U.S. Department of Energy

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

Drip Shield Creep and Environmental Degradation Update

Presented to:
Nuclear Waste Technical Review Board

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Objectives

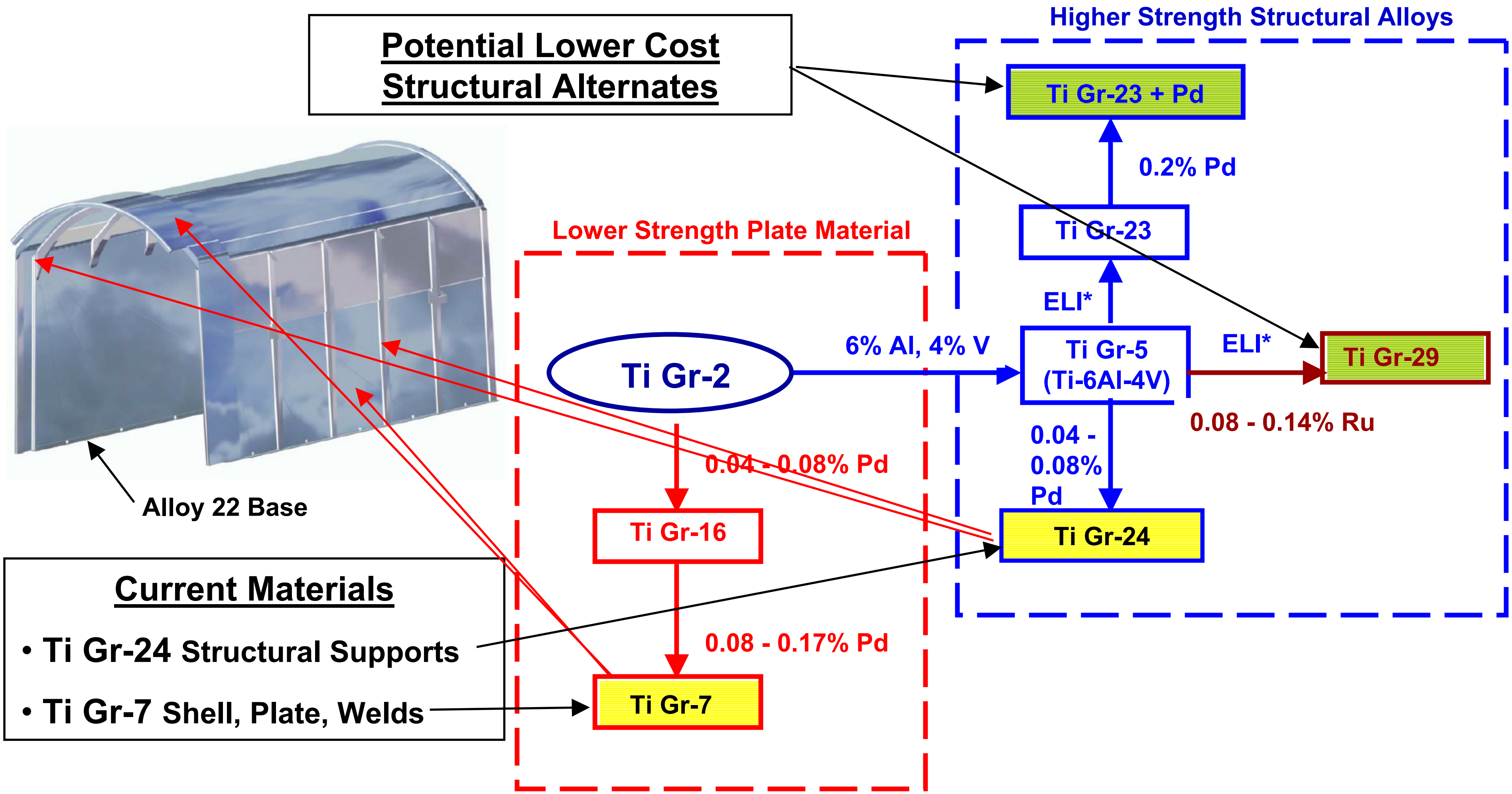
- Describe drip shield materials selection basis
- Review
  - Environmentally induced cracking susceptibility of drip shield titanium alloys
  - Effect of creep on drip shield performance
  - General, localized and galvanic corrosion of drip shield materials
- Conclusions

Selection of Titanium for Drip Shield (DS)

- **DS materials selection based on series of YMP sponsored materials experts meetings & evaluations***
  - **Selection of corrosion resistant materials narrowed to Alloy 22 for WP and Ti Gr-7 or Gr-16 for DS in 1999**
    - » Selection based on expected corrosion performance, defense in depth, fabrication ease, handling issues, cost impact and estimated lifetime
- **Ti Gr-24 (or Gr-29) selected later for DS structural supports**
  - **Literature indicates excellent general and localized corrosion performance**
- **Titanium alloys evaluated on other repository programs (including Canadian, Japanese and German programs)**

*** 1) Peer Review Report on Selection Criteria for the Yucca Mountain Project Waste Package Container Material, December 14, 1998,**
2) Selection of Candidate Container Materials for the Conceptual Waste Package Design for a Potential High Level Nuclear Waste Repository at Yucca Mountain, UCRL-ID-112-58, 1993,
3) Waste Package Materials Selection Analysis, BBA000000-01717-0200-00020 REV 01, Table 7.3.1.2-1, 1997,
4) Waste Package Containment Barrier Materials and Drip Shield Selection Report", B00000000-01717-2200-00225 REV 00, 1999

Current and Potential Alternate DS Materials



Small Pd or Ru additions greatly enhance corrosion resistance

*ELI = Extra Low Interstitial (lower Fe, O and N gives higher toughness)

Environmentally Induced Cracking Susceptibility of DS Alloys

Environmental Cracking of DS Alloys

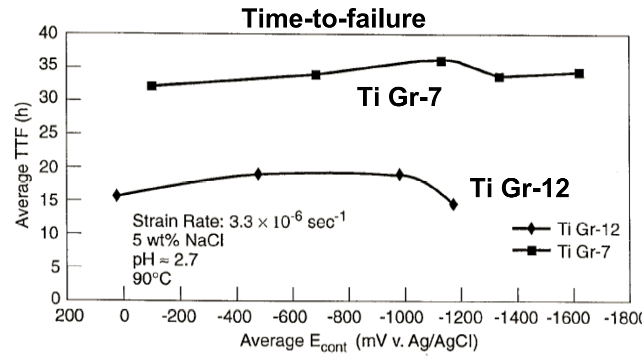
- **DS alloys highly resistant but may not be immune to Hydrogen Induced Cracking (HIC) and Stress Corrosion Cracking (SCC)**
- **Prior relevant testing includes:**
  - **German* slow strain rate tests (SSRT) of Ti Gr-7 in 5 M NaCl brine at 170°C**
    - Concluded: Ti Gr-7 base metal and welds not sensitive to SCC
  - **NRC funded SSRT of Ti G- 2, Gr-7 and Gr-5 in deaerated 95^{o}C, 1 M NaCl with and without 0.1 M NaF ****
    - No SCC (or HIC) in notched specimens without 0.1 M NaF
    - With 0.1 M NaF, potential HIC observed for all three alloys
      - Ti Gr-5 (basis for Ti Gr-24/29) more susceptible than Ti Gr-7
    - Aerated repository conditions and extended period of dry oxidation will provide HIC margin and resistance to fluoride effects

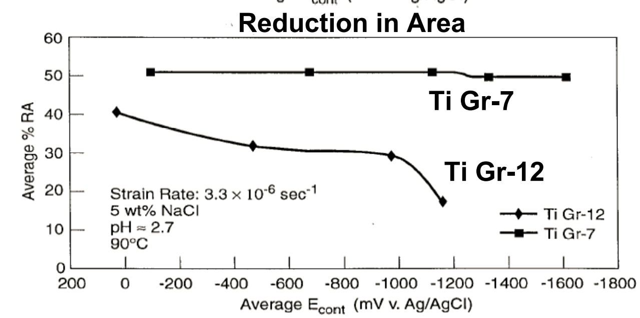
*** Smailos et al, Enresa final report, EC-Contract NO. F14W-CT95-0002, 1999**

