SYMPOSIUM CC

Nuclear Waste Containment Materials

April 19, 2001

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*Invited paper
SESSION CC1: CORROSION AND OTHER CHEMICAL ASPECTS
Chair: Daniel Yerkes
Thursday Morning, April 19, 2011
Golden Gate C1 (Merrit)

8:30 AM CC1.1
NAIVE COMPETITION BETWEEN CATHODES IN A TWO-ELECTRODE AQUEOUS SYSTEM WITH A NICKEL-CONTAINING MEMBRANE
J. A. McClelland, A. P. Sayer, and J. G. G. Smith
University of Manchester Institute of Science and Technology, Manchester, England

8:45 AM CC1.2
A CORROSION STUDY OF ARCHAEOLOGICAL FERROUS ALLOYS FROM THE BASSEY SITES.
University of Exeter, UK

9:00 AM CC1.3
LONG-TERM PASSIVE BEHAVIOR OF ALLOY 22
Osvaldo Pascual, Darrell Dunn, Sean Brossard, and Gustavo Cingolani
Center for Nuclear Waste Regulatory Analyses, San Antonio, TX

9:30 AM CC1.4
APPLICATION OF PASSIVE DURABILITY TO THE DESIGN OF THE OUTER LINING OF A NUCLEAR WASTE CONTAINER
J. A. B. J. de Groot, P. H. M. van den Heuvel, and H. van der Velden
Technische Universiteit Delft, Netherlands

9:45 AM CC1.5
THE INFLUENCE OF NICKEL-MODIFIED FERRITE SECOND PHASE ON THE PASSIVE DURABILITY OF TYPE 304 Stainless Steel
J. A. McClelland, A. P. Sayer, and J. G. G. Smith
University of Manchester Institute of Science and Technology, Manchester, England

10:00 AM CC1.6
THE VERIFICATION OF PASSIVE DURABILITY IN MODEL PLUGS AND GEOMATERIALS
J. A. McClelland, A. P. Sayer, and J. G. G. Smith
University of Manchester Institute of Science and Technology, Manchester, England
10:15 AM CC16
BIOMIMETIC DEVELOPMENT ON IRRADIATED STAINLESS STEEL FUEL CLADDINGS IN A HOT CELL ENVIRONMENT D.F. Brehm, F.F. Roberto, P.J. Pinkerton, INEL, Idaho Falls, ID; S.M. Frank, Argonne National Laboratory-West, Idaho Falls, ID.

The effect of ionizing radiation on biomimetic film formation is a subject of debate in the nuclear waste storage community. Biomimetic film development on the surfaces of spent nuclear fuel (SNF) claddings is essential to establishing whether or not microbial influenced corrosion (MIC) impacts the long term stability of SNF. An experimental study was recently performed which showed microbial biomfilm growth occurring on irradiated Type 304 stainless steel cladding tubes within an analytical hot cell environment. The experiments involved introducing 22 species of bacteria, in a nutrient rich media, to test vessels containing irradiated cladding tube sections. Though the measured dose rate at the surface was rather low, ca. 47 rad/hr, the overall radiation field exceeded 200 rad/hr (gamma and beta radiation). The larger field was formed by placing dislodged irradiated stainless tubes in four flasks at the corners of a square test tube rack housing the test vessels. This arrangement was utilized to simulate the radiation fields associated with fresh spent nuclear fuel. The total dose received by some of the flasks was over the order of 0.5 Mrad over the course of the three month study. The microbes used were originally isolated, cultured and identified from water samples collected from the Idaho National Engineering and Environmental Laboratory (INEEL). During the experiment, microbially influenced corrosion was observed in several test vessels and this microbially influenced corrosion was confirmed. The presence and activity of the microorganisms were determined using a portable probe designed to measure microbial activity. Several controls were maintained to account for microbiological contamination during the entire length of the study. Our observations indicate that biomimetic film does in fact form on the irradiated tubes within the context of this analytical hot cell study. This provides evidence that MIC is a possibility in the storage and permanent disposition of SNF in repository environments.

