



Advisory Committee on Nuclear Waste and Materials (ACNW&M) Questions on Corrosion of the Waste Package and Spent Nuclear Fuel Dissolution

**In Response to Staff Presentations to ACNW&M in 182nd Meeting,
September 18 – 20, 2007**

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engineered barrier system in post-closure, ENG 1, ENG 3 and ENG 4
of Division of High-Level Waste Repository Safety of NRC and
Center for Nuclear Waste Regulatory Analyses (CNWRA)**

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ACNW&M General Comment

“The most important considerations in any corrosion discussions to the Committee are: (1) what radionuclides (at what activity) are released from the Waste Package (WP), and (2) how are they released. The following questions are directed towards these considerations.”



Examples of Releases and Release Modes

- What is potentially released depends on physical state and chemistry of spent nuclear fuel (SNF) radionuclides:
 - Rapid release of gap and grain boundary radionuclide inventory, such as C-14, I-129, Cs-135, and Tc-99.
 - High solubility radionuclide inventory, such as I-129 and Tc-99 (release controlled by SNF dissolution rate).
 - Low solubility radionuclide inventory, such as Np-237, Pu-(239-240), and Am-241 (release controlled by solubility limit or colloids).
- Potential release modes:
 - Advective or diffusional, depending on groundwater flow rates through perforations or cracks of the WP caused by corrosion
 - Advective or diffusional release is also in series with SNF dissolution rate or radionuclide solubility limit (or colloids).



Question (Q) 1: Use of Temperature as a Time Surrogate

- Experiments at temperature to simulate long times were not used for NRC corrosion and SNF studies.
- Temperature could be used as a time surrogate, as rates of important chemical reactions increase predictably with temperature (e.g., Arrhenius relationship).
- Range of calculated repository temperatures, $\sim 35 - 240$ °C ($\sim 95 - 464$ °F), used in experiments for
 - Kinetics of general corrosion
 - Localized corrosion criteria
 - Kinetics of SNF dissolution



Q 2: Potential Staff Use of Corrosion Experiments Conducted since 2003 in License Application (LA) Review and Performance Assessment (PA)

- Use of CNWRA information to assist LA review depends on what information is provided in LA.
- Independent information could be used to assist LA review for areas such as:
 - Data and model justification
 - Data uncertainty
 - Model uncertainty
 - Model support
- Topics investigated on Alloy 22, since 2003, include (references in the end):
 - General corrosion
 - Seepage groundwater crevice corrosion
 - Dust deliquescence corrosion
 - Stress Corrosion Cracking (SCC)
 - Microbially influenced corrosion
 - Effects of fabrication processes



Q 3: Application of WP Passivation Studies

- **Passive film persistence** – Chromium-rich oxide film results in low general corrosion rates.
 - Thermodynamic analyses used to assess long-term stability of passive film (Jung, et al, 2007; Mintz, et al, 2007).
 - Analogs: Josephinite, meteorite, and reactor steam generator materials were assessed to understand long-term passivity (Jung, et al, 2007; Ahn, et al., 2007).
- **Anodic sulfur segregation** – Although sulfur may remain on the surface during corrosion and destabilize passive film, molybdenum may dissolve sulfur and chromium promotes repassivation.
 - Scratched metal exposed to solutions containing sulfides or thiosulfates may experience sulfur-enhanced general corrosion (i.e., Jung, et al, 2007; Ahn, et al., 2007).
 - Sulfur impurity may be up to 100 ppm. Detrimental effects of sulfur segregation can be reduced by reduction of initial sulfur content in the alloy (e.g., 1 ppm) (Jung, et al, 2007; Ahn, et al., 2007).
- **Alpha radiation effects** – Effects on passivity appear limited.
 - No significant source of alpha particles to contact the passive film. Alpha particles inside WP cannot penetrate through the WP under nominal conditions, and there is no other significant source of external alpha-particles.
 - Possible alpha particle source is from early-failed adjacent WP, or from portion of adjacent WPs subjected to corrosion or mechanical failure. Unlikely geometry is required for possible effect.
 - Limited analyses are being performed, to support review of DOE's Features, Events, and Processes (FEPs).



