Use of Coupled Multi-Electrode Arrays to Advance the Understanding of Selected Corrosion Phenomena

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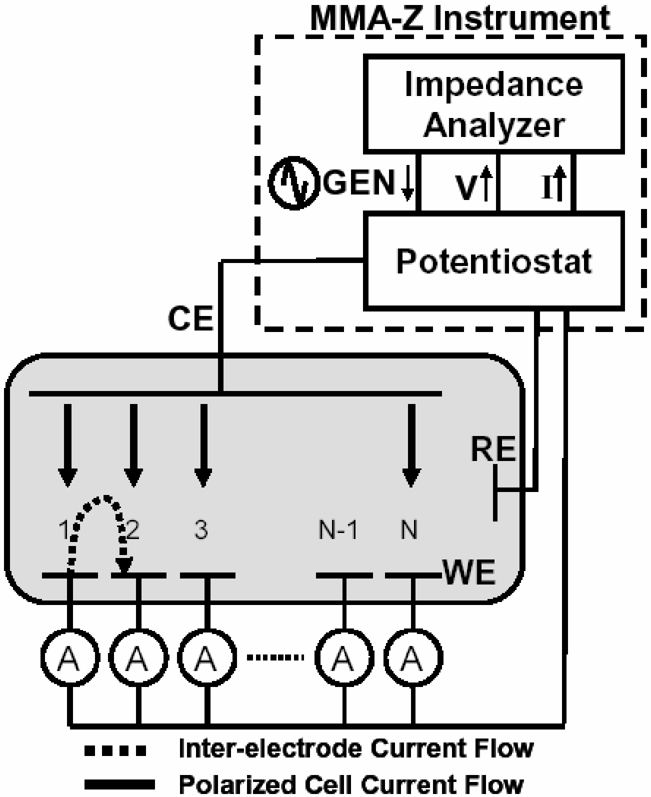
Local Electrochemical Processes

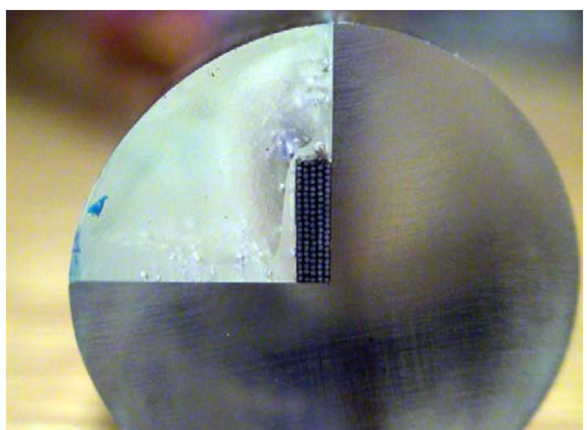
- Local electrochemical processes differ significantly from global process averaged over entire surfaces.
- Many methods exist to probe local processes:
  - Scanning or localized EIS
  - Scanning vibrating probe
  - Multi-Electrode Arrays
  - Scanning electrochemical microscopy

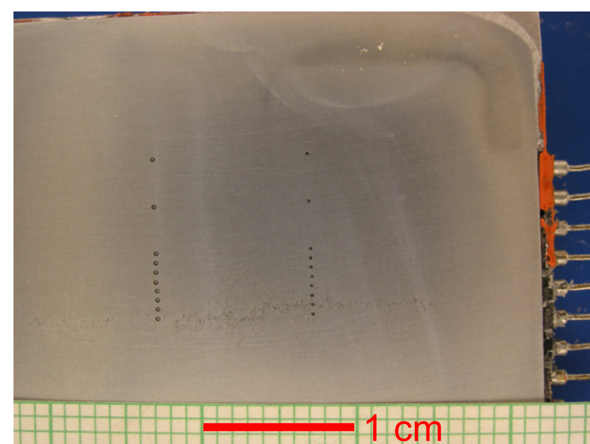
Coupled Multi-Electrode Arrays



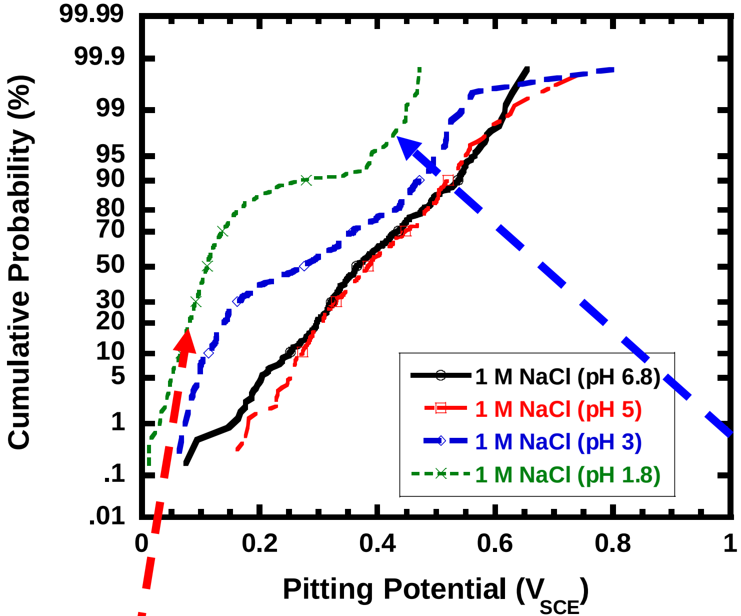
Cooper et. al. CORROSION/2006 (2006)

- Constructed from nominally identical electrodes or a combination of different materials to simulate compositional and structural heterogeneous surfaces. (i.e., Al-Cu)
- Allow temporal and spatial measurements of electrochemical processes simultaneously
- **Far Spaced MEAs** – Allow high throughput experiments
  - Eliminates variations in test environment
- **Close spaced MEAs** - Simulates a planar electrode
  - Electrodes close enough to allow chemical and electrochemical coupling of electrodes
- **Embedded Sensor MEAs** – monitor behavior of corrosion on a planar electrode surface.



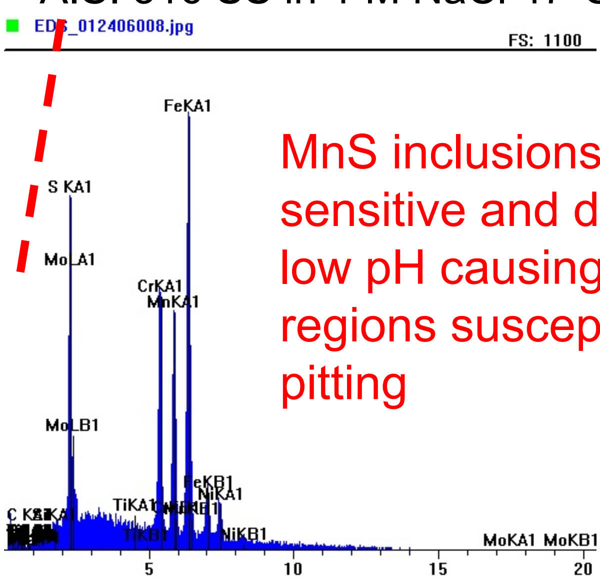


Far Spaced Electrodes: High Throughput Testing

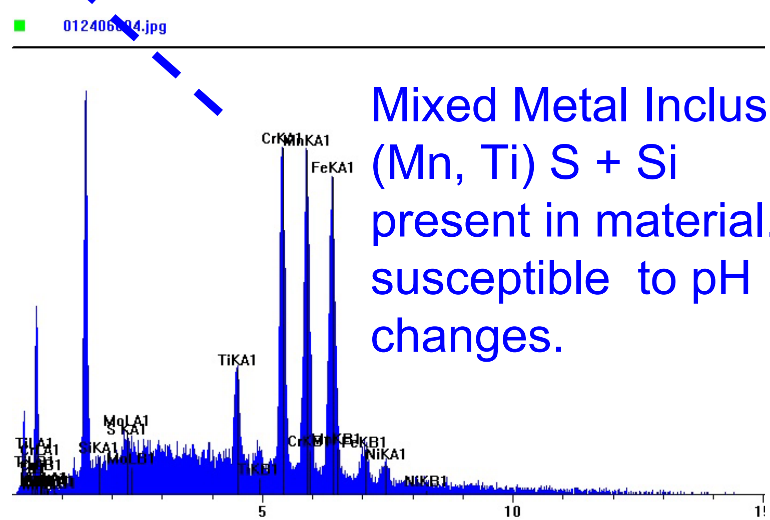


AISI 316 SS in 1 M NaCl 47^{o}C

- **Materials have a statistical distribution of flaws that control electrochemical properties (i.e., pitting potential). Causes distribution in E_{pit}.**
- **High throughput testing elucidates information about different portions of the underlying microstructure.**



MnS inclusions are pH sensitive and dissolve at low pH causing occluded regions susceptible to pitting



Mixed Metal Inclusions (Mn, Ti) S + Si present in material. Less susceptible to pH changes.

Potential and Chemical Coupling

Potential Coupling

$E_{Applied/Measured} = E_{Interface} + V_{Ohmic}$

The Ohmic Potential can be predicted using Newman's solution:

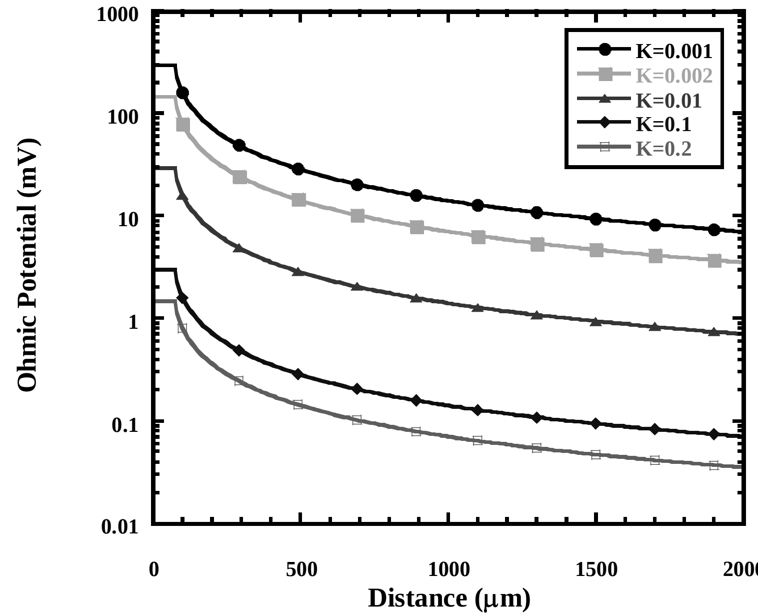
$$\frac{\Phi}{\Phi_o} = 1 - \left(\frac{2}{\pi}\right)\cdot \tan^{-1}(\xi)$$

$$I = 4K\cdot r_o\cdot \Phi_o$$

$$r = r_o\cdot\sqrt{\left(1+\xi^2\right)\cdot(1-\eta)^2}$$

J. Newman JECS. (1966)

Φ=Ohmic potential (V)
Φ_o=Maximum ohmic potential (V)
ξ=Distance from center of disk, in elliptical coordinates (cm)
η=Second elliptical coordinate (in this case = 0)
r = Normalized distance from center of disk (cm)
I=Total current from disk (A)
K=Solution conductivity (Ω-1-cm-1)
r_o=Radius of electrode (cm)



