SYMPOSIUM CC

Nuclear Waste Containment Materials

April 19, 2001

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SESSION CC1: CORROSION AND OTHER CHEMICAL ASPECTS
Chair: Daniel McCright
Thursday Morning, April 19, 2001
Golden Gate C1 (Marriott)

8:30 AM CC1.1
NATIVE COPPER IN PERMIAN MUDSTONES FROM SOUTH DEVON: A NATURAL ANALOGUE OF COPPER CANISTERS FOR HIGH-LEVEL RADIOACTIVE WASTE. A.E. Milodowski, M.T. Styles, British Geological Survey, Keyworth, Nottingham, UNITED KINGDOM; L. Werme, Swedish Nuclear Fuel and Waste Management Company, Stockholm, SWEDEN; V.M. Oversby, VMO Konsult, Stockholm, SWEDEN.

The Swedish geological disposal concept for spent fuel is a multibarrier system consisting of a corrosion-resistant canister, compacted bentonite buffer, and 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 geochemical 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. Native copper sheets, associated with uranium mineralisation, occur within concretions hosted by smectitic Permian red-bed mudstones in south Devon, United Kingdom, and have been studied as a natural analogue of copper canisters enclosed by bentonite. The copper sheets (1–2 mm thick) grew within reduction spots formed by the localised reduction of ferric oxides. Petrographical analysis shows they developed before the host rocks achieved maximum compaction. The regional burial history indicates that this would have been achieved before the end of the Lower Jurassic. The copper sheets display complex alteration and subsequent mineral growth on their surfaces—initially copper oxides (indicating oxidising groundwater conditions), followed by dissolution of associated native silver and the growth of fringes of copper and nickel arsenides and sulphides, and uranium silicate (indicating later, more reducing porewaters). This alteration and subsequent mineralisation also pre-dates compaction and is geologically old. Despite corrosion, a significant proportion (30–80% of the original thickness) of the copper sheets has been preserved. This demonstrates that copper metal can persist in a saturated and compacted smectitic clay environment for over 176 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, Stéphane Lequien, Laboratoire Pierre Süe CEA/CNRS, CE Saclay, Cedex, FRANCE; Gérard Béranger, Laboratoire Roberval, Université de Technologie de Compiëgne, Compiëgne Cedex, FRANCE.

One of the elements of the engineered barrier which could be used in the future French radioactive waste geological repositories is a low alloyed steel container's overpack. Thus, the understanding of the 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 analogues 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 mechanisms. So, artifacts of different compositions and structures and coming from the same archeological site (same burying environment) are investigated. Transverse cross-sections of archaeological artifacts embedded in soil are examined. On one hand, composition and metallographic structure of the remaining metal are determined. On the other hand, the different oxide scales are analyzed with different original analytical methods like micro diffraction with synchrotron radiation. Particularly, the corrosion modes and the original surface of the artifacts are evidenced. The quantity of corroded metal is deduced. 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
LONG TERM PASSIVE BEHAVIOR OF ALLOY 22. Osvaldo Pensado, Darrell Dunn, Sean Brossia, and Gustavo Cragnolino, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX.

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 corrosion 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 importance is the possibility for these vacancies to accumulate at the metal/film interface leading to film detachment and possible film spalling. A heuristic model for film spalling is proposed to estimate container lifetimes. According to the dissolution model and because of the low vacancy diffusivities at 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 degree of congruency in the passive dissolution of alloy 22 (Ni-22Cr-13Mo-3W-5Fe). This study demonstrates that extrapolation of short-term behavior (of the order of days, months, years) to long-term performance (thousands of years) must be supported by mechanistic understanding of the dissolution phenomena.
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. 0207009 and does not necessarily reflect the views or regulatory position of the NRC.

