



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



Effect of Anions on the Passive Film Properties and Localized Corrosion Behavior of Alloy 22

210th Meeting of the Electrochemical Society

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Objective

- **To study corrosion resistance of Ni-Cr-Mo alloy in high temperature brines**
- **To study the effect of anions on the passive film properties of alloy C-22**
- **To study the effect of anions on the localized corrosion susceptibility of alloy C-22**
- **To investigate the correlation between the localized film breakdown and the electronic properties of the passive film**



Approach

- **Cyclic Polarization (with and without crevice former)**
 - Electrochemical parameters of alloy/environment, e.g. open circuit potential, breakdown potential, repassivation potential
 - Basis for further experiments, e.g. constant potential crevice corrosion tests, electrochemical impedance analysis
- **Constant Potential Crevice Corrosion Test**
 - Highly aggressive, accelerated crevice corrosion test
 - ◆ Applied potential more positive than repassivation potential
 - ◆ Teflon covered ceramic with multi-crevice assembly (MCA)
 - Current-time measures corrosion initiation, propagation, stifling and arrest
- **Electrochemical Impedance Spectroscopy (without crevice former)**
 - Resistance and capacitance of passive films
 - Thickness of the passive films (all of space charge layer is associated with the full thickness of the passive film)
- **Mott-Schottky Analysis (without crevice former)**
 - Electronic properties, concentration and type of charge carriers, defects in passive films



Experimental Details

Material Alloy C-22 (Ni-Cr-Mo Alloy)

Composition

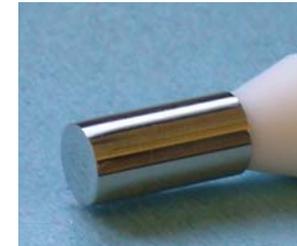
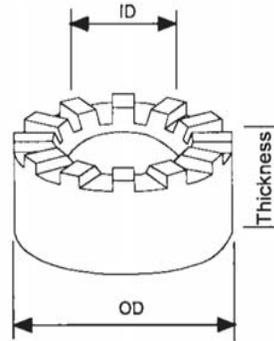
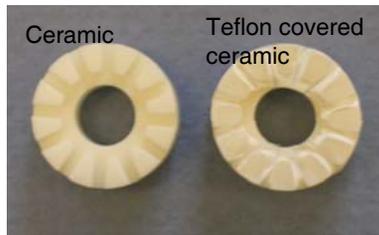
	C	Co	Cr	Fe	Mn	Mo	Ni	P	S	Si	V	W
Alloy 22	0.0035	0.7167	21.0	3.9	0.2306	13.3	BAL	0.011	0.0039	0.0264	0.0128	2.9

Environment

<i>Solution</i>	<i>T, °C</i>
4M NaCl	100
<i>Effect of Nitrate in Chloride Solution</i>	
4M NaCl + 0.6 M KNO ₃	100
4M NaCl + 2 M KNO ₃	100
<i>Effect of Sulfate in Chloride Solution</i>	
4M NaCl + 0.4 M Na ₂ SO ₄	100
<i>Effect of Chloride in Sulfate Solution</i>	
1M Na ₂ SO ₄	100
1M Na ₂ SO ₄ + 0.1M NaCl	100
1M Na ₂ SO ₄ + 1M NaCl	100



Test Cell and Specimen



Localized Corrosion Study

Passive Film Study



Procedure

Cyclic Polarization/without crevice

Cathodic reduction at -1.0 V-sce for 30 min
Open circuit potential till it stabilizes (1h)
Start scan 50 mV below OCP
Reverse scan at 5 mA/cm²
Scan Rate: 0.1667 mV/sec

Electrochemical Impedance Spectroscopy (EIS)

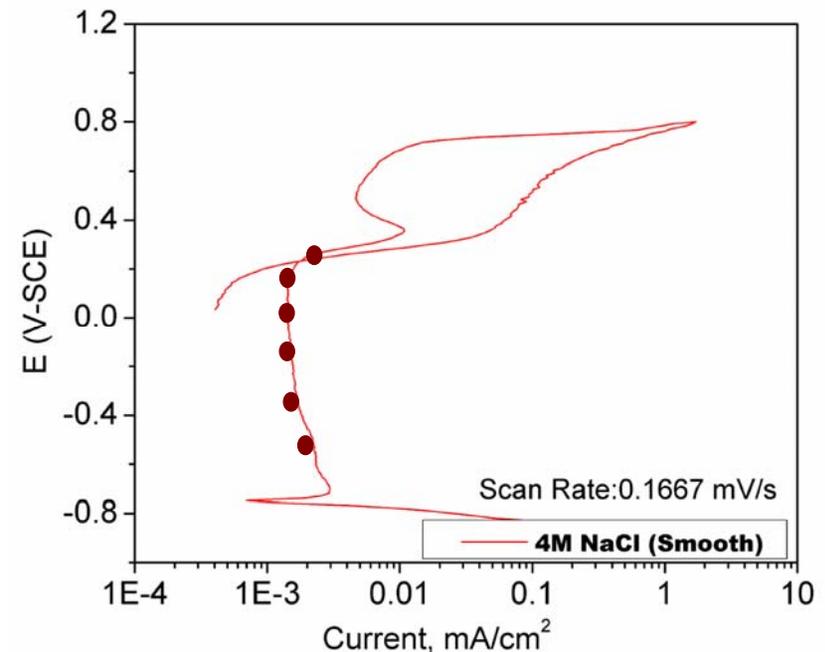
Cathodic Reduction at -1.0 V-sce for 30 min
Step the potential in the passive range, hold for 2 h, perform EIS at that potential
Step the potential 200 mV and repeat step 2

Parameters for EIS

Frequency range: 65 KHz to 10 mHz
Peak to peak potential: 10 mV
Potentials: picked from fwd-reverse scans

Cyclic Polarization/with crevice former

Open circuit potential till it stabilizes (12-24 h)
Start scan 50 mV below OCP
Reverse scan at 5 mA/cm²
Scan Rate: 0.1667 mV/sec

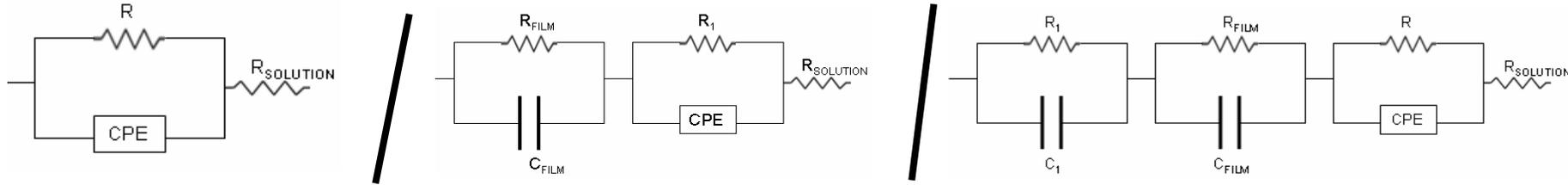


Forward –reverse scan of Alloy C-22 in 4M NaCl (de-aerated) at 100 °C



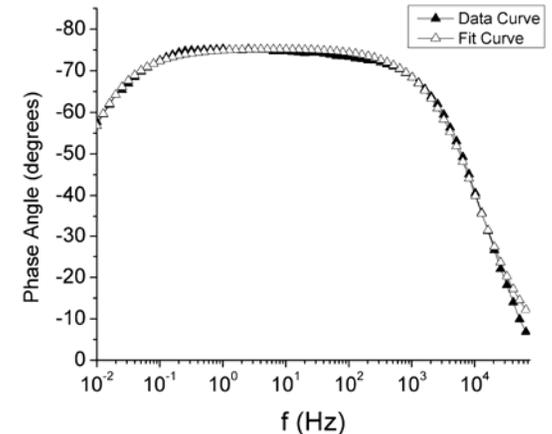
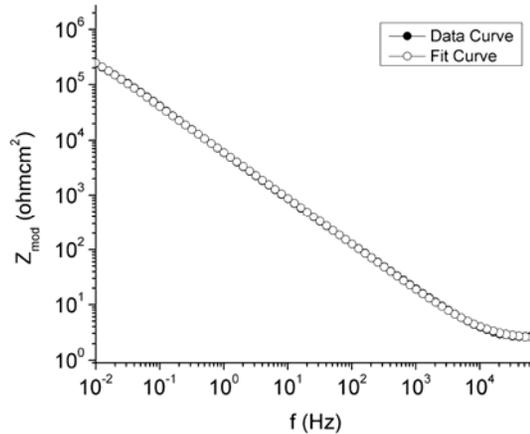
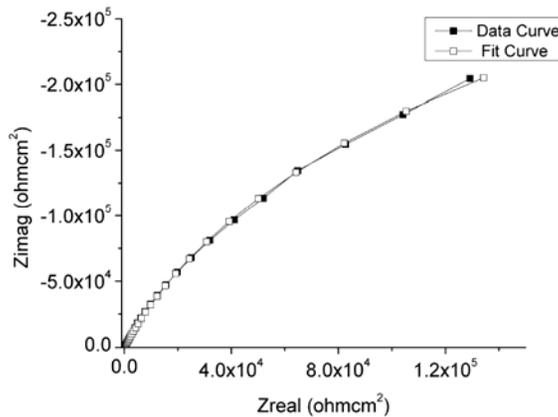
EIS Analysis

