SYMPOSIUM CC
Nuclear Waste Containment Materials
April 19, 2001

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

8:30 AM CC1.1

The Swedish geological disposal concept for spent fuel is a multi-barrier system consisting of a corrosion-resistant canister, compacted bentonite buffer, and a burial up to 700 m in granitic rock. Performance Assessment (PA) requires the canister to resist corrosion for approximately 100,000 years, to allow the radioactivity to decay to acceptable risk levels. Copper was identified as a suitable canister material because of its stability over a wide range of geochanical conditions in the repository environment. However, prediction of its behaviour over the PA timescale, based only on theoretical calculations and short-term experimental observations, may be uncertain. Confidence can be improved by studying similar natural systems (natural analogues) that have been operative over a long period of time. Natural copper sheets intensely weathered with uranium mineralization, occur within concretions hosted by smectite Permian red-bed mudstones in south Devon, United Kingdom, and have been studied as a natural analogue of copper canisters enclosed by bentonite. The results demonstrated that copper can persist in a weathered and compacted smectic clay environment for over 170 million years.

8:45 AM CC1.2
A CORROSION STUDY OF ARCHAEOLOGICAL FeRROUS ANALOGUES FOR THE UNDERSTANDING OF THE STEEL OVERPACK BEHAVIOR IN GEOLOGICAL REPOsITORIES. Delphine Neff, Philippe Dillmann, Séléphine Lequien, Laboratoire Pierre et Marie Curie, CNRS, CE Saclay, Cedex, France; Gérard Hénin-Aubry, Laboratoire d’Informatique et de Géologie, Université de Technologie de Compiegne, Compiègne Cedex, France.

One of the elements of the engineered barrier system that could be used in the future French radioactive waste geological repositories is a low alloyed steel of the FLF type. The behaviour of such a steel can be understood using experimental studies on corrosion and long-term corrosion of this kind of steel in clay environment is of major interest. Because it is difficult to simulate in a laboratory the time scales involved in the repositories, the study of archaeological analogies can bring useful information about corrosion kinetics and products. The aim of this study is to better understand if the metal composition (minor alloying elements, second phase particles) and the structure of the steel play a determining role in the corrosion processes. So, the study of different analogues and structures and coming from the same archeological site (same browning environment) are investigated. Transverse cross-sections of archaeological artifacts embedded in soil are examined. On one hand, composition and metallic structure of the remaining metal are determined. On the other hand, the different oxide scales are analyzed with different original analytical methods like micro fraction with synchrotron radiation. Particularly, the corrosion modes and the original surface of the iron artefacts are studied. The quality of glass is a key point. For objects coming from the same environment, this later value can be compared with the metal structure and its composition.

9:00 AM CC1.3

The hypotheses of uniform and stoichiometric dissolution used to predict the lifetime of proposed high-level waste disposal containers made of Ni-Cr-Mo alloys, in the absence of environmental and electrochemical conditions leading to localized corrosion and stress cracking, are evaluated based on the point defect model for passive dissolution. The model indicates that the predominant charge conduction mechanism through the oxide film formed on Ni-Cr-Mo alloys (mainly composed of chromium oxide for alloys with Cr content greater than 12 weight percent) is interstitial transport of metal cations. Injection of interstitials into the film is accompanied by the creation of vacancies in the alloy. Possible consequences of this vacancy creation on the container lifetime are discussed. Of particular interest is the possibility for these vacancies to act as the met al/film interface leading to film detachment and possible spallation. A heuristic model for film spalling is proposed to estimate container lifetimes. According to the dissolution model and because of the low vacancy diffusivity and near room temperatures in the metal substrate, away from the passive film, long-term dissolution is necessarily stoichiometric. Analyses of solution chemical composition using capillary electrophoresis are reported to evaluate the frequency of occurrence of vacancy in the passive dissolution of alloy 22 (Ni-22Cr-13Mo-3W-Fe).

Acknowledgments:
This paper was prepared to document work performed on behalf of the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Material Safety and Safeguards, under Contract No. 0290769 and does not necessarily reflect the views or regulatory position of the NRC.

9:15 AM CC1.4
MINIMALISTIC POTENTIALS FOR PROPAGATION OF PITTINg CORROSION OF COPPER IN CHLORIDE-CONTAINING SOLUTIONS, SIMPLIFIED TREATMENT. Claus Tassen, Swedish Corrosion Institute, Stockholm, Sweden; Kimmo Kallio, Royal Institute of Technology, Stockholm, Sweden.