Q 4: Basis for Dust Deliquescence Corrosion

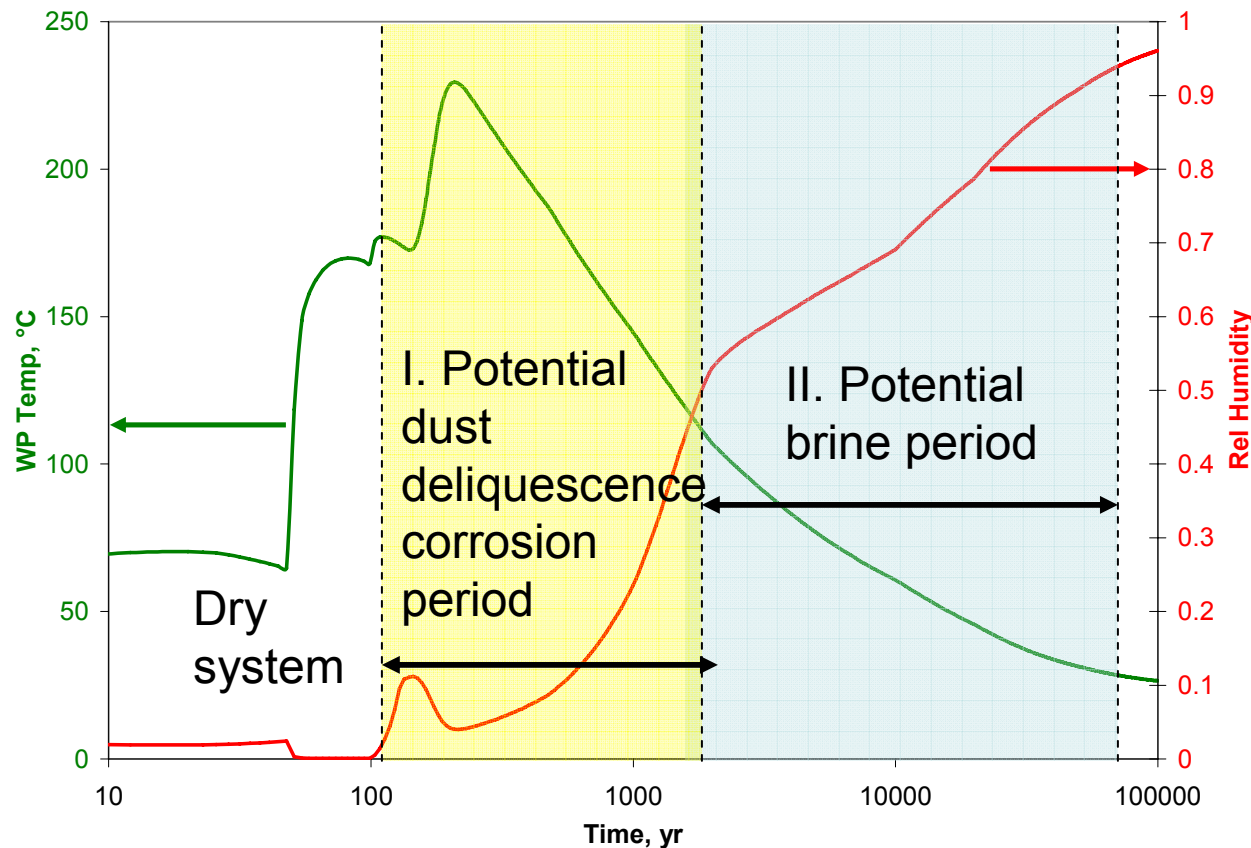
- Staff needs to review basis for potentially included and excluded FEPs.
- Alloy 22 corrosion testing in salt brines (potential composition of dust deliquescence brines) shows that general corrosion could occur (Yang, et al., 2007). Models of cathodic capacity of Alloy 22 in dust deliquescence brines (Shukla, et al. 2007) support the experimental observations.
- During the potential brine period, dust will be present. Although corrosion by seepage groundwater may dominate, dust deliquescence effects on general corrosion contribute to variability and uncertainty in PA.



