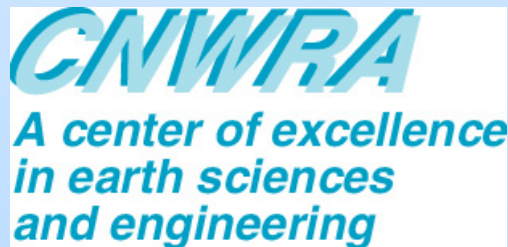


Factors Influencing the Uniform and Localized Corrosion of Alloy 22

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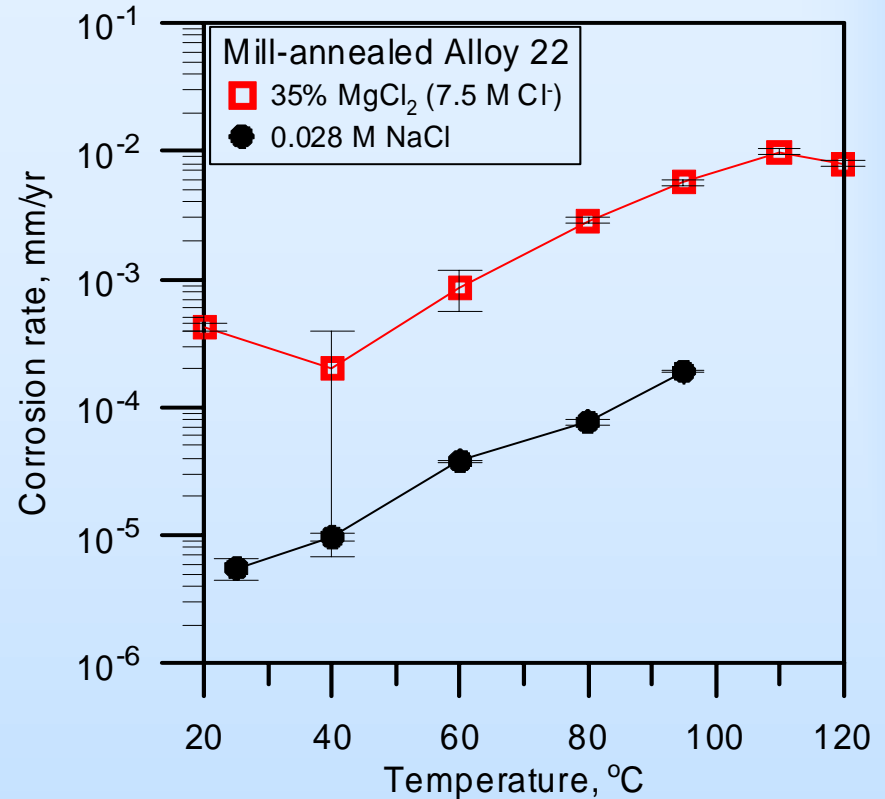
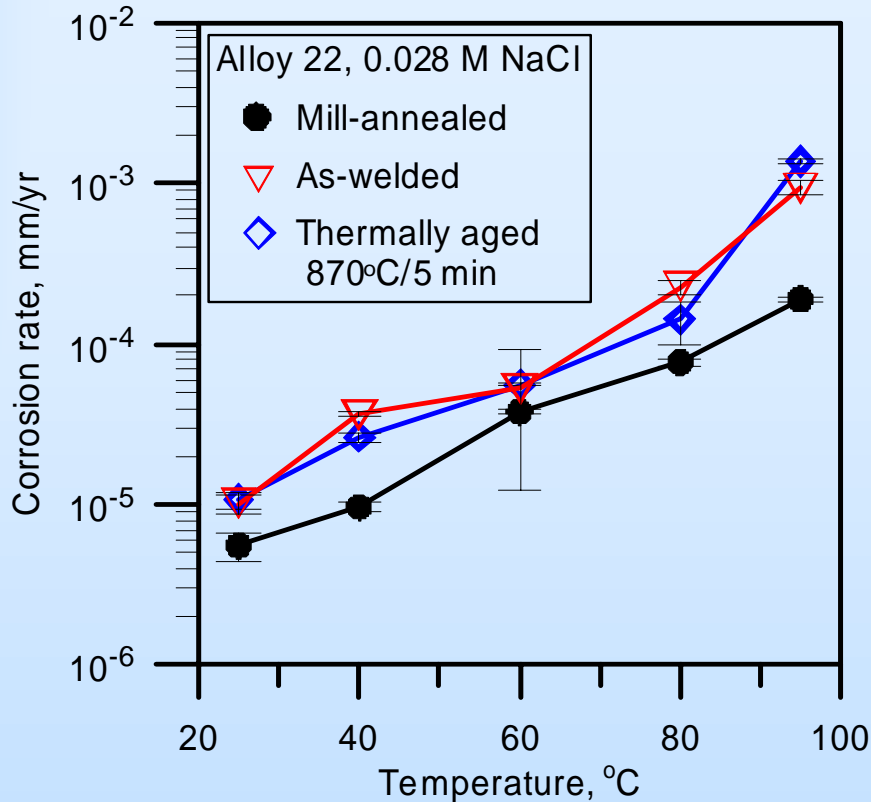
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Corrosion Processes and Evolution of the Environment