**** Pan et al., CNWRA 2003-02, Section 4.2**

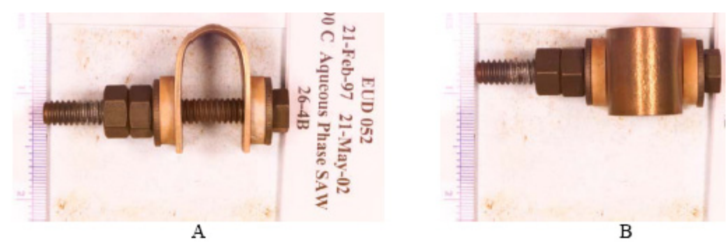
Environmental Cracking of DS Alloys

- **YMP SSRT* on cathodically polarized Ti Gr-7 and Gr-12 (Gr-2 + .7 Ni, .3 Mo) in 90°C, 5 wt % NaCl, pH ~2.7**
  - **Times-to-failure (T-T-F) and ductility for Ti Gr 7 not significantly influenced by very negative potentials**
    - **Highly resistant to HIC**
  - **Ti Gr-12 showed significant drop in ductility and lower T-T-F at very negative potentials indicative of HIC.**
- **YMP U-bends of Ti Gr-7, 16 and 12 exposed in LLNL brines for 0.5-5.5 years****
  - **No SCC in Ti Gr-7, Gr-16 in 60-90°C SDW, SAW & SCW brines*** (0 to ~0.1 M F, pH ~3 to 10)**
  - **SCC in as-welded Ti Gr-12 90˚C SCW (contains ~ 0.1 M F)**





Typical Un-Cracked Ti U-bend Specimen after 5 years Exposure to SAW at 90˚C



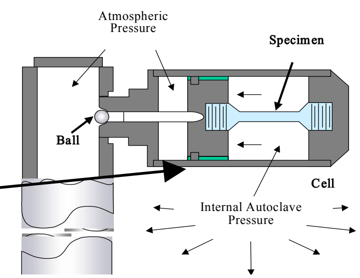
Exposed in LLNL Long Term Corrosion Test Facility (LTCTF)

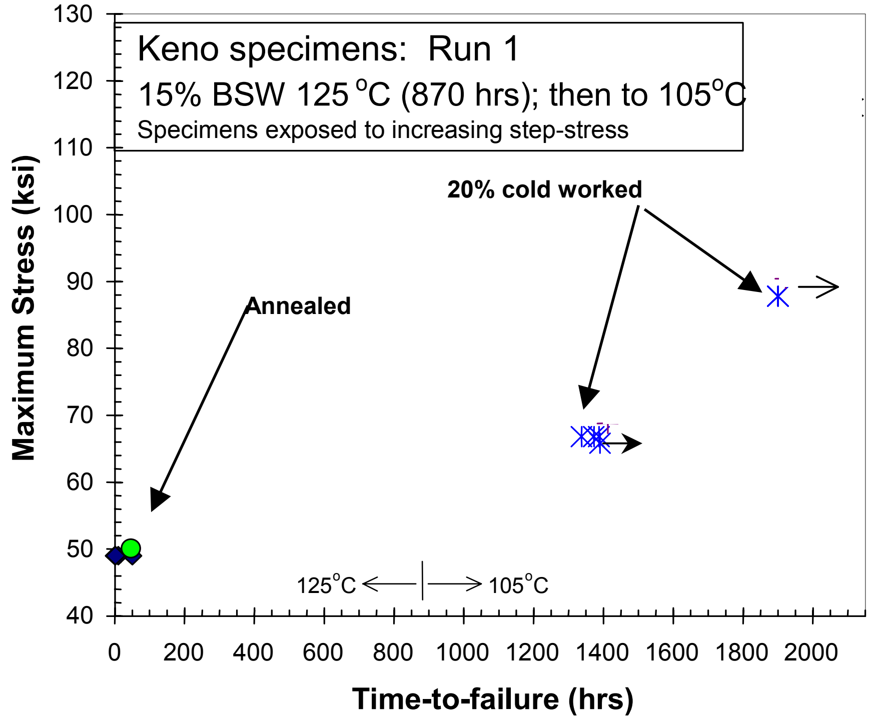
***Roy et al., Corrosion 2000, Paper 00188, **Fix et al Paper 04551, Corrosion 04, ***SAW = Simulated Acidified Water, SCW = Simulated Concentrated Water, SDW = Simulated Dilute Water**

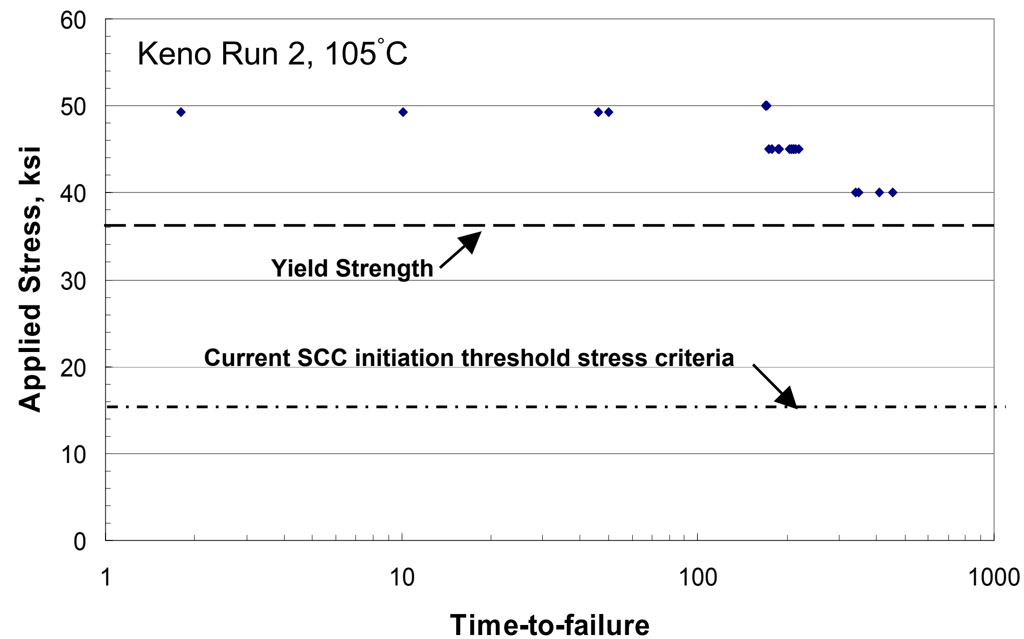
Environmental Cracking of DS Alloys

- Two GE constant load Ti Gr-7 SCC initiation test campaigns*
  - 15% BSW (~7500X J-13, pH ~12)

