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

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Newer Alloy 22 Data and Their Relevance to High-Temperature Localized Corrosion

Presented to:

Nuclear Waste Technical Review Board

Workshop on Localized Corrosion of Alloy 22 in Yucca Mountain Environments

Presented by:

Raul B. Rebak

Senior Scientist, Lawrence Livermore National Laboratory

25-26 September 2006

Las Vegas, NV

Data Generators - LLNL

- Gregory E. Gdowski
- Susan A. Carroll
- Tiangan Lian
- Suvasis Dixit
- Sean J. Felker
- Joel R. Hayes
- Sarah K. Roberts
- Philip D. Hailey
- Kirk J. Staggs
- Christine A. Orme

Outline

- Introduction
- Environment (Felker Report)
  - What type of Na and K solutions are possible at high temperature?
- Autoclave Tests (Dixit Report)
  - General and crevice corrosion susceptibility
- Anodic Polarization at High Temperature
  - What nitrate over chloride ratio is necessary to inhibit crevice corrosion?
- Conclusions

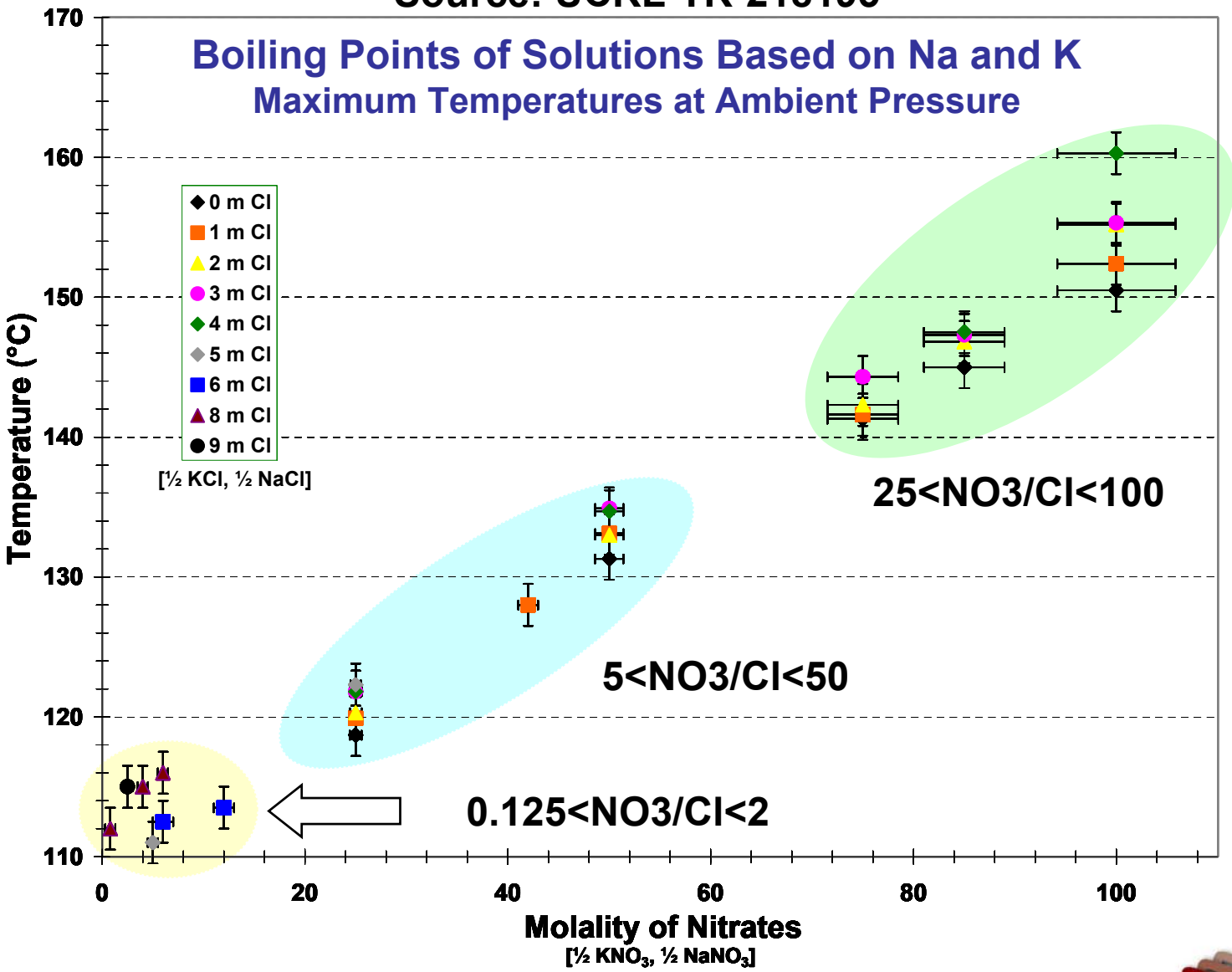
Introduction

- N06022 is susceptible to crevice corrosion in chloride-containing aqueous solutions
- Susceptibility is influenced by chloride concentration, temperature, electrochemical potential and nitrate concentration
- Nitrate inhibits crevice corrosion initiation and propagation
- A minimum ratio of [NO3]/[Cl] may be needed for localized corrosion inhibition
- At T < 120°C, this ratio may vary between ½ to 2, depending on other experimental variables

Environments Based on K and Na Salts (Felker Report)

Brine Compositions at High Temperature

Source: UCRL-TR-218195



Notes on Environments for K and Na Brines

- **Using Na and K salts, it is not possible to make chloride-rich brines that would have boiling temperatures higher than 120°C**
- **All Na and K based brines with boiling temperatures higher than 120°C will have [NO3]/[Cl] ratios higher than 5**
- **Crevice corrosion was not observed in Alloy 22 using short-term tests at [NO3]/[Cl] ratios higher than 2**
  - **Except for the closed autoclave tests, which were performed at [NO3]/[Cl] ratios lower than those for stable solutions**

Autoclave Experiments (Dixit Report)

Why the Autoclave Experiments?

