Modeling the effects of solution chemistry on the localized corrosion of engineering alloys

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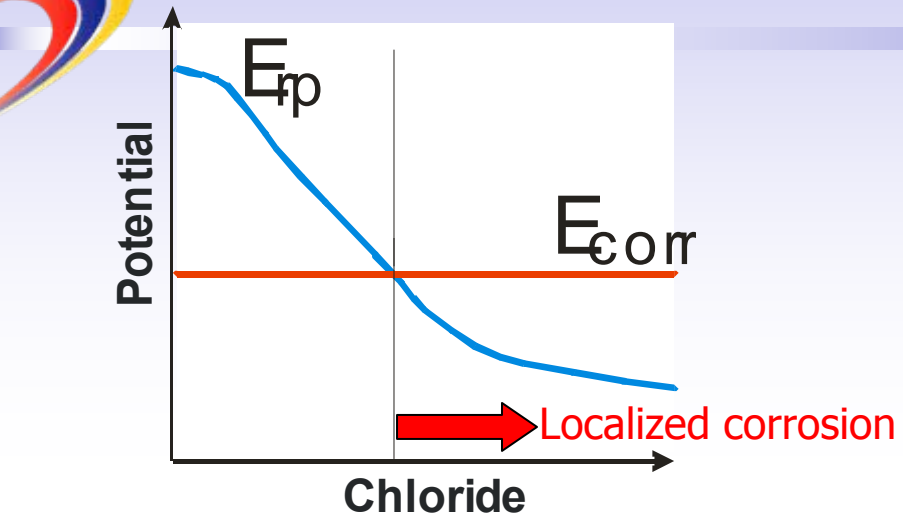
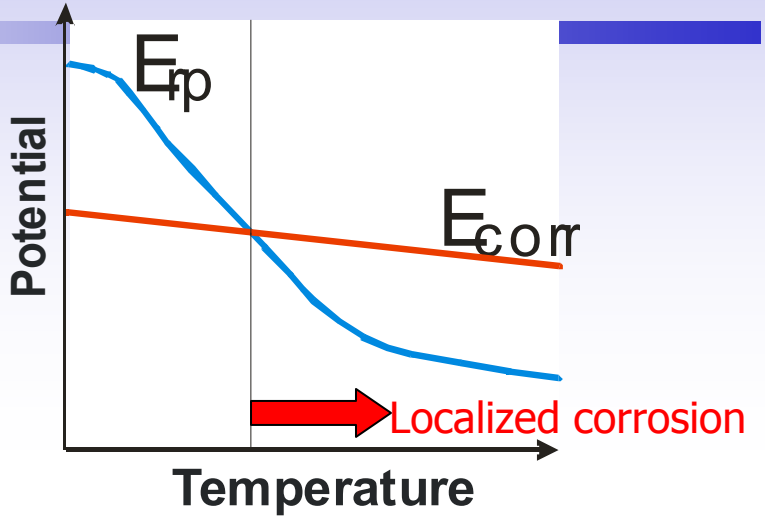
Problem

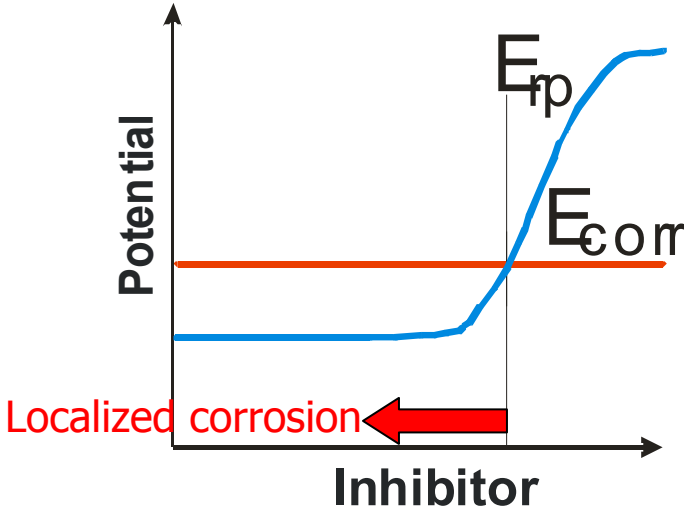
- Localized corrosion shows great complexity as a function of
  - Chemical species in aqueous environments
  - Concentrations of components
  - Temperature
  - Composition and microstructural features of the alloy, etc.
- Focus area: Modeling the effect of aggressive (chloride) and inhibitive ions (oxyanions)
- Engineering approach: Predict two characteristic potentials as a function of environmental conditions
  - Corrosion potential
  - Repassivation potential

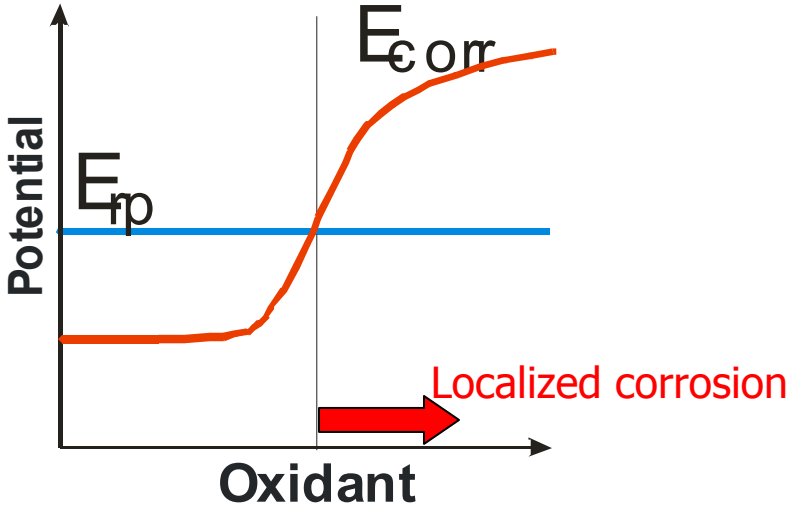
Predicting localized corrosion:

Repassivation and corrosion potentials versus environmental conditions





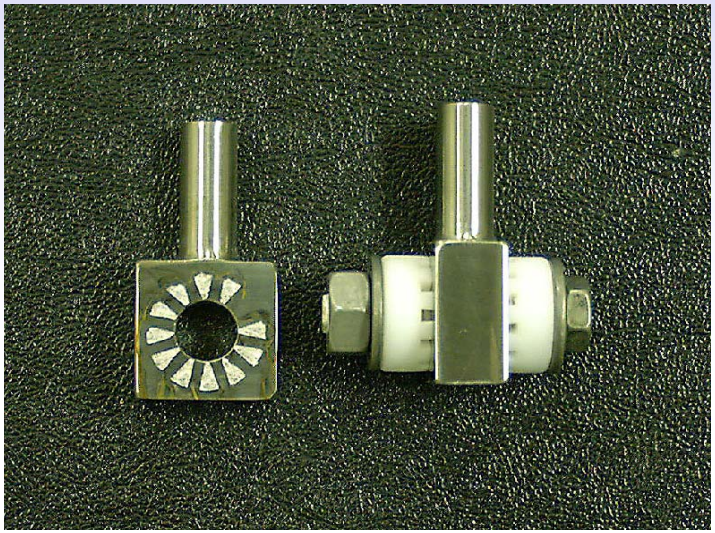




Scope

- Develop an experimental matrix of repassivation potentials for alloy – chloride – oxyanion combinations
- Reproduce and correlate the data using a mechanistic model
- Generalize the model in terms of alloy composition to be able to predict the localized corrosion of alloys that have not been experimentally investigated