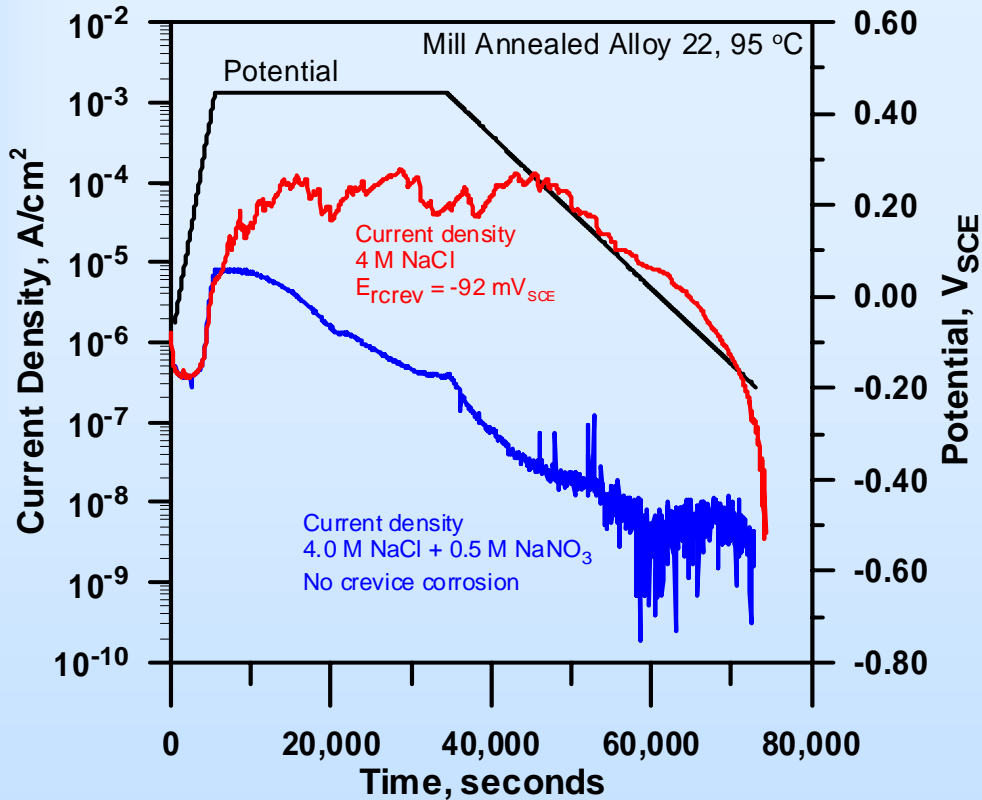
- Passive Dissolution
 - Temperature
 - Metallurgical condition
- Loss of Passivity
 - Temperature
 - Chloride concentration
 - pH
- Localized Corrosion
 - Temperature
 - Aggressive and inhibiting species
 - Metallurgical condition

Uniform Corrosion and Temperature



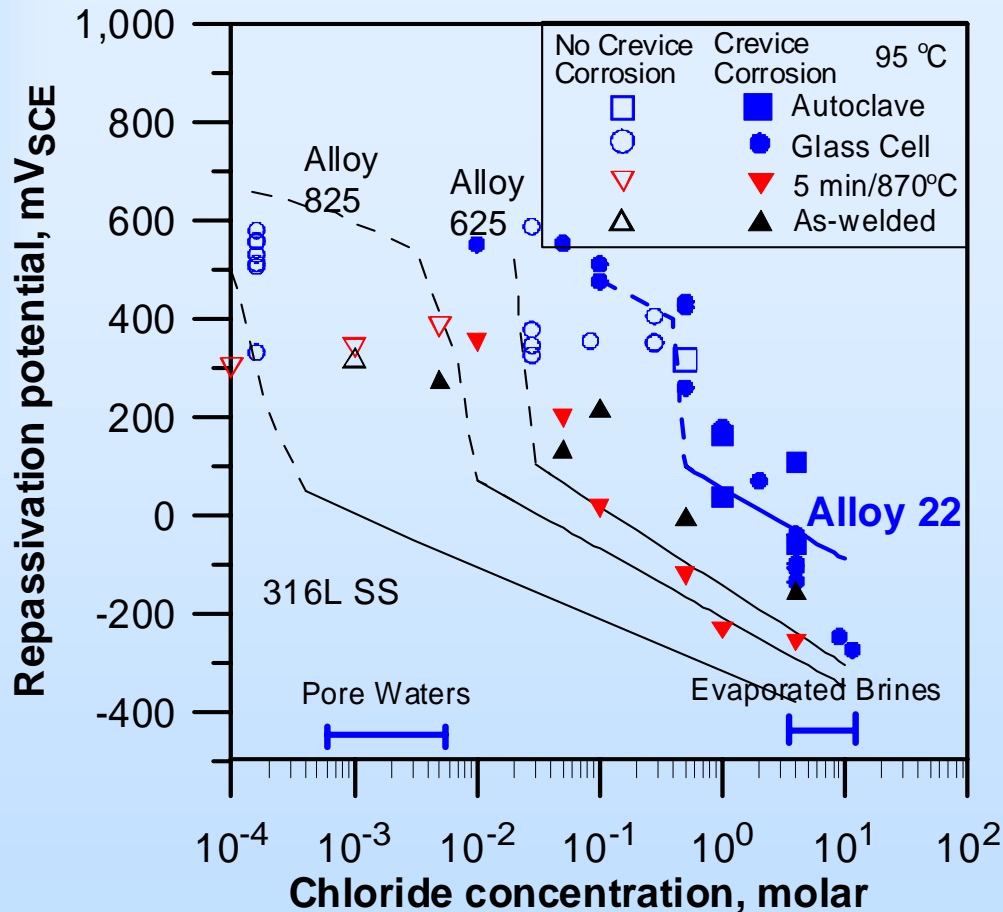
- Passive corrosion rates depend on temperature and metallurgical condition
- Accelerated uniform corrosion limited to acidic concentrated chloride solutions that are not expected within the emplacement drifts

