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U.S. Department of Energy
Office of Civilian Radioactive Waste Management

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Update on Titanium Drip Shield

Presented to:
Nickel Institute Workshop No. 6

Presented by:
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Objectives

- Describe drip shield materials selection basis and configuration
- 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)

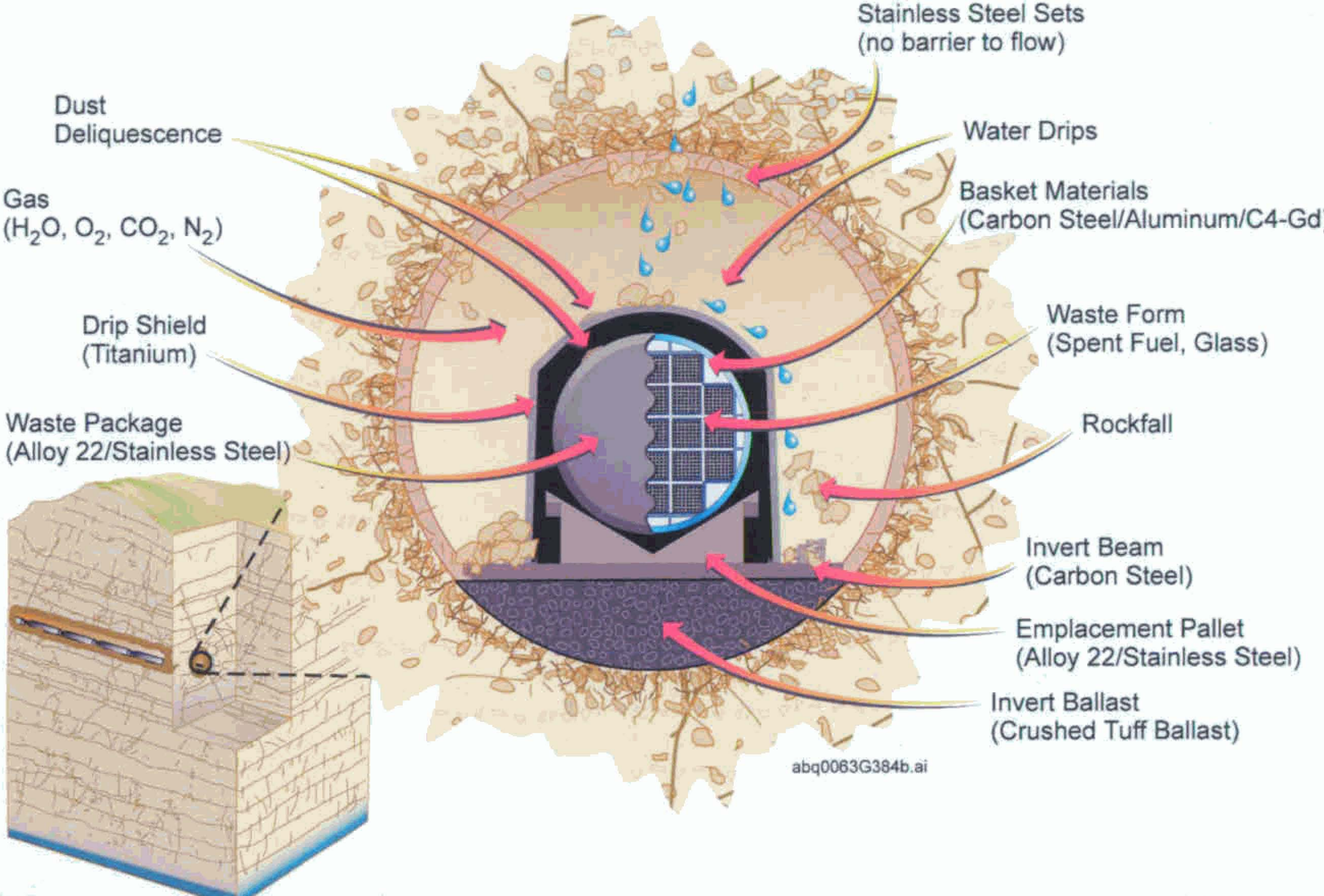
- **DS materials selection based on series of Yucca Mountain Project (YMP) sponsored material experts meetings & evaluations***
  - **Selection of corrosion resistant materials narrowed to Alloy 22 for WP and Ti Gr-7 or Gr-16 for DS in 1999**
    - Selection based on expected corrosion performance, defense 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

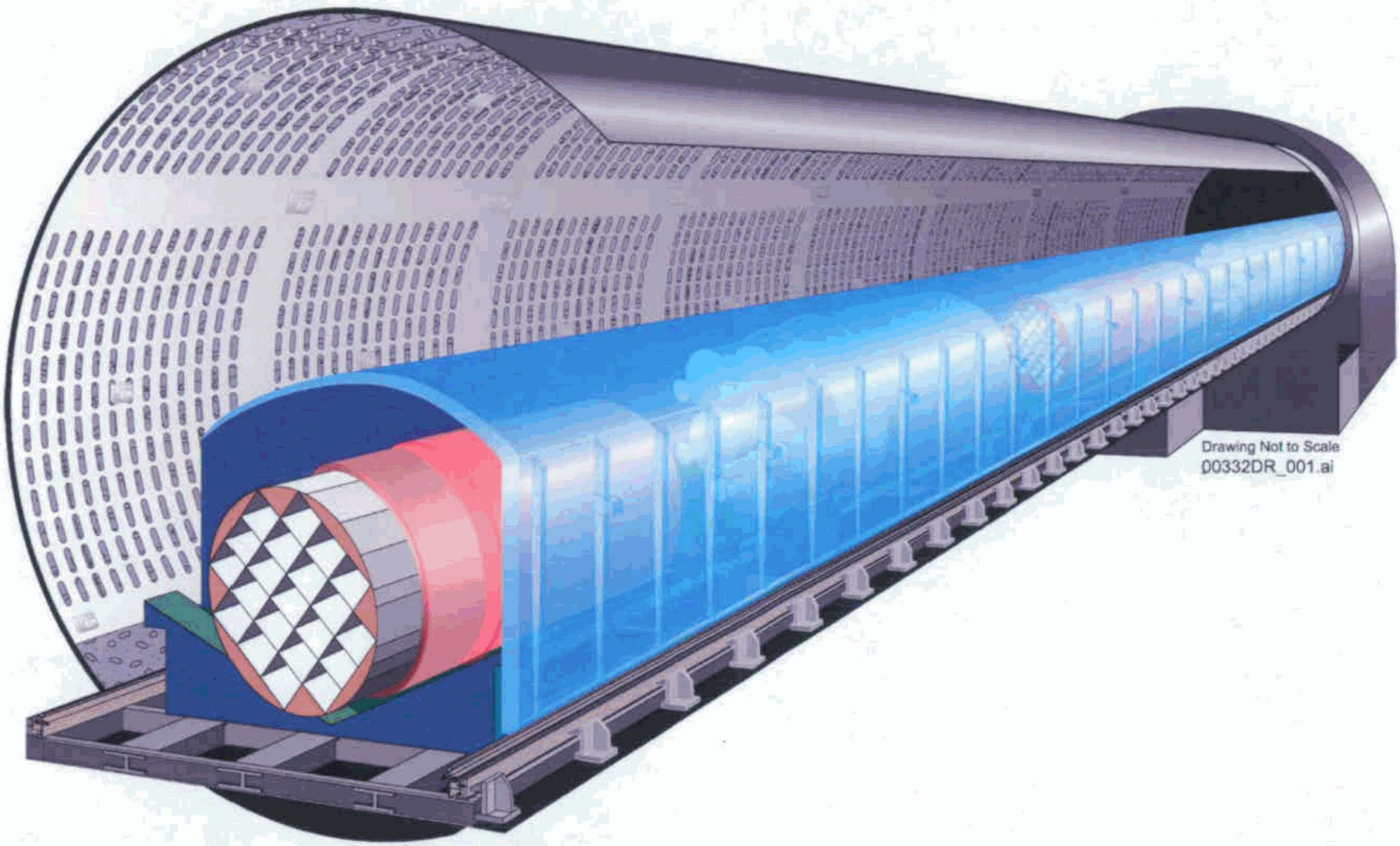
Drip Shield Functions

- Primary drip shield functions are
  - Divert any dripping (seepage water) around waste package into invert
  - Protect waste package from rock fall and long-term drift collapse

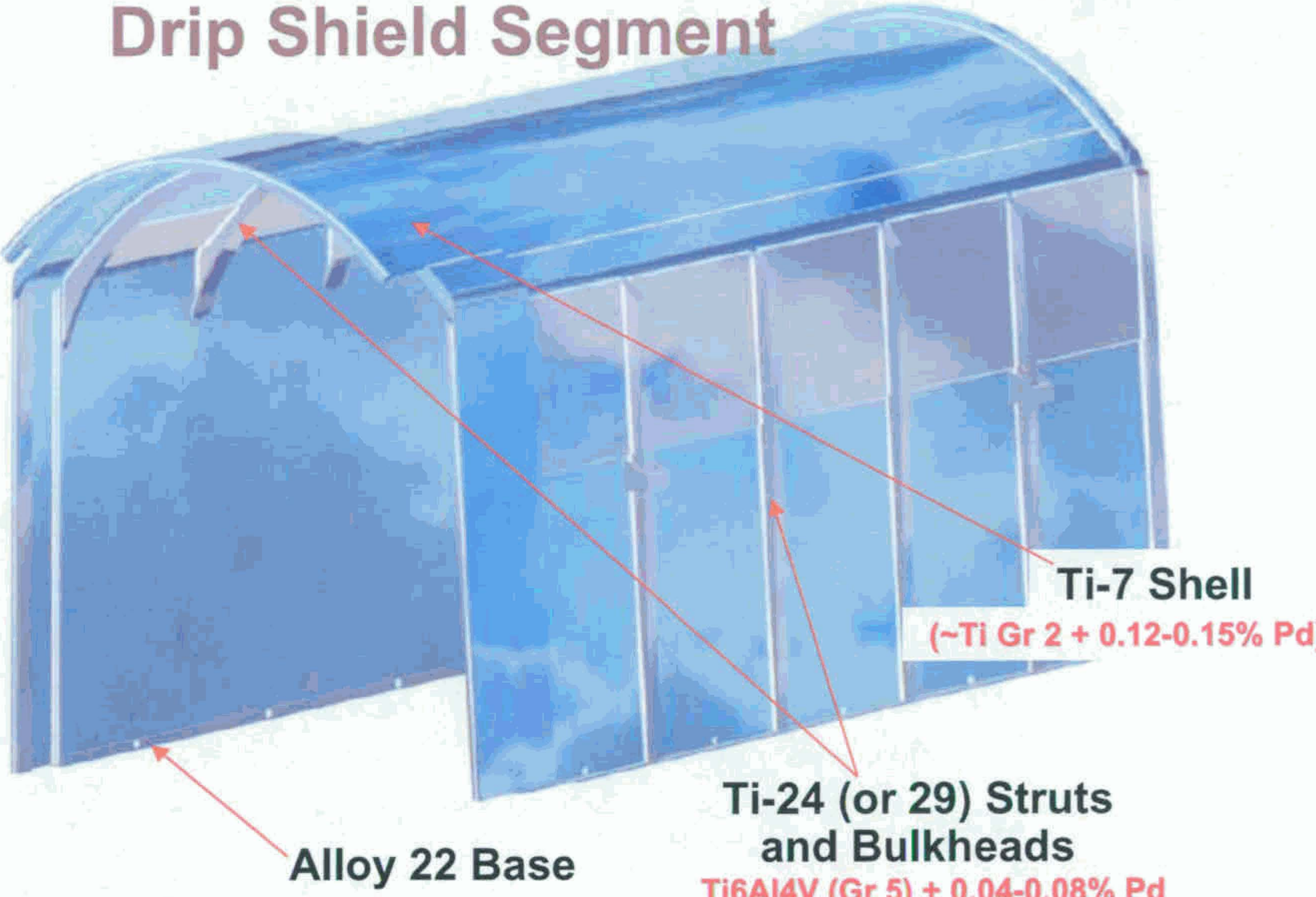
Waste Package and Drip Shield Environments



