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EVOLUTION OF CHEMISTRY AND ITS EFFECTS ON THE CORROSION OF ENGINEERED BARRIER MATERIALS

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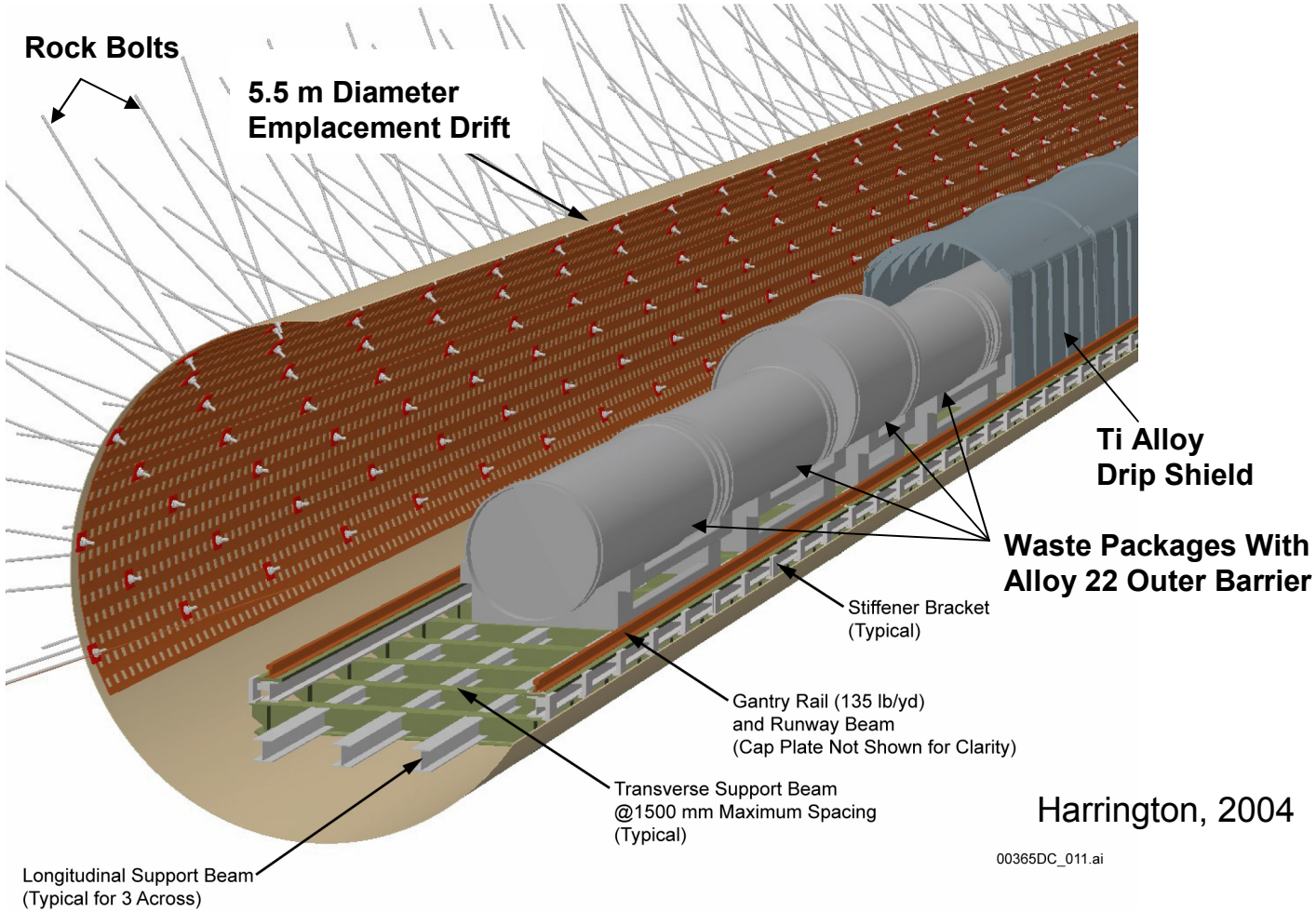
Outline

- Background
- Objectives
- Approach
- Water Chemistry
- Thermodynamic Simulations
- Laboratory Testing
- Conclusions