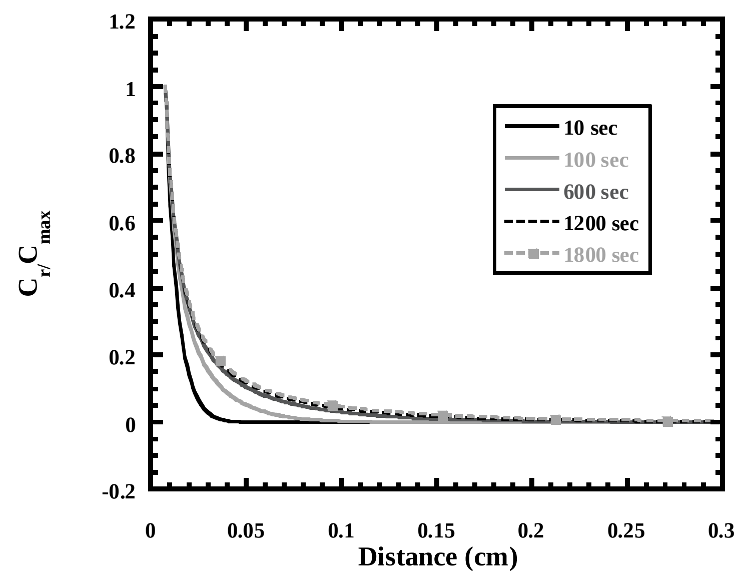
Chemical Coupling

Regions in the vicinity of electrochemically active sites where hydrolysis occurs.
Chemical gradient predicted by Carslaw and Jaeger

$$\frac{C_r}{C_{pit}} = \frac{a}{r} * erfc\left(\frac{r-a}{2\sqrt{Dt}}\right)$$

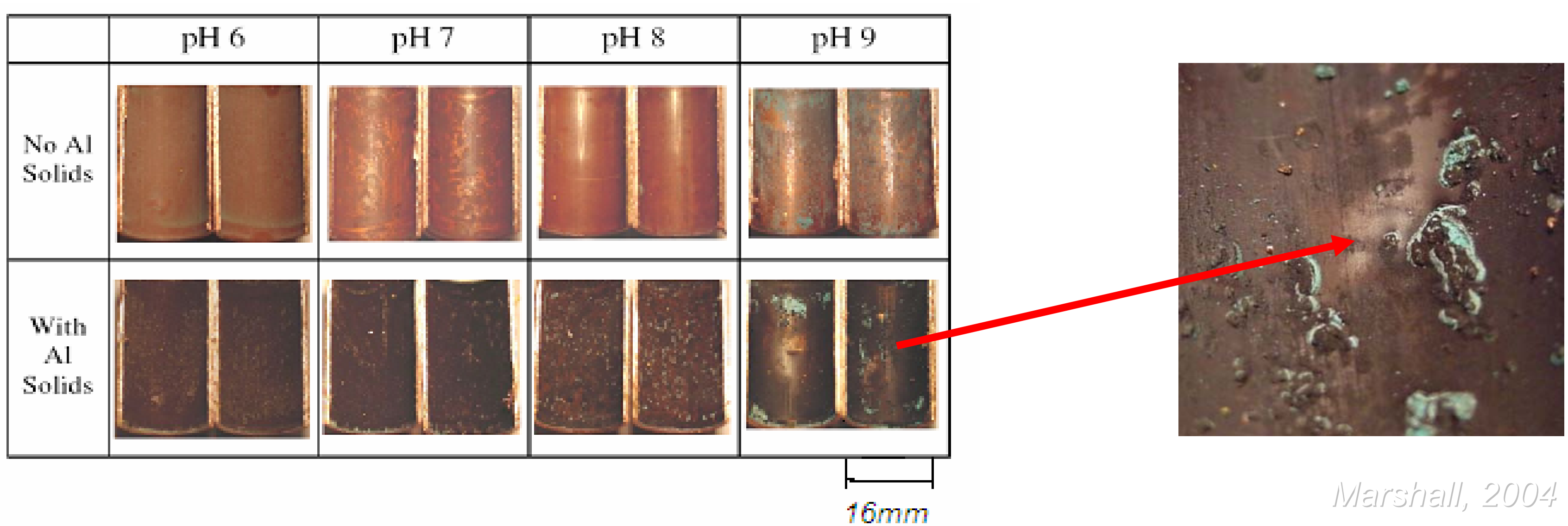
Where:
C_r = concentration at a distance r from the pit mouth (Moles/l)
C_{pit} = concentration inside the pit (Moles/l)
a = radius of the pit (cm)
r = radial distance away from the pit mouth (cm)
erfc = complementary error function
D = diffusion coefficient of the diffusion ion (cm^2/s)
t = time (seconds)

H. S. Carslaw and J. C. Jaeger (1978)



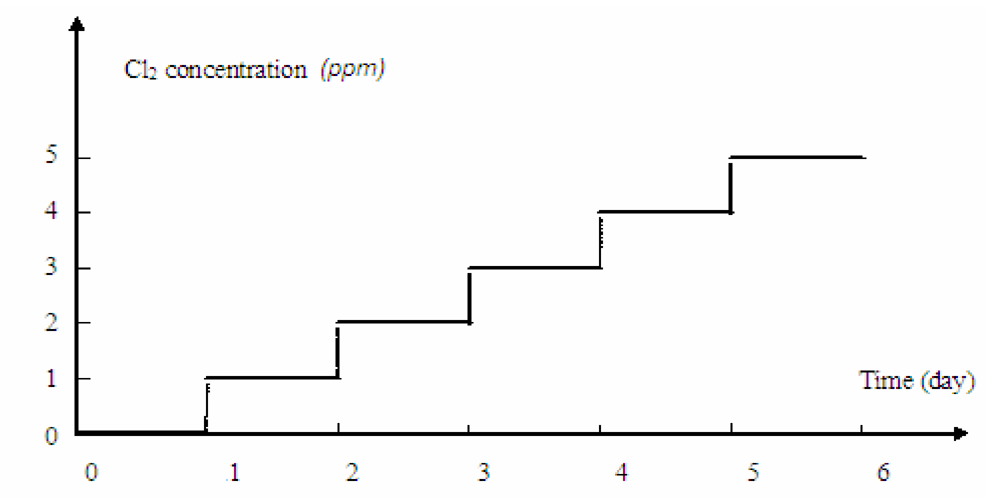
Interplay between Water Chemistry and Electrochemical Properties if Copper

- Study the fundamental mechanism of copper pitting, elucidate electrochemical properties as a function of: chlorine, aluminum, pH, sulfate, chloride, susceptible v.s. unsusceptible waters etc.
- Circumstantial evidence of susceptible water chemistries emerging but not firmly linked to key electrochemical properties associated with pitting;
- High PH: from pH = 8 to somewhere below PH = 10;
- High Chlorine (5 ppm) and High Aluminum (2 ppm Al-$Al(OH)_3$) accelerate copper pitting by synergistic reactions that cause potential rise and accelerated chlorine reduction.

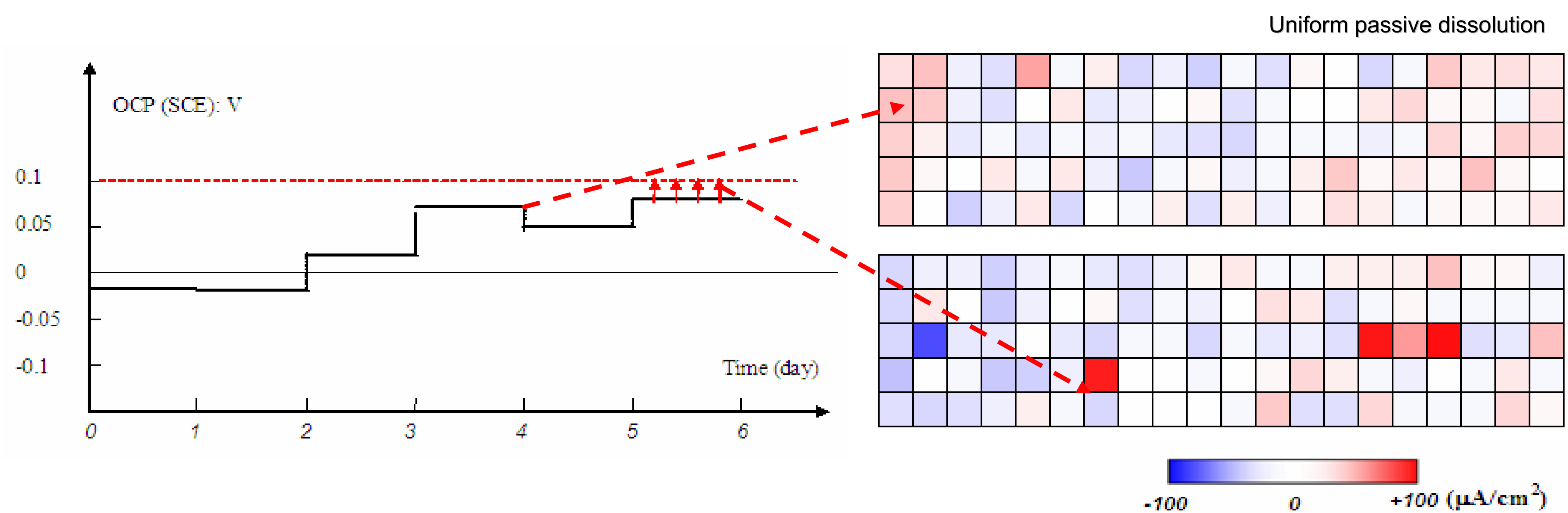


Need: Investigate the spatial development of persistent or switching local anodes as a function of water chemistry.

