# Developments in High-Level Radioactive Waste Disposal Containers Materials Through

# 25 Years of MRS Symposia

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# Outline

- Historic review of papers on container materials and waste package designs since 1st MRS Symposium in November 1978 until the present Symposium
- Brief overview of evolution of environmental conditions in different geological formations proposed for high-level radioactive waste disposal
- Brief review of evolution of waste package designs
- Corrosion and metallurgical studies of container materials presented in 213 papers in the MRS Symposia
  - Experimental [131]
  - Modeling [24]
  - Performance assessment and life estimates [26]
  - Reviews and general descriptions [32]

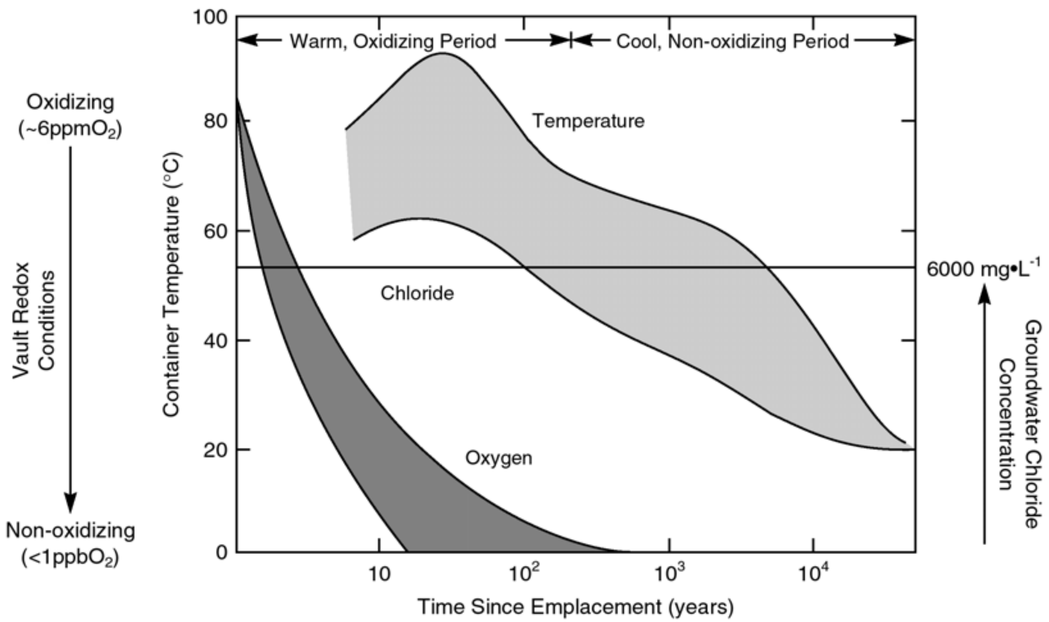
# Classes of Container Materials Studied

- Carbon steel, low alloy steel, and cast iron [62]
- Austenitic stainless steels [20]
- Copper [36]
- Titanium alloys (include drip shield studies) [29]
- Nickel-base alloys [47]
- Others materials [20]

In addition, a number of papers [13] are comparative reviews or studies on several materials listed above

Note: The numbers indicate the number of papers in which a given class of materials is studied. The total is greater than 213 papers because several papers deal with more than a single class of materials

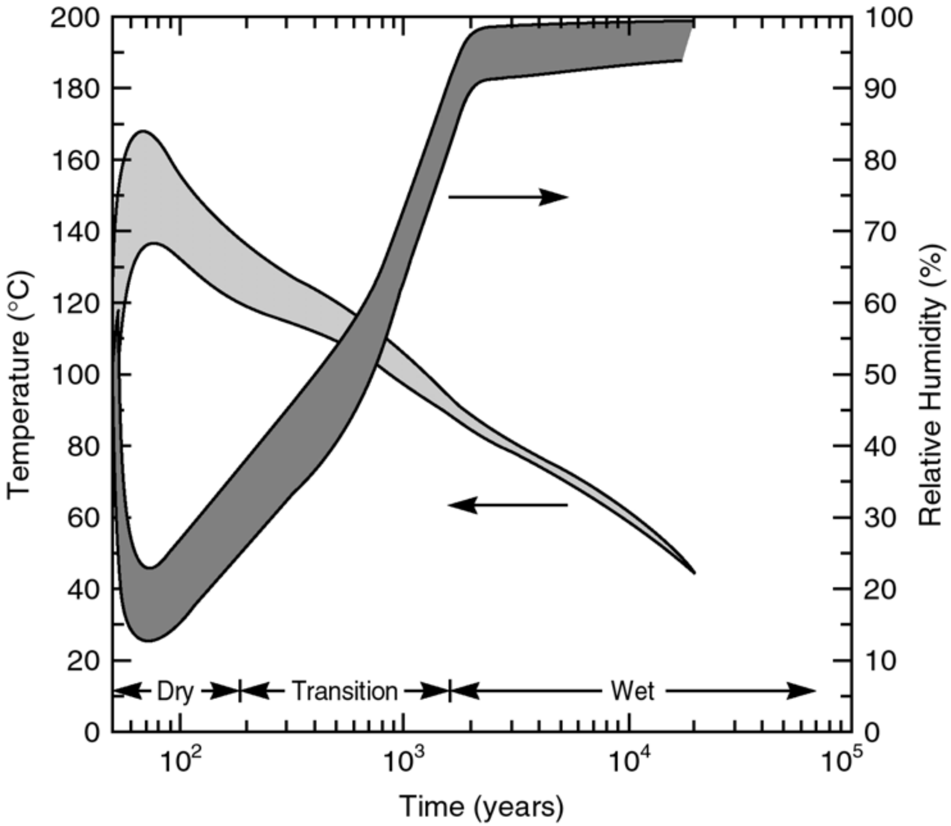
# Evolution of Environmental Parameters in a Repository Located in the Saturated Zone




King et al.(1993); Shoesmith et al. (1995)

- Schematic evolution for a potential Canadian waste repository in granitic rock
- After a peak arising from radionuclide decay heat the temperature decreases
- The chloride concentration is fixed to a typical value for saline underground water
- Oxygen is consumed (< 1 ppb) at times bounded by the reaction with organic material and with Fe(II) present as biotite