Constant Load (Keno) test module located in autoclave





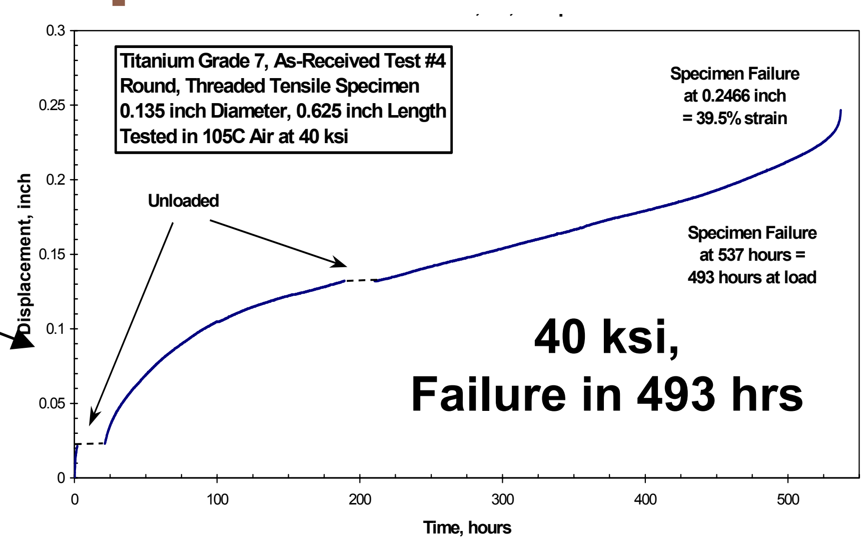


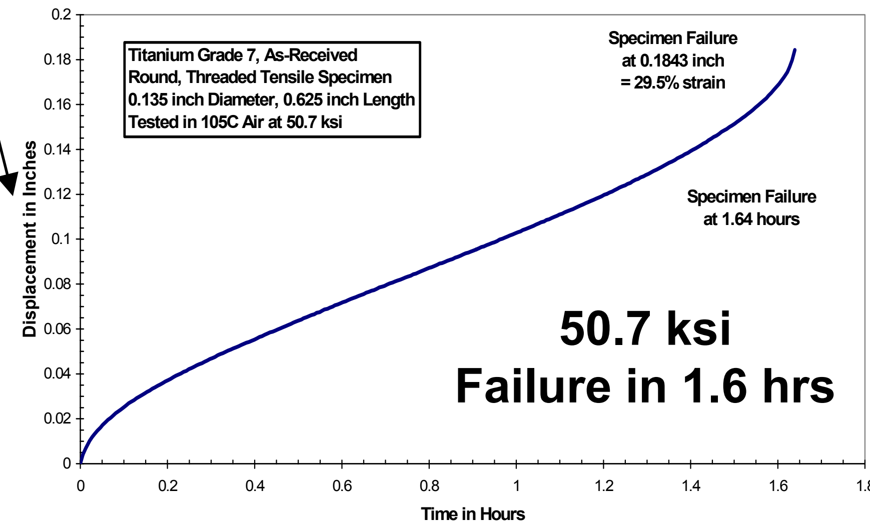
- Failure in annealed Ti Gr-7 at 125˚C at ≥ 48 ksi (~1.4YS)
- No cracking in 20%-Cold Worked Ti Gr-7 at 88 ksi (~1.2 YS)
- Annealed specimens fail at over-yield stresses in ~2-500 hours
- Tests at lower applied stress levels being initiated

* Young, et al, Proceedings, 11th Int'l Conference on Environmental Degradation, Paper No. 72115, 2003

Comparison of Failure Times in SCC Tests with Air Creep Rupture Results

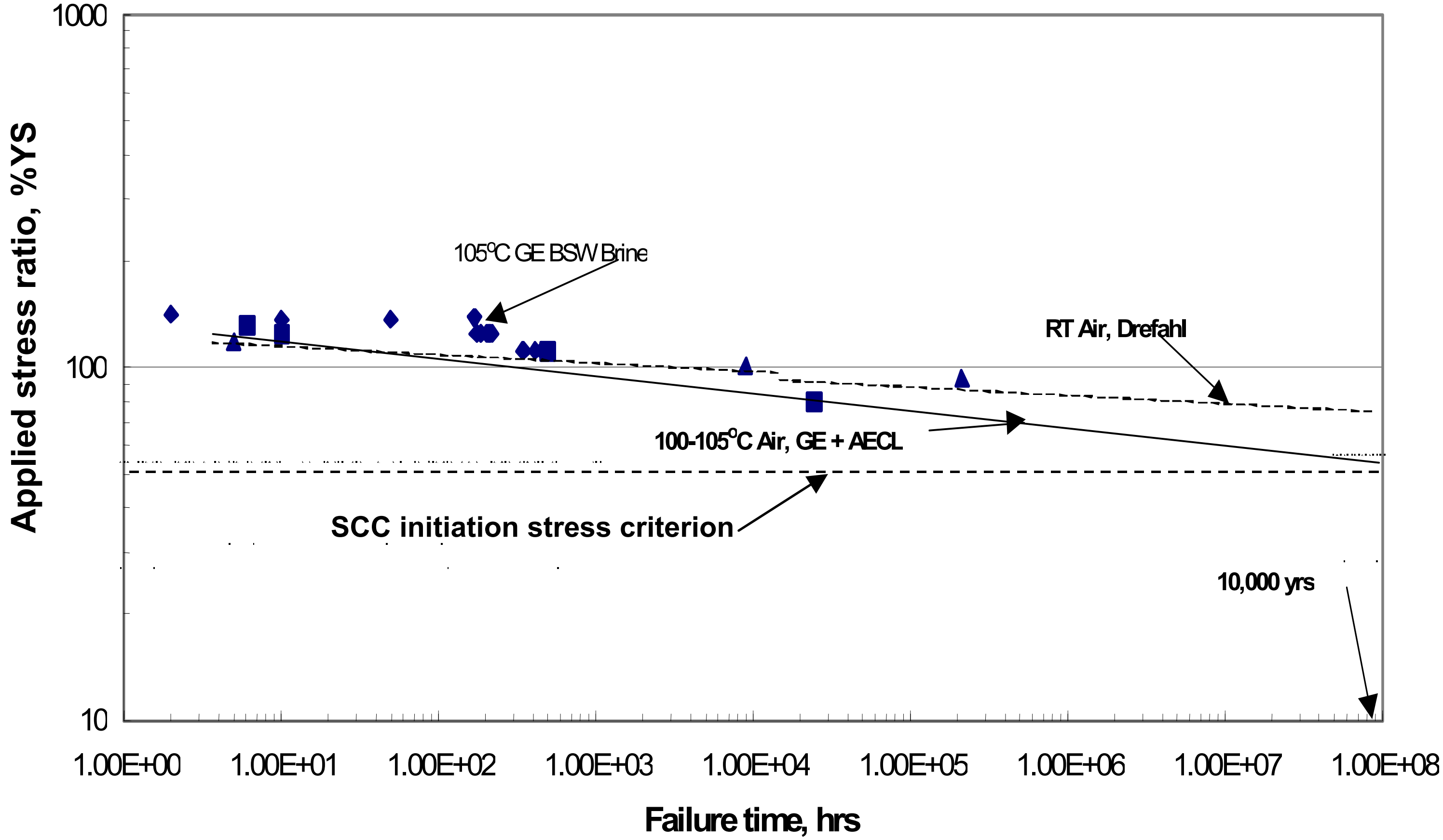
- Because of short brine failure times, air creep tests run
  - Typical Ti Gr 7 creep ruptures in air at 105°C at $\geq$ 110% YS*
  - Other 100°C air tests** indicate creep at $\geq$ 60% YS
- Specimen failure times in brine and air overlap at similar stresses
- Necessary to determine if failures due to SCC or creep rupture





*Andresen et al., 12th Int'l Conference on Environmental Degradation, Salt Lake City, August 14-18, 2005, **Dutton et al., Preliminary Analysis of the Creep Behaviour of Nuclear Fuel-Waste Container Materials, AECL-11495, COG-95-560-1, 1996

Comparison of Constant Load Failure Times in 15% BSW Brine with Air Creep Rupture Results*

