DR-1274-2

UCID--20499

DE85 013241

Spent Fuel Cladding Corrosion under Tuff Repository Conditions - Initial Observations

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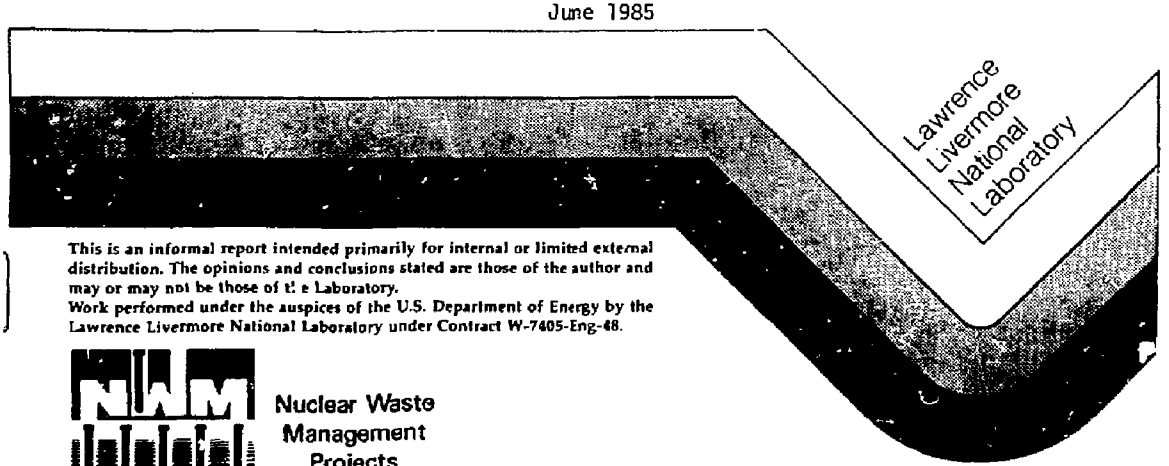
June 1985



Nuclear Waste
Management
Projects

SPENT FUEL CLADDING CORROSION UNDER TUFF REPOSITORY CONDITIONS - INITIAL OBSERVATIONS

The basic objective of any nuclear waste repository is to safely isolate the waste from the biosphere. "Safely isolated" is defined by regulatory limits which state that the waste package will not release more than one part in 10^5 per year of the radionuclide inventory present at 1000 years following the end of the containment years.[1] The waste package consists of a number of engineered barriers designed to meet the regulations. In the case of spent reactor fuel, the cladding may provide a useful contributing barrier to radionuclide release. Therefore, the Lawrence Livermore National Laboratory (LLNL) is sponsoring the Zircaloy Cladding Degradation study presently being carried out by Westinghouse Hanford Company (WHC). LLNL is responsible for high level nuclear waste package development for the tuff repository as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project.

The WHC program is investigating corrosion and stress corrosion cracking of Zircaloy-2 and 4 in two model tuff repository environments using an experimental approach in which the repository environment is reproduced as accurately as possible, including temperature, radiation field, water chemistry and materials associations.[2] Post-experimental sample evaluation utilizes or will utilize sophisticated SEM/STEM, Auger surface analysis/ion milling, and trace element (e.g., ^{14}C) release to detect, locate and measure the effects of corrosion. The experiments themselves are being conducted using actual spent fuel and repository materials at repository conditions. The short experimental time (i.e., one year) is being compensated for by sensitive measuring techniques. Characterization of any corrosion found will be used to understand the mechanisms involved for extrapolation purposes.

Prepared by Nevada Nuclear Waste Storage Investigations (NNWSI) Project participants as part of the Civilian Radioactive Waste Management Program. The NNWSI Project is managed by the Waste Management Project Office of the U.S. Department of Energy, Nevada Operations Office. NNWSI Project work is sponsored by the Office of Geologic Repositories of the DOE Office of Civilian Radioactive Waste Management.

Chemical-electrochemical corrosion is being investigated using spent fuel cladding bundles which include crevices and dissimilar metal contacts characteristic of a spent fuel package. Stress corrosion cracking is being investigated using a "C-ring" test apparatus and will be followed by a pressurized cladding section experiment series (these results will be reported at a later date). The aqueous environments being modeled could occur in an unbreached container with breached fuel containing water after 90-100 years or in a breached container after more than 1,000 years when the repository has cooled to <95°C. The first environment is modeled with deionized water in an autoclave at 170°C and the second uses reference tuff area well water equilibrated with tuff at 90°C. Spent fuel and defueled cladding produce radiation fields approximating the expected repository levels after ~100 and ~1000 years, respectively.