Localized Corrosion Tests



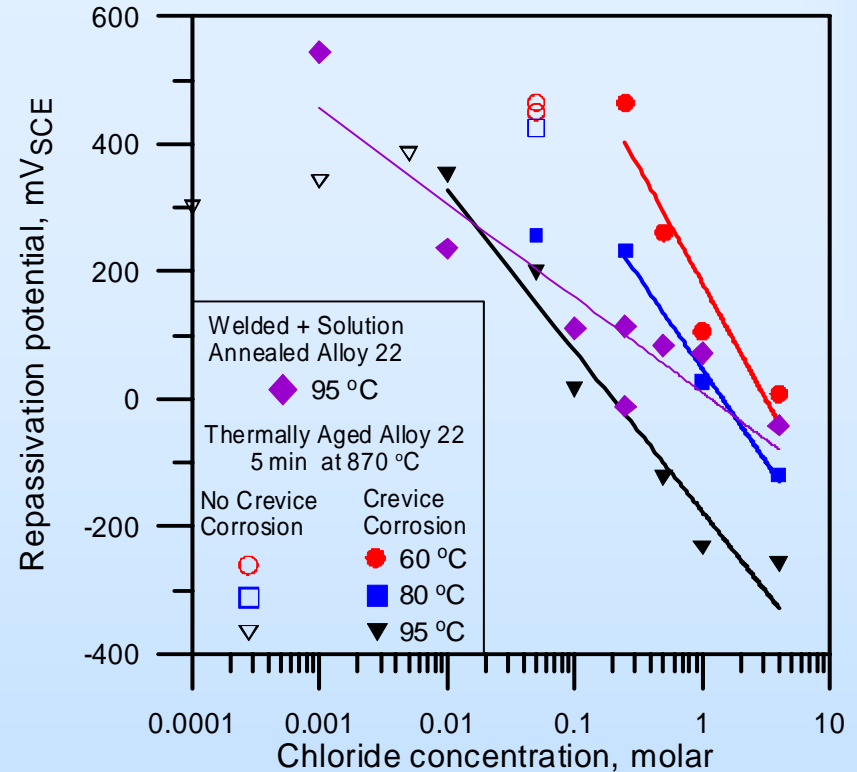
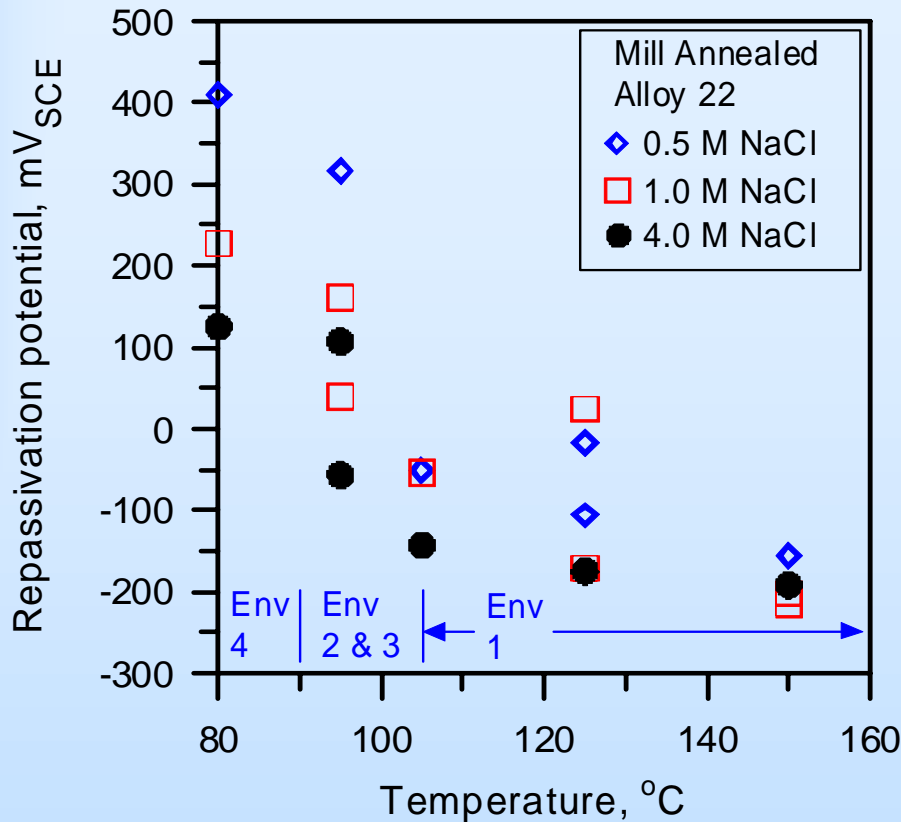
- Electrochemical tests used to measure repassivation potential for assessing crevice corrosion
- Evaluate inhibiting effects of nitrate, bicarbonate, carbonate, and sulfate
- Evaluate effects of fabrication processes such as welding, postweld heat treatments, and thermal exposures
- Long-term potentiostatic and open circuit tests used to validate repassivation potential