Development of Local Anodes

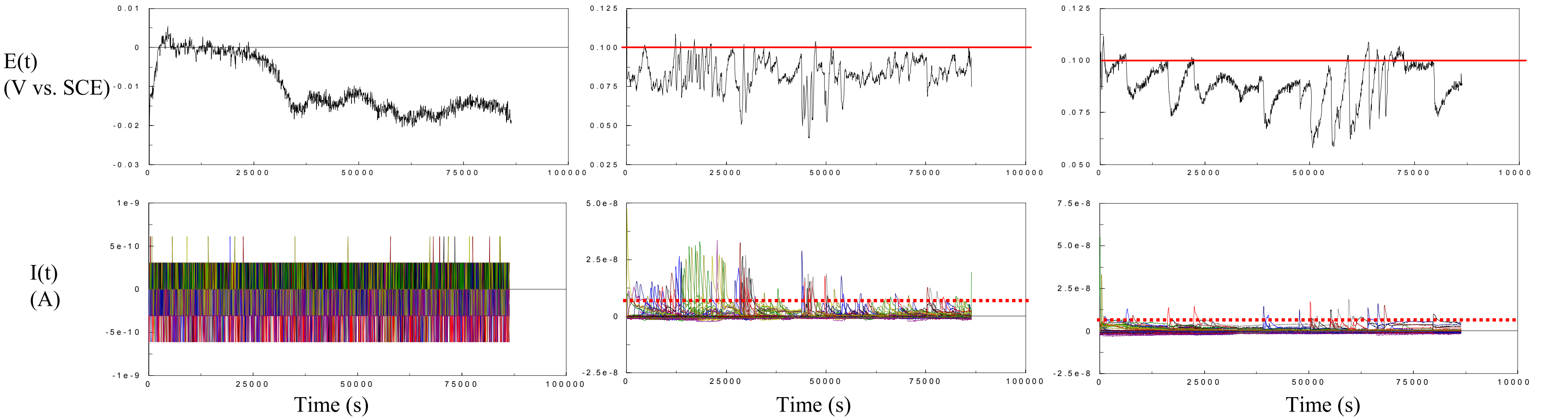


Close packed array was set up in flat cell to simulate the vertical inside of copper pipe. 2 ppm Al-$Al(OH)_3$ was added in synthetic water, and pH was adjusted to 9.2. Starting from 0 ppm, Cl_2 was increased by 1 ppm per day to 5 ppm by adding NaClO solution into test water.



pH = 9 Synthetic Water, 2 ppm Al-Al(OH)$_3$ added

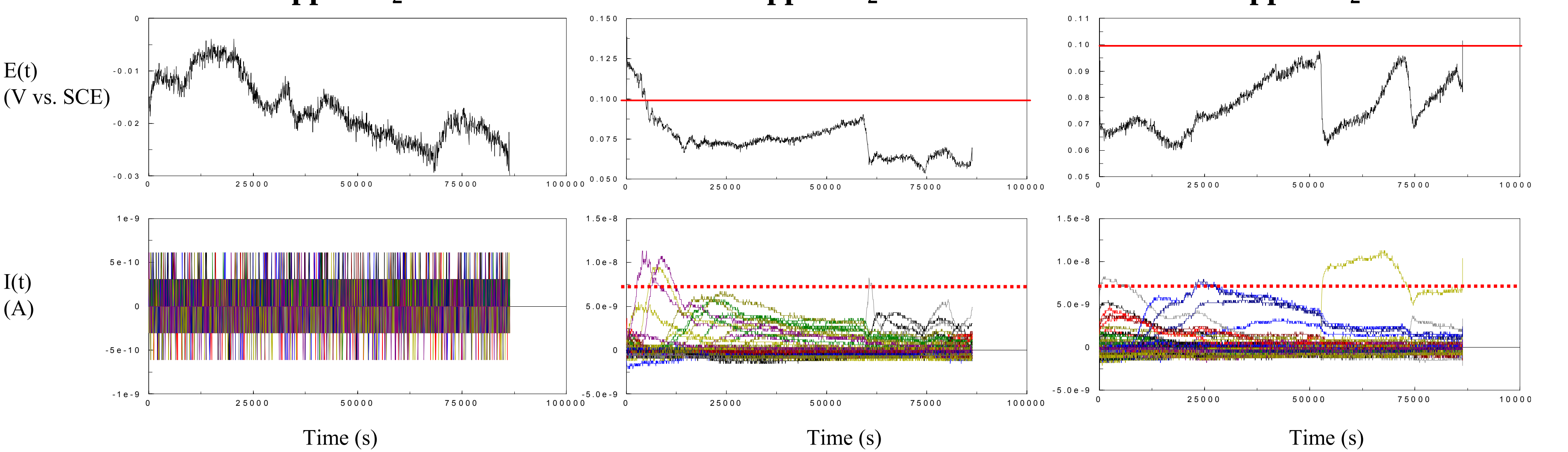
1 ppm Cl_2 | **3 ppm Cl_2** | **4 ppm Cl_2**



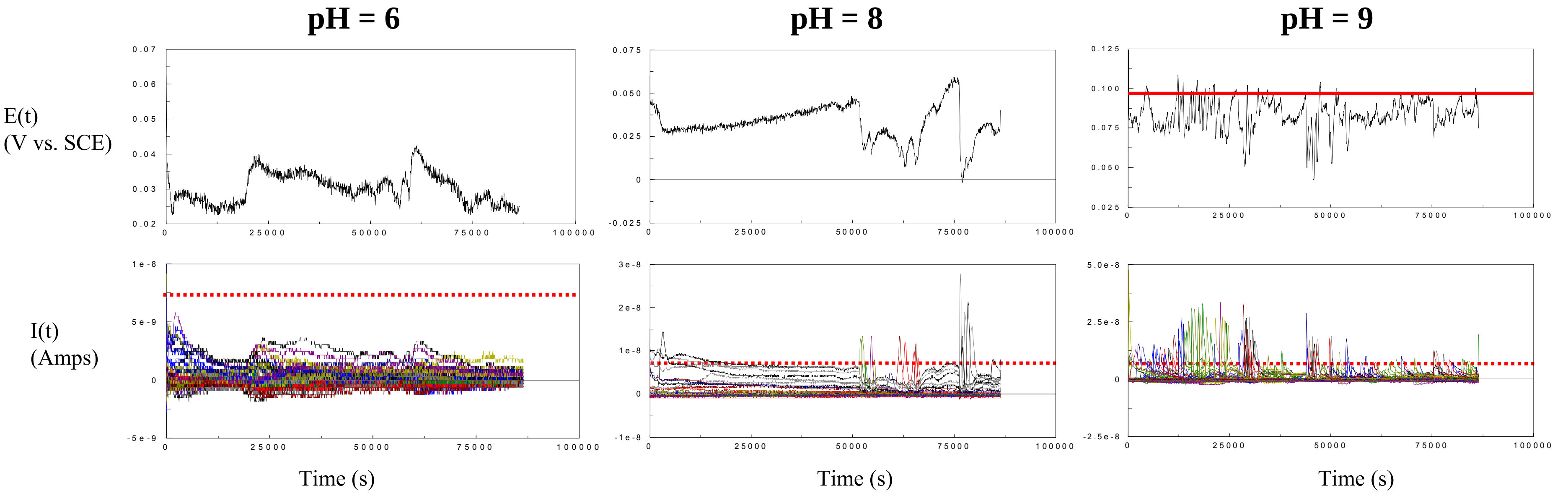
Critical line: ***Potential: 100 mV*** (vs. SCE) (solid line); ***Current density: 40 μA/cm²*** > 20 mpy (i.e. 200 mpy) (dash line)

pH = 9 Synthetic Water, No Aluminum added

1 ppm Cl_2 | **3 ppm Cl_2** | **4 ppm Cl_2**



Chlorinated Synthetic Water (3 ppm Cl_2), 2 ppm Al-Al$(OH)_3$



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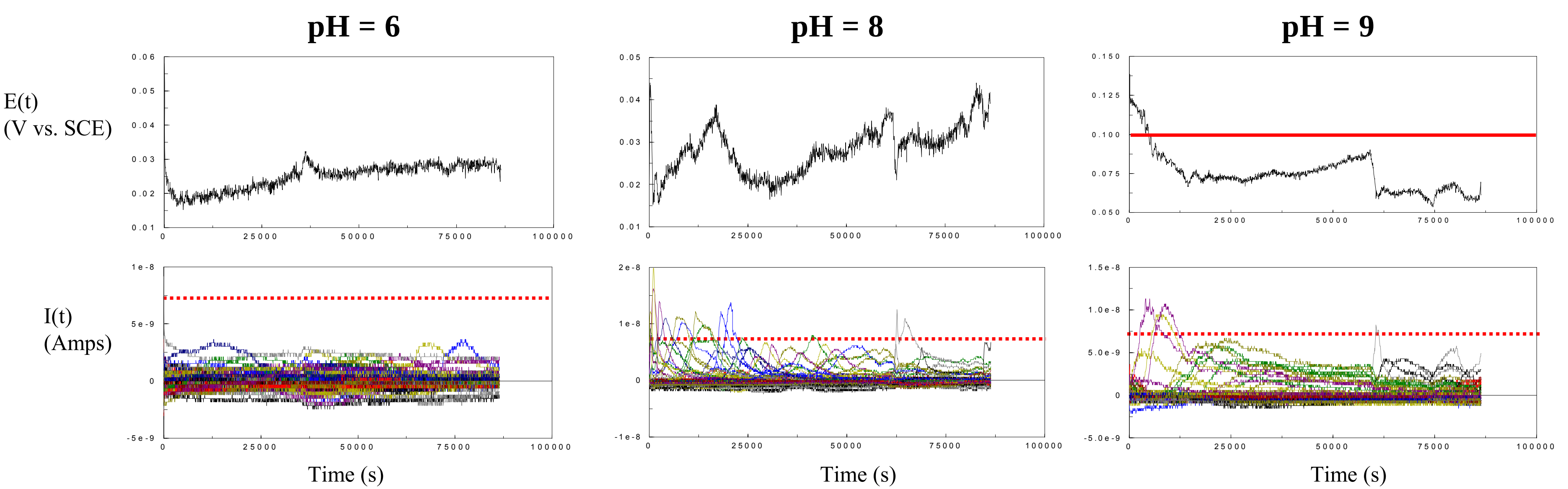


Conditions for Pit Initiation Identified

Number of Wires with Pitting Events Greater than 40 µA/cm²

No Aluminum in synthetic water

$[Cl_2]$ (ppm)	pH = 6	pH = 7	pH = 8	pH = 9
5	0	2	2	4
4	9	1	4	4
3	0	0	19	4
2	4	2	21	7
1	0	0	0	0
0	0	0	0	0

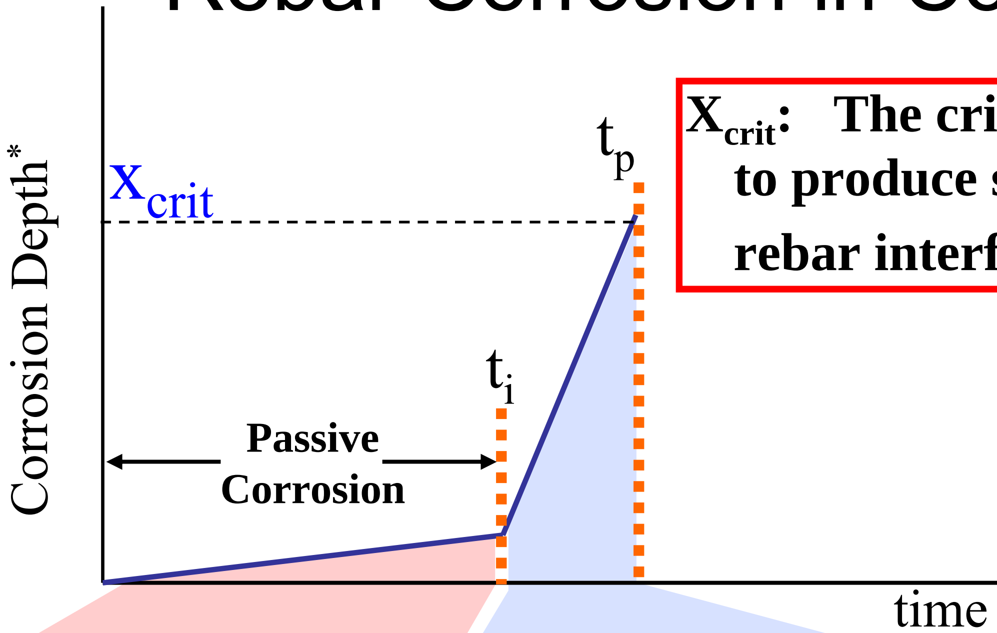
2 ppm Aluminum in synthetic water

$[Cl_2]$ (ppm)	pH = 6	pH = 7	pH = 8	pH = 9
5	0	4	9	11
4	3	2	7	26
3	5	13	24	83
2	0	10	19	0
1	0	2	0	0
0	0	0	0	0

