Modeling of Inhibitor Release from Epoxy Coating with Hydrotalcites Using Finite Element Method

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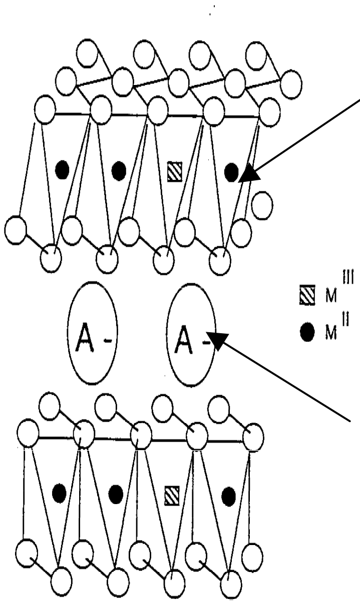
Inhibition by Ion Exchange Using Hydrotalcites

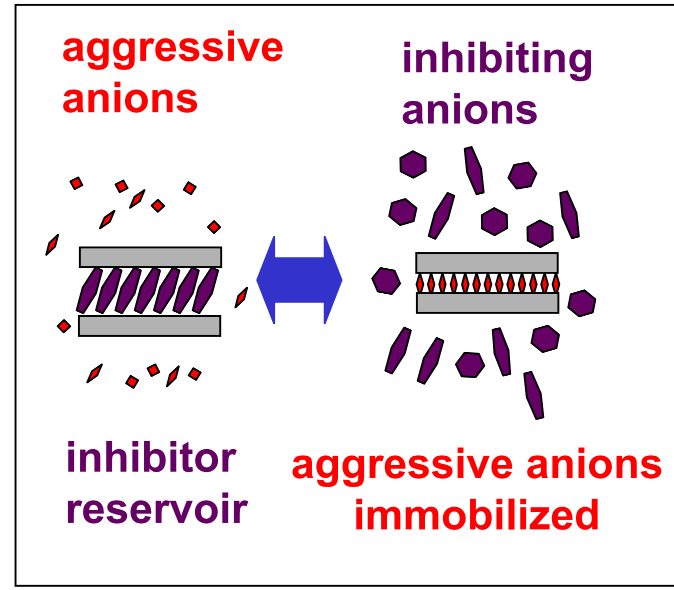


Host layer: double metal hydroxide:
Al-Mg, Al-Li, Al-Zn, Al-Ni . . .

- high temperature thermal stability
- anion selectivity
- exchange kinetics

Anion interlayer: OH^-, CO_3^{2-}, NO_3^-, VO_3^-, $V_{10}O_{28}^{6-}$, CrO_4^{2-}, $Fe(CN)_6^{3-}$, $S_2O_8^{2-}$, MoO_4^{2-}, MnO_4^{2-}, . . .

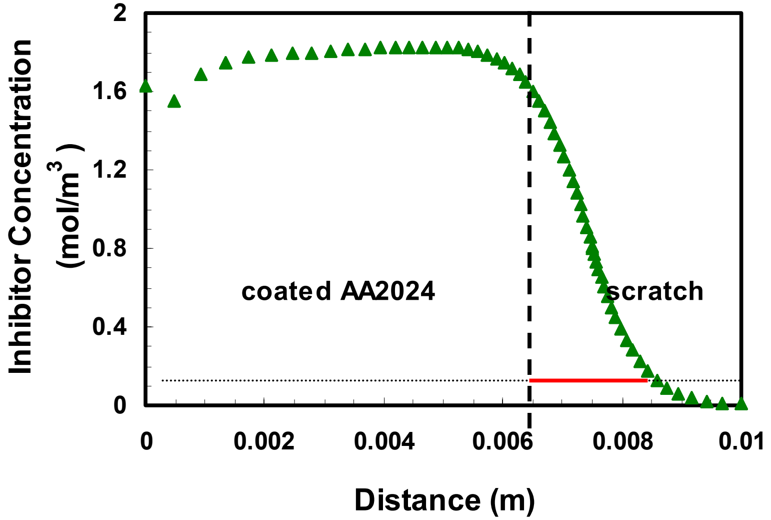
- inhibitors
- sensing ions, e.g. pH
- hydrophilic