Background

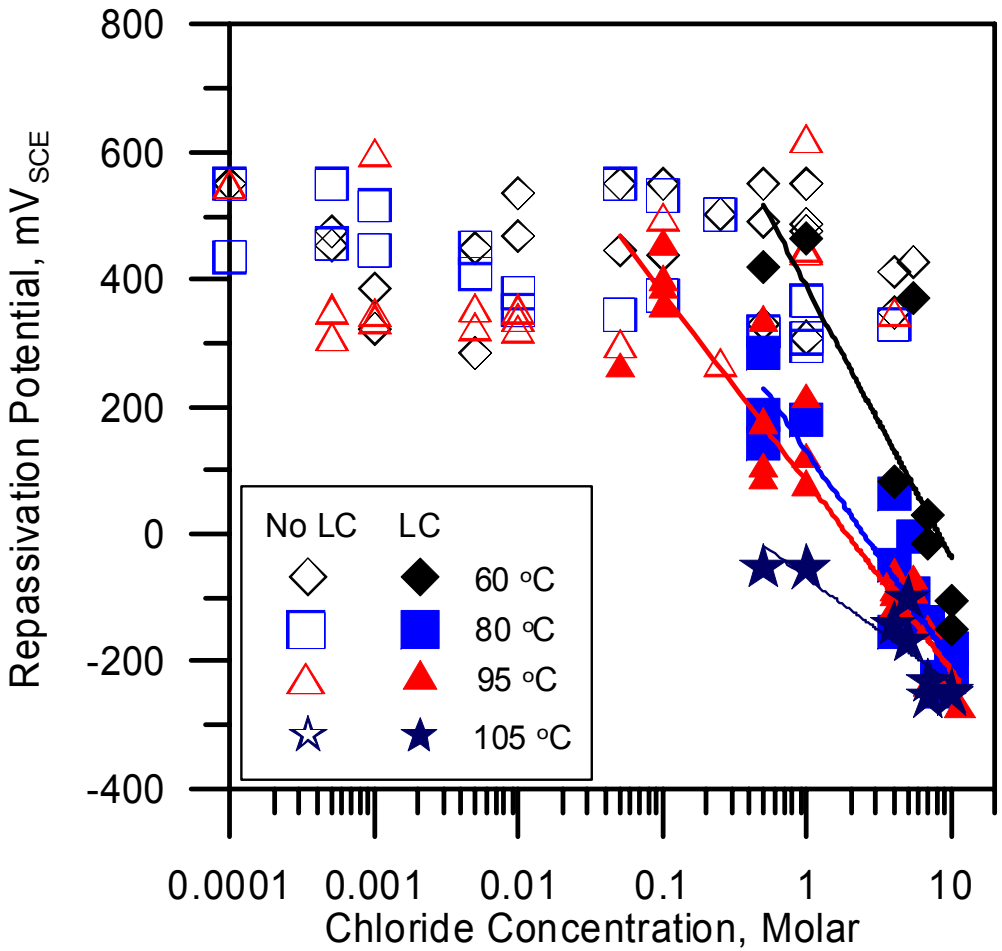
- U.S. Nuclear Regulatory Commission (NRC) preparing to review a potential license application for a high-level nuclear waste repository at Yucca Mountain, Nevada
- Center for Nuclear Waste Regulatory Analyses (CNWRA) tasked with providing technical assistance to the NRC.
- CNWRA is conducting technical investigations including assessment of waste package performance