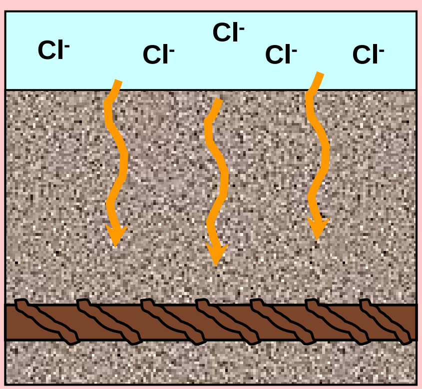
A rapid lab screening method?

Criterion:
The current density measured on a single wire exceeded 40 µA/cm² (20 mpy) at least once during the test;
If 1/10th of area pitted, then >200 mpy

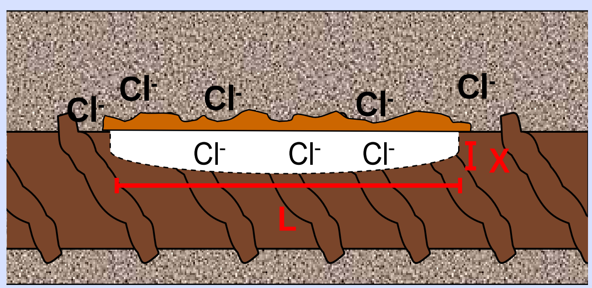
Rebar Corrosion in Concrete: Background



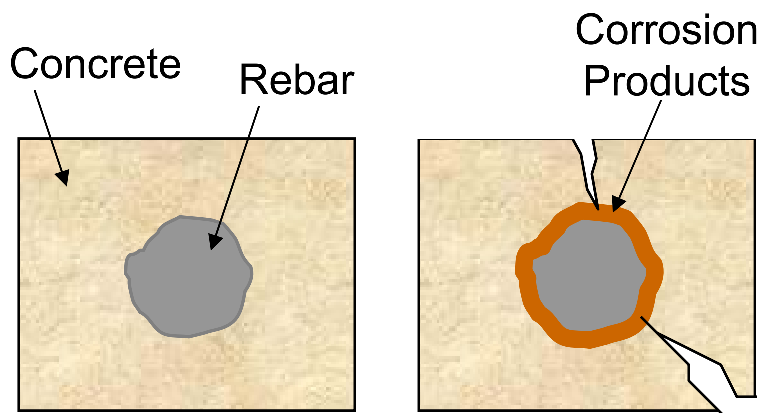
X_{crit}: **The critical depth of corrosion attack required to produce sufficient corrosion products at the rebar interface to crack the surrounding concrete**



t_i = concrete quality, alloy composition



t_p = alloy quality, corrosivity environment, electrochemical conditions



Time

<u>Time to Spalling</u>

(when $X > X_{crit}$)

$$\boxed{t_{failure} = t_i + t_p}$$

*After: K. Tuutti, *Corrosion of Steel in Concrete*. Swedish Cement and Concrete Research Institute: Stockholm. p. 18,51, 1982.

Corrosion Propagation: Impact on Concrete Structures

x_{crit} = *Corrosion Depth Required to Damage Concrete*

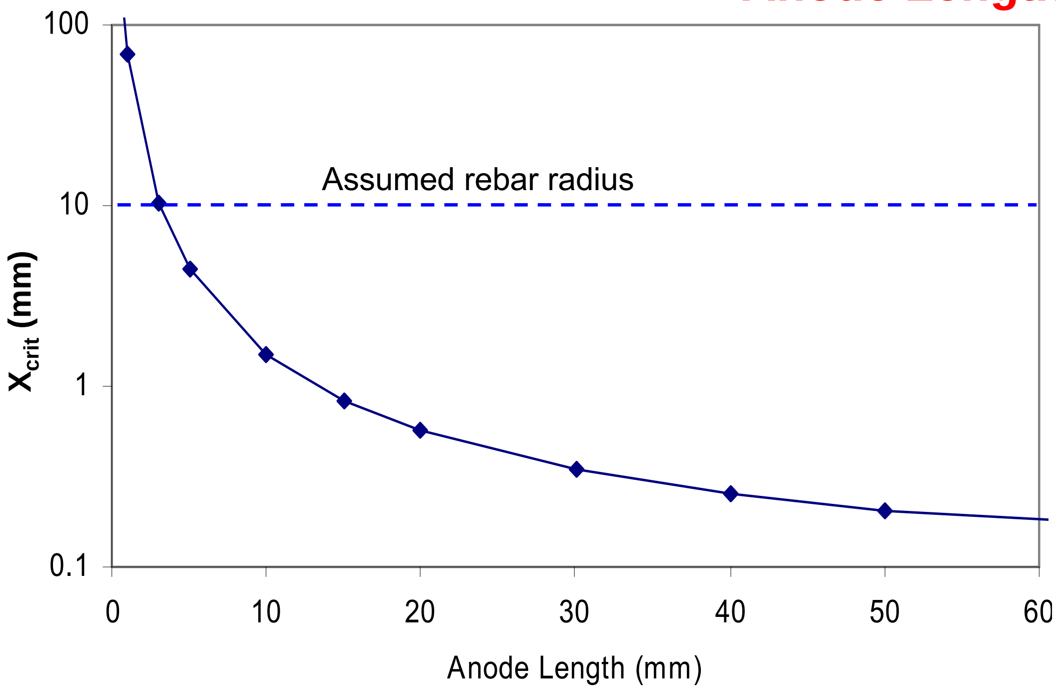
- **Degree of localization impacts concrete cracking**
  - For carbon steel an empirical relationship has been found*
- **Effect of new rebar alloys**
  - Higher aspect ratio corrosion morphology
  - Unique metal-to-oxide conversion rate
  - MEA's utilized to study anode length of new rebar alloys developed during lateral growth of corrosion damage

$$x_{crit} = 0.011\left(\frac{C}{\phi}\right)\left(\frac{C}{L}+1\right)^{1.8}$$

Concrete Cover C = 50 mm

Rebar Radius ϕ = 10 mm

Anode Length

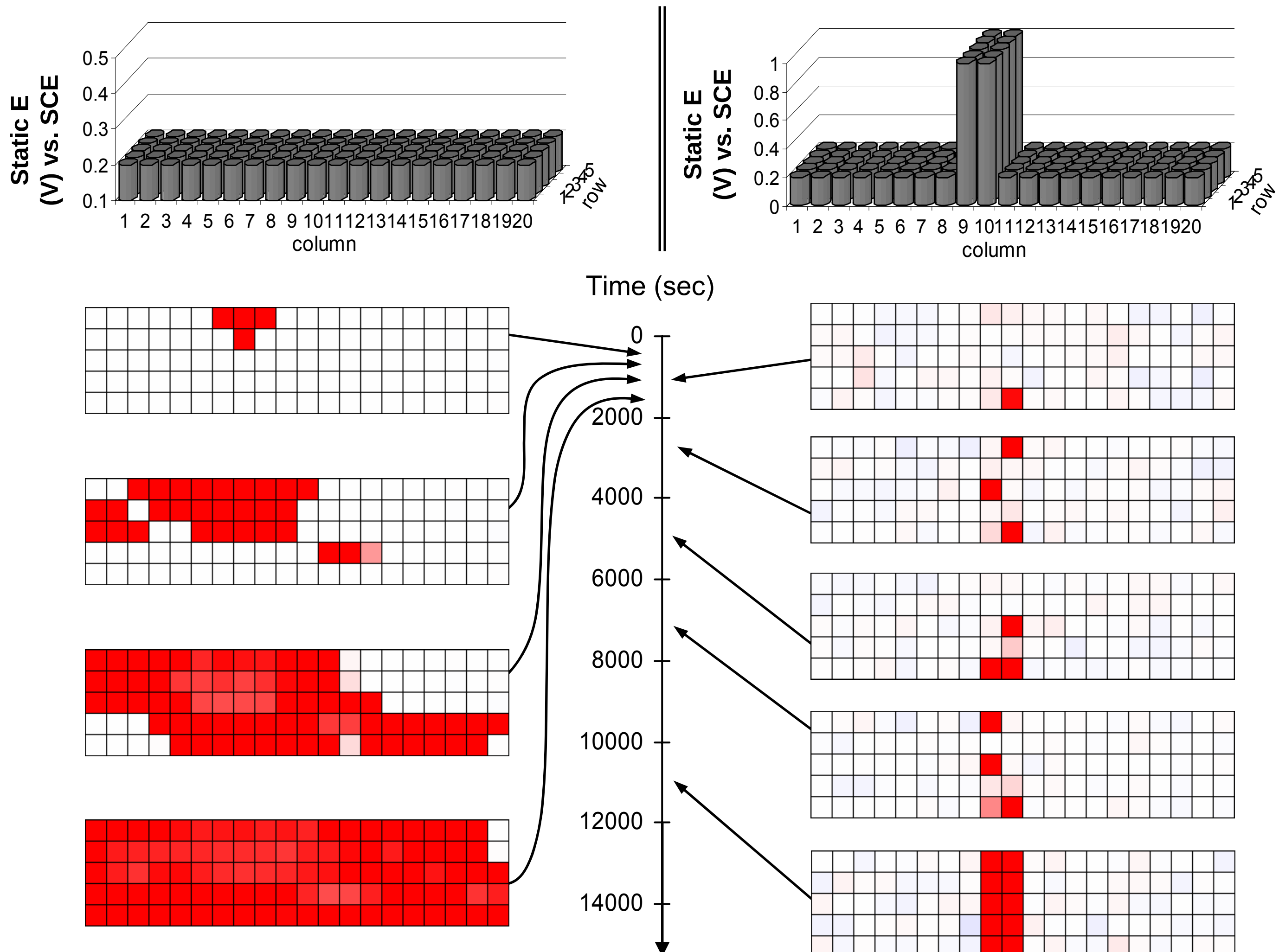


*A.A. Torres-Acosta and A.A. Sagues. Concrete Cover Cracking with Localized Corrosion of Reinforcing Steel. In 5th CANMET/ACI. 2000. Barcelona: ACI Intl.