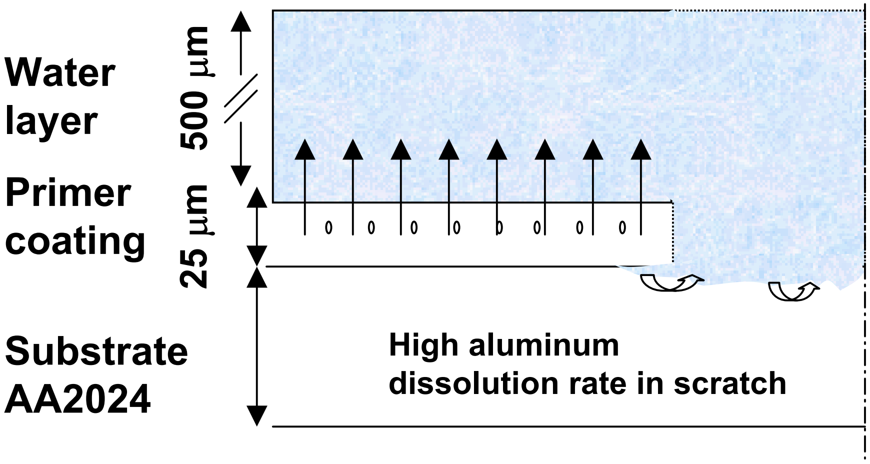
Hydrotalcites compound released inhibiting anions and immobilized aggressive anions

$[M_{1-x}M'_x(OH)_2]^{x+}(X)_{x/m}.nH_2O$, where M=Zn(II), M′=Al(III) and $X=[V_{10}O_{28}]^{6-}$ (decavanadate)

Model the Scratch on Coating

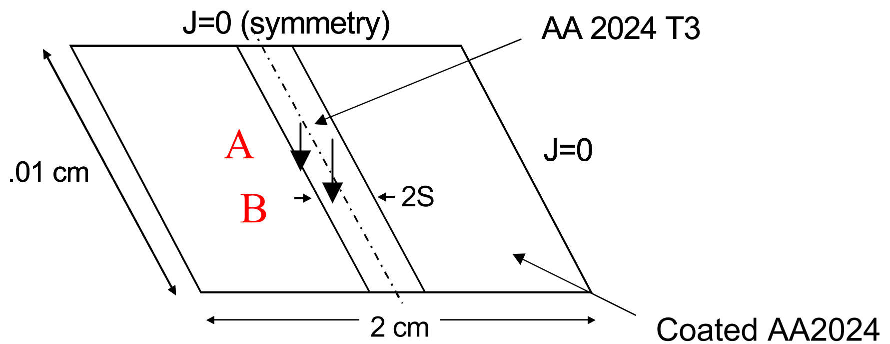


Inhibitor is released and transports horizontally



(Figure not to scale)

Sample Geometry



J = Electric Flux

Figure not to scale

Model and Assumptions

- Transport modes: diffusion and migration
- Complex reaction system
  - Electrochemical reactions

    $Al \rightarrow Al^{3+} + 3e^-$ anodic reaction

    $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ cathodic reaction

  - Chemical reactions/processes

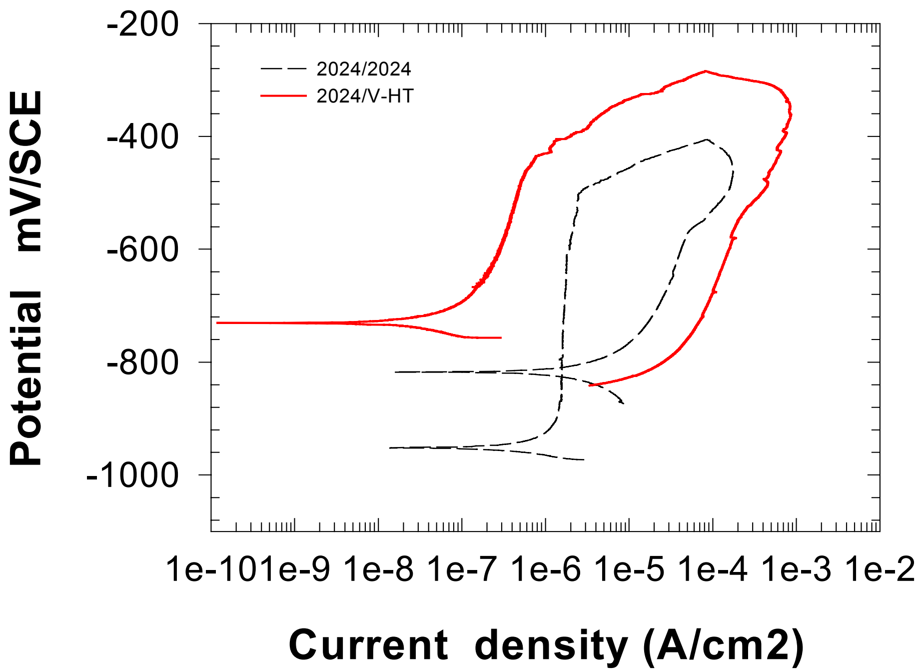
    $Al^{3+} + yH_2O = Al(OH)_y^{3-y} + yH^+$ hydrolysis