- **The latest autoclave experiments were designed as a follow-on of previous tests to determine the general corrosion rate of Alloy 22 at temperatures higher than 150°C**
- **Creviced specimens were included in the autoclaves to test the hypothesis that a [NO3]/[Cl] ratio higher than 0.5 would not initiate crevice corrosion in Alloy 22**
- **The autoclave experiments were not designed to mimic the high nitrate brines expected for the in-drift environment**

Autoclave Experiments

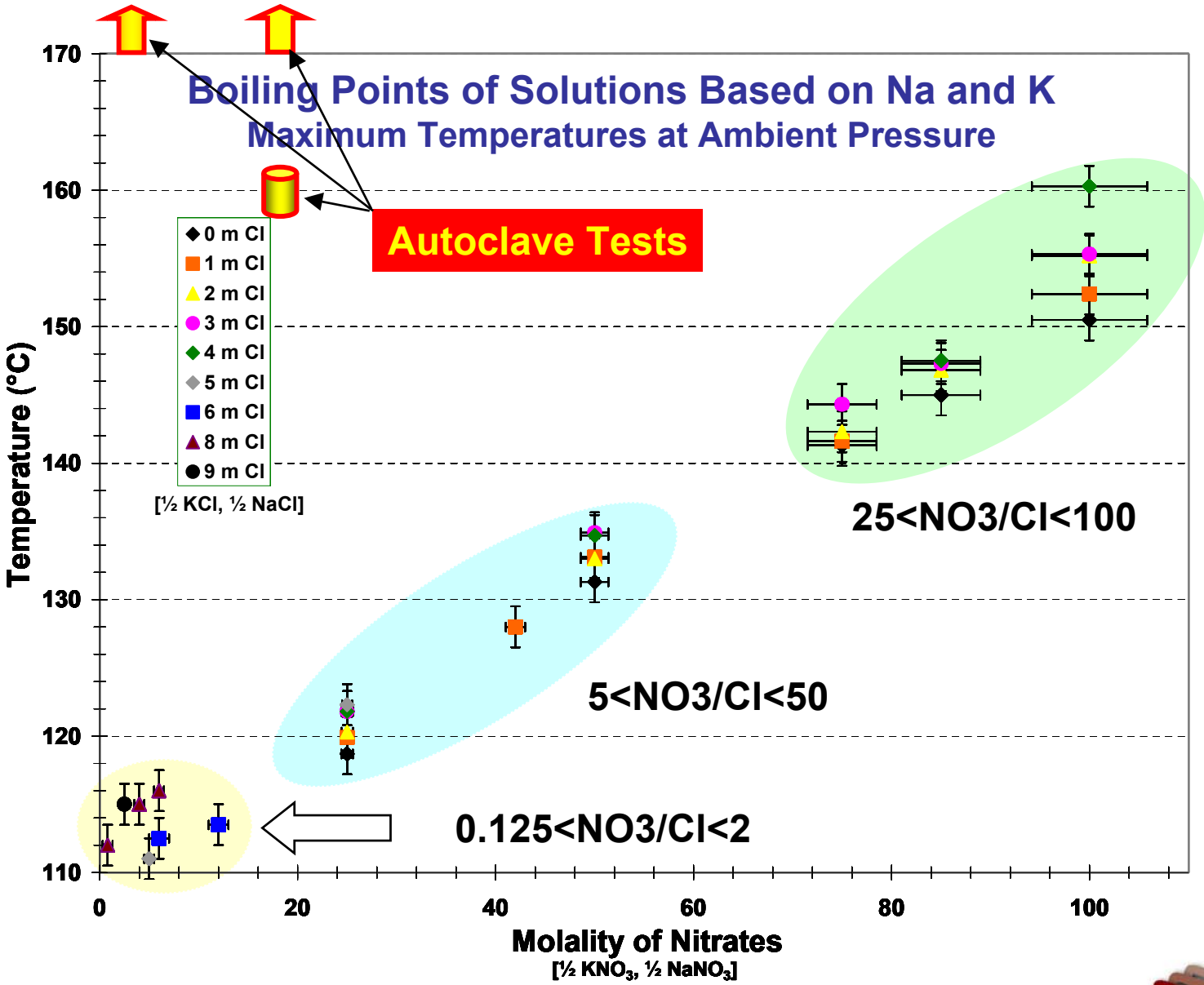
Details in the Dixit Report (UCRL-TR-217393)

- **Alloy 22 specimens, all non-welded polycrystalline material**
- **Three types of specimens**
  - **Pucks (5/8” diameter 3 mm thick discs – ASTM G 61)**
    - **Non-creviced for surface analysis**
  - **50 µm thick foils**
    - **Non-creviced for corrosion rate by weight loss**
  - **50 µm thick foils**
    - **Creviced for crevice corrosion initiation studies**
    - **Crevice former = alumina 12-tooth washer. No PTFE tape**

Autoclave Experiments

- Autoclaves purged with nitrogen before heaters turned on
- **Autoclave 1**
  - 160°C
  - 2.5 *m* NaCl + 3.4 *m* $NaNO_3$ + 15.1 *m* KNO_3, [NO3]/[Cl] = 7.4
  - Crevice corrosion initiation was not anticipated, but occurred
- **Autoclave 2**
  - 220°C
  - 2.5 *m* NaCl + 3.4 *m* $NaNO_3$ + 15.1 *m* KNO_3, [NO3]/[Cl] = 7.4
  - Crevice corrosion initiation was not anticipated, but occurred
- **Autoclave 3**
  - 220°C
  - 6.4 *m* NaCl + 3.2 *m* KNO_3, [NO3]/[Cl] = 0.5
  - Crevice corrosion initiation may be expected, and occurred

Brine Compositions at High Temperature



Autoclave Experiments

- **Specimens tested in the vapor and liquid regions in each autoclave**
- **Total of 30 specimens per autoclave**
  - **Pucks = 8 (4 in the vapor and 4 in liquid)**
  - **Weight-loss Foils = 12 (6 in vapor and 6 in liquid)**
  - **Creviced Foils = 10 (4 in vapor and 6 in liquid)**
- **Total testing time was 267 days (9 months)**
  - **Tests started 9-13 September 2004**
  - **Autoclave heaters turned off 22 June 2005**

Three Type of Results from Autoclave Tests

- Crevice corrosion initiation susceptibility
- Surface deposits and corrosion products composition information
- Corrosion rate by weight loss

Crevice Corrosion (CC) Results from Autoclave Experiments

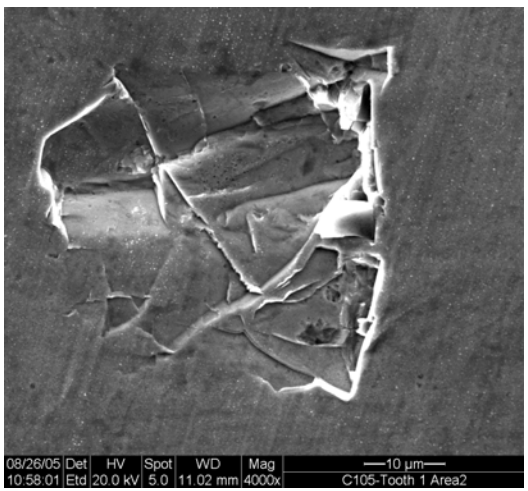
- The creviced specimens showed deposits from dissolved crevice formers
- Specimens exposed to all the tested conditions had crevice corrosion both in the vapor and liquid phases
  - Autoclave 1 (160°C), [NO3]/[Cl] = 7.4
  - Autoclave 2 (220°C), [NO3]/[Cl] = 7.4
    - At 220°C, less attack in the liquid than in the vapor
    - There was less attack at 220°C than at 160°C (same electrolyte)
  - Autoclave 3 (220°C), [NO3]/[Cl] = 0.5
    - Similar amount of crevice corrosion for Autoclave 2 and 3 (same temperature, different electrolyte)