Experimental Methods



Performed at Southwest Research Institute

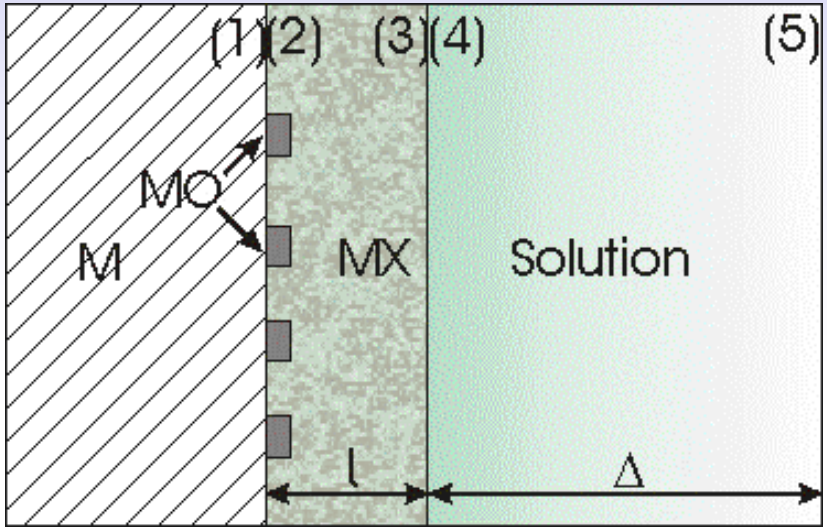
- Repassivation potential measured using crevice corrosion specimens
- Tests are designed to initiate crevice corrosion and measure potential at which crevice corrosion stops
- Methods:
  - Cyclic potentiodynamic polarization (CPP)
  - Potential staircase

Experimental database: Combined effect of Cl^- and inhibitors

- Matrix of:
  - Inhibiting anions:
    - Molybdates
    - Hydroxides
    - Vanadates
    - Sulfates
    - Nitrates
    - Nitrites
  - Alloys:
    - 316L
    - 600
    - 690
    - 254SMO
    - 2205
    - 825
    - S-13Cr
    - 22

Calculating repassivation potential

- Potential below which stable pitting or crevice corrosion do not occur
- Relatively insensitive to surface finish as well as prior pit depth as long as the pit depth exceeds a certain minimum value



- The model simulates electrochemical processes in a pit or crevice in the limit of repassivation

Fundamentals of the E_{rp} model

- The expressions can be solved in the limit E -> E_{rp}

$$1+\sum_j\left[\left(\frac{i_{rp}}{i_p}-1\right)\frac{l_j''}{i_{rp}}\right]\theta_j^{n_j}\exp\left(\frac{\xi_j F E_{rp}}{RT}\right)=\sum_i\frac{k_i''}{i_{rp}}\theta_i^{n_i}\exp\left(\frac{\alpha_i F E_{rp}}{RT}\right)$$

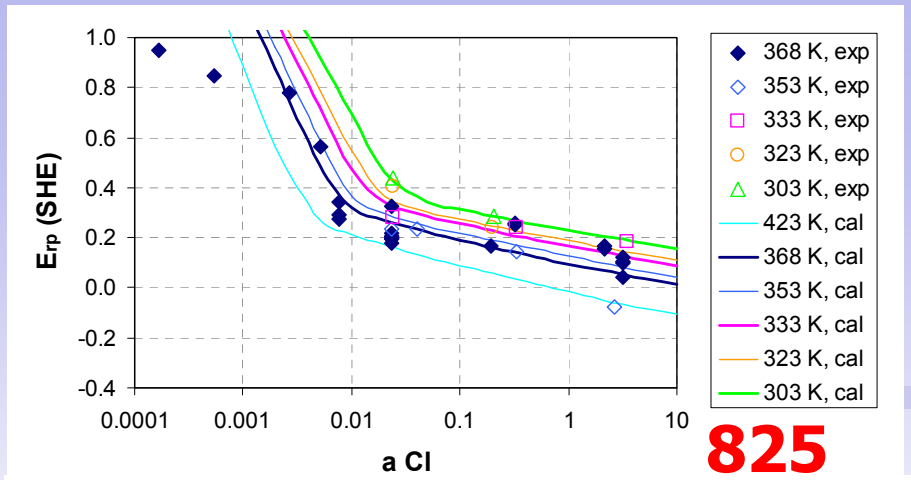
Contributions of water and inhibiting species, which participate in oxide formation in the repassivation process

Contributions of aggressive species, which form complexes with metal species

Fundamentals of the E_{rp} model

- Model parameters
  - Parameters for metal dissolution reactions mediated by the adsorption of aggressive species
    - Gibbs energy of activation
    - Reaction order with respect to aggressive species
  - Parameters for the formation of oxide mediated by the adsorption of water or inhibitor species
    - Gibbs energy of activation
    - Electrochemical transfer coefficient
- Activities of aqueous species are calculated from a thermodynamic electrolyte model

E_{rp} in Cl solutions: Alloys 825, 690, and 316L



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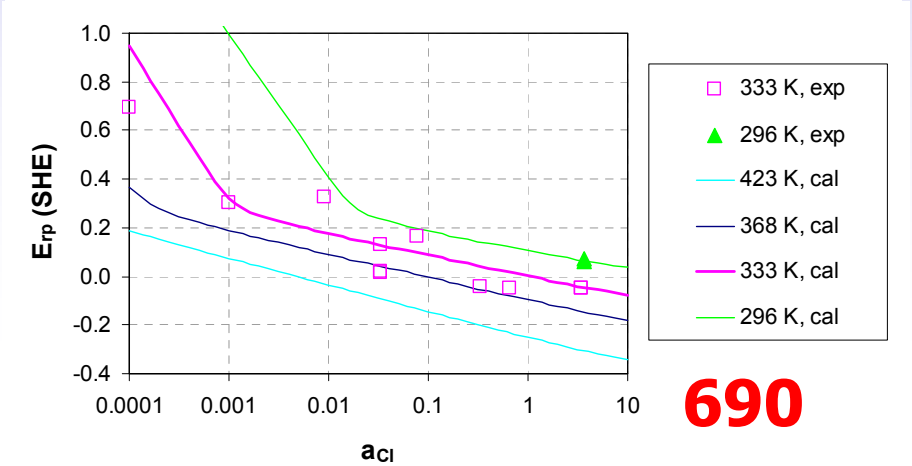