Localized Corrosion Susceptibility



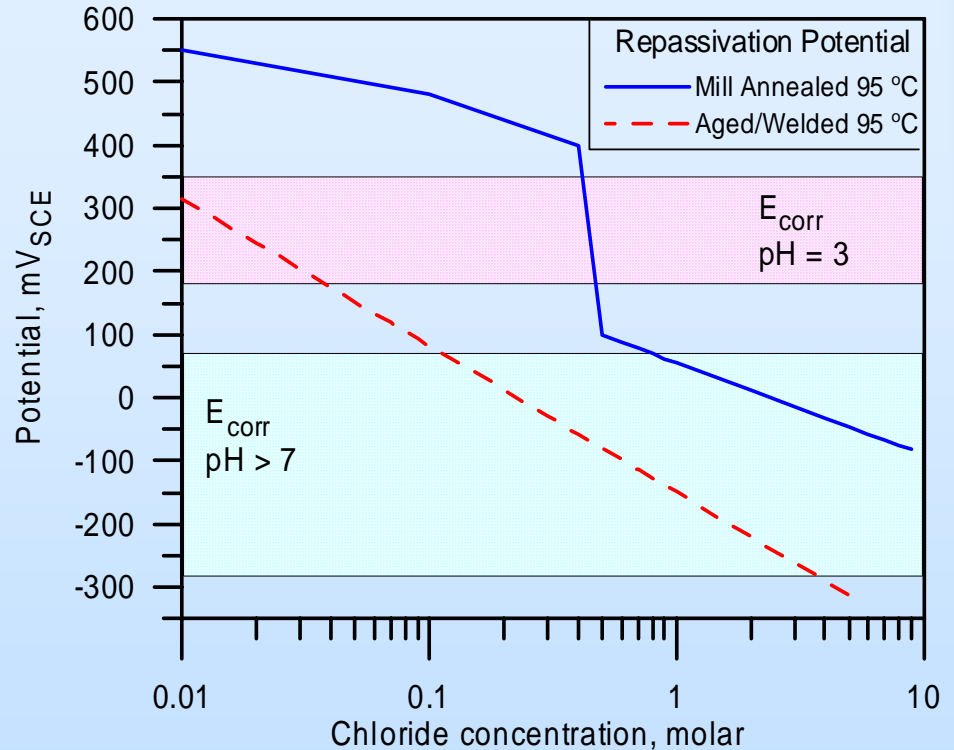
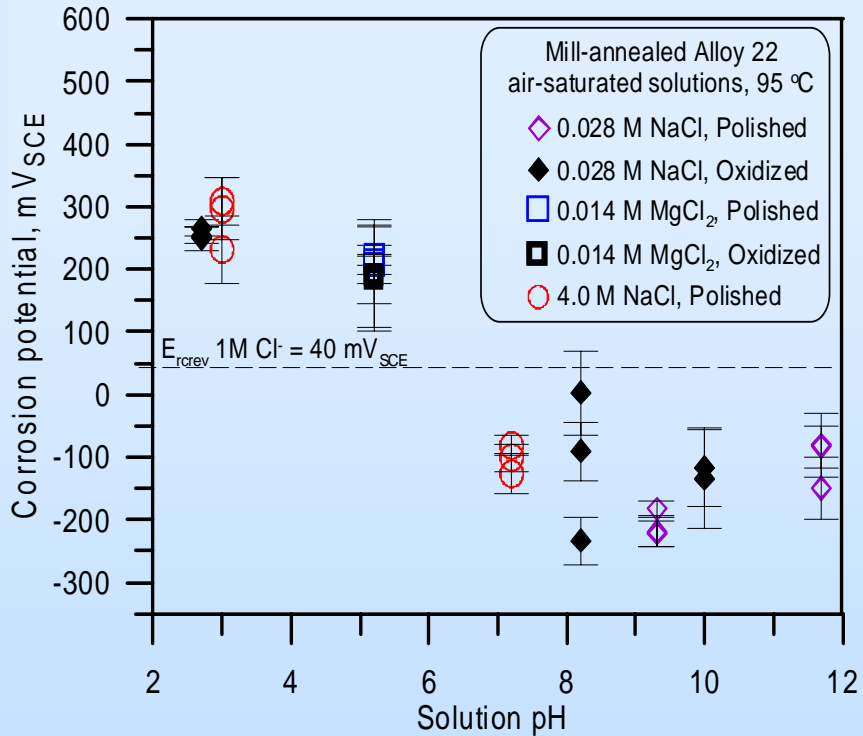
- Crevice corrosion repassivation potential used as critical potential for the long-term initiation of localized corrosion
- Repassivation potential mainly dependent on alloy Mo content
- Localized corrosion resistance reduced by welding and short exposures at elevated temperatures (~ 800 °C)