9:15 AM CC1.4
MINIMUM POTENTIALS FOR PROPAGATION OF PITTING CORROSION OF COPPER IN CHLORIDE-CONTAINING SOLUTIONS, SIMPLIFIED TREATMENT. Claes Taxen, Swedish Corrosion Institute, Stockholm, SWEDEN; Ignasi Puigdomenech, 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 which calculates activities from concentrations. When pitting of copper is observed or when copper is corroding and not undergoing pitting corrosion, the surface is generally covered by one or more layers of corrosion products. The innermost of these layers is composed of cuprous oxide. When pitting corrosion occurs, this oxide is frequently, but not always, observed at the bottom of the pit. To determine limits for where copper is immune to pitting corrosion we study cases where some cuprous oxide is formed at the site of oxidation, but at a fraction that is insufficient to completely cover the underlying metal. We find that the detrimental effect of chloride can be explained by an enhanced solubility of cuprous oxide due to complex formation with chloride. In solutions containing hydrogen carbonate and chloride we find that the detrimental effect of chloride, to some extent, is counteracted by the facilitated transport of protons in the form of carbonic acid, outwards from the slightly acidified pit solution. Compared to experimentally-determined potentials for breakdown of passivity, found in the literature, the calculated minimum potentials for propagation show good agreement for the pure chloride solutions. For mixed chloride/hydrogen carbonate solutions the calculations indicate that pitting corrosion can propagate at potentials much lower than the potentials where breakdown of passivity has been observed.

9:30 AM CC1.5
INFLUENCE OF TEMPERATURE ON THE PITTING BEHAVIOR OF CANDIDATE CONTAINER MATERIALS FOR THE DISPOSAL OF HLW IN BOOM CLAY. Bruno Kursten, Frank Druyts, SCK•CEN, The Belgian Nuclear Research Center, Waste and Dispoal Unit, Mol, BELGIUM.

The localized corrosion behavior of austenitic stainless steels AISi 316L hMo and UHB 904L was evaluated in solutions containing chloride, sulfate, and thiosulfate at near-neutral pH simulating deep geological clay environments. These stainless steels are considered as candidate container materials for the disposal of high-level nuclear waste and spent fuel for the Belgian repository concept in an underground clay environment. The experiments were conducted at 16, 90, and 140°C in oxidized synthetic interstitial Boom clay water with chloride concentrations ranging from 50 to 10000 mg/L, varying sulfate concentrations of 216 and 5400 mg/L, and thiosulfate concentrations ranging from 2 to 200 mg/L. The experiments at 140°C were conducted in an autoclave system. The vessel wall is used as the counter electrode and an internal reference electrode was designed: the electrode consisted af a silver wire onto one end of which a AgCl layer was deposited electrolytically; this wire is placed inside a heat-shrunk Teflon tube which is seperated from the test

electrolyte by means of a ceramic plug (MgO-ZrO_2); the Teflon tube is then filled with 0.1M KCl. Cyclic potentiodynamic polarization measurements were used as an electrochemical technique to compare the pitting behavior of the tested stainless steels. The E_{np}- and E_{pp}-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_{np} and E_{pp} 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 after electrochemical testing. The formed pits have a rose-like appearance due to subsurface growth.

10:15 AM CC1.6
BIOFILM DEVELOPMENT ON IRRADIATED STAINLESS STEEL FUEL CLADDINGS IN A HOT CELL ENVIRONMENT. D.F. Bruhn, F.F. Roberto, P.J. Pinhero, INEEL Research Center, 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 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 dissolved irradiated nuclear fuel dispensed 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 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 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 deposition of SNF in repository environments.

10:30 AM CC1.7
BACTERIAL IMPACTS ON ALLOY 22, A CANDIDATE NUCLEAR WASTE PACKAGING MATERIAL, UNDER SIMULATED REPOSITORY CONDITIONS. Joanne Horn, Sue Martin, Brett Masterson, Diedre Sharkey, Dave Fix, 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 and thereby decrease their useful lifetime as barrier materials. Evaluation of potential Microbiological 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 presterilized), material coupons, and a continual feed of simulated YM groundwater. Periodically, material coupons were analyzed for chemical and surfacial characterization. Alloy 22 coupons exposed for one and two years at room temperature in reactors containing non-sterile YM rock demonstrated accretion of silaceous scales, with what appear to be underlying areas of corrosion. Coupons exposed for one year under identical but sterile conditions demonstrate some corrosive effects, but less so than Alloy 22 incubated under non-sterile conditions for the same time period.