Creviced Specimens - Autoclave 1

Vapor

[NO3]/[Cl] = 7.4
160°C

Liquid



Liquid
C105

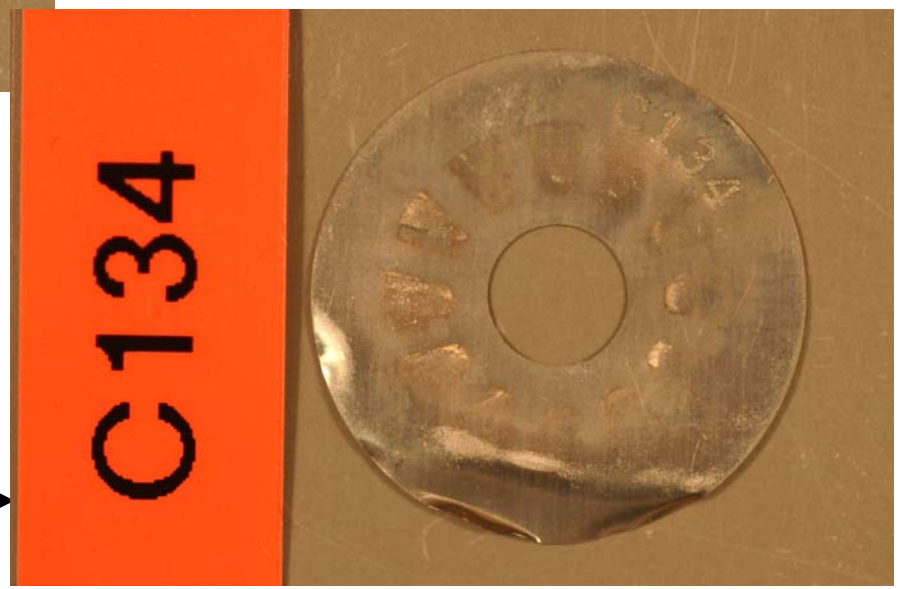
X4000 Mag.

Creviced Specimens - Autoclave 2

Vapor

[NO3]/[Cl] = 7.4
220°C

Liquid

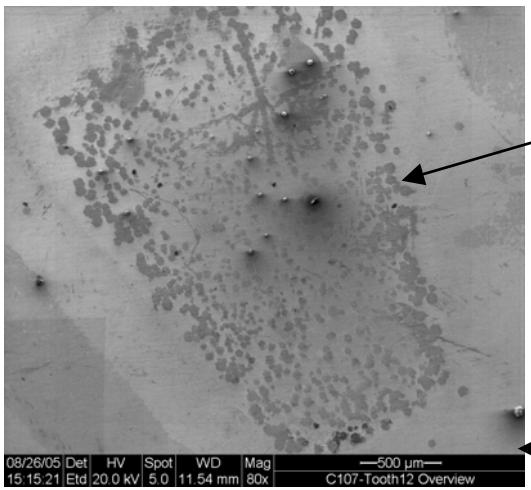


Creviced Specimens - Autoclave 3

Vapor

[NO3]/[Cl] = 0.5
220°C

Liquid



Deposits

Liquid
C107

X80 Mag.

Auger and XPS Surface Analysis Results from Autoclave Experiments

- Strong signals for O, C, Al and Si (Auger)
  - Al and Si are foreign elements
- Metals from the solution such as Na, K and in lower levels Ca and Mg also detected (Auger)
- Profiles show thinner surface oxides in the vapor (15 nm) than in the liquid (30 to 500 nm) (Auger)
- AC 1 samples have the thinnest oxides (Auger)
- Ni, Cr, Fe and W were detected on the surface as oxides or hydroxides (XPS)

Corrosion Rate Results from Autoclave Experiments

- All the weight-loss foils in the three autoclaves showed mass gain even after up to 30 acid cleaning steps
- Weight difference between before-and-after tests was small (10 to 70 µg) (equivalent to -10 nm/year)
- Little or no general corrosion after 9 months at 160°C and 220°C
- Corrosion potential (E_{corr}) was not measured
  - E_{corr} was probably not in the transpassive region since little corrosion was observed

Notes From Autoclave Tests Results

- All the creviced specimens in the three autoclaves showed crevice corrosion initiation
- Tests were conducted in environments that are physically impossible in the repository
- Unanticipated crevice corrosion results from AC 1 and AC2 where [NO3]/[Cl] = 7.4
- Short-term, fully immersed, cyclic potentiodynamic polarization would have predicted that at [NO3]/[Cl] = 7.4 crevice corrosion would not have occurred up to ~120°C
- To reach a stable solution at 160°C in a repository-type environment the ratio of [NO3]/[Cl] has to be near 100

Why Did Crevice Corrosion Occur in the Autoclave Tests?

- There are several possible explanations
  - Chemical modification in the electrolyte or in the passive film due to the crevice former dissolution
  - At the temperature the tests were performed a higher absolute amount of nitrate may be needed to provide inhibition
    - The ratio to provide inhibition may be temperature dependent
- There may still be a need to investigate, under physically attainable natural conditions, the effect of time on crevice corrosion initiation and propagation (stifling) for [NO3]/[Cl] higher than 1 in dust-like environments (Na and K brines)

Repassivation Potential Tests in K and Na Based Brines Short-Term Testing

$NaCl + KCl + NaNO_3 + KNO_3$ Brines

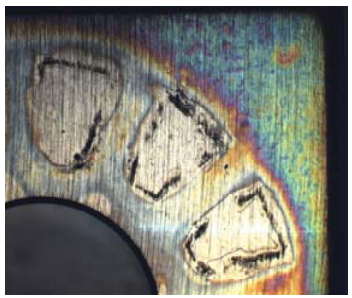
- Binary, ternary and quaternary salt mixtures 110°C to 150°C
- Solutions included
  - From pure Cl (8 *m*) to pure NO3 (42 *m*)
  - Mixtures Cl and NO3 at [NO3]/[Cl] from 0.005 to 100
  - More than 30 solution compositions tested
    - Some pHs adjusted with HCl
- Short-term electrochemical tests
  - Cyclic potentiodynamic polarization (ASTM G 61)
  - Tsujikawa-Hisamatsu Electrochemical (THE)
  - Constant potential tests