Q 5 and 6: Corrosion During Dust Deliquescence and Brine Periods

- In the dust deliquescence corrosion period capillary retention of dust deliquescence brines by rock dust may reduce the amount of brine that contacts a metal surface, but does not prevent corrosion from occurring (He, et al., 2007).
- In the brine period, temperatures appear high enough to form concentrated brines that may cause crevice corrosion. Simultaneously, general corrosion continues. General corrosion rates are generally insensitive to brine concentrations.

WP Environment and Corrosion Modes



(After Pensado, 2006)

- Persistence of long-term passive film in general corrosion (I, II, and longer period)
- Dust deliquescence corrosion (I)
- Seepage water brines - crevice corrosion (II)

(100 °C = 212 °F)



Q 7: Role of Stress Corrosion Cracking

- SCC could potentially have an effect by allowing a limited amount of water into tight cracks in the WP.
- Formation of SCC requires carbonate/bicarbonate solution concentrations that are not expected in the potential repository (e.g., Chiang, et al., 2007). CNWRA analysis supports that SCC is an unlikely process (e.g., Chiang, et al, 2007).
- Uncertainties associated with SCC model abstraction are considered in TPA (Leslie and Grossman, 2007).



Q 8: Chemical Mechanisms for WP and DS Corrosion.

- Corrosion most is the likely process to penetrate the WP.
- General corrosion likely will occur over a longtime.
- General corrosion may eventually create large enough opening in WP to support advective release.
- Passivity loss for enhanced general corrosion:
 - Impurity segregation (e.g. sulfur), corrosion product accumulation, or stress developed
 - Long-term dissolution and no repassivation



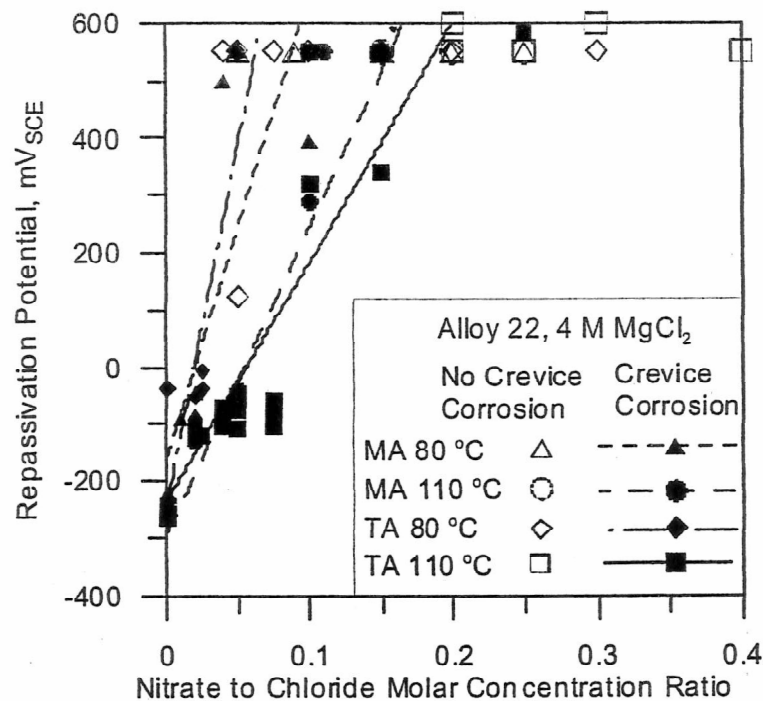
Q 9: Nitrates in the Repository

There are two likely sources of nitrates in the potential repository:

- Atmospheric aerosols could be entrained in ventilation air and deposited, together with dust particles, on the waste package surface during the preclosure period.
 - The soluble fraction of atmospheric aerosols over continental landmasses typically is dominated by nitrate, sulfate, ammonium, and sodium (e.g., Seinfeld, 1986).
 - Nitrate concentrations in leachates of dust samples taken by the U.S. Geological Survey from the Exploratory Studies Facility at Yucca Mountain range from several tens to about 1800 ppm (Bechtel SAIC Company, LLC, 2004).
- Nitrate dissolved in groundwater.
 - Nitrate concentrations reported by the U.S. Geological Survey (Yang, et al., 1996, 1998, 2003) for porewaters extracted from rock samples taken from the unsaturated zone of YM and vicinity typically are in the tens of ppm.
 - Although these porewaters are initially dilute, evaporation may increase or decrease the concentrations of dissolved constituents, including nitrate salts.