10:45 AM CC1.8
THE RESISTANCE OF PURE COPPER TO STRESS CORROSION CRACKING IN REPOSITORY ENVIRONMENTS. Bo Rosborg, Rosborg Consulting, Nykoping, SWEDEN; Lars Werme, Svensk Karnbranslehantering AB (SKB), Stockholm, SWEDEN.

The risk for stress corrosion cracking of the copper canister 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 has been shown that stress corrosion cracking can occur in copper (of commercial quality). This is not a very sensational circumstance considering todays knowledge, and does not in any way disqualify copper as a material for the canister. Most materials, if not all, show susceptibility under some circumstances. The objective 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 phenomenon as stress corrosion cracking. The 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 a practicable way of approach. Thus, one is referred to indirect 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 nitrite 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 nitrite solution, it cannot be claimed that stress corrosion cracking has occurred in the synthetic groundwater.

11:00 AM CC1.9
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 Karnbranslehantering AB (SKB), Stockholm, SWEDEN.

Svensk Karnbranslehantering (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 immune 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 groundwaters 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 groundwaters 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 Comisin Chilena de Energa 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 at 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 analysis as one of the tools to characterize the corrosion products that formed. In either laboratory, it was possible to identify copper sulfide by X-ray diffraction. Clear sulfide sulphur was, however, identified in some of the XPS spectra recorded by CCHEN. The results from the two studies will be reviewed and the possible consequences for copper corrosion in reducing, sulfide-containing water will be discussed future studies suggested.

11:15 AM CC1.10
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. Estill, 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) anodic dissolution at film-rupture sites by coupling to reduction of dissolved oxidizers at nearby exposed passive surfaces, (4) metallurgical triggering of brittle crack initiation by anodic dissolution at film rupture sites, and (5) brittle crack growth by continued anodic dissolution at the crack tip coupled to nearby passive crack-wall and/or exposed outer surfaces. Progress in defining these steps from previous models, developing algorithms to describe and link the steps into an improved more-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 CC1.11
COMPOSITION EFFECTS ON STRENGTH AND HYDROGEN-ASSISTED FRACTURE IN 22Cr-13Ni-5Mn WELDS. B.P. Somerday, C.H. Cadden, and S.H. Goods, Sandia Natl Labs, Livermore, CA.

The nitrogen-strengthened, austenitic stainless steel 22Cr-13Ni-5Mn was designed for applications that require high strength and corrosion 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 effect of weld composition on strength and hydrogen-induced cracking in 22-13-5. 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 are fabricated from 22-13-5 in nitrogen 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. Weld strengths are evaluated from tensile tests in air at 25°C. Hydrogen-assisted fracture in 22-13-5 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 is supported by the U.S. Dept of Energy under contract # DE-AC04-94L85000.

11:45 AM CC1.12
CORROSION TESTING OF Gd-DOPED INTERMETALLICS CONSIDERED AS MATERIALS FOR CONSTRUCTING NUCLEAR WASTE STORAGE CANISTERS. Tedd Lister, Carolyn S. Watkins, Patrick J. Pinhero and Ron Mizia, INEEL Research Center, Idaho Falls, ID.

Presently there is a debate in the waste container community about choosing a suitable material for the permanent internment 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 remain 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 focussed 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 potentiodynamic 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 potentiodynamic 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 Afternoon, April 19, 2001
Golden Gate C1 (Marriott)

