosure without requiring sampling and the risk of contaminating the laser laboratory. The sensitivity of the system was found to be comparable to that obtained from samples placed directly at the end of the fiber (without the fiber). This optical fiber system represents a prototype remote sensor for field applications in which photoacoustic measurements could be performed in a ground water environment.

P4.5 ABSTRACT WITHDRAWN

P4.6

THE APPLICATION OF POSITRON EMISSION TOMOGRAPHY TO THE STUDY OF MASS TRANSFER IN FRACTURED ROCKS. D Gilling¹, N.I. Jefferies¹, M.R. Hawkesworth² and D Parker². ¹AEA Decommissioning and Radwaste, Harwell Laboratory, Oxon, OX11 0RA, ²University of Birmingham, Edgbaston, Birmingham, UK.

Water flow in hard rocks takes place dominantly in fractures. In order to predict the transport of dissolved radioelements through a fractured rock it is necessary to determine the geometry of the fracture network and the hydraulic properties of individual fractures.

Several laboratory techniques, such as tracer migration tests and fracture impression methods, have been used previously to study mass transfer in individual fractures. This paper describes an alternative technique for studying mass transfer in a single fracture. Positron emission tomography (PET) offers the potential for visualising quantitatively the migration of dissolved tracers. The position in space of a positron-emitting nuclide can be determined by the simultaneous detection of the two collinear positron-electron annihilation gamma rays.

Two conservative tracers have been used in these experiments: ^{18}F and ^{22}Na . Preliminary experiments involved the flow of water through simulated fractures. Three experiments have been performed, and demonstrate that PET is well suited to this application. Mathematical modelling has been undertaken in conjunction with these experiments.

P4.7

MIGRATION OF RADIONUCLIDES IN GEOLOGIC MEDIA: FUNDAMENTAL RESEARCH NEEDS. D. T. Reed, Argonne National Laboratory, Argonne, IL 60439; F. J. Wobber, Office of Health and Environmental Research, U.S. Department of Energy, Washington, DC 20555; and J. M. Zachara, Pacific Northwest Laboratory, Richland, WA 99352.

Fundamental research needs relating to the understanding of radionuclide migration will be presented. The focus will be on long-term research needs that correspond to existing and anticipated waste management problems within the DOE. Aspects of this research currently being addressed by the Surface Science Program will be summarized.

This work is supported by the Office of Health and Environmental Research, Subsurface Science Program, under DOE contract W-31-109-ENG-38.

P4.8

THE EFFECT OF EXPERIMENTAL CONDITIONS ON THE MODIFIED LANGMUIR ISOTHERM ADSORPTION PARAMETERS. Wilfred L. Polzer, Los Alamos National Laboratory, Los Alamos, NM; M. Gopala Rao, Howard University, Washington, DC; and Hector R. Fuentes, University of Texas at El Paso, El Paso, TX.

The adsorption of solutes on geologic media is usually described in term of isotherms. The isotherm parameters are coupled to transport codes to account for the retardation of reactive solutes under flow conditions. Isotherms, though theoretically based, are considered empirical and thus their parameters depend on the conditions for which they were determined. Therefore, the use of the isotherm as a predictive tool is predicated on the basis that conditions in which the model will be applied are similar to those in which their parameters were determined. In this study relationships between Modified Langmuir isotherm parameters and experimental parameters (conditions) were derived through thermodynamic considerations for binary ion exchange adsorption. Based on these relationships, an unique set of isotherm parameters can be defined by a minimum and necessary set of experimental conditions. These conditions are the solid-liquid ratio, the initial concentration of the target solute in the solid phase, and the initial concentration of the competing solute in the liquid phase. The effect of these initial conditions have been qualitatively verified from literature data. The results of this study indicate that, in principle, unique sets of isotherm parameters can be predicted from a known set of experimentally determined parameters for conditions not experimentally evaluated. Therefore, the above derived relationships between isotherm parameters and experimental parameters provide a means to reduce significantly the effort needed to model the movement of reactive solutes in the environment.

P4.9

NONIDEALITY EFFECTS ON ION EXCHANGE BEHAVIOR OF THE ZEOLITE MINERAL CLINOPTILOLITE. Roberto T. Pabalan, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX 78228-0510.

The presence of laterally-extensive zones of zeolitized tuff

underlying the proposed high-level nuclear waste repository at Yucca Mt., Nevada, has focused attention on the potential role of zeolite minerals, particularly clinoptilolite, in sorbing radionuclides and thereby retarding their migration. Published geochemical studies on zeolite minerals at Yucca Mt. indicate lateral and vertical variations in zeolite compositions. Ion exchange between zeolites and aqueous solutions depends on factors including aqueous solution ionic strength and compositions of both the aqueous and zeolite phases. Therefore, variations in zeolite compositions observed at Yucca Mt., as well as natural or repository-induced changes in groundwater chemistry, may result in variations in the effectiveness of the zeolite minerals as retardation agents.

Experiments conducted to study ion exchange between clinoptilolite and aqueous solutions of alkali and alkaline earth cations can provide a quantitative basis for evaluating the role of zeolites in the retardation of radionuclides in the Yucca Mt. system. Experimental data indicate that the systems exhibit nonideal behavior, particularly for reactions involving mixed valence exchanges. The data can be interpreted using excess Gibbs energy models for the aqueous solution and zeolite phases to account for nonideality in the system. These models allow reliable predictions of ion exchange behavior at other ionic strengths and relative concentrations, and provide a foundation for the interpretation of ion exchange equilibria in multicomponent systems.

P4.10

EFFECTS OF MINERALOGY ON SORPTION OF Sr AND Cs ONTO CALICO HILLS TUFF, R. E. Meyer, W. D. Arnold, F. I. Case, G. D. O'Kelley, and J. F. Land, Oak Ridge National Laboratory, Oak Ridge, TN.

Sorption and desorption measurements were made of strontium and cesium onto clinoptilolite and Calico Hills tuff. The object was to see whether there was a correlation between sorption of strontium and cesium onto Calico Hills Tuff and the sorption of strontium and cesium onto clinoptilolite based on the content of clinoptilolite in the Calico Hills Tuff. If sorption onto Calico Hills Tuff is solely due to the presence of clinoptilolite, then the ratios of the sorption ratios on tuff to those on clinoptilolite at similar conditions should be the weight fraction of the clinoptilolite on the tuff. Since the tuff contained about 50% clinoptilolite, the ratios would be expected to be about 0.5 if sorption was due solely to clinoptilolite. The experimental evidence showed that the ratios were generally near 0.5 for both cesium and strontium sorption and that ion-exchange processes were operative for both the clinoptilolite and the tuff. However, the ratios differed to a small extent for the different conditions, and there were indications that other sorption processes were involved.

P4.11

ESTIMATION OF THE MIGRATION PARAMETERS FOR THE BOOM CLAY FORMATION BY PERCOLATION EXPERIMENTS ON UNDISTURBED CLAY CORES. M. J. Puy, M. Monsecour, A. Fonteyne, SCK/CEN Mol (Belgium); and H. Yoshida, PNC Tokyo (Japan)

The safety assessment of the repository for high level radioactive waste in the Boom clay formation requires reliable data for the migration parameters. The results of the percolation experiments on undisturbed clay cores drilled from the formation are reported.

The undisturbed clay cores are drilled perpendicular and parallel to the stratification of the formation to study the isotropic of the formation. To represent as close as

possible the real situation in-situ interstitial clay pore water is used as percolating liquid.

Parameter values for bromine, iodine and tritiated water are presented.

Darcy velocity and effective stress are used as variables. Anisotropic of the formation is demonstrated for the hydraulic conductivity, but trivial for the dispersion parameters.

A general relation between the apparent dispersion constant, the diffusion accessible porosity and the Darcy velocity is given.

The experimental set-up and the interpretation method is briefly described.

P4.12

MIGRATION OF RADIONUCLIDES IN FRACTURE COLUMNS. Pirkko Holttä, Maritta Hakanen, University of Helsinki, Department of Radiochemistry, Helsinki, Finland; and Aimo Hautajarvi, Technical Research Centre of Finland, Nuclear Engineering Laboratory, Helsinki, Finland.

Radionuclides transported with ground water flowing through the fractures may be delayed by interactions with the fracture surfaces. Migration of radionuclides in natural fractures was studied under well defined laboratory conditions using tonalite drill core columns having fracture running parallel to the axis.

Synthetic ground water was pumped through the fracture by a peristaltic pump and tracers were injected as a pulse. The effluent was continuously fed to the fraction collector for the determination of break through concentration of the tracer.

The hydrodynamic characterization of the columns was performed using tritiated water, perchlorate and chloride ions as non-sorbing tracers. Strontium and neptunium were used to study retardation of radionuclides on fracture surfaces.

The experimental set-up is described and break through curves of non-sorbing tracers, strontium and neptunium are presented. Results were interpreted by means of model calculations.

P4.13 ABSTRACT WITHDRAWN

P4.14

THE INFLUENCE OF TRACE ELEMENTS IN CONSOLIDATED SEDIMENTARY ROCKS ON THE MIGRATION BEHAVIOUR OF RADIONUCLIDES. W. Bode, GSF - Institut für Tief Lagerung, Braunschweig, Fed. Rep. of Germany; and B. Bode, Lahstedt, Fed. Rep. of Germany

The migration velocity of dissolved radionuclides through consolidated sedimentary rocks depends upon the characteristics of the ground water and also substantially upon the retention properties of the rock, taking the different ions into consideration. Besides the petrophysical properties, such as permeability, porosity, degree of separation and specific surface, the chemical and mineralogical composition of the rocks influences the retention or retardation of the dissolved radionuclides in the ground water flow. Several reports have been issued on the topic of the influence of the chemical main components. This factor was observed when preparing the de-

scribed samples. The effects of trace amounts of 15 elements in the rock on their R_s , R_d resp. K_D values of the dissolved radionuclides of the elements C (as carbonates), namely, Se, Sr, Tc, I, Cs, Pb, Ra, Ac, Pa, U, Np, Pu, Am, and Cm were investigated and discussed. For this purpose the Fe, Mn, Sr, Ba, Pb, Cu, Zn, Ni, Cr, V, Cd, B, P and F contents as well as the organic carbon in the rocks were compared to the sorption/desorption coefficients of the above mentioned 15 radionuclides and listed in x-y diagrammes (a total of 225).

While the height of the amounts of most trace elements has no or only a slight influence on the retention properties of most radionuclides, a distinct correlation between the height of the amount of trace elements and the height of the distribution coefficients was found for some radionuclides.

P5.1

EFFECTS OF HEAT TREATMENT ON THE MICROSTRUCTURE OF A FULLY SIMULATED NUCLEAR WASTE GLASS. Terese V. Palmiter, I. Joseph, and L. David Pye, Institute of Glass Science and Engineering, NYS College of Ceramics at Alfred University, Alfred, NY.

Samples of a fully simulated nuclear waste glass, both oxidized and reduced, were heat treated for three hours at 600, 700, 800 and 900°C. Microstructural features in untreated as well as heat-treated glasses were studied using transmission electron microscopy. Elemental analysis by energy dispersive spectroscopy (EDS) was used to identify components of crystals observed.

Long-term heat treatments of 45 days at 10°C above T_g (430-460 °C) were conducted. Transmission electron microscopy revealed microphase separation in these glasses. EDS was used to further study these phases.

P5.2

EFFECTS OF HIPING TIME, TEMPERATURE, AND PRESSURE ON ICPP EXPERIMENTAL WASTE FORM PROPERTIES. B. A. STAPLES, Westinghouse Idaho Nuclear Company, Idaho Falls, ID 83403, D. V. MILEY, EG&G Idaho Company, Idaho Falls, ID 83403

At the Idaho Chemical Processing Plant glass-ceramic waste forms are being developed for the immobilization of calcined high-level radioactive waste. In this action simulated calcine and glass-forming additives are hot isostatically pressed (HIPed) under various processing conditions to form the glass-ceramics.

A full 2^3 factorial design with centerpoint experiment was performed to investigate the effects of HIPing time, temperature, and pressure on the durability of the glass-ceramic as measured by the 14-day MCC-1 static leach test. Effects were also determined on phase composition as measured by solid state analytical techniques and on density. The results of the experiment indicate that a significant time-temperature interaction influences the leaching properties and phase composition of the glass-ceramics. Based on the results of this experiment it is recommended that glass-ceramics be prepared at 1050°C and 12000 psi for at least four hours. It is also recommended that response surface techniques be used to analyze the dependence of glass-ceramic leachability on HIPing time and temperature.

P5.3

LEACH RATE EXCURSIONS IN BOROSILICATE GLASSES: EFFECTS OF GLASS AND LEACHANT COMPOSITION. Aaron Barkatt, S. A. Olszowka, W. Sousanpour, M. A. Adel-Hadadi, R. Adiga, Al. Barkatt, G. S. Marbury, and S. Li, The Catholic University of America, Washington, D.C.

Transient increases in leach rate have been observed in the cases of certain borosilicate glasses upon exposure to aqueous media. Increases of this type have not been detected in glasses with a lower alkali and higher Al content, or in a neutral bicarbonate medium.

P5.4

R777 GLASS INITIAL DISSOLUTION RATE MEASUREMENTS USING A HIGH TEMPERATURE SOXHLET DEVICE. F. Delage, J.L. Dussossoy, SDHA/SEMC, CEN-Vairinó, BP171, 30205 Bagnols-sur-Cèze Cedex, France.

The corrosion of glasses in aqueous media was described by the general rate equation proposed by Grambow, in its simplest form, this equation may be written as: $V = V_0(1 - a(H_4SiO_4)/a^*(H_4SiO_4))$.

The purpose of this investigation was to measure the initial dissolution rate (V_0) of R777 nuclear glass between 80 and 250°C and to deduce activation energies of reaction.

Leaching solutions were maintained far from equilibrium by using a dynamic leaching apparatus: the High Temperature Soxhlet device (HTS).

The corrosion rates were defined by weight loss measurements and by silicon, boron, sodium and lithium analysis in the leachate. Under all temperature conditions, the dissolution rates were linear with time. The initial dissolution kinetics, calculated from weight loss (before and after scraping off the surface layer) and from silicon, boron, sodium and lithium release, follows an Arrhenius-type law. Activation energies range from 55 to 62 kJ/mol according to the element. This slight discrepancy is attributed to a more pronounced retention factor of certain elements in alteration layer with increasing temperature. The mean activation energy of reaction (about 57 kJ/mol) is typical of a surface-controlled reaction. This energy is unique on the studied temperature range.

P5.5

APPLICATION OF THE GRAMBOW MODEL TO LEACH TEST DATA ON WEST VALLEY GLASSES. X. Feng, I. S. Muller, Hsing-yie Ting, I. L. Pegg, and P. B. Macedo, The Vitreous State Laboratory, The Catholic University of America, Washington, D. C. 20064.