    $V_6O_{28}^{6-}{}_{(HT)} = V_6O_{28}^{6-}{}_{(sol)}$ inhibitor release

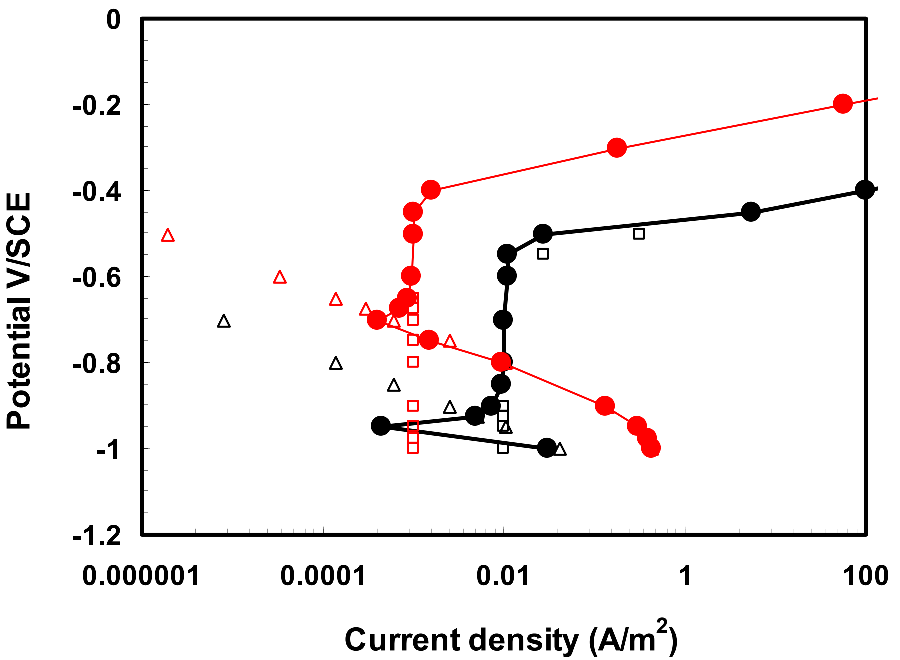
    $Cl^-_{(sol)} = Cl^-_{(HT)}$ chloride gettering

- Mass balance (11 chemical species)
- Electrical charge balance (electrochemical reaction)
- Solution electroneutrality (Na^+ to neutralize)

Electrochemical Boundary Conditions



AA2024-T3 with/without exposure to V/HT in simulated scratch cell, 0.1 M NaCl



Simulated kinetics model

Modeling and Simulation System Development

Numerical calculation

- Finite element method (ANSYS)