10:30 AM CC17
BACTERIAL IMPACTS ON ALLOYS 22, A CANDIDATE NUCLEAR WASTE PACKAGING MATERIAL, UNDER SIMULATED REPOSITORY CONDITIONS. Jeanne Henn, Sue Martin, Brett Masterson, David Poe, Lawrence Livermore Laboratory, Livermore, CA.

The U.S. Department of Energy has been charged with assessing the suitability of a potential geologic nuclear waste repository at Yucca Mountain (YM), NV. Microorganisms, both those endogenous to the repository site and those introduced as a result of construction and operational activities, may contribute to the corrosion of metal nuclear waste packaging materials and thereby reduce their useful lifetime as barrier materials. Evaluation of potential Microbiologically Influenced Corrosion (MIC) on candidate waste package materials was undertaken in reactor systems incorporating the primary elements of the repository: YM rock (either non-radioactive or radioactively treated), material coupons, and a continual feed of simulated YM groundwater. Periodically, material coupons were analyzed for chemical and surface characterization. Alloys 22 coupons exposed for up to two years at room temperature in reactor core simulated non-radioactive YM rock demonstrated aeration of scales, with what appear to be underlying areas of corrosion. Coupons exposed for one year under identical but non-aerated conditions demonstrate some corrosive effects, but less so than Alloys 22 incubated under non-aerated conditions for the same time period.

10:45 AM CC18
THE RESISTANCE OF PURE COPPER TO STRESS CORROSION CRACKING IN REPOSITORY ENVIRONMENTS. Bo Rosborg, Rosborg Consulting, Nykoping, SWEDEN; Lars Werme, Svensk Kärnbränslehandlning AB (SKB), Stockholm, SWEDEN.

The risk for stress corrosion cracking of the copper cuvettes in the final repository for high-level radioactive waste in Sweden is low. However, it is a desire to try to elucidate and if possible quantify this minor risk. It is known that stress corrosion cracking of copper occurs in copper (of commercial quality). This is not a very sensational circumstance considering today's knowledge, and does not in any way disqualify copper as a material for the cuvettes. Most materials, if not all, show susceptibility to localized corrosion. The purpose of this work is to assure that these circumstances do not appear in the intended application. It is of course exceedingly difficult to predict life of the order of hundreds of thousands years, in particular concerning such life-limiting phenomena as stress corrosion cracking. Consumption of material is none or minor during the attack, which does not allow material balances to be used to predict life as for general corrosion. Nor give crack growth rate measurements straight off applicability to the problem. Thus, one is referring to the methods and extrapolations. Available information from own and others work will be discussed together with possible methods to estimate the resistance of pure copper to stress corrosion cracking in repository environments. An attempt to rationalise available crack growth rate data will be made. Electrochemically controlled slow strain rate testing of pure copper was performed in a sodium nitrate solution, known to give stress corrosion cracking, and in a synthetic groundwater of pH 9. For reasons of comparison, testing was also performed in air. Whereas the occurrence of stress corrosion cracking as expected was clear in the sodium nitrate solution, it cannot be claimed that stress corrosion cracking has occurred in the synthetic groundwater.

11:00 AM CC19
SULFIDE CORROSION OF COPPER CANISTER FOR SPENT FUEL DISPOSAL. Ivan Escobar, Carmen Silva, Eric Silva, Comision Chilena de Energia Nuclear (CChEN), Santiago, CHILE; Lars Werme, Svensk Kärnbränslehandlning AB (SKB), Stockholm, SWEDEN.