Chemical durability data determined from PCT (modified MCC3) tests on a large number of glass compositions around the present West Valley reference glass show several interesting features. An essential basis for developing materials behavior predictions over repository-relevant time scales is mechanistic modeling which must be capable of explaining the salient features of the glass dissolution process. In this paper we present results on the extent to which the Grambow GLASSOL code is able to represent the leach behavior exhibited by our data on West Valley glasses and, in particular, the sharp transition in durability that we observe with very small changes in glass composition. Analysis of leachate compositions using the PHREEQE geochemical code has shown that for the glasses in the more durable region a silica phase with a log K value approaching that of quartz is consistently close to saturation whereas in the less durable glass region the same phase is consistently under saturated. Furthermore, the set of minerals close to saturation was significantly different for each of the two regions. The GLASSOL results for the more durable glasses are in reasonable agreement with the data when experimentally derived values for the input parameters are used. The forward rate is obtained from short-time, low S/V data and the log K_{102} value and residual affinity are obtained from long-term data at high S/V (10,000/m).

P5.6

EFFECTS OF COMPOSITION VARIATIONS ON MICROSTRUCTURE AND CHEMICAL DURABILITY OF WEST VALLEY REFERENCE GLASS. A. C. Rucchele, X. Feng, H. Gu, I. S. Muller and I. L. Pegg, The Catholic University of America, Washington, D. C.

Glasses suitable for high-level nuclear waste vitrification must meet a number of requirements including processability, durability, and phase stability. Our new data indicate that the West Valley reference 5 composition meets these requirements: it is phase stable over the expected range of melter temperatures and residence times and only minimal (<1 vol%) secondary phase formation, consisting predominantly of iron-group spinels, is expected in the canister cooled glass. Leach tests have shown little or no effect on durability of spinel levels in excess of 2 vol%. However, natural process variations during production will produce a range of glass compositions around the nominal composition. In this paper we report on the effects of composition changes around reference 5 on the phase stability upon heat treatment and the consequent effects on chemical durability. Since variations in the waste-stream levels of most major components can be accommodated by adjusting the quantities of the glass-forming additives we focus here on a group of components for which this is generally not the case: Ca, Cr, Mn, Ni, Th, U, S, P, and Fe. While many of these components are present at below 1 wt% they could have potentially significant indirect effects on product durability due to enhancement of secondary phase formation.

P5.7 ABSTRACT WITHDRAWN

P5.8

MEASUREMENTS OF RADON EMISSIONS FROM NUCLEAR WASTE. G. Espinosa, H. Hu and V. M. Castaño, Instituto de Física UNAM, Apartado Postal 20-364, México, D.F. 01000, México.

Radon gas is a product of the nuclear decay of Plutonium. Therefore, it is important to realize that, besides the obvious protection of the solid nuclear waste, it is necessary to prevent leaking of radioactive gases such as Radon, which could permeate through several materials normally used in nuclear waste management.

In this work we present a study of the diffusion of Radon through concrete with different compositions and also various commercially available steels.

The results allow us to determine the best conditions for having a safe handling and managements of nuclear waste that produces Radon.

P5.9

CHARACTERISTICS OF MIGRATION OF ^{85}Sr AND ^{137}Cs IN ALKALINE SOLUTION THROUGH SANDY SOIL. Toshihiko OHNUKI, Department of Environmental Safety Research, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan.

Characteristics of migration of ^{85}Sr and ^{137}Cs in the solution of pH 12 through coastal sandy soil have been investigated by both column and batch tests. Desorption behaviors of the ^{85}Sr and ^{137}Cs by the sandy soil in both column and batch tests were examined by sequential extraction techniques, in order to study difference in the adsorption behavior of the ^{85}Sr and ^{137}Cs under dynamic (column) and static (batch) conditions. Contributions of

the constituents of the sandy soil to the adsorption of the ^{85}Sr and ^{137}Cs were tested in batch tests.

Approximately 85 percent of the ^{137}Cs were unexchangeably adsorbed by the sandy soil in the column test, and the portion of the ^{137}Cs adsorbed unexchangeably adsorbed by the sandy soil in the column test was greater than that in the batch test. Most of the ^{85}Sr were adsorbed exchangeably with the sandy soil under both static and dynamic conditions. The desorption behaviors of the ^{137}Cs adsorbed by kaolinite and by sericite resembled to that by the sandy soil. Most of the ^{85}Sr were adsorbed exchangeably by kaolinite, chlorite, sericite and MnO_2 being similar to desorption behavior of ^{85}Sr by the sandy soil.

Therefore, major constituents of the sandy soil contributing adsorption of ^{137}Cs would be kaolinite and sericite, and those contributing adsorption of ^{85}Sr would be kaolinite, chlorite, sericite and manganese dioxide.

PS.10

STUDIES OF THE EFFECTS OF DEGRADATION PRODUCTS ON THE SORPTION OF TIN AND RADIUM. J. A. Berry, G. M. N. Baston, K. A. Bond, C. M. Linklater and N. J. Pilkington. AEA Decommissioning and Radwaste, Harwell Laboratory, Oxfordshire, OX11 0RA, UK

The effects on sorption by geological media caused by the presence of materials derived from a cementitious repository have been studied. This work includes an investigation of the influence of cellulosic degradation products on the sorption of tin and radium on London clay and Caithness flagstones and also considers the sorptive behaviour of radium as a function of calcium concentration.

In the study concerning cellulosic degradation products, experimental conditions were chosen to simulate those expected close to a cementitious repository (pH 11) and at the edge of the zone of migration of the calcium plume (pH 8). Work was carried out (i) under baseline conditions in the absence of organic materials (ii) with gluconate, acting as a well-characterized simulant (iii) with authentic cellulosic degradation products.

These experimental studies were complemented by thermodynamic modelling work.

This investigation has shown that the sorption of tin can be affected by the presence of cellulosic degradation products whereas the sorption of radium is unaffected. The sorptive behaviour of radium is however strongly influenced by the calcium concentration.

The present work provides further evidence of the need to take account of such factors in safety assessment modelling.

PS.11

DEVELOPMENT OF HIGH-TEMPERATURE UV-VIS-NIR SPECTROSCOPY FOR THE MEASUREMENT OF FREE ENERGIES OF COMPLEXATION AT ELEVATED TEMPERATURES. P. Robough, P. Grant, R. Torres, and R. Silva, Nuclear Chemistry Division, Livermore National Lab, Livermore, CA 94550.

We have developed instrumentation capable of measuring optical absorption spectra over a wavelength range of 200-1200 nm and a temperature range of 20-100°C. A solution contained in a quartz cell is controlled at elevated temperatures and pressures in a dry-block heater assembled in a glovebox. Spectral interrogation of the sample is performed remotely with a Guided Wave Model 200 fiber-optic spectrometer. Changes in metal-ligand coordination induce small wavelength and intensity shifts in absorption spectra, and such data allow the computation

of stability constants (free energies of complexation) via regression techniques.

High-temperature measurements of radionuclide stability constants are of importance in a speciation database for waste disposal in an underground repository. Thermodynamic studies at five temperatures between 20-100°C have been completed using the lanthanide Pr as an actinide analog. The ligands chosen for initial study were acetate and diglycolate. At 25°, the Pr-ac system exhibits two metal complexes over a log β range of -1.5-3; the Pr-diglycolate system comprises three complexes with log β_1 from 5-12.

The results of these experiments will be presented, and trends in the temperature variation of thermodynamic parameters will be discussed. Although most of the present data are novel, some comparisons with prior literature values are possible. Agreement in these instances is quite good and serves as a validation of the current technique.

PS.12

APPLICATION OF SPHAGNUM PEAT FOR IMMOBILIZING RADIOACTIVE AND HAZARDOUS CONTAMINANTS IN THE SUBSURFACE

E. A. Longmuir, D. G. Brinkman, and B. Thomson, University of New Mexico, Albuquerque, NM; E. G. Eiler, Los Alamos National Laboratories, Los Alamos, NM

Lanthium mill tailings contain anomalously high concentrations of radionuclides, heavy metals, non-metals, and organic compounds used during solvent extraction of uranium ore. Leachate generated from uranium mill tailings has contaminated groundwater in the United States and Canada. This paper describes the results of an experimental study, coupled with thermodynamic modeling to evaluate the effectiveness of sphagnum peat in removing dissolved concentrations of As, Mo, NO_3^- , Se, and U within sulfuric acid-leach uranium tailings, near Gunnison, Colorado, U.S.A. These contaminants are stable as oxyanions under acidic and relatively oxidizing conditions within the tailings pore fluid. Favorable geochemical properties of sphagnum peat, which make this carbonaceous material suitable as a permeable barrier, include high cation-exchange capacity, abundance of acidic functional groups, and moderately high surface area. In batch experiments, amounts of contaminant removal were typically above 95 percent, resulting in contaminant decreases of four orders of magnitude. Much of this removal is attributable to ion exchange and complexation primarily with carboxylic functional groups under acidic (pH 3.5) and relatively oxidizing conditions. Calculated distribution coefficients of five weight percent sphagnum peat, for carbohydrates, alcohol, pyridine, and toluene are 200, 8, 37, and 11 mg, respectively. These calculations, along with other experimental data, suggest that sphagnum peat and other types of solid organic matter are strong adsorbents for most hydrophobic organic contaminants. Further sorption and sorption-desorption experiments are being conducted to evaluate the effectiveness of sphagnum peat to remove mixed organometal complexes of U, Pu, and Am from solution.

PS.13

DIFFUSION MEASUREMENTS OF RADIONUCLIDES IN SITE-SPECIFIC SEDIMENT/GROUNDWATER-SYSTEMS. Hans Meier, Erwin Zimmerhackl, Günter Zeitler, and Plus Nenge, Staatl. Forschungsinstitut für Geochemie/Außenstelle des Geologischen Landesamtes, Bamberg, FRG.

For understanding and predicting movements of radionuclides released from the planned underground radioactive repository at Gorleben, Federal Republic of Germany, in addition to batch and column measurements diffusion experiments have been carried out.

In the paper results of systematic measurements on the diffusion of radionuclides (U-235, Ra-226, Pb-210, Ni-63) through sandy, marlaceous and clayey sediment rocks from strata overlying the Sorleben salt dome are presented. The rate of diffusion was measured in a cell consisting of a sediment disc between two chambers filled with groundwater one of which contained the diffusing nuclide.

It is shown that, among other parameters, diffusion coefficients could be derived in the region of steady-state diffusion. Additionally, with the help of a special transport model measurements yielded distribution coefficients which agree with sorption/desorption ratios obtained from batch tests. Moreover, it is demonstrated that the diffusion behaviour of nuclides such as Pb and Ni can be enhanced enormously in sediment rocks by complex forming agents.

P5.14

IMMOBILIZATION OF RADIOACTIVE STRONTIUM IN CONTAMINATED SOILS BY PHOSPHATE TREATMENT. K. H. Kim, The University of Tennessee, Knoxville, and S. Y. Lee, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Radioactive strontium (^{90}Sr) has been recognized as one of the most abundant radionuclides in the contaminated areas on the Oak Ridge Reservation (ORR) and at other U.S. Department of Energy facilities. Strontium-90 has a relatively short half-life but has relatively high mobility under acidic soil conditions. Most of the soils on the ORR have weak acidic reactivity. Such soil conditions resulted in the leakage of ^{90}Sr near waste disposal areas. An in situ treatment of phosphate and metal (calcium, aluminum, or iron) solutions was selected for a feasibility study as a potential technology for ^{90}Sr immobilization.

The results showed that more than 99% of very dilute ^{90}Sr ($<10^{-4} \text{ M}$) was coprecipitated with metal phosphate compounds. The optimum concentration of phosphate and metal was 0.1 M with a 1:1 molar ratio, and the coprecipitation was favored at a pH between 6 and 7 in batch experiments with and without soil. Column experiments revealed a noticeable reduction of ^{90}Sr leachability in metal- and phosphate-treated samples. The reduction was more noticeable when calcium was introduced first than when phosphate was introduced first in the calcium-phosphate system. The opposite was observed for other metal-phosphate systems. Although the amount of ^{90}Sr reduction did not differ much among the metal phosphates, aluminum and iron phosphate would be more stable at a lower pH. However, selection of a metal as a coprecipitator would be dependent upon site characteristics. For example, if contamination had extended to the organic-rich zone of the soil, treatment with calcium phosphate would be a better choice. Nonetheless, the experimental results suggest that in situ containment of ^{90}Sr would prevent groundwater contamination and lead to eventual decommissioning of the sites through the natural decay process of ^{90}Sr .

P5.15

INFLUENCE ON THE TRANSPORT PROPERTIES OF REDOX-SENSITIVE ELEMENTS (E.G. TECHNETIUM) BY MICRO ENVIRONMENTS AND MICROORGANISMS. Hanskarl Brühl, Asaf Pekdeger & Andreas Winkler, Freie Universität Berlin, Berlin, West Germany.

Technetium is the lightest radio element of the periodic system (No. 43). While primordial Tc doesn't exist in nature any longer, it is produced in nuclear reactors with 6.13 % of the fission products. Tc-99 has a half life of $2.13 \text{ E}+5$ years. In aqueous solutions, Tc (IV) and (VII) are the most important valence states; other states are only stable in connection with complexing ligands.

A very low retardation of Tc(VII) occurs during transportation through aquifers under oxidizing conditions. Combined with the long half life this

is the reason for Tc's great hazard potential. Therefore, if there is migration from the disposal site, Tc is one of the problematic elements. Under reducing conditions on the contrary Tc (IV) is more or less immobile.

In laboratory experiments Tc was immobilized under certain circumstances, although oxic conditions could be measured. The transport behaviour of redox-sensitive elements is not only ruled by the geochemical "frame conditions" which can be measured within the macro environment. The micro environments which may develop for example on the mineral surfaces often turn out to be a very strong factor controlling the transport properties (here immobilisation). Besides microbial activities showed a strong influence on the fixation of Tc. Thus immobilisation behaviour of Tc strongly depends on micro environments and on microbial metabolism.

P5.16

THERMODYNAMIC MODELLING AND AQUEOUS CHEMISTRY IN THE $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ SYSTEM. Alan Atkinson, John A. Hearne, and Clive F. Knights, AEA/Technology, Building 429, Harwell Laboratory, Didcot, Oxon, OX11 0RA, UK.

The chemical properties of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system are important for understanding and predicting the behaviour of Portland cements in cementitious wasteforms and radioactive waste repositories. Solids of known average composition in this system have been synthesised by the co-hydrolysis of mixed alkoxides. The solids have been equilibrated with water at 25°C and the composition of the aqueous phase characterised. A thermodynamic model for the system has been developed by extending an earlier model of solid solutions in amorphous gels to include aluminium compounds. The model accounts for most of the experimental data and predicts that the main influence of aluminium is to form a hydrogarnet solid solution of general composition $\text{C}_3\text{A}_x\text{H}_{4-3x}\text{S}_2$. The model can be used to predict the chemistry of hydrated cements and the interaction of cements with groundwaters.