Engineering software development

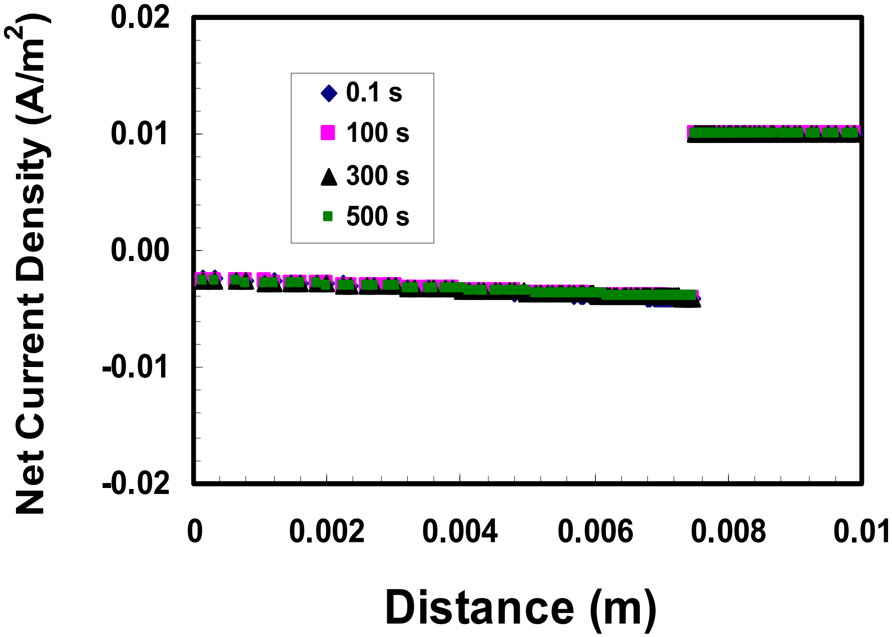
- C++ Object Oriented Programming
- Open source codes and executable files available on web (IT IS FREE)

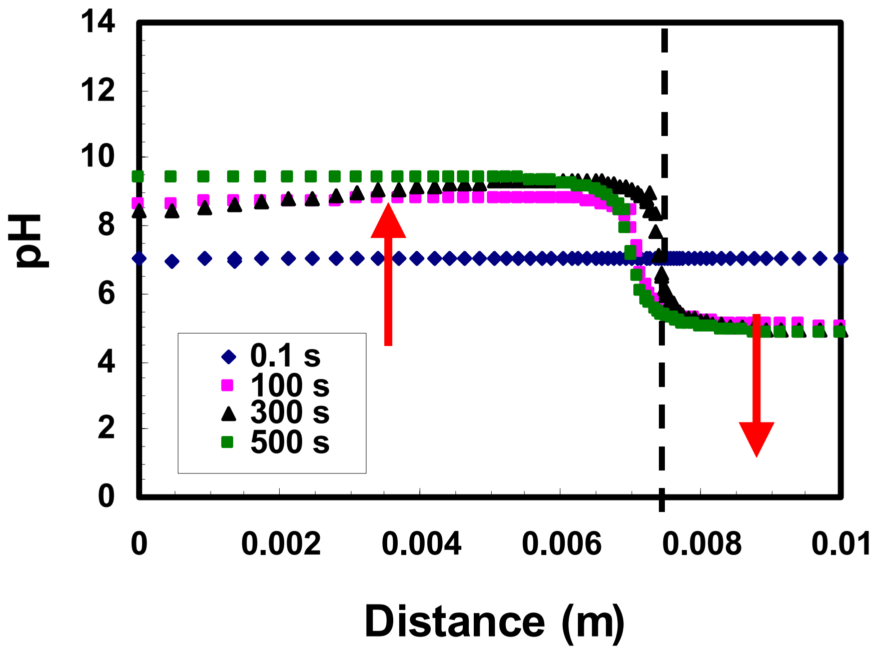
  http://www.virginia.edu/cese/research/crevicer/
- Encourage different researchers to use for the specific purposes
- 1994-present at University of Virginia lead by R.G. Kelly