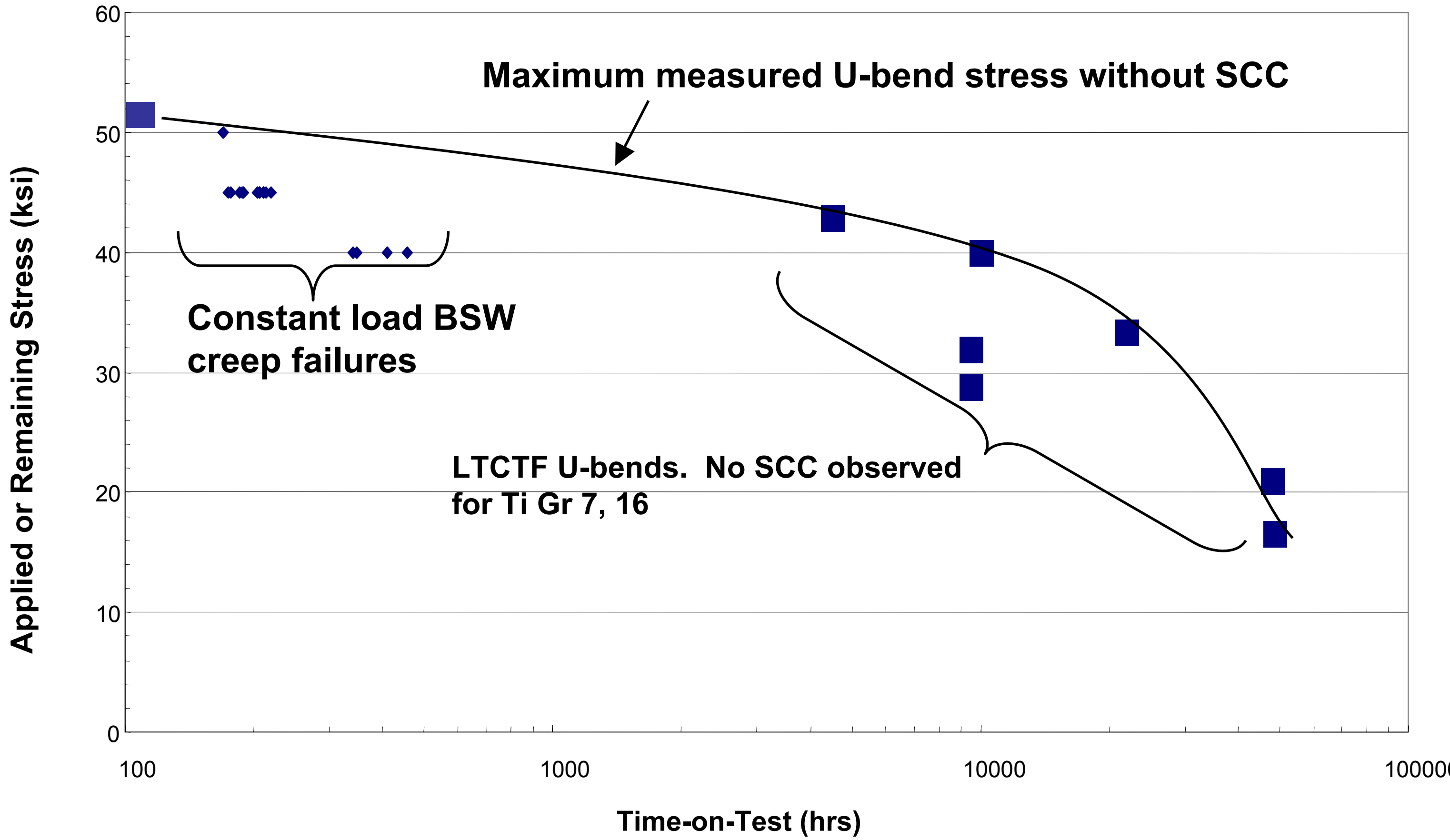


- **Constant load brine failures due to creep rupture rather than SCC**
- **Significant margin between minimum stress without SCC initiation and threshold stress criterion**

*Andresen et al., 12th Int'l Conference on Environmental Degradation, Salt Lake City, August 14-18, 2005, Dutton et al., Preliminary Analysis of the Creep Behaviour of Nuclear Fuel-Waste Container Materials, AECL-11495, COG-95-560-1, 1996, Drefahl et al., Titanium Science and Technology (G. Lutjering, U.Zwicker and W. Bunk, editors), Deutsche Gesellschaft fur Metallkunde E.V.., Germany.

Stress Versus Time-on-Test in Brines

Constant Load Tests in 105^oC, 15% BSW; U-Bend Test in 60-90^oC SAW, SCW, SDW



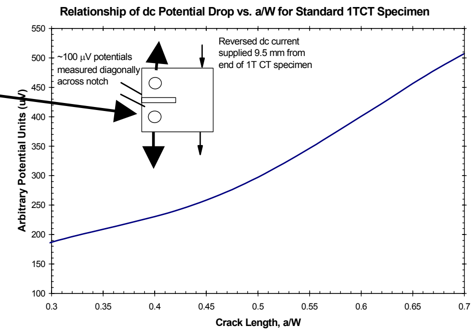
- **Constant load specimens fail by creep rupture but U-bends exhibit no SCC initiation after 0.5-5.5 years exposure**
  - **Maximum U-bend stresses (from X-ray diffraction)* drop over time from creep relaxation**
- **Stress relaxation beneficial in reducing rock fall impact residual stresses**

*Lambda Research Report 1181-12611, MOL.20051031.0202

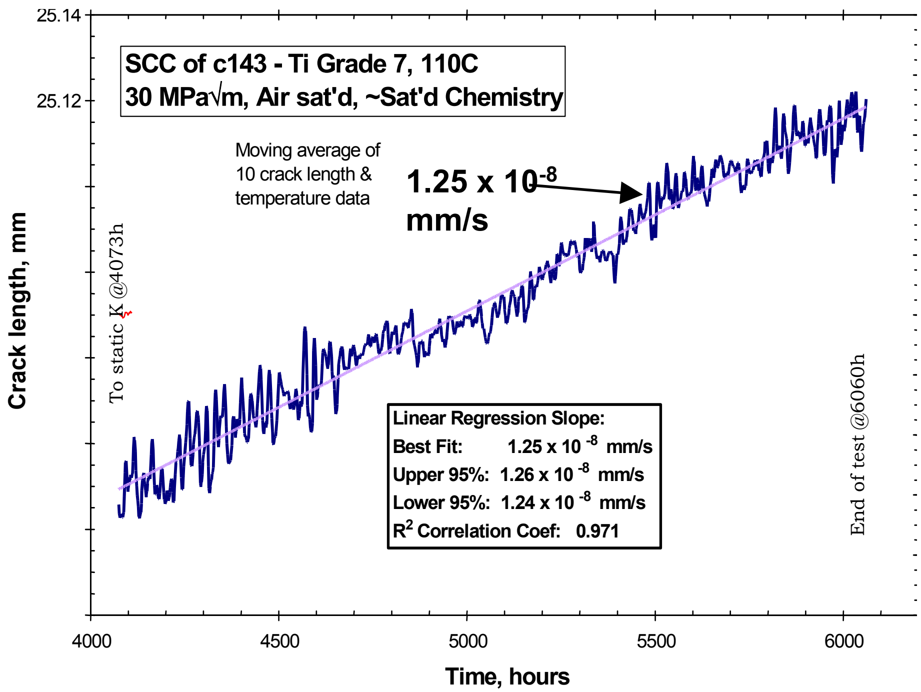
Comparison of Crack Growth Rates in BSW and SCW Brines versus Air Creep Rate Results

Ti Gr-7 Crack Growth in 110°C in Air and BSW

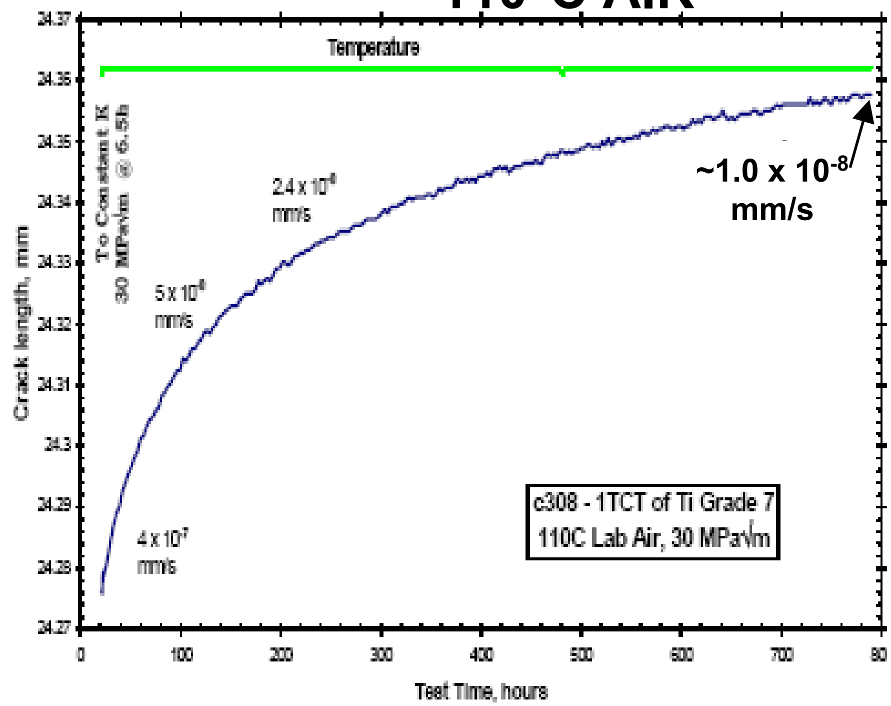
- Fracture mechanics type fatigue pre-cracked compact tension specimen
  - Growth monitored using DC potential drop