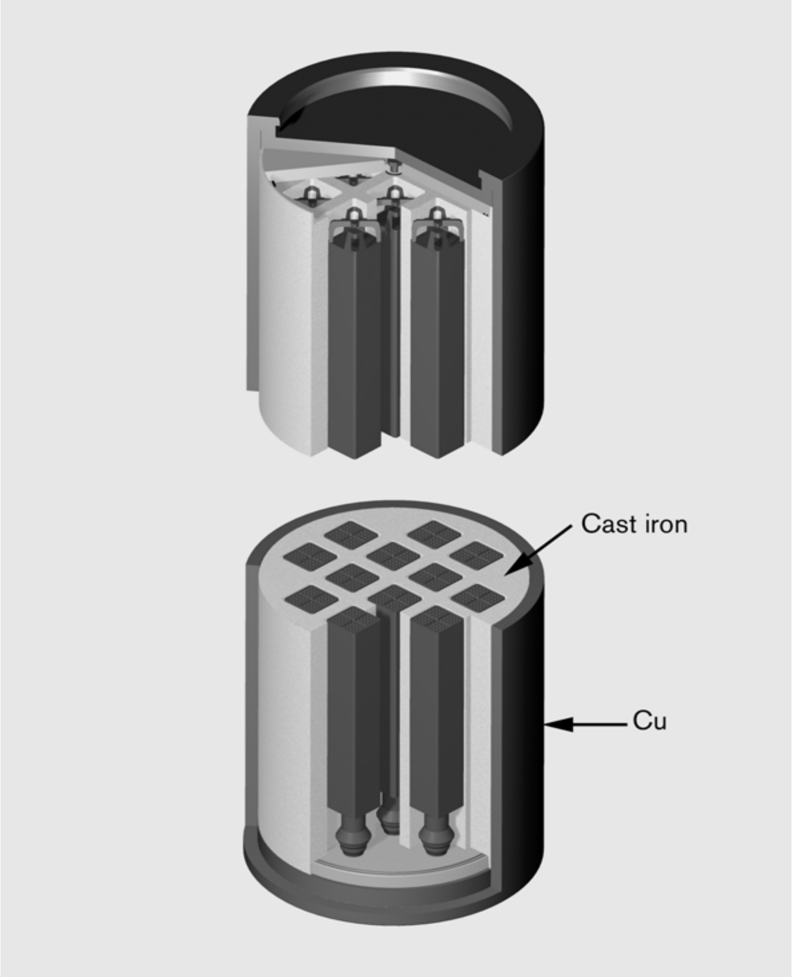
# Evolution of Environmental Parameters in a Repository Located in the Unsaturated Zone




Waste Package and Drip Shield Corrosion Technical Basis Document No. 6. Bechtel SAIC (2003)

- Estimated evolution for a potential repository at Yucca Mountain
- The temperature decreases after a peak at about 50 years
- Relative humidity in emplacement drifts increases after the dry period to values close to saturation
- The chemical composition of the aqueous environment (i.e., [$Cl^-$], [$NO_3^-$], [$HCO_3^-$], …) in contact with the waste package changes with time due to evaporation of groundwater and deliquescence of deposited salts

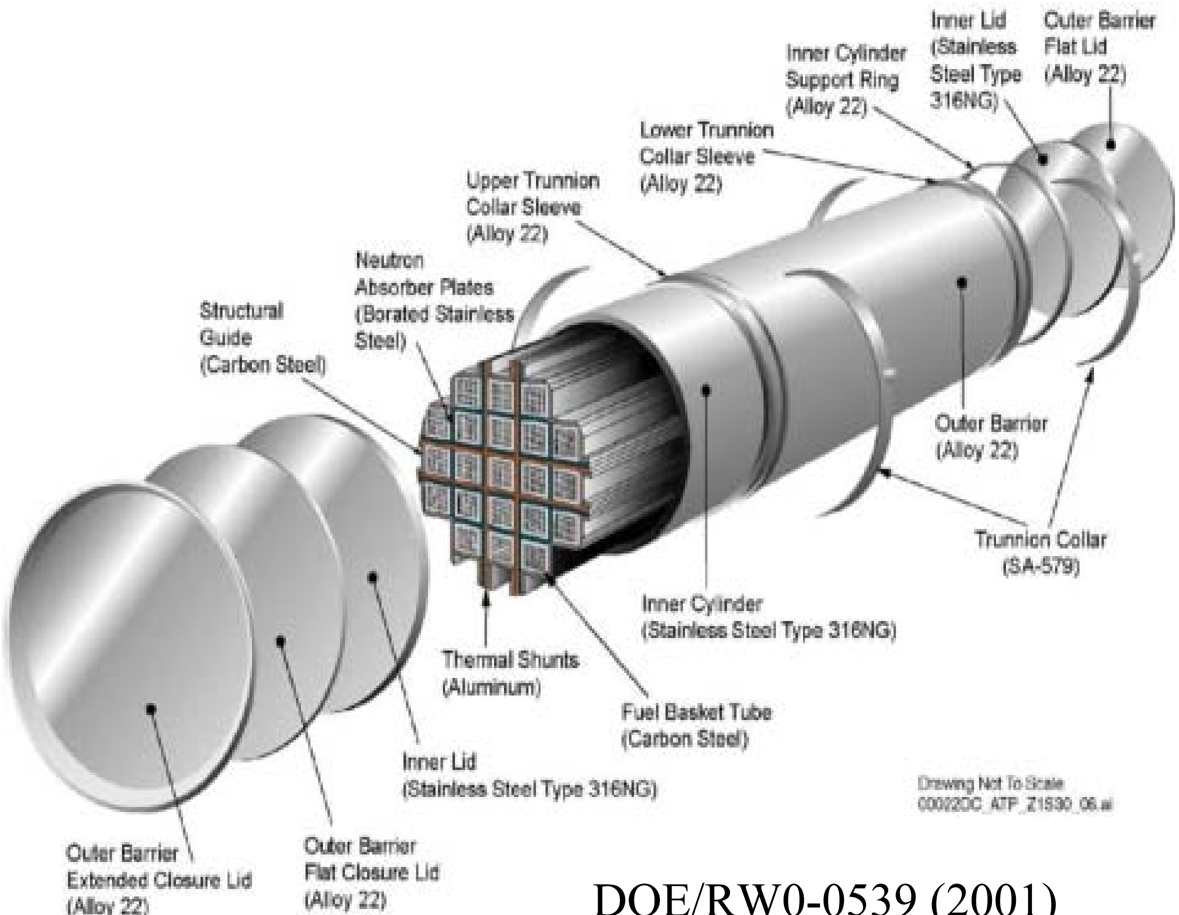
# Waste Package Design for the Proposed Swedish Repository