Drip Shields Emplaced in Drift



Drip Shield Segment



DS is post-weld stress relieved for 2 hours at 1100°F and air cooled

Drip Shield Illustration

Drip Shield Materials

Plates- Ti-7

Connector, Bulkheads, Beams & Stiffeners - Ti-24

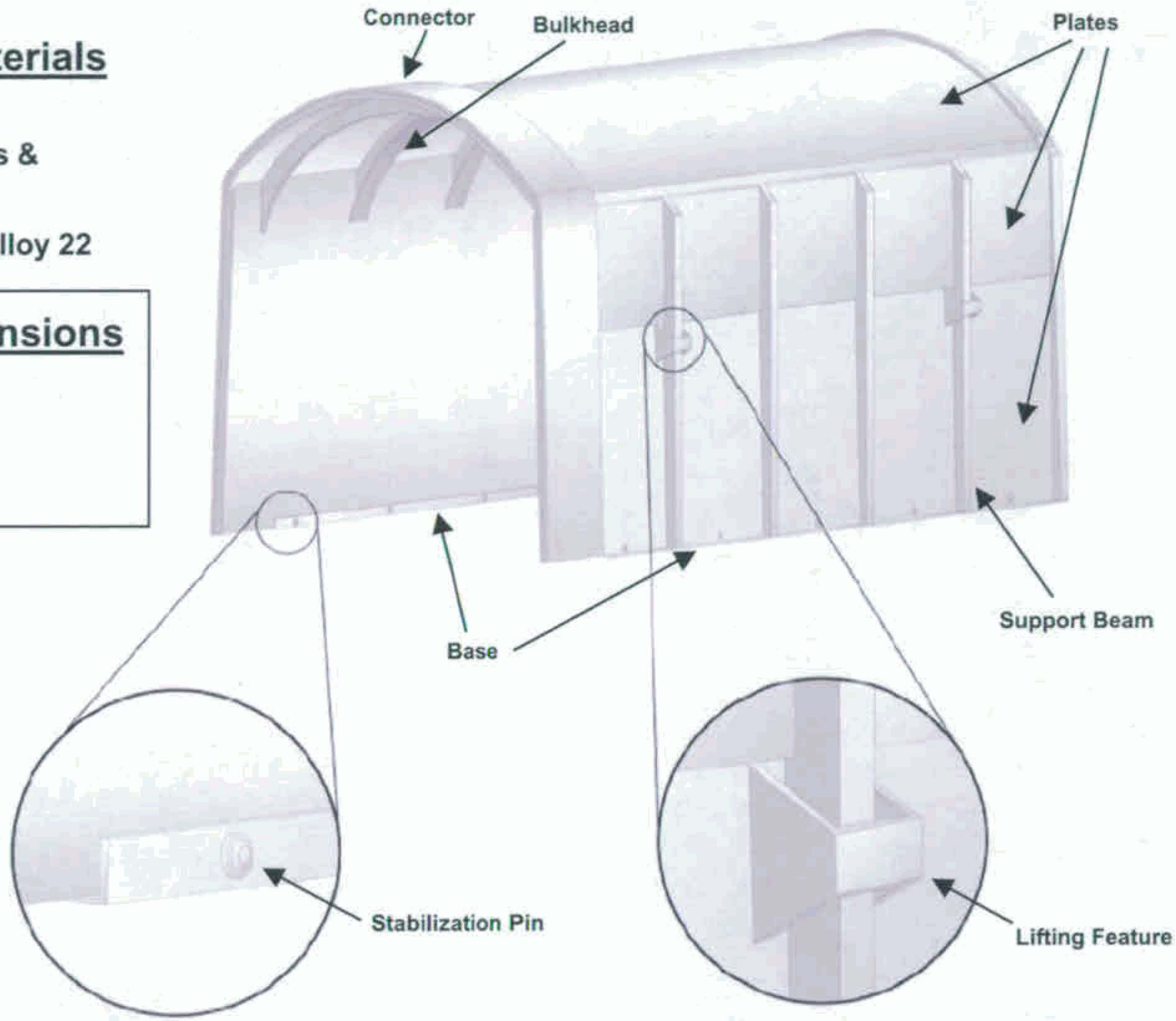
Bases & Stabilization Pins - Alloy 22

Drip Shield Dimensions

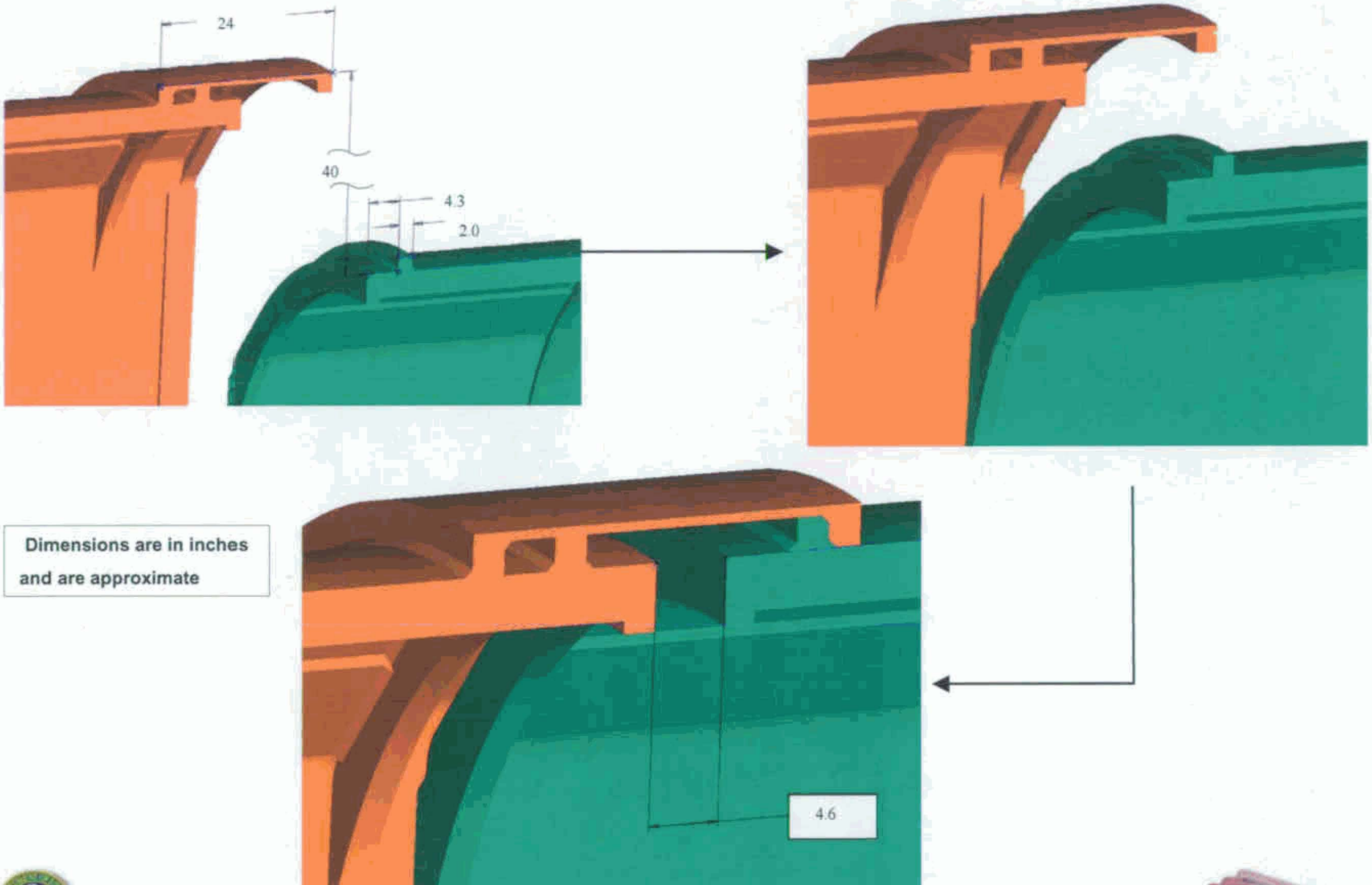
Maximum Height ≈ 114" (9.5')

Maximum Length ≈ 228" (19')

Weight ≈ 11,000 lb

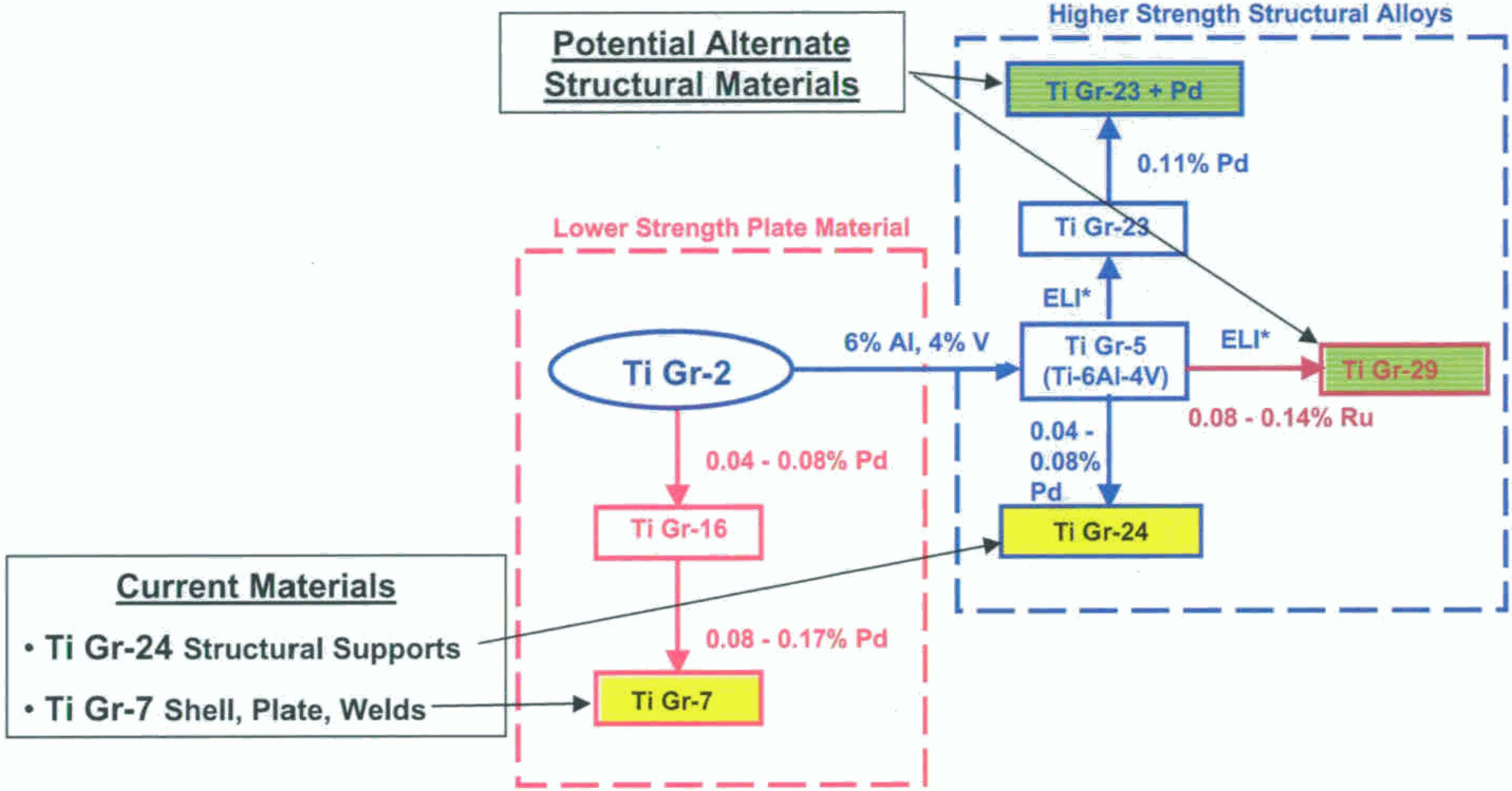


Drip Shield Interface



Dimensions are in inches and are approximate

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

Drip Shield Stress Corrosion Cracking

- **As emplaced, drip shield resistant to SCC**
  - Stress relief annealed
  - No dynamic loading
- **SCC is possible under seismic and rockfall loads**
  - SCC does not compromise water diversion function
  - Tightness and tortuosity of cracks limits flow
  - Potential for mineral/corrosion product plugging.