Corrosion Propagation: Lateral Spreading

Carbon Steel: Corrosion spreads rapidly across the MEA surface

316L Stainless Steel: No spreading is seen from preferentially activated sites

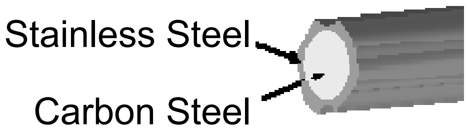


Carbon Steel Saturated $Ca(OH)_2$ + 0.2 M NaCl

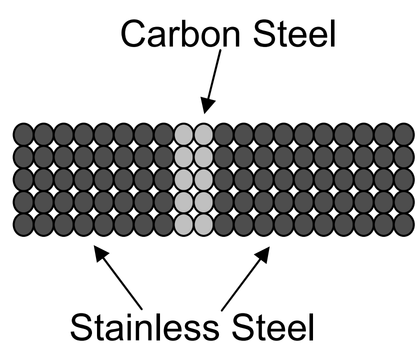
316L Stainless Steel H_20 + 3 M NaCl

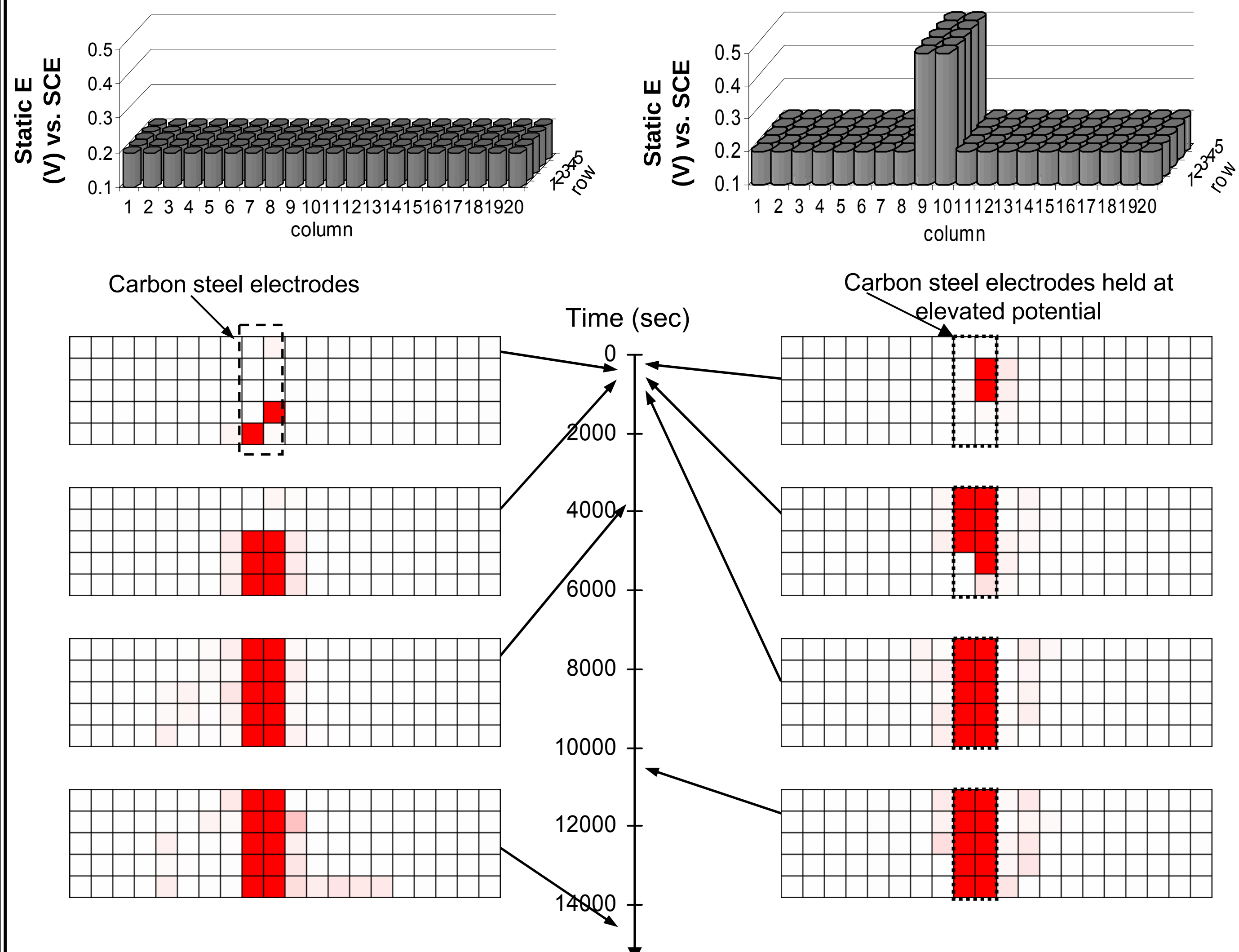
Corrosion Propagation: Simulated Clad Rebar

Clad Rebar



- An MEA was constructed to simulate a “defective” Stainless Steel clad over carbon steel rebar
- Can corrosion at the breech propagate to the clad layer?



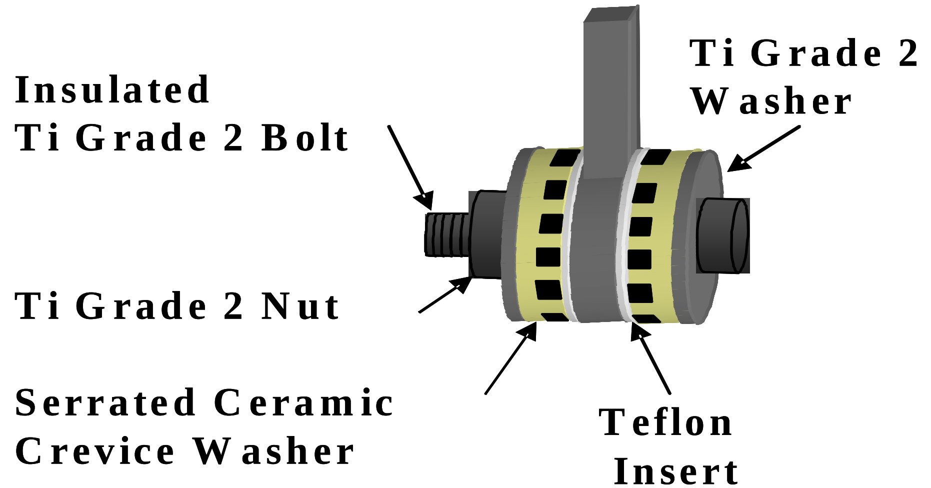


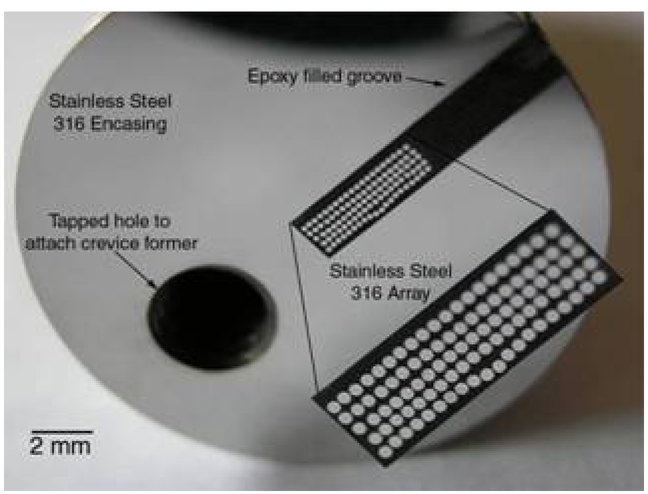
Simulated Clad
Sat. $Ca(OH)_2$ + 0.2M NaCl

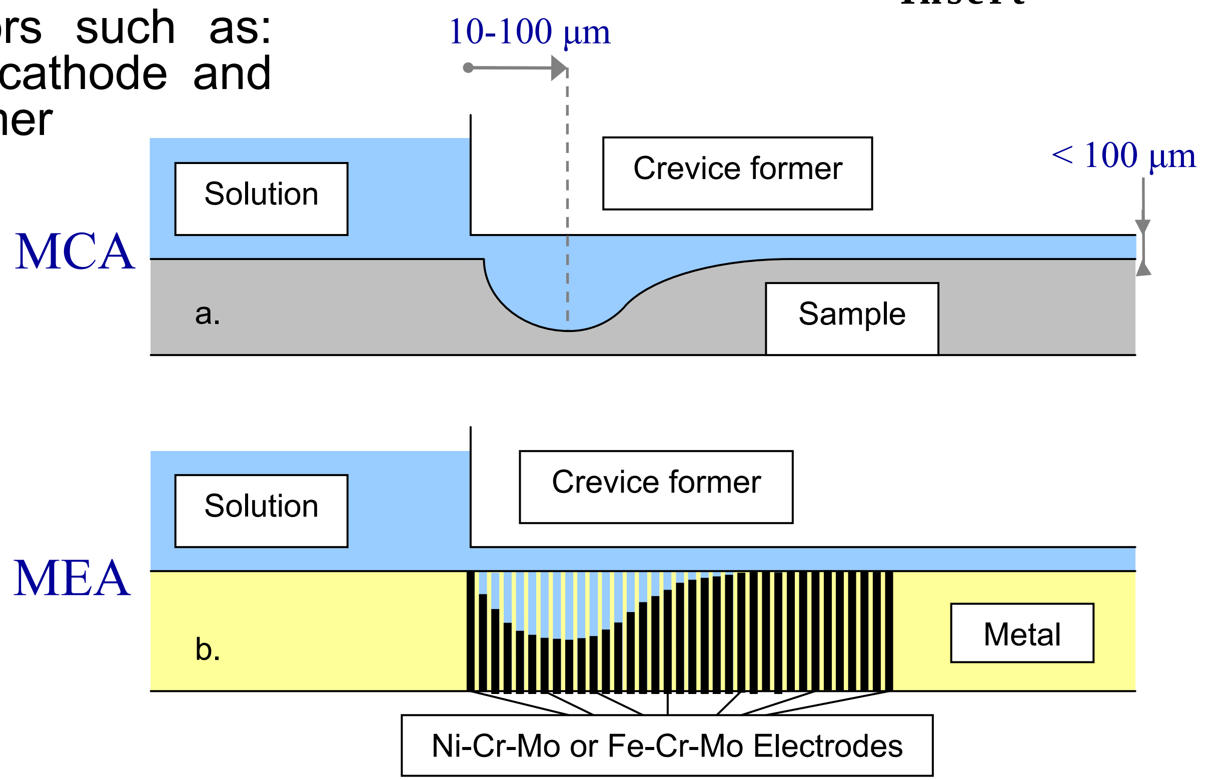
Simulated Clad
Sat. $Ca(OH)_2$ + 0.2M NaCl