Localized Corrosion and Temperature



- Repassivation potential decreases with temperature, chloride concentration and welding or thermal aging indicating increasing susceptibility to crevice corrosion

Corrosion and Repassivation Potentials



Based on regression equation that does not include effects of inhibiting anions

Repassivation Potential Parameters

Localized Corrosion

- $E_{\text{corr}} > E_{\text{rcrev}}$
- $[\text{Cl}^-] > [\text{Cl}^-]_{\text{crit}}$
- $[\text{Inhibitor}] < (0.1-0.2)[\text{Cl}^-]$
- $T > T_{\text{crit}}$

$$E_{\text{crit}} = E_{\text{rcrev}}$$

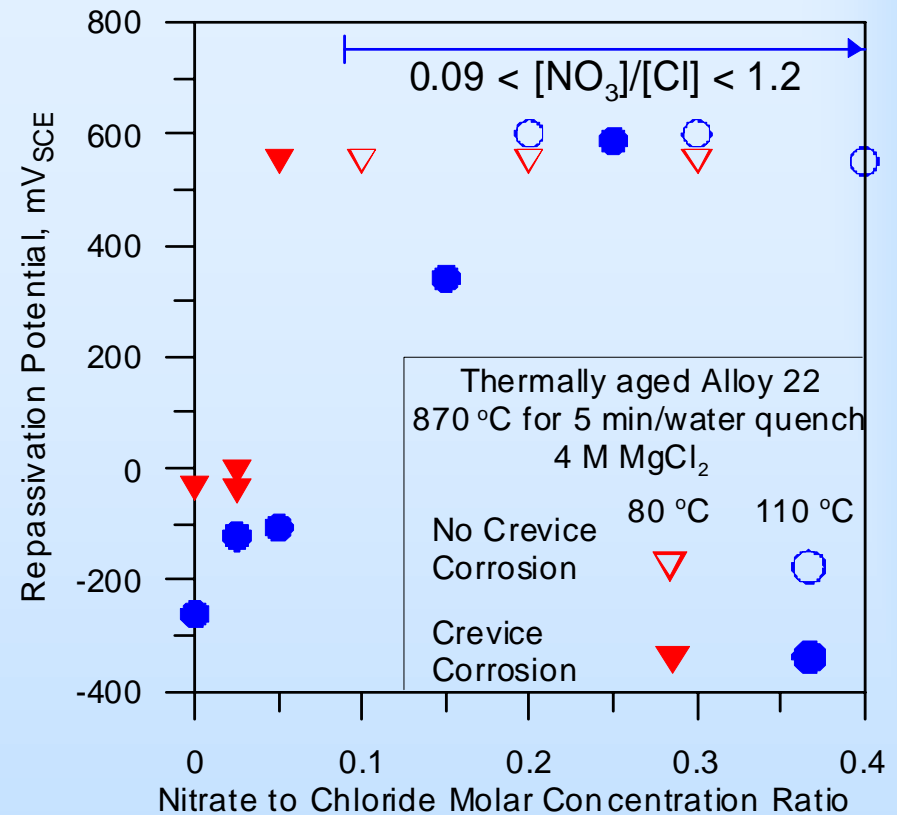
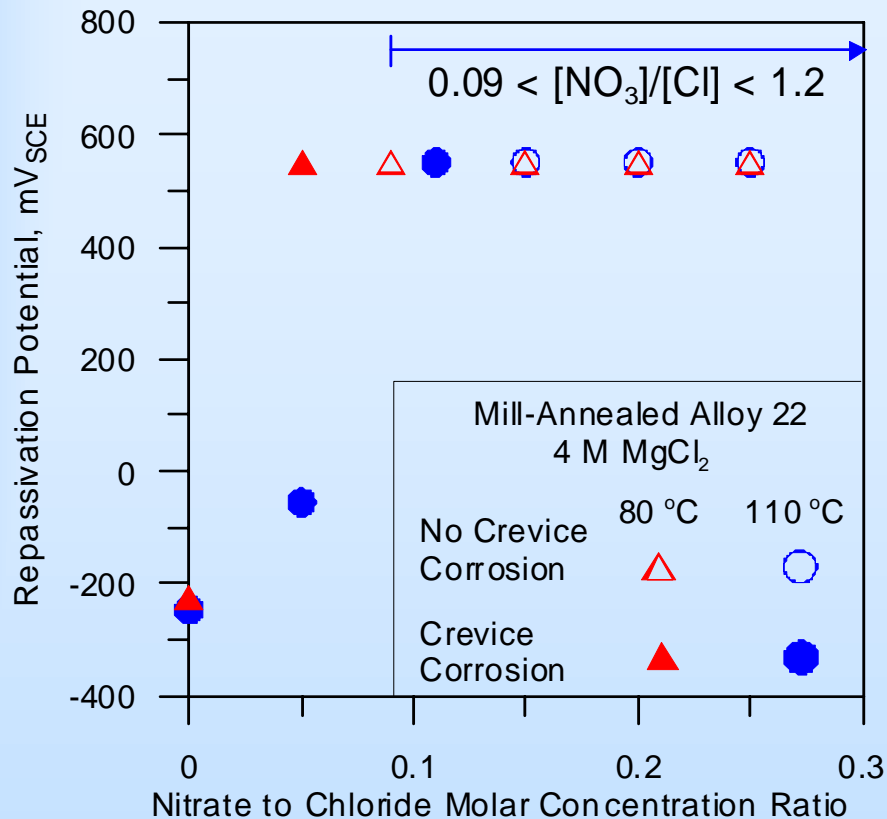
$$E_{\text{rcrev}} = E_{\text{rcrev}}^0(T) + B(T) \log[\text{Cl}^-]$$