Environmental Cracking of DS Alloys

- **DS alloys highly resistant 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 with no SCC initiation**
  - **NRC funded notched SSRT of Ti G-2, Gr-7 and Gr-5 in deaerated 95°C, 1 M NaCl with and without 0.1 M NaF ****
    - No SCC (or HIC) 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

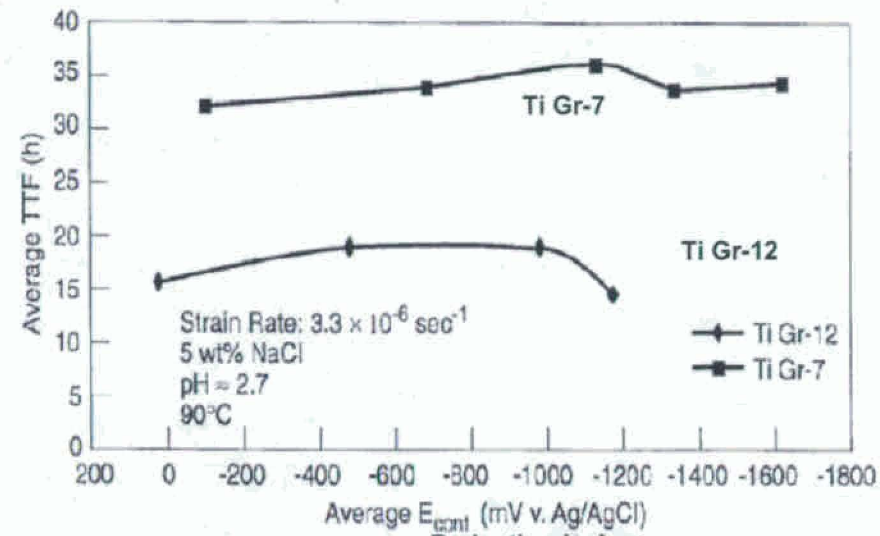
* Smailos et al, Enresa final report, EC-Contract NO. F14W-CT95-0002, 1999

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

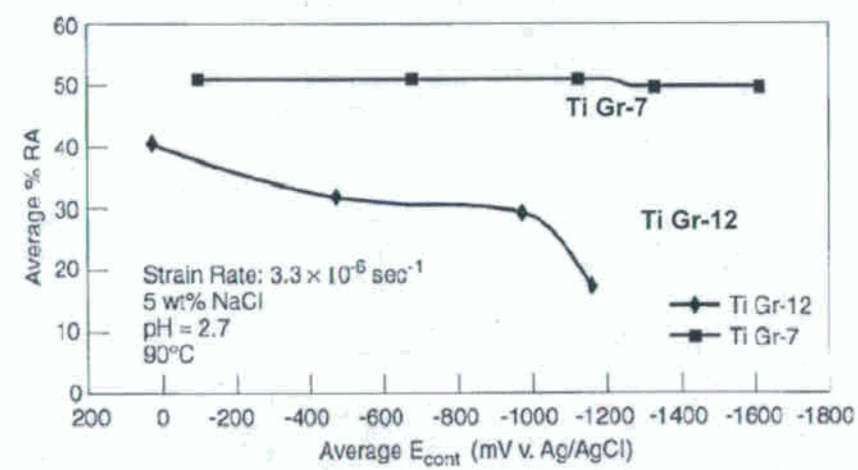
Environmental Cracking of DS Alloys

- **YMP SSRT* on cathodically polarized Ti Gr-7 and Gr-12 in 90°C, 5 wt % NaCl, pH ~2.7**
  - **For Ti Gr-7, time-to-failure (T-T-F) and ductility not significantly influenced by 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.**

Time-to-failure



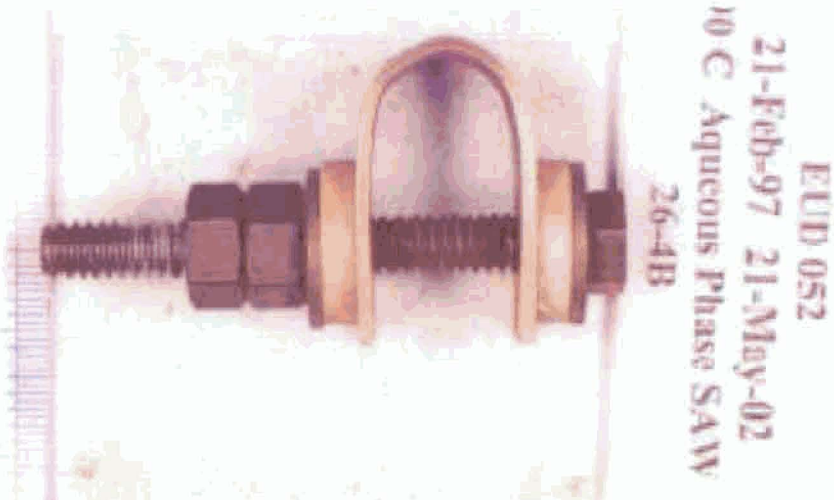
Reduction in Area



*Roy et al., Corrosion 2000, Paper 00188

Environmental Cracking of DS Alloys

- Ti Gr-7, 12 and 16 U-bends exposed up to 5.5 years in LLNL Long Term Corrosion Test Facility (LTCTF)*
  - No SCC in Ti Gr-7 or 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 in 90°C SCW (contains ~ 0.1 M F)



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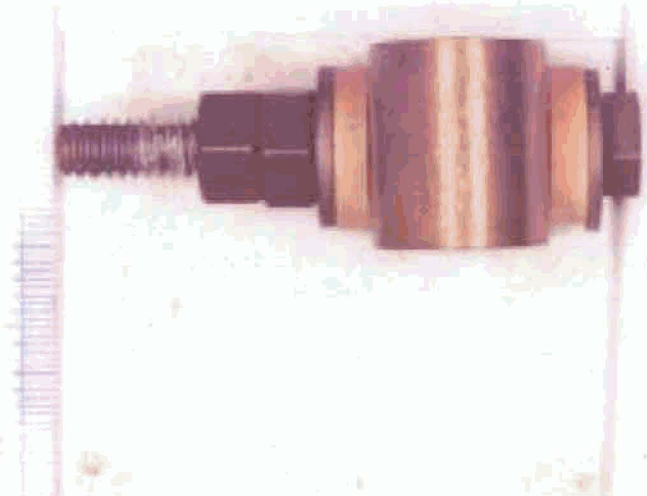


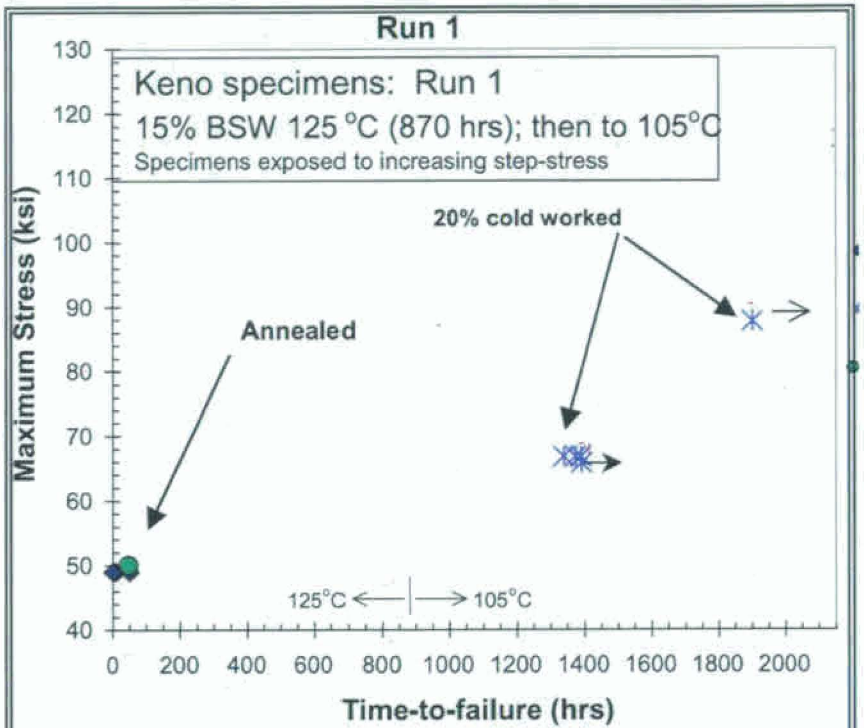
B

Un-cracked Ti U-bend specimen after 5 years exposure to SAW at 90°C

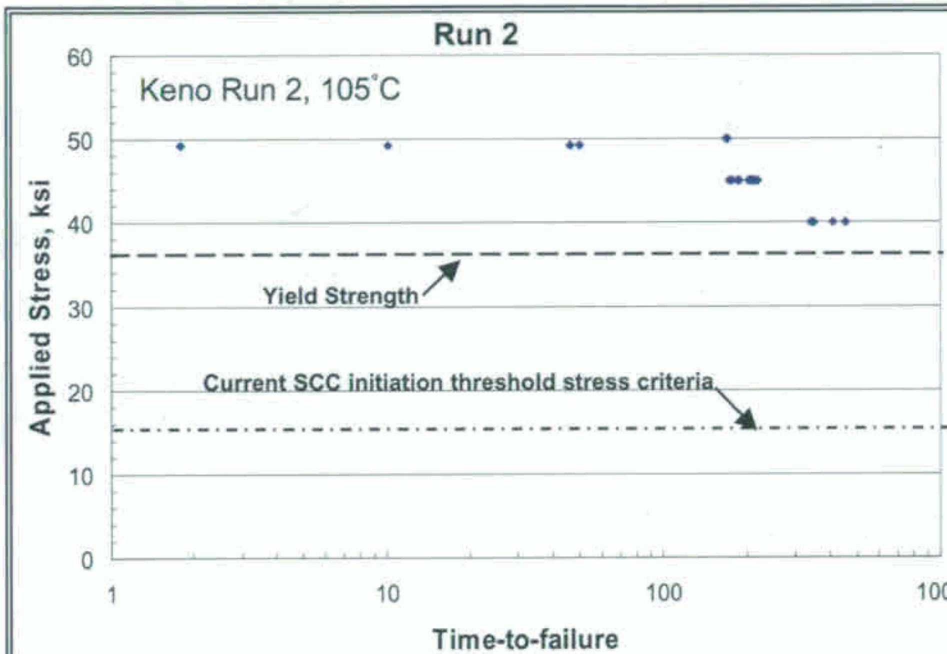
*Fix et al Paper 04551, Corrosion 04, **SAW = Simulated Acidified Water, SCW = Simulated Concentrated Water, SDW = Simulated Dilute Water

Environmental Cracking of DS Alloys

- **Two GE constant load Ti Gr-7 SCC initiation test campaigns***
  - 15% basic saturated water (BSW) [~7500X J-13, pH ~12, 105-125°C]



- Failure in annealed Ti Gr-7 at 48-50 ksi, (~1.4 x yield strength [YS])
- No cracking in 20%-Cold Worked Ti Gr-7 at 88 ksi (~1.2 YS)