Multi-Crevice Assembly vs. MEA

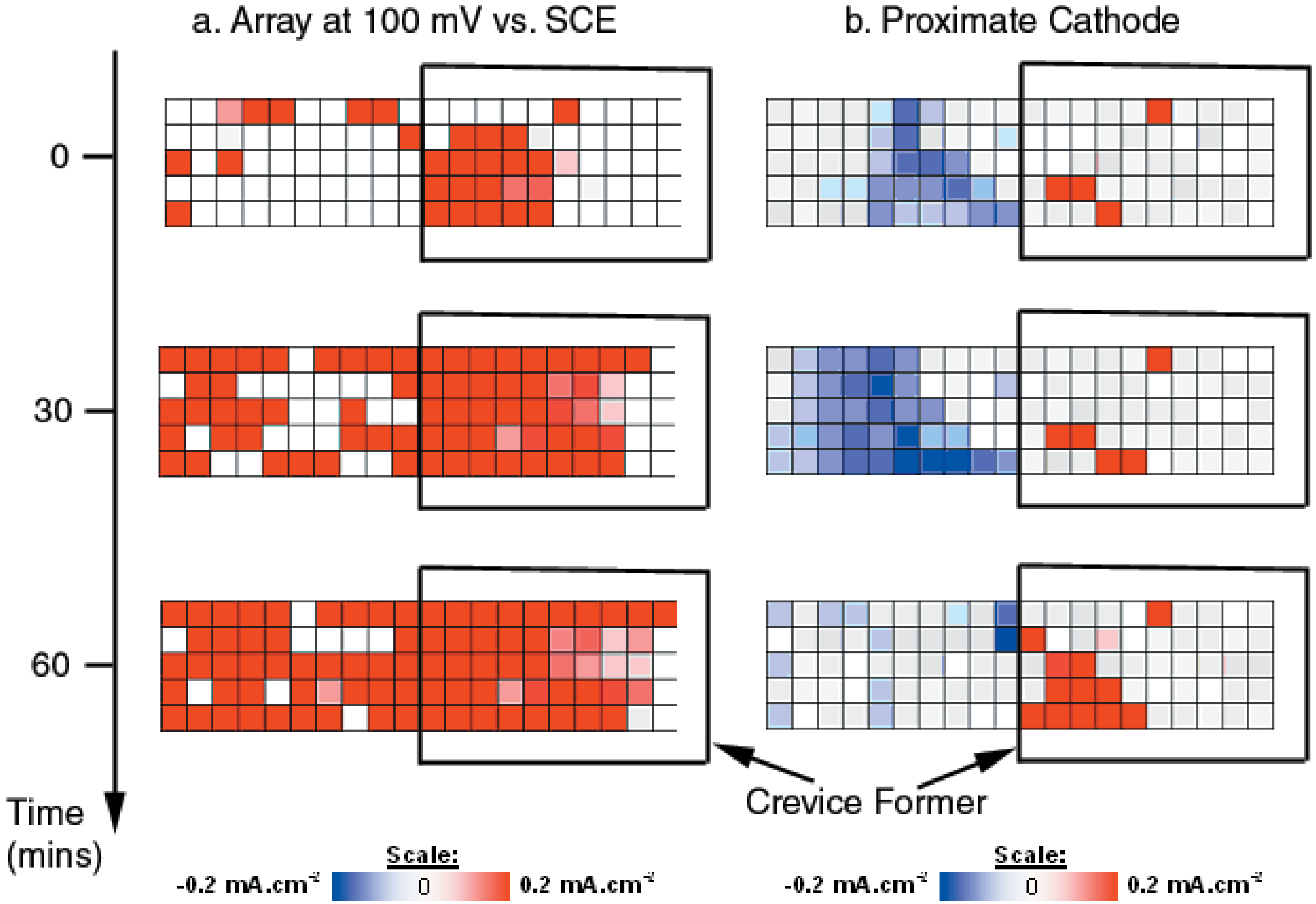
- The array is flush-mounted in a metallic rod of the same material, resulting in a metallic surface-volume ratio similar to that of MCA
- Array provides detailed spatial-temporal resolution, important as crevice corrosion behavior is very dependant on position
- Easier study of effects on initiation and propagation of some factors such as: proximate cathode, limited cathode and semi-permeable crevice former







Crevice Corrosion & Proximate Cathode



- 316 SS
- $E_{Applied}$ stepped 50 mV/hour starting at 0 V_{SCE}
- 1 M NaCl 47^{o}C

- Pitting and Crevice Corrosion
- Pitting occurs randomly outside crevice

- The proximate cathode (-400 mV_{SCE}) outside the crevice inhibits the initiation of crevice corrosion at 100 mV_{SCE}

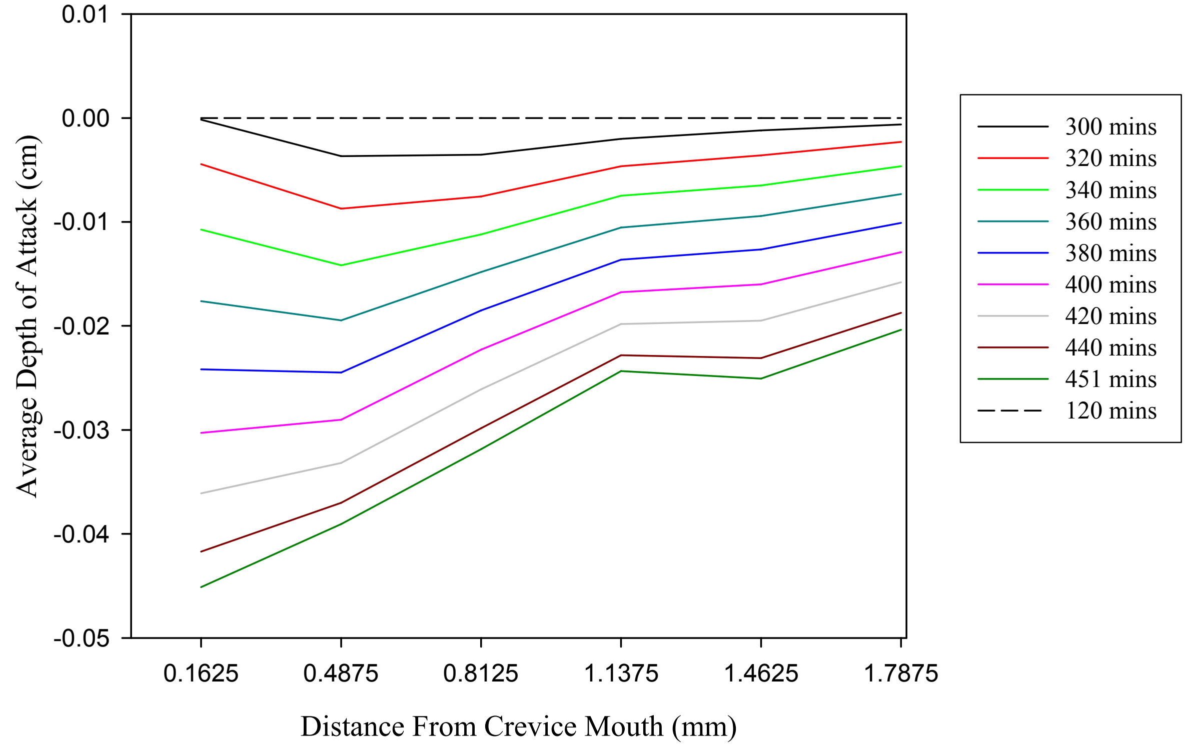
Crevice Corrosion Analysis

- From Faraday's Law:

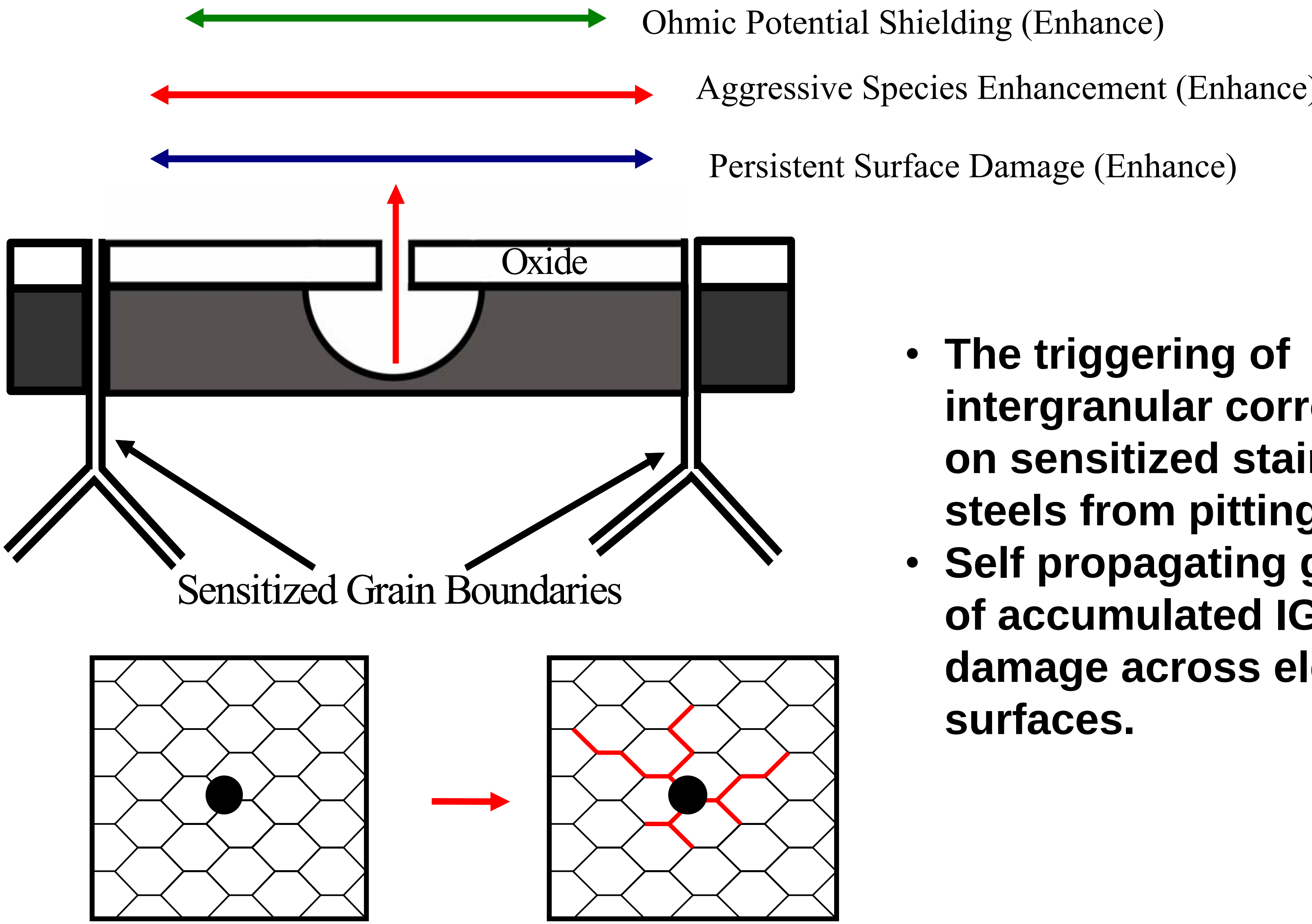
$$d = \frac{C \cdot EW_{316SS}}{F \cdot \rho_{316SS} \cdot \pi \cdot r^2}$$