- Experimental Impedance data were simulated with $R_p//CPE$ electrical analog circuit to get resistance and capacitance of the passive film*



CPE: Constant Phase Element
 R1/C1: Metal/Oxide interface
 R2/C2: Oxide /Solution interface

Various equivalent circuits considered; one on far left above used for this analysis



Representative simulation curves of Nyquist, Bode magnitude and Bode phase plots of experimental impedance data set

- Simulation Software: Zsimpwin/Zview

* Rodriguez, M.A. Carranza, R.M., Rebak, R.B., "Influence of halide ions and alloy microstructure on the passive and localized corrosion behavior of alloy 22", Metallurgical and Materials Transaction A, V. 36A, p.1179



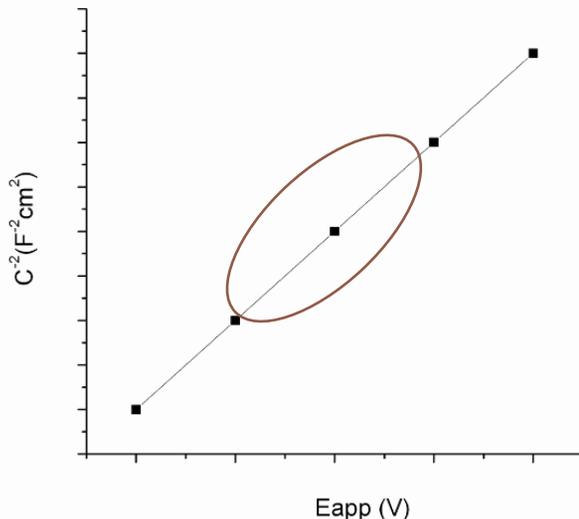
M-S Analysis

- Capacitance at the semiconductor/solution interface $C^{-1} = (C_{sc} + C_{ss})^{-1} + C_{dl}^{-1}$

- Classical Mott-Schottky theory assumes $C^{-1} = C_{sc}^{-1}$ at high frequency ($f > 1 \text{ KHZ}$)

- Capacitance is calculated by (assuming $\alpha=1$)
$$C = \frac{-1}{\omega \text{Im}(Z)}$$

- M-S relation can apply only when $1/C$ vs. E and $1/C^2$ vs. E are linear



- Extrapolation of E_{app} to $1/C^2 = 0$ gives E_{fb}

- Flat band potential is the applied potential where semiconductor band bending is minimized, the potential distribution and concentration of charge carriers are uniform in oxide from metal to the surface

$$\frac{1}{C_{sc}^2} = \frac{-2}{\epsilon\epsilon_0 e N_A A^2} \left(E - E_{fb} - \frac{\kappa T}{e} \right) \quad \text{p-type film}$$

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon\epsilon_0 e N_D A^2} \left(E - E_{fb} - \frac{\kappa T}{e} \right) \quad \text{n-type film}$$

- Thickness is calculated by

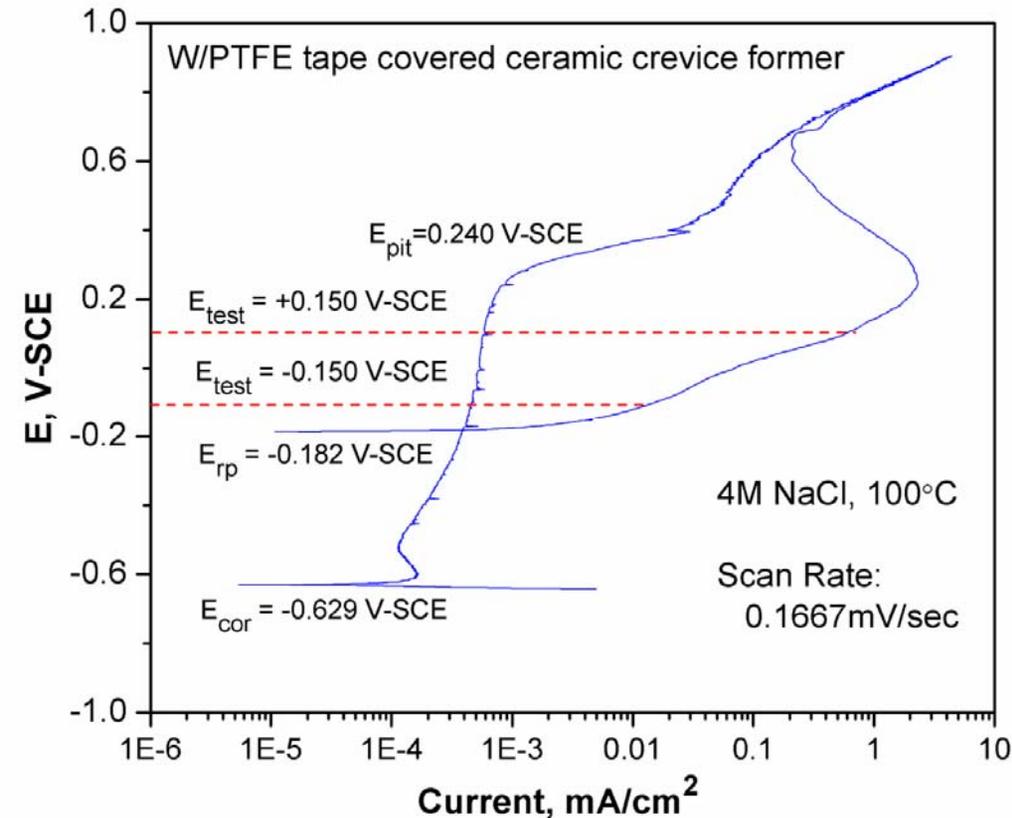
$$L_{ss} = \frac{\epsilon\epsilon_0}{C}$$