1:30 PM CC2.1
THEORETICAL STUDY OF THE GRAIN BOUNDARY SEGREGATION IN COPPER. P.A. Korzhavyi, B. Johansson, Royal Inst of Technology, Dept of MS&E, Stockholm, SWEDEN; A.Y. Lozovoi[a], A. Alavi, Univ of Cambridge, Dept of Chemistry, Cambridge, UNITED KINGDOM. [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 phosphorous, due to segregation of these impurities towards the grain boundaries. In the present work we perform a systematic study of the segregation energy of the $3sp$ impurities (Al, Si, P, and S) to the $\Sigma = 5(310)[001]$ 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 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 impurities in Cu.
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 CC2.2
CALPHAD APPROACH TO STABILITY AND AGING OF CANDIDATE ALLOYS FOR THE YUCCA MOUNTAIN PROJECT. P.E.A. Turchi, LLNL (L-353), Livermore, CA; L. Kaufman, Dept. of MS&E, MIT, Cambridge, MA; Z.-K. Liu, Dept. of MS&E, 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_2Cr-type may play a major role on micro-structural evolution and properties of the as-cast 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 statics and kinetics of phase transformation in YMP-type alloys, including C-22, C-4, 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_3Mo). We then present a comparative study of phase fractions versus temperature, and of solidification based on the Scheil-Gulliver model for the nominal composition of several YMP candidate alloys. We also discuss preliminary results on predicted TTT diagrams for the formation of Ni_2Cr 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 measurement of lattice constant versus time for several 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-7405-ENG-48, and supported by the Yucca Mountain Site Characterization Project at LLNL.

2:00 PM CC2.3
THERMAL STABILITY OF C-22 ALLOY WELDS. Todd A. Palmer and Tammy S. Edgecumbe Summers, Lawrence Livermore National Laboratory, Livermore, CA; R. Rodger Seeley and Raúl B. Rebak, Haynes International Inc., Kokomo, IN.

A Ni-Cr-Mo-W alloy (UNS N06022) is being considered for long-term nuclear waste storage containters 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 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, are thus expected. These microstructural changes 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 Tetrahedrally Close Packed (TCP) phases, such as P, μ, and σ. 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, as-welded samples have been aged at elevated temperatures (430, 590, 650, 700, and 760°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 PHOSPHOROUS ON CREEP IN PURE COPPER. Henrik C.M. Andersson, Facredin Seitisleam, Rolf Sandström, Swedish Institute for Metals Research, Stockholm, SWEDEN.

Spent nuclear fuel in Sweden is planned to be disposed of by encapsulation in double-walled canisters consisting of iron and copper, respectively, and placed deep in the bedrock. The main function 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 reactions within the spent fuel is estimated to be about 80-90°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 has been to investigate the creep behaviour 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 has been investigated. Copper with <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 P failed at an elongation greater than 20%, most of them at 30-40%. The main creep rupture mechanisms were found to be cavitation and microcracking at the grain boundaries. Master curves for extrapolation 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.
Claes-Goran Andersson, Svensk Karnbranslehantering 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 1050mm and are 4830mm 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 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 installation of prototype Reduced Pressure Electron Beam Welding at SKB's Canister Laboratory located in Oskarshamn. 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 EB weld. It appears however, that 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 frequencies yielding a satisfactory imaging of both 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 specimens, an ultrasound with a frequency range of 4-5 MHz was suitable for the HAZ while satisfactory images of the FZ could be obtained using a frequency range of 2-3 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 PA-233, NP-237 AND Pu-240 ONTO BENTONITE OVER A WIDE pH RANGE.
Toru Nagaoka, Yoshitomo Watanabe, Central Research Institute of Electric Power Industry, Bio-science Dept, Chiba, JAPAN; Takayuki Sasaki, Kyoto Univ, Research Reactor Institute, Osaka, JAPAN; Tiit Kauri, National Research Council Canada, Ottawa, CANADA.

Distribution coefficients (Kd) were determined under various pH conditions to investigate adsorption behaviors of the radionuclides, Pa-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 Kds are pH-Eh dependent according to the chemical form of the nuclides. In the absence of EDTA, the Kd for Pa-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 Kds for Pa-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 1mM or more. For Np-237, there were little changes in Kds 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 (Marriott)

CC3.1
AB INITIO CALCULATION OF FISSION PRODUCTS SOLUTION ENERGY IN URANIUM DIOXIDE.
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, Caesium, 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 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 à l'Energie Atomique, Section de Recherches de Métallurgie Physique, CEA/SRMP, Saclay, FRANCE; C. Meis, Commissariat à l'Energie Atomique, CEA/DCC-DPE-SPCP, Saclay, FRANCE; D. Ghaleb, Commissariat à l'Energie Atomique, CEA/DCC-DRRV-SCD, 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 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 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 ionic sites 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 eV), point defects (intertitials, 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 α-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.