Q 9:Nitrates in the Repository (Cont.)

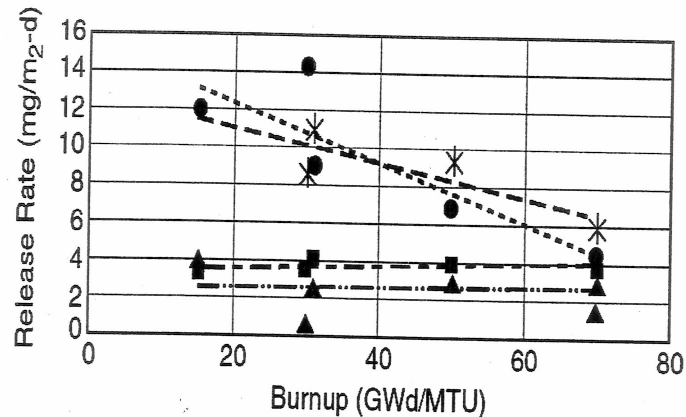
E_{repass} vs. NO_3 (Dunn, et al, 2005)



**Crevice Corrosion Repassivation
Potentials for Mill-Annealed and Thermally Aged
Alloy 22**

Q 10: Dissolution Rates for High Burnup Fuel

- Available information indicates that high burnup SNF does not increase the dissolution rate.



■ T 25°C, CO₃ 0.02 ▲ T 25°C, CO₃ 0.0002
 ● T 75°C, CO₃ 0.02 ✱ T 75°C, CO₃ 0.0002
 --- Linear (T 75°C, CO₃ 0.0002) - - - - - Linear (T 75°C, CO₃ 0.02)
 - - - - - Linear (T 25°C, CO₃ 0.0002) - · - · - Linear (T 25°C, CO₃ 0.02)

Spent Nuclear Fuel Dissolution Rate As a Function of Burnup Under Different Temperatures (T) and Molar Total Carbonate Concentrations (CO₃).

(Jain, et al., 2004)

- Available information indicates that:

- prior dry oxidation of high burnup SNF may increase surface area, to increase dissolution rates (Ahn, 1996).

- hydride formation (Pan, et al, 2007; Ahn, et al., 2007) does not affect dissolution rate, except potentially altering surface area.

75 °C (167 °F); 25 °C (77 °F);
mg m⁻² d⁻¹ = 1.42x10⁻⁹ lb in⁻² d⁻¹



Q 11: Use of SIMFUEL Data

- Dissolution rates of SNF, unirradiated UO_2 , and SIMFUEL are undistinguishable for similar environmental conditions. Thus, dissolution experiments using unirradiated UO_2 or SIMFUEL are considered appropriate (Ahn and Mohanty, 2007; Jegou, et al., 2001; Shoesmith, 2000; Serrano, et al., 1998).
- Radiolysis effects on SNF dissolution may be significant in reducing environments. The potential Yucca Mountain repository is oxidative, not reducing, with abundant buffered oxygen available. Therefore, radiolysis is anticipated to have a negligible effect on an oxidized system.
- Uncertainties regarding the geometry of alpha particle emission after potential container failure appear low but are being considered (Ahn and Mohanty, 2007; Jain, et al., 2004).



Q 12: Long-Term Spent Nuclear Fuel Behavior

- **Long-term stability of irradiated UO_2 matrix** – Other than chemical degradation (e.g. dissolution), ongoing work in Europe indicates long-term stability of crystal structure/integrity and stable radionuclide distributions.
- **Physical degradation** – Physical degradation could come from alpha displacement damage or mechanical failure, sometimes assisted by chemical process such as hydration in the irradiated UO_2 or hydrogen embrittlement in cladding.
- **Stability of cladding** – Cladding could be subject to gross rupture or perforations (e.g., pin holes and hairline cracks) by applied stress, hydrogen embrittlement, or corrosion through time.
- **Hydriding** – Hydrogen embrittlement in cladding comes from the formation of a brittle zirconium-hydrogen compound (i.e. hydride). Existing hydrides after reactor discharge could be reoriented radially under applied stress. More radial hydrides could form by absorption of hydrogen during corrosion, which could reduce cladding ductility or cause slow crack propagation.