The underlying principles, thermodynamic parameters (of solid phases and liquid species) and predictions of the model are compared with those of cement chemistry models from other workers.

P5.17

MIGRATION OF CESIUM, STRONTIUM AND COBALT IN WATER-SATURATED CONCRETES. Kazuya Idemitsu, Hirotaka Furuya, Ryuji Tsutsumi, Sigeaki Yonezawa and Yoshiro Inagaki, Kyushu University, Fukuoka, JAPAN; and Seichi Sato, Hokkaido University, Sapporo, JAPAN.

Diffusivities of Cs, Sr and Co were measured in several kinds of water-saturated concretes. The measured penetration profile of every tracer was composed of two parts. Those were steep slope near the surface and gradual slope in deep part. This profile was successfully explained by considering two diffusion paths in concrete. One diffusion path was fissure which width was few microns and another was network of submicron pores. The volume of submicron pores was approximately 90% of total space volume in every concrete. The orders of magnitude of apparent diffusivities for all tracers were 10^{-12} - $10^{-11} \text{ m}^2/\text{s}$ through the fissure and 10^{-16} - $10^{-15} \text{ m}^2/\text{s}$ through the network of pores. The difference between diffusivities through two paths was supposed to be caused by large specific area and small constrictivity of the network of submicron pores.

THE EFFECT OF SILICA FUME AND WATER-TO-CEMENT RATIO ON THE HYDRAULIC CONDUCTIVITY OF CEMENT-BASED GROUT. A.A. Al-Manaseer, M. Onofrei, M.N. Gray and B. Shenton, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada R0E 1L0

In situ experiments at AECL's Underground Research Laboratory in Canada have demonstrated that a specially developed cement-based grout consisting of Canadian Type 50 cement, silica fume and superplasticizer can seal very fine fissures of less than 50 μm in granitic rock. Studies are now in progress to determine the longevity of these materials, with special emphasis on long-term hydraulic characteristics. This paper describes progress in these studies. The hydraulic conductivity, k_f , of a reference grout (90% Type 50 cement, 10% silica fume, water-to-cement (w/c) ratio between 0.4 and 0.8) are compared with those of the same grout with no silica fume. The k_f has been assessed with the grouts under compressive and tensile stresses using specially designed radial flow permeameters.

The tests have confirmed that k_f of the intact reference grout is 2 to 3 orders of magnitude higher than that typically observed for intact granitic rock (10^{-12} m/s). Also, the data show that the sealing properties of the cement grout are improved by adding silica fume and by reducing the value of the w/c ratio, that is, by decreasing connected capillary pore space in the grout.

The hydraulic conductivity data coupled with field work and other laboratory data strongly suggest that the reference grout can be successfully employed to seal finely fractured rock in the vicinity of a nuclear fuel waste disposal vault.

P5.19

SENSITIVITY OF A CEMENTITIOUS GEOCHEMICAL MODEL TO CHANGES IN THE GIBB'S FREE ENERGY OF THE COMPONENTS. Mark A. Gardiner and Craig A. Givens, IT Corporation, Albuquerque, NM

Because experimental thermodynamic data for many phases used in modeling cementitious materials have been unavailable, calculated data have typically been used instead. However, many times the quality of the data is suspect, and differing values have been reported for the same mineral by different researchers. In this paper, the sensitivity of a particular cementitious model to changes in the Gibb's free energy of its components is assessed.

The cementitious model chosen was comprised of the phases tobermorite, ettringite, hydrogarnet, portlandite and Na- and K- residual alkalis. These phases were chosen either because they have actually been documented as present in cementitious materials or because they may serve as reasonable proxies for actual phases. The amount of change in Gibb's free energy chosen was determined by the range of reported free energy values in the literature, the error associated with those values, and by estimating the effect low degrees of crystallinity would have on the phases chosen to proxy for actual cementitious phases (e.g., in the case of C-S-H).

Results of the modeling indicate that, as expected, changing the Gibb's free energy of minor and/or highly soluble phases causes little change in the predicted sealing performance of the grout, while changing the free energy of the dominant C-S-H phase causes the greatest change. Further, changing the free energy of the dominant silicate hydrate phase in the model by as little as 0.5% could alter the predicted performance of the material by as much as an order of magnitude. Differences in free energy as low as 0.25% between calculated and experimentally determined values can be obtained for silicates using the method of Chermak & Rimstidt (1989), using the sum of polyhedral contributions. However, this work suggests that these errors may or may not be too great, depending on the performance criteria of the grout.

P5.20

EFFECTS OF CHLORITE ALTERATION ON URANIUM REDISTRIBUTION IN KOONGARRA, AUSTRALIA. Takashi Murakami, and Hiroshi Isobe, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan, and Robert Edghill, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234, Australia

Rock samples at various depths in Koongarra have been examined mineralogically to understand the process and mechanisms of the alteration of chlorite, one of the major minerals of the uranium ore host rock. The alteration of chlorite occurs as a function of depth: chlorite is transformed to vermiculite, through regularly interstratified chlorite/vermiculite. The transformation is characterized by Fe oxidation, Fe loss, and K and Ti gain. The Fe released from chlorite reprecipitates to form iron minerals, possibly ferrihydrite. Vermiculite is then replaced by kaolinite (and possibly smectite), further releasing Fe.

On the millimeter scale, the alpha-autoradiography study has shown that uranium concentrations are qualitatively proportional to the extent of the alteration. e.g., chlorite grains are lower in uranium concentration and altered chlorite grains, higher. On the meter scale, the X-ray diffraction study has revealed that the abundance of chlorite, vermiculite, and kaolinite corresponds well to the low, intermediate, and high uranium concentration zones, respectively. This strongly suggests that the process, mechanisms, and kinetics of the chlorite alteration affect the uranium migration in Koongarra. The crystal and physical chemistry of chlorite and its altered products well accounts for the uranium redistribution.

P5.21

COMPARISON OF TUFF, GRANITE, AND BASALT AS HIGH-LEVEL REPOSITORY HOST ROCKS: LITHOLOGIC FACTORS INFLUENCING FLUID COMPOSITIONS. G. C. Ulmer, V. J. Grassi, A. Lee, D. E. Grandstaff, Geology Dept., Temple University, Philadelphia, PA 19122

Although most variations in (silicate) rock composition do not strongly alter the nature of fluids resulting from water-rock interactions (Grandstaff et al., 1990), hydrothermal experiments and examination of natural analogs have revealed that for siliceous rocks (>70% SiO_2), there are some host rock parameters that may affect the composition of groundwaters resulting from rock-water reactions in a high-level nuclear waste repository. Among these factors are crystallinity and ferrous iron content.

In Dickson rocking autoclave experiments at 300°C the fO_2 produced by reactions with glass-rich (>90% glass) tuffaceous rocks is 3-5 orders of magnitude more oxidizing than those with holocrystalline granite or basalts. This difference will certainly affect corrosion of container materials; affect on solubility and mobility of radionuclides, such as U, Np, and Tc, must also be considered. Reactions of glassy tuffaceous rocks also produce higher dissolved silica concentrations and lower pH values. Lower pH values will also increase rates of container corrosion; the higher SiO_2 values may produce different, but possibly beneficial secondary minerals such as zeolites that would sorb radionuclides or quartz that would decrease porosity. Tuffaceous silicic rocks generally are low in ferrous iron (<2% FeO). Thus, they have low redox buffer capacity which might be quickly exhausted by reaction with oxidized groundwaters entering the repository.

The combination of lower pH, more oxidized redox potential, and lower redox buffer capacity may render tuffaceous rocks less than desirable for host rocks for a nuclear waste repository.

P5.22

HIGH-TEMPERATURE ANNEALING OF NATURAL UO_2 . Janusz Janczok and Rodney C. Ewing, University of New Mexico, Albuquerque, NM 87131.

Four powdered samples of natural UO_2 (uraninite) were annealed in a reducing atmosphere up to 1200°C. U^{4+} to U^{6+} ratio and degree of crystallinity varied from sample to sample. The initial unit cell parameter values ranged from 0.5463 to 0.5385 nm. Three samples consisted of a mixture of UO_{2+x} and $\text{UO}_{2.25}$ as determined by BSE

images and X-ray diffraction analysis. Small amounts of the UO₂ 25 occur in all samples after annealing. Only the sample with the lowest initial unit cell parameter recovered fully after annealing ($a = 0.5465$ nm at 1200°C). The thermal recovery curve of this sample resembles that of synthetic U₄O₉. Also the changes in density are most dramatic in this sample ($\Delta\rho/\rho = 21\%$). The changes in the unit cell parameter with temperature for all samples (up to 750°C) consist of phenomena that can be explained by the annealing of point defects in both sublattices: 1.) migration of oxygen interstitials at 300°C; 2.) order-disorder transformation at 450°C; 3.) changes in the U sublattice at 600-750°C. Beginning at 600-750°C U⁶⁺ reduction associated with the second order transformations dominates the change in unit cell parameter.

Because of their geological age (600-300 m.y.) all samples experienced similar α -decay dose followed by self-annealing. However, oxidation is more important in creating defects within uraninite structure than α -decay damage due to self-irradiation.

P5.23

ON THE COMPARISON OF THE EFFECT OF pH ON THE SOLUBILITY OF AN UNIRRADIATED UO₂ IN BOTH PERCHLORATE AND CHLORIDE TEST SOLUTIONS. INFLUENCE OF THE SOLID MORPHOLOGY. E. Torrero, I. Casas, M. Aguilar, J. de Pablo, J. Giménez, Dep. Chem. Engineering, UPC, Barcelona, Spain; and J. Bruno Dep. Inorg. Chem., KTH, Stockholm, Sweden.

The solubility of a powdered crystalline uranium dioxide has been studied under reducing conditions, at 25 °C, using chloride and perchlorate as test solutions.

The solid composition and its morphology have been followed by X-ray Powder Diffraction (XPD) and Scanning Electron Microscopy (SEM).

The results obtained have shown an increase of the solubility at acidic pH values when chloride is used instead of perchlorate as ionic medium, whereas no significant difference is observed at neutral to alkaline pH values.

The XPD and SEM observations point to the fact that at acidic pH values the UO₂ particles suffer a degradation process that increases drastically the total surface area of the solid, which has been measured by the BET method, correlating in this way the solubilities obtained.

The uranium concentrations determined at 1 and 5 mol dm⁻³ chloride concentrations are also compared in order to assess the influence of this anion in the leaching process.

P5.24

Direct Analysis of Time Dependent Fundamental Solution in Three-Dimensional Transient Advection Diffusion by Boundary Element Method. Ryuji Kawamura, Information and Mathematical Science Laboratory, Inc., 2-43-1, Ikebukuro, Toshima-ku, Tokyo 171

The advective diffusion analyses have been applied to many fields of science and engineering, such as a dispersion of chemically reacting (first order reaction) substance, thermal conduction in fluid, electromagnetic field caused by a moving magnet, electron transport in semiconductors, underground migration of radioactive waste, and so on. In solving the transient advective diffusion equations by the boundary element method, however, time integrations of fundamental solution appear in the boundary integral equation, which makes the

BEM application to advective diffusion problems difficult. Therefore, the method has been approximated in the past relevant publications. The paper describes the method to carry out the time integrals of fundamental solution analytically, and the usefulness of the technique is demonstrated with several examples. The formalization are applicable not only to the advective diffusion but also to thermal conduction with constant flow. The results are obtained from the examples compared with analytical solutions or with the results from other numerical codes. Further, migration of nuclides with decay chain on constant groundwater velocity are treated comparison with results of the finite element method.

P5.25

THREE-DIMENSIONAL VISUALIZATION: A MEANS OF OPTIMIZING ANALYSIS OF TECHNICAL INFORMATION FOR A GEOLOGIC REPOSITORY FOR HIGH-LEVEL NUCLEAR WASTE. Donald H. Alexander^a, E. Richard Hill^b, John L. Smoot^c, Dennis R. Smith^c, Karen Waldo^c, Kenneth G. Eggert^d, and Kenneth M. Krupka^b.

Computer graphics systems that provide interactive display and manipulation of three-dimensional data are powerful tools for analysis, communication, and organization of technical information required for characterization and design of a geologic repository for nuclear waste. Greater understanding is possible through visualization of the geometric and property relationships of geologic information for a proposed site, engineering data for the surface and subsurface facilities, and the results of performance assessment modeling.

Commercially-available, graphics software was used to interactively visualize and analyze the results of three-dimensional, transport-model simulations of hypothetical radionuclide release from spent-fuel canisters placed in a geologic repository located at Yucca Mountain, Nevada. The concentration contours of the subsurface radionuclide plumes are shown in three-dimensional space. The software incorporates models for the interpolation and extrapolation of data over the three-dimensional space of interest. Users may assess the three-dimensional distribution of data and modeling results by interactive zooming, rotating, slicing, and peeling operations on models of the site and proposed repository.

- (a) U.S. Dept. of Energy, Washington, DC
- (b) Pacific Northwest Laboratory, Richland, WA
- (c) Dynamic Graphics, Inc., Bethesda, MD
- (d) Los Alamos National Laboratory, Los Alamos, NM

P5.26

MODELLING THE CHEMICAL BEHAVIOUR OF RADIONUCLIDES IN WASTE DISPOSAL IN GRANITE. R. Fabrice, BRGM, Orléans, FR, G. Ouzounian, ANDRA, Fontenay-aux-Roses, FR.

Radionuclides in nature as other elements are mainly transported by water as single or complexions. In order to elaborate safety models, the limiting concentrations of radionuclides in water have been determined. The only mechanism taken into account is the control of aqueous concentrations of the elements by the equilibrium with minerals. Absorption and ionic exchange are considered as additional retardation factors. The calculation was performed with the code CEQSY in which equilibrium state is reached by the Gibbs free energy minimisation, constrained by mass balances. The model was applied to a granitic system, with two different engineered barriers. Temperature is varied with the distance to the waste which delivers Sr, U, Pu, Np, Th, Ra, Se. The behaviour of these elements appears to be independent of the engineered barriers materials, and strongly dependent on temperature effect on mineral solubilities.