Background
Drift Emplacement



Harrington, 2004

Background
Localized Corrosion

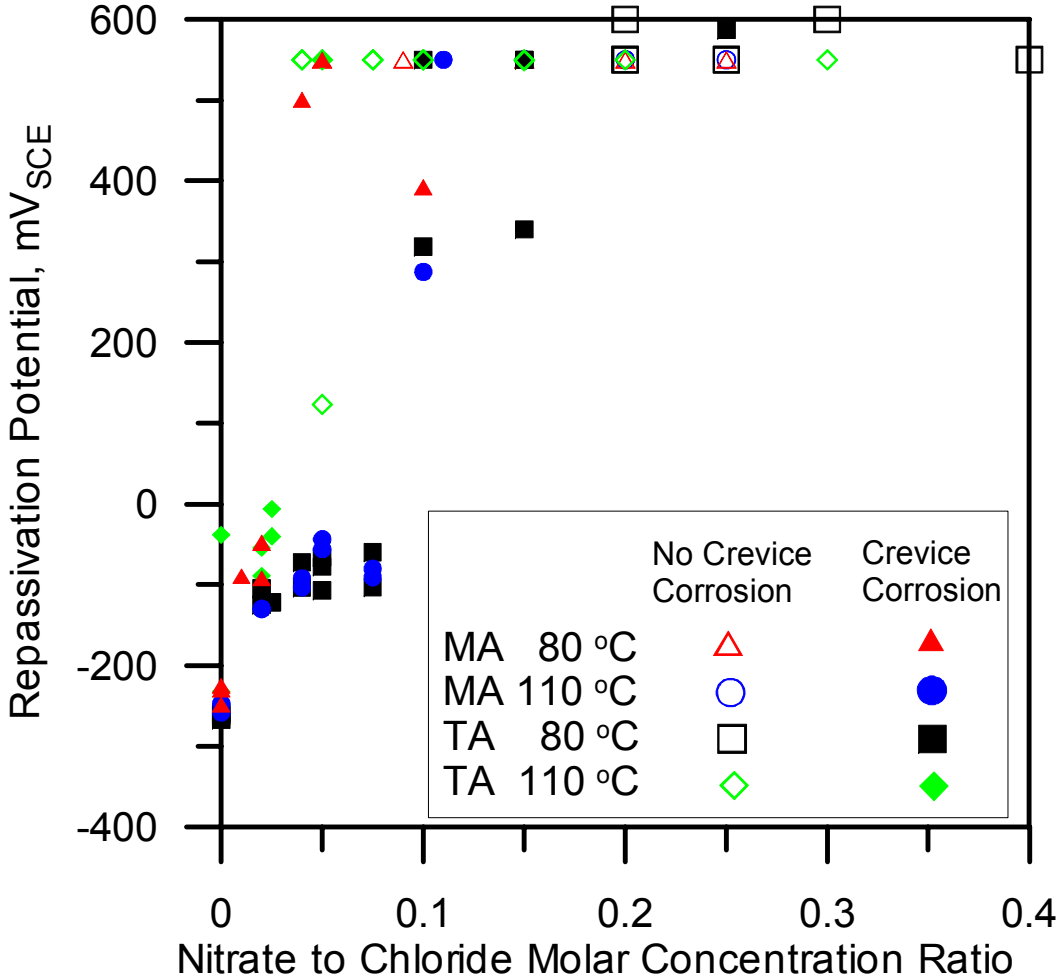


Localized corrosion susceptibility of Alloy 22 increases with temperature, chloride concentration, and anodic potentials

Dunn, et al. (2005)

$^{o}F = (^{o}C \times 9/5) + 32$

Background
Effect of Inhibitors

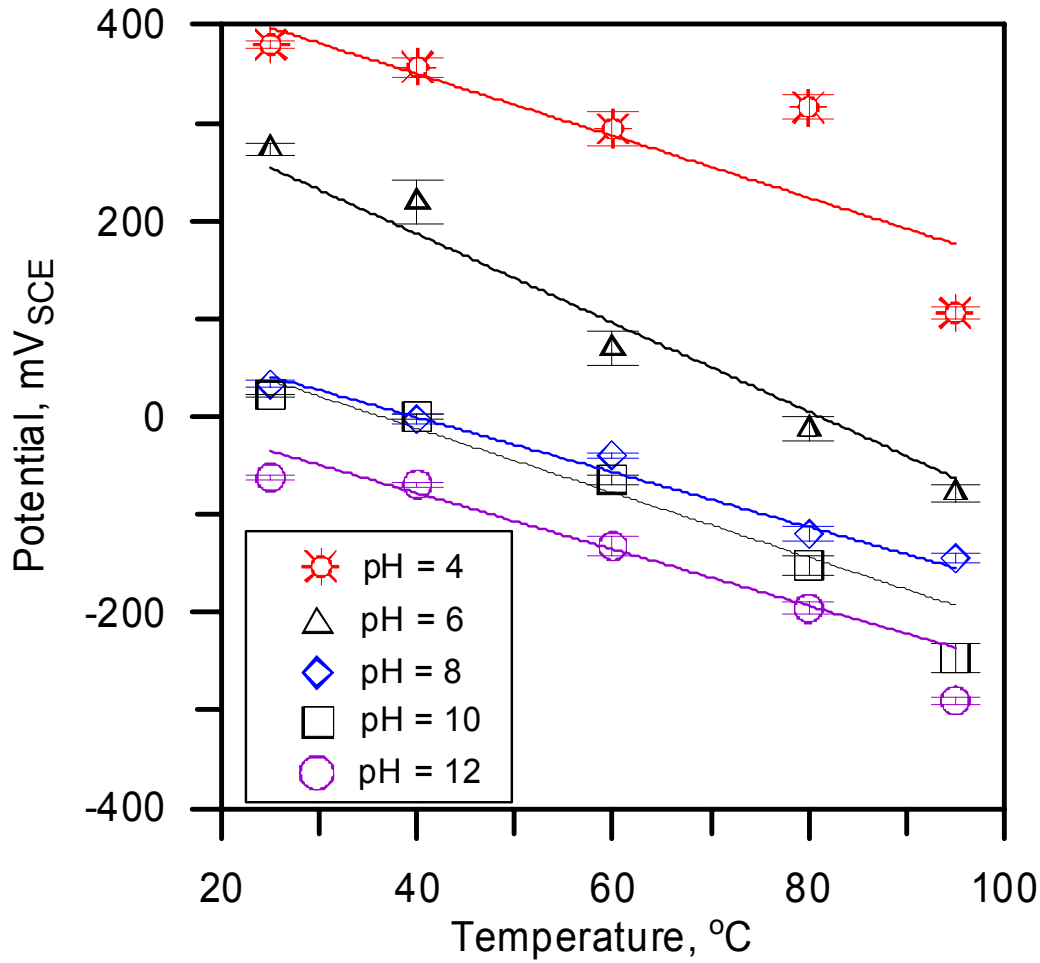


- Localized corrosion of Alloy 22 inhibited at nitrate to chloride molar concentration ratios > 0.1
- Sulfate, carbonate, and bicarbonate also act as inhibitors

He, et al. (2006)

$^{o}F = (^{o}C \times 9/5) + 32$

Background
Corrosion Potential



- Corrosion potentials for Alloy 22
- Anodic potentials necessary for the initiation of localized corrosion of Alloy 22 only observed in acidic solutions

$^{o}F = (^{o}C \times 9/5) + 32$

Objectives

- Evaluate the evolution of environmental conditions on the engineered barrier surfaces
- Determine the effects of environmental conditions on the performance of the waste package outer container material