$$E_{\text{rcrev}}^0(T) = A_1 + A_2T;$$

$$B(T) = B_1 + B_2T$$

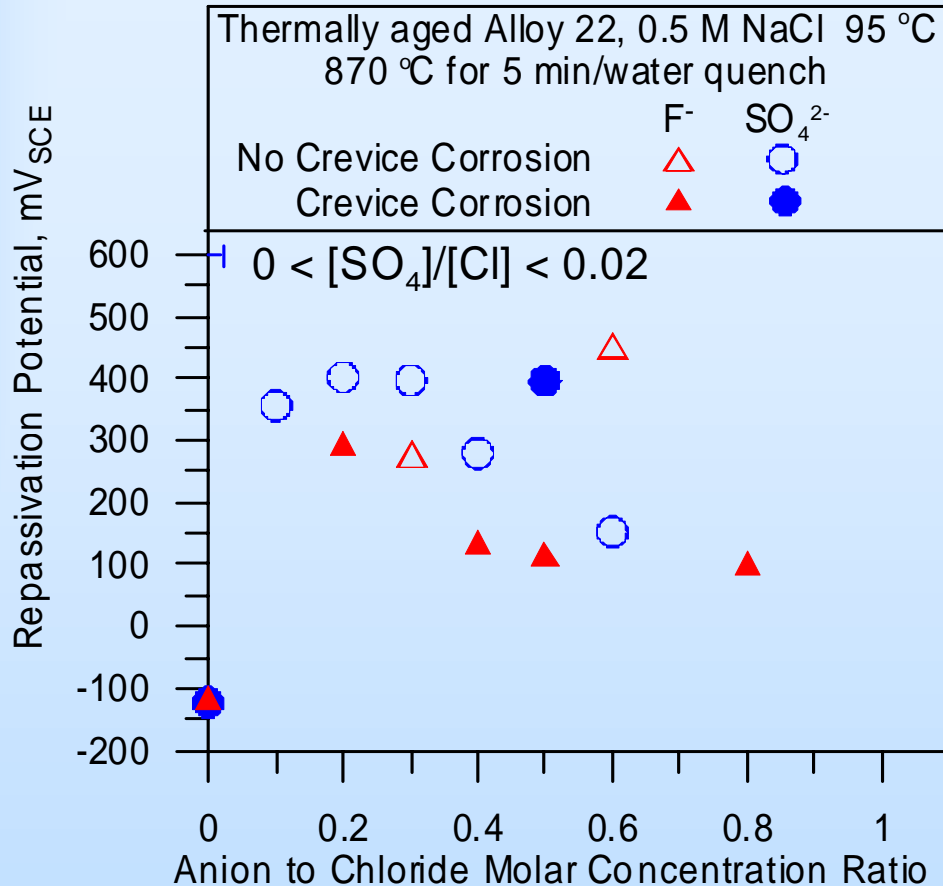
Metallurgical Condition	T (°C)	$[\text{Cl}^-]_{\text{crit}}$ (M)	$[\text{INH}]/[\text{Cl}^-]_{\text{crit}}$	A_1 (mV _{SCE})	A_2 (mV/°C)	B_1 (mV)	B_2 (mV/°C)
Mill annealed (as-received)	80 to 125 °C	0.5	0.1	1,300	-13.1	-362.7	2.3
Thermally Aged 5 min at 870°C Water Quench	60 to 95 °C	0.25 to 0.01	0.2	800	-10.0	-584.2	3.7