With EW_{316SS} = 25.4
and ρ_{316SS} = 7.87

- The charge is derived from the net current. Close to the crevice mouth, the cathodic current contribution will be minimal
- The derived depth of attack profile evolution is in agreement with the IR drop model

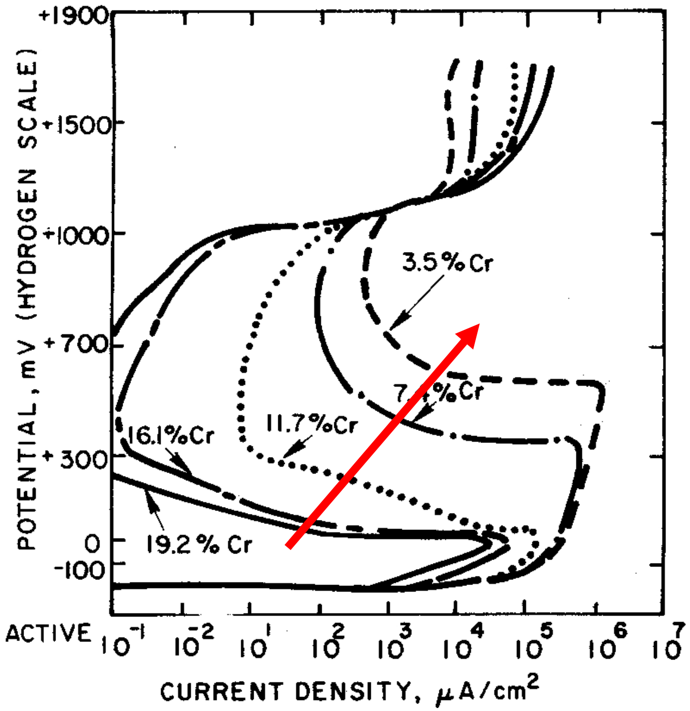


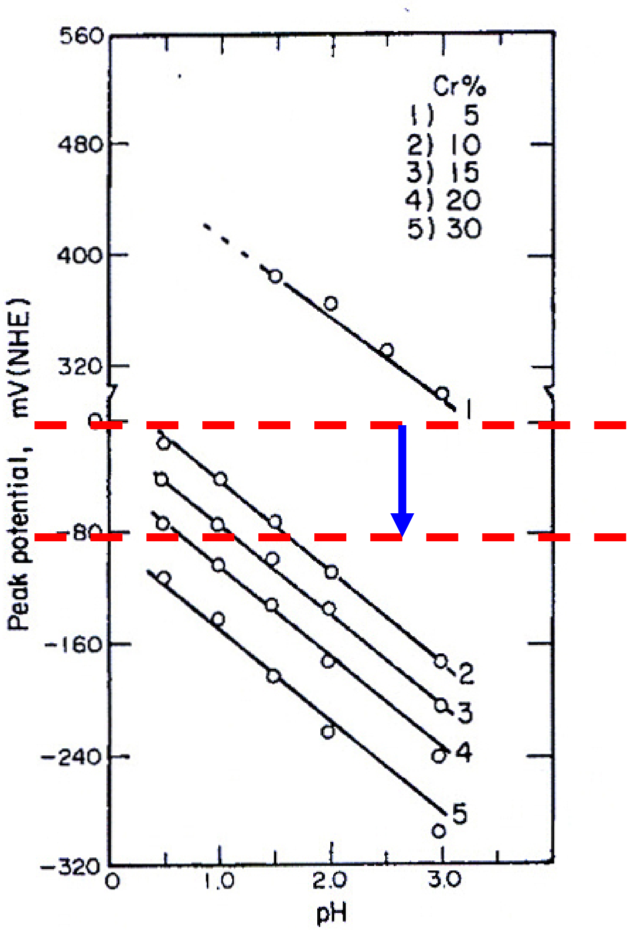
Spreading of Intergranular Corrosion by Cooperative Interactions



- **The triggering of intergranular corrosion on sensitized stainless steels from pitting sites.**
- **Self propagating growth of accumulated IGC damage across electrode surfaces.**

Initiation of IGC From Localized Pitting

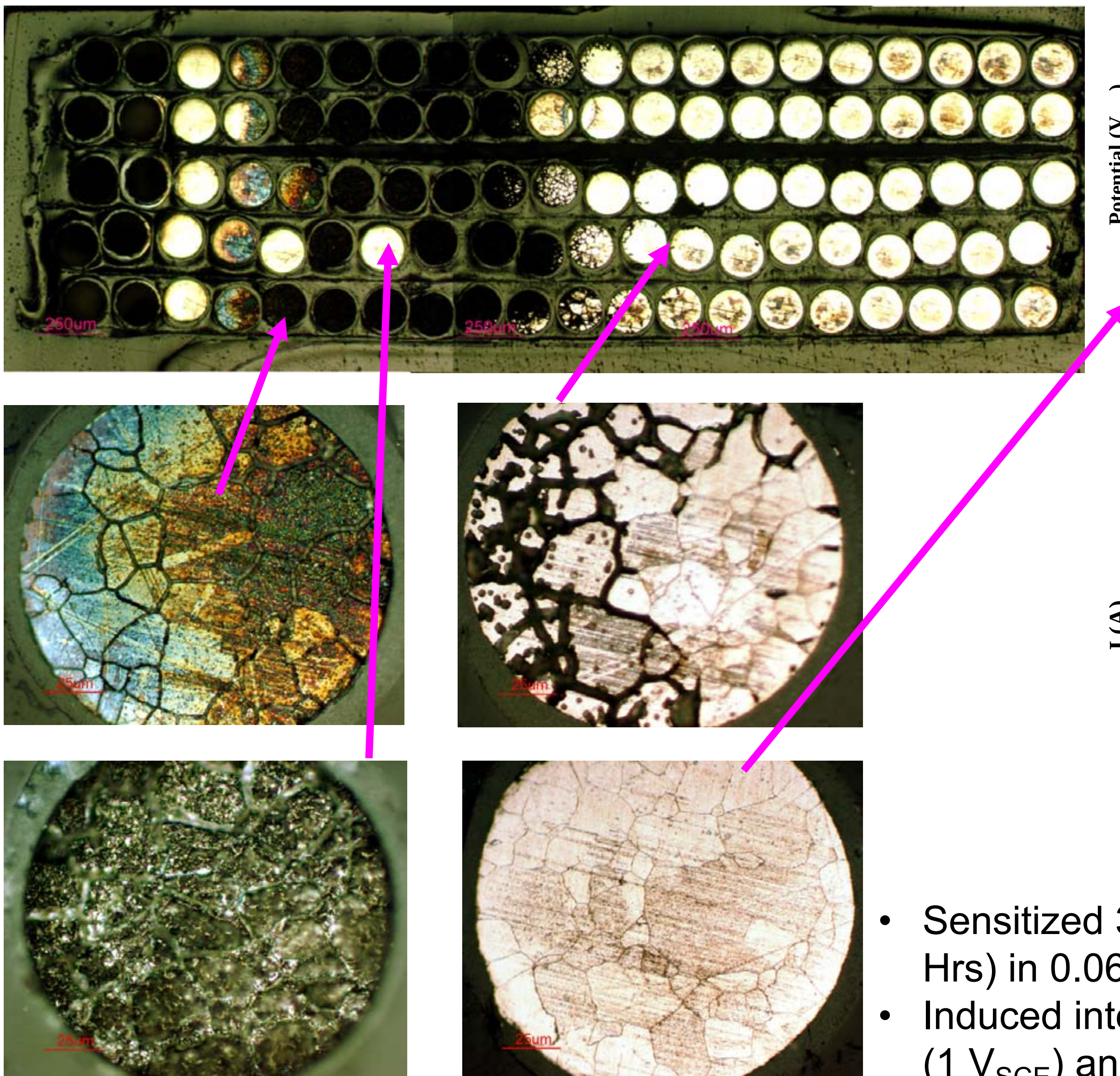


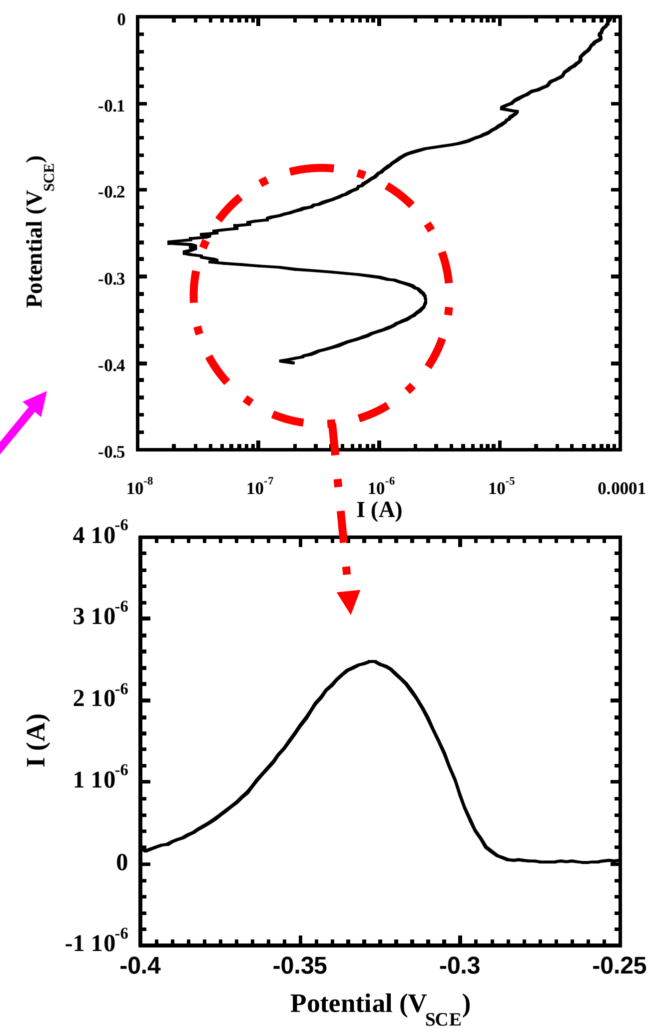


- E_{Flade} **increases with decreasing [Cr].**
- E_{Flade} **increases with decreasing pH.**
- **G.B. with lowest [Cr] most susceptible to initiation and continued growth.**

Ohmic potential can cause the applied potential on surrounding surface to drop from a passive potential into an active range