110°C BSW



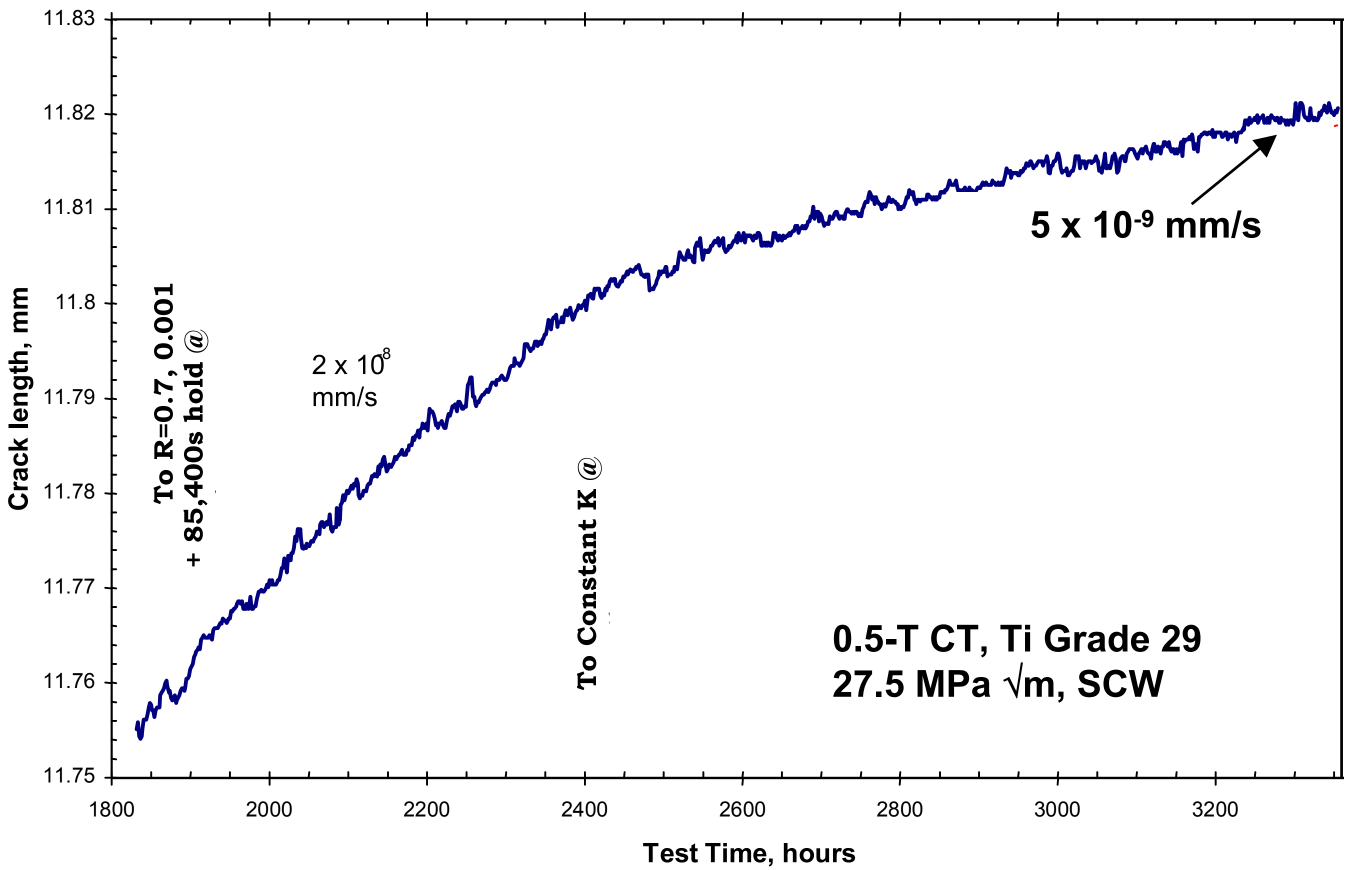
110°C AIR



- Constant load crack growth rates similar in air and BSW
- Consistent with significant creep component for Ti Gr-7 growth

*Andresen et al., 12th Int'l Conference on Environmental Degradation, Salt Lake City, August 14-18, 2005

Ti Grade 29 Crack Growth in 150°C SCW



- **Ti Gr 29 (analog for Ti Gr 24) growth rate* much higher than Ti Gr 7**
- **Since Ti Gr 29 significantly more creep resistant, crack growth likely due to SCC**
  - **Air control test planned to confirm crack growth mechanism**

***Andresen et al., 12th Int'l Conference on Environmental Degradation, Salt Lake City, August 14-18, 2005**

Effects of Creep on DS Performance

Effects of Creep on DS Performance

- **As-emplaced DS resistant to creep and SCC**
  - **Stress relief annealed condition**
- **Two significant loading scenarios**
  - **Scenario 1: Rock rubble loads in lithophysal zones**
    - **May lead to DS creep rupture and/or collapse**
  - **Scenario 2: Seismic induced rockfall in non-lithophysal zones**
    - **Residual stresses may initiate and propagate SCC**
    - **Seepage water pooling may increase flow rate through cracks**
      - **However, cracks form at dent periphery not bottom of dent****
- **Scenarios analyzed using literature benchmarked and conservative creep power laws***
  - **Calculations* indicate DS performance acceptable**

*Creep Deformation of the Drip Shield, CAL-WIS-AC-000004 REV 0, **ANL-WIS-PA-000002 REV 05, FEP 2.1.03.10.0B

Effects of Creep on DS Performance

Rock Rubble Loading

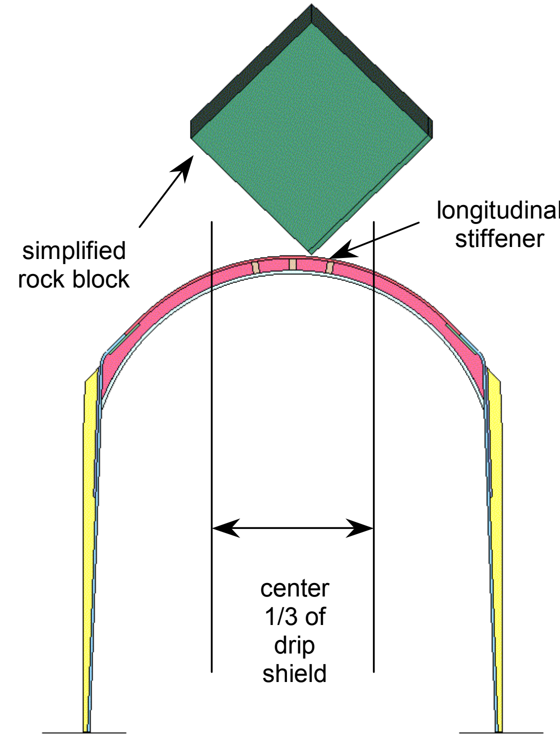
- **Maximum calculated creep strains less than 5%**
  - Acceptable limit is 10%
    - ~Onset of tertiary creep