Werme (1999)

- Corrosion resistance to the aqueous environment provided by the outer copper canister
- Mechanical strength under the hydrostatic pressure expected to prevail in the repository provided by a cast nodular iron insert
- Vertical borehole emplacement in the crystalline bedrock with a bentonite clay backfill surrounding the canister

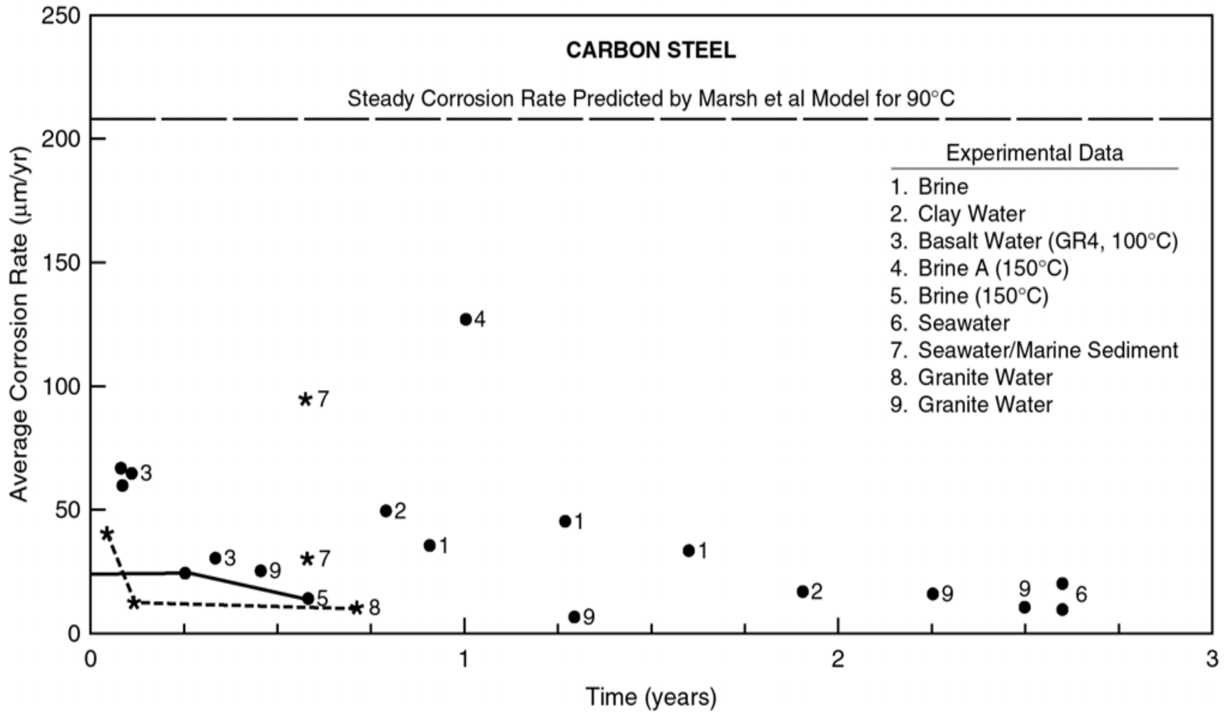
# Waste Package Design for the Potential Repository at Yucca Mountain




DOE/RW0-0539 (2001)

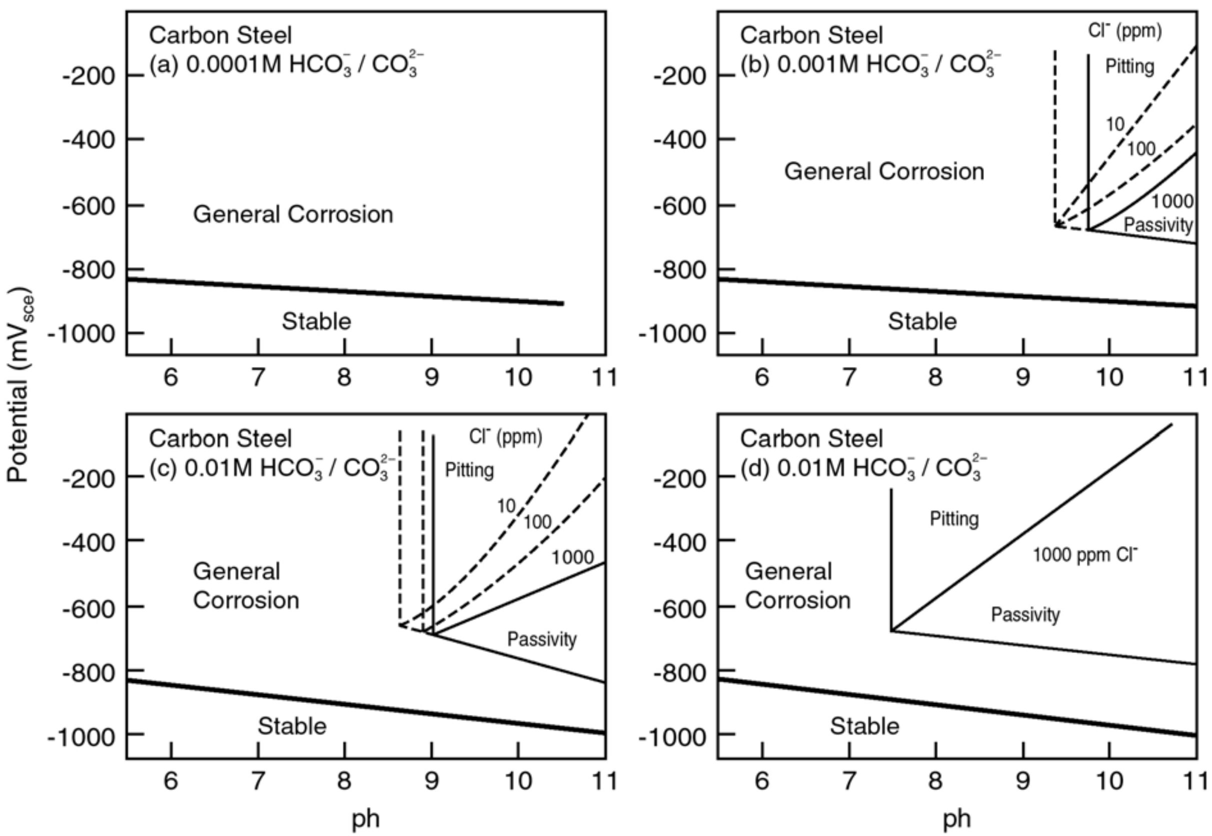
- Outer disposal made of Alloy 22 to provide resistance to aqueous corrosion
- Inner disposal container made of Type 316NG to provide structural strength
- Horizontal emplacement in drifts with a Ti alloy drip shield to limit water seepage and rockfall