Electrochemical Corrosion Scoping Experiment

The scoping experiment, which was designed to provide some initial data and to refine the experimental procedure, exposed defueled cladding bundles sitting in a layer of crushed tuff to 90°C J-13 well water for two, six, and 12 months. The water level was maintained to midway up the cladding bundle. The cladding used in this experiment was discharged from Turkey Point Unit 3, with an average core burnup of 25.7 MWD/MTU. Each section read ~700 mR/hr at ~2" with the self-field of each bundle of seven sections on the order of ~5 R/hr. This compares to a field of about 4 R/hr expected after 1000 years in this repository. Zircaloy-4 end plugs prevented the interior of the cladding section from contacting the aqueous environment. The bundles were held together by a 304L SS (reference container material) wrap and a 300-series stainless hose clamp. Following each experiment, the bundle was dismantled, photographed and samples selected for more detailed examination.

Discussion of Results

Other than white encrustations of silica and calcium carbonate at the water-air interface and a slight staining observed occasionally at the contact

between the 304L SS wrap and the cladding sections, no macroscopic physical change was observed. Metallographic sections were evaluated with both an optical microscope and an SEM capable of handling radioactive specimens. The sections studied were fabricated so that they cut across cladding-cladding and cladding-304L SS contact areas and the water-air interface. Comparison with n n-contact areas revealed no sign of selective corrosion in the contact or interface areas. Comparison at magnifications to 10,000X of material exposed to the conditions of the experiment with unexposed material again gave no indication that corrosion had taken place. Because of the observed variation of oxide thickness (factor of two) and roughness of the oxide/metal interface (~1 μm) on spent fuel cladding, these comparative observations would not have detected less than a few microns of corrosion unless there was a distinct texture produced by corrosion in the model repository environment. The pH and conductivity measurements made on the water during the course of the experiments showed some scatter but on the average remained constant (8.65 ± 0.30, 750 ± 200 mho) during the duration of the experiments. Zirconium remained below about 10 ppb for the duration of the experiments. These results are consistent with the very low values (on the order of angstroms per year) for oxidative corrosion of zirconium and its alloys observed by others when extrapolated to these experimental conditions.[3]

The next set of experiments will use fueled cladding from H. B. Robinson discharged in 1974 with 28.0 MWD/MTU average burnup. These cladding bundles will include sections with polished patches where the oxide film is removed down to bare metal providing a baseline condition. Using Auger surface analysis in conjunction with ion milling, oxidation corrosion can be measured accurately to within a few hundred angstroms, greatly lowering the detection limit for measuring the rate of homogeneous corrosion of Zircaloy-4 spent fuel cladding. This polished surface simulates a condition of an abraded fuel rod and provides an excellent surface on which to observe pitting and galvanic corrosion where it contacts 304L SS.

Conclusion

The initial evaluation of samples from two, six, and 12-month electrochemical corrosion experiments indicated no Zircaloy-4 corrosion at a detection sensitivity of 1-2 μm of corrosion per year.

To improve the sensitivity of the experiment, baseline conditions (e.g., beginning with a polished metal surface) will need to be established that are expected to make it possible to resolve corrosion on the scale of hundreds of angstroms. Examples are the development of such measurements as film depth determination via Auger surface analysis/ion milling and Zr and ^{14}C released into the aqueous corrosion environment. Characterization of any corrosion found will be used to understand the mechanisms involved. This will allow extrapolation of results to predict cladding lifetime under repository conditions.

References

1. Federal Register, Vol. 48, No. 120, 10CFR60, "Disposal of High-level Radioactive Wastes in Geologic Repositories Technical Criteria," Nuclear Regulatory Commission, Final Rule, June 21, 1983.

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3. Rothman, A. J., "Potential Corrosion and Degradation Mechanisms of Zircaloy Cladding on Spent Nuclear Fuel in a Tuff Repository," Lawrence Livermore National Laboratory, UCID-20172, September 1984.