ϵ : Dielectric constant of Cr_2O_3 oxide, 30

ϵ_0 : Permittivity of vacuum



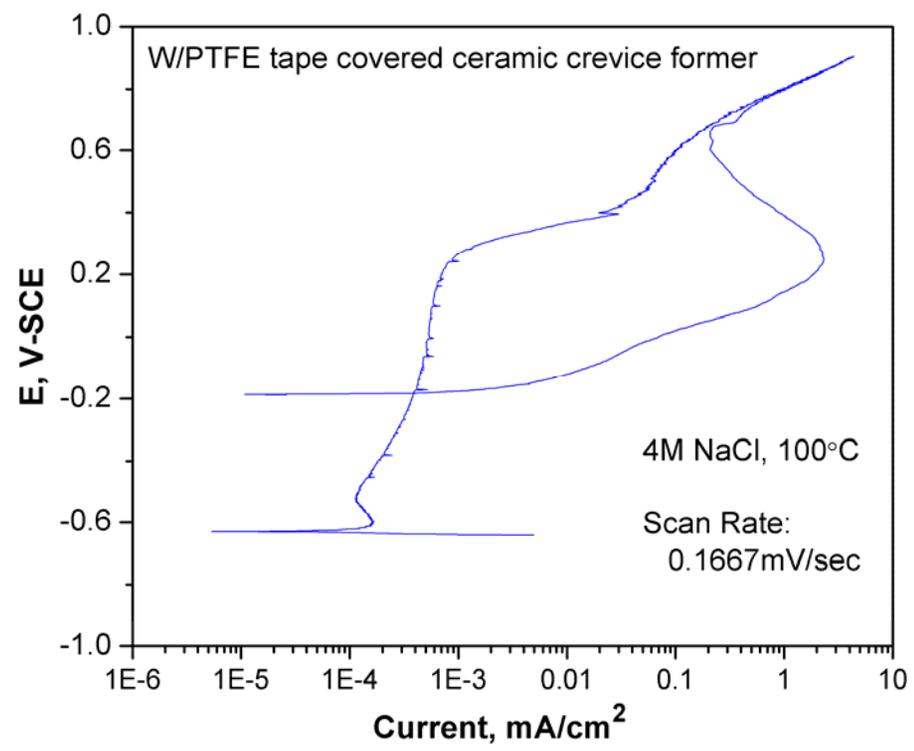
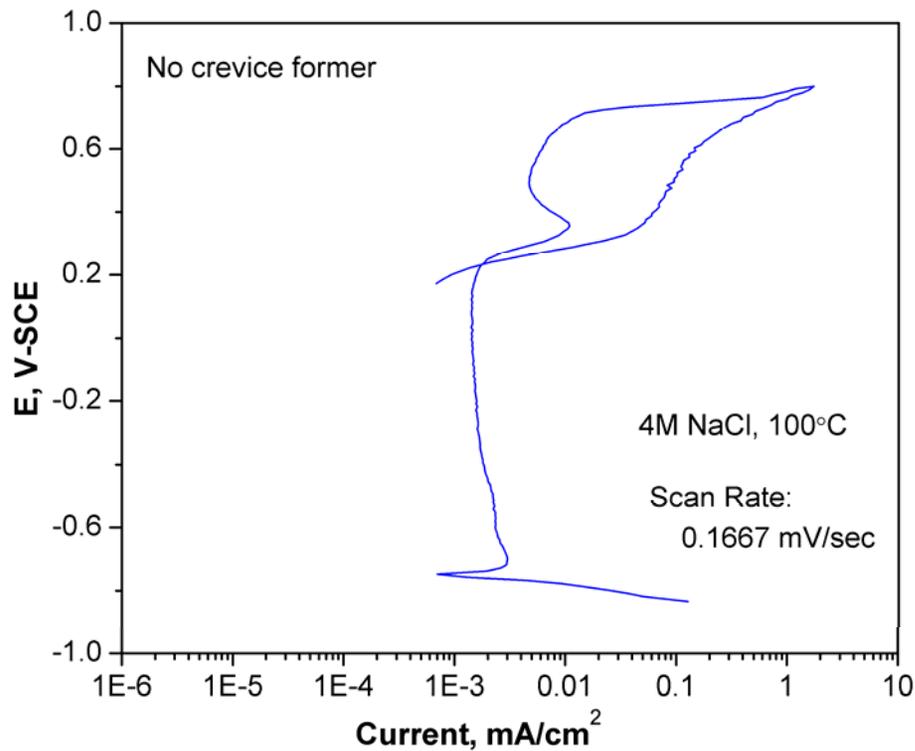
Cyclic Potentiodynamic Polarization Test



- Forward and reverse scan
- Measure E_{corr} , E_{br} , E_{rp}
- Results are basis for crevice corrosion tests
 - Increase of current
 - Visible damage under crevice former
 - $E_{applied} > E_{rp}$
- E_{test} is 30 to 50mV above $E_{rp(MCA)}$
 - $E_{rp} = -0.182 \text{ V-SCE}$
 - $E_{test} = -0.150 \text{ V-SCE}$
 - $E_{test} = +0.150 \text{ V-SCE}$



Corrosion Behavior in Hot Chloride Brines



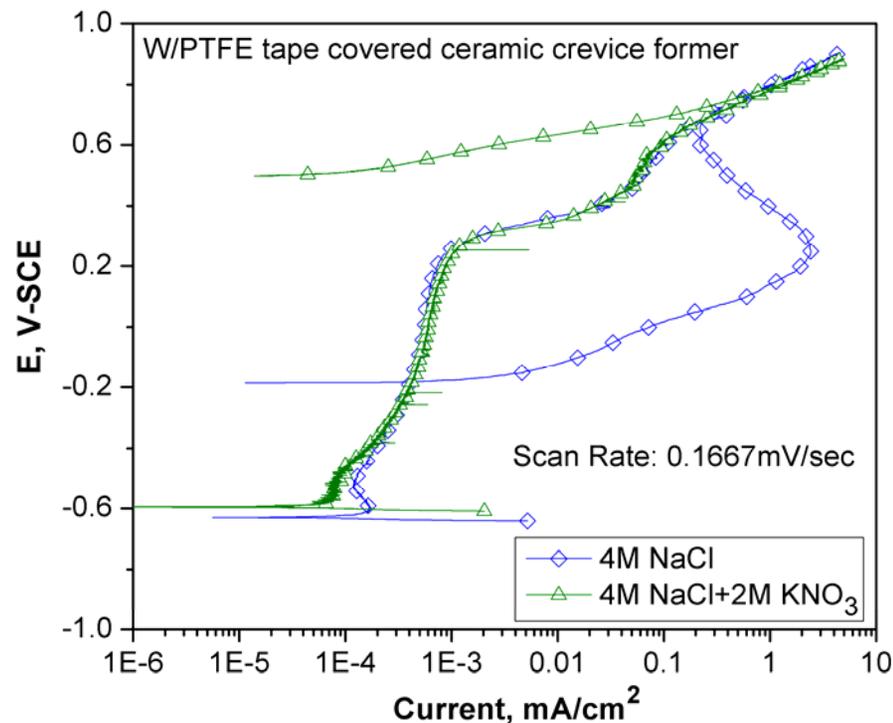
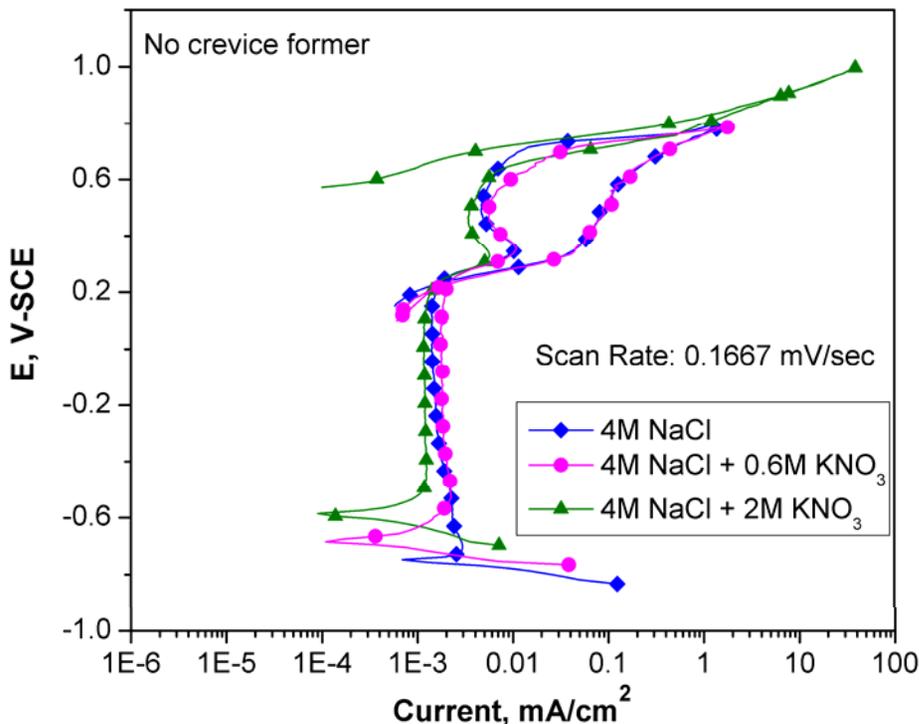
- Both conditions (with and without crevice former) showed similar passive behavior in hot 4M NaCl brines
- Breakdown potential for both occurs at the same level (~ 0.200 V-sce) but the amount of corrosion for crevice assembly is more (larger hysteresis)
- Crevice assembly ($E_{rp, crevice} = -0.182$ V-sce) repassivated at a much lower potential, ~ 400 mV more negative than smooth samples ($E_{rp, smooth} = 0.231$ V-sce)
- Minor effects of crevice former prior to passive film breakdown, and greatest effect of crevice former is on repassivation behavior