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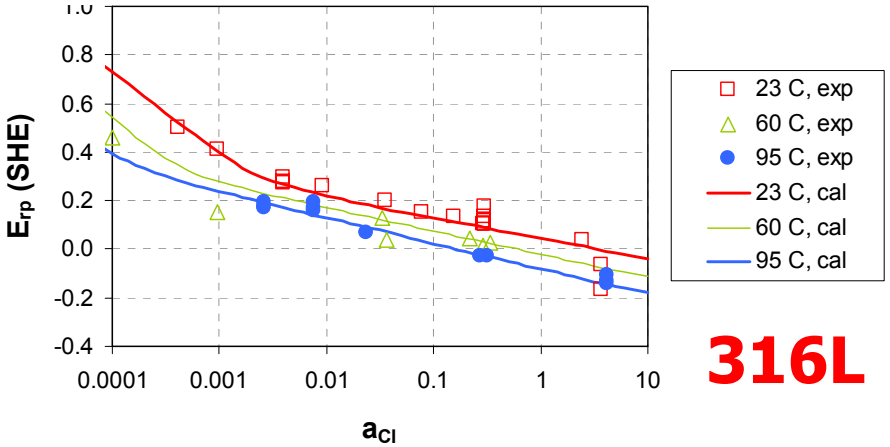
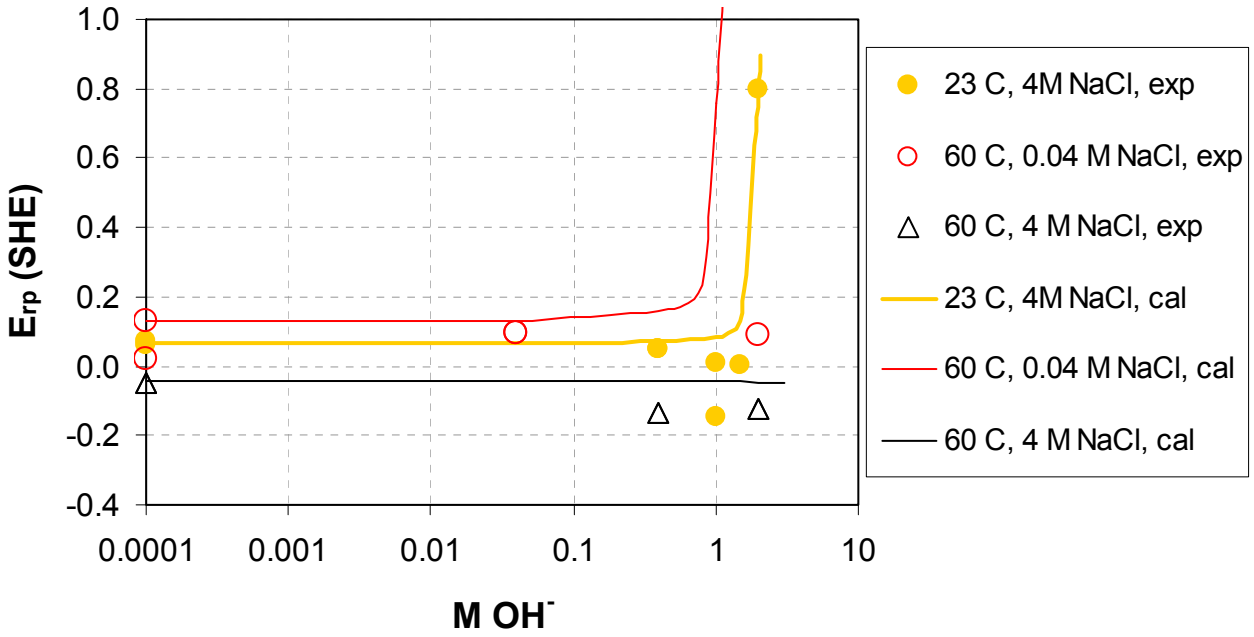


316L

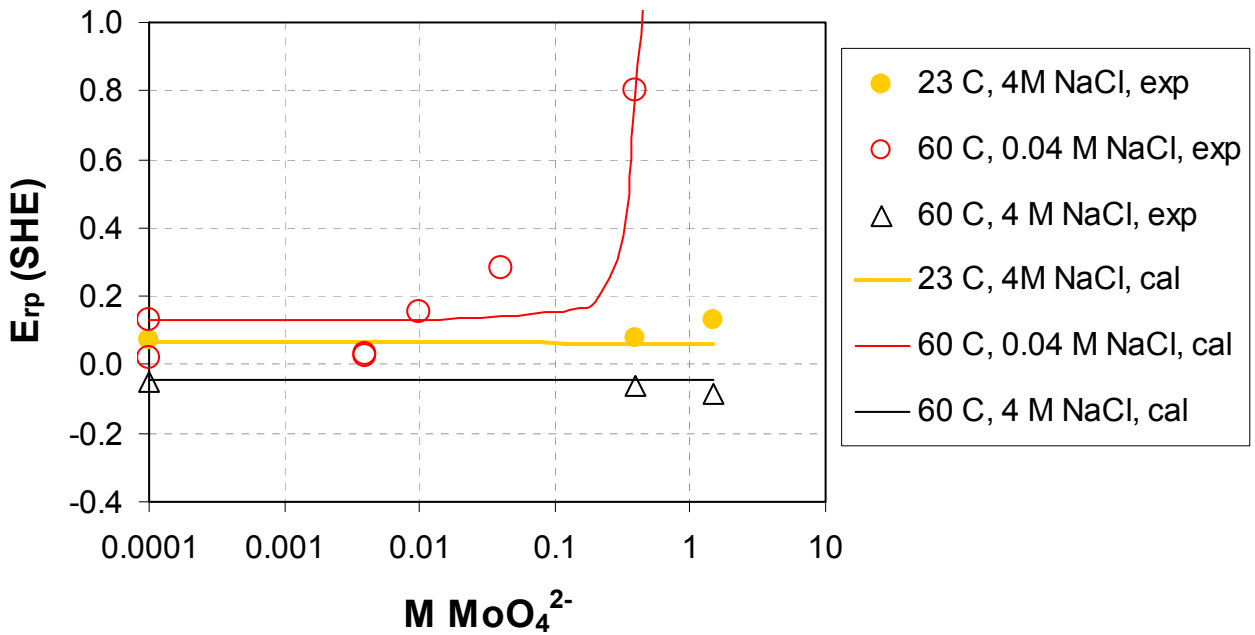
- The slope changes as a function of chloride activity
- The steep portion of the slope is more pronounced for more corrosion resistant alloys