Svensk Kärnbränslehandtering (SKB) has chosen copper as the corrosion barrier material in the waste package for disposal of spent nuclear fuel in Sweden. The reason for this choice is the high resistance of copper to corrosion in oxygen free water over a relatively wide pH range. Some species in the groundwater may upset the stability and dissolved sulfides are one of the most important ones in deep geologic host rocks. In SKB's safety analyses, the extent of the sulfide-induced corrosion has been evaluated from mass balance considerations only. The reason for this is that the sulfide content in Swedish groundwater is generally very low and, also, there are few experimental studies of the kinetics of sulfide corrosion of copper. Recently, the Swedish Nuclear Power Inspectorate (SKI) and Comision Chilena de Energia Nuclear (CChEN) have published electrochemical studies of copper corrosion in sulfide containing water with special relevance for nuclear waste disposal. Studsvik Materials AB (Studsvik) performed the work published by SKI. Both laboratories used similar techniques and the results revealed interesting similarities and differences. In the work performed by CChEN, XPS was also employed. The sulfur corrosion product layers formed after exposing electrochemically reducing potentials for times up to one hour. Most of these data were not included in their previous publication. Studsvik used considerably longer exposure times and used energy dispersive X-ray microprobe analysis in one of the tests to characterize the corrosion products. The work performed in both laboratories used similar techniques and the results revealed interesting similarities and differences. In the work performed by CChEN, XPS was also employed. The sulfur corrosion product layers formed after exposing electrochemically reducing potentials for times up to one hour. Most of these data were not included in their previous publication. Studsvik used considerably longer exposure times and used energy dispersive X-ray microprobe analysis in one of the tests to characterize the corrosion products. The work performed in both laboratories used similar techniques and the results revealed interesting similarities and differences. In the work performed by CChEN, XPS was also employed. The sulfur corrosion product layers formed after exposing electrochemically reducing potentials for times up to one hour. Most of these data were not included in their previous publication. Studsvik used considerably longer exposure times and used energy dispersive X-ray microprobe analysis in one of the tests to characterize the corrosion products. The work performed in both laboratories used similar techniques and the results revealed interesting similarities and differences.
The nitrogen-strengthened, austenitic stainless steel 29C_13N_5.5Mn was designed to have high strength and corrosion resistance. Work in the literature demonstrates that 29-13-5 exhibits good resistance to hydrogen-induced cracking; however results are limited particularly for welds. The objective of this study is to characterize the tension on strength on hydrogen-induced cracking in 29-13-5. Of particular importance are changes in composition that result during electron-beam welding due to evaporation of elements such as nitrogen and manganese. Electron-beam welds were fabricated from Type 316L and helium atmospheres of varying gas pressures to produce different weld-metal compositions. Gas-tungsten arc welds in 29-13-5 are also produced to provide a baseline comparison to the electron-beam welds. Weld strengths are evaluated from tensile tests in air at 25°C. Hydrogen-assisted fracture in 29-13-5 welds is characterized from notched tensile specimens that are charged in high-pressure hydrogen gas to a uniform concentration at 300°C then tested in air at 25°C.

This work was performed by the U.S. Dept of Energy under contract DE-AC04-94AL85000.

11:45 AM CC1.12 CORROSION TESTING OF GD-DOPED INTERMETALLIC CONSIDERED AS MATERIALS FOR CONSTRUCTING NUCLEAR WASTE STORAGE CANISTERS, Todd Lister, Carolyn S. Watkins, Patrick J. Pichner and Ron Mann, INEL Research Center, Idaho Falls, ID.

Presently there is a debate in the waste container community about choosing materials for the final barrier for the waste of nuclear waste. Many issues need to be considered, e.g., corrosion susceptibility, weldability, machinability, and neutron absorbance. The possibility for corrosion in the proposed permanent repositories is real because the facilities are not anticipated to be kept completely dry over its lifetime, which U.S. Department of Energy (DOE) has set at 10,000 years. Leaching of radioactive materials must be considered along with criticality issues for the leached material. Incorporation of neutron poisons such as Gd is one method being considered to solve criticality issues. Our work has focused on the corrosion behavior of two classes of Gd-containing materials: a Type 316L stainless steel, and a C-22, Ni-based alloy, doped with Gd. Gd concentrations up to 6 weight percent were inspected. We examined Gd-containing the Ni-based alloy in both cast and plasma-sprayed forms. Corrosion tests were performed using cyclic potentialdynamic scans adapted from ASTM standard procedures. Following the corrosion tests, samples were analyzed by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) to determine changes in microstructure and elemental composition, respectively. Preliminary results in 100 mM HCl solutions show that Gd phases in both materials are susceptible to corrosion. For the Type 316L stainless steels, the pitting corrosion susceptibility is directly related to the weight percent of Gd added to the base material. In the Ni-based alloys, corrosion was localized to Gd-rich phases and the potentialdynamic scans do not show pitting behavior. It is suspected that corrosion was limited to Gd phases directly exposed to the electrolyte. For the plasma-sprayed coatings, the corrosion behavior was very similar to the cast samples and may present a cost-effective method of constructing waste containers.