Maximum creep strains 10,000 years after emplacement

Realization	Creep Strain (%)
1	4.20
2	1.74
3	2.01
4	3.11
5	1.28
6	2.95

Rock Fall Impact

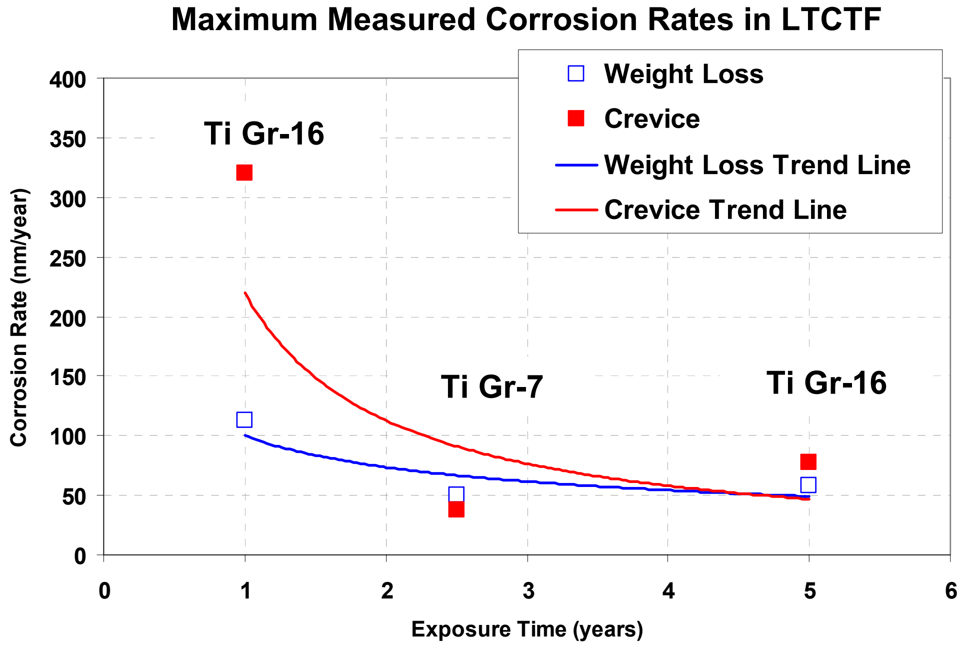
- **Residual stresses >50% YS**
  - Through-wall SCC can occur
  - Creep/stress relaxation calculation indicates SCC unlikely
    - Stresses relax below 50% of YS in less than 100 years at 30˚C
    - Stresses relax below 65% of YS in less than 10 years at 150°C
    - Consistent with measured U-bend stress versus time results

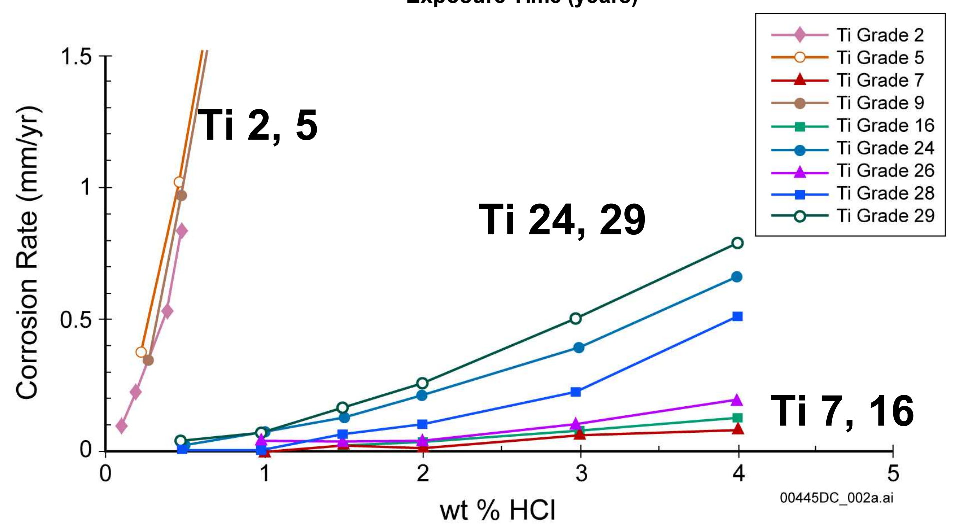


General, Localized and Galvanic Corrosion of DS Alloys

Drip Shield General Corrosion

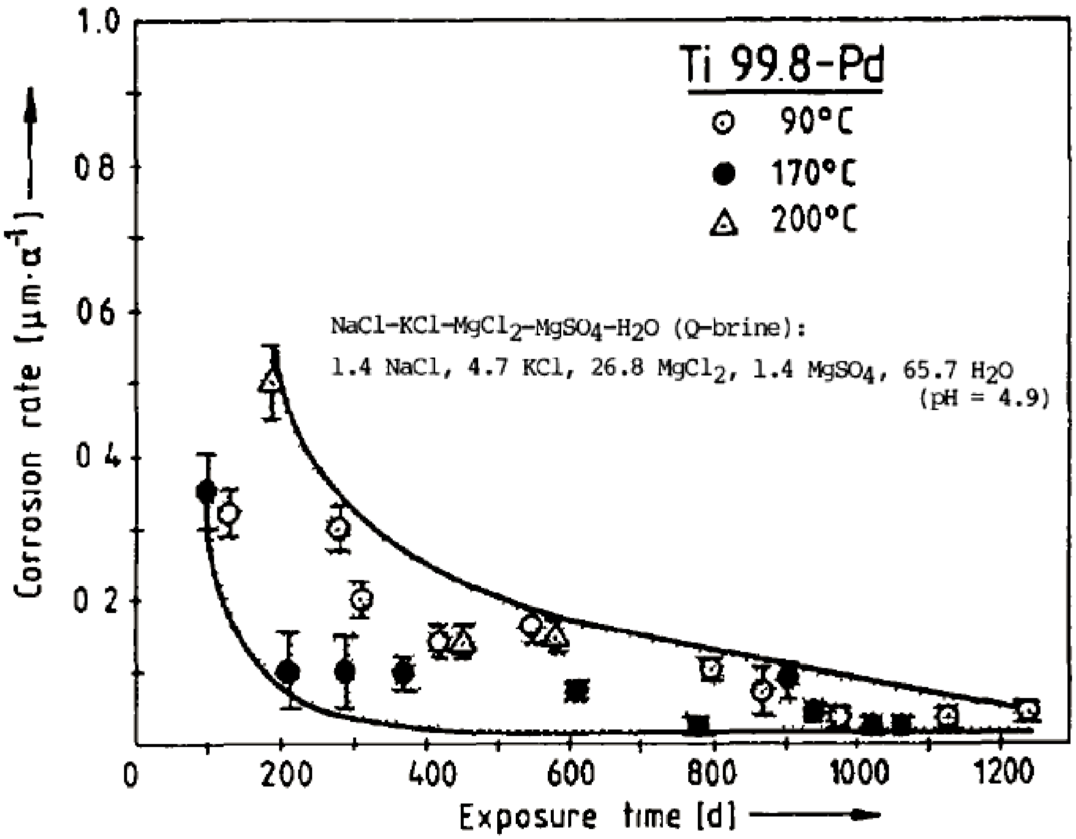
- **Ti-Gr 7 Plate Material***
  - One year Ti Gr-16 exposed specimens used for PA (Performance Assessment)
    - Corrosion rate decreases with time* – not used in PA
    - Ti-7 more resistant than Ti-16
    - Median value of <10 nm/yr after 2.5 years exposure
- **Ti-24/29 Supports****
  - Accelerated tests in acidic chloride media indicate GC rate is 4-5x Ti-7 GC Rate**
    - Still extremely low