Alloy 690: E_{rp} for Cl^- - OH^- systems



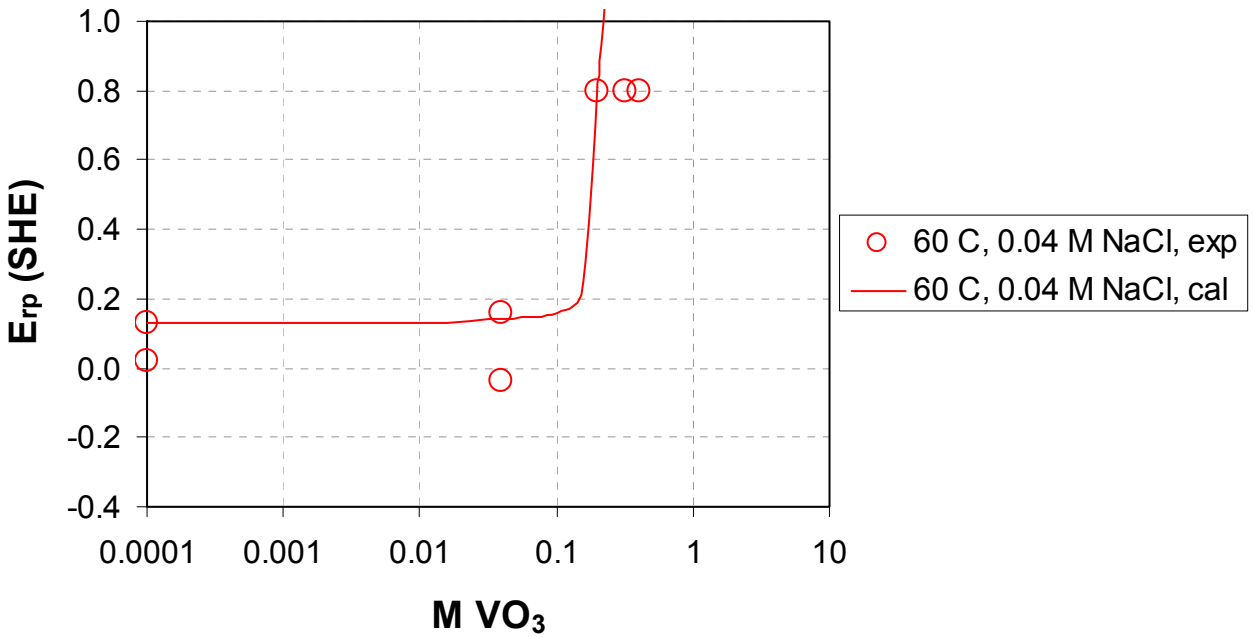
- Steep increase in slope indicates inhibition at a certain OH^- concentration
- At some conditions, inhibition cannot be achieved due to solubility limits

Alloy 690: E_{rp} for Cl^- - MoO_4^{2-} systems



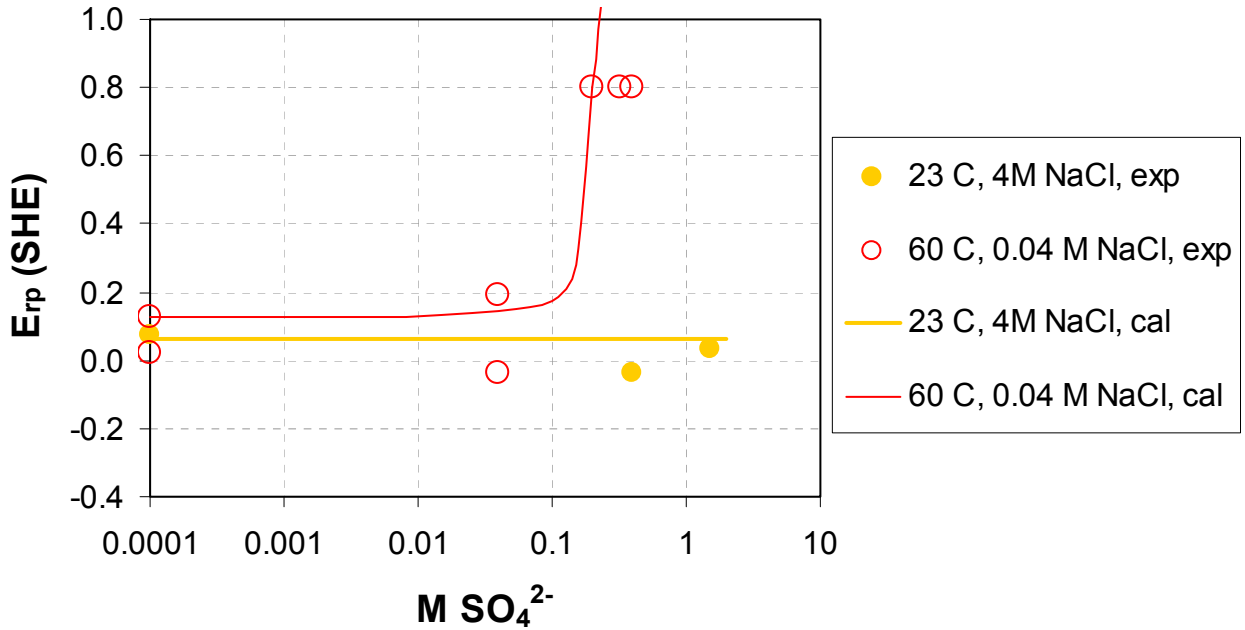
- Transition occurs at somewhat lower concentrations of molybdates than hydroxides
- Solubility limits are also significant

Alloy 690: E_{rp} for Cl^- - VO_3^- systems



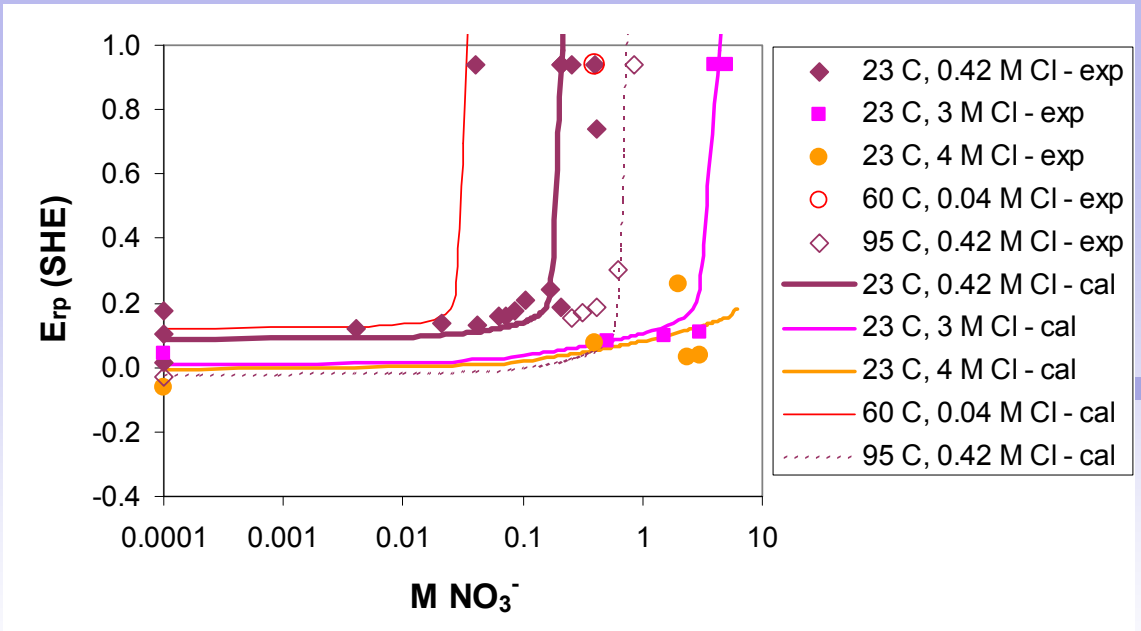
- Transition occurs at still lower concentrations of the inhibitor than in the case of molybdates