Computing facility

- PC is enough
- Super computer might be needed for the long term simulation

I(x) and pH Evolution

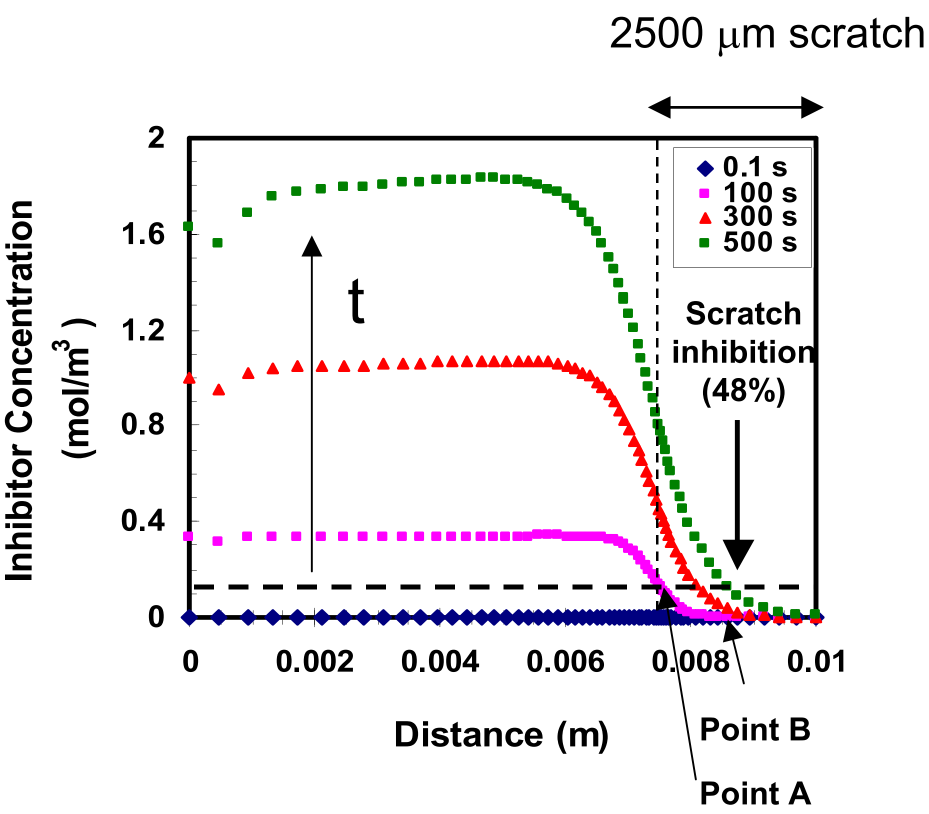


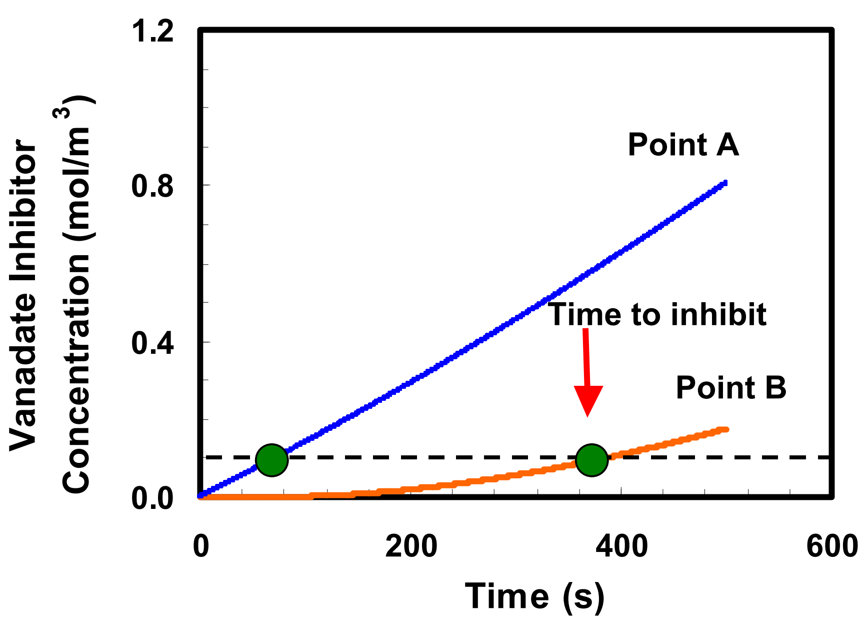


2500 μm scratch, 500 μm water layer,