Effect of Nitrate addition in Chloride Solutions



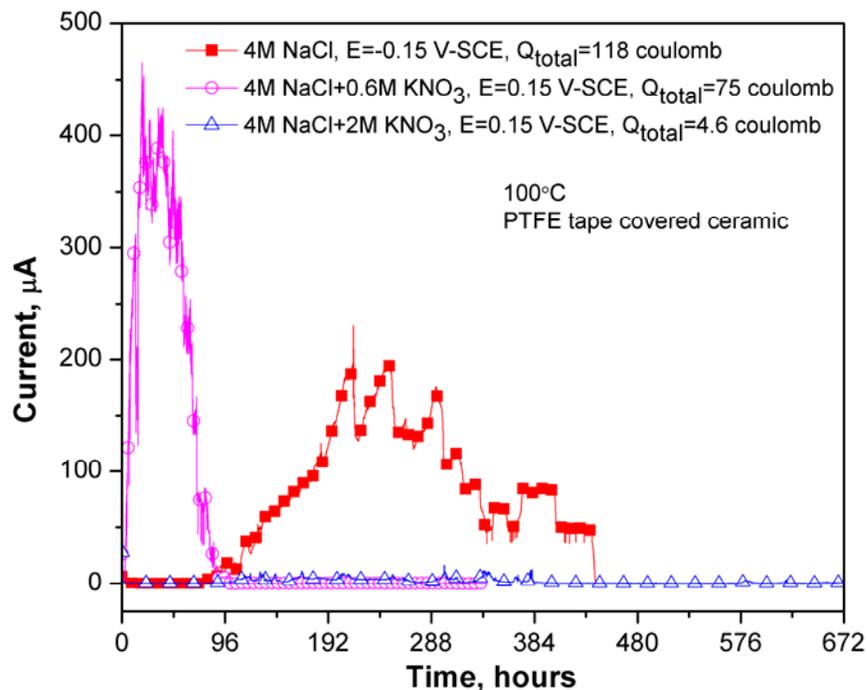
Effect of Nitrate Addition in Chloride Solution



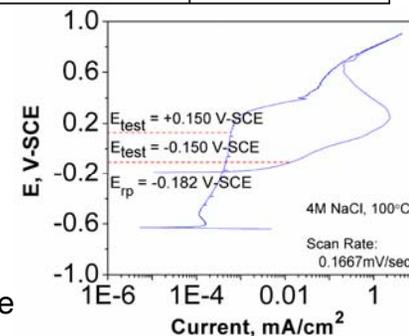
- Slight increase in E_{corr} with addition of nitrate
- With 0.6M NO_3^- addition
 - No significant nitrate effect, i.e. similar corrosion behavior in terms of i_{pass} , E_{br} , E_{rp} , hysteresis loop
- With 2M NO_3^- addition
 - Similar corrosion behavior until passive film breakdown
 - With nitrate, repassivation was nearly immediate with and without crevice former
 - Repassivation potential for smooth sample increased by around 300 mV whereas the repassivation potential for the MCA increased by around 500 mV



Effect of Nitrate Addition in Chloride Solution



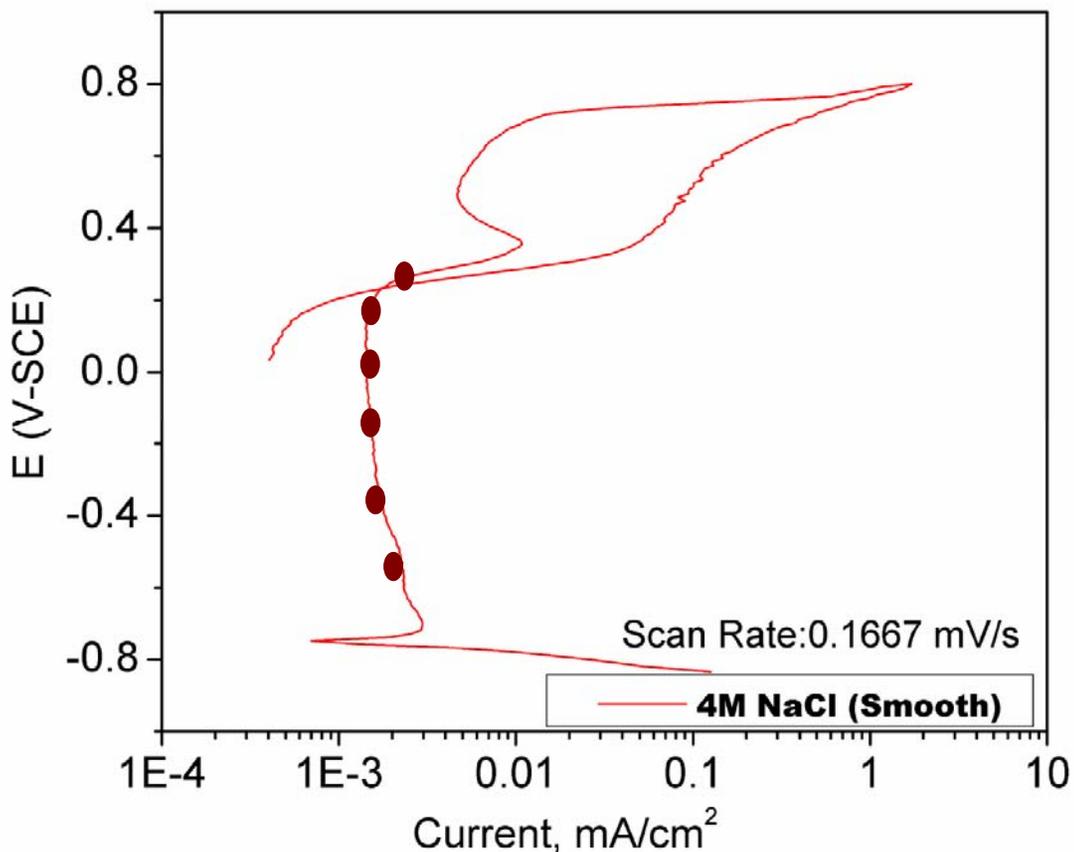
	4M NaCl E=-0.150 V	4M NaCl + 0.4M NaNO ₃ E=-0.150 V	4M NaCl + 0.6M KNO ₃ E=+0.150 V	4M NaCl + 2M KNO ₃ E=+0.150 V
Incubation (hours)	43.6 (9 to 112 for 7 tests)	>240	1.4 (1.5, 1.3)	98.3 (93.7, 102.8)
I_{max.} (µA)	161 (118 to 195 for 4 tests)	n/a	450	13 (15, 10)
Q_{total} (coulomb)	>90.7 (118, 59.8, >94.2)	No corrosion	75	3.9/28 days (4.6, 3.1)



- Effect of 0.4M NO₃⁻ at E = -0.150 V-sce (same potential applied for straight sodium chloride brine)
 - Crevice corrosion initiated after 10 days, No crevice corrosion observed with nitrate
- Effect of 0.6 M NO₃⁻ at E = + 0.150 V-sce
 - 300 mV more positive potential than straight chloride solution
 - Crevice corrosion initiated earlier, maximum current was greater and damage prior to repassivation somewhat less
- Effect of 2M NO₃⁻ at E= + 0.150 V-sce
 - 300 mV more positive potential than straight chloride solution
 - Nitrate increased incubation time, lowered the maximum current significantly and decreased the damage prior to repassivation



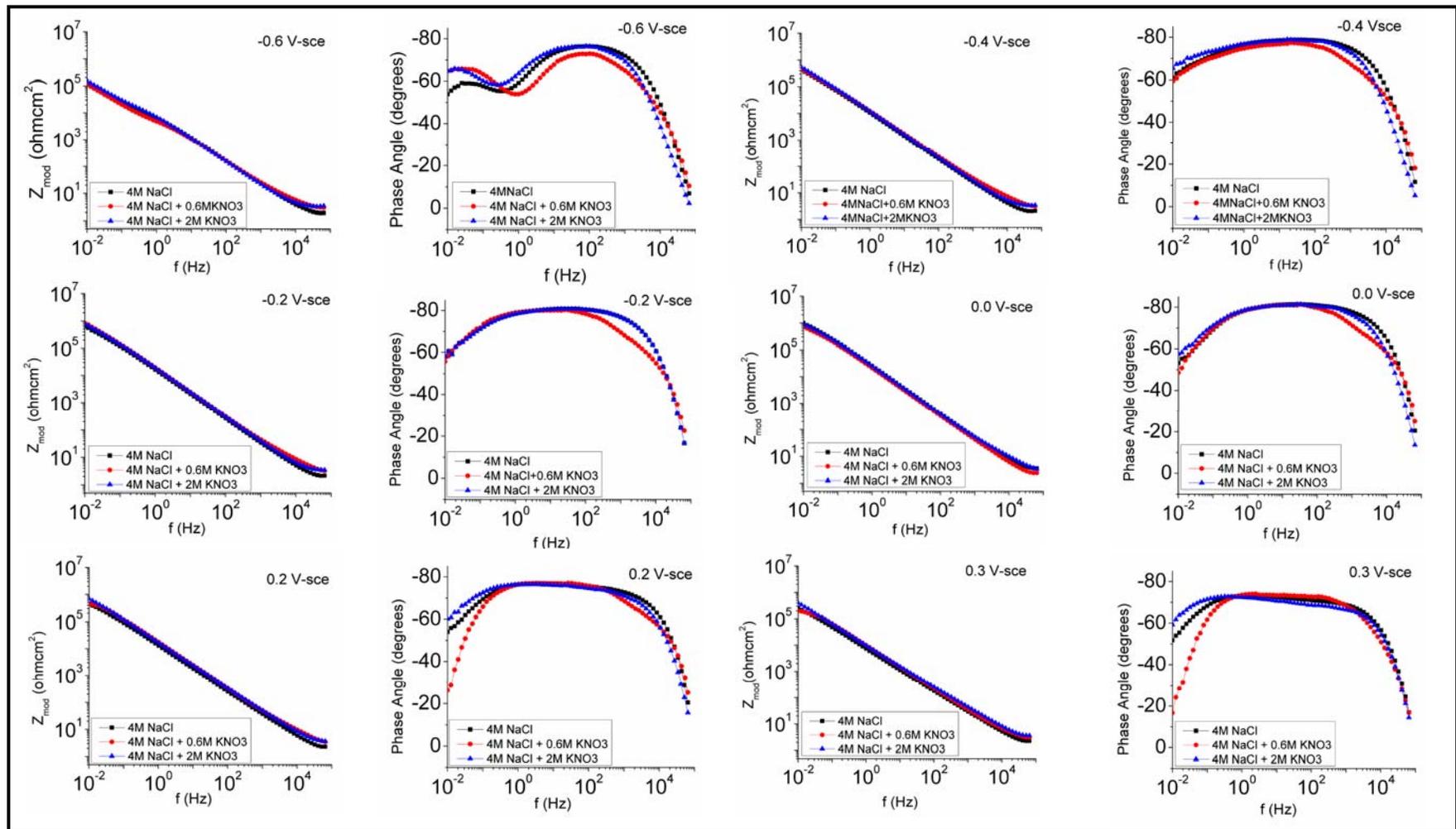
Electrochemical Impedance Spectroscopy (EIS)