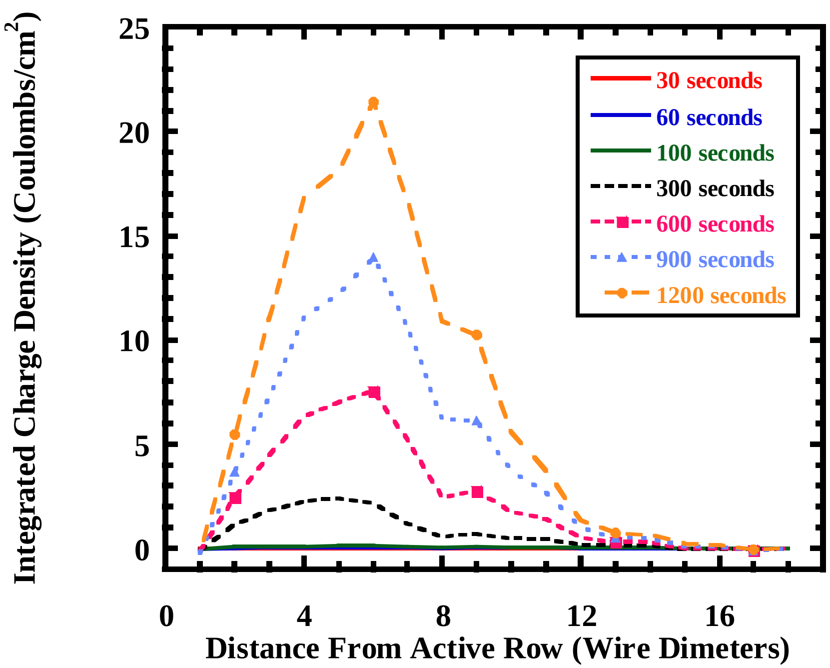
Pits trigger IGC on sensitized stainless steel

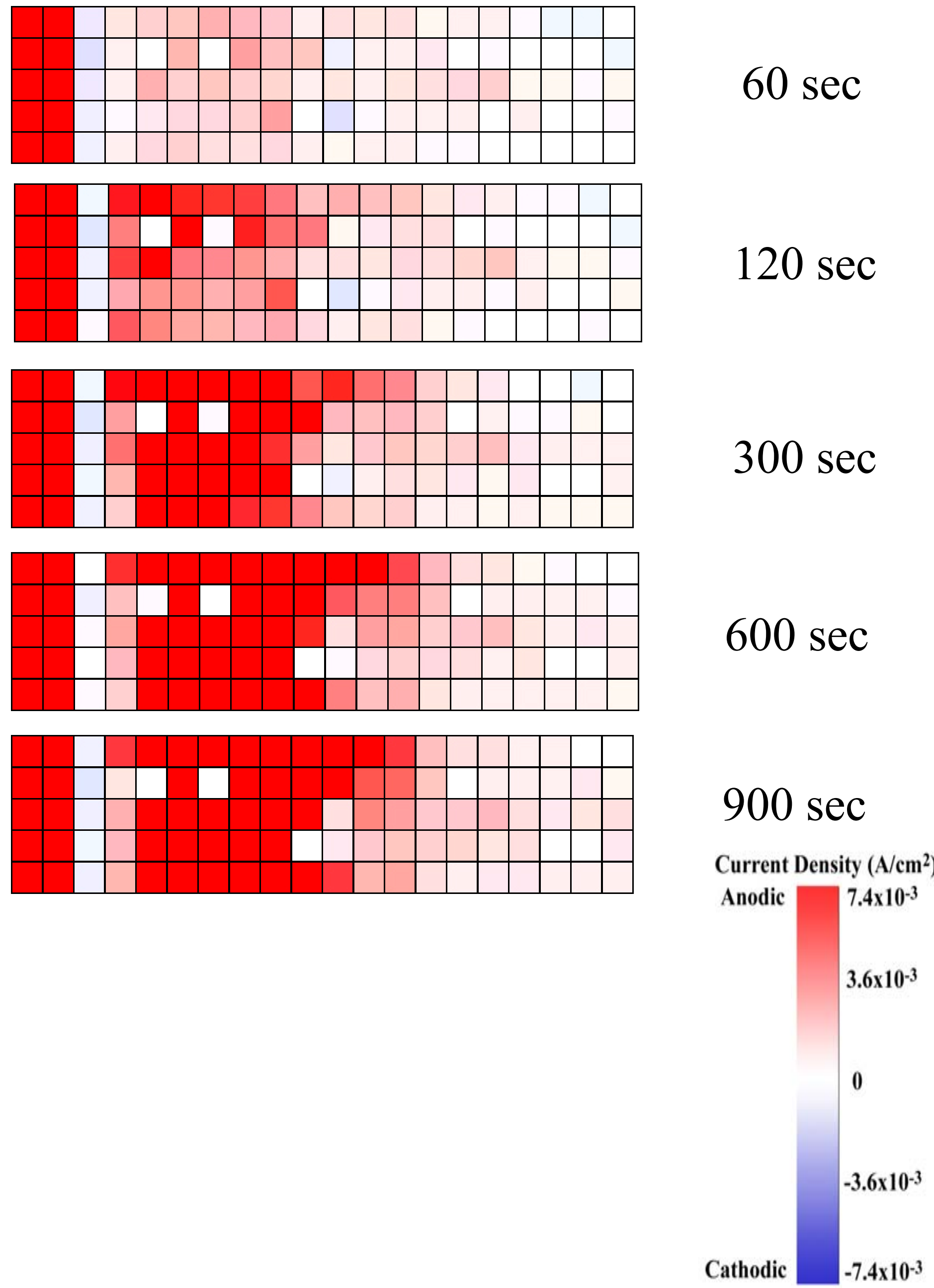




- Sensitized 304 (1030°C 1 hour and 621°C 48 Hrs) in 0.06 M HCl 60°C
- Induced interaction experiments: Rows 1 and 2 (1 V_{SCE}) and remaining electrodes (-0.29 V_{SCE})

Measured Accumulated IGC Damage





- **Visually observed accumulated damage matches current and charge measured with MEA.**
- **Damage spreads with time beyond predicted region of accumulated damage by ohmic potential drop-solution enhancement**

Predicted Regions of IGC

- Using Newman's solution for a disk in an insulator we can predict the ohmic potential drop produced by active pitting.

$$\frac{\Phi}{\Phi_o} = 1 - \left(\frac{2}{\pi}\right)\cdot \operatorname{atan}(\xi)$$

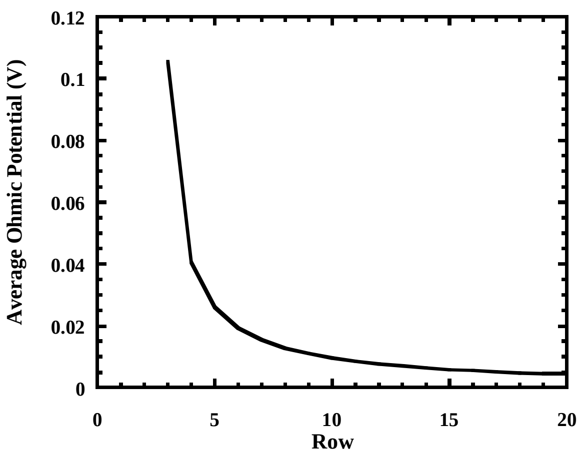
$$I = 4K\cdot r_o\cdot \Phi_o$$

$$r = r_o\cdot\sqrt{\left(1+\xi^2\right)\cdot(1-\eta)^2}$$

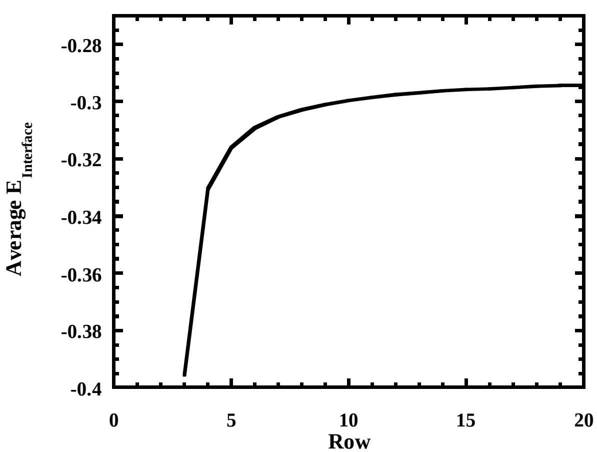
- Assume that an array is a radial slice of this model.
- Using these equations, some experimental values, and potentiodynamic curves the region of IGC damage can be predicted.

$I = 1.25\ A/cm^2$

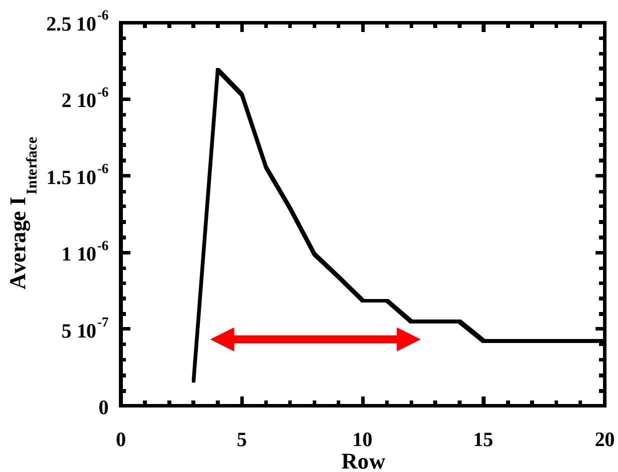
$K = 0.027\ ohm^{-1}cm^{-1}$



V_{ohmic}



$E_{Interface} = E_{applied} - V_{ohmic}$



Predicted Region of IGC

Conclusions

- Synthetic water containing 2 ppm Aluminum shows a specific set of conditions where pit initiation occurs.
- Allow the determination of anode lengths for different high performance rebar materials cause by the propagation and growth characteristics of the material. The lateral growth behavior of these materials is monitored on MEAs.
- Pitting corrosion can trigger IGC on stainless steels through ohmic potential shielding and localized solution enhancement. Lateral growth of IGC can self propagate across electrode surfaces.

ACKNOWLEDGEMENTS

- The concrete project was sponsored by the VTRC (Virginia Transportation Research Council). The support and helpful discussions with Dr. Gerardo Clemeña and Dr. Steve Sharp are gratefully acknowledged.
- The crevice corrosion work was supported by the Office of Science and Technology and International of the U.S. Department of Energy, Office of Civilian Radioactive Waste Management is gratefully acknowledged. The work was performed under the Corrosion and Materials Performance Cooperative, DOE Cooperative Agreement Number: DE-FC28-04RW12252
  - The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OST&I.
- Dr. Harold T. Michels and Copper Development Association Inc. provided financial support for pitting of Cu studies.
- The United States Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering supported intergranular corrosion studies under contract DEFG02-00ER45825 with Jane Zhu as contact monitor.
- Special thanks to Scribner Associates, Inc. for instrument and software support.