Nuclear Waste Technical Review Board

INTERNATIONAL WORKSHOP ON LONG-TERM EXTRAPOLATION OF PASSIVE BEHAVIOR

Alberto Sagüés

September 10, 2001

1

Outline of Presentation

- Background for International Workshop (why, when, who, what)
- Results (possible anomaly/failure mechanisms; ideas for new research)
- What's next

2

Issue

- Unprecedented extrapolation of long-term corrosion performance of chosen alloy for many thousands of years
  - Alloy 22 owes its corrosion resistance to the phenomenon of passivity
  - Limited experience with Alloy 22: commercially available less than two decades
  - Other alloys (e.g. Stainless steels, Aluminum alloys) also rely on passivity, but engineering experience with them spans only about a century

3

Workshop Goals

- Assemble workshop of experts from around the world to propose:
  - Plausible mechanisms by which Alloy 22 passive layer could degrade in long term leading to increased corrosion rates
  - Plausible mechanisms for shifts in open circuit / critical potentials or other long term processes that could lead to localized corrosion in Alloy 22
  - Ideas for experimental or theoretical work to address these mechanisms
- Broaden awareness within corrosion community of Yucca Mountain corrosion issues

4

Workshop Time and Place

- 1½-day workshop was held July 19, 2001, and morning of July 20, 2001, in Arlington, Virginia.
- The following material from the workshop is on the Board's website (www.nwtrb.gov):
  - List of workshop participants
  - Background material and questions sent participants before the workshop
  - Transcripts of the workshop

5

Workshop Participants

Ugo Bertocci		USA
Gustavo A. Cragnolino	Center for Nuclear Waste Regulatory Analyses (Southwest Research Institute)	USA
Alison J. Davenport	University of Birmingham	UK
Jerome Kruger	Johns Hopkins University, Emeritus	USA
Digby D. Macdonald	The Pennsylvania State University	USA
Barry R. MacDougall	National Research Council Canada	Canada
Philippe Marcus	L'Ecole Nationale Superieure de Chimie de Paris	France
Roger C. Newman	University of Manchester Institute of Science and Technology	UK
Howard W. Pickering	The Pennsylvania State University	USA
Robert A. Rapp	Ohio State University, Emeritus	USA
Norio Sato	Hokkaido University, Emeritus	Japan
Toshio Shibata	Osaka University, Emeritus	Japan
Susan Smialowska	Ohio State University, Emeritus	USA
Hans-Henning Strehblow	Heinrich-Heine University Duesseldorf	Germany

6

"Plausible Mechanisms*"

- Passive corrosion may proceed at different rates for various alloy components, leading to vacancy buildup at the metal-film interface. This could cause oxide spalling and increase overall corrosion rate.
- Particularly if the pH is high, molybdenum may dissolve preferentially and compromise passivity. Similar processes in transpassive dissolution of high-Mo alloys.
- Changes in the composition of the metal (e.g., Cr depletion) near the metal surface-passive layer interface may exacerbate corrosion.

* Emphasis on long-term passive dissolution effects

7

"Plausible Mechanisms*" (continued)

- The outer hydroxide film may play a stabilizing effect on the inner barrier film. Possibly adverse evolution of the outer film, for example due to cyclic conditions, should be considered.
- The roughness of the metal surface-passive layer interface may increase during passive dissolution, eventually affecting corrosion rate.
- Corrosion products from passive dissolution accumulate on the WP surface, creating a layer of (likely hydrated) metal ions. If this layer acts as an anion-selective membrane, it may promote localized corrosion.
- Much remains to be known about nature and composition of the passive film.

* Emphasis on long-term passive dissolution effects

8

"Plausible Mechanisms*" (continued)

- Deposition of passive-corrosion debris on the WP surface over long times could lead to long-term upward drift of the open-circuit potential
- p-type barriers can result in increased open circuit potential under radiation.
- Anodic segregation of sulfur (or other) impurities may occur at the metal-passive layer interface as passive dissolution progresses.
- Possible detrimental synergistic effects of Cl^- and F^- ions, especially under cyclic exposure conditions.

9

* Emphasis on localized corrosion

"Plausible Mechanisms*" (concluded)

- Expect large scatter in pitting potentials when they are elevated as in Alloy 22.
- Passive layers formed initially by air oxidation may protect less well than water-formed films against aqueous conditions if aggressive anions are present.
- Processes in deep crevices are poorly understood.
- Time spent at (or above) ~800ºC can have large effects on critical potential, possibly because of segregation at grain boundaries.

* Emphasis on localized corrosion

10

Research/Analysis Ideas

- Perform corrosion tests and surface analytical investigations under worst-case repository conditions.
- Examine thickness, composition, and structure of passive film as a function of potential, time, and anion (e.g., Cl^-, F^-) concentration.
- Study passive films produced in air or steam from 100º-250ºC over long times to determine their nature and whether they can survive in aqueous environments containing aggressive anions.
- Study metastable pitting by measuring electrochemical noise at environmental extremes that may develop in a repository.

11

Research/Analysis Ideas (continued)

- Develop theoretical treatment of the effect of environment on Cl^- transport through the passive layer under an electric field to examine the buildup of metal chloride at sites of local film disruption.
- Compare electrochemical properties (i.e., potential) of fresh coupons with coupons exposed to simulated repository environments for years.
- Examine kinetics of redox reactions on the passive layer and transport processes in the passive layer.
- Simulate effect of surface roughness, then validate with short-term measurements of roughness.
- Investigate accumulation of vacancies.

12

Research/Analysis Ideas (concluded)

- Perform laboratory studies of the behavior of Alloy 22 with increasing amounts of impurities (e.g., intentionally added sulfur).
- Study mechanisms of local depassivation by ions other than Cl^- (e.g., F^-).
- Use capillary electrophoresis for measuring solution composition to evaluate possible preferential dissolution of alloying elements.
- Use high-resolution passive current density measurements over extended periods.
- Evaluate possible vacancy accumulations by resistivity measurements of thin metal foils.

13

Future

- Symposium participant summaries are being collected; Board will decide how to disseminate.
- Board findings, conclusions, and recommendations (if any) on corrosion will be forthcoming.

14