*Forward –reverse scan of Alloy C-22 in 4M NaCl (deaerated) at 100 °C
Potentials to perform EIS were picked from these scans*



Effect of Nitrate Addition in Chloride Solution

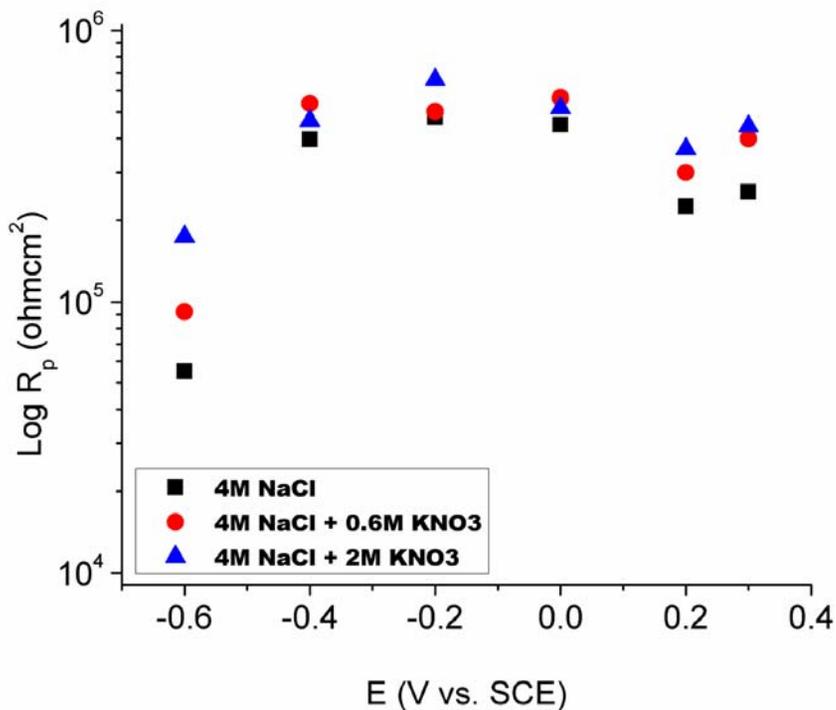


Montage of Bode phase/magnitude plots at various potential in 4M NaCl, 4M NaCl + 0.6M KNO₃, 4M NaCl+ 2M KNO₃ at 100° C

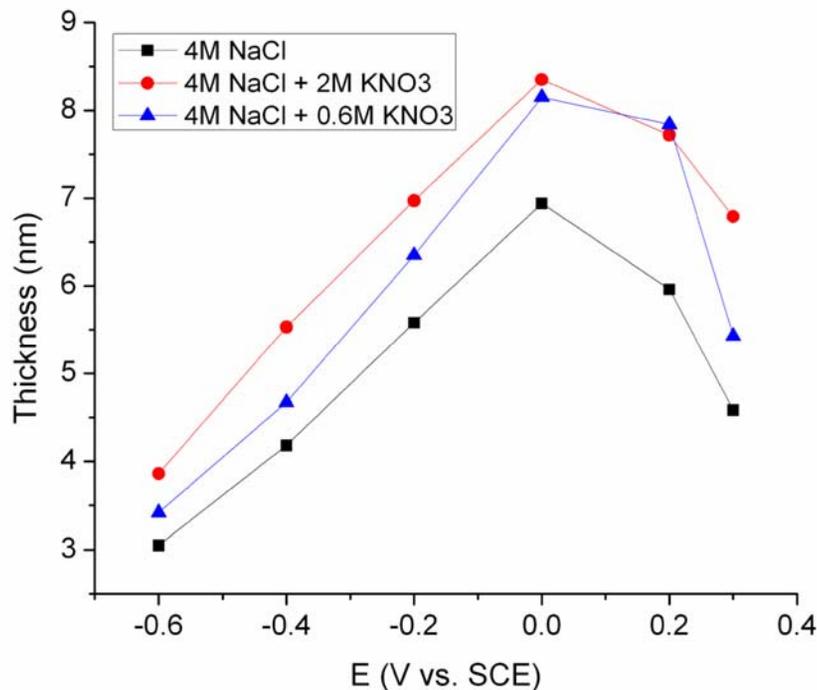
- In all solution, at $E = -0.6$ V-sce, passive film shows two time constants; second not seen at subsequent higher voltages
- The total impedance of the passive film with 2M NO₃⁻ addition was greater compared with straight chloride solution
- The total film impedance increased as the potential is increased, reached maximum at 0.0 V-sce (almost similar impedance values at -0.2, 0.0 and 0.2V-sce) and decreased at 0.3 V-sce



Effect of Nitrate Addition in Chloride Solution



Polarization resistance of the passive film as a function of nitrate/chloride ratio at different voltages



Passive film thickness as a function of nitrate/chloride ratio at different voltages

- Film resistance and thickness shows more dependence on potential for all the solutions
- Passive film resistance and thickness did not show much dependence on anion effect in the passive region
- The change in passive film thickness with the addition of 2M KNO₃ brine to hot sodium chloride brine was to higher values at all potentials
- The film thickness reaches a highest at 0.0V-sce and shows considerable less thickness at 0.3 V-sce (a transpassive region)