Results from a simplified model of pitting corrosion of copper in chloride-containing waters are presented. The model is applicable for solutions with chloride concentrations between 0.02 M and 0.50 M. The lower concentration limit is set by the neglect of cupric species and of potential differences between the inside of the pit and the bulk solution. The upper concentration limit is set by the model treatment of the effects of the solution potential on the rate of pit growth. The results are compared with available experimental data for systems containing hydrochloric acid. The model is shown to predict the time to passivation, found in the literature, for solutions containing sodium chloride, as well as for solutions containing hydrochloric acid. The model is shown to predict the time to passivation, found in the literature, for solutions containing sodium hydroxide.

9:30 AM CC1.5
INFLUENCE OF TEMPERATURE ON THE PITTINg BEHAVIOR OF CANDIDATE CONTAINER MATERIALS FOR THE DISPOSAL OF HUd IN BOOM CLAY. Bruce Kusent, Frank Drakey, SCK·CEN, The Belgian Nuclear Research Center, Waste and Disposal Unit, Mol, Belgium.

The localized corrosion behavior of austenitic stainless steels AISI 316L, 316Ti, and UH3 004L was investigated in solutions containing chloride, sulfide, and nitrite. The behavior of these solutions in the presence of HCl, NaCl, and HNO3 was also analyzed. The localized corrosion behavior of these solutions was examined in a domestic aqueous electrolyte. The vessel was made of stainless steel, which was designed for the electrode construction of a stainless steel wire on a metal substrate, which is a AgCl layer was deposited electrolytically; this wire is placed inside a heat-shrunk Teflon tube which is separated from the test...
electrolyte by means of a ceramic plug (\( \text{MgO-ZrO}_2 \)); the Test tube is then filled with 0.1M KCl. Cyclic potential-determining polarization measurements were made on an electrochemical system to determine the pitting behavior of the tested stainless steels. The \( E_{p_{corr}} \) and \( E_{p_{pitt}} \) values were generally found to be slightly higher for the stainless steel UHB 904L, indicating a higher resistance to localized corrosion. Pitting is initiated more easily with increasing temperature. Increasing the temperature caused \( E_{p_{corr}} \) and \( E_{p_{pitt}} \) to shift to lower potentials (shift towards the active region) for both stainless steels. The surface of each specimen was investigated by Optical Microscopy and Scanning Electron Microscopy (SEM). The formed pits have a rose-like appearance due to subesequent growth.

10:15 AM  CC11.6
BIOFILM DEVELOPMENT ON IRRADIATED STAINLESS STEEL FUEL CLADDINGS IN A HOT CELL ENVIRONMENT. D.F. Bruhn, 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 biofilm formation is a subject of debate in the nuclear waste storage community. Biofilm 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 biofilm growth occurring on irradiated Type 304 stainless steel cladding hulls 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 hull sections. Though the measured dose rate at the hull surfaces was rather low, ca. 47 rad/h, the overall radiation field exceeded 200 rad/h (gamma and beta radiation). The larger field was formed by placing discolored irradiated nuclear fuel disassembled into 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 bacteria was on the order of 8.5 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 Nuclear Technology and Engineering Center (INTEC) spent fuel storage pools at the Idaho National Engineering and Environmental Laboratory (INEEL). During the experiment, media, and hull surfaces were sampled periodically to monitor biological activity. Several controls were maintained to account for microbiological contamination during the entire length of the study. Our observations indicate that biofilms do in fact form on the irradiated hulls within the context of this analytical hot cell study. This provides evidence that MIC is a possibility in the storage and permanent depositions of SNF in repository environments.

10:30 AM  CC11.7
BACTERIAL IMPACTS ON ALLOY 22, A CANDIDATE NUCLEAR WASTE PACKAGING MATERIAL UNDER SIMULATED REPOSITORY CONDITIONS. Jeanne Horn, Sue Martin, Brett Masterson, DeJuan Paul, 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, 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 undermine 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-sterile or sterilized), material coupons, and a continual feed of simulated YM groundwater. Periodically, material coupons were analyzed for chemical and surficial characterization. Alloy 22 coupons exposed for one year in room temperature reactors containing non-sterile YM rock demonstrated accretion of siliceous scales, with what appear to be underlying areas of corrosion. Coupons exposed for one year under identical but sterile conditions demonstrated some corrosive effects, but less so than Alloy 22 incubated under non-sterile conditions for the same time period.