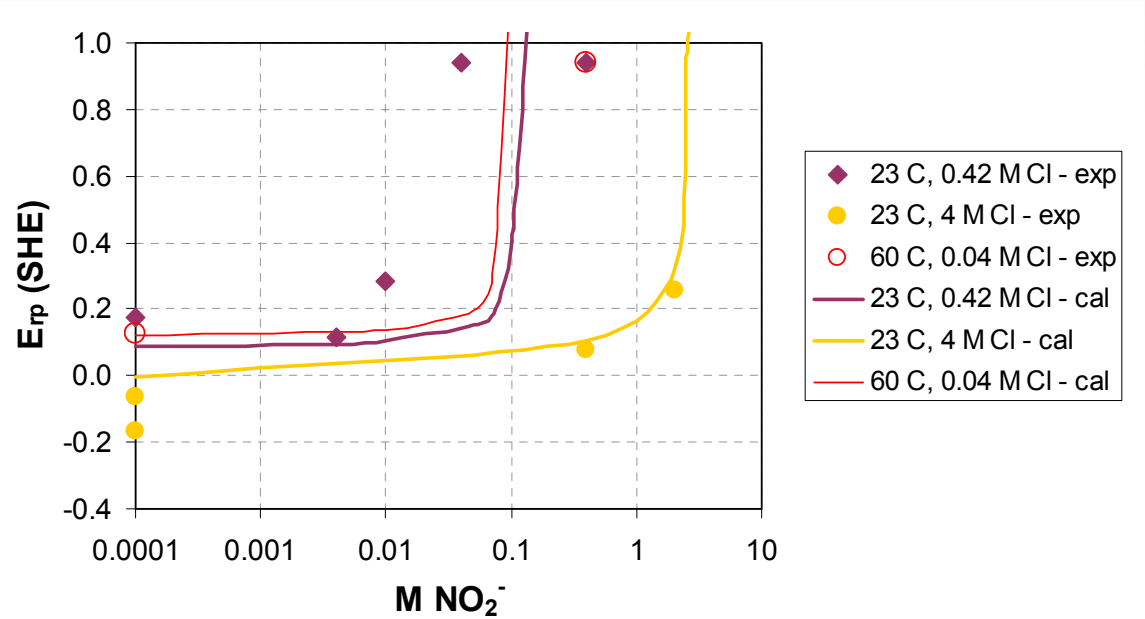
Alloy 690: E_{rp} for Cl^- - SO_4^{2-} systems



- Sulfates are reasonably effective for alloy 690 even though they are less effective than other ions for 316L

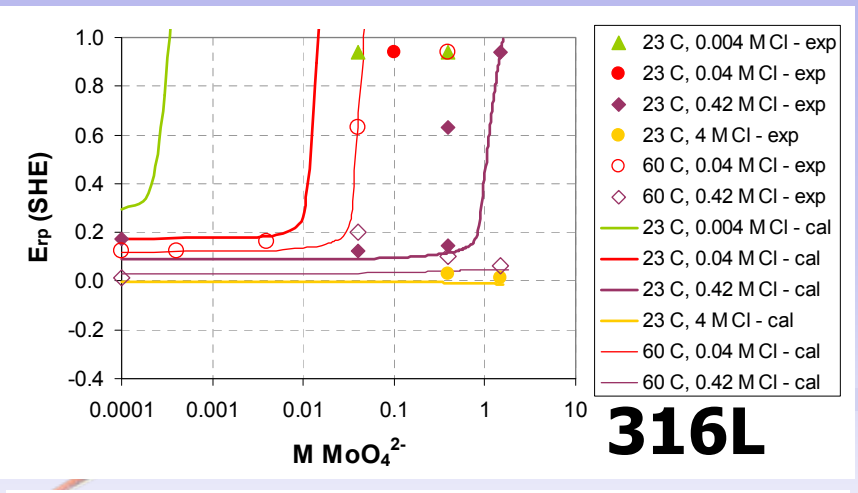
316L stainless: Nitrates vs. nitrites



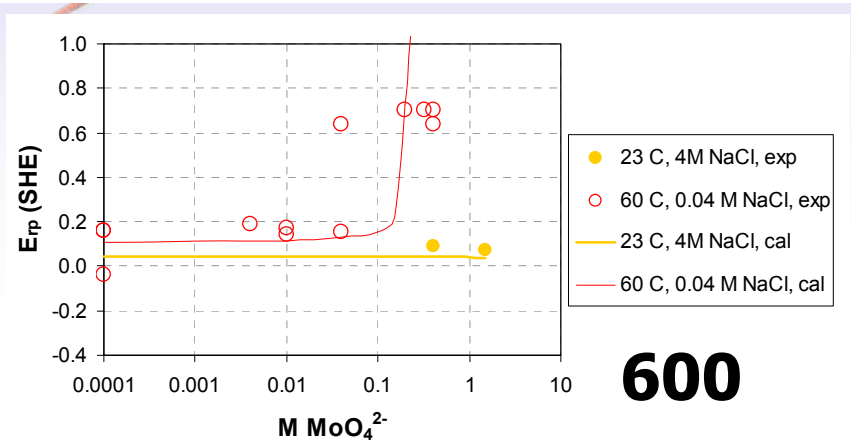


- Both nitrates and nitrites are effective as inhibitors
- Solubility limits at high Cl concentrations may favor nitrites

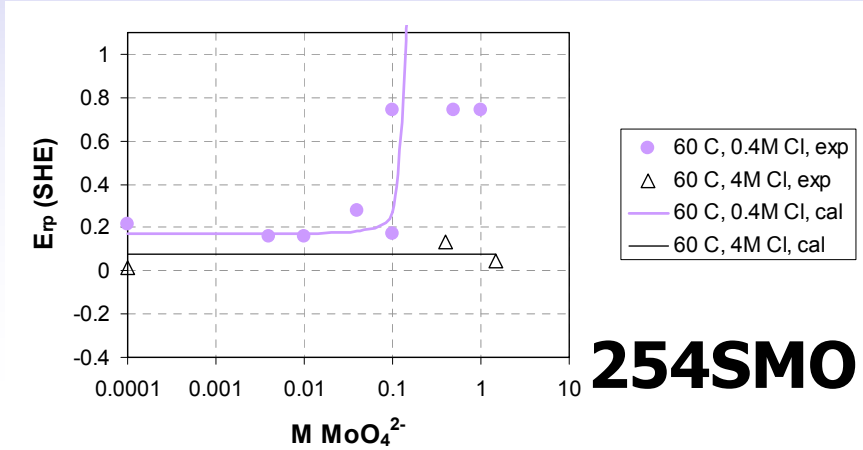
Effect of molybdates on E_{rp} of various alloys: Transition depends on the corrosion resistance of the alloy; patterns are similar