Approach

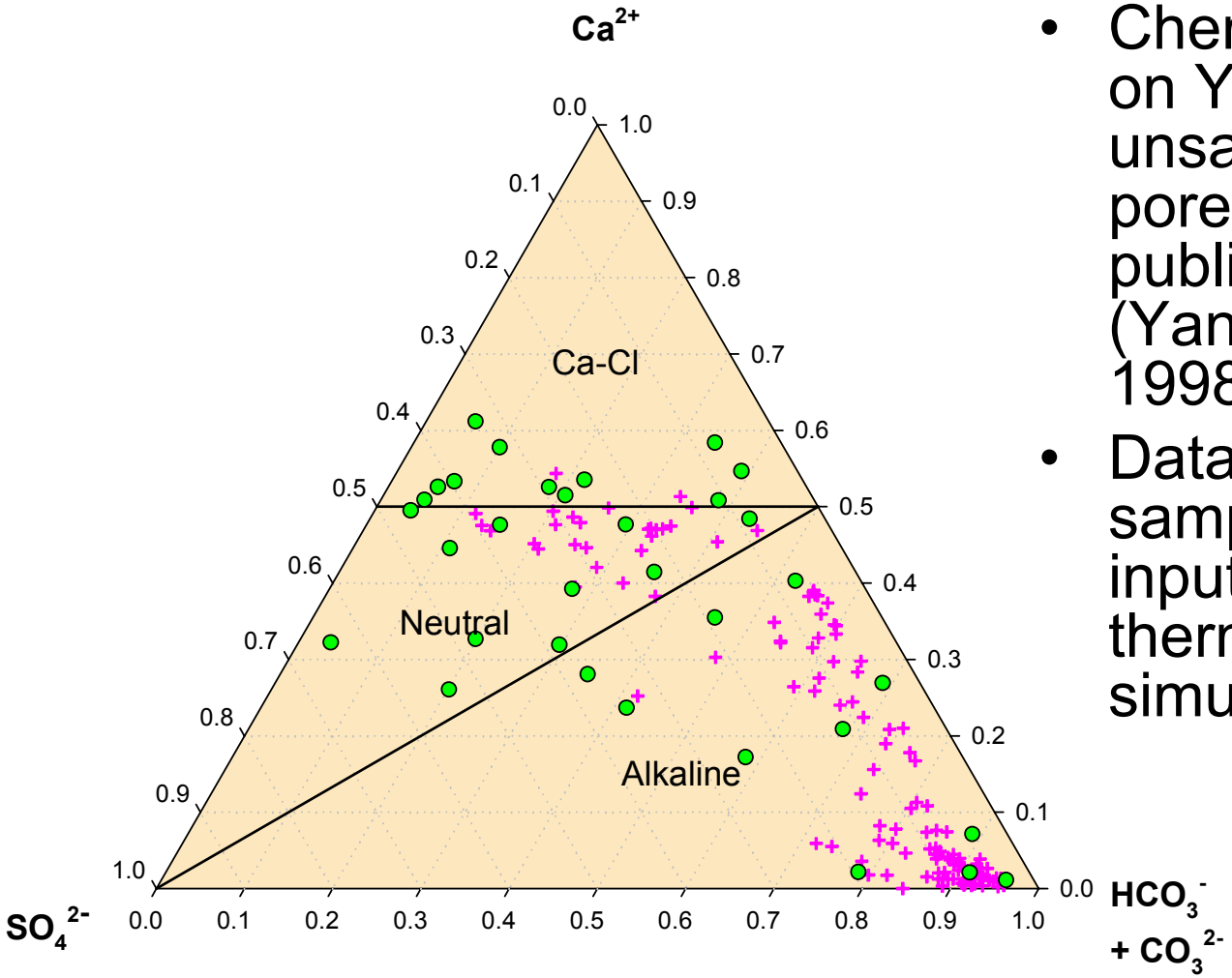
Modeling

- Thermodynamic simulations of evaporation, supplemented by chemical divide analyses, conducted to determine evolution of water chemistry
- Compositions of Yucca Mountain unsaturated zone pore waters belonging to three water types (calcium-chloride, neutral, and alkaline) used as inputs to thermodynamic simulations