Summary/ Nitrate Addition in Chloride Solution

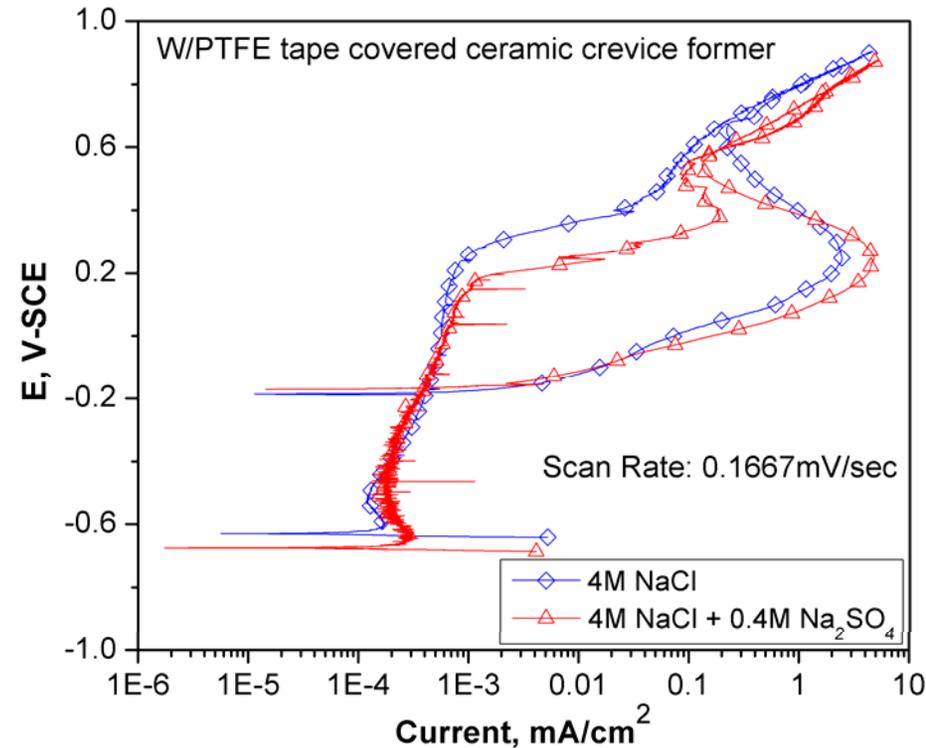
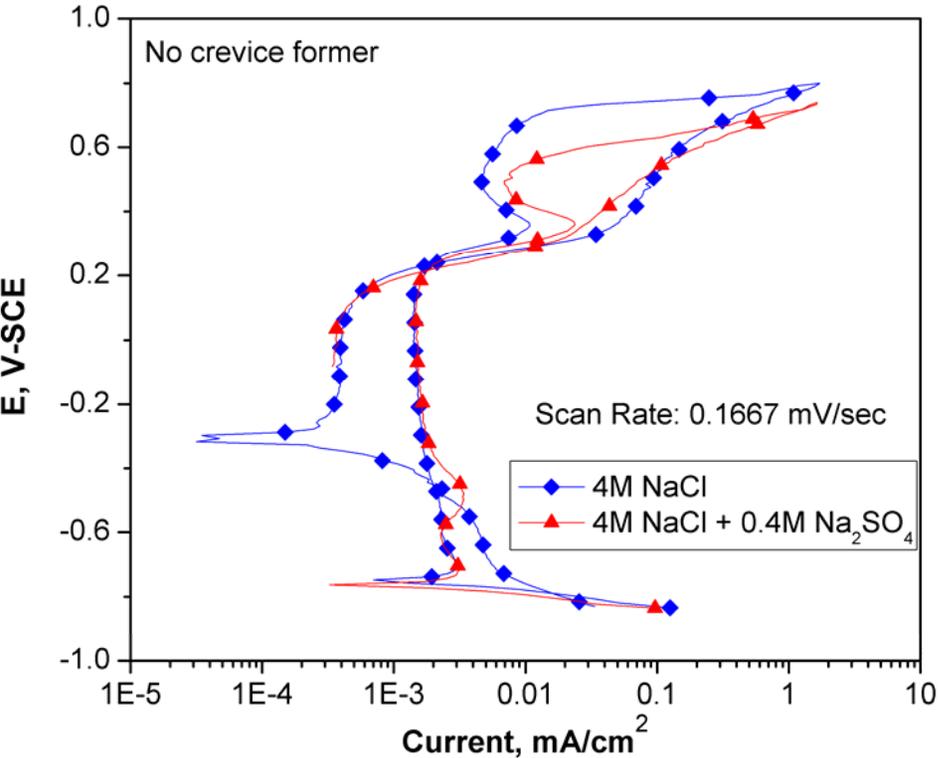
- **Forward-reverse scans show that repassivation potential was significantly higher with 2M NO₃⁻ salt additions to chloride solution**
 - **Beneficial effect of nitrate was greater with increasing NO₃⁻/Cl⁻ ratio**
- **Constant potential, crevice corrosion tests suggest that the incubation time with addition of nitrate is significantly more than in straight chloride solutions**
 - **Addition of NO₃⁻ can retard or even stop the crevice corrosion of alloy C-22**
- **Impedance studies showed that nitrate modestly increases the film thickness and resistance**
- **Based on above tests, nitrate has shown greater impact on repair and repassivation behavior than on the passive film when it is not damaged**



Effect of Sulfate Addition in Chloride Solution



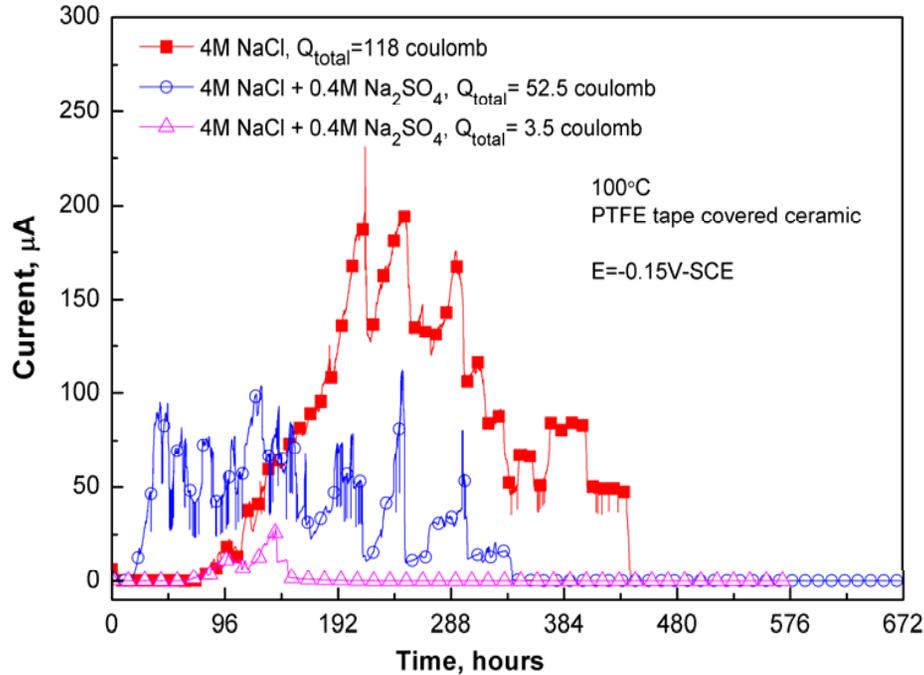
Effect of Sulfate Addition in Chloride Solution



- Effect of 0.4M SO₄²⁻
 - Corrosion behavior did not change with the addition of 0.4M sulfate
 - Same i_{pass} , E_{br} , E_{rp} recorded for both the samples
 - The hysteresis loop showed lesser damage after film breakdown but the impact not great



Effect of Sulfate Addition in Chloride Solution

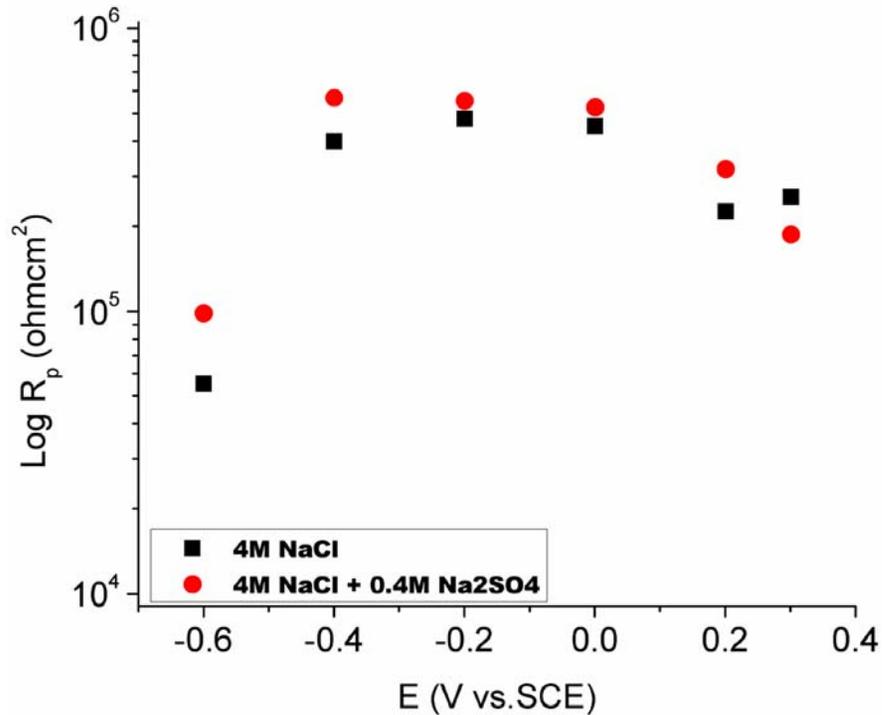


	4M NaCl	4M NaCl + 0.4M Na ₂ SO ₄
Incubation (hours)	43.6 (9 to 112 for 7 tests)	47.1 (65.3, 14.2, 61.8)
I_{max.} (µA)	161 (118 to 195 for 4 tests)	65 (103, 27)
Q_{total} (coulomb)	>90.7 (118, 59.8, >94.2)	28 (62.5, 3.5)