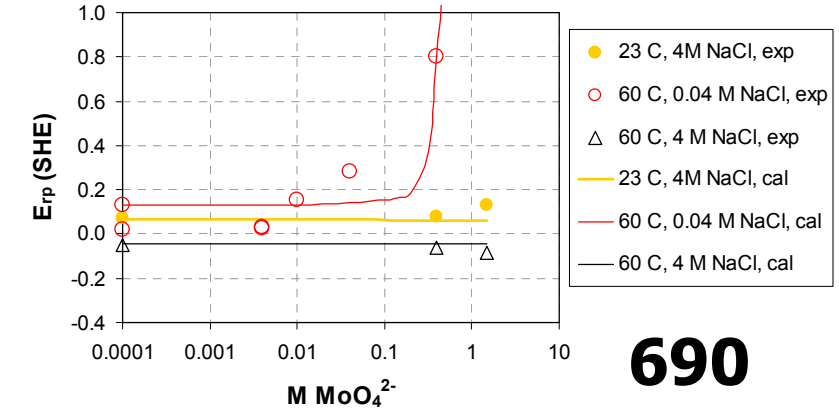
316L



600



254SMO



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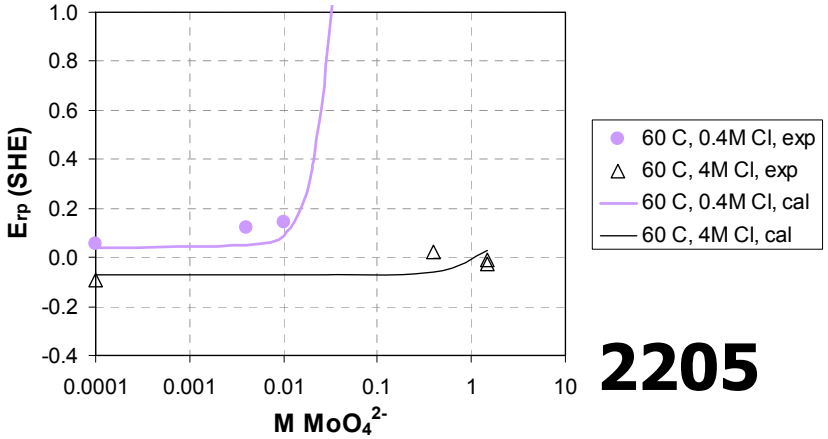

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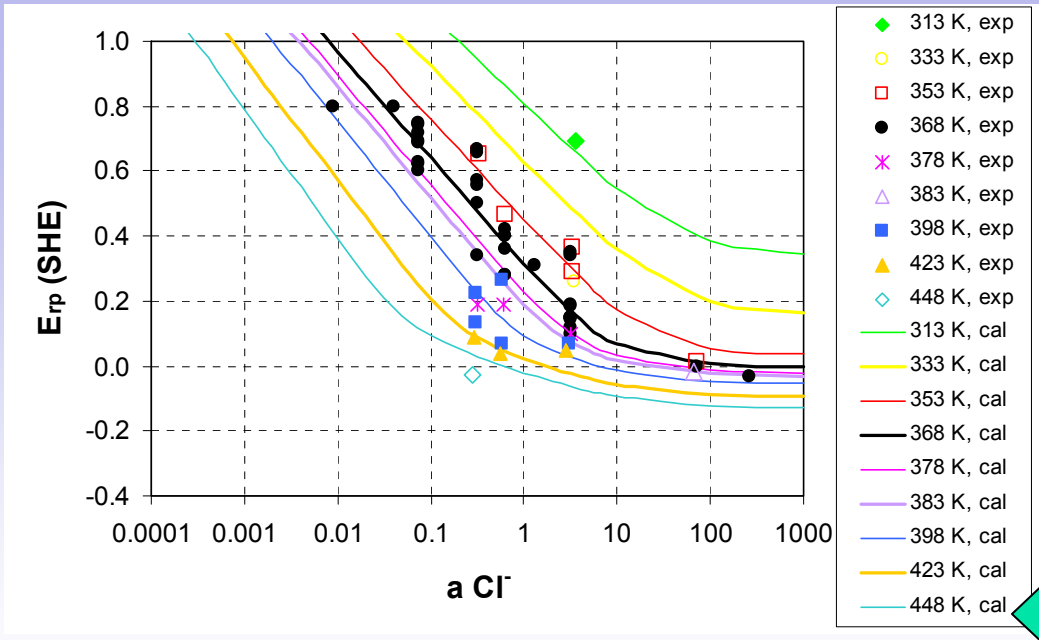
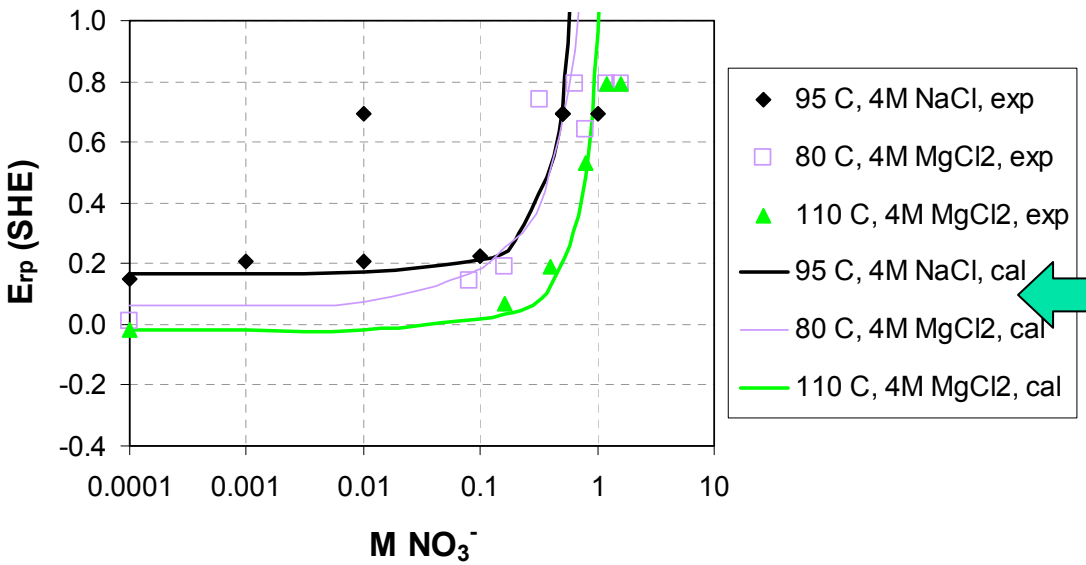
Alloy 22 in Cl^- - NO_3^- solutions