SESSION CC2: PHYSICAL AND PROCESSING ASPECTS
Chair: Allen C. Lingenfelter
Thursday, April 19, 2011
Golden Gate C1 (Marriott)

130 PM CC2.1 THEORETICAL STUDY OF THE GRAIN BOUNDARY SEGREGATION IN COPPER, P.A. Kozhukhay, B. Johansson, Royal Inst. of Technology, Dept. of MSE, Stockholm, SWEDEN; A.Y. Leavitt, A. Aliev, Univ. of Cambridge, Dept. of Chemistry, Cambridge, UNITED KINGDOM; A. A. also at Queen’s University, School of Mathematics and Physics, Belfast, UNITED KINGDOM

The mechanical properties of dilute copper alloys, which are intended for nuclear waste containers, are very sensitive to the presence of small amount of impurities such as sulfur and phosphorus, due to segregation of these impurities towards the grain boundaries. In the present work we present a systematic study of the segregation energy of the S and Cu impurities (Al, Si, P, and S) to the Σ = 5/2(110) [001] symmetrical tilt grain boundary in Cu using ab initio pseudopotential calculations based on density functional theory. We find that the segregation tendency increases when going from Al to P. Aluminim is found to anti-segregate from the grain boundary. Silicon has a very small segregation energy, whereas in the case of P and S we obtain moderate and strong segregation tendency, respectively. We also report on the calculated atomic structure of the core region of clean and segregated grain boundaries, as well as on the preferential segregation sites for P and S. This work is supported by SKB AB, The Swedish Nuclear Fuel and Waste Management Company, and by the EPSRC through Grant No. L08380.

1:45 PM CC2.3 CALPHAD APPROACH TO STABILITY AND AGING OF CANDIDATE ALLOYS FOR THE YUCCA MOUNTAIN PROJECT. P.A. Turchi, LLNL (Livermore), C.A. L. Kaufman, Dep. of MSE, MIT, Cambridge, MA; Z.-K. Liu, Dep. of MSE, The Pennsylvania State University, University Park, PA.

The precipitation over long time of phases such as complex tetrahedrally close packed intermetallics and ordered compounds of Ni_3X type may play a major role on microstructural evolution and properties of the maste material used in the waste packages for the Yucca Mountain Project (YMP). After a brief review of the CALPHAD methodology, we present the results of a comparative study on stability and kinetics of phase transformation in YM-type alloys, including C-22, C-44, C-276, and alloy 59. We first show that excellent agreement is achieved between assessed and calculated phase diagrams for the three major binary alloys, Ni-Cr, Ni-Mo, and Cr-Mo. Additional validation of the thermodynamic database is performed by comparing calculated and assessed sections of phase diagrams in the case of ternary Ni-Cr-Mo alloys and of the pseudo-binary Ni-(Cr,Mo). We then present a comparative study of phase fractions versus temperature, and of solidification based on the Scheil-Gulliver model for several YMP candidate intermetallic compounds. We also discuss preliminary results on predicted TTT diagrams for the formation of Ni-Cr ordered phase in the binary Ni-Cr alloy and of the complex P phase in ternary Ni-Cr-Mo alloys. The results are compared with those from both the current models and the experiments in terms of time for complete of one or another phase precipitation over long time of annealing temperatures in the case of Ni-Cr and on preliminary determination of the experimental TTT diagram in the multi-component case.