# Carbon Steel – General Corrosion



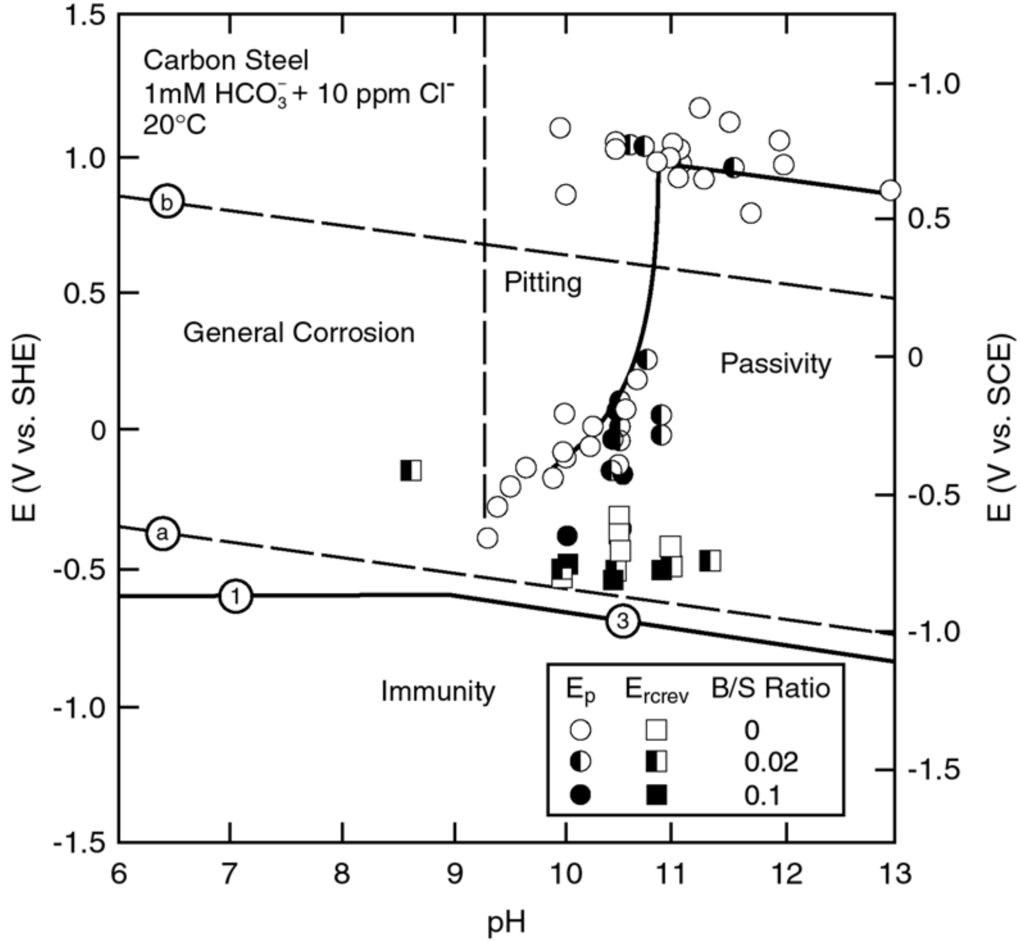

- Corrosion allowance material proposed for repository environments in the saturated zone
- March et al. (1987) developed a model for general corrosion and compared with experimental results of immersion tests from a variety of sources

# Carbon Steel - Passivity and Pitting Corrosion



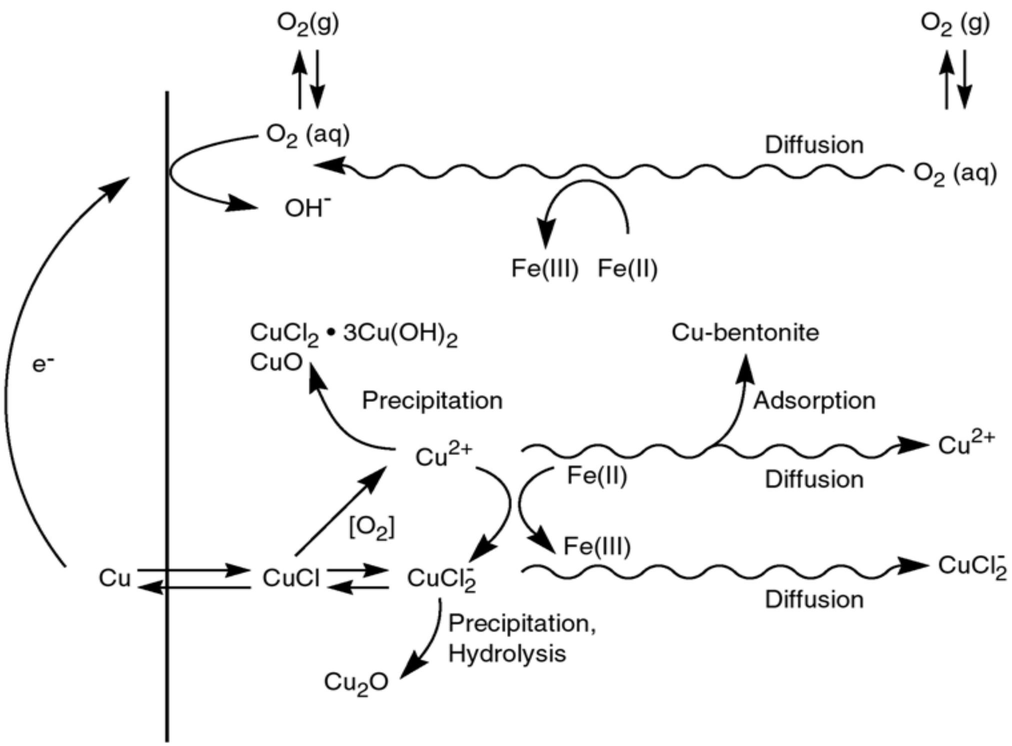

- Corrosion behavior of carbon steel is strongly dependent on pH
- Marsh et al. (1985) showed that carbon steel exhibits passivity above a pH which is dependent on $[HCO_3^-]$ and becomes susceptible to pitting corrosion in the presence of $Cl^-$ above a critical potential