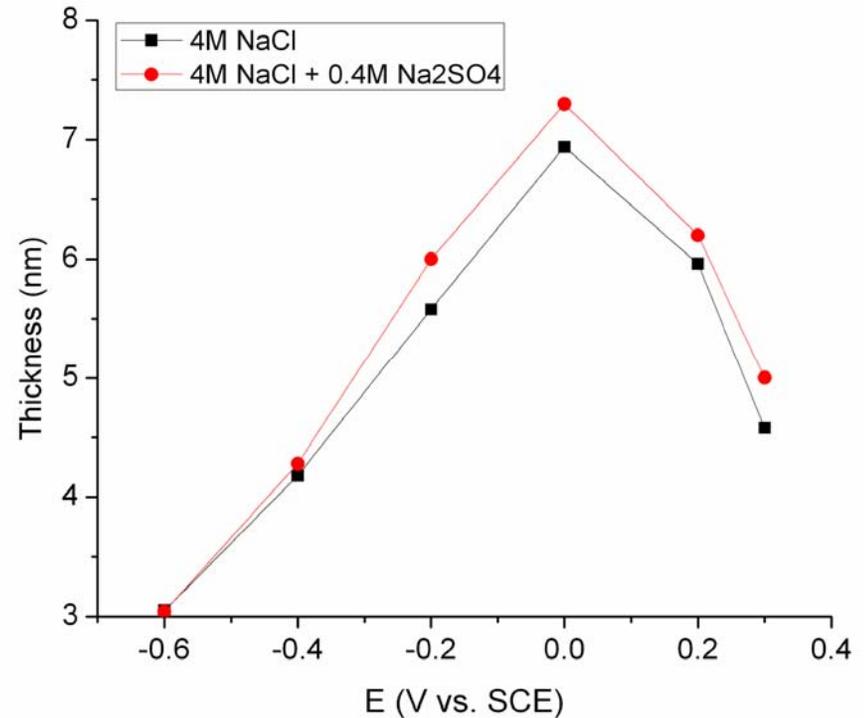
- Effect 0.4M SO₄²⁻ at E= -0.150 V-sce
 - Incubation time approximately the same
 - Addition of sulfate decreased the maximum corrosion current during crevice corrosion
 - With sulfate, less damage (coulombs) prior to repassivation
 - Sulfate does not stop the initiation crevice corrosion, but it decreased the severity of crevice corrosion in 4M NaCl solution at 100°C



Effect of Sulfate Addition in Chloride Solution



Polarization resistance of the passive film as a function of nitrate/chloride ratio at different voltages



Passive film thickness as a function of nitrate/chloride ratio at different voltages

- With SO_4^{2-} addition

- Impact of potential on the passive film resistance was found to be greater than effect of anions
- Polarization resistance increases from -0.6 V-sce, reaches a maximum value at -0.4 V-sce and shows the same resistance values at -0.4, -0.2 and 0.0 V-sce and decreases at 0.2 and 0.3 V-sce
- Film thickness shows highest thickness at 0.0 V-sce and decreases with further increase in potential



Summary/ Sulfate Addition in Chloride Solution

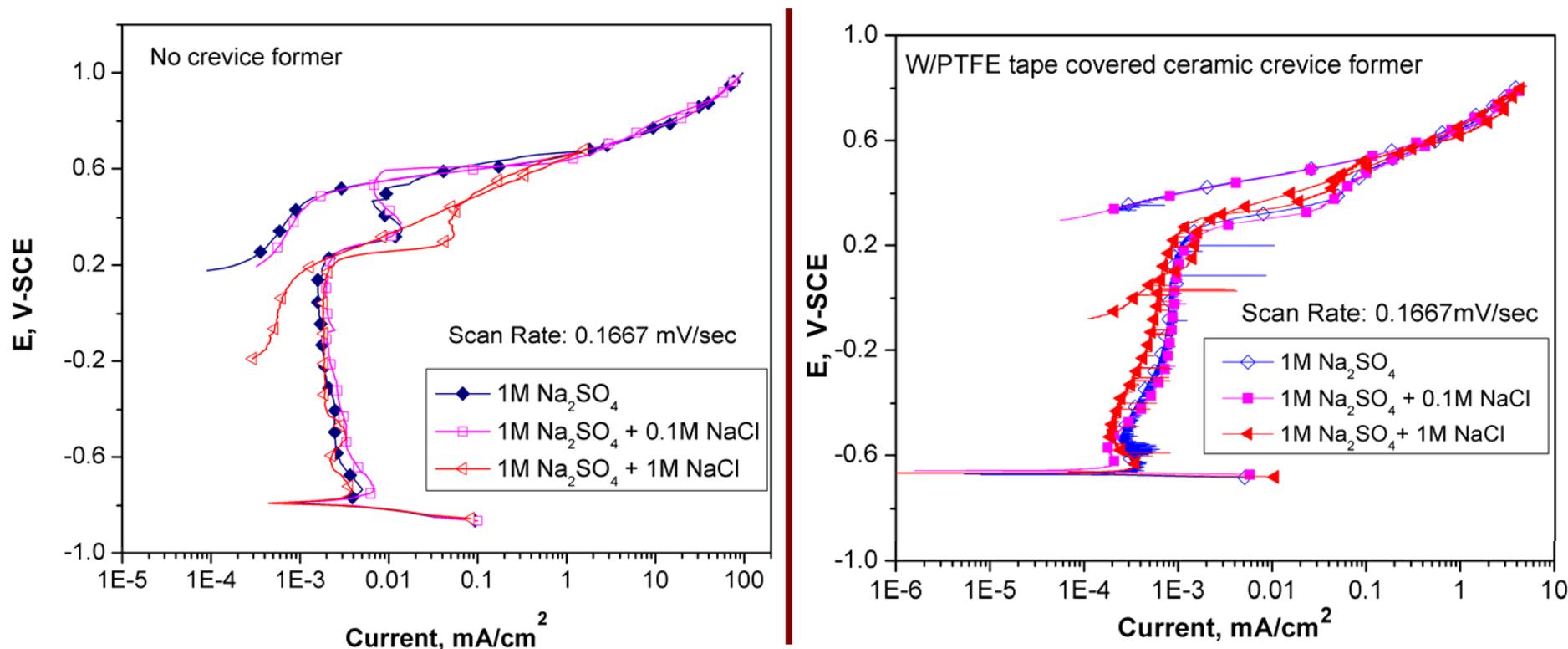
- **Forward-reverse scans did not show observable change with the addition of sulfate**
- **Constant potential crevice corrosion tests showed that sulfate did make an impact once the passive film breaks (longer incubation time, fewer coulombs to repassivate)**
- **Impedance tests showed that sulfate addition did not have observable effect on film resistance and thickness**
- **Based on above tests, sulfate did not show marked affect on the film properties in the present ratio of ($\text{SO}_4^{2-}/\text{Cl}^-$: 0.1:1), but sulfate did decrease the damage by crevice corrosion**



Effect of Chloride Addition in Sulfate Solution



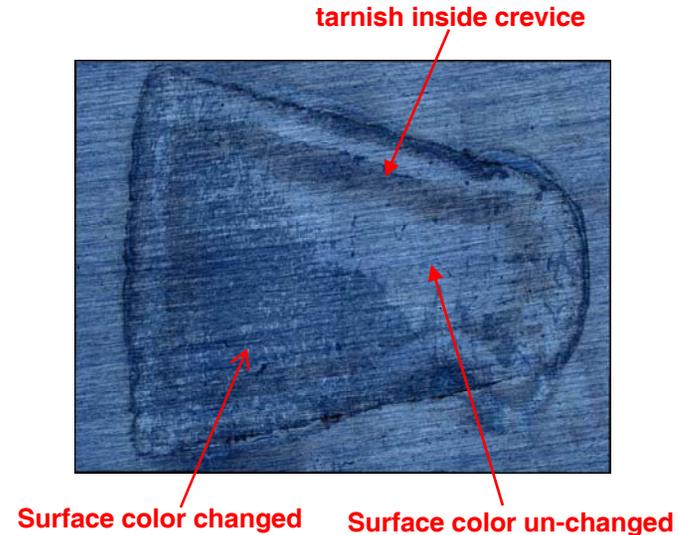
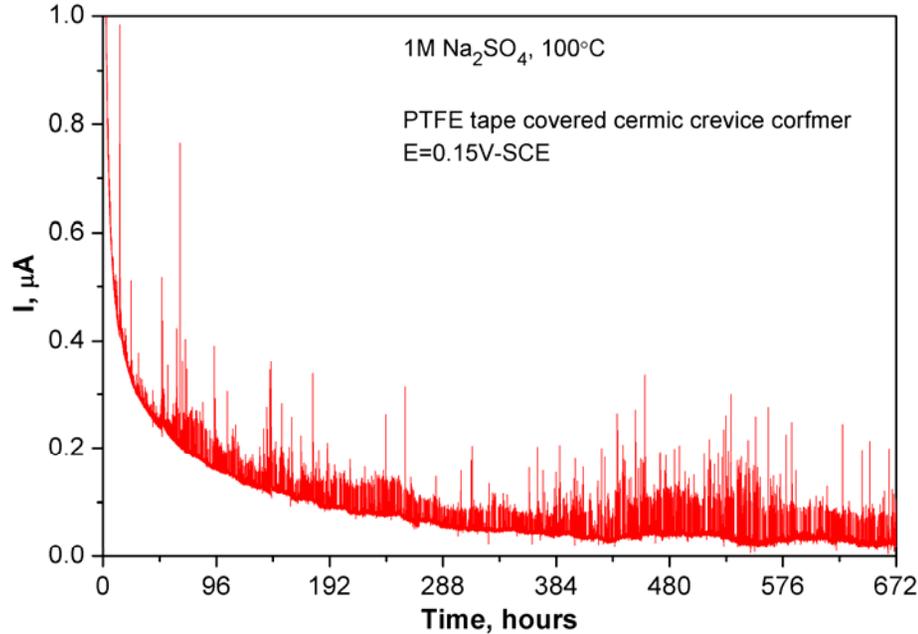
Effect of Chloride Addition in Sulfate Solution