Nitrate Inhibits Localized Corrosion



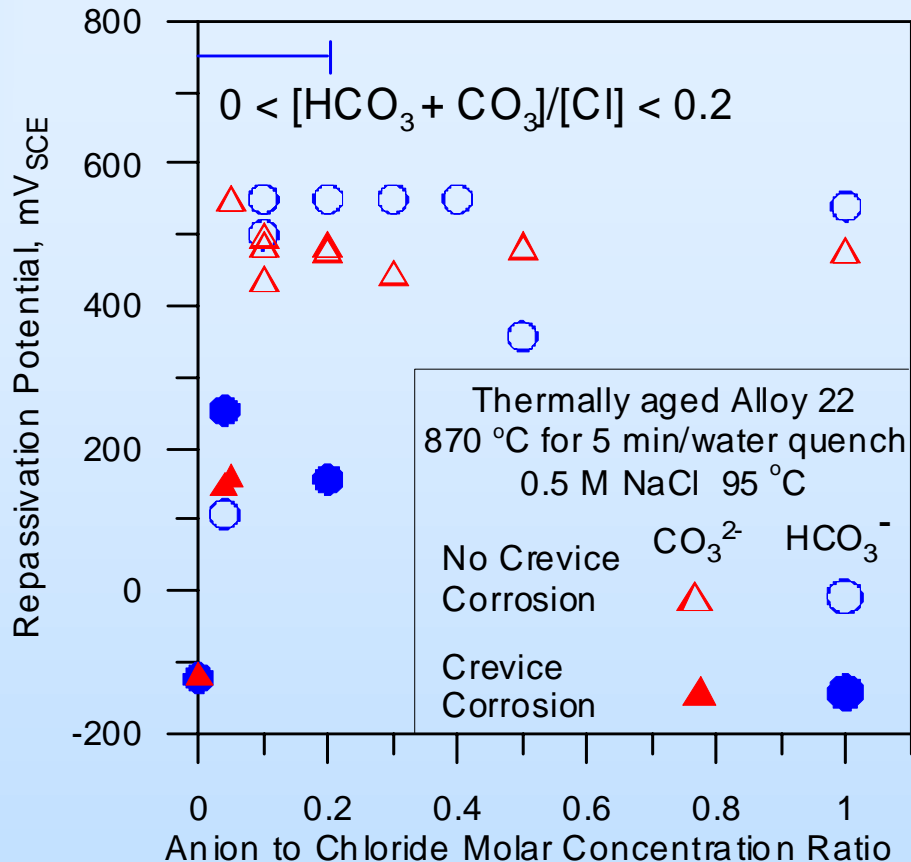
- Nitrate inhibits localized corrosion of mill annealed and thermally aged Alloy 22 at very low nitrate to chloride molar concentrations ratios
- Likely nitrate to chloride concentration ratios in evaporated brines are sufficient to inhibit localized corrosion