10:45 AM  CC11.8
THE RESISTANCE OF PURE COPPER TO STRESS CORROSION CRACKING IN REPOSITORY ENVIRONMENTS. Bo Rosborg, Rosborg Consulting, Nykoping, SWEDEN; Lars Wermel, Svensk Kärnbrunnshämtning AB (SKB), Stockholm, SWEDEN.

The stress corrosion cracking (SCC) mechanism is thought to follow the following steps: (1) passive film rupture under plastic tensile strain, (2) passive film healing and repassivation at film rupture sites, (3) monodic dissolution at film rupture sites by coupling to reduction of dissolved calcium at nearby exposed passive surfaces, (4) metastable triggering of brittle crack initiation by monodic dissolution at film rupture sites, and (5) brittle crack growth by continued monodic dissolution at the crack tip coupled to nearby passive crack-wall and/or exposed outer surfaces. Progress in defining these steps from previous works, developing algorithms to describe and link the steps into an improved model credible model, and experimental work to better define and confirm the model for predictive modeling at Yucca Mountain will be described in this paper.

11:00 AM  CC11.9
SULFUR CORROSION OF COPPER CANISTER FOR SPENT FUEL DISPOSAL. Ivan Escobar, Carmen Silva, Eric Silva, Comision Chilena de Energia Nuclear (CCHEN), Santiago, CHILE; Lars Wermel, Svensk Kärnbrunnshämtning AB (SKB), Stockholm, SWEDEN.

Swensk Kärnbrunnshämtning (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 that copper is impervious to corrosion in oxygen free water over a relatively wide composition range. Some species in the groundwater may upset this stability and dissolved sulfides are one of the most important ones in deep granitic groundwater in Sweden. 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 for surface analysis of the corrosion product layers formed after exposing electrochemically to reducing potentials for times up to one hour. Much of those data were not included in their previous publication. Studsvik used considerably longer exposure times and used energy dispersive X-ray microprobe and AES as one of the tools to characterize the corrosion product that formed. In either laboratory, it was possible to identify copper sulfide by X-ray diffraction. Clear sulfide sulfurn was, however, identified in some of the XPS spectra reported by CCHEN. The results from the two studies will be reviewed in order to clarify the possible effects of copper corrosion in reducing, sulfide-containing water will be discussed future studies suggested.

11:15 AM  CC11.10
MODELLING THE STRESS CORROSION CRACKING BEHAVIOR OF CORROSION-RESISTANT CONTAINER ALLOYS FOR THE YUCCA MOUNTAIN PROJECT. Denny A. Jones, University of Nevada, Reno, NV and Lawrence Livermore National Laboratory; John C. Beall, Lawrence Livermore National Laboratory, Livermore, CA.

The stress corrosion cracking (SCC) mechanism is thought to follow the following steps: (1) passive film rupture under plastic tensile strain, (2) passive film healing and repassivation at film rupture sites, (3) monodic dissolution at film rupture sites by coupling to reduction of dissolved calcium at nearby exposed passive surfaces, (4) metastable triggering of brittle crack initiation by monodic dissolution at film rupture sites, and (5) brittle crack growth by continued monodic dissolution at the crack tip coupled to nearby passive crack-wall and/or exposed outer surfaces. Progress in defining these steps from previous works, developing algorithms to describe and link the steps into an improved model credible model, and experimental work to better define and confirm the model for predictive modeling at Yucca Mountain will be described in this paper.

11:30 AM  CC11.11
The nitrogen-strengthened, austenitic stainless steel 29Cr-13Ni-5Mo was developed for high temperature weldability and creep resistance. Work in the literature demonstrates that 22 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 unstressed hydrogen-induced cracking in 22 13–5. Of particular importance are changes in composition that result either in electron beam welds due to evaporation of elements such as nitrogen and molybdenum. Electron-beam welding is the most widely used process in the oceans and helium atmospheres of varying gas pressures to produce different weld metal compositions. Gas-tungsten arc welds in 22 13–5 are also produced to provide a baseline comparison to the electron-beam welds. Welding parameters differ from those in tests in air at 25°C. Hydrogen-assisted fracture in 22 13–5 welds is characterized from a notched tensile specimen, which is charged in high-pressure hydrogen gas to a uniform concentration at 300°C then tested in air at 25°C. This work is supported by the U.S. Department of Energy under contract DE-AC04-94AL85000.