*Hua et al., A Review of Titanium Grade 7 and Other Titanium Alloys in Nuclear Waste Repository Environments, Corrosion, Vol 61, No. 10, pp. 987-1003, 2005, ANL-EBS-MD-000004, REV 02; **R.W. Schutz, Platinum Group Metal Additions to Titanium: A Highly Effective Strategy for Enhancing Corrosion Resistance, Corrosion Vol 59, No. 12, pp.1043-1057, 2003

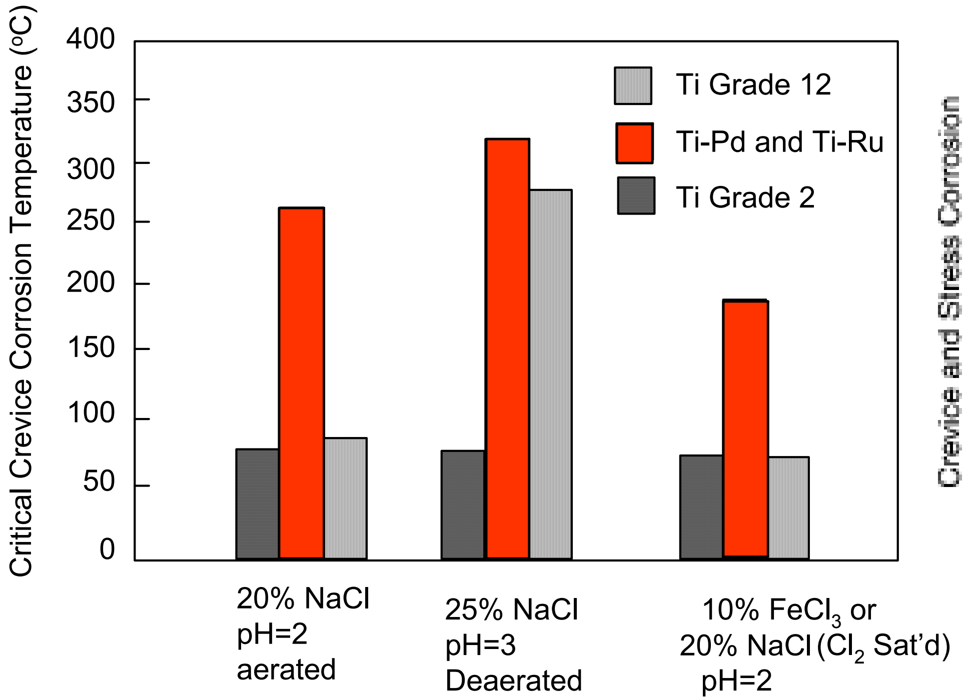
Ti Grade 7 General Corrosion in Q-Brine*



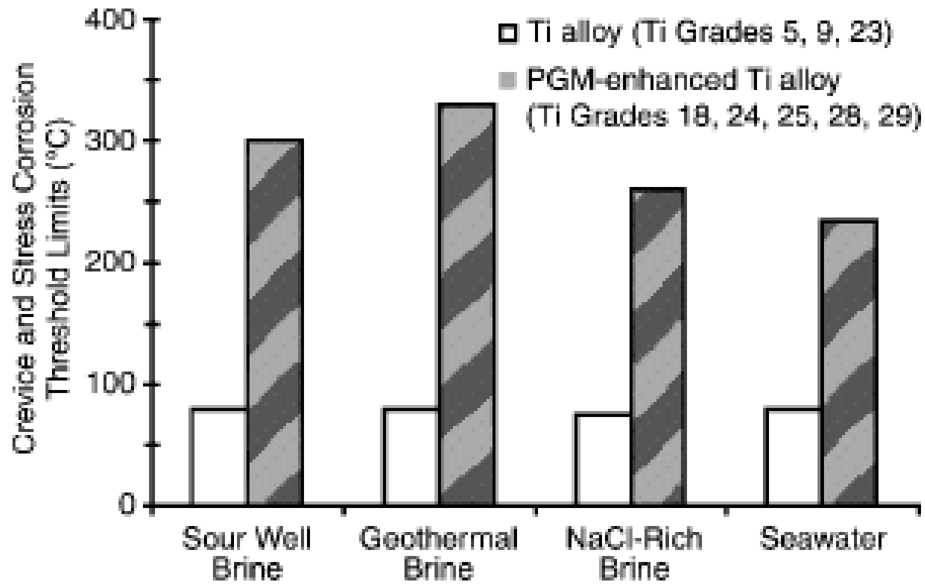
- **General corrosion in Q-Brine consistent with LTCTF results**
- **Rate is temperature independent up to 200°C**

***** E. Smailos, R. Köster**,** Corrosion studies on selected packaging materials for disposal of high level wastes, **IAEA-TECDOC-421,** PROCEEDINGS OF A TECHNICAL COMMITTEE MEETING ON MATERIALS RELIABILITY IN THE BACK END OF THE NUCLEAR FUEL CYCLE ORGANIZED BY THE INTERNATIONAL ATOMIC ENERGY AGENCY AND HELD IN VIENNA, 2-5 SEPTEMBER 1986

Critical Crevice Temperatures for Ti-Pd and Ti-Ru Containing Alloys



Creviced Ti-Gr 7, 12 and 16 in a range of aggressive acidic and highly oxidizing chloride environments*



Crevice and stress corrosion temperature thresholds for alpha-beta alloys (e.g., Ti Gr-24 and 29) in aqueous chloride media**

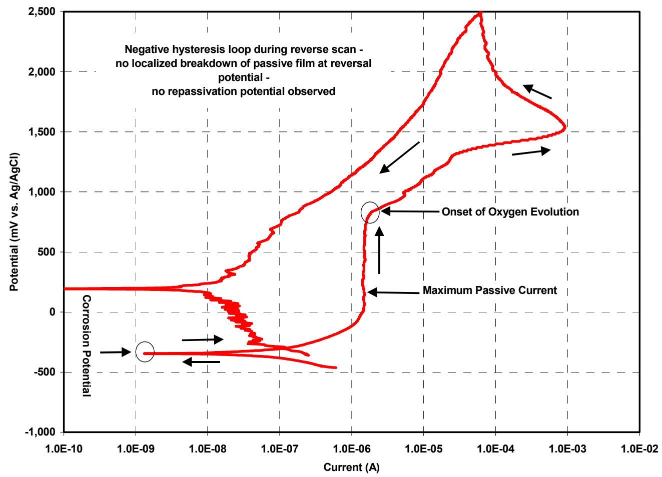
- **Ti-Gr 7, 24 and 29 highly resistant to crevice corrosion in chloride brines**

*Schutz, R.W., "Ruthenium Enhanced Titanium Alloys: Minor Ruthenium Additions Produce Cost Effective Corrosion Resistant Commercial Titanium Alloys, "Platinum Metals Review, 40 (2), 54-61, 1996

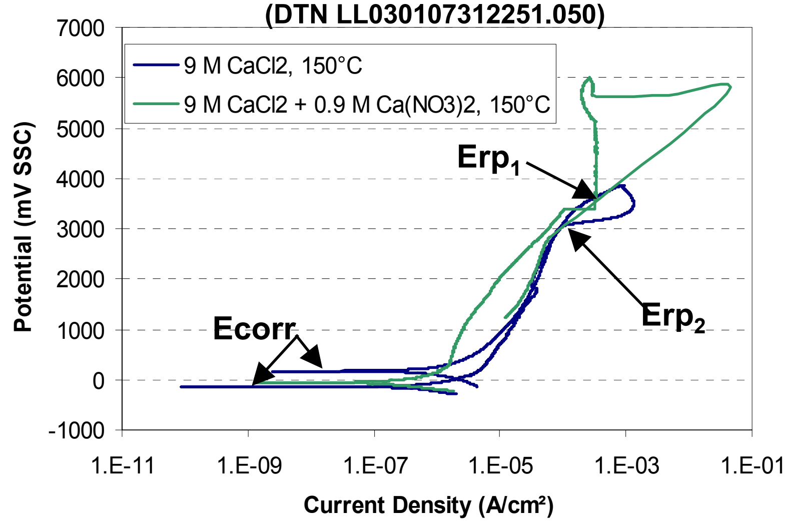
**Schutz, R.W., "Platinum Group Metal Additions to Titanium: A Highly Effective Strategy for Enhancing Corrosion Resistance", Corrosion, Vol 59, No. 12, pp. 1043-1057, 2003