Effects of Sulfate and Fluoride



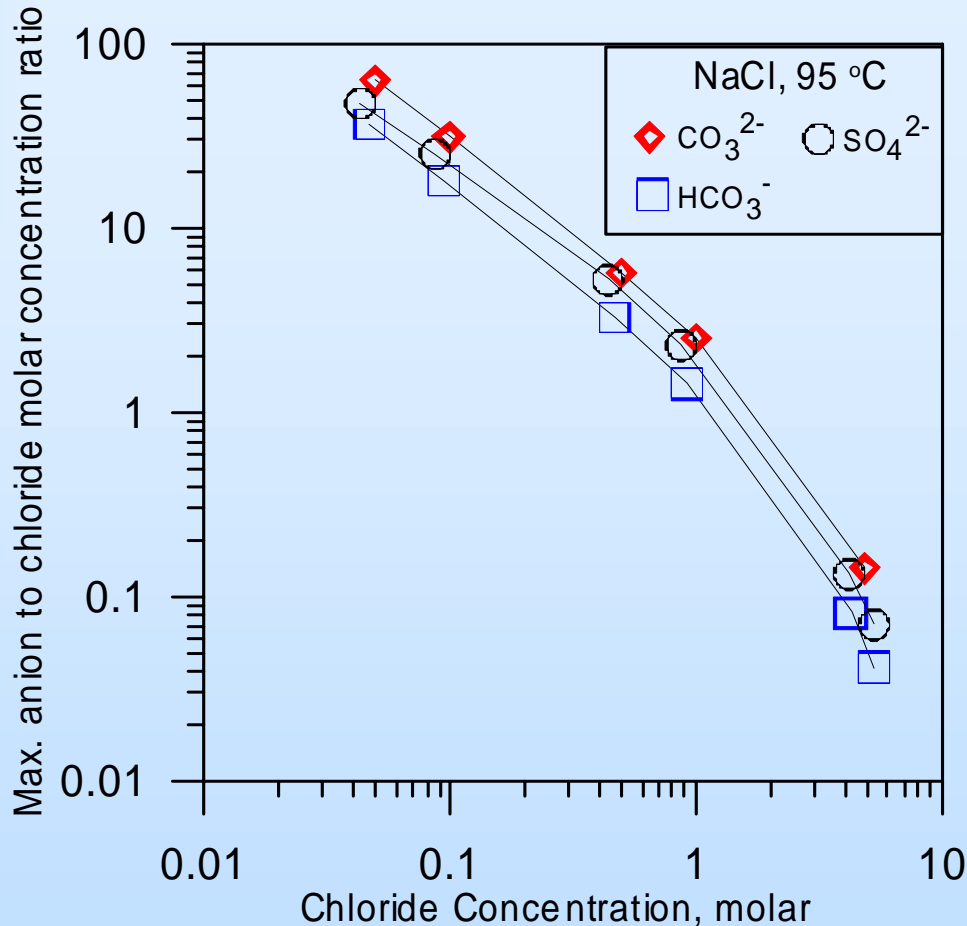
- Thermally aged Alloy 22
- Sulfate inhibits localized corrosion at sulfate to chloride molar concentration ratios ≥ 0.1
- Fluoride may dilute the detrimental effect of chloride but does not inhibit localized corrosion
- Fluoride does not enhance the effect of chloride up to molar concentration ratios of 1.0

Carbonate and Bicarbonate as Localized Corrosion Inhibitors



- Thermally aged Alloy 22
- Both carbonate and bicarbonate inhibit crevice corrosion
- Likely carbonate + bicarbonate to chloride ratios in evaporated brines may inhibit localized corrosion

Inhibitor Concentrations



- Speciation calculations show that the maximum oxyanion concentrations decrease with increasing chloride concentration
- Nitrate is highly soluble and can act as an inhibitor in concentrated chloride solutions
- $0.09 \leq [\text{NO}_3^-]/[\text{Cl}^-] \leq 1.2$
 - Assuming no CaNO_3^+ or NaNO_3^+ complexes
- $0.1 \leq [\text{INH}]/[\text{Cl}^-] \leq 1.2$
 - $[\text{INH}] = [\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$
- Localized corrosion is inhibited if $[\text{INH}]/[\text{Cl}^-] \geq 0.1$ to 0.2

Environment and Metallurgical Factors

Environment or Metallurgical Factors	E_{corr}	E_{rcrev}
$[\text{NO}_3^-]$ or other inhibitors increase	(0)	(+)
pH increase	(-)	(0)
$[\text{Cl}^-]$ increase	(-)	(-)
T increase	(-)	(-)
$[\text{HCO}_3^-]$ increase (inhibiting and increases pH)	(-)	(+)
$[\text{S}_2\text{O}_3^{2-}]$ or other reduced sulfur species (from SRB*) increase	(-)	(-)
E_h^\dagger (from air and radiolytic species) increase	(+)	(0)
Aging of passive film	(+)	(0)
Precipitation of intermetallic phases at grain boundaries	(0)	(-)
Segregation of alloying elements in welds	(0)	(-)
*SRB—sulfate reducing bacteria; $^\dagger E_h$ —redox potential (+) Increase in E_{corr} or E_{rcrev} (-) Decrease in E_{corr} or E_{rcrev} (0) No change in E_{corr} or E_{rcrev}		

Summary

- Passive corrosion rates are dependent on temperature and metallurgical condition but are low ($<10^{-4}$ mm/yr) under steady state conditions
- Accelerated uniform corrosion of Alloy 22 was observed in acidic, concentrated chloride solutions at high temperatures, however, such conditions are not expected within the emplacement drifts
- The localized corrosion susceptibility of Alloy 22 depends on chloride concentration, concentration of inhibitors, temperature, and metallurgical condition
- Nitrate, carbonate, bicarbonate, and sulfate were found to inhibit localized corrosion of Alloy 22 when present in sufficient concentrations relative to chloride
- The nitrate to chloride molar concentration ratio necessary to inhibit localized corrosion is in the range of 0.1 to 0.2 and is slightly dependent on chloride concentration, temperature, and metallurgical condition

Acknowledgements

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