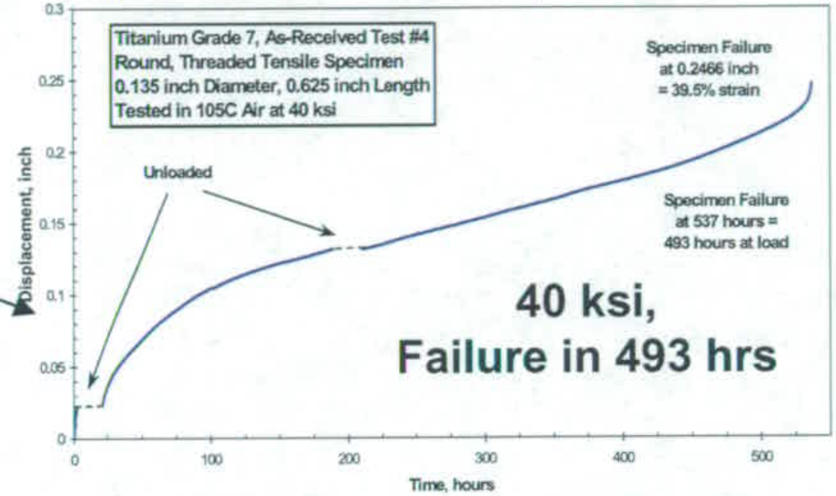


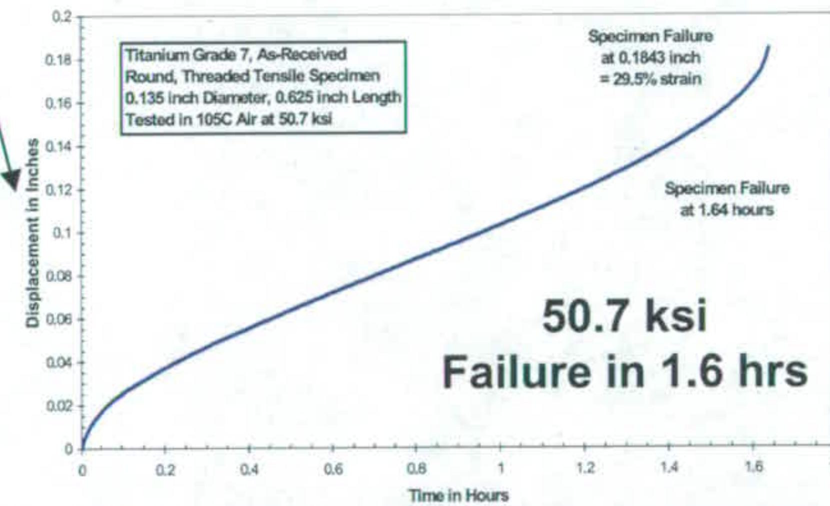
- Annealed specimens failed at over-yield stresses in ~2-500 hours
- Tests at lower applied stress levels now underway

* 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

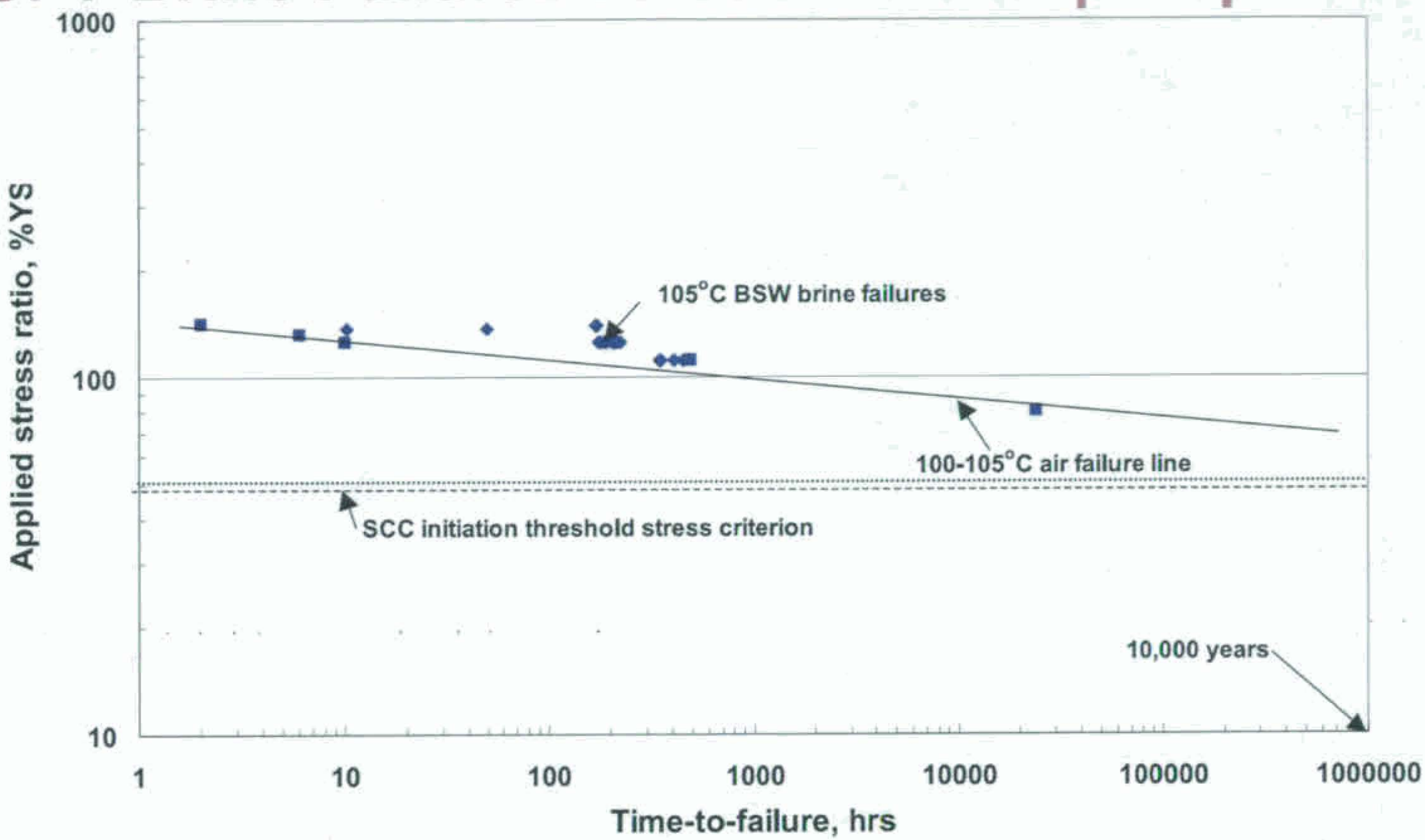
- **Because of short brine failure times, air creep tests run**
  - **Ti Gr-7 creep curves in air at 105°C at ≥ 110% YS***
  - **Other 100°C air tests** indicate creep at ≥ 60% YS**
- **Specimen failure times in brine and air overlap at similar stresses**
- **Necessary to determine if failures due to 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

Ti Gr-7 Brine Failures versus Air Creep Rupture Results*



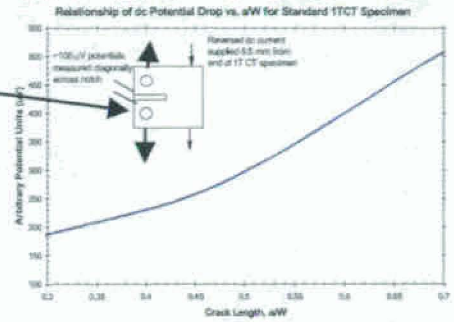
- Constant load brine failures due to creep rupture rather than SCC
  - Fractography also consistent with ductile failure
- Significant margin between minimum stress without SCC initiation and threshold stress criterion

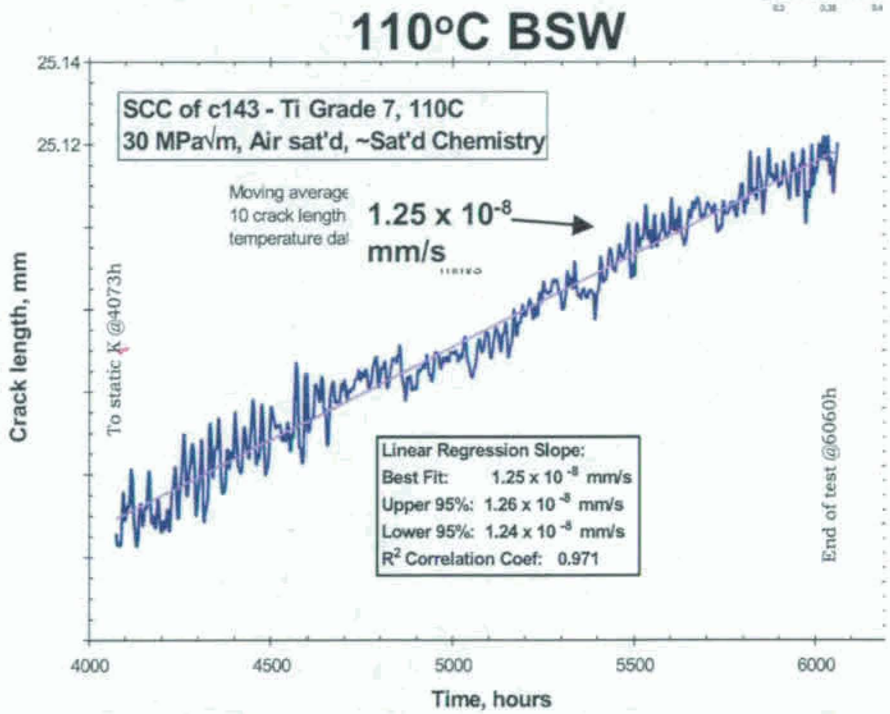
*Andresen et al., 12th Int'l Conference on Environmental Degradation, Salt Lake City, August 14-18, 2005, Dutton et al., Preliminary Analysis of the Creep Behaviour of Nuclear Fuel-Waste Container Materials, AECL-11495, COG-95-560-1, 1996, Drefahl et al., Titanium Science and Technology (G. Lutjering,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

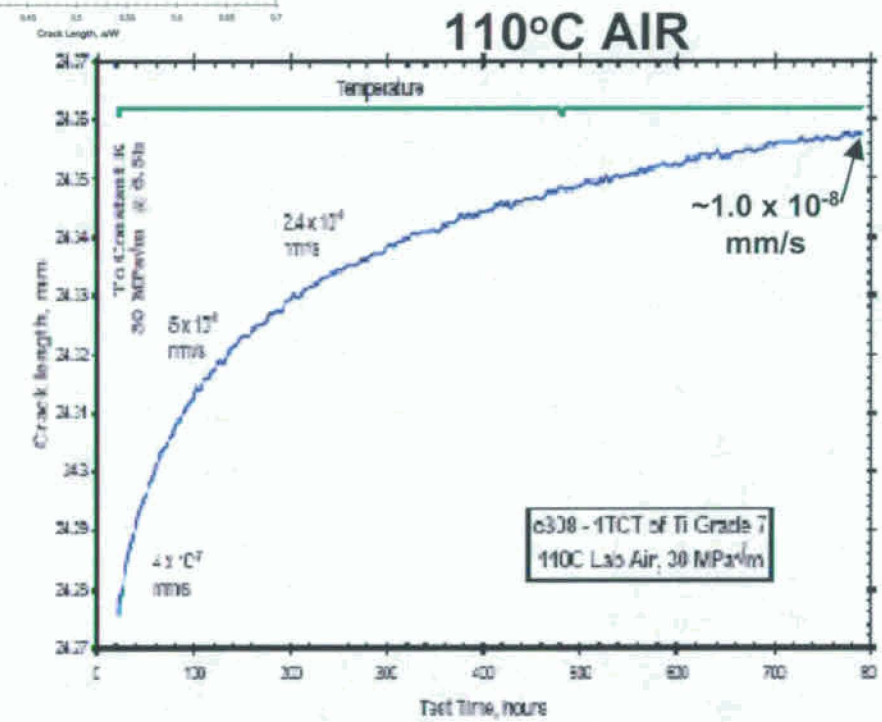
Crack Growth Rates in BSW and SCW Brines