# Carbon Steel – Pitting and Crevice Corrosion



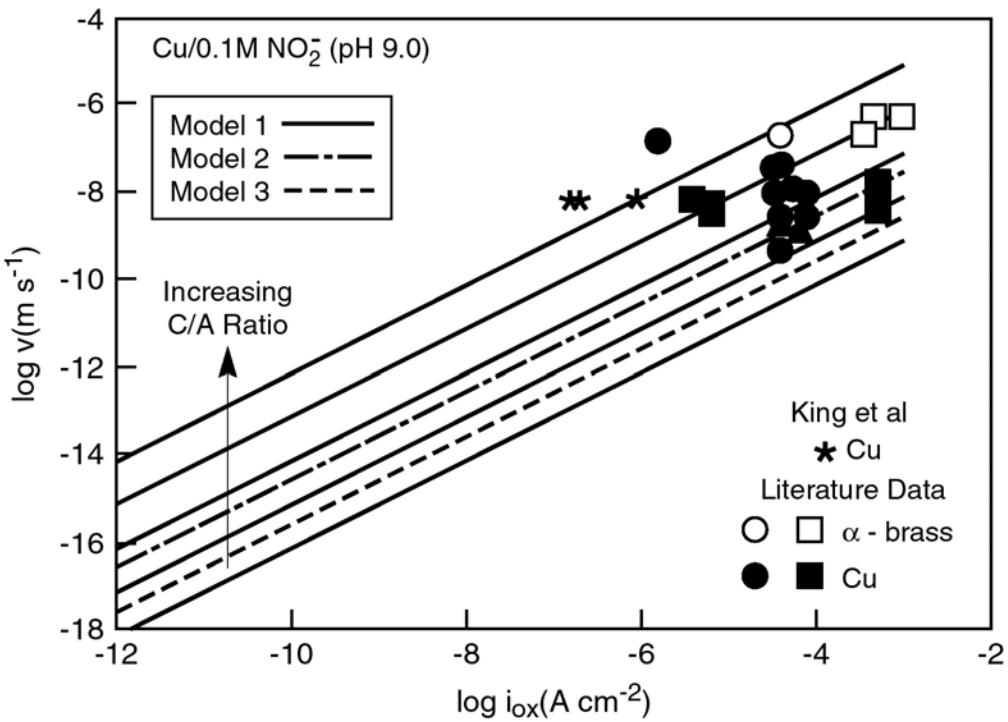

- Nakayama and Akashi (1991) showed that carbon steel in the presence of bentonite is susceptible to crevice corrosion at potentials even lower than those for pitting corrosion
- The crevice corrosion susceptibility increases with increasing bentonite/solution ratio
- Localized corrosion of carbon steels can be avoided only in fully deaerated environments

# Copper – Corrosion Modeling



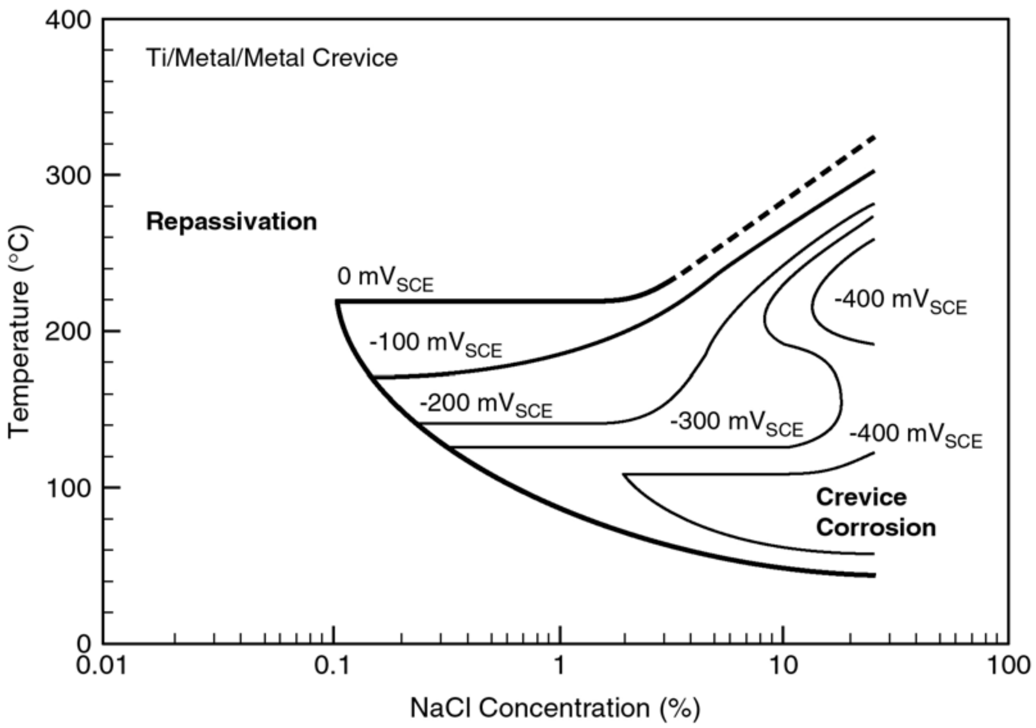

- King et al. (1993, 1995) developed a model for Cu corrosion in $O_2$-containing chloride solutions including chemical, electrochemical, and mass transport processes
- The model estimates the corrosion potential and uniform corrosion rates, as well as the initiation of pitting corrosion