Acknowledgments
This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405ENG-48, and supported by the Yucca Mountain Site Characterization Project at LLNL.

2:00 PM CC2.3 THERMAL STABILITY OF C-276 ALLOY WELDS, Todd A. Palmer and Thomas S. Edgecombe-Summers, Lawrence Livermore National Laboratory, Livermore, CA; R. Rodger Seeley and Radu B. Rebak, Hughes International Inc., Kokomo, IN.

A Ni-Cr-Mo-W alloy (UNS N06092) is being considered for long-term nuclear waste storage containers in the current Yucca Mountain Site Characterization Project design. Welding plays an important role in both the fabrication of these containers and their final closure prior to emplacement in the repository. Conditions within the repository, according to current predictions, are characterized by temperatures in the vicinity of 201°C for a period of several thousand years. Changes in the weld metal microstructure, caused by the heat generated from radiative decay of the waste, can significantly alter the mechanical properties of the welds. Previous observations of the as-welded microstructure of N06092 alloy welds exhibit significant segregation of the primary alloying elements and the presence of Tetrahedrally Close Pack (TCP) phases, such as Cu-P, Cu-S, and Cu-Se. These phases are products of the thermal cycles experienced by the weld metal and degrade the corrosion resistance of the base metal. Relatively little is known about the effects of subsequent long-term thermal aging on the microstructural, mechanical, and corrosion properties of these welds. In order to determine the microstructural stability in Gas Tungsten Arc (GTA) welds of this alloy, annealed specimens have been aged at elevated temperatures (400, 550, 650, 700, and 800°C) for times up to 40,000 hours. Such long times and high temperatures are then correlated with uniaxial tension properties, Charpy impact toughness, and corrosion properties in aggressive reducing and oxidizing environments. Based on these observations, a preliminary estimation of the stability of the weld metal microstructure for conditions in the repository will be made.

2:45 PM CC2.4 INFLUENCE OF PHOSPHORUS ON CREEP IN PURE COPPER, Henrik C.M. Andersen, Faridin Setiahardjo, Rolf Sandström, Swedish Institute for Metals Research, Stockholm, SWEDEN.

Sputtered copper in Sweden is planned to be disposed of by encapsulation in double-walled canisters consisting of iron and copper, respectively, and placed in the bedrock. Therefore, further investigation of the outer copper canister is to provide corrosion resistance and the gap between the copper and the iron canister is initially 1.2 mm.
When the canister is exposed to a slowly increasing external pressure this gap will close. The temperature of the canisters due to the nuclear reaction heat and spent fuel is estimated to be about 80-80°C during the first 100-200 years. This temperature is enough to promote creep in the copper canister. Thus the gap will close by creep and the maximum strain has been estimated to 4%. The aim of this project is to investigate the creep behavior of copper with different phosphorous content and assess the suitability as a canister material. Uniaxial creep tests have been performed at 175°C for extruded oxygen-free copper and the effect of different contents of phosphorous was investigated. Creep curves with 0.1 ppm phosphorous content showed significantly lower creep life and ductility than batches with higher P content. An increase of the P content to 29 ppm increased the creep life and ductility, but a further increase did not affect the properties much further. All tests except those with a phosphorous content of less than 1 ppm failed at an elongation greater than 30-40%. The main creep rupture mechanisms were found to be cavitation and microcracking at the grain boundaries. For creep curves with P≤0.1 ppm are provided for creep rupture as well as for 5% and 10% creep strain.

3:00 PM CC2.5
THE DEVELOPMENT OF ADVANCED WELDING TECHNIQUES FOR SEALING NUCLEAR WASTE CONTAINMENT CANISTERS. Chig-Gorr Anderson, Swen Kibrandschalking AB (SKB), Stockholm, SWEDEN; Richard E. Andrews, TWI Ltd, Abington, Cambridge, UNITED KINGDOM.