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

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



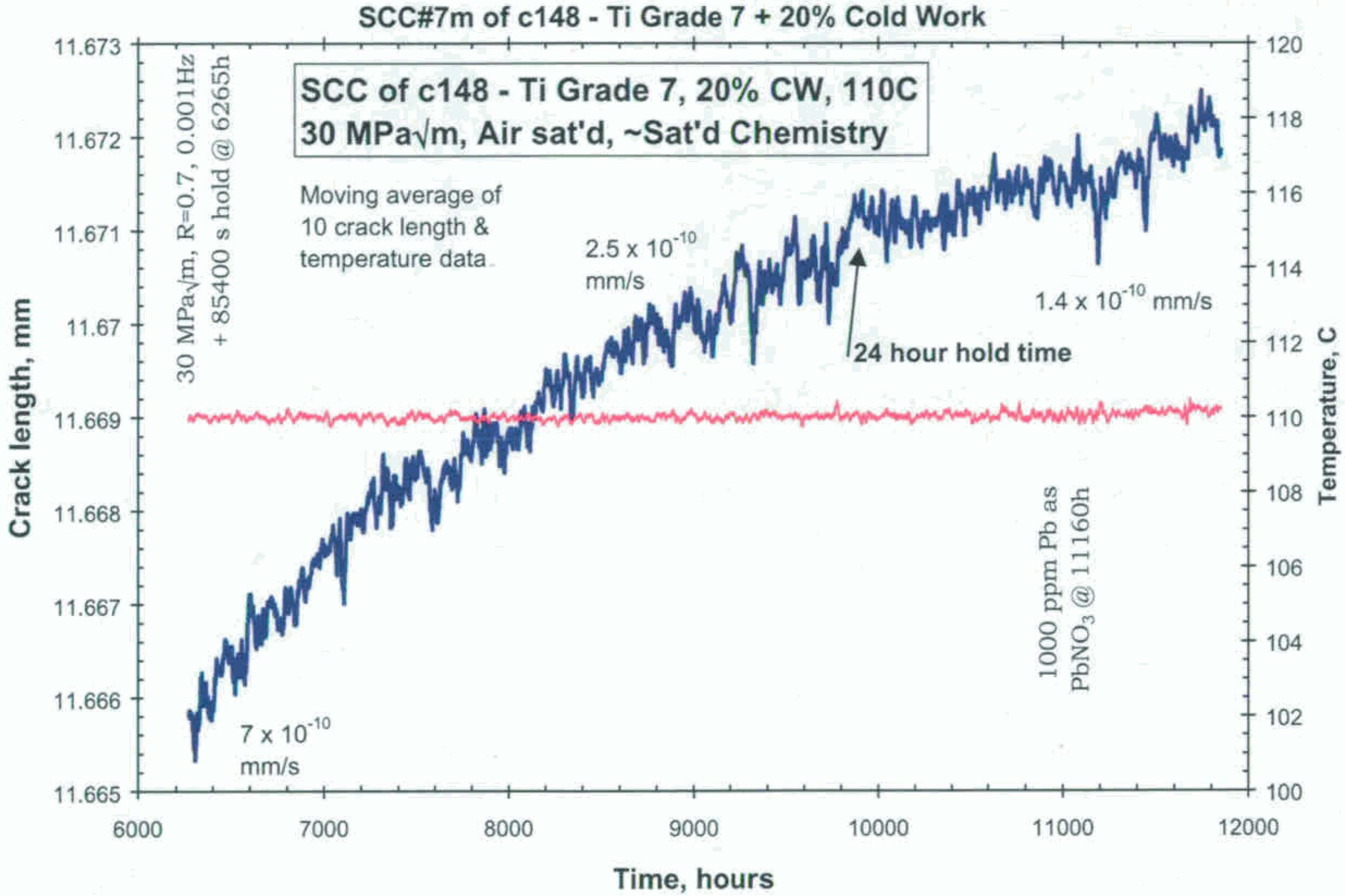




- Annealed Ti Gr-7 constant load crack growth rates similar in air and BSW
- Consistent with significant creep component for Ti Gr-7 growth

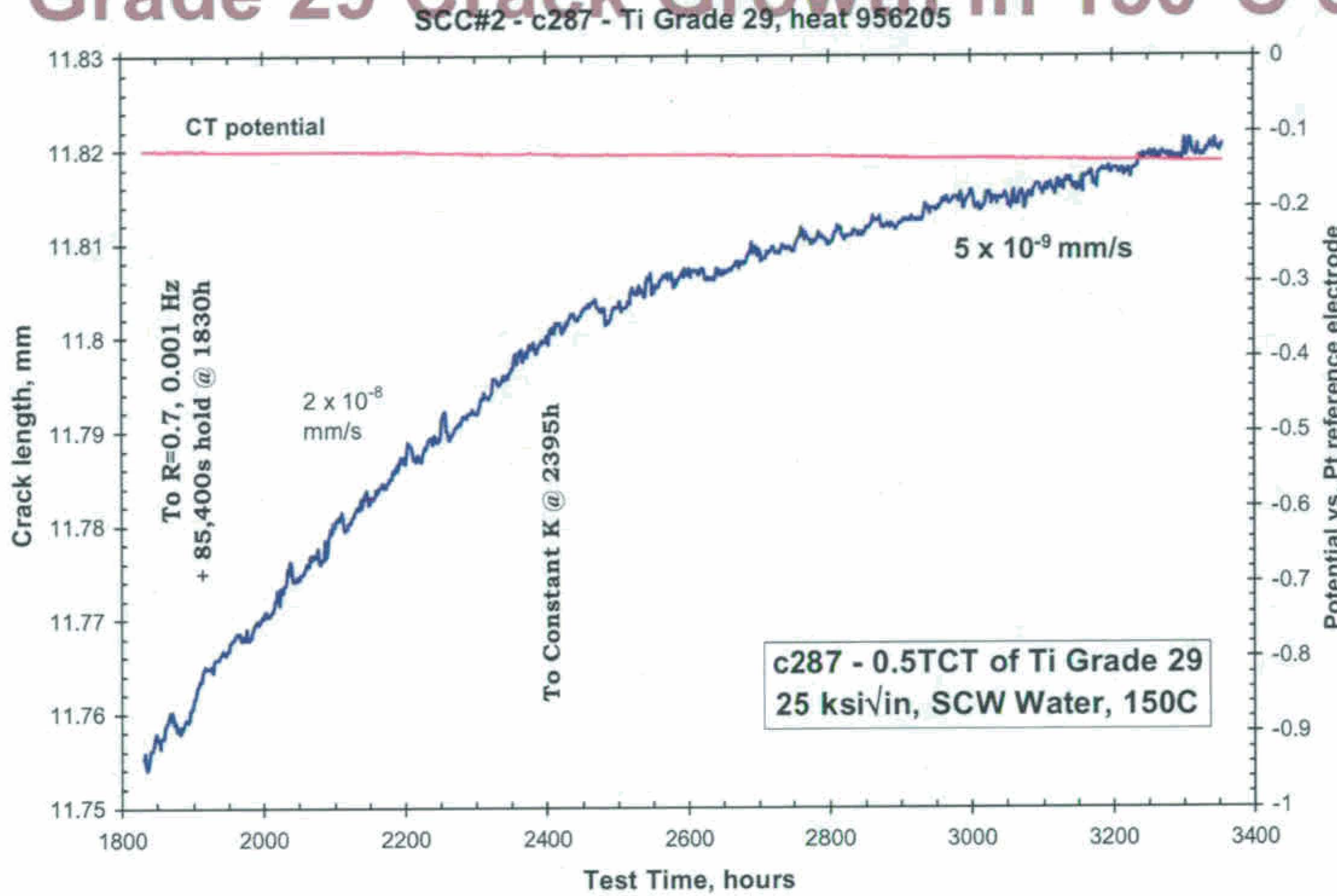
*Andresen et al., 12th Int'l Conference on Environmental Degradation, Salt Lake City, August 14-18, 2005

Cold-worked Ti Gr-7 Crack Growth in 110°C BSW



•Cold-worked Ti Gr-7 highly resistant to SCC growth in BSW Brine

Ti Grade 29 Crack Growth in 150°C SCW



- Ti Gr-29 significantly more creep resistant than Ti Gr-7 *
- Therefore, crack growth observed in Ti Gr-29 likely due to SCC

*Andresen et al., Proceedings 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

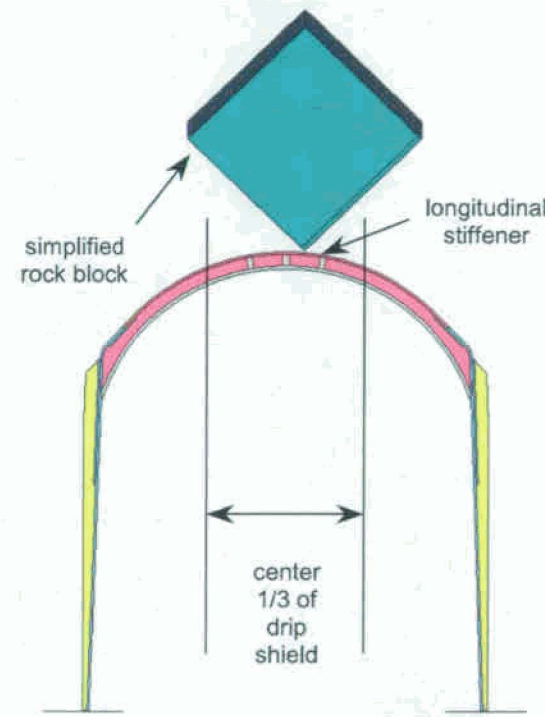
- Maximum calculated creep strains less than 5%
  - Acceptable limit is 10%
    - ~Onset of tertiary creep

Rock Fall Impact

- Residual stresses >50% YS
  - Through-wall SCC can occur
  - However, 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