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

Presently there is a debate in the waste container community about choosing the primary glass for the waste form 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 containers are not anticipated to be retrieved or removed within 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: Type 316 stainless steel, and a C-22, Nb-based alloy, doped with Gd. Gd concentrations up to 6 weight percent were investigated. We examined Gd-containing the Nb-based alloys in both cast and plasma-sprayed forms. Corrosion tests were performed using cyclic potential/cycling 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 μM HCl solutions show that Gd phases in both materials are susceptible to corrosion. For the Type 316 stainless steels, the pitting corrosion susceptibility is directly related to the weight percent of Gd added to the base material. In the Nb-based alloys, corrosion was localized to Gd-rich phases and the potential/cycling scans do not show pit formation 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, 2001

Golden Gate C1 (Marriott)

1:30 PM CC2.1 THEORETICAL STUDY OF THE GRAIN BOUNDARY SEGREGATION IN COPPER. P.A. Kozhikhoi, B. Johansson, Royal Inst. of Technology, Dept. of MSE, Stockholm, SWEDEN; A.Y. Lezovoy, P.A. Alain, Univ. of Cambridge, Dept. of Chemistry, Cambridge, UNITED KINGDOM. "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 phosphorous, due to segregation of these impurities towards the grain boundaries. In the present work we performed a systematic study of the segregation behavior of the 3p impurities (Al, Si, P, and S) to the Σ = 5 [100] [001] symmetrical tilt grain boundary in Cu using ab initio pseudo-potential calculations based on density functional theory. We find that the segregation tendency increases when going from Al to S. Aluminum 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 preferable segregation sites for P and S. This work is supported by SKB A.B., The Swedish Nuclear Fuel and Waste Management Company, and by the EPSRC through Grant No. L083800.

1:45 PM CC2.2 CALPHAD APPROACH TO STABILITY AND AGING OF CANDIDATE ALLOYS FOR THE YUCCA MOUNTAIN PROJECT. P.F. Dargusch, LLNL (L-1335), Livermore, CA; L. Kaufman, Dep. of M&SE, MIT, Cambridge, MA; Z-K Liu, Dept. of M&SE, The Pennsylvania State University, University Park, PA.

The precipitation over long time of phases such as complex meta-stable solid phase transformations ordered and changed compositions of Ni3Cr-type may play a major role on micro-structural evolution and properties of the target materials 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 structures and kinetics of phase transformation in Fe-3Cr type alloys, including C-22, C-4, C-276, and alloy 69. We first show that an excellent agreement is achieved between measured 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 measured assessed phases 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 Schel-Gulliver model formalism. General compositional restrictions among experimental data are also discussed on preliminary results on predicted TTT diagrams for the formation of Ni2Cr ordered phase in the binary Ni-Cr alloy and of the complex phase ternary Ni-Cr-Mo alloys. The results are compared with those of other composite materials, and are expected to be useful for timescale for same 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 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-22 ALLOY WELDS. T.C. Palmer and Tammy S. Edgecombe-Summers, Lawrence Livermore National Laboratory, Livermore, CA; R. Rodger Seeley and Raul D. Rebak, Hughes International Inc., Kokomo, IN.

A Ni-Cr-Mo-W alloy (UNS N06022) 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 in the repository, according to current predictions, are characterized by temperatures in the vicinity of 200°C for a period of several thousand years. Changes in the weld metal microstructure, caused by the heat generated from radioactive decay of the waste, is expected to cause microstructural changes to result in changes in the corrosion and mechanical properties of the welds. Previous observations of the as-welded microstructure of N06022 alloy welds exhibit significant segregation of the primary alloying elements and the presence of Tetrahedra Close Packed (TCP) phases, such as P, y, and . 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 estimate the microstructural stability in Gas Tungsten Arc (GTA) welds of this alloy, annealed specimens have been aged at 650°C (1500°F) 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, Facred Setlheim, Rolf Sandström, Swedish Institute for Metals Research, Stockholm, SWEDEN.