# Copper - Stress Corrosion Cracking



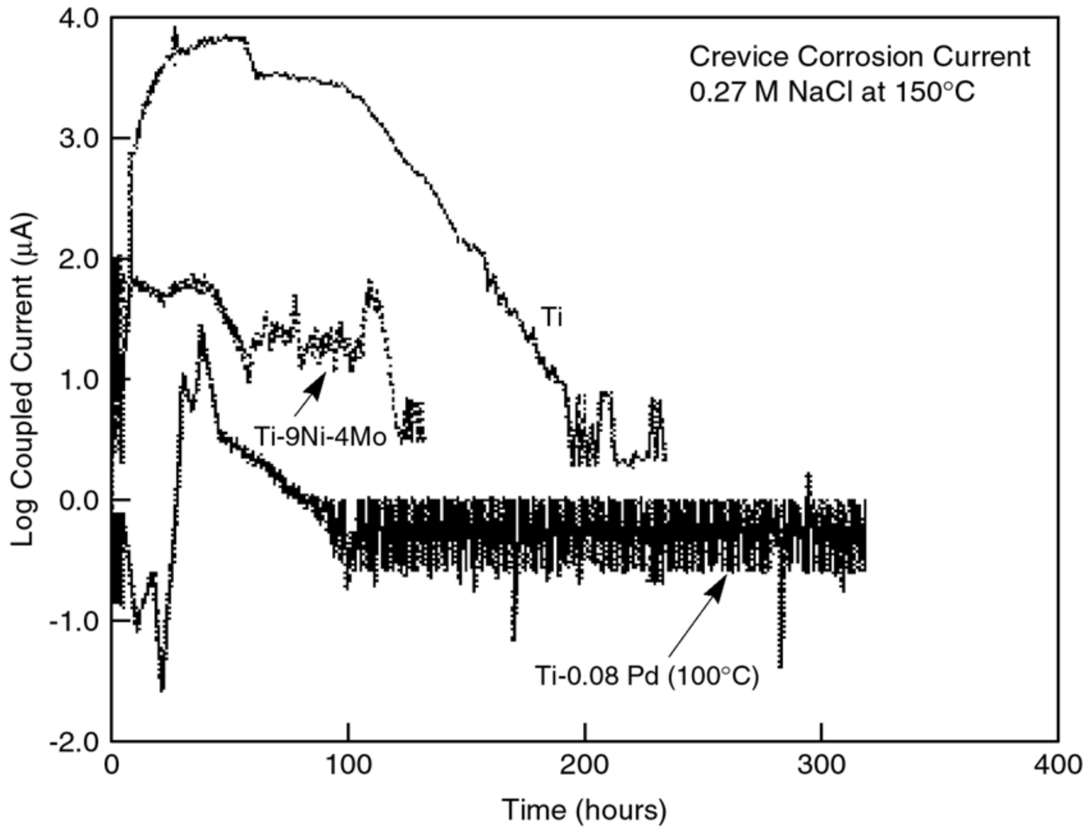

- King et al. (1998) studied the SCC of Cu in $NO_2^-$ solutions and compared their results with literature data and model estimates
- $NO_2^-$ can be produced initially by γ-radiolysis of moist air and later by microbial activity
- Three models
  - 1 - Film rupture anodic dissolution
  - 2 - Film-induced cleavage
  - 3 - Tarnish rupture
- Good agreement with Model 1 for high cathode/anode surface ratio

# Titanium – Crevice Corrosion



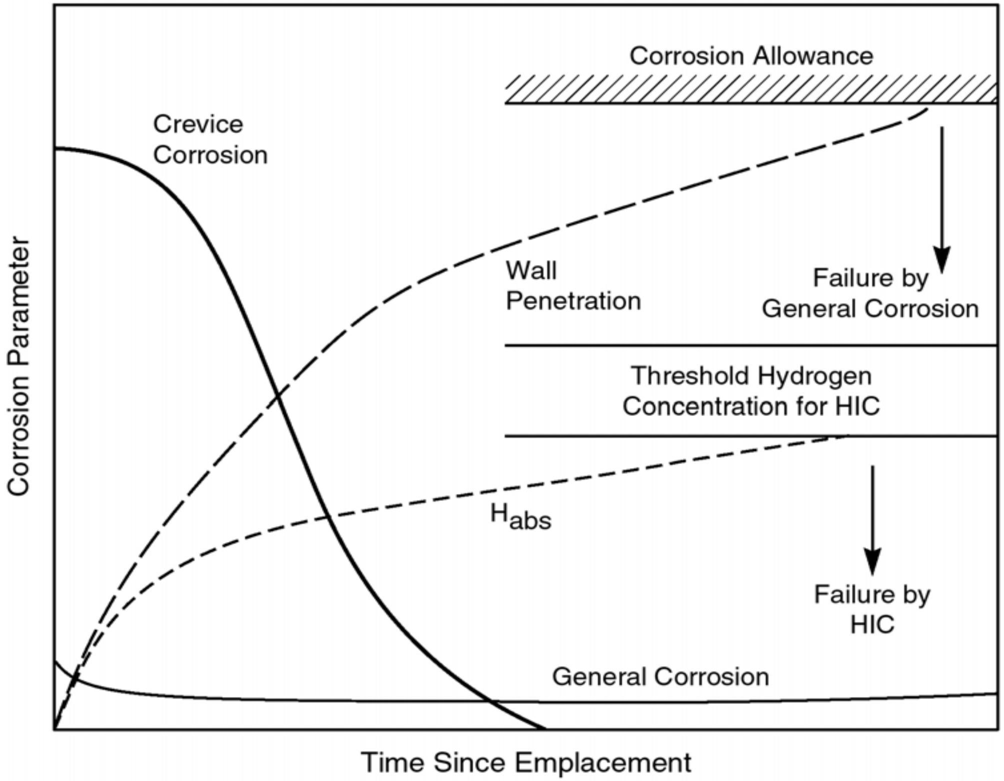

- Tsujikawa and Kojima (1992) used the repassivation potential ($E_{rcrev}$) to define map for susceptibility to crevice corrosion as a function of T and $[Cl^{-}]$
- The boundary lines define regions of passivity in the map for different values of the corrosion potential as the enabling parameter
- The approach can be used for many Ti alloys but the data is limited to commercial purity Ti and it cannot be extended to other Ti alloys