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

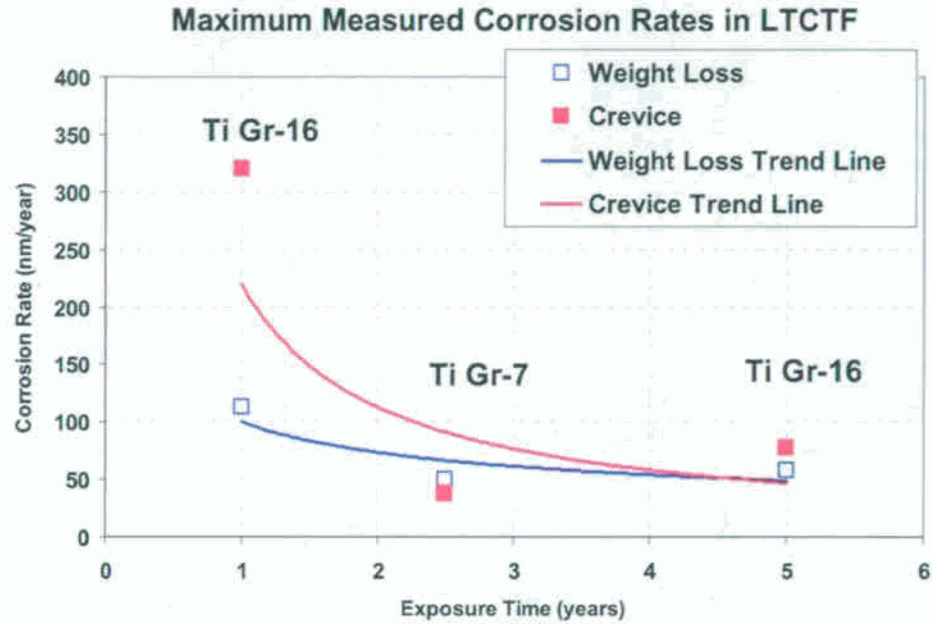


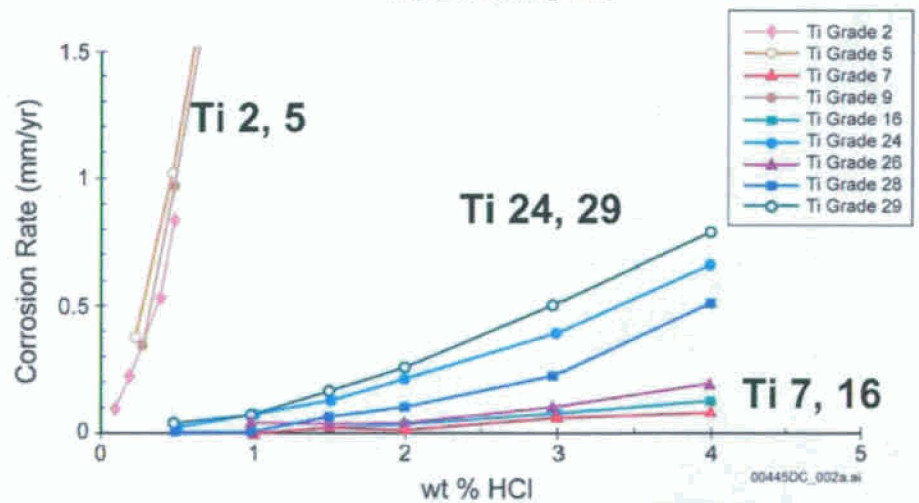
General, Localized and Galvanic Corrosion of DS Alloys

Drip Shield General Corrosion

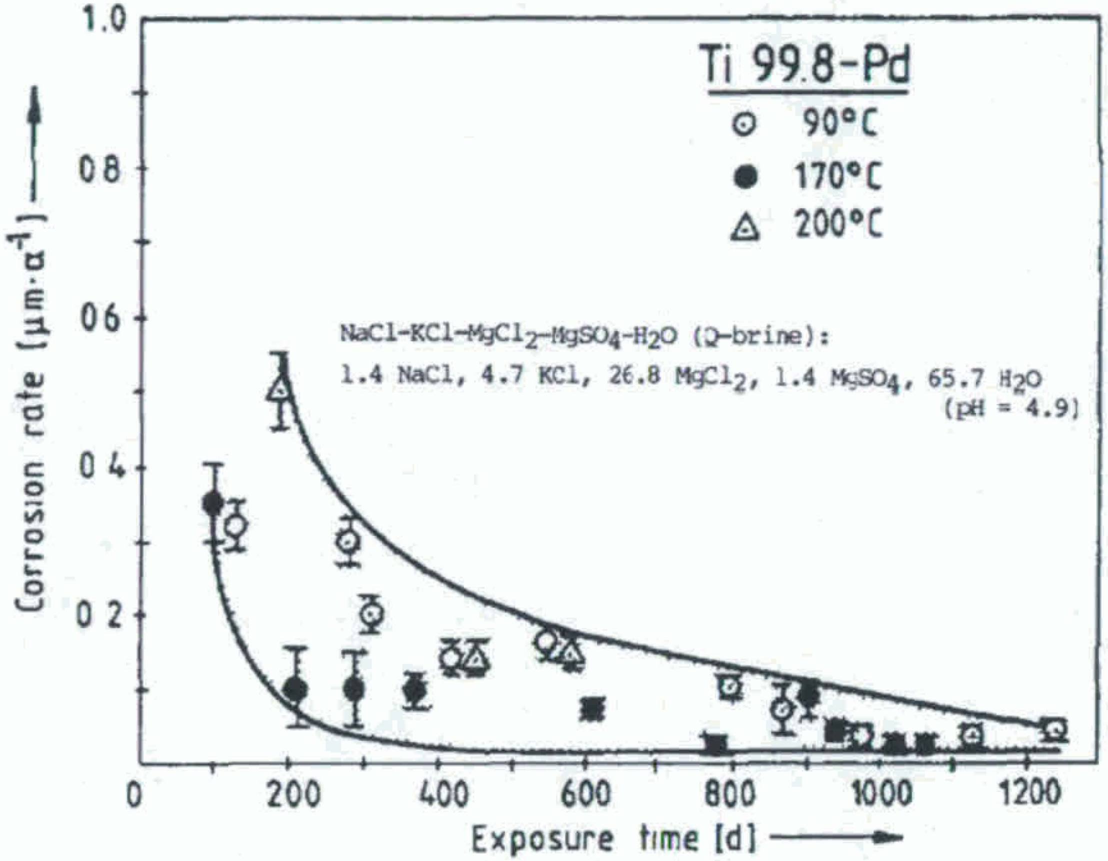
- **Ti Gr-7 Plate Material***
  - One year Ti Gr-16 exposed specimens used for PA (Performance Assessment)
    - Corrosion rate decreases with time* – not used in PA
    - Ti-7 more resistant than Ti-16
    - Median value of <10 nm/yr after 2.5 years exposure
- **Ti Gr-24/29 Supports****
  - Accelerated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

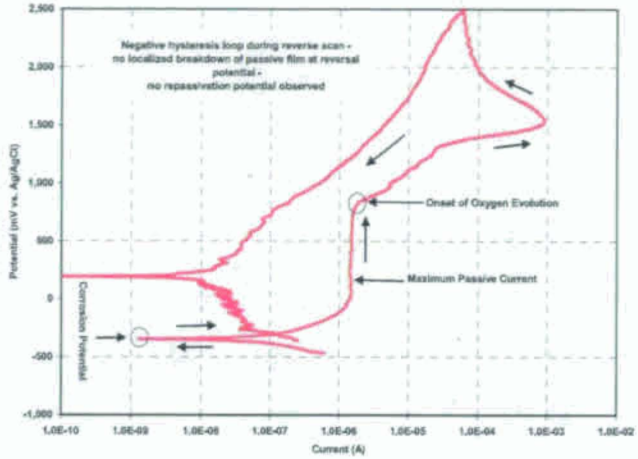


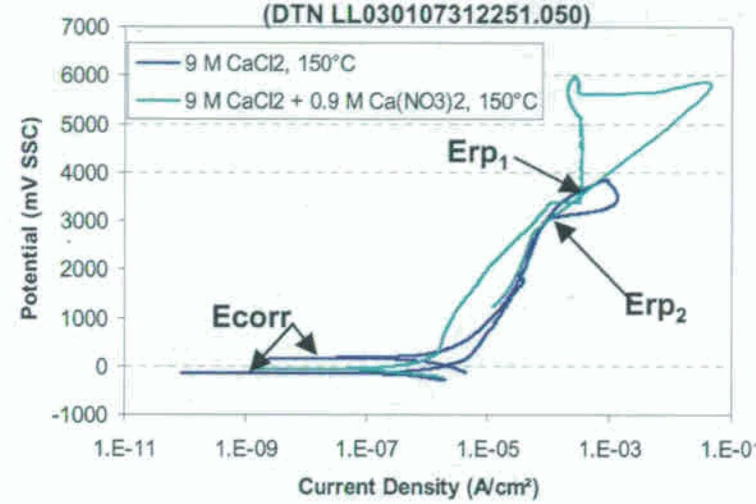
- General corrosion in Q-Brine consistent with LTCTF results
- Rate is temperature independent up to 200°C

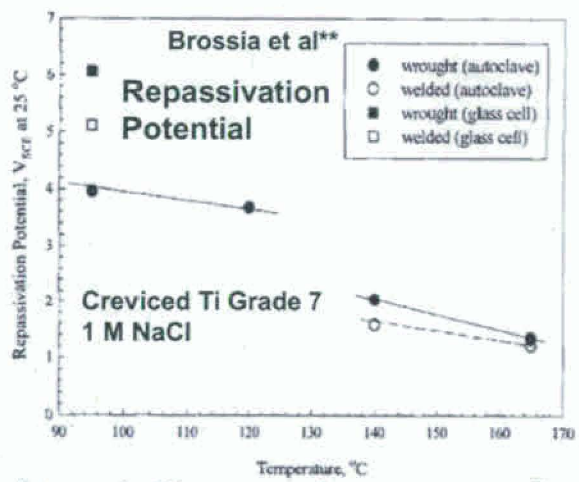
* E. Smailos, R. Köster, Corrosion studies on selected packaging materials for disposal of high level wastes, **IAEA-TECDOC-421**, Proceedings of a Technical Committee Meeting on Materials Reliability in the Back End of the Nuclear Fuel Cycle, Organized by the IAEA, Vienna, 2-5 September, 1986

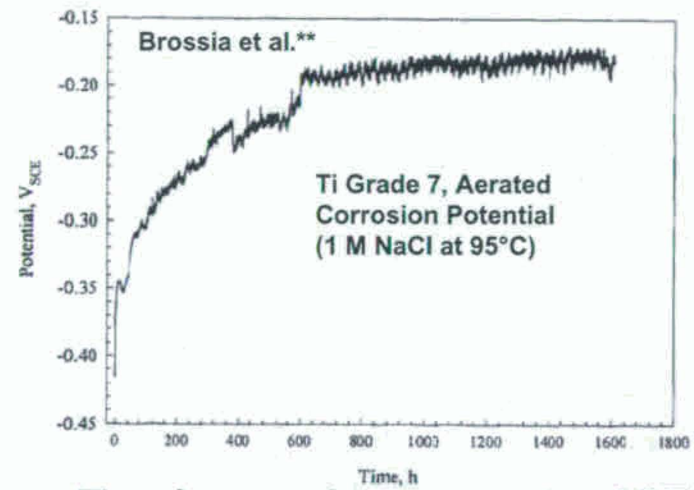
Localized Corrosion of Ti Gr-7 at High Temperatures