DIFFUSION POROSITY AND DIFFUSIVITY OF RADIONUCLIDES IN GRANITIC ROCKS. PART II: DIFFUSIVITY AND ELECTRICAL RESISTIVITY MEASUREMENTS IN ROCK MATRIX AROUND FRACTURES
 Heikki Kumpulainen, Arto Muurinen and Kari Uusheimo, Technical Research Centre of Finland, Reactor Laboratory, SF-02160 Espoo, Finland

Microfracturing of rock matrix around permeable fractures was studied experimentally from drill core samples around major fractures. The methods used were diffusion measurements using ^{36}Cl tracer and electrical resistivity measurements on samples saturated with 1M NaCl solution. Rock samples were granite around a partially filled carbonate fracture from the depth of 333 m and gneiss around a slickenside fracture.

The apparent diffusivities were approximately of the same order of magnitude. None of the changing parameters i.e. salt concentration of the solution, rock and fracture type or distance from the fracture surface had any clearly systematic effect on the apparent diffusivities.

The effective diffusivities and porosities, on the contrary, depended strongly on the salt concentration of water used to saturate the rock samples and on the measurement techniques.

P5.28

RADIOACTIVE TRACER STUDY PERFORMED IN A DIPOLE GEOMETRY IN A HIGHLY CONDUCTIVE FRACTURE ZONE.
Johan Byegård, Gunnar Skarnemark, Mats Skälberg, Dpt. of Nuclear Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden.

A radioactive tracer experiment has been performed in a highly conductive fracture zone, where a dipole geometry was obtained by pumping up water from an isolated part at the fracture zone in a borehole and then leading the water down to the same fracture zone in another borehole. Tracers were injected to this system and the breakthrough was registered in the pumping borehole and at two other boreholes at each side of the dipole.

Anions ($^{127}\text{I}^-$ and $^{82}\text{Br}^-$) and complexed metal ions ($^{51}\text{Cr-EDTA}$, $^{59}\text{Co-EDTA}$, $^{111}\text{In-EDTA}$, $^{140}\text{La-DOTA}$, $^{160}\text{Tb-EDTA}$, $^{169}\text{Yb-EDTA}$ and $^{177}\text{Lu-DOTA}$) were injected and their properties as non-sorbing tracers were evaluated. Besides that, studies of slightly sorbtive cations ($^{22}\text{Na}^+$, $^{59}\text{Co}^{2+}$, $^{86}\text{Rb}^+$ and $^{201}\text{Tl}^+$) were also performed. $^{99\text{m}}\text{TcO}_4^-$ and its chemical analogue $^{186}\text{ReO}_4^-$ were also injected in order to study the behaviour of Tc at low redox-potentials.

Breakthrough are obtained for Re and for all metal complexes and anions. Some differences in the recovery yields can be seen. No transport of cations can be observed, except for Na, although observation has been made for a long time. In contrary to Re any breakthrough of Tc can not be observed. This indicates that the injected TcO_4^- is completely reduced, probably to TcO_2 , and sorbed.

P5.29

TEMPERATURE INDUCED REDOX FRONT IN THE NEAR FIELD OF A REPOSITORY FOR SPENT FUEL.

Allan T. Emsen
 Department of Nuclear Chemistry
 Chalmers University of Technology
 S-41296 Göteborg
 Sweden

Simulations with the CHERCH program show that under certain circumstances, irreversible processes in the rock - groundwater system may cause oxidizing conditions to occur in a great part of the near field of a repository for spent nuclear fuel. This in turn has implications for the stability of copper containers, as well as for solubilities of radionuclides in the groundwater.

Generally, the groundwater in deep Swedish rock is strongly reducing. Since it is formed from rain entering the ground, and the rain is oxidizing, there has to be processes which reduce the water while it moves downwards. Minerals containing iron are supposed to be important contributors to these processes.

The reducing properties of the groundwater are supposed to make corrosion of the copper containers for spent nuclear fuel extremely slow. It has been proposed, however, that in the case of a container failure, radiolysis will create oxidizing conditions, since several of the radionuclides are much more soluble under oxidizing than reducing conditions. Radionuclides might be released at rather high concentrations. In that case, the processes leading to reducing conditions in ordinary groundwater are supposed to restore the reducing properties within the repository or in the rock very close to it. This will decrease the solubilities by several orders of magnitude, and thus the radionuclides should be prevented from entering the environment.

The processes in the rock - groundwater system are, however, poorly understood. The groundwater is in equilibrium or close to equilibrium with a few minerals. On the other hand it is far from equilibrium with respect to other minerals, which are observed in the fracture walls, and which are known to react readily with the groundwater. Further, equilibrium models have been able to predict relationships

P5.30

CRITICAL CHLORIDE CONCENTRATIONS FOR PITTING OF AUSTENITIC AND HIGH-NICKEL ALLOYS. R. Daniel McCrae, Joseph C. Farmer, and Dennis L. Fleming, Lawrence Livermore National Laboratory, Livermore, CA.

Several austenitic and high-nickel alloys are being considered as candidate materials for fabrication of high-level radioactive waste containers. Austenitic alloys include 304 and 316L stainless steel, Alloy 825, and Hastalloy C-22. The pitting potentials of these alloys are being determined at various chloride concentrations from potentiodynamic polarization tests. The critical chloride concentration coincides with a precipitous drop in pitting potential. These tests are being conducted in accordance with procedure recommended by ASTM G-93. Data will be discussed in the context of existing theoretical models for pit initiation.

P5.31

STATISTICALLY DESIGNED LEAD CORROSION EXPERIMENTS FOR NUCLEAR WASTE DISPOSAL. P. Mani Mathev and P.A. Krueger, Containment Analysis Branch, Atomic Energy of Canada Limited, Pinawa, Manitoba ROE 1L0

The Canadian Nuclear Fuel Waste Management Program is evaluating two basic supported-shell container concepts for used-fuel immobilization. One concept uses a compacted particulate material within the container to support the thin corrosion-resistant shell. The other concept, called "the metal-matrix concept", uses a cast-in-place metal matrix for shell support. A corrosion-resistant metal-matrix could provide an additional barrier to radionuclide release from a breached container.

This paper describes studies of galvanic corrosion of lead, a candidate matrix metal, coupled with ASTM Grade-2 titanium, a candidate container-shell material. In these studies the fractional factorial statistical design of Box-Behnken was used to develop mathematical relationships between the independent variables and the corrosion rate of lead. The results of two series of tests are reported. In the first series the effect of three variables, namely, the ionic strength of simulated Canadian Shield groundwater, titanium-to-lead surface area ratio and the diameter of exposed lead, was investigated. In the second series the third variable of the first test series, the diameter of exposed lead, was replaced by the exposure time. Mathematical expressions

were defined for the lead corrosion rate as a function of the independent variables.

The results show a decrease in lead corrosion rate with increasing exposure time. The rate increases with increasing ionic strength and titanium-to-lead surface area ratio. An increase in the diameter of exposed lead does not appear to affect the corrosion rate.

P5.32

UNCERTAINTIES IN CONTAINER FAILURE TIME PREDICTIONS. R. E. Williford, Pacific Northwest Laboratory, Richland, WA.

Stochastic variations in the local chemical environment of a geologic waste repository can cause corresponding variations in container corrosion rates and failure times, and thus in radionuclide release rates. This paper addresses how well the future variations in repository chemistries must be known in order to predict container failure times that are bounded by a finite time period within the repository lifetime. Temporal variations in local chemistries are modeled by a type of random walk called fractional Brownian motion, with a Hurst exponent $H=0.72$ developed from 2000 years of climatological observations. In this restricted and idealized study, uniform and localized corrosion processes are modeled by a generic, power-law equation that admits variations both in corrosion rates and mechanisms, but is limited to the continuous immersion case. The analysis is relative because no absolute corrosion rates or failure times are computed; only the propagation of uncertainties through the above model are treated. Preliminary results indicate that a 4000 to 5000 year scatter in predicted container failure times may be possible if repository chemistries can be known to within ± 5 to $\pm 10\%$ over the repository lifetime. These are small uncertainties compared to current estimates.

Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RL0 1830.

P5.33

AN ADVANCED COLD PROCESS CANISTER DESIGN FOR NUCLEAR WASTE DISPOSAL. Heikki Raiko, Technical Research Centre of Finland, Nuclear Engineering Laboratory; and Jukka-Pekka Salo, Teollisuuden Voima Oy.

Teollisuuden Voima Oy (TVO) has recently delivered to the Finnish authorities a new technical plan for encapsulation of spent nuclear fuel. The so-called cold process technique will replace earlier used KBS-3 type encapsulation process.

The work for optimization of the encapsulation process has been in progress since 1987. The purpose of the studies has been to develop a method for encapsulation in which elevated temperatures are not required for producing a copper canister of sufficient structural stability. Molten lead casting is in the cold process substituted by solid granulate canister filling material. By this way the design and operation of the conditioning plant can be simplified thus resulting in increased safety and improved economics.

An advanced cold process canister design, ACPC-design, is presented in Fig. 1 and Fig. 2. The structure consists of a steel canister as a load bearing element, with an outer corrosion shield of oxygen-free copper. The wall thickness for the copper shell is 60 mm and for the steel shell 55 mm correspondingly. The outer copper lid is to be sealed using electron beam welding. The inside steel lid is designed to be leak-tight only during the sealing weld process of the copper lid.

The canister will be filled with granular material, such as lead shots, glass beads or quartz sand. Laboratory tests have been performed with lead shots and quartz sand. A density of 6.76 kg/dm^3 can be reached with lead shots having a diameter of 1.5 mm. For quartz sand, grain sizes between 0.5 - 2 mm, a density of 1.5 kg/dm^3 is possible.

The main conditions for the canister design are the following ones:

- When designing the cold process encapsulation plant, the maximum radiation level on the outer surface of the canister was selected to be abt. 100 mSv/h.

- The maximum temperature on the outer surface is limited to $+100^\circ\text{C}$ because of the chemical stability of the highly-compacted bentonite in the deposition hole. Allowable heat load per canister is abt. 1200 W.

- The mechanical design load for the canister is 15 MPa external pressure. The maximum design pressure is assumed to be distributed evenly and acting on all faces of the vessel.

- The maximum tensile strain in copper material is limited to 1%. According to the numerical analysis performed, if the copper shell has a 1 mm gap all over the inside joint against the steel shell and the copper liner is pressed against the steel shell, the local maximum plastic (positive) strain in copper material is limited to 1%.

The mechanical dimensioning of the copper/steel canister is made according to the Finnish standards (SFS) for pressure vessels. It was found that the inner shell could be produced commercially out of cast or pressure vessel steels. If needed there are practical possibilities to increase the design pressure of the canister.

Thermal strains and stresses induced in the copper layer of the canister during the cooling period of the canister in the deposition hole were studied and found out to be of very little significance. Also the effect of corrosion product expansion on pressure loads were evaluated and found not to be a dimensioning factor.

P5.34

EVALUATION OF THERMAL CONDUCTIVITY OF BACKFILL MATERIAL VIA A TRIAL FUNCTION TECHNIQUE. Xu, D.M., Yong, R.N., and Mohamed, A.M.O., Geotechnical Research Centre, McGill University, Montreal, Canada.

It is known that the thermal conductivity of a soil is a function of its moisture content. With the existence of temperature gradients in a soil medium, the moisture in the medium will redistribute itself to new equilibrium values to conform with the applied temperature gradient. Subsequently, the new moisture content distribution will affect the temperature distribution in the soil medium. This process indicates the coupling effect between the temperature and moisture distribution in a porous medium.

In this study, a trial function technique is used to obtain an analytical solution for the temperature distribution. The merit of this method not only lies in its simplicity but also offers an analytical formulation in a form that permits one to clearly visualize the significance of the physical parameters e.g. thermal conductivity. Since the thermal conductivity of the soil material is not always known in advance, therefore one task of the solution technique is to determine its value. In using the trial function technique, the task can be fulfilled in a manner which used the data pertaining to heat front movement.

A series of tests have been performed at the Geotechnical Research Centre on backfill material under imposed temperature gradients. It has been demonstrated that the water content distribution during the transient process does not affect the temperature distribution. The trial function technique has been applied to calculate the thermal conductivity of the backfill material. Using the calculated values and the proposed method of solution the temperature profiles have been calculated. The comparison between the theoretical prediction of the temperature profiles and the experimentally measured temperature profiles shows good agreement except in the vicinity of the heating boundary, where a thin thermal boundary layer exists. The vaporization process in this thin layer contributes to the turbulent effect which can be modeled by using a thermal shock condition. The vaporization process has not been taken into account in the method of solution.

P5.35

MODELLING STUDIES OF SORPTION OF URANIUM AND PLUTONIUM IN THE FAR-FIELD OF A NUCLEAR WASTE REPOSITORY. A. Haworth, S.M. Sharland and C.J. Tweed, Radwaste Disposal R&D Division, AEA Decommissioning and Radwaste, AEA Technology, Harwell Laboratory, Didcot OXON OX11 0RA.

Sorption can greatly retard the migration of dissolved radionuclides from a radioactive waste repository to the biosphere. Many safety-assessment models for radioactive waste disposal make use of a linear sorption isotherm derived from experiment. However, for some systems, the observed isotherm values can vary greatly with measurement technique. It is therefore important to investigate such effects in order to appreciate possible limitations of this approach in safety assessments.

In this paper, modelling studies of sorption of radionuclides onto geologic materials are described. These models aim to simulate various experiments which measure R_d , both to aid interpretation of the results and to validate the model formulation and database. The HARPHRQ code (which uses the geochemical code PHREEQS), first used to model 'batch' sorption experiments. HARPHRQ contains several sorption models, including surface complexation models which take into account electrostatic and other chemical interactions between the aqueous species and surface. The choice of model depends on the precise system under consideration. The parameterised HARPHRQ models are then used directly in simulations of 'through-diffusion' experiments with the CHEQMATE code.

This modelling approach has previously been applied to sorption of uranium onto London clay. In the current paper, this model is extended by addition of organic materials and the results are compared with experiment. Similar studies of plutonium sorption onto far-field materials are also presented.

P5.36

DESIGN AND TENTATIVE RESULTS OF REDOX CAPACITY MEASUREMENTS OF GRANITIC ROCKS AND MINERALS. Veijo O. Pirkonen. Technical Research Centre of Finland, Geotechnical Laboratory, P.O. BOX 108, SF-02150, Espoo, Finland.

This document presents a procedure and preliminary results of redox capacity measurements with granitic rocks and minerals. The on-line autoclave technique was used. Oxygen uptake was measured as a function of Fe(II) reduction in the solid phase.

In a test run with pulverized granodiorite, dissolved oxygen was measured on line with a particular electrode designed for that purpose. Redox reactions between rock (BET $1.0 \text{ m}^2/\text{g}$) and granite water in NTP conditions reached a diffusion controlled reaction state within two weeks. The maximum reaction rate was measured during a two days period when $3.0 \times 10^{-10} \text{ mol l}^{-1} \text{ s}^{-1}$ of oxygen and $5.8 \times 10^{-9} \text{ mol l}^{-1} \text{ s}^{-1}$ of Fe(II) were consumed. 17 % of Fe(II) in solid phase was oxidized before the diffusion phase. At this stage the oxygen pressure was increased up to 100 bar. Three weeks later, minor amount (0.07 %) of Fe(II) was oxidized. According to the result, the measured maximum redox capacity of pulverized granodiorite is 0.001 mmol/g (BET $1.0 \text{ m}^2/\text{g}$). A theoretical maximum redox capacity could be one order of magnitude greater.