# Titanium Alloys – Crevice Corrosion



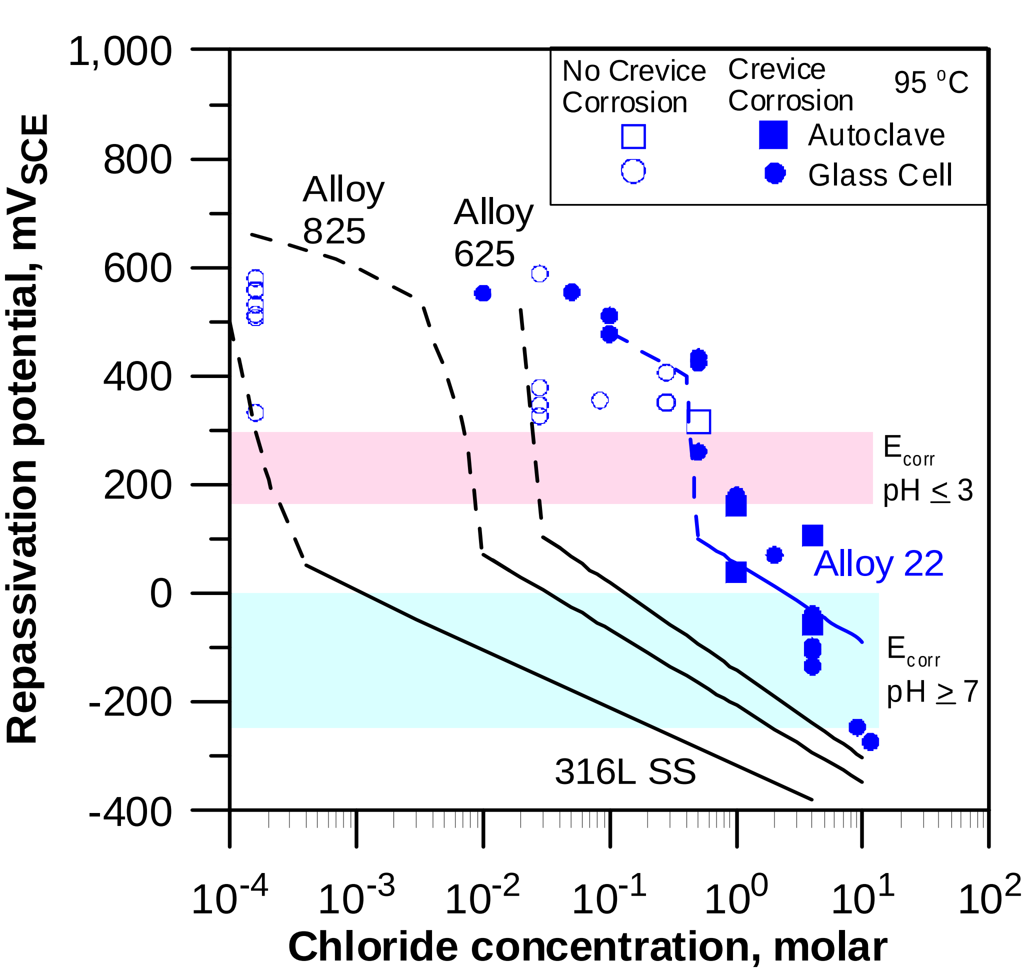

- Shoesmith et al (1995) used the evolution of the current density between a crevice specimen and a planar electrode to assess the development of crevice corrosion
- In an air-saturated NaCl solution Ti-16 (Ti-0.08Pd) repassivates significantly faster than Ti and Ti-12 (Ti-9Ni-4Mo)

# Titanium - Summary of Degradation Processes



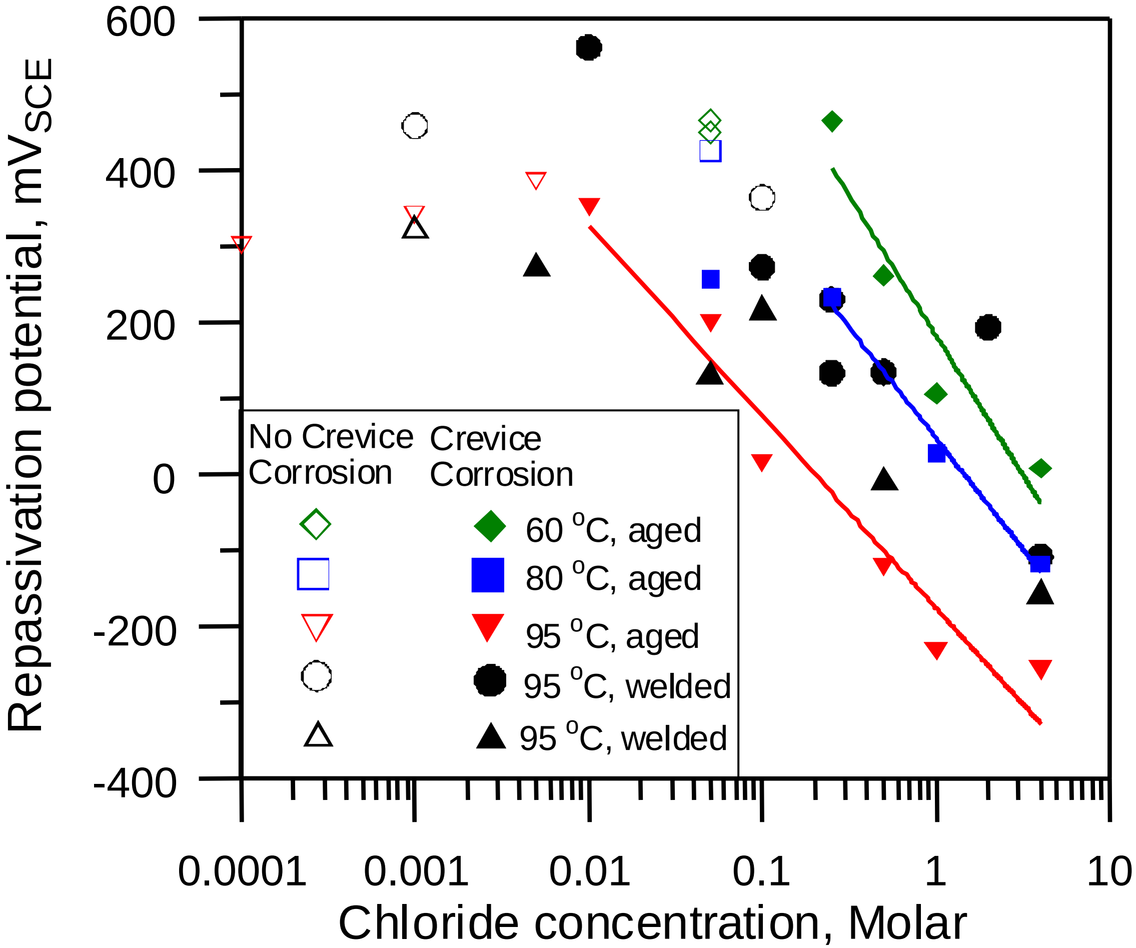

- Shoesmith et al. (1995) summarized the potential degradation processes that may affect Ti containers in the Canadian Shield
- It was concluded that uniform corrosion and hydrogen-induced cracking were the most probable failure processes but container life is estimated to be greater than $10^6$ years