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





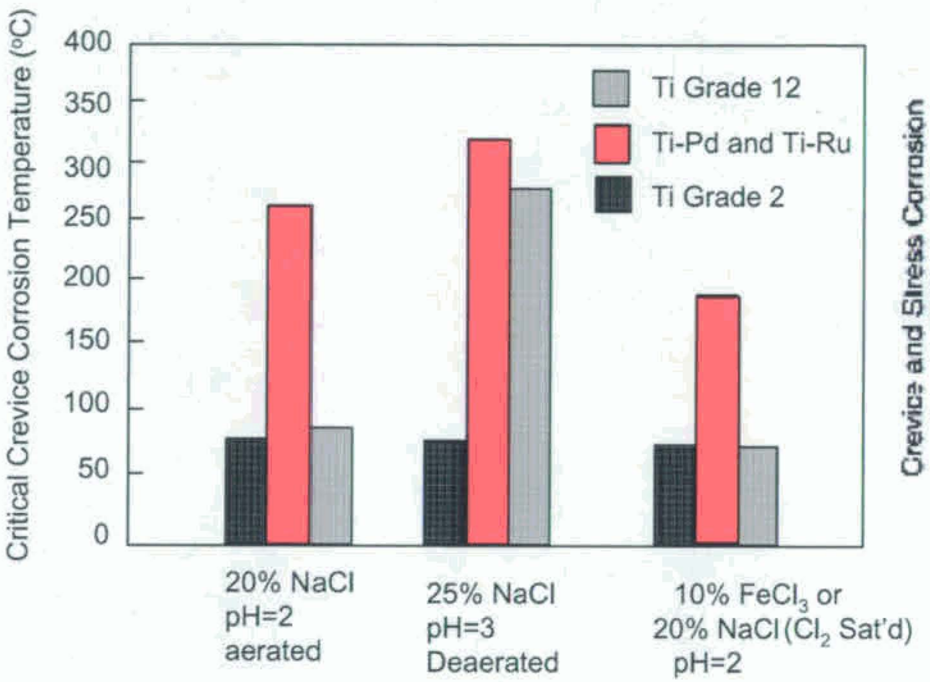




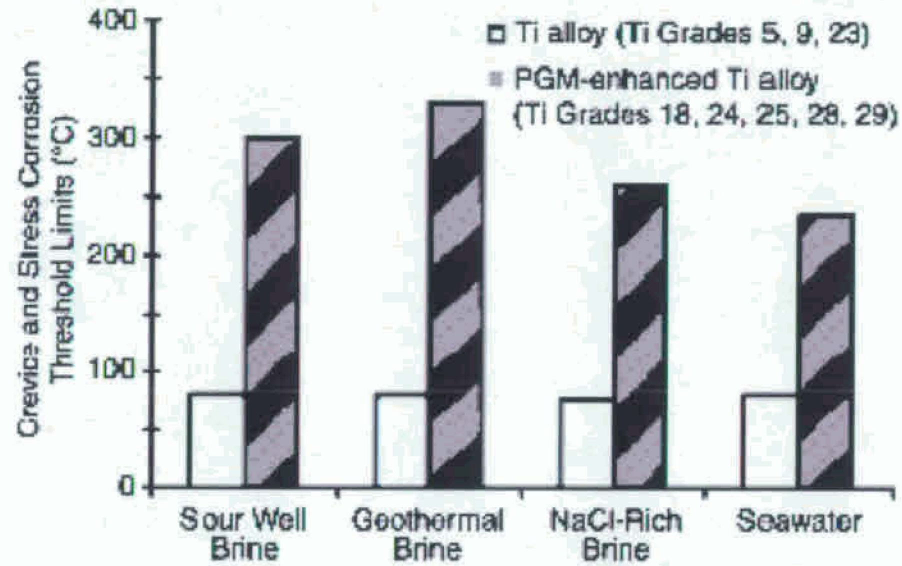
- **Localized Corrosion margin ($\Delta E = E_{crit} - E_{corr}$) very large up to 165°C***

*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

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**

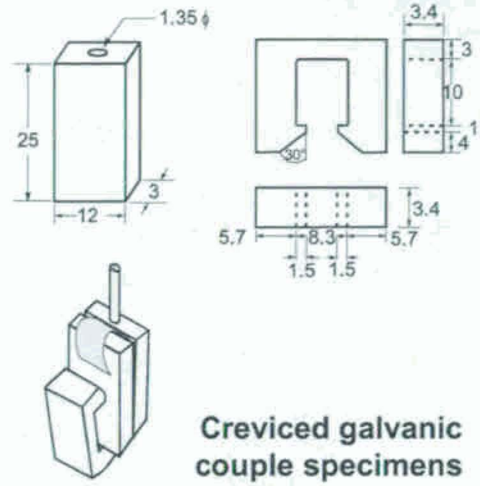
*Schutz, R.W., "Ruthenium Enhanced Titanium Alloys: Minor Ruthenium Additions Produce Cost Effective Corrosion Resistant Commercial Titanium Alloys, "Platinum Metals Review, 40 (2), 54-61, 1996

**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

Galvanic Corrosion of Ti Gr-7

Ti Gr-7/Alloy 22 Galvanic Couples

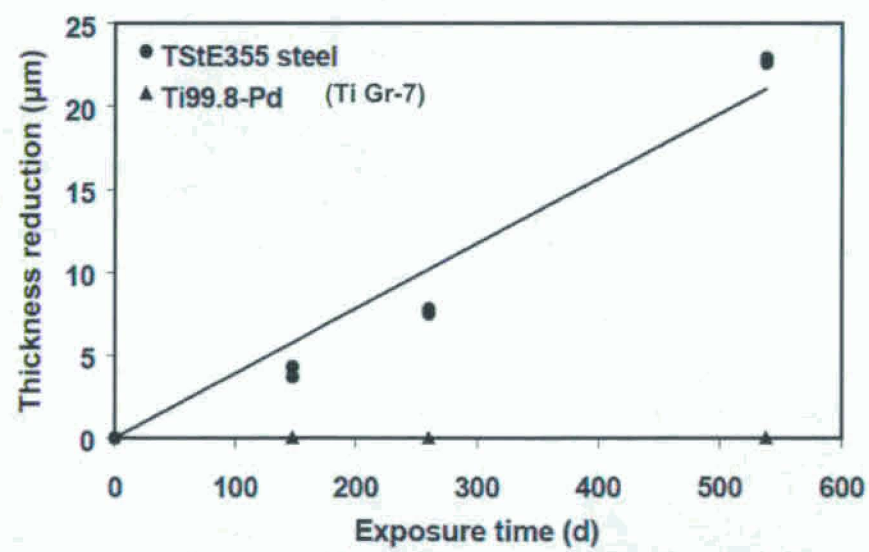
- A series* of creviced, galvanic couples tested in non-deaerated 90°C SCW
  - No evidence of galvanic or crevice corrosion after 350 - 500 hours exposure



Creviced galvanic couple specimens

Ti Gr-7/Carbon Steel Tight Contact Couples

- Ti Gr-7/carbon steel couples** 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

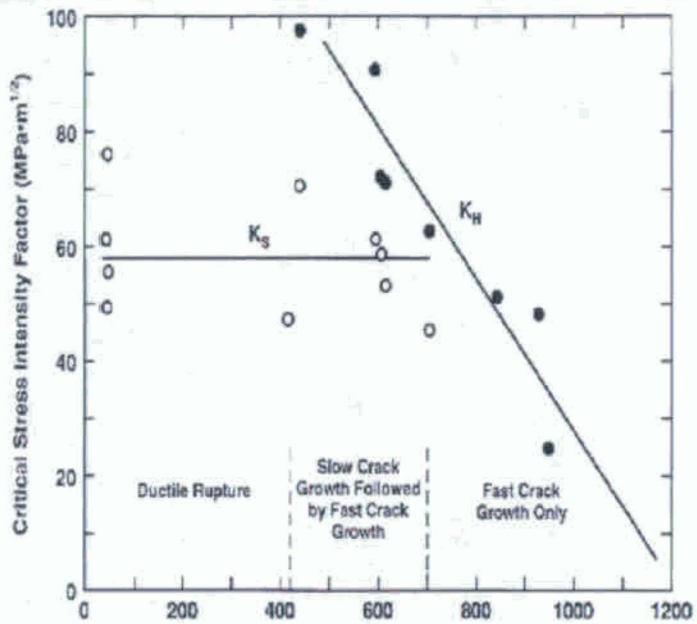
- Titanium DS alloys highly resistant to SCC and HIC in likely repository environments
- General corrosion rates extremely low and temperature independent to at least 200°C
- Large localized corrosion margins - LC not expected under repository relevant conditions
- Accelerated galvanic corrosion not 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

Backup Slides

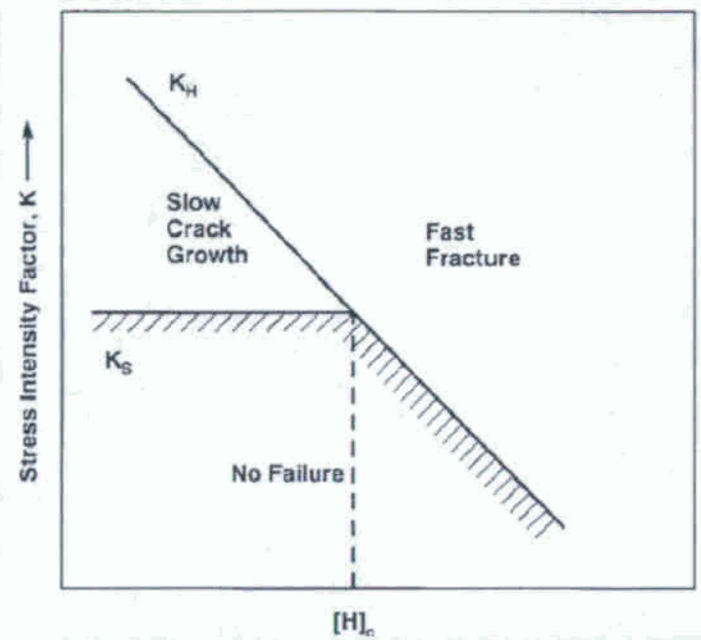
Modeling of Hydrogen Induced Cracking

Hydrogen Induced Cracking of Ti Alloys

ANL-EBS-MD-000006 REV 02



Clarke et al. 1995



Shoesmith et al. 1995

Critical Hydrogen Concentration (H_C)

- Ti Grade 2: 500 ~ 800 μg/g (Clarke et al. 1995)
- Ti Grade 16: 1,000 ~ 2,000 μg/g (Ikeda and Quinn 1998)
- Ti Grade 7: Should be at least 1,000 μg/g (YMP)
- Ti Grade 5: 200 μg/g for pre-cracked specimen
- 1,000 μg/g for smooth specimen (Hardie et al., 1999)
- Ti Grade 24: Estimated as 400 ~ 600 μg/g (YMP)
- Ti Grade 29: Estimated as 400 ~ 600 μg/g

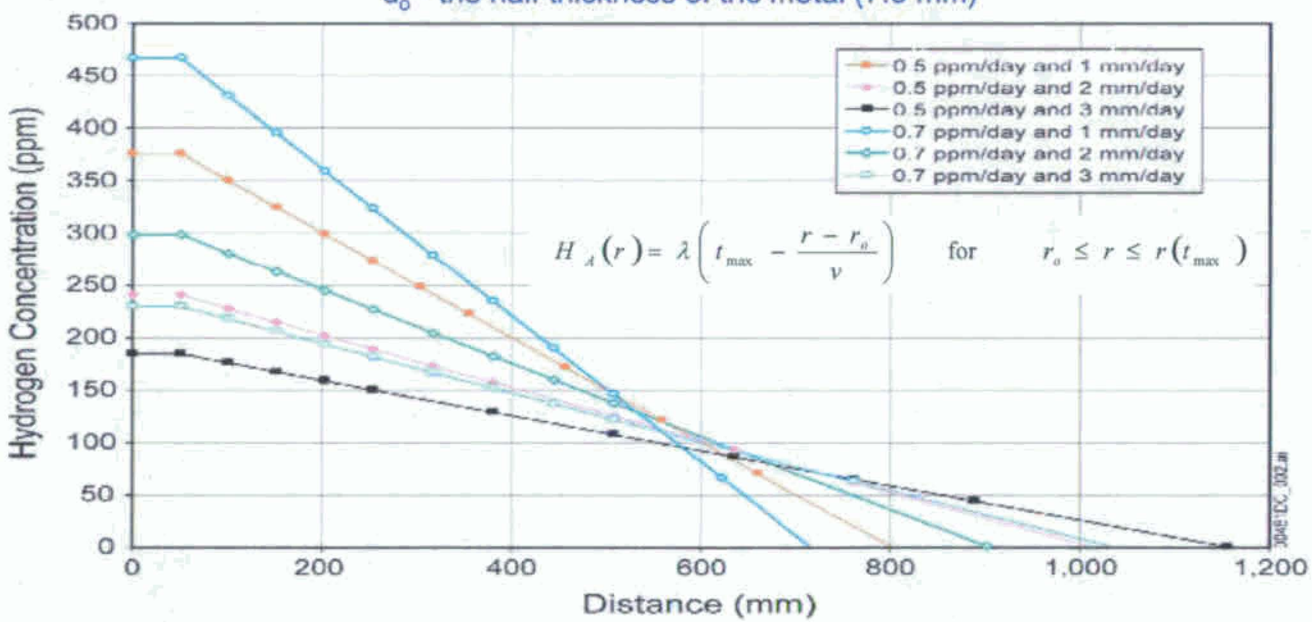
Estimated hydrogen content in 10,000 years

$$H_A = 4\times10^{6} f_h \cdot R_{uc} \cdot t\, [M_{ti} (d_o - R_{uc} \cdot t)]^{-1}$$

$$H_{A(10,000\ years)} = 124\ \mu g/g \ll H_C = 1,000\ \mu g/g \text{ (from general corrosion)}$$