Cyclic Polarization: Na and K Brines at 110°C

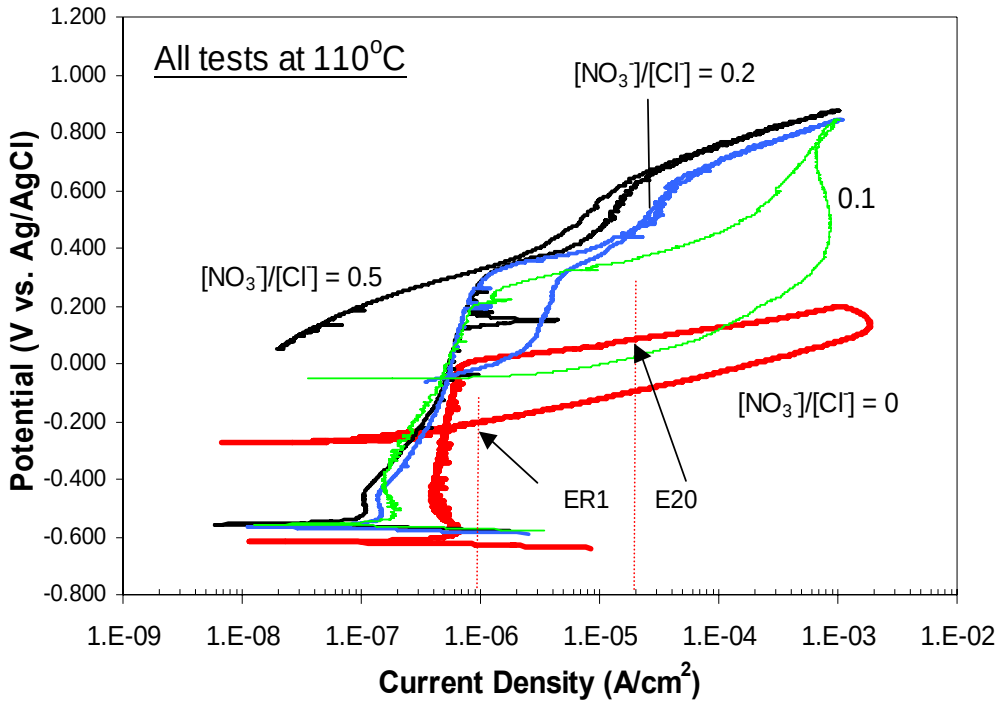
[NO3]/[Cl]= 0

[NO3]/[Cl]= 0.1

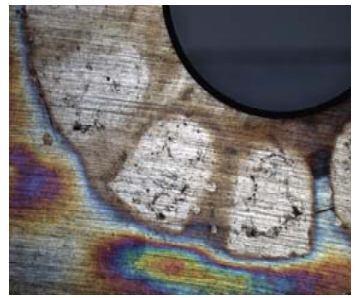
[NO3]/[Cl]= 0.2



Increase in [NO3]/[Cl] ratio resulted in shrinking of the hysteresis loop and drove the crevice corrosion attack deeper under the crevice former