P5.37

THE WIPP BIN-SCALE CH TRU WASTE TEST PROGRAM: INITIATION
Martin A. Molecke, Sandia National Labs., Albuquerque, NM.

The Waste Isolation Pilot Plant (WIPP) is scheduled to become the first operating nuclear waste repository in the United States. The first contact-handled transuranic (CH TRU) wastes to be shipped to and emplaced in the WIPP will be incorporated into a series of scientific tests. A WIPP bin-scale TRU waste test has been set up and recently initiated, to specifically provide needed waste degradation/gas generation data to the WIPP performance assessment program, in anticipation of first actual (radioactive) waste receipt. This paper: a) provides a technical description of the ongoing test program and associated equipment; b) characterizes the types of TRU wastes used in these tests; c) reviews the initial gas-generation data obtained for the baseline-reference (non-waste) segment of the test; and, d) provides a status report on the WIPP and its related scientific programs.

This bin-scale program involves the testing of about 600 drum-volume (440 liter) of actual CH TRU wastes contained

within about 124 separate test bins. A test bin is a specifically designed, extensively instrumented, metal container, approximately $1.2 \text{ m} \times 1.2 \text{ m} \times 0.9 \text{ m}$ in size, to allow for the periodic sampling of gases, to control the internal bin pressures, and to safely isolate the radioactive wastes.

Test gas samples will be obtained periodically from each bin and quantitatively analyzed for gases generated by multiple waste degradation mechanisms and released as a function of time. Gases to be quantified also include potentially hazardous volatile organic compounds released by the wastes, of environmental safety and Environmental Protection Agency (EPA) hazardous-waste concerns.

P5.38

COUPLED THERMO-HYDRAULIC BEHAVIOR AROUND ACCESS SHAFT SEALED WITH BACKFILL MATERIAL
J. OKAMOTO*, K. HARA*, N. SASAKI*, K. ISHIHARA* and Y. SAWAGUCHI*
* Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, JAPAN
* KAJIMA Corporation, Akasaka, Minato-ku, Tokyo, JAPAN

Groundwater flow from the repository to the surface through the sealed access shaft is considered to be induced by the heat generated from HLW. It is important to estimate the effect of this heat generation on groundwater flow.

This paper presents the evaluation of this groundwater flow in the vicinity of the access shaft filled with backfill material by using the coupled thermo-hydraulic model. According to the current design, backfill material within the shaft will be compressed 5 to 15 times every 20 cm with a vibrating compactor with 60 kg tamper during construction. Dry density and porosity of backfill material were determined from the experimental results and the construction condition. Hydraulic conductivity was determined from the experimental results for various mixtures of bentonite and sand. With respect to thermal properties of backfill material for the tunnel sealing, the properties used in Stripa Project were adopted.

Transient coupled thermo-hydraulic FEM analysis was carried out for the axisymmetric model. The repository was assumed to be located at 1000 m depth, and the access shaft was located at the center of the repository.

The results showed that hydraulic gradient of groundwater flow along the sealed shaft was approximately 1/1000 at the time 1000 years after closure of the repository.

P5.39

BENTONITE-GROUNDWATER INTERACTION IN INERT NITROGEN ATMOSPHERE. Anna Nystrom, Irene Lunden, Dep. of Nuclear Chemistry, Chalmers University of Technology, Goteborg, SWEDEN

A study concerning the influence of bentonite (MX-80) on the chemical composition of synthetic granitic groundwater has been performed under inert nitrogen atmosphere.

The study included one statically, and two dynamically leached bentonite samples. In one of the dynamically leached samples an addition of 1% copper powder was made.

Water samples were drawn after 12, 18, 25, and 41 days. The samples were then analyzed with respect to the total concentrations of K, Na, Mg, Ca, Cu, Fe, Al, and Si using atomic absorption spectrometry. The concentrations of Cl^- , NO_3^- , and SO_4^{2-} were measured using ion chromatography. pH and Eh measurement were performed inside the nitrogen filled glovebox,

whereas alkalinity was measured outside using backtitration.

As a comparison calculations were made using the geochemical codes PHREEQE and DISSOL.

P5.40

CHARACTERISTICS OF BOOM CLAY AS SEALING AND BACKFILLING MATERIAL. Geert T.C. VOLCKAERT, Frank T.L. VANDERVOORT, SCK/CEN, Mol, Belgium

In Belgium the SCK/CEN is studying the geological disposal of high level radioactive waste in the Boom clay formation. In such an argillaceous repository the backfilling and sealing features will be multiple.

A preliminary selection study has shown that highly compacted Boom clay is potentially a suitable sealing and backfilling material. It is a logic choice to try to re-use the excavated clay because of its evident geochemical compatibility and easy availability.

Therefore an experimental program was set up to determine the main sealing properties of highly compacted boom clay.

The results of the measurement of volumetric swelling, swelling-pressure and hydraulic conductivity are reported. The density and initial degree of saturation are used as variables. Models are proposed for the relation between density and swelling-pressure and for the relation between density and hydraulic conductivity.

The influence of hydro-thermal conditions on the swelling and hydraulic properties are indicated.

The experimental set-up and the procedure are briefly described.

P5.41

A REVIEW PROCESS AND A DATABASE FOR WASTE-PACKAGE DOCUMENTS

CHARLES G. INTERRANTE*, CARLA A. NESSINA**, AND ANNA C. FRAKER***

*Nuclear Regulatory Commission, Washington, DC 20555

**Consultant, 9800 Marquette Drive, Bethesda, MD 20817

***National Institute of Standards and Technology, Gaithersburg, MD 20899

The work reported here is part of a program conducted by the Nuclear Regulatory Commission on the efficacy of proposed plans for radionuclide containment for long-term storage of high-level nuclear waste (HLW). An important element of that program is the review and evaluations of available literature on components of a waste package. A review process and a database have been developed and tailored to provide information quickly to an individual who has a question about a particular material or component of a waste package. The database is uniquely suited to serve as a guide to indicate special areas where data and information needs exist on questions related to radionuclide containment. Additions to the database are made as information becomes available, and this source is as current as the published literature. A description of the review process and the database is given.

P5.42

EFFECT OF OXYGEN TRANSPORT AND RESISTIVITY OF THE ENVIRONMENT ON THE CORROSION OF STEEL.

E. Escalante, U. Bertocci, National Institute of Standards and Technology, Gaithersburg, MD; and T. Oka, Nippon Steel Corp. Japan

This study is directed at investigating the rate of corrosion and its spatial distribution, that develop under conditions where transport of oxygen and conductivity of the environment are controlled over a wide range, including low conductivity as expected in the Yucca Mountain environment. The

results indicate that the corrosion rate of steel is directly related to the rate of oxygen transport over several orders of magnitude, and increasing conductivity by one order of magnitude increases corrosion rate by a factor of two or three. Of greater significance is the result that indicates that as conductivity of the environment decreases, and corrosion rate decreases, the degree of localized attack increases.

P6.1 ABSTRACT NOT AVAILABLE

P6.2

PHASE RELATIONS OF THE URANYL OXIDE HYDRATES AND THEIR SIGNIFICANCE TO THE DISPOSAL OF SPENT FUEL

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

The geochemical modelling of the corrosion of spent fuel requires a knowledge of the alteration products. Becquerelite has been identified as an alteration product of spent fuel (Bates, *et al*, 1990). Uraninite (UO_{2+x}) is a natural analogue for the long term behavior of spent fuel in an aqueous environment. The corrosion of uraninite produces a complex assemblage of alteration products, including the hydrous uranyl oxides known as the becquerelite group of minerals. The becquerelite group has a layer-type structure with water and exchangeable cations occupying interlayer sites.

Sobry (1971) proposed a substitutional scheme for the alteration of the becquerelite minerals through the coupled substitution of interlayer water and aqueous ions. Dehydration of these phases is also an important alteration process.

Our analysis of Sobry's scheme using a ternary diagram (UO_3 - H_2O - MO , $M = Ca, Pb, Ba, Na_2, K_2$, etc.) explains some of the complexity observed in natural systems. The becquerelite group minerals generally coexist with curite, $Pb_2U_5O_{17} \cdot nH_2O$, a precursor to uranyl phosphates suggesting curite may play a critical role in the alteration sequence. Clarkeite, $(Na_2Ca)U_2O_7$, may be important at elevated temperatures and high ionic strengths. The sequence of formation of uranyl phases during the corrosion of spent fuel probably depends more strongly on kinetics than on thermodynamics.

P6.3

DISSOLUTION BEHAVIOUR OF USED CANDU FUEL UNDER REDUCING CONDITIONS. J.C. Tait, S. Stroes-Gascoyne, W.H. Hocking, A.M. Duclos, R.J. Porth and D.L. Wilkin, AECL, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada.

The dissolution behaviour of used CANDU fuel in aqueous solutions has been examined under mildly reducing conditions at 100°C for periods of about one year. The objectives were to study a 'breached container' scenario by investigating the effects of various container components and groundwaters on the dissolution of used CANDU fuel. The components studied were titanium (container material), carbon steel (fuel bundle support basket) and aluminosilicate glass beads (container infill material). Leaching solutions included deionized water (DIW) and synthetic saline groundwaters, some of which had been pre-equilibrated with Na-bentonite (buffer material).

The presence or absence of glass beads or carbon steel did not appear to significantly affect solution concentrations of ^{137}Cs , ^{90}Sr , ^{99}Tc , ^{238}U or Pu/Am . Radionuclide concentrations were one to two orders of magnitude higher in saline groundwaters than in DIW. Releases from clad fuels were higher than those from fuel fragments. It appears

that once mildly reducing conditions are established in the leachant, further radionuclide release from the fuel is inhibited and radionuclide concentrations in solution become virtually constant. Measurements of the oxidation state of some of the leached fuel segments, using X-ray photoelectron spectroscopy, show a surface composition of less than UO_2 , below the postulated threshold for oxidative dissolution. Scanning electron microscopy examination of some fuels has indicated accelerated grain-boundary attack in saline groundwaters, in agreement with the enhanced dissolution rates and higher solution concentrations for most radionuclides.

P6.4

RESULTS FROM LONG-TERM DISSOLUTION TESTS USING OXIDIZED SPENT FUEL. Charles N. Wilson, Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352.

Two semi-static dissolution tests using oxidized PWR spent fuel specimens are being conducted under ambient hot cell conditions in Nevada Test Site J-13 well water and unsealed fused silica vessels. The test specimens were oxidized at 250°C in air to bulk oxygen-to-metal (O/M) values of 2.21 and 2.33. Following an initial 191 day test cycle, the specimens were restarted in fresh J-13 water for a second long-term test cycle. Results through the first 40 months of Cycle 2 are compared with results from similar tests at 25°C and 85°C using unoxidized spent fuel specimens.

Uranium concentrations in the oxidized fuel tests reached steady-state values of 10-12 $\mu\text{g}/\text{mL}$ versus 1-2 $\mu\text{g}/\text{mL}$ with unoxidized fuel tested at 25°C. Higher concentrations were also observed for Am, Cm and Np in 0.4- μm filtered samples from the oxidized fuel tests compared to the unoxidized fuel tested at 25°C, while Pu concentrations were not affected by the fuel oxidation state. Initial ^{99}Tc releases increased to approximately 0.9% of specimen inventory as a result of oxidation. Smaller increases in initial ^{90}Sr and ^{129}I release were observed as a result of oxidation and initial ^{137}Cs release was not significantly affected by fuel oxidation. The longer term continuous release rates of ^{99}Tc , and apparently ^{129}I , were also increased as a result of fuel oxidation. The effects of fuel oxidation on apparent ^{137}Cs and ^{90}Sr release rates in later samples were small and less than the effects of temperature.

This work was supported by Lawrence Livermore National Laboratory as part of the Yucca Mountain Project (YMP) Waste Package Task. The YMP is part of the U.S. Department of Energy Civilian Radioactive Waste Management Program.

P6.5

RADIATION INDUCED DISSOLUTION OF UO_2 . Hilbert Christensen, Studsvik Nuclear, 611 82 Nyköping, Sweden.

Radiolysis of water produces radicals and molecules, amongst them the oxidizing species H_2O_2 and OH-radicals and, in aerated solutions, also O_2 . These species are probably responsible for the oxidation and dissolution of UO_2 observed in a number of experiments. In order to be able to model the effect of water radiolysis on the dissolution of fuel in the disposal vault it is essential to study the oxidation mechanism. In the present investigation the effect of the oxidizing species has been studied separately using suitable scavengers.

A polished specimen of UO_2 was immersed in water and irradiated at ambient temperature with Co-60 gamma radiation. After irradiation the uranium which had dissolved or precipitated elsewhere than the solid surface, was measured, and the oxidation of the surface was determined, using ESCA and SIMS.

In 50 mM H_2O_2 (no irradiation) the corrosion rate was $<4 \mu\text{g cm}^{-2} \text{d}^{-1}$ after 6 d exposure at pH 8. Corresponding rates for oxidation by O_2 and OH radicals were about $3 \mu\text{g cm}^{-2} \text{d}^{-1}$. (Dose rate about 700 Gy/h.)

P6.6

UO_2 MATRIX DISSOLUTION RATES AND GRAIN BOUNDARY INVENTORIES OF Cs, Sr, AND Tc IN SPENT LWR FUEL. W. J. Gray and D. M. Strachan, Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352.

Experimental methods have been developed for measuring the grain-boundary inventories of radionuclides and for determining whether the UO_2 matrix of spent light-water reactor (LWR) fuel dissolves congruently. Measuring the grain-boundary inventories first involves low-temperature (150°C to 200°C) air oxidation, which occurs preferentially along the grain boundaries, making the fuel fragments friable and easily separated into individual grains. With the grain boundaries thus exposed, the associated inventories of radionuclides can be completely dissolved and measured. Tests to date show that grain-boundary inventories of Cs and Tc are approximately equal to gap inventories, as expected. Other radionuclides and other fuels are being tested.

To determine whether the UO_2 matrix of spent fuel dissolves congruently, the fuel is pulverized without preoxidation. This produces individual grains and subgrains (somewhat more transgranular fracture occurs than with partially oxidized fuel) that are subsequently tested in a flow-through column. Water is pumped through the column at a rate (0.1 to 1.0 mL/min) where the concentration of U in the column effluent remains far below saturation. This allows the forward reaction rate of the UO_2 matrix to be measured and, by measuring the concentrations of other radionuclides in the column effluent, the degree of congruency of the dissolution process can be determined. Data obtained to date show that the fractional dissolution rate of Cs exceeds that of U by no more than about 20%, in contrast to tests with multigrain fuel fragments, which suggest Cs dissolution rates two or more times greater than U dissolution rates even after testing periods lasting several years.