Testing

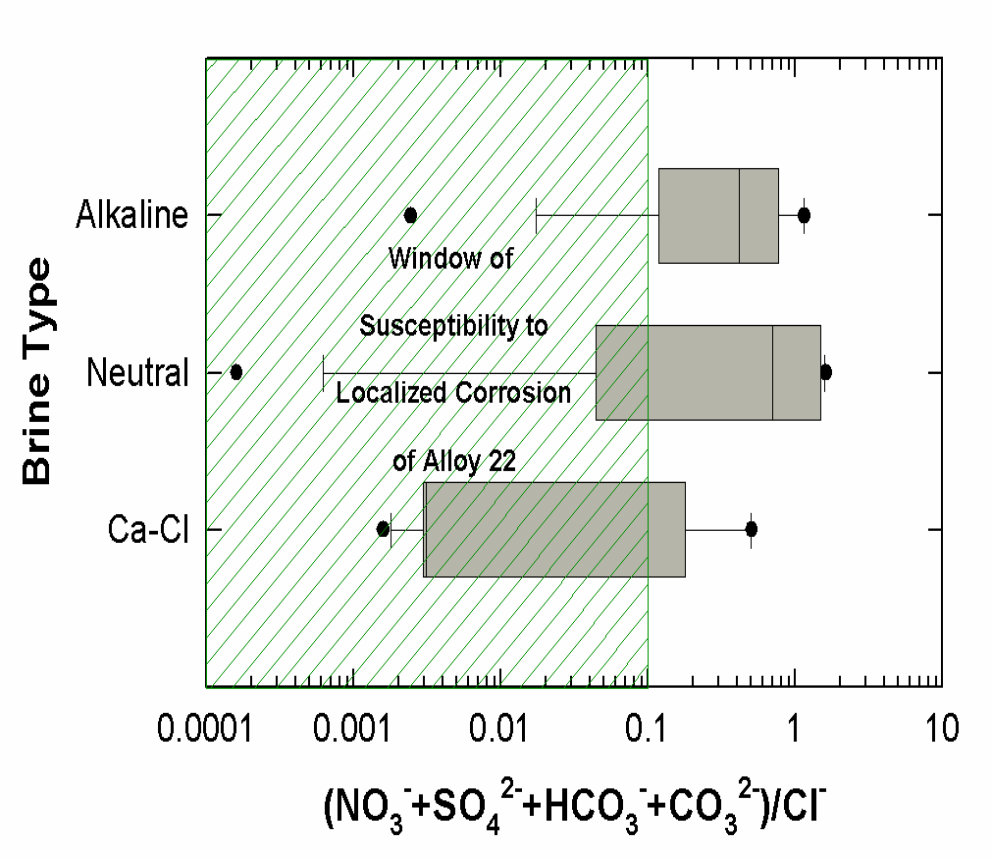
- Heater tests conducted by the CNWRA with initially dilute calcium-chloride, neutral, and alkaline waters synthesized from reagent grade chemicals
- Deposits analyzed to determine composition and evaluate the effects on waste package container materials
- Results compared to previous tests where effects of water chemistry were systematically explored

Water Chemistry



- Chemistry data (+) on Yucca Mountain unsaturated zone pore waters published by USGS (Yang, et al., 1996, 1998, 2003)
- Data on selected samples (●) used as input to thermodynamic simulations

Thermodynamic Simulations



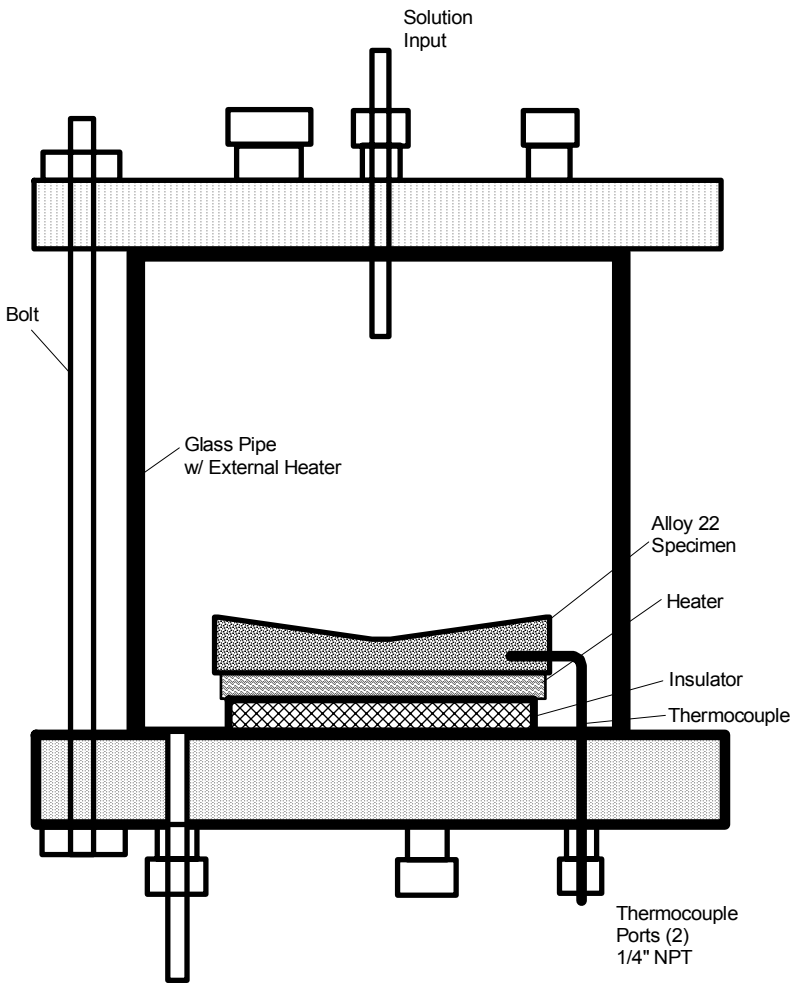
- Water chemistry after evaporation and precipitation
- Brines formed from alkaline and neutral water chemistries not as aggressive as brines from Ca-Cl water chemistries

