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

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Workshop on Localized Corrosion of Alloy 22 in Yucca Mountain Environments

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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

Boiling Points of Solutions Based on Na and K
Maximum Temperatures at Ambient Pressure

Molality of Nitrates
Temperature (°C)

[½ KNO₃, ½ NaNO₃]
[½ KCl, ½ NaCl]

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 $\frac{[NO_3]}{[Cl]}$ 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 NaNO₃ + 15.1 m KNO₃, [NO₃]/[Cl] = 7.4
- Crevice corrosion initiation was not anticipated, but occurred

**Autoclave 2**
- 220°C
- 2.5 m NaCl + 3.4 m NaNO₃ + 15.1 m KNO₃, [NO₃]/[Cl] = 7.4
- Crevice corrosion initiation was not anticipated, but occurred

**Autoclave 3**
- 220°C
- 6.4 m NaCl + 3.2 m KNO₃, [NO₃]/[Cl] = 0.5
- Crevice corrosion initiation may be expected, and occurred
Brine Compositions at High Temperature

Boiling Points of Solutions Based on Na and K
Maximum Temperatures at Ambient Pressure

Temperature (°C) vs. Molality of Nitrates

- 0 m Cl
- 1 m Cl
- 2 m Cl
- 3 m Cl
- 4 m Cl
- 5 m Cl
- 6 m Cl
- 8 m Cl
- 9 m Cl

[½ KNO₃, ½ NaNO₃]
[½ KCl, ½ NaCl]

Auto clave Tests

Temperature (°C)

0 0.125<NO₃/Cl<2
5<NO₃/Cl<50
25<NO₃/Cl<100
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), \([\text{NO}_3]/[\text{Cl}] = 7.4\)
  - Autoclave 2 (220°C), \([\text{NO}_3]/[\text{Cl}] = 7.4\)
    - 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), \([\text{NO}_3]/[\text{Cl}] = 0.5\)
    - Similar amount of crevice corrosion for Autoclave 2 and 3 (same temperature, different electrolyte)
Creviced Specimens - Autoclave 1

[NO$_3$]/[Cl] = 7.4
160°C

Vapor

Liquid

C121

C144

C105

X4000 Mag.
Creviced Specimens - Autoclave 2

[NO3]/[Cl] = 7.4
220°C

Vapor

Liquid
Creviced Specimens - Autoclave 3

[NO3]/[Cl] = 0.5
220°C

Vapor

Liquid

Deposits

Liquid C107

X80 Mag.

C120

C137
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 + NaNO₃ + KNO₃ 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

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

No Crevice Corrosion

Crevice Corrosion
Type I

Type II

Ca + K + Na Brine
ER1 = 463, 525

4 m CaCl₂

N06022 Welded PCA
NaCl + KCl + NaNO₃ + KNO₃
(High Cl = 8 m
High NO₃ = 42 m)
110°C

ER1 - CPP
Average CPP
CRP - THE
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 KNO₃ + 38 m NaNO₃
  - 1 m KCl + 36 m KNO₃ + 36 m NaNO₃

- **150°C**
  - 1.5 m KCl + 1.5 m NaCl + 50 m KNO₃ + 50 m NaNO₃
  - 0.5 m KCl + 0.5 m NaCl + 50 m KNO₃ + 50 m NaNO₃

- 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 NO3 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 [NO3]/[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
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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

Solution Level

Non-Welded

Welded

Weld

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} ≥ E_{crit}, crevice corrosion is possible.

**Diagram:**
- Potential (mV, SSC) vs. Current Density (A/cm²)
- Parameters: E20, E200, ER10, ER1, ERCO
- Conditions: N06022, JE1635 ASW MCA 5 M CaCl₂ 90°C, CPP Method

**Notes:**
- E_{corr} is the steady-state corrosion potential in naturally aerated brines.