P6.7

SIMFUEL DISSOLUTION STUDIES IN GRANITIC GROUNDWATER UNDER OXIC CONDITIONS, AT 25 °C. Jordi Bruno and Amaia Sandino, Dept. of Inorganic Chemistry, Royal Institute of Technology, S-100 44, Stockholm.

As a result of a collaboration between the Swedish and the Finnish nuclear waste management programs we are at the present studying the dissolution of SIMFUEL in a wide array of groundwater compositions and temperatures.

In this presentation we will discuss the results obtained on the dissolution of SIMFUEL in non-saline groundwaters, under oxic conditions and at 25 °C.

The SIMFUEL pellets have been prepared by Chalk River Nuclear Laboratories to simulate the chemical composition of UO_2 spent fuel at two different burnups, 30 and 50 MVd/Kg respectively. Two non-saline granitic groundwaters have been used in these experiments, the so-called Allard groundwater and a more complete groundwater which reflects more realistically the composition of groundwater in equilibrium with granitic bedrock. The experiments have been performed in three different ways: batch replenishment under slightly oxic conditions, batch without replenishment under constant pO_2 , and continuous flow-through under constant pO_2 .

The results show a completely different release mechanism if the supply of oxidants is limited (batch replenishment closed oxic system) or if there is a continuous supply of oxidants (batch non-replenishment open system). The implications of these different mechanisms on the dissolution of the minor components of SIMFUEL will be discussed in the light of this and surface spectroscopic data of the reacted phases.

- A DESCRIPTION OF THE KINETICS AND MECHANISMS WHICH CONTROL THE RELEASE OF HLW ELEMENTS FROM SYNROC.** K.L. Smith, K.P. Hart, G.R. Lumpkin, P. McGinn, J. Bartlett, P. Lam and M.G. Blackford, Australian Nuclear Science and Technology Organisation, Lucas Heights Research Laboratories, Sydney, Australia.

Dissolution tests were conducted on a well characterised Synroc C specimen (a polyphase titanate ceramic wasteform) containing 10 wt % simulated waste. The effect of temperature and leachant composition on the mechanisms and kinetics of the dissolution of HLW elements from Synroc were investigated by leaching Synroc samples in doubly deionised water at 70 and 150°C; and in silicate and carbonate solutions at 70°C. Optical metallography, SEM, TEM, XPS and X-ray diffraction were used before and after the dissolution experiments, to characterise the primary and secondary phases in and on the Synroc samples and to describe the morphological and chemical changes which occurred. Chemical changes in the leachants were analysed using ICP/Mass Spectrometry.

These studies allow some interpretation of Synroc leaching behaviour. The titaniferous surface layers which form on the primary perovskite and hollandite phases during dissolution tests are of particular interest, as these appear to alter local pH (i.e. form micro-environments). Analysis of the leaching data has established that these surface layers can reduce the release of HLW elements from Synroc and that variations in temperature and leachant composition can hinder the formation of these secondary phases.

Thermodynamic calculations have been used to predict the speciation of elements in solution and the stability of the solid secondary phases, at the temperatures and in the leachants used in this study.

P7.1 ABSTRACT NOT AVAILABLE

P7.2

- HEAT-PIPE EFFECT ON THE TRANSPORT OF GASEOUS RADIONUCLIDES RELEASED FROM A NUCLEAR WASTE CONTAINER.** W. Zhou, P. L. Chambré, T. H. Pigford, & W. W.-L. Lee, Department of Nuclear Engineering, University of California and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

We present analytical studies of the transport of gaseous species released from a spent-fuel waste package, as affected by a heat-pipe of counterflowing liquid and vaporized ground water in the surrounding rock. A heat-pipe is caused by nuclear waste heating which vaporizes pore water near the waste, releasing vapor into the fractures. Driven by its pressure gradient, the vapor flows away from the waste and condenses where the rock is cooler. Because of capillary pressure gradient due to non-uniform liquid saturation, the condensate flows towards the waste surface through the porous rock. We first develop analytical solutions for the time-dependent transport of energy and fluid from the waste container surface to the surrounding fractured porous rock. From the mass fluxes of liquid and vapor, we solve the advective-diffusive transport of a gaseous species released from the waste. The major assumptions are quasi-steady-state, local thermodynamic equilibrium, no noncondensable gases, and no sorption. Our results include the extent of the heat-pipe zone as function of time, the vapor velocity distribution in the heat-pipe zone, radionuclide concentration in water vapor, and the flux of radionuclide at the waste surface normalized to the surface concentration. We find that the vapor velocity in the heat-pipe zone is 1000-fold greater than the local air velocity if there were no heat pipe. If the gaseous species release mechanism maintains a near-constant concentration of gaseous species in the gas outside and near the waste container surface, the mass rate of transport of that species would be increased 1.3 to 7 times greater than if there were no heat pipe. However, if the release rate of the gaseous species is affected little by the concentration of that species outside the container, the heat-pipe can have little effect on the transport rate of that species.

P7.3

- Release and Transport of Gaseous C-14 from a Nuclear Waste Repository in an Unsaturated Medium.** W. B. Light, E. D. Zwielen, T. H. Pigford, P. L. Chambré & W. W.-L. Lee, Department of Nuclear Engineering, University of California and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

We study the release of ^{14}C released as $^{14}\text{CO}_2$ from partly failed nuclear waste containers by analyzing the flow of gas out of and into the container in a nuclear waste repository in an unsaturated rock. We analyze the transport of released $^{14}\text{CO}_2$ with gas-phase advection and dispersion. We calculate cumulative release of ^{14}C from the entire repository and inhalation dose to a maximally exposed individual.

Waste containers will be filled with inert gas before they are sealed. Due to decay heat, temperature of the container increases. The increased temperature causes the gas pressure inside the container to increase, and inert gas could leak out through a penetration, carrying with it gaseous radioactive material such as $^{14}\text{CO}_2$. Because the waste cools, due to the decay of the heat source, and because of the loss of inert gas through the penetration, the pressure drops. The pressure inside the container will eventually fall below atmospheric pressure and air will leak in. Gas flow is analysed by steady viscous flow of an ideal gas through a single equivalent hole. We also analyse air flowing into the container and the simultaneous release of radioactive gases is by counter-current diffusion.

Using time-dependent release rates, we calculate advective-diffusive transport of the released ^{14}C in air flowing through surrounding rock. Transport of $^{14}\text{CO}_2$ is retarded by absorption of CO_2 in vadose water. We calculate $^{14}\text{CO}_2$ concentrations in the gas phase as it moves towards the ground surface, $^{14}\text{CO}_2$ release rate and above-ground $^{14}\text{CO}_2$ concentrations when diluted by atmospheric dispersion. The dose to a maximally exposed individual is very low, approximately 1% of background, for the peak release at a gas Darcy velocity of 0.04 m/a.

P7.4

- WASTE STORAGE IN THE VADOSE ZONE AFFECTED BY WATER VAPOR CONDENSATION AND LEACHING.** J. W. Cary, G. W. Gee, G. A. Whyatt, Pacific Northwest Laboratory, Richland, WA.

One of the major concerns associated with waste storage in the vadose zone is that toxic materials may somehow be leached and transported by advecting water down to the water table and reach the accessible environment through either a well or discharge to a river. Consequently care is taken to provide barriers over and around the storage sites to reduce contact between advecting water and the buried waste form. In some cases it is important to consider the intrusion of water vapor as well as water in the liquid phase. Water vapor diffuses through porous material along vapor pressure gradients. A slightly lower temperature, or the presence of water soluble components in the waste favors water condensation resulting in leaching of the waste form and advection of water soluble components to the water table. A simple analysis is presented which allows one to estimate the rate of vapor condensation as a function of waste composition and back fill material. An example using a cementitious waste form surrounded by concrete and gravel layers is presented. The use of thermal gradients to offset condensation effects of water soluble components in the waste form is discussed. Thermal gradients may be controlled by design factors that alter the atmospheric energy exchange across the soil surface, or that interrupt the geothermal heat field.

Contribution from the Pacific Northwest Laboratory, operated for DOE by Battelle Memorial Institute, Richland, WA 99352. This research was funded by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

P7.5

- AQUEOUS DIFFUSION IN UNSATURATED MATERIALS.** James L. Conca, WSU Tri-Cities; and Judith Wright, Pacific Northwest Laboratories, Richland, WA 99352.

Aqueous diffusion coefficients (D) were experimentally

determined in a variety of unsaturated gravel, soil and whole rock that are potential backfill and host rock materials. The electrical conductivity was measured on the samples after hydraulic steady-state was achieved, and the diffusion coefficient calculated using the Nernst-Einstein equation. D in several soils from the Hanford Site ranged from $2.5 \times 10^{-10} \text{ m}^2/\text{sec}$ ($2.5 \times 10^{-6} \text{ cm}^2/\text{sec}$) at a volumetric water content of 30.7%, to $2.4 \times 10^{-12} \text{ m}^2/\text{sec}$ ($2.4 \times 10^{-8} \text{ cm}^2/\text{sec}$) at a volumetric water content of 5.5%. D in four types of angular gravel ranged from $2.7 \times 10^{-11} \text{ m}^2/\text{sec}$ ($2.7 \times 10^{-7} \text{ cm}^2/\text{sec}$) for a 6.3-9.5mm angular tuff gravel at a volumetric water content of 7.6%, to $1.6 \times 10^{-13} \text{ m}^2/\text{sec}$ ($1.6 \times 10^{-9} \text{ cm}^2/\text{sec}$) in a 6.3-9.5mm angular granitic gravel at a volumetric water content of 0.50%. D in two samples of Calico Hills tuff were $1.51 \times 10^{-10} \text{ m}^2/\text{sec}$ ($1.51 \times 10^{-6} \text{ cm}^2/\text{sec}$) and $1.66 \times 10^{-11} \text{ m}^2/\text{sec}$ ($1.66 \times 10^{-7} \text{ cm}^2/\text{sec}$) at volumetric water contents of 30.9% and 29.3%, respectively. Variations in D result primarily from differences in water content which depend mainly on particle size/aperture distribution, and only secondarily on material type unless the surfaces are hydrophobic.

P7.6

REFORMULATION OF A SYSTEM PERFORMANCE ASSESSMENT PROCESS

K. V. Dornuth
AECI Research
Whiteshell Laboratories
Pinawa, Manitoba, Canada

The assessment of the long-term performance of a nuclear waste disposal facility, based on criteria of public safety, requires integration of information developed by several different groups with a wide range of disciplines and analytical methods. The assessment process must ensure that available knowledge and data from the field and laboratory are consistently and reliably incorporated in the analysis to meet the requirements of the site selection team, the designers, and the regulators. A complete demonstration of the performance assessment process is being prepared for a hypothetical used fuel disposal vault in plutonic rock. The analysis uses site-specific information from a field research area in the Canadian Shield, particular specifications for engineered system components, vault characteristics based on a comprehensive conceptual engineering study, and biosphere characteristics typical of the Shield.

P7.7

PRELIMINARY MODEL OF REPOSITORY CHEMISTRY FOR THE WASTE ISOLATION PILOT PLANT. L. H. Brush, Sandia National Laboratories, Albuquerque, NM; D. Grbic-Galic, Stanford University, Stanford, CA; D. T. Reed, Argonne National Laboratory, Argonne, IL; X. Tong, Stanford University; R. H. Vreeland, West Chester University, West Chester, PA, and R. E. Westerman, Pacific Northwest Laboratory, Richland, WA.

The design-basis, defense-related, transuranic (TRU) waste to be placed in the Waste Isolation Pilot Plant (WIPP) could produce as much as 1,500 moles of gas per drum of waste. Gas production could pressurize the repository to 150 atm (lithostatic pressure), and perhaps higher.

Anoxic corrosion of metals and microbial degradation of cellulose are the processes of greatest concern, but radiolysis could also be important. Several proposed backfill additives may remove or prevent the production of some of the expected gases. We describe these processes, laboratory and modeling studies to quantify them, and preliminary results of these studies.

Because of the heterogeneous nature of design-basis waste, the Eh and pH of any brine present in WIPP disposal rooms

could vary significantly over short distances after reacting with the waste.

The WIPP Project is investigating gas production and its consequences, and is considering engineered alternatives, including reprocessing the waste, to reduce gas production rates and/or potentials. Reprocessing would also reduce the range of Eh and pH expected for the repository.

P7.8

ON THE PROBLEM OF CONSISTENCY OF CHEMICAL THERMODYNAMIC DATA BASES. Hans WANNER, OECD Nuclear Energy Agency, Data Bank, 91191 Gif-sur-Yvette, France.

There has been considerable concern in recent years about the fact that thermodynamic data bases used to calculate the behaviour of radionuclides in the geosphere have been found to lack consistency. In some cases, efforts have been taken to improve to level of consistency by applying basic thermodynamic laws to recalculate equilibrium constants, enthalpies or entropies. It appears obvious that thermodynamic data bases must conform to the laws of chemical thermodynamics; however, this is no guarantee for a high quality of the data presented neither for the compatibility of the data with experimental evidence. The intention of this paper is to present the different levels of consistency that should be considered when producing a high quality thermodynamic data base.

1. Consistency with the fundamental laws of thermodynamics.
2. Consistency with auxiliary data: The procedure that leads to the evaluation of chemical thermodynamic data from experimental measurements often requires the use of auxiliary data. Among these are the protonation constants of ligands, redox potentials, or formation constants of additional species that may be present in the solutions investigated.
3. Consistency within a chemical model: Measurements on complex aqueous systems can often be interpreted with different chemical models. Unless there is compelling evidence in favour of one of the models, it does not really matter which model is chosen. However, the use of one model excludes the use of the other.
4. Consistency in the data correction procedures: A generally applicable data base contains values that refer to standard conditions and to a reference temperature. Auxiliary data used for the extrapolation of experimental data to standard and reference conditions, must be applied together with the thermodynamic parameters of a standard state data base. Otherwise, the application of even high quality data bases may lead to incorrect results.

Theoretical discussions and examples for each point mentioned above will be provided in the full paper.

P7.9

QUANTIFYING THE EFFECTS OF UNCERTAINTY IN THERMODYNAMIC MODELLING. J.M. Bealby, A.Dawes and D.Reed, WS Atkins Engineering Sciences, Epsom, UK

The use of predictive computer-based models to supplement field and laboratory experimentation is well established in post-closure risk assessment methodology. Such models greatly aid interpretation of complex disposal systems and can provide useful data in situations where direct measurement is impractical. However the assignment of confidence to the results of modelling is a difficult task, owing to the uncertainties inherent throughout the modelling procedure. In the derivation of results from chemical equilibrium simulations for example, a series of discrete steps can be traced, each with its own associated degree of uncertainty. This series includes: source experimental data for fundamental thermodynamic constants, bias introduced during database compilation, selective use of auxiliary information during modelling or data transformation, the modelling process itself and "geochemical judgement" exercised on the results.