The Swedish Nuclear Fuel and Waste Management Co (SKB) is making great progress in the many aspects of the disposal of operational waste resulting from electricity production in Swedish power plants. A part of this programme has involved research into methods of encapsulation of waste in canisters. These canisters will be stored in a deep repository located at a depth of 500 meters. SKB have designed and manufactured cylindrical canisters that can withstand the operational stresses and are sufficiently corrosion resistant to provide a service life of 100,000 years. The canisters, which have a diameter of 150mm and are 4800mm long, consist of a 50mm thick copper outer corrosion barrier and a close fitting nodular cast iron insert to provide mechanical strength. A very high integrity joint is essential to seal the bases and lids of these canister to avoid possible leaks and voids. Canister fabrication at this location. Thick wall copper is difficult to weld due to its excellent thermal conductivity and initially in the mid 1980's the only method considered to be viable was high power electron beam welding. Development of this process at TWI has resulted in the establishment of prototype Reduced Pressure Electron Beam Welding at SKB's Canister Laboratory located in Ockelsham. This equipment is being used in welding trials to establish a production canister welding procedure. In 1991 an alternative solid phase welding process called Friction Stir Welding (FSW), which had the potential for producing high integrity welds in 50mm copper was invented at TWI. SKB commissioned TWI to explore the feasibility of FSW for welding bases to canisters. A full size experimental welding machine has been designed and built which has demonstrated the SKB now has an alternative or complementary method for canister sealing and also the repair of defective welds.

3:15 PM CC2.6
ULTRASONIC IMAGING AND EVALUATION OF ELECTRON BEAM WELDS IN COPPER CANISTERS. Tadeusz Stepinski, and Ping Wu, Uppsala University, Signals and Systems, Uppsala, SWEDEN.

This paper presents our recent research concerned with ultrasonic imaging of electron beam (EB) welds, sealing copper canisters for spent nuclear fuel. The main purpose of this research was obtaining high quality ultrasonic images enabling reliable assessment of the EB welds. A high quality ultrasonic image, with well pronounced both heat-affected zone (HAZ) and fusion zone (FZ) is required for the evaluation of less than 0.1mm. However, the HAZ and FZ cannot be satisfactorily imaged simultaneously using one ultrasonic transducer since the satisfactory contrast in both zones cannot be obtained at the same time. Since the size of grains in the host material, HAZ and FZ differs very much (usually grains are fine in the host material, get bigger in the HAZ, and become coarse in the FZ), the contrast, defined by the scattering patterns is different for different zones. To obtain a satisfactory contrast in the image, the ultrasonic scattering from the material has to be limited by choosing a wavelength proper for the inspected microstructure (e.g. grain size, elasticity). In the paper we present our solution to the problem - using an annular array consisting of two elements with different center frequencies, yielding signals from the HAZ and FZ of an EB weld, simultaneously. A number of transducers was used in an experimental study to find appropriate frequency ranges for imaging the different zones. The results have demonstrated that, for the EB welds in our annular array a frequency range of 4-8 MHz was suitable for the HAZ while satisfactory images of the FZ could be obtained using a frequency range of 3.5 MHz. An annular array with elements operating in the above frequency ranges yield clear images of the layered structure of an EB weld.

3:30 PM CC2.7
THE EFFECT OF EDTA ON THE ADSORPTION BEHAVIOR OF PA-237 AND Pu-240 ONTO BENTONITE OVER A WIDE pH RANGE. Toru Naganum, Yoshitomo Watanabe, Central Research Institute of Electric Power Industry, Bio-science Dept, Chiba, JAPAN; Takayuki Sasuki, Kyoto Univ, Research Reactor Institute, Osaka, JAPAN; Tat Kaori, National Research Council Canada, Ottawa, CANADA.

Distribution coefficients (Kd) were determined under various pH conditions to investigate the sorption behavior of the radionuclides, Pa-237, Pu-239 and Pu-240, interacting with bentonite. There are significant differences in adsorption behavior among these radionuclides over the wide pH range. All Kd are pH-Eh dependent according to the chemical nature of the nuclides. In the absence of EDTA, the Kd for Pa-237 was ranged from 1,210 to 34,000 over the wide pH range while ranging from 29 to 900 for Pu-237 and from 1,100 to 150,000 for Pu-240. On the other hand, the Kd for Pa-237 and Pu-240 in the presence of EDTA were decreased with increasing concentration of EDTA and dramatically reduced to around 100 at EDTA concentrations of 1mm or more. For Pu-237, there were little changes in Kd's even if the EDTA concentration was increased. These results show that the radionuclide migration could be enhanced by contaminant EDTA in the nuclear waste.