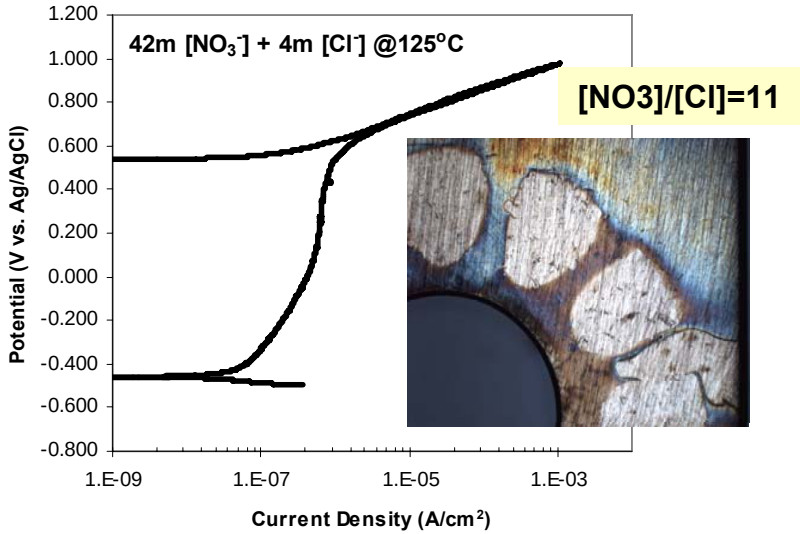
[NO3]/[Cl]= 0.3

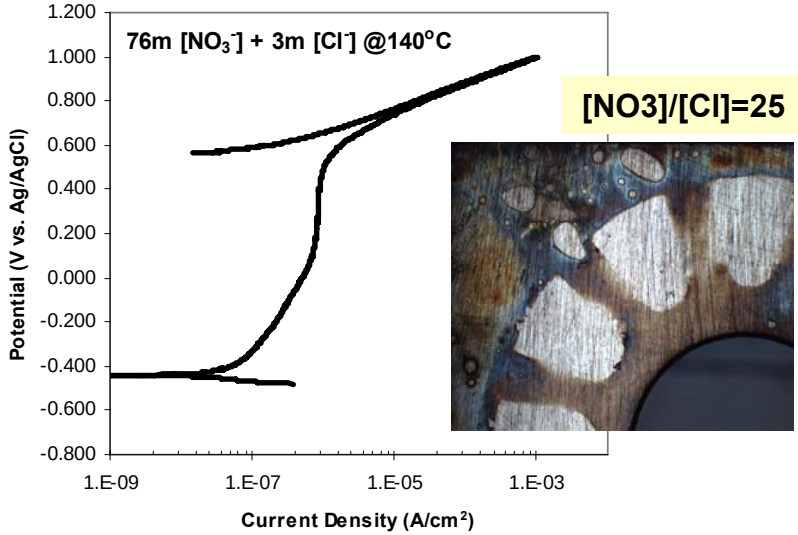


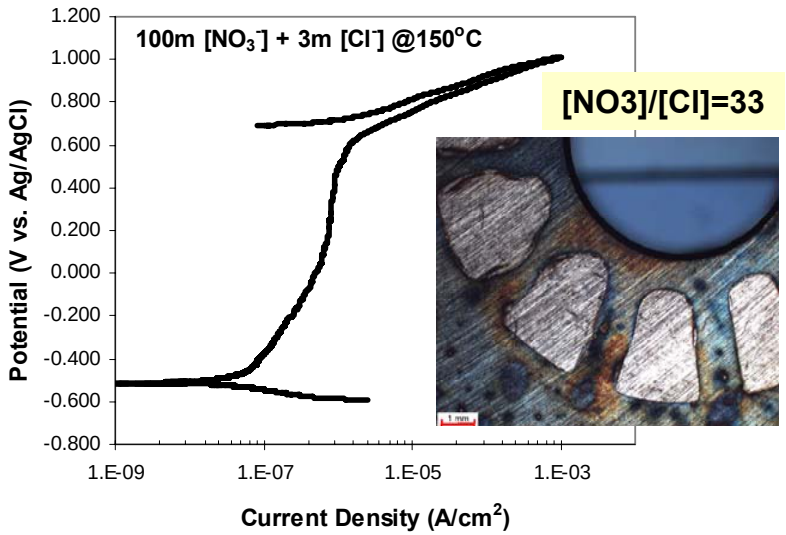
[NO3]/[Cl]= 0.5

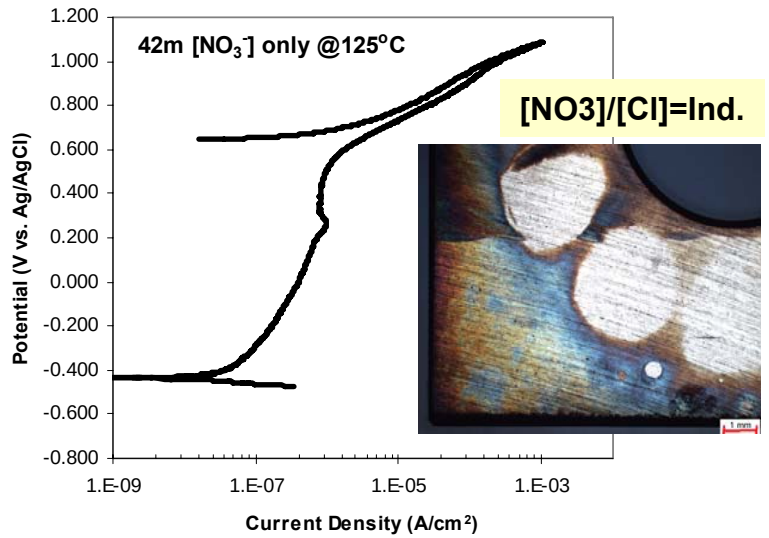
[NO3]/[Cl]= 1

High Nitrate Na and K Brines, 125°C to 150°C



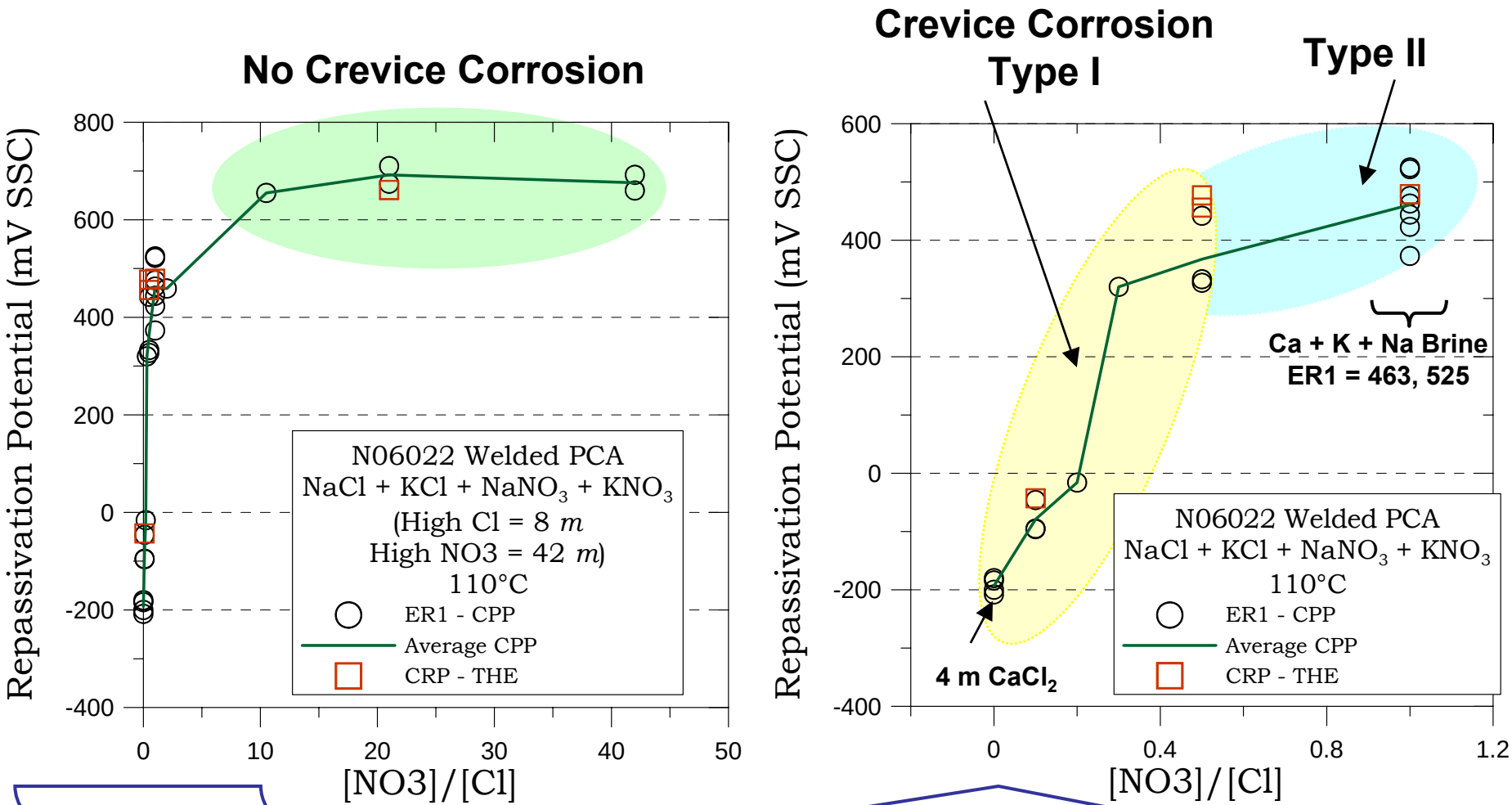




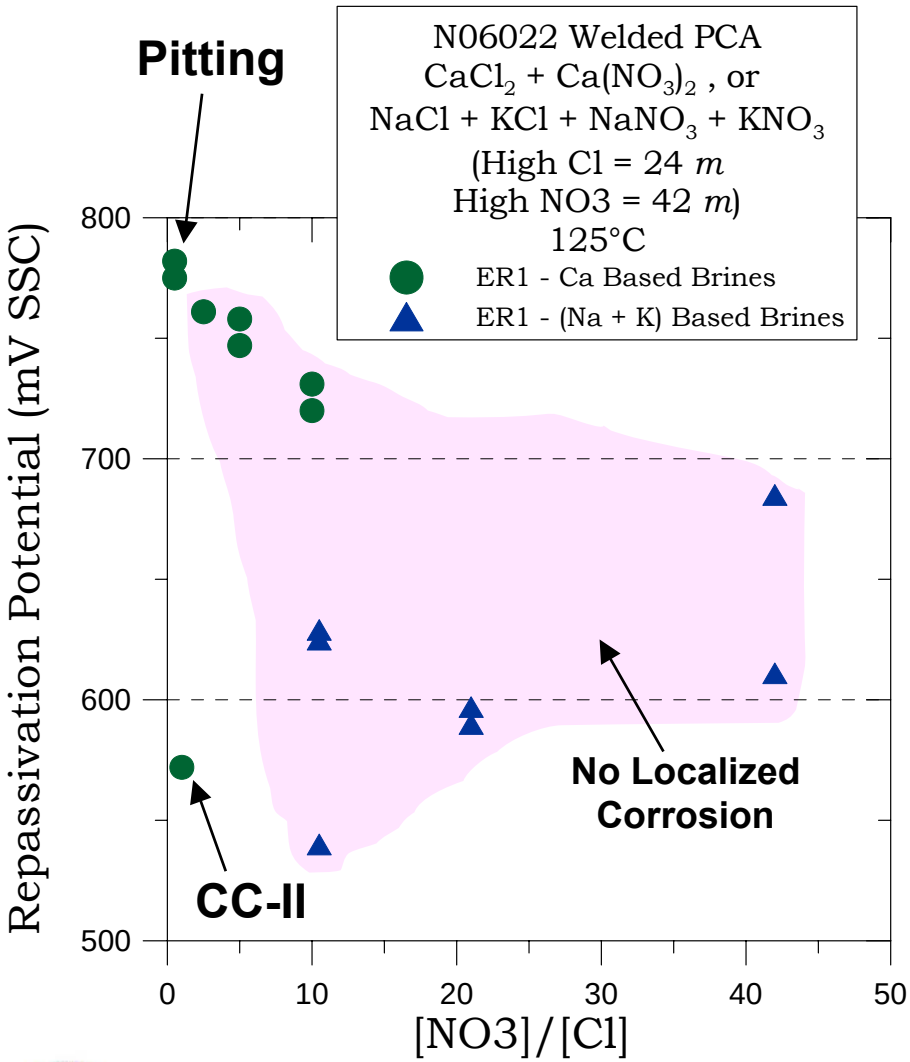


No Localized Corrosion in Any High NO3 Brine

Repassivation Potential, Na and K Brines, 110°C

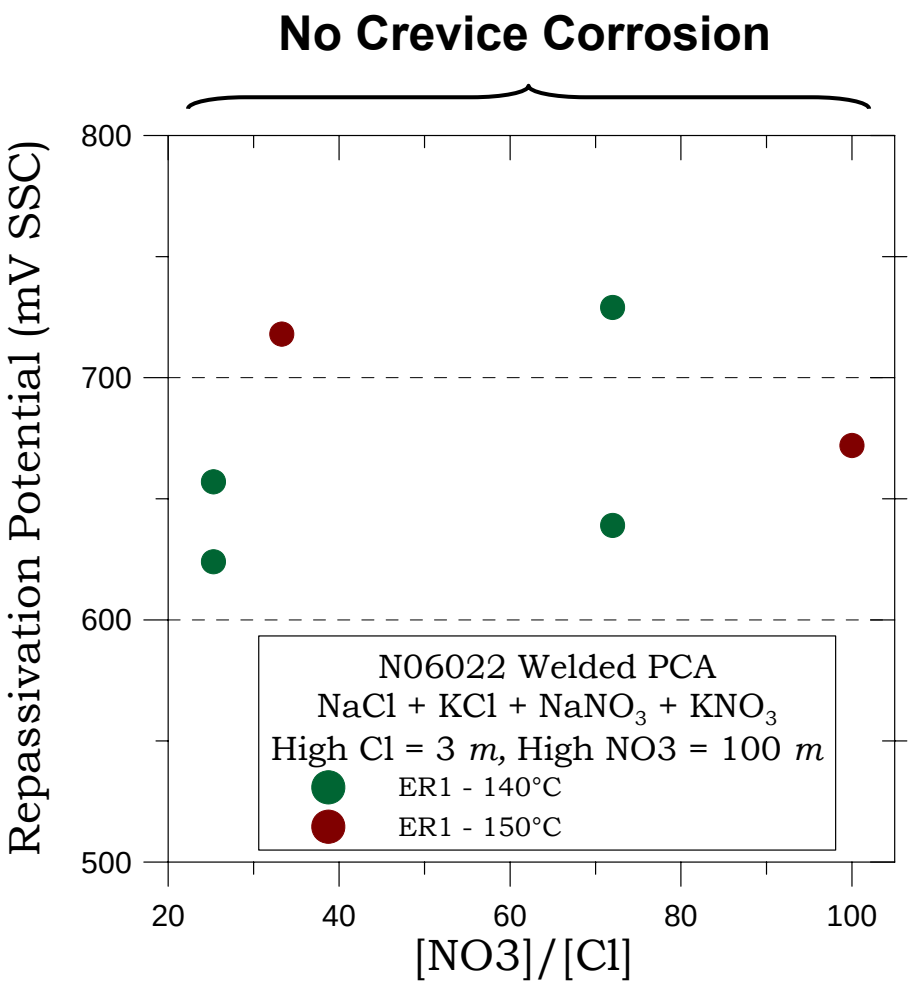


Repassivation Potential, Ca and Na + K Brines, 125°C



- **Localized corrosion occurred only at [NO3]/[Cl] ratio of 0.5 (pitting corrosion) and at ratio of 1 (CC-II)**
- **For all other ratios higher than 1, no localized corrosion**
  - **Type I crevice corrosion is shiny and of crystallographic appearance**
  - **Type II crevice corrosion is dull and happens at high anodic potentials (~>300 mV)**

Repassivation Potential, Na + K Brines 140°C and 150°C



- **140°C**
  - **3 m KCl + 38 m KNO_3 + 38 m $NaNO_3$**
  - **1 m KCl + 36 m KNO_3 + 36 m $NaNO_3$**
- **150°C**
  - **1.5 m KCl + 1.5 m NaCl + 50 m KNO_3 + 50 m $NaNO_3$**
  - **0.5 m KCl + 0.5 m NaCl + 50 m KNO_3 + 50 m $NaNO_3$**
- **No localized corrosion in any of the tested conditions**

Conclusions for Localized Corrosion Tests in Na and K Brines

- Repassivation potential results shown were determined in fully immersed specimens in the bulk electrolyte
- Forced corrosion using a potentiostat (unlimited cathodic reaction)
- At atmospheric pressure, crevice corrosion was not observed for [NO3]/[Cl] ratios higher than 1
- Most detrimental range of temperature for Alloy 22 regarding localized corrosion would be below 120°C where lower [NO3]/[Cl] ratios could be naturally reached

Final Remarks

- Inhibiting effect of NO_3 is active at high temperatures
- Results shown are for fully immersed specimens in the electrolyte
  - The amount of brine on the container will be small
- Crevice corrosion is inhibited at $[NO_3]/[Cl]$ ratios in the order of 0.5 to 2 and higher
- Dust deliquescence brines will be highly concentrated (or the activity of water in the brine will be low)
  - The amount of metal that such brine can dissolve is minimal
- Current results continue to support the localized corrosion model for degradation of the waste package