This paper describes attempts made to identify, isolate and, where possible, quantify the effects of the above uncertainties on the results of

speciation/solubility calculations. The approach is demonstrated through a case study of direct relevance to risk assessment of deep disposal sites in the United Kingdom.

P7.10

A NOVEL CONCEPTUAL MODEL FOR THE FLOW AND TRANSPORT IN FRACTURED ROCK. Aimo Hautajärvi, Veikko Taivassalo and Seppo Vuori, Technical Research Centre of Finland, Nuclear Engineering Laboratory, Helsinki, Finland

Consistent and realistic interpretation of hydraulic and tracer test data from a field experiment has been attempted. Reasonably good results were obtained by applying novel modeling approach.

Strongly varying fracture aperture guides the water to flow preferentially in some parts of the fracture plane, in the so called channels. Flow velocity differences in different parts of channels turns out to affect also the break-through curves essentially. The molecular diffusion across the flow field smooths out the velocity differences of the migrating solute and the dispersion diminishes in confined channels and there exists an instationary phase of dispersion.

In the developed hydraulic model the channeling degree together with the aperture variation along the channel is taken into account as a factor which is the ratio of the aperture from transmissivity measurements and the aperture from a tracer test. The transport model takes into account the coupling of molecular diffusion and advection in a velocity field. The velocity field is approximated by a linear field where velocity increases from zero to the maximum velocity over a characteristic width. Each channel has a specific dispersion behavior and the total route dispersion is obtained by summing the contribution from individual channels.

The developed concept and models have been applied to predict and interpret field experiments aimed to investigate transport over long distances in highly conductive fracture zones. The tests belong to the case 5 of the INTRAVAL project and experiments have been performed at the Finnsjön research area in Sweden.

P8.1

CONTAINER MATERIALS FOR HIGH-LEVEL NUCLEAR WASTE AT THE PROPOSED YUCCA MOUNTAIN SITE. R. Daniel McCright, Lawrence Livermore National Laboratory, Livermore, CA 94550.

Candidate container materials for high-level nuclear waste packages to be emplaced at the proposed Yucca Mountain repository site are being considered for their long-term resistance to corrosion, oxidation, embrittlement, and other kinds of degradation. Selection criteria have been established, and a method has been developed for recommending a material for advanced container design activities. An extensive compilation of the degradation phenomena for six candidate materials is complete, and further studies have begun on the degradation modes affecting additional candidate materials. Phenomenological models for predicting container degradation rates are being advanced for environmental conditions applicable to Yucca Mountain. An experimental program is underway to evaluate the susceptibility of container materials to localized corrosion, stress corrosion cracking, and enhancement of corrosion and oxidation attack by gamma radiation. Initial evaluations of container fabrication and welding processes have identified some processes that appear to alleviate some long-term corrosion susceptibility concerns.

P8.2

REPASSIVATION METHOD TO PREDICT LONG TERM INTEGRITY OF LOW ALLOY TITANIUM USED FOR NUCLEAR WASTE PACKAGE. Shigeo Tsujikawa and Yoichi Kojima, The University of Tokyo, Tokyo, JAPAN.

Long term corrosion resistance is evaluated for G-2 and G-12 titanium as a candidate of the high-level nuclear waste packages.

The repassivation potential for crevice corrosion E_p , in comparison with the well known spontaneous potential, E_{sp} , of a metal passivated in given environment, allows conclusions to be drawn whether it performs "permanent" or does not.

This repassivation method is extended to determine critical conditions in terms of NaCl concentration and temperature for specimens kept at a electrode potential which is more noble than E_p and is included in E_{sp} ranges.

Thus obtained NaCl concentration - temperature - crevice corrosion - map could predict critical conditions for the titanium used in geologic formations.

P8.3

HYDROGEN EVOLUTION FROM CORROSION OF IRON AND STEEL IN INTERMEDIATE LEVEL WASTE REPOSITORIES.

R. Grauer, Paul Scherrer Institute, Villigen PSI, Switzerland; B. Knecht, Nagra, Baden, Switzerland; P. Kreis and J. P. Simpson, Sulzer Innotec Ltd, Winterthur, Switzerland.

H_2 evolution is an important issue in the design and safety assessment of repositories for low and intermediate level waste. The gas evolved is expected to arise mainly from the anaerobic corrosion of steel (in the waste itself, as waste package and in the form of rebar) in the cementitious environment of the repository near-field. A review of the literature shows that an upper limit for the hydrogen evolution from corrosion under these conditions is $200 \text{ mmol m}^{-2} \text{ a}^{-1}$ (general corrosion rate below $1 \mu\text{m a}^{-1}$) at pH values above 12, steel being in the stable passive state at all electrode potentials within the stability domain of water. Because the actual values of the hydrogen evolution rate are expected to be at least an order of magnitude lower than this upper limit, direct measurements of the hydrogen evolved were carried out in closed cells in alkaline (NaOH, model cement porewaters) as well as other environments with a sensitivity better than $0.2 \text{ mmol m}^{-2} \text{ a}^{-1}$ for durations of several thousand hours at a temperature of 22°C .

The H_2 evolution rate was below $10 \text{ mmol}(H_2)\text{m}^{-2}\text{a}^{-1}$ in the alkaline environments considered at times of more than 300 h; it was below the detection limit for a model porewater characteristic of a relatively fresh cement, decreasing with time to approx. $2 \text{ mmol}(H_2)\text{m}^{-2}\text{a}^{-1}$ for a 0.1 mol/l NaOH solution at 6000 h and increasing with time to $2 \text{ mmol}(H_2)\text{m}^{-2}\text{a}^{-1}$ at 9000 h for a model cement porewater characteristic of an aged cement, demonstrating that it cannot be assumed that the hydrogen evolution rate will decrease in anaerobic environments. In a slightly alkaline chloride environment the rate was in the range 5 to $10 \text{ mmol}(H_2)\text{m}^{-2}\text{a}^{-1}$ at times between 5000 and 8000 h.

The hydrogen evolution rates observed are of such a magnitude that they cannot be neglected in the design and safety analysis of low/intermediate level waste repositories.

P8.4

ENVIRONMENTAL EFFECTS ON LOCALIZED CORROSION OF HIGH LEVEL NUCLEAR WASTE CONTAINER MATERIALS. Gustavo Cragnolino, Narasim Sridhar, Center for Nuclear Waste Regulatory Analyses, SWRI, San Antonio, TX; and Walter J. Machowski, Southwest Research Institute, San Antonio, TX.

Localized corrosion, including pitting and crevice corrosion, is one of the most important modes of degradation of the high level nuclear waste containers used for

long-term geologic disposal. In attempting to predict the performance of the container materials in a natural environment that varies with time, it is essential to understand the effects of environmental variables on localized corrosion quantitatively. This quantitative understanding will also enable a rational technique for extrapolation of data generated in aggressive, laboratory environments to less aggressive natural environments. Finally, it is also essential to evaluate the validity of parameters generated from laboratory testing for long-term prediction.

This paper presents pitting data from electrochemical polarization tests on the effect of environmental variables: Cl⁻, F⁻, NO₃⁻, SO₄²⁻, and temperature. A 2-level, full factorial experimental design is used to evaluate interaction between variables. The parameters used to assess pitting corrosion are pitting and repassivation potentials, and the difference between the two. The applicability of repassivation potentials to predict long-term behavior is also examined. The three alloys studied in this work include AISI 304L stainless steel, Incoloy[®] alloy 825, and Hastelloy[®] alloy C-22.

8 - Incoloy is a registered trademark of Inco Alloys International
Hastelloy is a registered trademark of Haynes International Inc.

P8.5

THE CRITICAL CONDITION FOR THE INITIATION OF LOCALIZED CORROSION OF MILD STEEL USED FOR NUCLEAR WASTE PACKAGE. Gen Nakayama and Masatsune Akashi, Research Institute, Ishikawajima-Harima Heavy Industries Co., Ltd., Tokyo, JAPAN

The general corrosion rate of mild steel is so small in neutral water environments that the appropriate corrosion allowance requirement can solve the practical problem. In alkaline water environments, however, mild steels can passivate themselves and often undergo the localized corrosion, such as pitting corrosion, crevice corrosion, etc., as stainless steels do in neutral water environments.

This paper describes a study of localized corrosion behavior of the mild steel, for assessing the long-term performance of high-level nuclear waste package in the geological disposal situations. The critical potentials for pitting and crevice corrosion and the critical pH for general corrosion-passivation transition were demonstrated for mild steel specimens in neutral and alkaline water environments. Effects of temperature, pH and chloride and other anion concentrations on the critical potentials as well as the critical pH were discussed. The initiation and propagation behavior of crevice corrosion was also analyzed under potentiostatic conditions.

It is concluded that the mild steels can undergo crevice corrosion even in the immunity region for pitting corrosion and that it is consequently undesirable for the mild steel to be used in the pH region above the critical pH.

P8.6

CORROSION PRODUCTS AND MECHANISMS IN LONG-TERM CORROSION OF COPPER ALLOYS. M. B. McNeil, Naval Coastal Systems Center, Panama City, FL 32407; and B.J. Little, Naval Oceanographic and Atmospheric Research Laboratory, NRTL, MS 39529

Copper and copper alloys are frequently used for service under conditions where short-term testing indicates that they should be adequately resistant to corrosion. In some cases involving

long-term survival the metals degrade by mechanisms which have not been replicated in the laboratory. These mechanisms, and specially those which are microbiologically controlled, are reviewed from the thermodynamic and kinetic points of view. Comparisons are made to related phenomena in high-nickel and high-iron alloys.

P8.7

EFFECT OF COMPACTED BENTONITE ON THE CORROSION BEHAVIOR OF CARBON STEEL AS A GEOLOGICAL DISPOSAL OVERPACK MATERIAL. A. Honda, T. Teshima, K. Tsurudome, H. Ishikawa, Y. Yusa and N. Sasaki, Power Reactor & Nuclear Fuel Development Co., Tokai-mura Ibaraki, 319-11, Japan.

Carbon steel is one of candidate overpack materials for high-level waste disposal in Japan. The corrosion rate of carbon steel in compacted bentonite is considered to be depend on the diffusion behavior of corrosive materials and corrosion products. Thus the corrosion rate in compacted bentonite is expected to be low even in the atmospheric condition.

Immersion tests of carbon steel in compacted bentonite were carried out under atmospheric condition. Carbon steel specimens were immersed in a compacted bentonite (dry density=0.8-1.6 g/cm³) mixed with aqueous solution. Mean corrosion rate and corrosion products were evaluated. Immersion tests in aqueous solution and in bentonite powder mixed with solution (bentonite slurry) were also conducted for comparison.

Mean corrosion rate in a compacted bentonite was lower than those in aqueous solution or in bentonite slurry. The corrosion rate in compacted bentonite increased as the density of bentonite decreased. No significant difference was observed among the corrosion rates in compacted bentonite with some kinds of aqueous solutions (chloride, sulfate, carbonate etc.). Prediction of general corrosion rate for carbon steel was also carried out on the basis of diffusion behavior of dissolved oxygen in bentonite.

P8.8

CORROSION OF COPPER-BASED MATERIALS IN IRRADIATED HIGH-HUMIDITY AIR SYSTEMS. D. T. Reed, Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439; and R. A. Van Konyenburg, Lawrence Livermore National Laboratory, Livermore, CA 94550.

The atmospheric corrosion of oxygen-free copper, 70/30 copper nickel, and aluminum bronze was investigated in an irradiated moist air environment. Experiments were performed in both dry and 40-50% RH air at 90° and 150°C. Corrosion rates were determined based on weight loss measurements. Corrosion products observed were analyzed and related to the irradiation environment. The experiments performed were sponsored by the Yucca Mountain Project and are needed to evaluate material performance in the expected environment.

P8.9

Stainless Steel Welds in Containers of Nuclear Waste. T.M. Devine, Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA

Welds of 308 stainless steel typically possess a two-phase microstructure which is thought responsible for their generally good resistance to sensitization. Actually, depending on the composition of the weld one of three markedly different weld microstructures will occur. Unfortunately, only one of these

microstructures is suitable for use in containers of nuclear waste. The other 2 types of microstructures are undesirable since one is susceptible to sensitization and the other to mechanical embrittlement. This paper describes the influence of weld microstructures on sensitization and embrittlement and identifies a compositional range that optimizes the performance of the weld.

P9.1

PARAMETERS OF GLASS DISSOLUTION IN INTEGRATED
EMS. Eliane Y. Verna and Nicole Godon, CEA, GEN VALRHO,
BP 171, 30205 Bagnols-sur-Cèze Cedex, France

Numerous leaching studies have been conducted during the last ten years to identify the basic mechanisms of glass corrosion in order to develop long-term behavior models. Considering the multiple parameters affecting a geological repository, however, integrated experiments simulating all the actual disposal conditions are necessary to check that all the key parameters are taken into account, to detect possible synergy effects and to qualify the model under realistic conditions.

Integral test mockups referred to as "TAV" experiments have been used in France to simulate several storage scenarios at 90°C under a pressure of 10 MPa. Simulated geological water is allowed to reach equilibrium with the test medium in a conditioning vessel before leaching the glass with a pseudo flow rate corresponding to samples of a low cm³ taken at 2 month intervals. The principal findings have been the following:

- Glass alteration is similar in French granite or salt, but much greater in clay.
- The backfilling material has a significant effect. Most clays constitute silica sinks and maintain a high long-term alteration rate. However, some highly siliceous bentonites do not accelerate glass alteration.
- In a granite medium at 90°C, the canister materials (NS 24, Hastelloy or AZS ceramic) are only slightly altered and have a minor effect on glass corrosion.
- The effects of fracturation of the glass block depend on the environmental conditions. In a granite medium where saturation conditions are quickly reached, the dissolved glass quantity increases by only a factor of 1.4 when the exchange surface area is multiplied by 10.
- Radioactive experiments with doped glass specimens have shown that a radiolysis does not modify the bulk glass dissolution rate, but that environmental materials do affect the actinide retention factor in the surface gel layer.
- Finally, an experiment has been in progress for over 7 years in a granite medium. After 3 years the corrosion rate dropped to about 2×10^{-3} g m⁻² d⁻¹ and depends only on the flow rate imposed by the sampling intervals.