- With 0.1M Cl⁻ addition
 - Did not show visible effect as compared to polarization behavior in straight sulfate
 - Same i_{pass} , E_{br} and E_{rp} were recorded
- With 1.0M Cl⁻ addition
 - Slightly lower E_{br} for both the samples
 - Repassivation behavior for both the samples decreased by 300 mV
 - Repassivation potential in straight sulfate (1M Na₂SO₄) 300 mV more than 4M NaCl



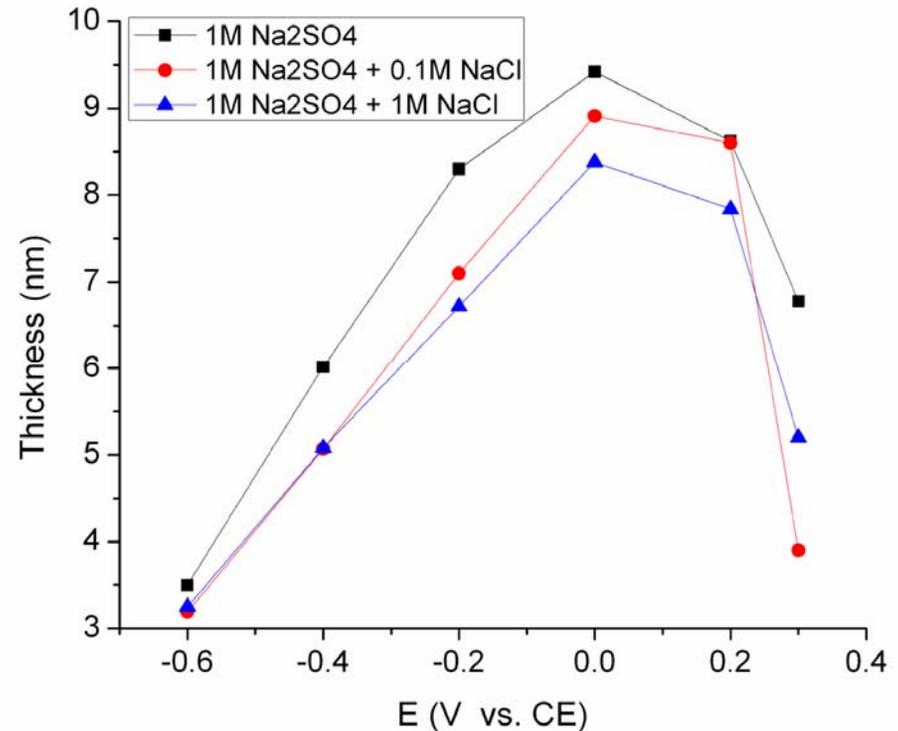
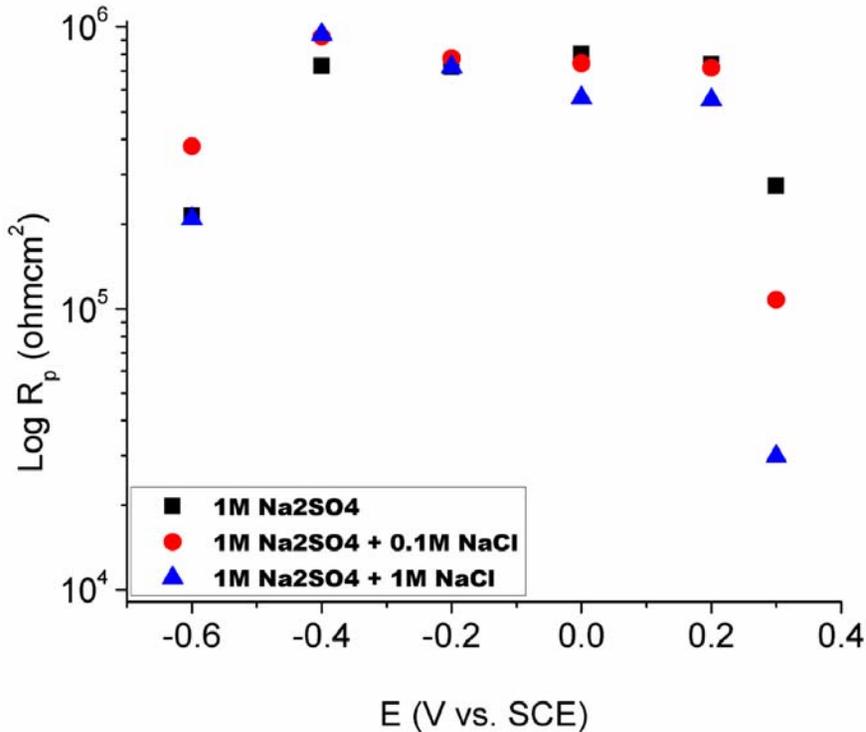
Effect of Sulfate Addition in Chloride Solutions



- Initial current dropped to 10 μA in 7 minutes, further dropped to 1 μA in 157 minutes, and stayed below 1 μA during the rest of the 28 day test
- No initiation of severe crevice corrosion in 28 days
- Superficial corrosion (less than 0.2 μm penetration) beneath the crevice feet
- Noise (current spikes) during the test are similar to those observed in chloride solutions
- Hypothesis is that many metastable pitting/crevice events occur but no stable, severe crevice corrosion initiated
- Work in progress on the effect of Cl⁻ in SO₄²⁻ solution



Effect of Chloride Addition in Sulfate Solution



Polarization resistance of the passive film as a function of nitrate/chloride ratio at different voltages

Passive film thickness as a function of nitrate/chloride ratio at different voltages

- Bode phase and magnitude plots similar to shown in nitrate effect in terms of phase angle change and resistance- capacitance response
- Film resistance increases with increase in potential, almost the same resistance values at -0.4, -0.2, 0.0 V-sce, and decreases with further increase in potential to transpassive region (0.3 V-sce)
- Film resistance lowest with addition of 1M NaCl in transpassive region at E=0.3 V-sce
- Cl⁻ shows detrimental effect of the passive film properties



Summary/ Chloride Addition in Sulfate Solution

- **Forward-reverse scans show that 0.1M Cl⁻ addition had no effect and 1M Cl⁻ addition decreased the corrosion resistance in 1M sulfate**
- **Constant potential test in straight sulfate with aggressive crevice assembly showed that sulfate did not initiate severe crevice corrosion over long exposure time**
- **Impedance studies showed that film resistance and thickness decreased when chloride content increased in sulfate solutions**
- **Based on above results, chloride is a detrimental anion for film formed on alloy C-22 and nitrate and sulfate anions can be beneficial depending upon their concentration**



Overall Summary

- Overall, effect of anions was greater on the repair-repassivation behavior than on the intact passive film properties
- Nitrate was more effective anion in comparison with sulfate in inhibition of crevice corrosion in chloride solutions
 - Beneficial effect of nitrate was greater with increasing $\text{NO}_3^-/\text{Cl}^-$ ratio
 - Sulfate addition resulted in longer incubation time, fewer coulombs to repassivate
- With chloride addition to sulfate solution, the repassivation potential was more negative



Future Directions

- **Perform long-term immersion tests (similar to localized corrosion tests) to observe changes in the passive film properties and evaluate correlation with localized corrosion**
- **Couple the above tests with surface analysis techniques like XPS depth analysis**



Acknowledgement and Disclaimer

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- **The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OCS.**