Laboratory Testing

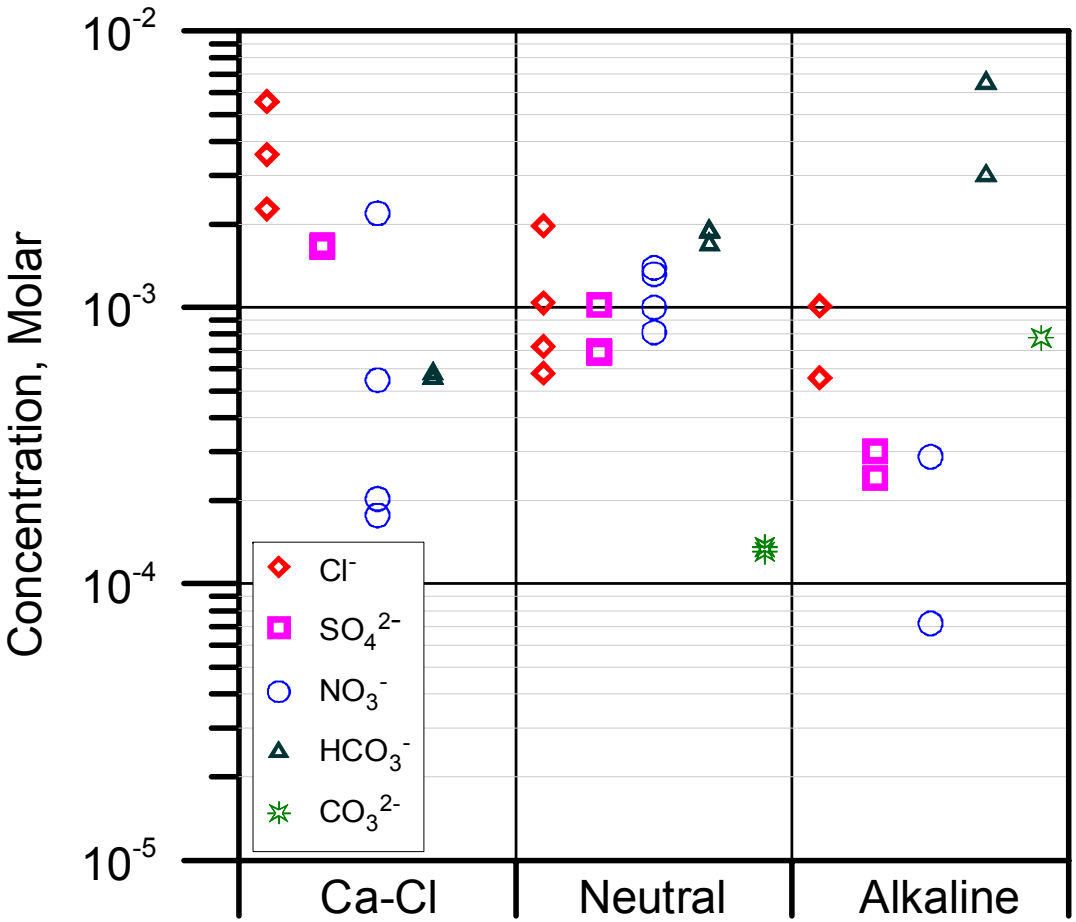
- Alloy 22 maintained at 110 °C [230 °F]
- Drip rate = 200 mL/day [0.05 gal/day] (approximately one drop every 15 seconds)