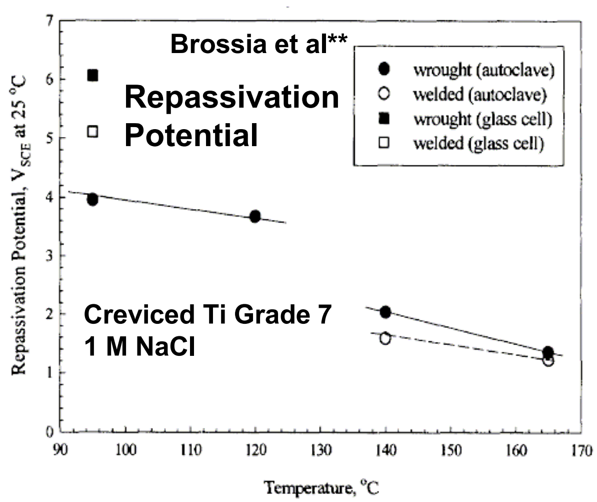
Localized Corrosion of Ti Gr-7 at High Temperatures

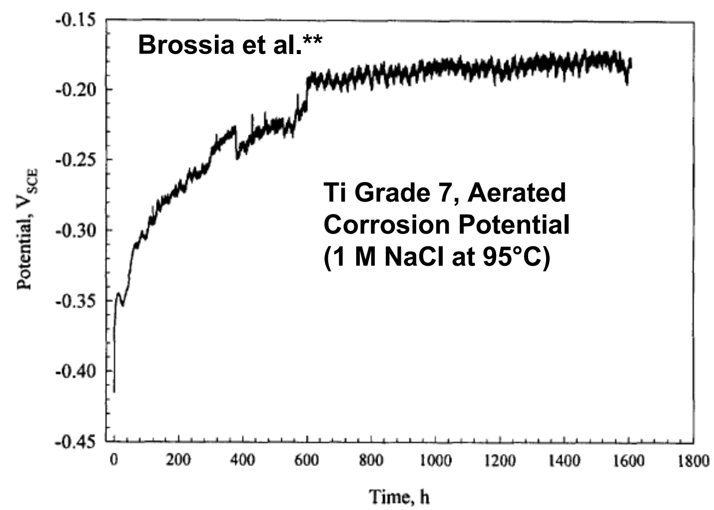
120°C Simulated Saturated Water
3.6 M KCl, 21.2 M $NaNO_3$, NO_3:Cl = 5.9*



LLNLCyclic Polarization
(DTN LL030107312251.050)







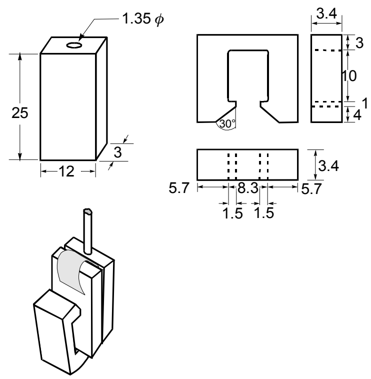
- **Localized Corrosion margin ($\Delta E = E_{crit} - E_{corr}$) very large up to 165°C***

***Hua et al., A Review of Titanium Grade 7 and Other Titanium Alloys in Nuclear Waste Repository Environments, Corrosion, Vol 61, No. 10, pp. 987-1003, 2005 **Brossia et al., Paper NO. 00211, Corrosion 2000, NACE**

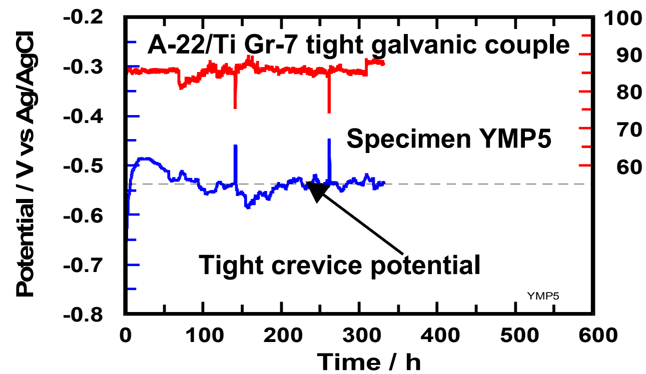
Galvanic Corrosion of Ti Gr-7

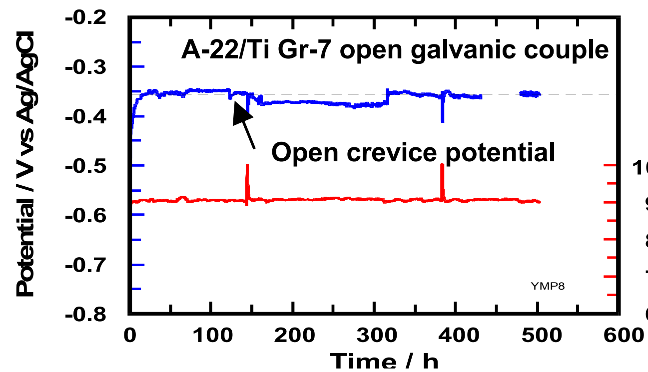
Ti Gr-7/Alloy 22 Galvanic Couples

- A series* of galvanic couples tested in non-deaerated 90˚C SCW
  - No evidence of galvanic or crevice corrosion
  - Tight crevice E_{corr} similar to uncreviced Ti Gr-7***
  - Open crevice E_{corr} lies between Alloy 22 and Ti Gr-7



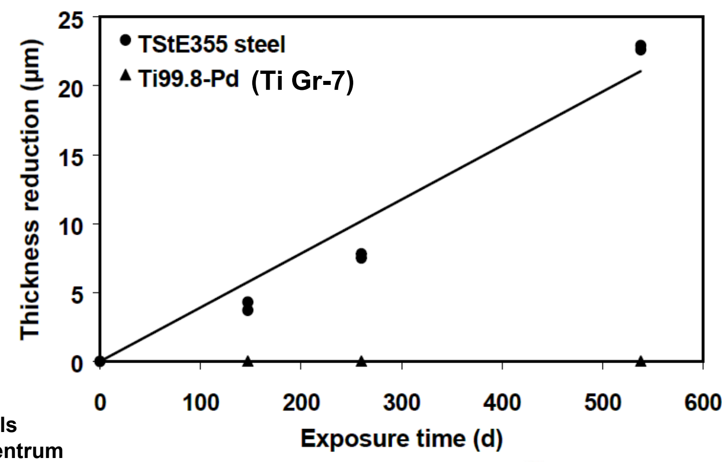
Creviced galvanic couple specimens





Ti Gr-7/Carbon Steel Tight Contact Couples

- Ti Gr-7/carbon steel couples** were exposed over 500 days in 150˚C, 26% NaCl, pH = 6.5
  - Ti Gr-7 corrosion rate remains very low, < 0.07 μm/yr
  - Metallography indicated no evidence of corrosion attack



*Ikeda et al., Corrosion of Dissimilar Metal Crevices in Simulated Concentrated Water Solutions at Elevated Temperatures, AECL-12167 REV 00, January 2003, **Smialos et., Long-Term Performance of Candidate Materials for HLW/Spent FuelDisposal Containers, Wissenschaftliche Berichte FZKA 6706. Fprscjimgszentrum Karlsruhe, 2002, ***ANL-EBS-MD-000004, REV 02

Conclusions

- Titanium DS alloys highly resistant to SCC and HIC in repository relevant environments
- General corrosion rates extremely low and temperature independent to at least 200°C
- Large localized corrosion margins – LC not expected under repository relevant conditions
- Accelerated galvanic corrosion not expected for Ti-Gr-7 couples between Alloy 22 or carbon steel
- DS creep deformation can occur under rock rubble loading but calculation shows resulting strains acceptable