Q 13: Risk Insights Radionuclide Release

- Fundamental risk insights (NRC, 2004) have not substantially changed in light of new information.
- Radionuclide release depends in part on extent of the surface-area opening on WP.
 - Small surface-area opening for groundwater entry into the failed WP.
 - Limited groundwater volume restricts the mobilization of radionuclides.
- The expected extent of surface-area opening for various corrosion modes includes:
 - General corrosion - loss of passivity gives relatively large opening; may lead to advective release
 - Crevice corrosion – restricted opening from susceptible water chemistry, tight crevice area of buckled DS and WP, and weld area; may lead to diffusional or advective release
 - Unlikely SCC – restricted area opening; may lead to diffusional release
- New internals of WP to reduce colloid production



References

- T. Ahn, H. Jung, X. He and O. Pensado, Understanding Long-Term Corrosion of Alloy 22 Container in the Potential Yucca Mountain Repository for High-Level Nuclear Waste Disposal, Third International Workshop on Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems, Pennsylvania State University (with OECD), State College, PA, May 14 – 18, 2007, U. S. Nuclear Regulatory Commission, NRC ADAMS ML071210581, also submitted for publication is special issue of Journal of Nuclear Materials
- T. Ahn and S. Mohanty, Dissolution Kinetics of Commercial Spent Nuclear Fuels in the Potential Yucca Mountain Repository Environment, U. S. Nuclear Regulatory Commission, NRC ADAMS ML070860209, 2007
- T. Ahn, F. Gaskins, D. Pomeroy and M. Bailey, Hydride Effects in the Cladding Performance for the Safe Geologic Disposal of High-Level Waste, ASTM Subcommittee C26.13, Spent Fuel and High Level Waste, Workshop on Hydride Re-Orientation in Zr Alloys, Costa Mesa, CA, 2007, NRC ADAMS ML063540231
- T. Ahn, Dry Oxidation and Fracture of LWR Spent-fuels, NUREG-1565, U. S. Nuclear Regulatory Commission, NRC ADAMS ML040150720, 1996
- Bechtel SAIC Company, LLC, Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier, ANL-EBS-MD-000001, Revision 01, Las Vegas, Nevada: Bechtel SAIC Company, LLC, 2004
- K. T. Chiang, D. S. Dunn, Y.-M. Pan, O. Pensado and P. K. Shukla, Stress Corrosion Cracking of Waste Package Material – Modeling and Experiments, CNWRA 2007-01, Center for Nuclear Waste Regulatory Analyses, 2006
- D. S. Dunn, O. Pensado, Y.-M. Pan, R. T. Pabalan, L. Yang, X. He and K. T. Chiang, Passive and Localized Corrosion of Alloy 22 – Modeling and Experiments, CNWRA 2005-02, Revision 1, Center for Nuclear Waste Regulatory Analyses, 2005
- D. S. Dunn, Y.-M. Pan, D. Daruwalla and A. Csontos, The Effects of Fabrication Processes on the Mechanical Properties of Waste Packages – Progress Report, CNWRA 2004-03, Center for Nuclear Waste Regulatory Analyses, 2003
- D. S. Dunn, Localized Corrosion Susceptibility of Alloy 22 in Chloride Solutions: Part 2-Effect of Fabrication Processes, Corrosion, Vol. 62, pp. 3-12, 2006



References (Cont.)