Alloy 22 Composition

Material	Ni	Cr	Mo	W	Fe	C
Alloy 22 2277-3-3266	57.8	21.40	13.60	3.00	3.80	0.004

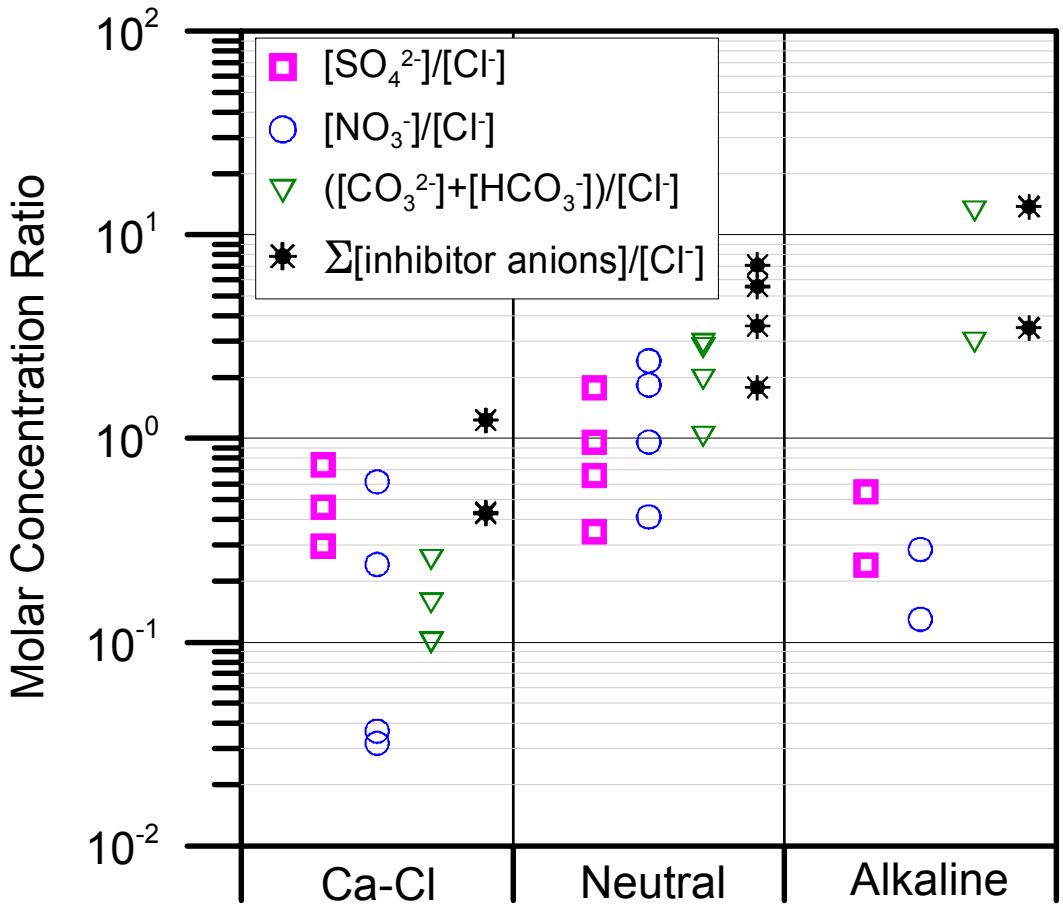


Test Solution Chemistry



- $[Cl^-]$ highest for Ca-Cl waters and lowest for alkaline waters
- All water compositions have nitrate, sulfate, and carbonate

Test Solution Chemistry

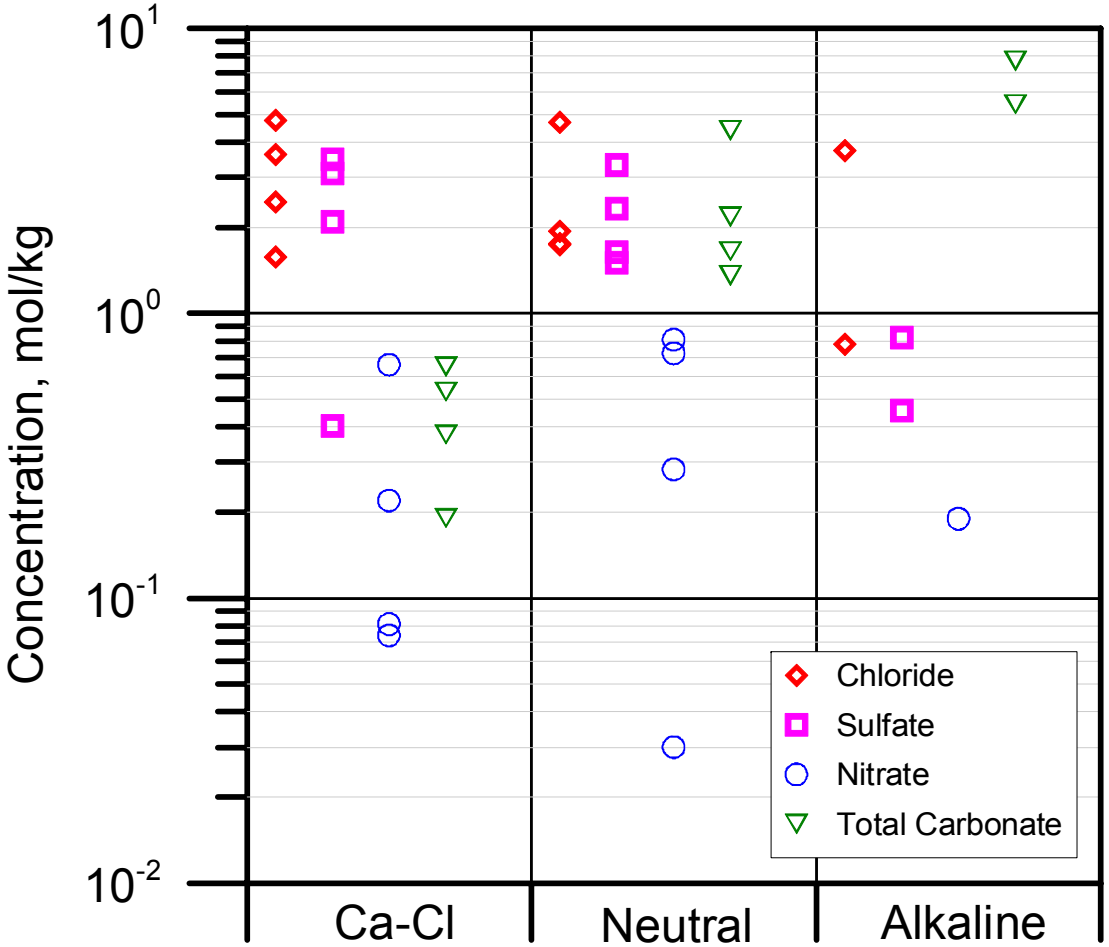


- Critical Σ[inhibitor anion]/$[Cl^-]$ ratio previously determined to be 0.1
- Inhibition possible by sulfate, nitrate, carbonate, and bicarbonate
- Chloride + bicarbonate solutions may promote SCC