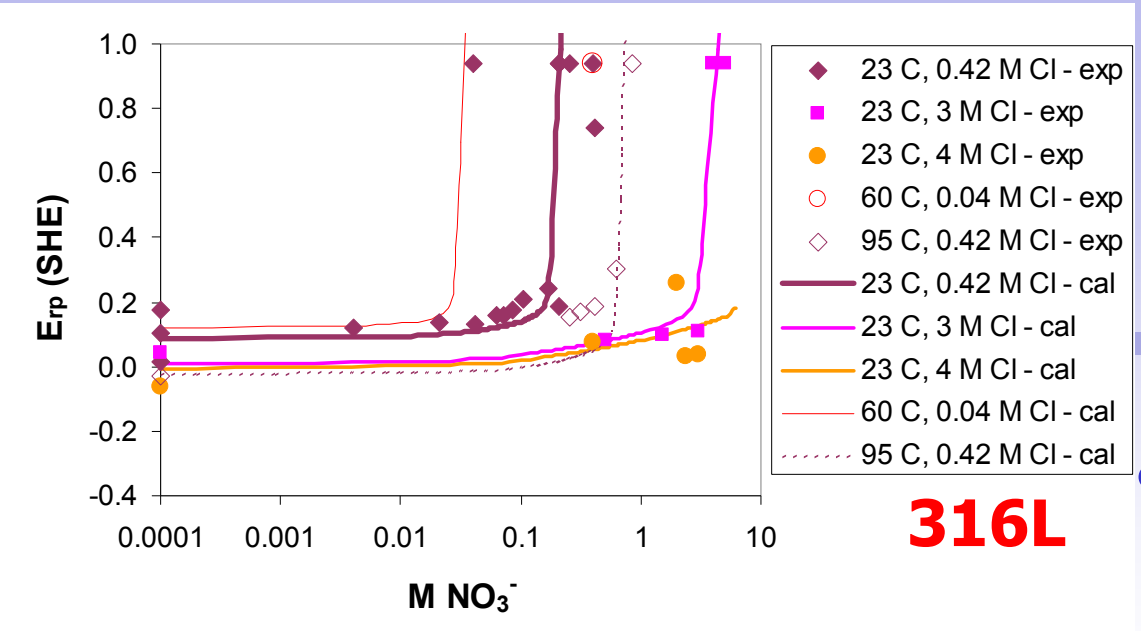


- The alloy is resistant to localized corrosion (high E_{rp} values)

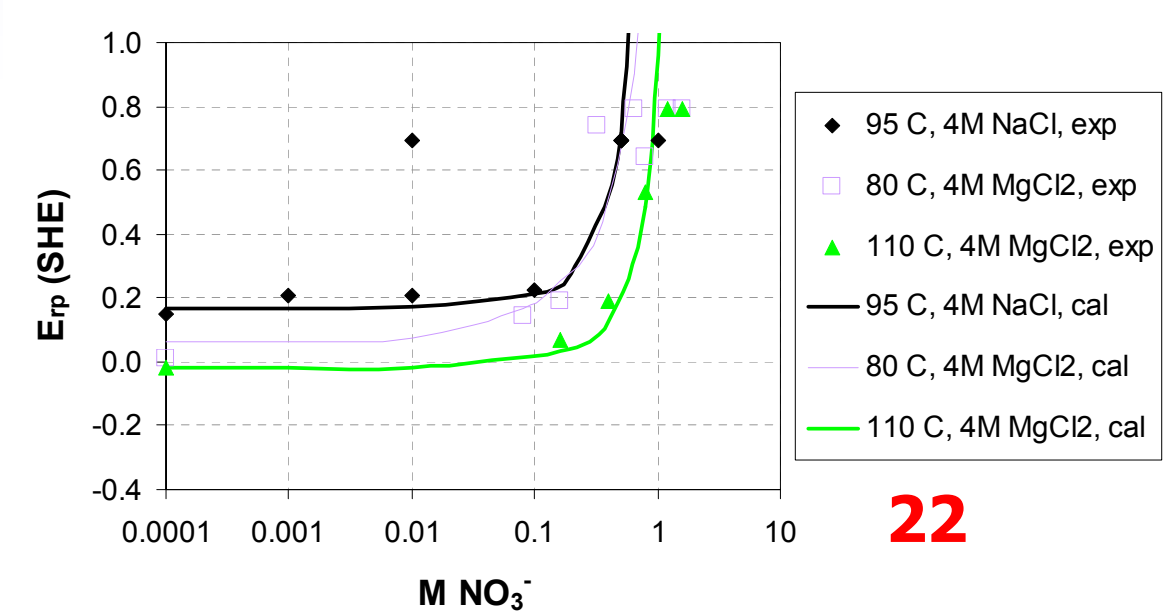


- Nitrates can inhibit even concentrated chloride solutions at high temperatures

E_{rp} in Cl^- - NO_3^- solutions: Alloys 316L and 22



316L



22

- Inhibition is easier for a more resistant alloy – inhibition can be achieved for alloy 22 at higher temperatures at high Cl concentrations

E_{rp} correlation
Step 1: Parameter for Cl-only systems

- Reaction orders and electrochemical transfer coefficients have generalized values
- Calculation of the Gibbs energy of activation
  - Baseline contribution for Fe-Ni-Cr alloys

$$\Delta g^{\neq}_{A,Cl}(Cr,Fe,Ni) = \Delta g^{\neq}_{A,Cl}(Fe)w^2_{Fe} + \Delta g^{\neq}_{A,Cl}(Ni)w^2_{Ni} - 6.789 w_{Cr} w_{Ni} + 132.3 w_{Cr} w_{Ni}$$

  - Increment due to the effect of Mo and W

$$\Delta g^{\neq}_{A,Cl}(Mo,W) = w_{Cr}(w_{Mo} + w_W)^{0.4}(488.55 x^{1.3}_{Ni} + 634.08 x^{1.3}_{Fe})$$