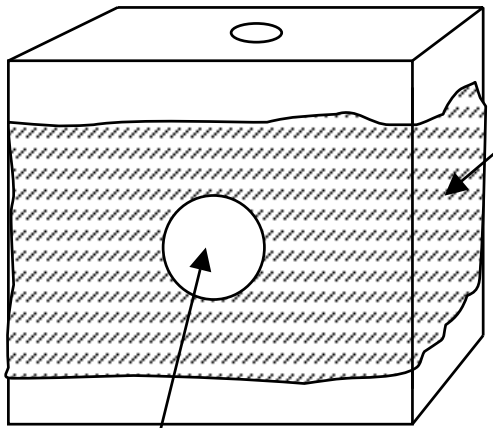
Acknowledgments

- **This work was performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract N° W-7405-Eng-48. This work is supported by the Yucca Mountain Project, which is part of the Office of Civilian Radioactive Waste Management OCRWM-DOE**

Backup Slides

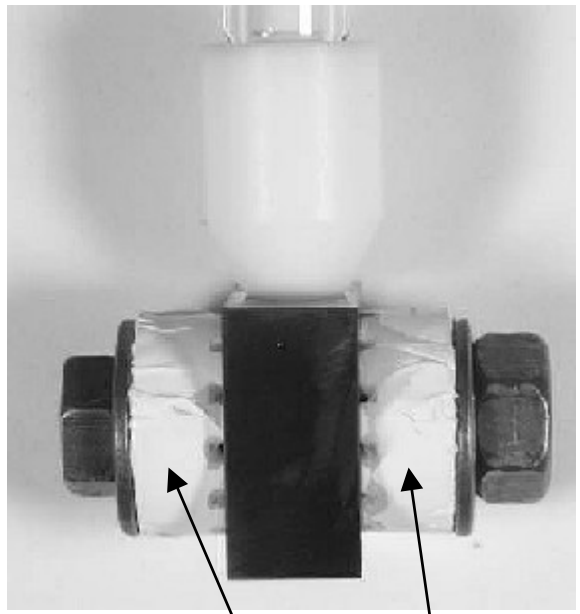
Alloy 22 Specimens Used Prism Creviced Assembly (PCA)