0.1 M NaCl, release rate (A4)

Inhibitor Concentration Evolution and Protection of the Scratch

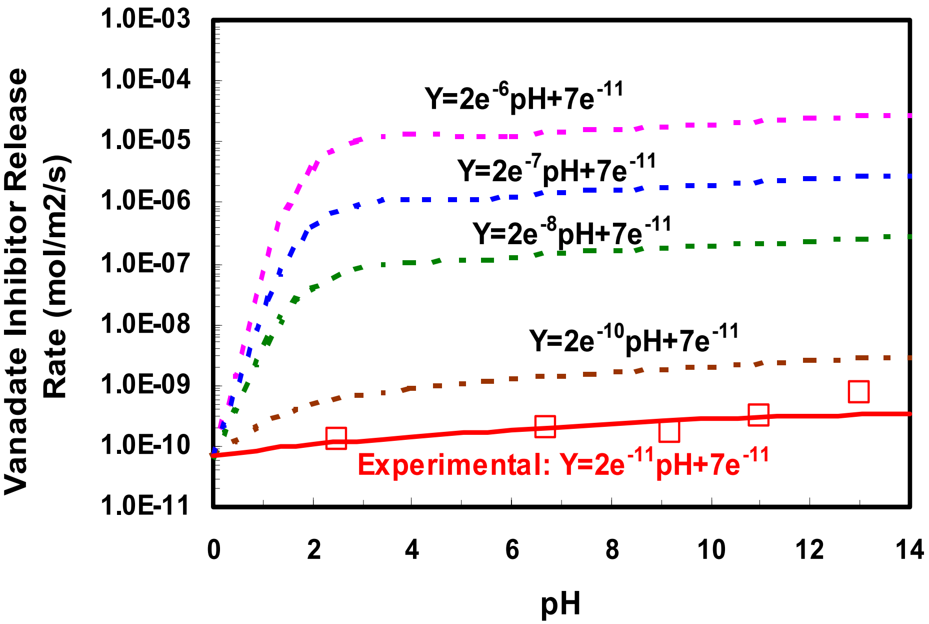


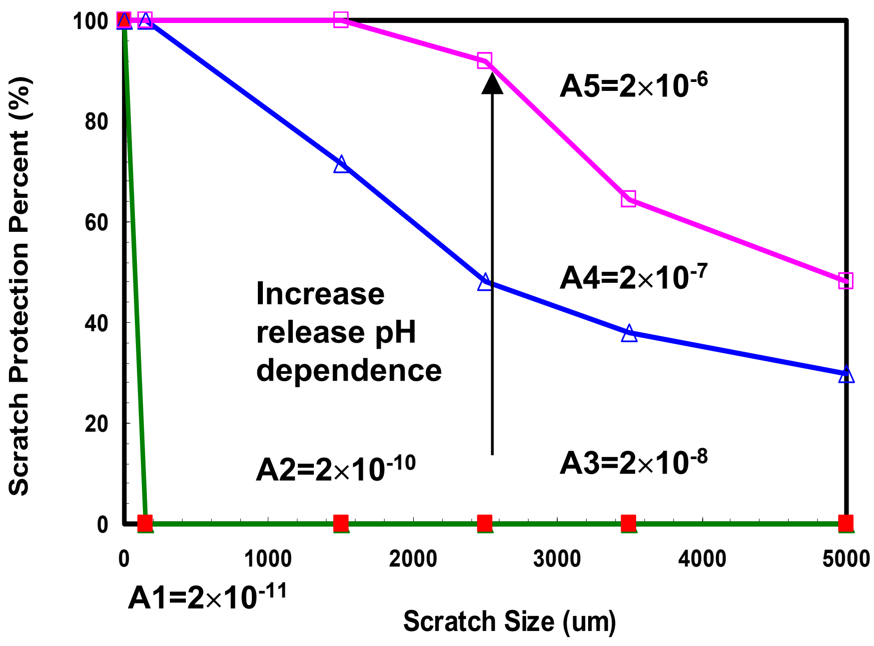


2500 μm scratch, 500 μm water layer, 0.1 M NaCl, release rate (A4)