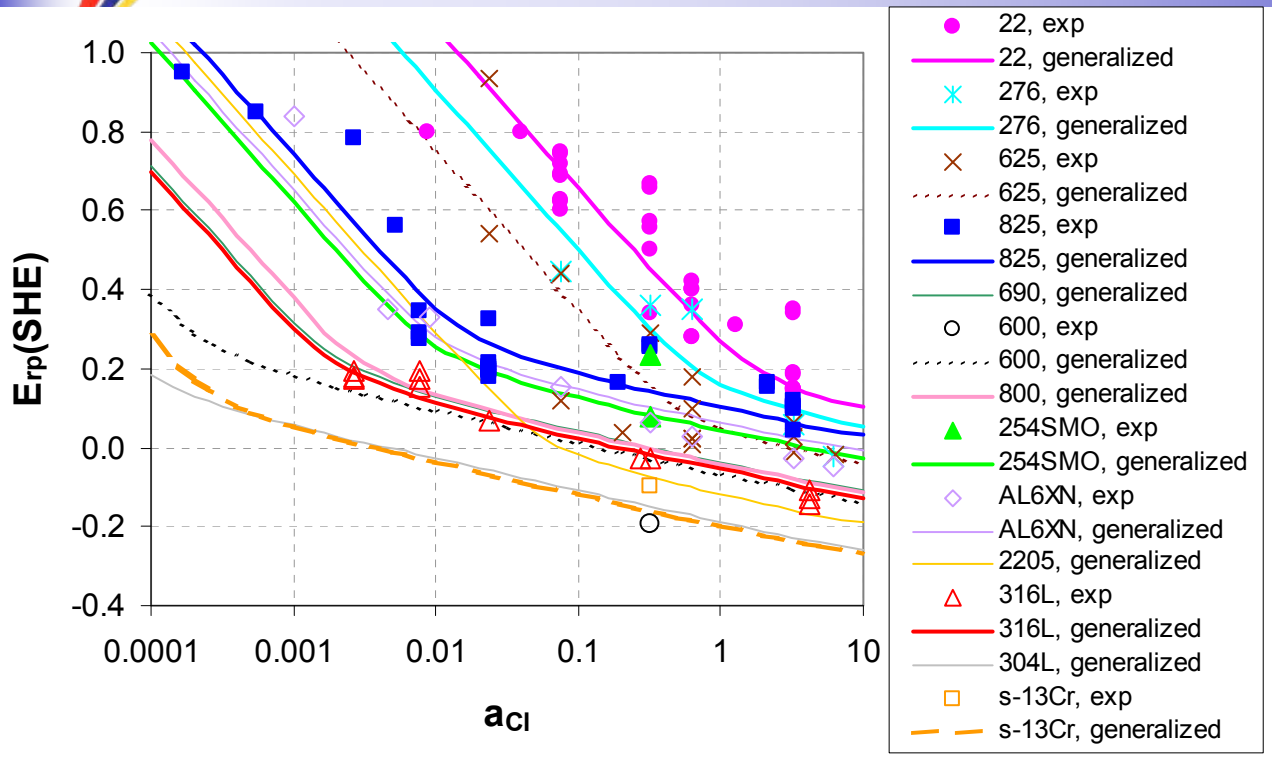
  - Increment due to N

$$\Delta g^{\neq}_{A,Cl}(N) = w_N w_{Cr}\left[1.967e6 w_{Mo} - 0.148e6(w_{Fe} + 2w_{Ni})\right]$$

  - Miscellaneous contribution of other elements

$$\Delta g^{\neq}_{A,Cl}(misc) = -1542 w_{Nb} w_{Cr}$$

Generalized correlation for predicting E_{rp} of Fe-Ni-Cr-Mo-W-N alloys



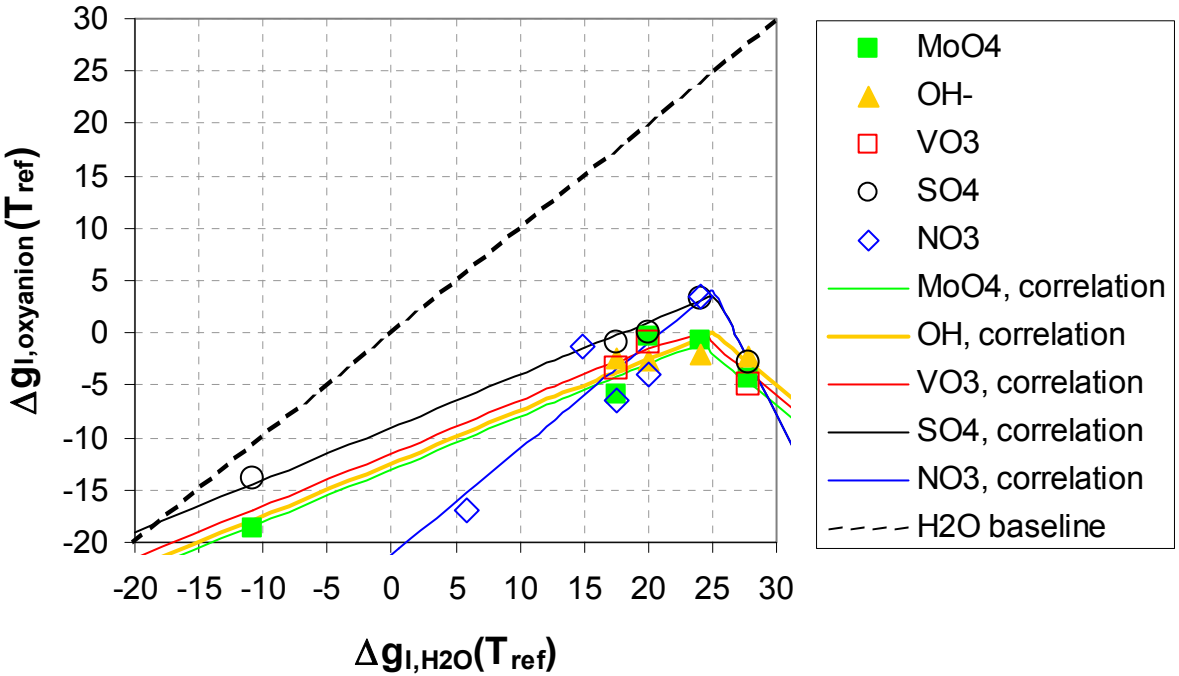
- Reproduces E_{rp} for 15 metals (13 stainless steels and nickel-base alloys, Ni, and Fe)
- Predictions have been verified from 296 K to 423 K

Example: T = 368 K

E_{rp} correlation
Step 2: Effect of oxyanions

- An alloy's tendency for repassivation in oxyanion-containing environments is correlated with that in oxyanion-free solutions
- A relationship exists between the Gibbs energy of activation for the formation of oxide due to the adsorption of oxyanions and that due to the adsorption of H_2O

E_{rp} correlation
Step 2: Effect of oxyanions



The symbols represent various alloys

- E_{rp} parameters for Cl – oxyanion solutions can be predicted based on alloy composition
- The quality of such a prediction is similar to the quality of individual correlation

Summary

- A matrix of repassivation potential data has been established for alloys 316L, 600, 690, 254SMO, 2205, 825, and S-13Cr in the presence of various combinations of Cl^- with OH^-, MoO_4^{2-}, VO_3^-, SO_4^{2-}, NO_3^- and NO_2^- ions
- A mechanistic E_{rp} model reproduces the data with good accuracy
- The model predicts the transition from the concentration range in which localized corrosion is possible to the region in which inhibition is expected
- The model can be used to predict the repassivation potential in complex process environments
- A generalized correlation makes it possible to predict E_{rp} for Fe-Ni-Cr-Mo-W-N alloys for which experimental data are not available