The mechanical properties of pure copper are not only due to the presence of a few impurities such as iron and phosphorus, but also due to the presence of very small amounts of other elements. The influence of these impurities on the creep behavior of copper has been investigated in previous studies. In particular, the influence of phosphorus on the creep behavior of copper has been studied. Phosphorus is a very impurity element in copper, and it has been shown that phosphorus can significantly improve the creep resistance of copper. In the present study, the influence of phosphorus on the creep behavior of copper is investigated in more detail. The results show that phosphorus can significantly improve the creep resistance of copper, and that the improvement is due to the formation of an intermetallic compound at the grain boundaries. The intermetallic compound is found to be a protective layer that reduces the rate of grain boundary diffusion, thereby decreasing the creep rate of copper.
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 of spent fuel is estimated to be about 800-900°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 investigated. Copper with phosphorous content less than 1 ppm failed at an elongation greater than 30%, most of them at 35-40%. The main creep rupture mechanisms were found to be cavitation and microcracking at the grain boundaries. The test results indicate that phosphorous is 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. Chieh-Gonn Anderson, Swen Krumvndehlshering 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 metres. 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 1000mm 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 preferential corrosion in 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 installation of prototype Reduced Pressure Electron Beam Welding at SKB's Canister Laboratory located in Oakham. 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 that 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 the basic characteristics. However, the HAZ and the 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 frequency, 5 MHz with the HAZ and 10 MHz with the 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 samples, an ultrasonic frequency range of 5-10 MHz was suitable for the HAZ while satisfactory images of the FZ could be obtained using a frequency range of 3.3 MHz. An annular array with elements operating in the above frequency ranges yielded clear images of the layered structure of an EB weld.

3:30 PM CC2.7
THE EFFECT OF EDTA ON THE ADSORPTION BEHAVIOR OF Pb-210, Np-237 AND Pu-240 ONTO BENTONITE OVER A WIDE pH RANGE. Tooru Nagano, Yoshitomo Watanabe, Central Research Institute of Electric Power Industry, Bi-science Dept, Chiba, JAPAN; Tokuyuki Sasaki, Kyoto Univ, Research Reactor Institute, Osaka, JAPAN; Tais Kashi, National Research Council Canada, Ottawa, CANADA.

Distribution coefficients (Kd) were determined under various pH conditions to investigate adsorption behavior of the radionuclides, Pu-233, Np-237 and Pu-240, interacting with bentonite. There are significant differences in adsorption behavior among these radionuclides over the wide pH range. All Kd s are pH-Eh dependent according to the chemical stability of the nuclides. In the absence of EDTA, the Kd for Pu-233 was ranged from 1,200 to 34,000 over the wide pH range while ranging from 20 to 900 for Np-237 and from 1,100 to 150,000 for Pu-240. On the other hand, the Kd's for Pu-233 and Pu-240 in the presence of EDTA were decreased with increasing concentration of EDTA and drastically reduced to around 100 at EDTA concentrations of 1 mM or more. For Np-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 McCright Thursday Afternoon, April 19, 2001 4:00 PM
Golden Gate C3 (McCright)

CC3.1
AB INITIO CALCULATION OF FISSION PRODUCTS SOLUION ENERGY IN URANIUM DIOXIDE. J.P. Crocombette, Sectio de Recherches de Météllurgie Physique, Commissariat a 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 Yttrine 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 interstitial positions whereas all other fission products are mainly located in uranium vacancies.

CC3.2
MOLECULAR DYNAMICS SIMULATION OF THE α-RECOIL NUCLEUS DISPLACEMENT CASCADE IN ZIRCONOLITE. L. Veiller, J.P. Crocombette, Commissariat a l'Energie Atomique, Sectio de Recherches de Météllurgie Physique, CEA/ SRCMP, Saclay, FRANCE; C. Mois, Commissariat a l'Energie Atomique, CEA/DGC, DPE-SPCP, Saclay, FRANCE; D. Ghaheb, Commissariat a l'Energie Atomique, CEA/DGC-DHIV-SCD, Marcoule, FRANCE.

Zirconolite (CaZr2Ti2O7) 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 decades of actinides, 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 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 confinement 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 ion 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 ionic 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 ($< 150$ 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 ($\geq 1$ 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.