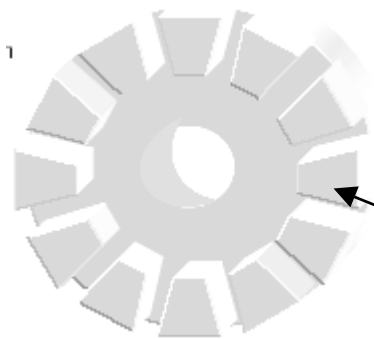
WELDED PCA SPECIMEN



GTAW Seam

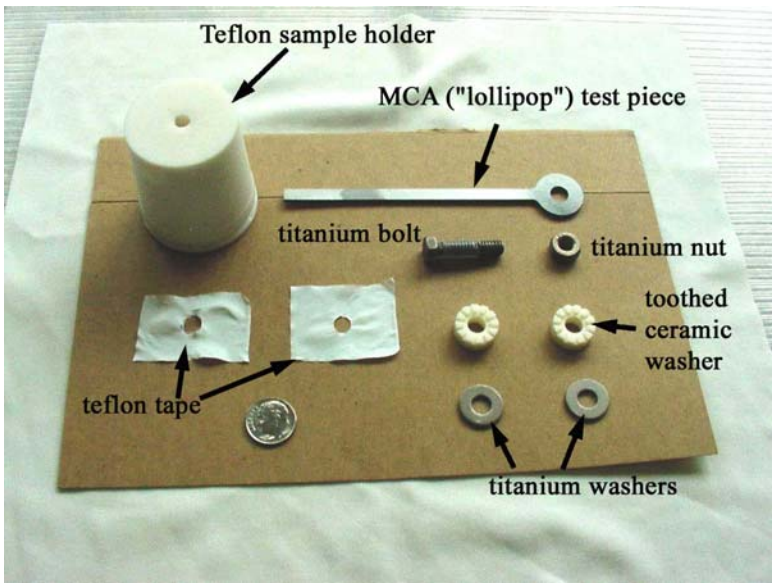
Hole for Crevice Formers

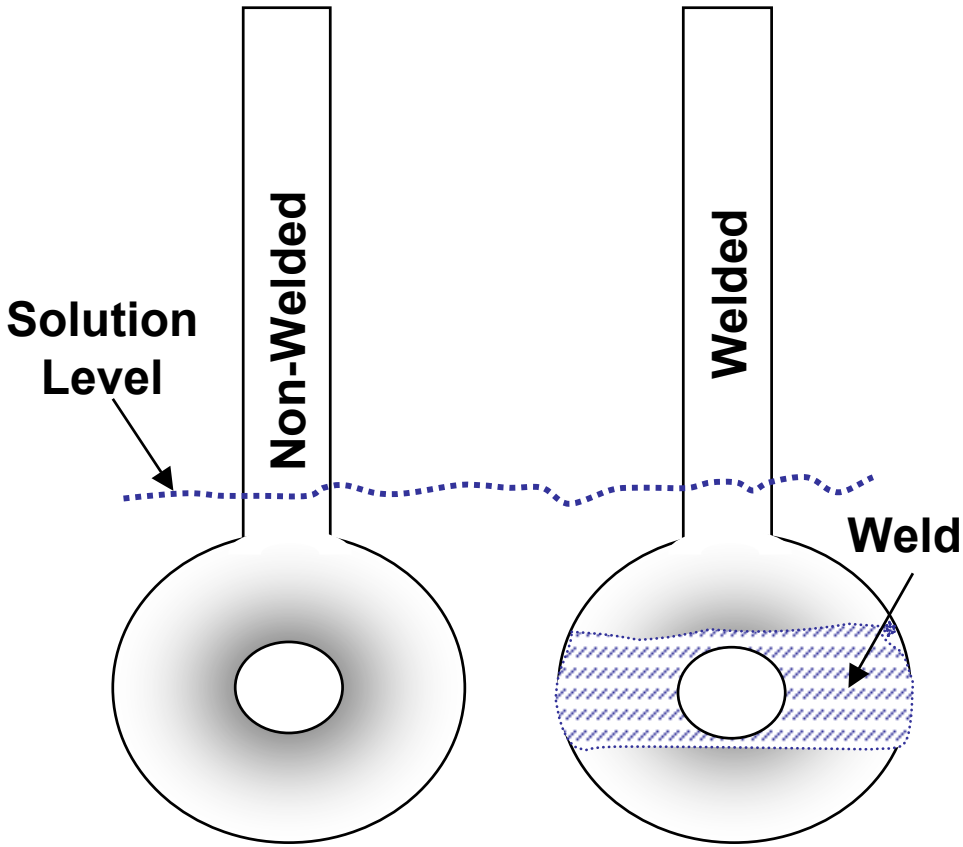




Two Crevice Formers With 12 Teeth Each ASTM G 48

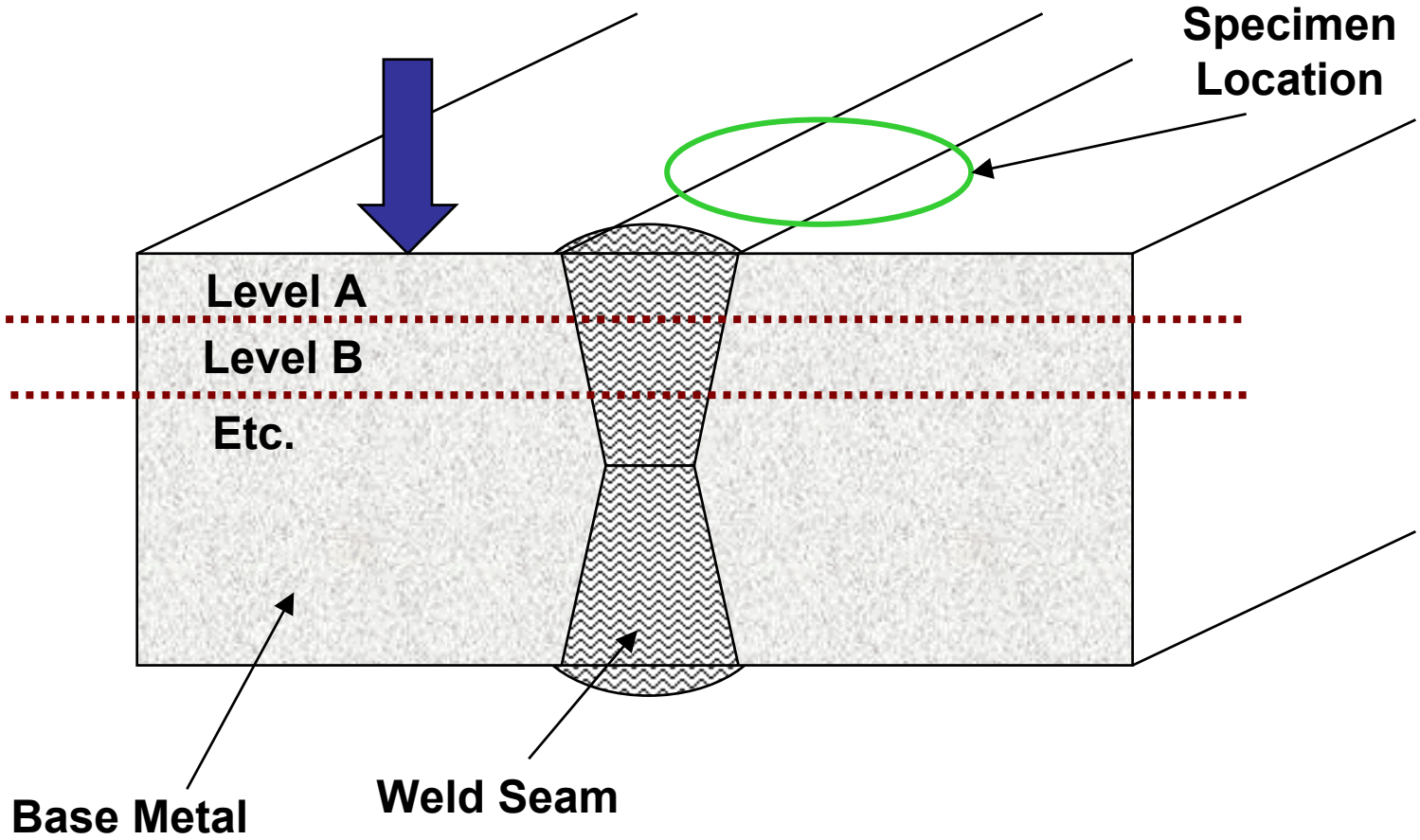
Alloy 22 Specimens Used



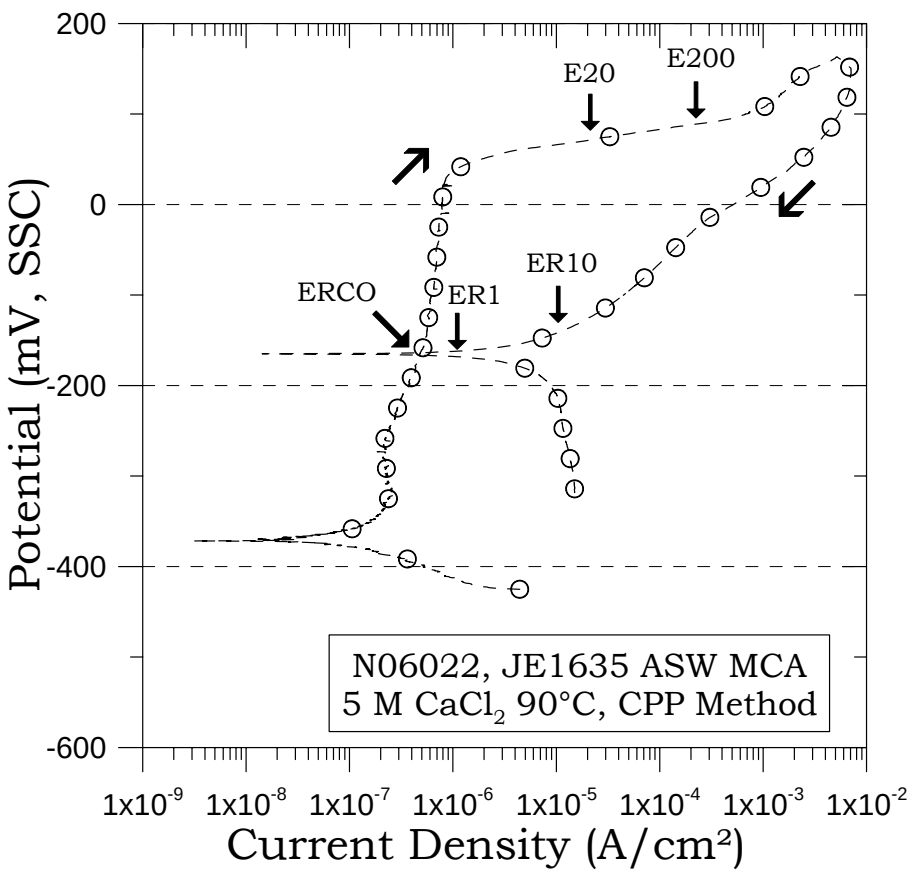


MCA or Lollipop Specimens

Corrosion Test Specimens Prepared from Plates



Explanation of Parameters



- E20 and E200 are parameters for breakdown potential
- ER10, ER1 and ERCO are forms of repassivation potential
- For Alloy 22, E_{crit} is taken as a Rep. Pot., usually ERCO
- E_{corr} is the steady-state corrosion potential in naturally aerated brines
- If $E_{corr} \geq E_{crit}$, crevice corrosion is possible