SESSION CC3: IN-ROOM POSTER SESSION
Chair: Daniel McElroy
Thursday Afternoon, April 19, 2001
4:00 PM
Gillian Grace C3 (Macmilli)
CC3.1
AD INIOTO CALCULATION OF FISSION PRODUCTS SOLUTION ENERGY IN URANIUM MELT CORE. J.P. Crocombette, Section de Recherches de Métallurgie Physique, Commissariat à l'Energie Atomique, Saclay, FRANCE.

Incorporation and solution energies of some fission products in uranium dioxide have been calculated ab initio using the plane wave pseudopotential method in the Local Density Approximation of the Density Functional Theoretical framework. We considered the incorporation of Helium, Krypton, Cesium, Strontium or Iodine in an interstitial (octahedral) position or their substitution for an uranium or an oxygen atom. Taking into account the formation energies of the insertion sites, one finds that helium atoms tend to be situated in the interstitial position whereas all other fission products are mainly located in uranium vacancies.

CC3.3
MOLECULAR DYNAMICS SIMULATION OF THE α-RECOIL NUCLEUS DISPLACEMENT CASCADE IN ZIRCONIOLITE. L. Veiller, J.P. Crocombette, Commissariat à l'Energie Atomique, Section de Recherches de Métallurgie Physique, CEA/SMNP, Saclay, FRANCE; C. Mays, Commissariat à l'Energie Atomique, CEA/DGC, DPE-SHCP, Saclay, FRANCE; D. Glaheb, Commissariat à l'Energie Atomique, CEA/DGC-DHR-BCD, Marcoule, FRANCE.

Zirconolite (CaZrTi_2O_7) has been proposed as a crystalline ceramic host for the long-term disposal of actinides from high level nuclear waste and from excess weapons-grade plutonium. The disintegration of radionuclides induces modifications of the crystallographic structure. During α-decay of α radio nuclides, localized cascades of displaced atoms can form as a result of ballistic collisions in the material mainly due to the emitted α-recoil nuclei. Under α-decay α-irradiation zirconolite undergoes a crystalline to amorphous transformation which is associated to a volume expansion. This radiation-induced swelling and amorphization could significantly deteriorate the efficiency of the containment in increasing the release rates of radionuclides during corrosion. We have focused our study on the understanding of radiation-induced structural changes at the atomic level. We have modelled the effects of displacement cascades due to α-recoil nuclei in zirconolite by molecular dynamics (MD) simulation. Calculations are based on a rigid-ion model using Buckingham potentials. Empirical potentials have been established for zirconolite to characterize the two body short-range interactions between different ionic pairs. We present the potential parameters fitted to the structural equilibrium properties of the crystal. This approach reproduces within 4% the characteristics of the cell parameters of zirconolite.

Using this established force field we have first evaluated the threshold displacement energies for ion sizes along different crystallographic
directions. Cationic threshold energies are in the range 25 to 53 eV. In a second part we have reproduced displacement cascades in MD simulations by accelerating one of the atoms of the cell. In simulations of low recoil energies \( \leq 150 \text{ eV} \), point defects (interstitials, vacancies) have been formed and stable Frenkel pairs were produced as the result of the existence of replacement collision sequences along cationic rows. To model the effect of the \( \alpha \)-decay recoil nucleus, series of MD simulations of high recoil energies \( \geq 1 \text{ keV} \) were performed. Damage mechanisms, defect production processes, stored energy and the degree of amorphization in cascades were investigated.

**CC3.3**  
Abstract Withdrawn.

**CC3.4**  
Transferred to CC2.7.