Where:

- H_A - the hydrogen content (g/mm^3)
- f_h - the fractional efficiency for hydrogen absorption (0.015)
- R_{uc} - the rate of general passive corrosion (mm/year)
- t - the time of emplacement (10,000 years)
- M_{Ti} - the atomic mass of Ti (47.9 g/mol)
- d_o - the half thickness of the metal (7.5 mm)



Conservative hydrogen distribution for 50 lbs carbon steel contacting Ti Gr-7 over a radius of 50.8 mm

Hydrogen Induced Cracking of Ti Alloys

- **Conservative Assumptions Used in Modeling:**

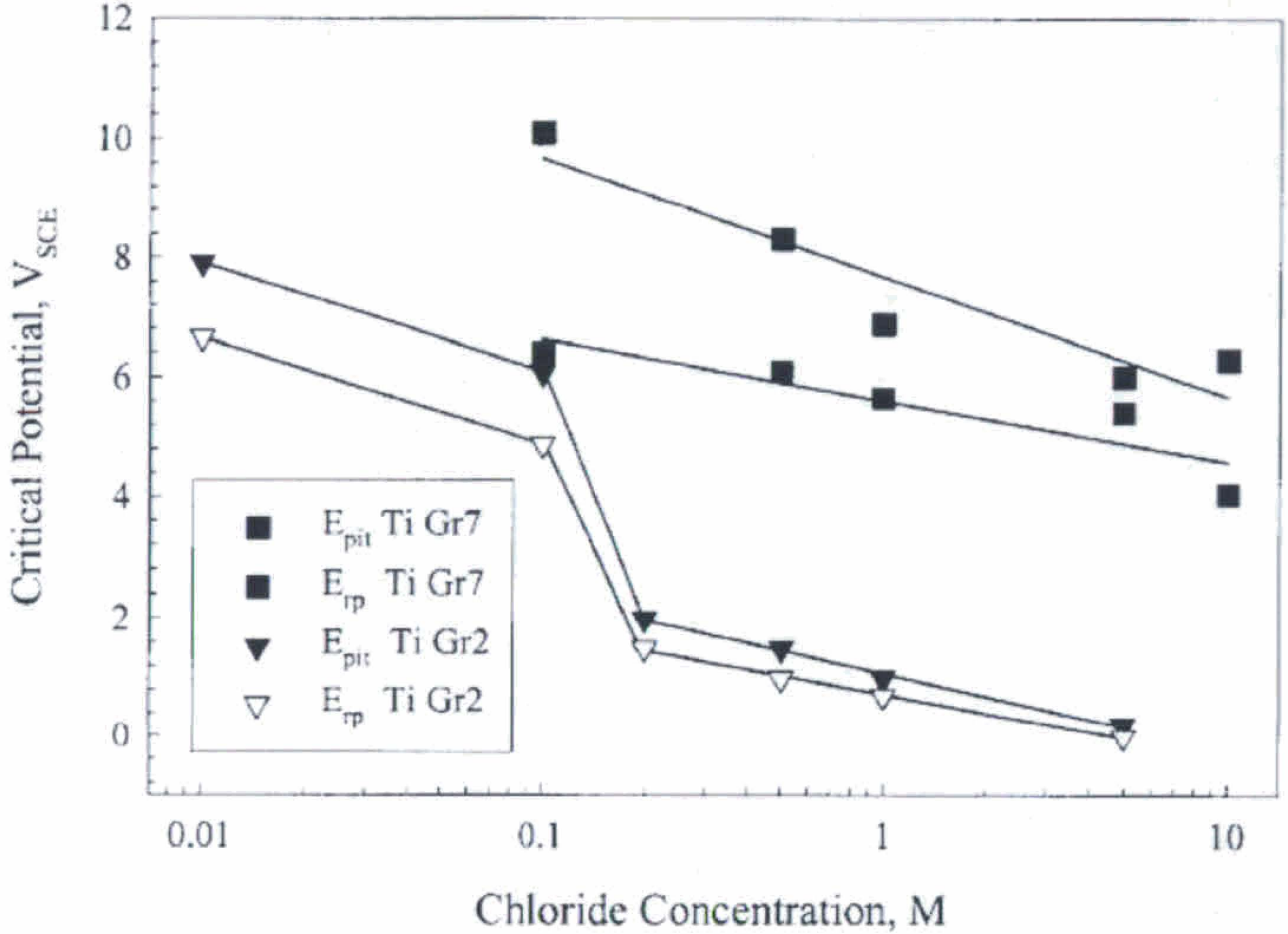
  - Assuming a f_h = 0.015 (0.005 - 0.015 per Okada 1983 under extreme conditions (< -1000 $mV_{(SCE)}$) unachievable in YMP).
  - Assuming constant corrosion rate: e.g. 5-year corrosion rate (77 nm/year) while in fact corrosion rate decreases with time.
  - Assuming immediate failure when $H_A \geq H_C$
  - Assuming hydrogen-in only.
  - H_C increases with temperature.

$$H_{A(10,000\ years)} = 124\ \mu g/g \ll H_C = 1,000\ \mu g/g$$

Test Type (Material)	1-Year (nm/yr) (Ti Grade 16)	2.5-Year (nm/yr) (Ti Grade 7)	5-Year (nm/yr) (Ti Grade 16)
Hydrogen Content after 10,000 Years (μg/g)	507	78	124

Localized Corrosion

Effect of Chloride on Repassivation Potential



*Brossia et al., Paper No. 01127, Corrosion 2001, NACE

Ti Gr-7 Potentiostatic Polarization in 5 M NaCl

- **Passive current density for creviced Ti Gr-7 exposed at 95°C to 5 M NaCl remains low**
  - 7.4×10^{-8} A/cm²

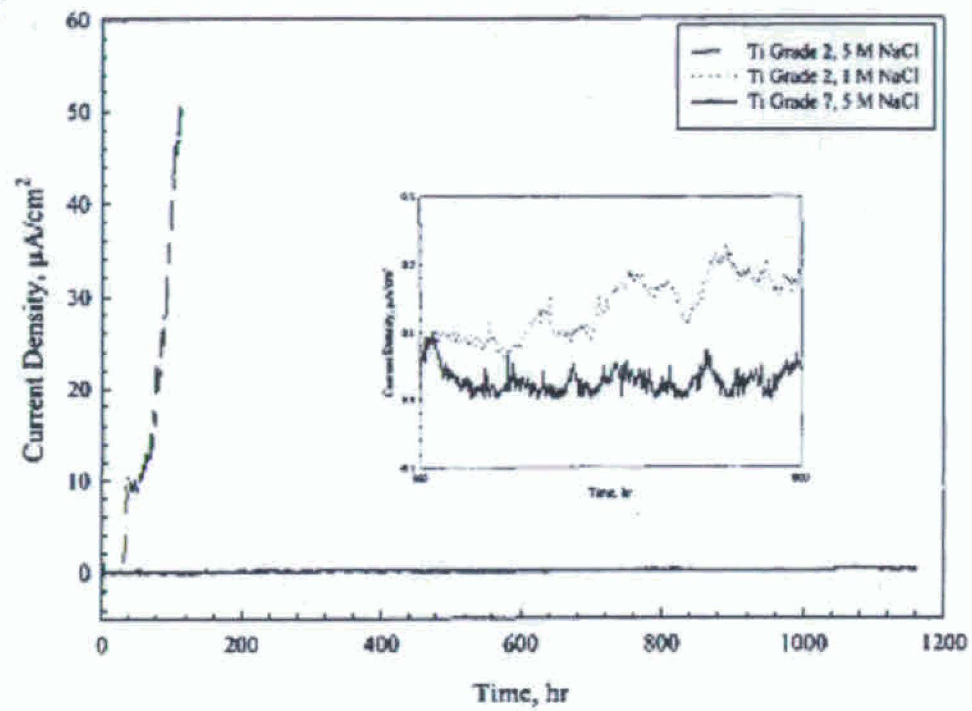


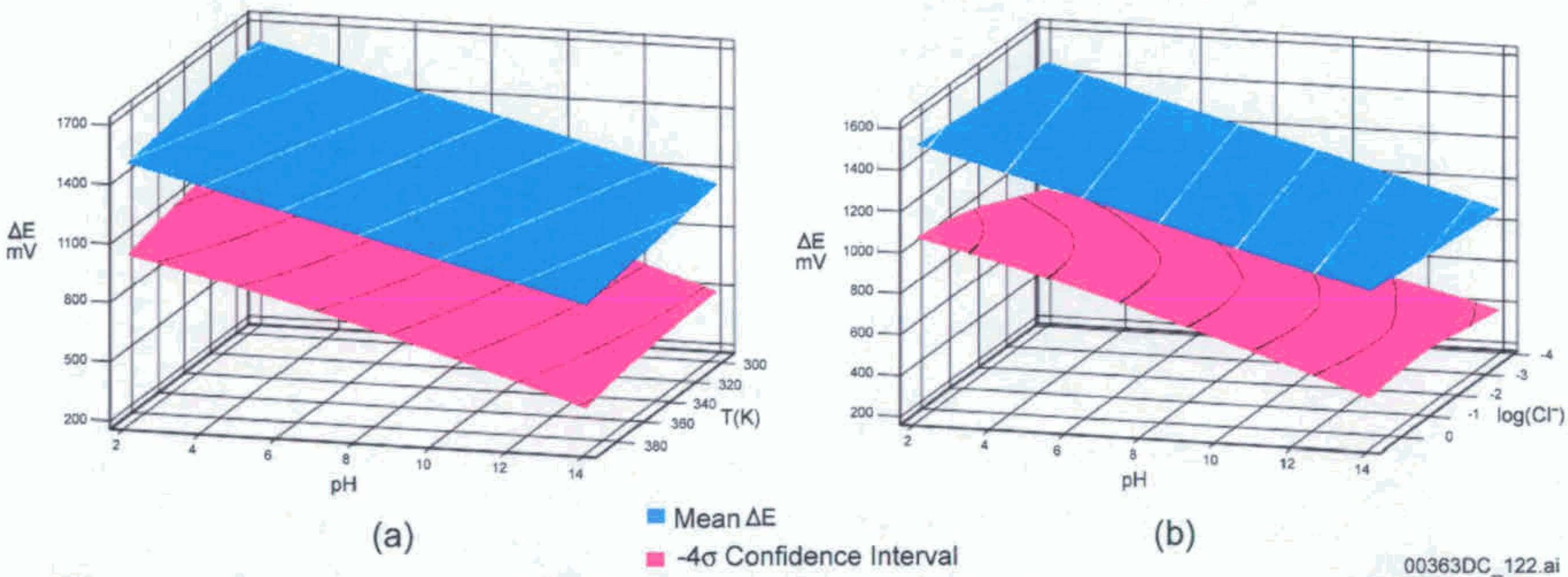
Figure 3: Current density as a function of time for creviced Ti Grades 2 and 7 in 5 M chloride solutions and creviced Ti Grade 2 in 1 M chloride solution. All tests conducted under deaerated conditions at 0 V_{SCE} and 95 °C. Inset figure shows expanded view of passive currents measured

Brossia et al., Paper No. 01127, Corrosion 2001, NACE

Drip Shield Localized Corrosion (LC)

- **Consistent with literature, YMP analysis* for repository relevant environments indicates LC will not initiate,** i.e., **$\Delta E = (E_{crit} - E_{corr}) > 0$, where:**

$$\Delta E = d_0 + d_1 \cdot T + d_2 \cdot \log(Cl^-) + d_3 \cdot pH$$



ANL-EBS-MD-000004, General Corrosion and Localized Corrosion of the Drip Shield