Test Results

- All solutions quickly boiled and evaporated, leaving a dry salt deposit.
- No salt deliquescence was observed at elevated temperature (110 ^{o}C [230 ^{o}F]) or after cooling to room temperature.
- No corrosion of the Alloy 22 specimen due to salt deposition was observed.

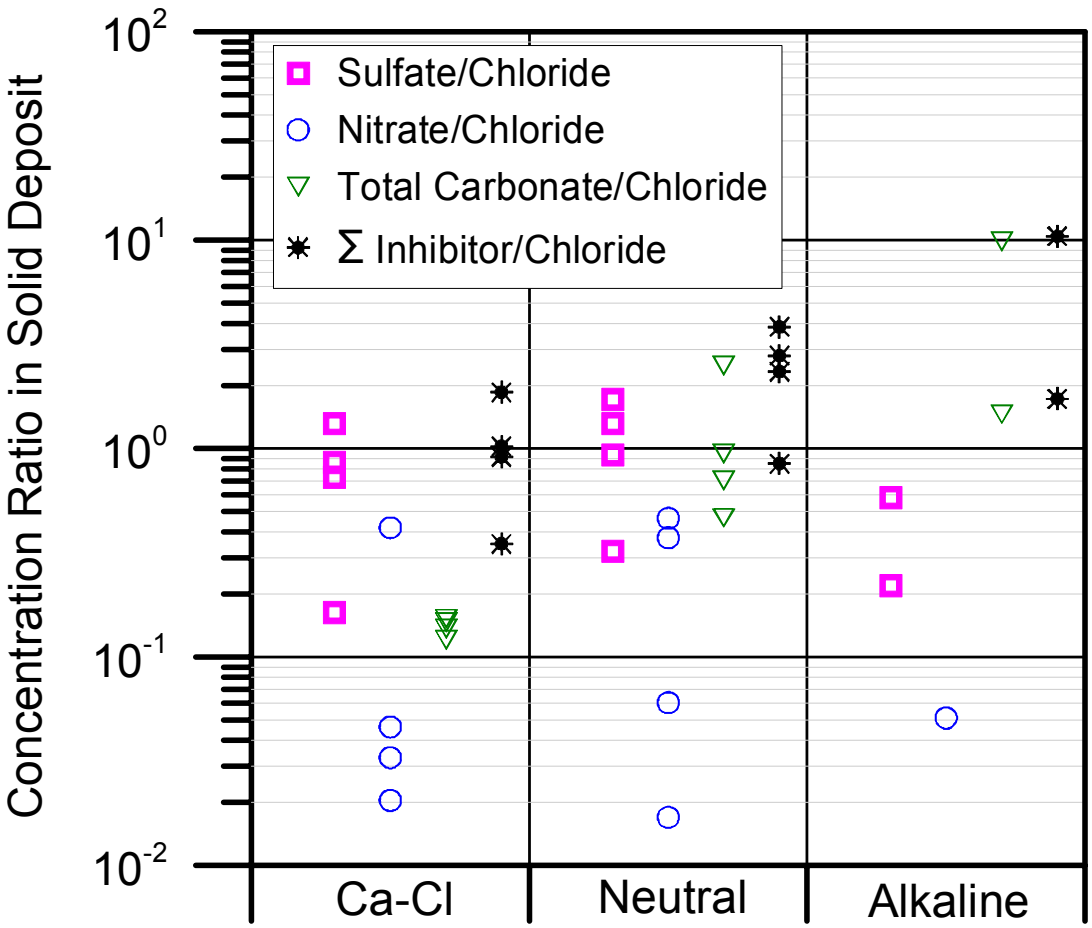
Salt Deposit Chemistry



- All deposits contained chloride, sulfate, nitrate, carbonate, and/or bicarbonate
- Salt deposit chemistry similar to starting water chemistry

mol/lb = (mol/kg)/2.204

Salt Deposit Chemistry



- Lower nitrate to chloride molar concentration ratios compared to initial solution values
- Overall concentration of inhibitors relative to chloride is retained

Conclusions

- Tests conducted using a wide range of solution compositions representative of calcium-chloride, neutral, or alkaline brines
- Formation of brines with boiling points greater than 110 °C [230 °F] was not observed
- Salt deposit composition was dependent on the composition of the initially dilute starting water
- Formation of deliquescent salt deposits or brines that promote either localized corrosion of Alloy 22 are not expected

Acknowledgement

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This presentation is an independent product of CNWRA and does not necessarily reflect the view or regulatory position of NRC.