Effect of Scratch Size and Inhibitor Release pH Dependencies

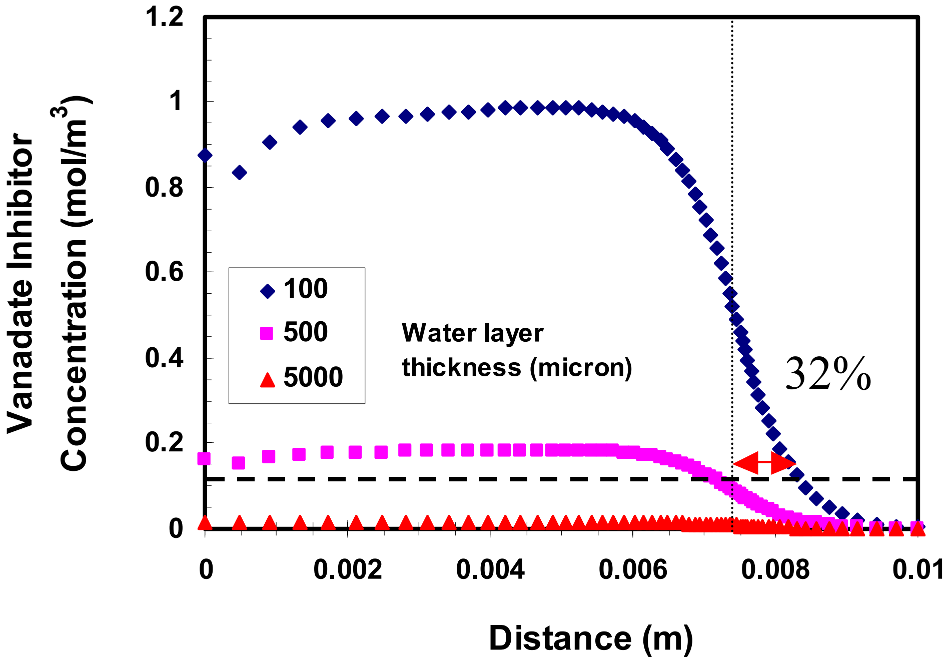
Y=A pH + C



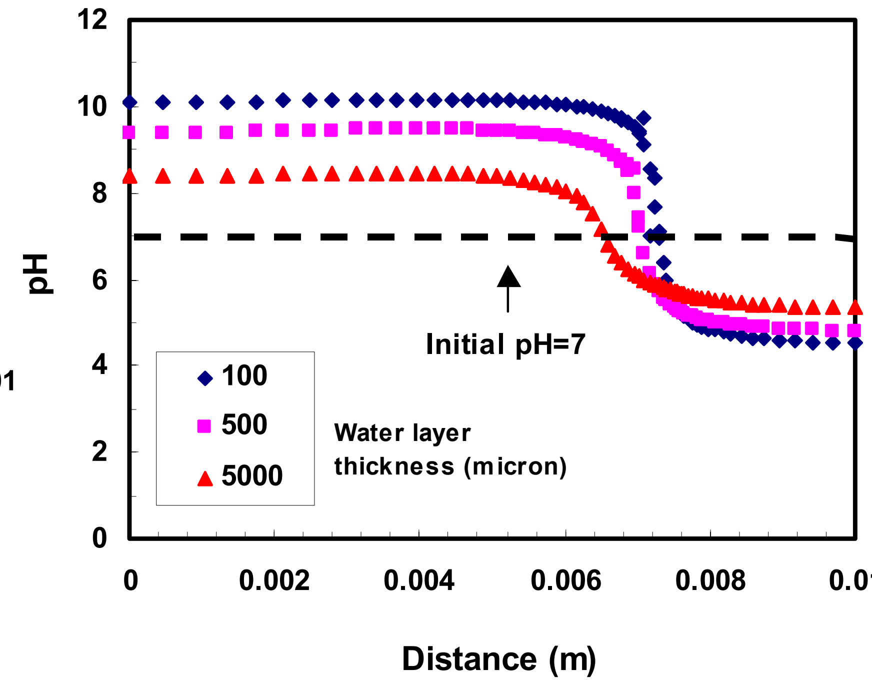


0.1 M NaCl, 500 μm water layer, 500 seconds

Increased Water Layer Thickness Slows Inhibition



Humid air: 100 μm water layer



[Cl^-] decrease is <10% in 500 s

2500 μm scratch, 0.1 M NaCl solution, release rate (A3), 500 seconds

Conclusions

- **We have extended the occluded corrosion mass transport model to atmospheric exposure of multifunctional coatings to include:**
  - **Anodic and cathodic reactions in a closed (open circuit) system**
  - **Al^{3+} hydrolysis**
  - **pH-dependent inhibitor release and Cl^- gettering**
  - **Provides a tool for design parameter evaluation**
  - **http://www.virginia.edu/cese/research/crevicer/**
- **The pH dependency of the inhibitor release is the primary controlling factor for protection of a scratch.**
  - **Larger pH dependencies are desirable**
- **Increases in water layer thickness have two compounding effects:**
  - **Slow the pH increase over the coating**
  - **Dilute the inhibitor concentration**