P9.2

NEAR-FIELD PERFORMANCE OF THE ADVANCED COLD
PROCESS CANISTER. J. O. Wernberg, SKB, Stockholm,
Sweden; and J.-P. Salo, TVO, Helsinki, Finland.

A near-field performance evaluation of a cold process canister for spent fuel disposal has been performed jointly by TVO and SKB. The canister, originally proposed by TVO, consists of an inner steel vessel as a load bearing element, with an outer corrosion shield of copper. In the analysis, internal (i.e. corrosion processes from the inside of the canister) as well as external processes (mechanical and chemical) have been considered both prior to and after canister breach.

The major conclusions for the evaluation are:

Internal processes cannot cause the canister breach under foreseen conditions, i.e. localized corrosion for the steel or copper canisters can be dismissed as a failure mechanism.

The evaluation of the effects of processes outside the canister indicate that there is no rapid mechanism to endanger the integrity of the canister. Consequently the service life of the canister will be several million years. This factor will ensure the safety of the concept.

Evaluation of post-failure behaviour was carried out. These analyses were focussed on low probability phenomena from faults in canisters.

P9.3

THE ROLE OF LABORATORY ANALOG EXPERIMENTS IN ASSESSING
THE PERFORMANCE OF WASTE PACKAGE MATERIALS.
J. C. Cunnane and J. K. Bates, Argonne National
Laboratory, Argonne, IL 60439.

There is an immediate need to develop an approach for credible assessment of waste package materials in an unsaturated repository environment. In this paper, which is based on a study conducted for the Repository Technology Program, the roles of laboratory analog experiments (i.e., laboratory simulation) and modeling (mathematical/numerical simulation) in satisfying the near-term needs are critically reviewed. Earlier laboratory analog experiments in a variety of saturated repository environments are reviewed and the results are interpreted in terms of their implications for future work of this type. In addition, some unanticipated and significant results for analog testing of borosilicate glass and UO₂ in unsaturated environments are presented. These include evidence for fluid film formation on glass surfaces in isothermal humid environments, accelerated reaction rates for the large SA/V ratios involved, spallation of the films and mobilization of radionuclides as solutes and colloids. These observations are interpreted in terms of current understanding of waste form reactions and the colligative properties of the fluid films that can form on the waste surface. The implications for the near-field scenarios that should be considered in waste package performance assessments are discussed. Also, conclusions are drawn concerning the role of analog testing at higher levels of system aggregation and the credibility of the results of waste package performance assessment modeling at the current stage of its evolution.

P9.4

ACTINIDE TRANSPORT IN TOPOPAH SPRING TUFF: PORE SIZE,
PARTICLE SIZE, AND DIFFUSION. Marilyn Bushholz ten Brink, Douglas
L. Phinney, and David K. Smith, Earth Sciences Department, Lawrence Livermore
National Laboratory, L202, P.O. Box 808, Livermore, Ca. 94550.

Diffusive transport rates for aqueous species in a porous medium are a function of sorption, molecular diffusion, and sample tortuosity. Single constant values for these parameters result in transport that can be modelled as Fickian diffusion with one diffusion coefficient. With heterogeneous natural samples, however, an understanding of the effect of multiple transport paths and sorption mechanisms is particularly important since a small amount of radioisotope traveling via a faster than anticipated transport path may invalidate the predictions of transport codes which assume average behavior.

Static-diffusion experiments (8 hrs) using aqueous ²³⁸U tracer in tuff saturated with groundwater indicated that U transport was faster in regions of greater porosity and that apparent diffusion coefficient values ranged from 10^{-12} to 10^{-18} cm²/s, depending on the scale (mm or μ m) over which concentration gradients were measured in the heterogeneous Topopah Spring tuff¹. If a significant fraction of actinides in high-level waste are released to the environment in forms that do not sorb to the matrix, they may be similarly transported along fast paths in porous regions of the tuff. To test this, aqueous diffusion rates in tuff were measured for ²³⁸U and ²³⁹Pu leached from doped glass for 183 days in groundwater (90°C, 80 ppb ²³⁸U, 20 ppb ²³⁹Pu). Actinide concentrations were measured with secondary ion mass spectrometry at 100 μ m steps (total 7 mm) from the interior to the exterior of a leachate-containing tuff vessel. ²³⁸U concentrations were above background (20 ppb) only within 200 μ m of the surface and ²³⁹Pu was below the detection limit (20ppm). This suggests that, for these conditions, transport along faster paths is a very small component of the bulk transport; however, additional measurements in more porous regions of the tuff vessel and within 100 μ m of the surface are needed for confirmation. The influence of heterogeneous porosity and colloidal species on actinide transport rates in these experiments will also be discussed.

¹Bushholz ten Brink, M.R., D. Phinney, K.D. McKeegan and V.M. Ovarby, 1989. Uranium transport in Topopah Spring Tuff: multiple diffusion paths. "Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere", Nov 6-10, 1989, Monterey, Calif.

Work performed under the auspices of the U.S. Dept. of Energy Office of Civilian Waste Management, Yucca Mountain Project Office, by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

P9.5
GAS FORMATION IN A HLW AND ILW REPOSITORY. EVALUATION AND MODELLING OF THE PRODUCTION RATES AND CONSEQUENCES ON THE SAFETY OF THE REPOSITORY. Francois Besous, CEA/IPSN/DAS, Fontenay-aux-Roses, France; and Sylvie Voiris, CEA/ANDRA, Fontenay-aux-Roses, France.

Present trends for disposal of HL and radioactive wastes have lead IPSN and ANDRA to estimate the hazards associated to gas formation in deep repositories. For this purpose, the main gas production mechanisms have been determined. Those are:

- Steel containers corrosion
- Radiolysis of conditioned waste matrix and water from wastes and near field
- Microbiological decomposition for ILW
- Heat generation (for HLW)

Production rates for each mechanism and type of waste as well as overall gas formation have been estimated, using calculation, experiments and literature review.

An attempt to model the gas pressure evolution and spreading into repository and near field has also been performed, considering the above mentioned formation processes and following transport mechanisms:

- gas dissolution and diffusion through near field and host rock
- dissolved gas dispersion by water convection
- two phase flow

First results for ILW and HLW will be given.

P9.6

PARAMETRIC SIMULATION OF ROCK SALT BEHAVIOUR RESULTING FROM DISPOSAL OF HIGH LEVEL RADIOACTIVE WASTE. D CARMELLE, MT GAUDEZ CEA SACLAY FRANCE, J MONIG GSF BRAUNSCHWEIG GERMANY, G OUZOUNIAN ANDRA/DESI FONTENAY AUX ROSES FRANCE and G SIMONET CEA FAR IPSN/DSMN FONTENAY AUX ROSES FRANCE.

An investigation of liberation and generation of gases from rock salt due to heat and gamma irradiation is undertaken in order to obtain some of the data which are needed for the development of long term safety concept for the disposal of high level waste in rock salt.

Our work is concerned with the influence of various parameters on the gas production, e.g. composition and grain size of the salt, total absorbed dose, dose rate, temperature and gas atmosphere. Some of these parameters have not been studied previously in detail.

The original gamma irradiator employing spent fuel elements and allowing to expose samples at temperatures up to 250°C will be described. Experimental results from some 150 experiments will be given. The two major gases found were CO₂, N₂O. CO, H₂, CH₄, Hydrocarbons, Cl₂, HCl, SO₂ were also detected. The dependence of the gas yields on the various parameters will be presented and discussed.

P9.7

EFFECTS OF ALPHA RADIATION ON UNSATURATED REPOSITORY ENVIRONMENT. E. Young and John K. Bates, Argonne National Laboratory, Argonne, IL 60439.

Radiation can effect glass performance in a repository site either by altering the glass structure and

performance characteristics or by interacting with the air and water vapor producing radiolysis products. Most studies of radiation effects on nuclear waste glass performance either have investigated the interaction of radiation with the solid glass or have assumed saturated aqueous conditions, i.e., the glass is covered with the leachate. These conditions are not representative of the geologically unsaturated environment anticipated at the Yucca Mountain repository site.

This study was carried out to determine the interaction of gamma and alpha radiation with water vapor in air. The gamma and alpha studies were carried out separately because gamma will be the primary type of radiation in the early years of the repository lifetime, and alpha will be the primary type in the later years. The extent of nitric and organic acid formation will be described. Evidence suggests that these acids are concentrated in the water films on the solid surfaces rather than transferred to the bulk water.

Work supported by the U.S. Department of Energy, ...

P10.1

THE EFFECTS OF MOISTURE REDISTRIBUTION AND TEMPERATURE ON THE LOAD-BEARING CAPABILITY OF A CLAY-BASED BACKFILL. S.C.H. Cheung and M.N. Gray, Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Est., Pinawa, Manitoba, Canada ROE 1L0; and R.N. Yong and A.M.O. Mohamed, Geotechnical Research Centre, McGill University, Montreal, Quebec, Canada H3A 2K6

To predict the mechanical performance of the backfill in a nuclear fuel waste disposal vault, the effects of temperature and moisture content on the backfill load-deformation characteristics must be known. Modified California Bearing Ratio (CBR) tests were used to obtain these data. The results show that the load-bearing capability of the backfill decreases with increasing water content and temperature. The load-deformation characteristics of the backfill are significantly affected by the distribution of water in the material, but the backfill should retain sufficient capacity to satisfy its mechanical design function.

P10.2

COMPRESSIVE BEHAVIOUR OF CLAY-BASED BACKFILL UNDER LARGE HYDRAULIC LOADING. H.T. Chan and K.C. Lau, Ontario Hydro, Civil Research Department, Ontario, Toronto, Canada M8Z 5S4.

In the proposed Canadian design of an underground repository for nuclear spent fuel, it is generally assumed that the shafts would be backfilled with a compacted clay-based material, probably a mixture of clay and/or crushed granite. At the closure of the disposal vault, the clay-based backfill may be subjected to a large hydraulic loading due to the disconnection of the dewatering system. As a result, a small annulus gap between the backfill and the wall of the shaft may develop and form a possible short circuit path for the migration of radionuclides from the vault to the biosphere. The development of this gap depends to a large extent on the compression characteristics of the backfill. The magnitude of this gap and the rate of self-healing of this gap are also a function of the characteristics of the backfill mix.

In order to study the behaviour of clay-based backfill mixes subjected to a large hydraulic loading, a high-pressure compression cell, with a maximum applied pressure of 7 MPa, was designed and constructed for performing compression tests on swelling and non-swelling compacted clay-based specimens. On the basis of preliminary compression and swelling test data, it was concluded that for a non-swelling clay the amount of compressive deformation caused by the hydraulic loading exceeded the

amount of elastic rebound. However, for a swelling clay (ie. 25% bentonite in the compacted specimen), the rebound due to elastic deformation and the swelling of the clay was greater than the compression.

PI0.3

APPLICATION OF ELASTO-PLASTIC MODEL TO MECHANICAL AND HYDRAULIC BEHAVIOR OF BUFFER MATERIAL UNDER WATER UPTAKE IN A REPOSITORY. T.FUJITA, K.HARADA, Y.YUSA, N.SASAKI, Power Reactor & Nuclear Fuel Development Co., Tokai-mura, Ibaraki 319-11, Japan.

Mechanical and hydraulic behavior of buffer material during water uptake in a repository is a major issue from the viewpoint of mechanical stability of engineered barriers. Coupled thermal-hydraulic-mechanical model of compacted bentonite has been developed to analyse mechanical behavior of engineered barriers during water uptake. This study presents the result of hydraulic-mechanical modelling and the simulations carried out on an engineered barrier system under water uptake.

Compacted bentonite swells with water uptake and builds up swelling pressure under restraint condition. The model used was as follows: (1) The water uptake was modeled as hydraulic diffusion. (2) Elasto-plastic model was applied to swelling behavior and deformation of compacted bentonite. (3) The water diffusivity and swelling coefficient were given as a function of water content, dry density and confining pressure, on the result of swelling tests of KUNIGEL-VI bentonite which contains 50 % montmorillonite. Using this model, the simulations were carried out on the case of water uptake from the whole surface of crystalline and sedimentary rock and from partial surface of these rocks.

The results were: (1) The hydraulic and mechanical behavior of compacted bentonite could be described by this model. (2) The distribution of the water content depends on the water access conditions. (3) The deformation of buffer material and the displacement of overpack were very small in the both cases.

PI0.4

HYGRO-THERMAL PERFORMANCE OF AN ENGINEERED CLAY BARRIER. A.P.S. Selvadurai, Department of Civil Engineering, Carleton University, Ottawa, Ontario, Canada, K1S 5B6.

This paper presents the results of a series of laboratory experiments which were conducted to establish the heat-induced moisture movement in a bentonitic clay buffer region. The buffer material is proposed as an engineered barrier which will isolate a heat emitting high level nuclear waste container from the emplacement borehole located in a deep rock repository. In the laboratory simulations, the borehole is located in a block of granitic rock and the moisture movement is induced by a cylindrical heater which is located along the axis of the compacted buffer. A series of thermocouple arrays located within the granite block monitor the time dependent progress of heat conduction within the granite rock. The moisture distribution within the buffer is determined by moisture content sampling at the termination of the test. The experimental results illustrate the time-dependent distribution of temperatures within the rock mass and the residual moisture distribution at the termination of the experiment. The experiments also assess the influence of moisture influx and an impervious barriers on the heat and moisture movement within the rock and the buffer material respectively.

PI0.5

DEVELOPMENTS FOR IN SITU TESTS ON COMPACTED BENTONITE BASED BUFFER MATERIALS. B.H. Kjartanson and M.N. Gray, AECL Research, Pinawa, Manitoba, Canada and B. Mullis, ERA Consultants, Edmonton, Alberta, Canada.

Full-scale buffer-container experiments will be conducted at AECL's Underground Research Laboratory (URL). These tests are intended to confirm that bentonite-based buffer can be compacted in situ to the densities required by the Canadian nuclear waste disposal concept and that the heat and moisture transfer properties of the buffer at full disposal-vault scale and under in situ boundary conditions can be reasonably predicted from small-scale surface laboratory measurements. This paper describes progress made towards the implementation of these experiments.

Results from tests in a large-scale emplacement borehole simulator show that the required buffer density can be attained using a specially developed compaction device and that instruments to measure temperature, total pressure, pore-water pressure and moisture content can withstand the compaction forces on the buffer. Ancillary tests have demonstrated that these instruments should have the durability needed for the year-long in situ high-temperature tests. The experiment room has been excavated in the URL and equipped with all the necessary facilities. Water inflow into the test borehole is so small as to be insignificant over the test period and the major effect expected in the buffer is moisture redistribution under the temperature gradients from the heater to the rock.

The developments in technology for the Buffer/Container experiments continue to show that the Canadian scheme for the construction and operation of a nuclear fuel-waste disposal vault is feasible. Further development and optimization of these technologies are required for viable implementation of the scheme at full vault scale.