# Ni-Cr-Mo Alloys – Localized Corrosion



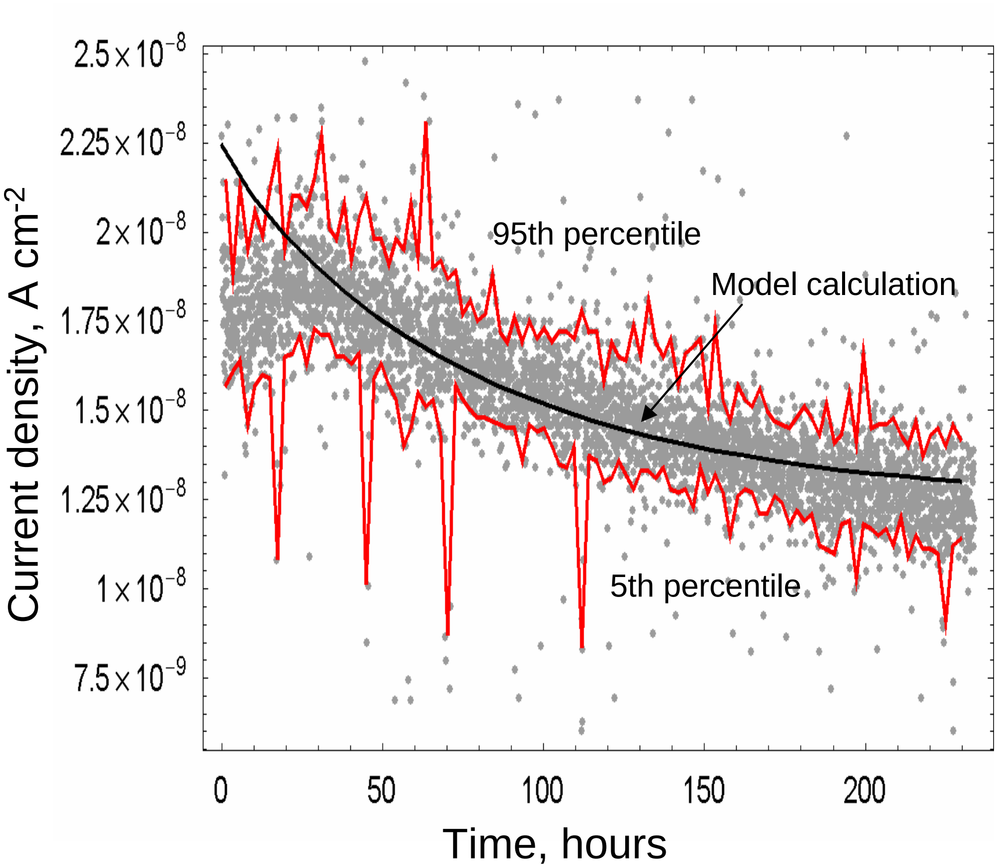

- Cragnolino et al. (2003) used the crevice corrosion repassivation potential as a critical potential for evaluating the long-term initiation of localized corrosion
- Alloy 22 in the mill annealed condition is quite resistant to localized corrosion in $Cl^-$ solutions compared to other alloys previously considered for the potential repository at Yucca Mountain
- Increased resistance with respect to other Ni-Cr-Mo alloys is due to the high Mo (and W) content of Alloy 22

# Alloy 22 Containers - Effect of Fabrication Processes




- Cragnolino et al. (2003) reported that fabrication processes such as welding and short-term thermal aging can increase the localized corrosion susceptibility
- Crevice corrosion is observed at lower $Cl^-$ concentrations and lower temperatures compared to the mill annealed condition

# Ni-Cr-Mo Alloys – Modeling of Passive Corrosion




Experimental data obtained using Alloy 22 in 0.028 M NaCl at 95 °C and 100 $mV_{SCE}$

- Pensado et al. (2002) developed an extension of the Point Defect Model for ternary Ni-Cr-Mo alloys considering a $Cr_2O_3$-rich passive film with Ni, Cr, and Mo (interstitial cations) as predominant charge carriers
- Computed a decrease in the current density (proportional to uniform corrosion rate) due to vacancy accumulation at metal-film interface until a steady state is reached
- A container lifetime extended beyond 10,000 years is estimated from experimental data and model calculations

# Evolution of Waste Package Materials and Designs

| Country | Waste Form | Env | Evolution of Outer Container | Inner Container or Metal Insert | Buffer/ Backfill | Life Estimates (Years) |
|---|---|---|---|---|---|---|
| Belgium | HLW | Red. | 316L SS | 304 SS | Bentonite | — |
| Canada | SNF | Red. | Ti,Cu→**Cu** | CS or Cast Fe Insert | Bentonite | >100,000 |
| Finland | SNF | Red | **Cu** | **Cast Fe Insert** | Bentonite | > 100,000 |
| France | HLW/SNF | Red. | SS? | Metal Insert | Bentonite | — |
| Germany | HLW | Red. | CS,Ti,Ni alloys | — | Salt? | — |
| Japan | HLW | Red. | CS,Ti,Cu→CS | — | Bentonite | > 1,000 |
| Spain | SNF | Red. | CS | — | Bentonite | — |
| Sweden | SNF | Red | Ti,Cu,$Al_2O_3$→**Cu** | **Cast Fe Insert** | Bentonite | > 1,000,000 |
| Switzerland | SNF/HLW | Red | **CS** (Cu) | — | Bentonite | > 10,000 |
| UK | ILW | Red. | CS? | — | — | 300 to 500 |
| USA | SNF/HLW | Oxid. | SS→ CS→**22** | None→825 →22 →**SS** | None | .> 10,000 |

# Summary

- Significant progress has been made during the last 25 years in the experimental evaluation of materials and design of containers for the disposal of high level nuclear waste
- Advances in modeling of corrosion processes and evaluating container performance have accompanied such evolution
- Although carbon steel is still considered for repositories in the saturated zone (reducing conditions), copper appears to be the material predominantly selected on the basis of thermodynamic considerations, experimental data, process models, and container lifetime estimates
- Alloy 22, an alloy resistant to corrosion as a result of the presence of an stable passive film, has been proposed as a container material for the oxidizing conditions prevailing in the unsaturated zone at Yucca Mountain
- Uncertainty still remains in long-term estimations of container life as a result of uncertainties related to the evolution of the aqueous environment contacting the waste packages and the stability of passive films

# Acknowledgments

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This work is an independent product of CNWRA and does not necessarily reflect the views or the regulatory position of the NRC