- X. He and D. S. Dunn, Crevice Corrosion Penetration Rates of Alloy 22 in Chloride Containing Waters – Progress Report, CNWRA 2006-01, 2005
- X. He, D. S. Dunn and A. A. Csontos. A Corrosion of Similar and Dissimilar Metal Crevices in the Engineered Barrier System of A Potential Nuclear Waste Repository, *Electrochimica Acta*, Vol. 52, pp. 7,556B7,569. 2007
- X. He and D. S. Dunn. A Crevice Corrosion Propagation Behavior of Alloy 22 in Extreme Environments. @ Proceedings of the CORROSION 2007 Conference. Paper No. 578. Houston, Texas: NACE International. 2007
- V. Jain, G. Cragolino and L. Howard, A Review Report on High Burnup Spent Nuclear Fuel – Disposal Issues, CNWRA 2004-08, Center for Nuclear Waste Regulatory Analyses, 2004
- C. Jegou, J. L. Paul and J. F. Lucchini, State of the Art of the Leaching and RN Release from Spent Fuel, Section 8.2 of Synthesis on the Long Term Behavior of the Spent Nuclear Fuel, C. Poinssot edited, CEA-R-5958 (E), Volume II Commissariat à l'Énergie Atomique, France, 2001
- H. Jung, T. Mintz, D. S. Dunn, O. Pensado and T. Ahn, A Review of the Long-Term Persistence of the Passive Film on Alloy 22 in the Potential Yucca Mountain Repository Environments, Center for Nuclear Waste Regulatory Analyses, NRC ADAMS ML072880595, 2007
- B. Leslie and C. Grossman, coordinator, Total-system Performance Assessment (TPA) Version 5.1 Module Descriptions and User Guide, Center for Nuclear Waste Regulatory Analyses, NRC ADAMS ML072710060, 2007
- T. Mintz, H. Gonzalez and Y.-M. Pan, An Examination of the Chromium-Rich Passive Film's Formation on Alloy 22 in Mildly Alkaline Environments, U. S. Nuclear Regulatory Commission, NRC ADAMS ML072960467, 2007
- Y.-M. Pan, K. S. Chan and D. S. Riha, A Probabilistic-Micromechanical Methodology for Assessing Zirconium Alloy Cladding Failure, *Mat. Res. Soc. Symp. Proc.*, Vol. 985, pp. 105 – 110, 2007
- J. R. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution*, New York, New York: John Wiley & Sons, 1986

References (Cont.)

- J. A. Serrano, V. V. Rondinella, J. P. Glatz, E. H. Toscano, J. Quiñones, P. P. Diaz-Arocas and J. Garcia-Serrano, Comparison of the Leaching Behavior of Irradiated Fuel, SIMFUEL, and Non-irradiated UO_2 Under Oxidic Conditions, *Radiochimica Acta*, Vol. 82, (1 – 4), pp. 33 – 37, 1998
- P. K. Shukla, R. Pabalan, T. Ahn, L. Yang, X. He and H. Jung, Cathodic Capacity of Alloy 22 in the Potential Yucca Mountain Repository Environment, Center for Nuclear Waste Regulatory Analyses, NRC ADAMS ML072780515
- N. Sridhar and G. Cragnolino, Evaluation of Analogs for the Performance Assessment of High-Level Waste Container Materials, CNWRA 2004-02, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX, 2004
- Shoesmith, Fuel Corrosion Processes Under Waste Disposal Conditions, *Journal of Nuclear Materials*, 282, (1), pp. 1 – 31, 2000
- U. S. Nuclear Regulatory Commission, Risk Insights Baseline Report, NRC ADAMS ML040560162, 2004
- I. C. Yang, G.W. Rattray and P. Yu, Interpretation of Chemical and Isotopic Data from Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada, Water-Resources Investigations Report 96-4058, Denver, Colorado: U.S. Geological Survey, 1996
- I. C. Yang, P. Yu, G.W. Rattray, J.S. Ferarese and J.N. Ryan, Hydrochemical Investigations in Characterizing the Unsaturated Zone at Yucca Mountain, Nevada." Water-Resources Investigations Report 98-4132, Denver, Colorado: U.S. Geological Survey, 1998
- I. C. Yang, Z.E. Peterman, and K.M. Scofield, Chemical analyses of Pore Water from Boreholes USW SD-6 and USW WT-24, Yucca Mountain, Nevada, *Journal of Contaminant Hydrology*, Vol. 1878, pp. 1– 20. 2003
- L. Yang, D. Dunn, G. Cragnolino, X. He, Y.-M. Pan, A. Csontos and T. Ahn, Corrosion Behavior of Alloy 22 in Concentrated Nitrate and Chloride Salt Environments at Elevated Temperatures, NACE Corrosion 2007 Conference & Expo, Paper No. 07580, NACE International, Houston, TX, 2007
- L. Yang, S. Birnbaum and G. A. Cragnolino, Microbially Influenced Corrosion Studies of Engineered Barrier System Materials, CNWRA 2005-01, Center for Nuclear Waste Regulatory Analyses, 2004



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