Mechanisms in the corrosion performance of dual polymer-zinc coated rebar

Alberto A. Sagüés

Acknowledgement: **Kingsley Lau**, Adrienne Accardi, Carlyn Krapf, Edward Lopez

Dept. of Civil and Environmental Engineering
University of South Florida
Tampa, Florida

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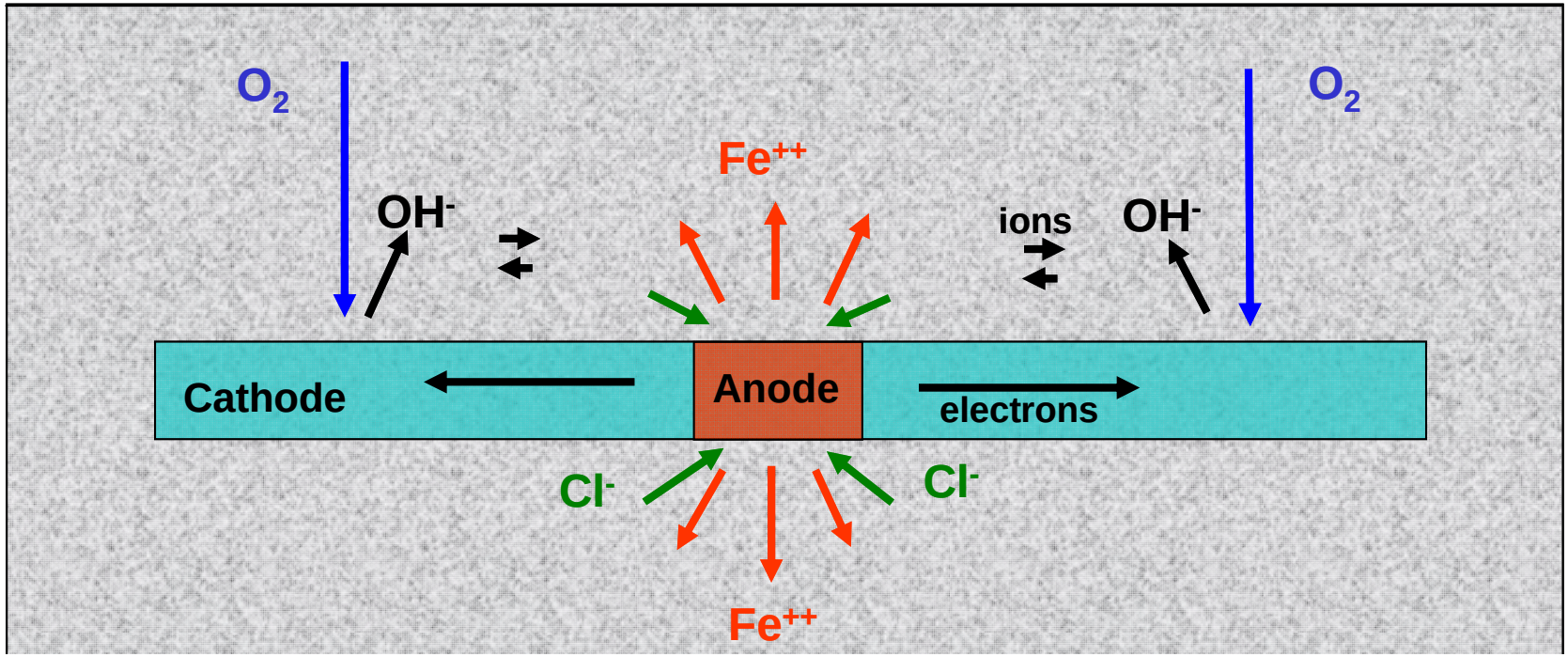
Corrosion of steel in concrete

- **Pore water (pH>~12.5) promotes steel surface passivity. Corrosion is negligible.**
- **Passivity disrupted if pH lower or if chloride (Cl^-) on steel surface is above a critical threshold value. Expansive corrosion products crack concrete.**
- **Most severe: Chloride in seawater or in deicing salts.**



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- **Two corrosion stages:**
  - **Initiation: Cl^- ions penetrate toward rebar, until threshold reached.**
  - **Propagation: Threshold reached, corrosion in progress until repair needed.**
- **Corrosion control:**
  - **Extend length of either or both stages.**

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Corrosion control: longer initiation stage

- **Concrete surface treatments:** less Cl^- at surface
- **Improved concrete quality:** slower Cl^- ingress
- **Thicker cover:** slower Cl- buildup at rebar surface
- **Alloy steel rebar**: elevated critical Cl- threshold
- **Cathodic prevention:** elevated critical Cl- threshold by cathodically polarizing rebar.

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Corrosion control: longer propagation stage:

- **Improved concrete quality:**
  - Higher electric resistance between anode cathode.
  - Slower Cl- flow to anode
- **Cathodic protection:**
  - Lower corrosion rate at anodic regions.
  - Lower/reverse chloride accumulation at anode; pH elevation.
- **Alloy steel rebar:**
  - Less expansive corrosion products.
  - Smaller anodic regions.
  - Less efficient cathodes.
- **Epoxy-coated rebar (ECR):**
  - Fewer, smaller anodic and cathodic regions (ideally at imperfections only)
  - Higher anode/cathode electric resistance.

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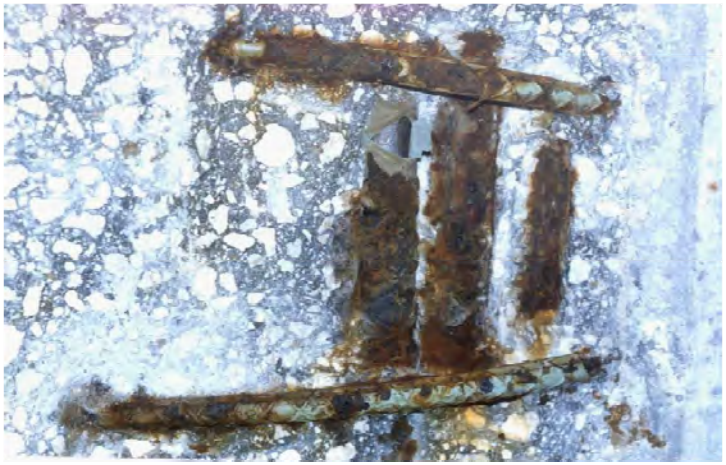
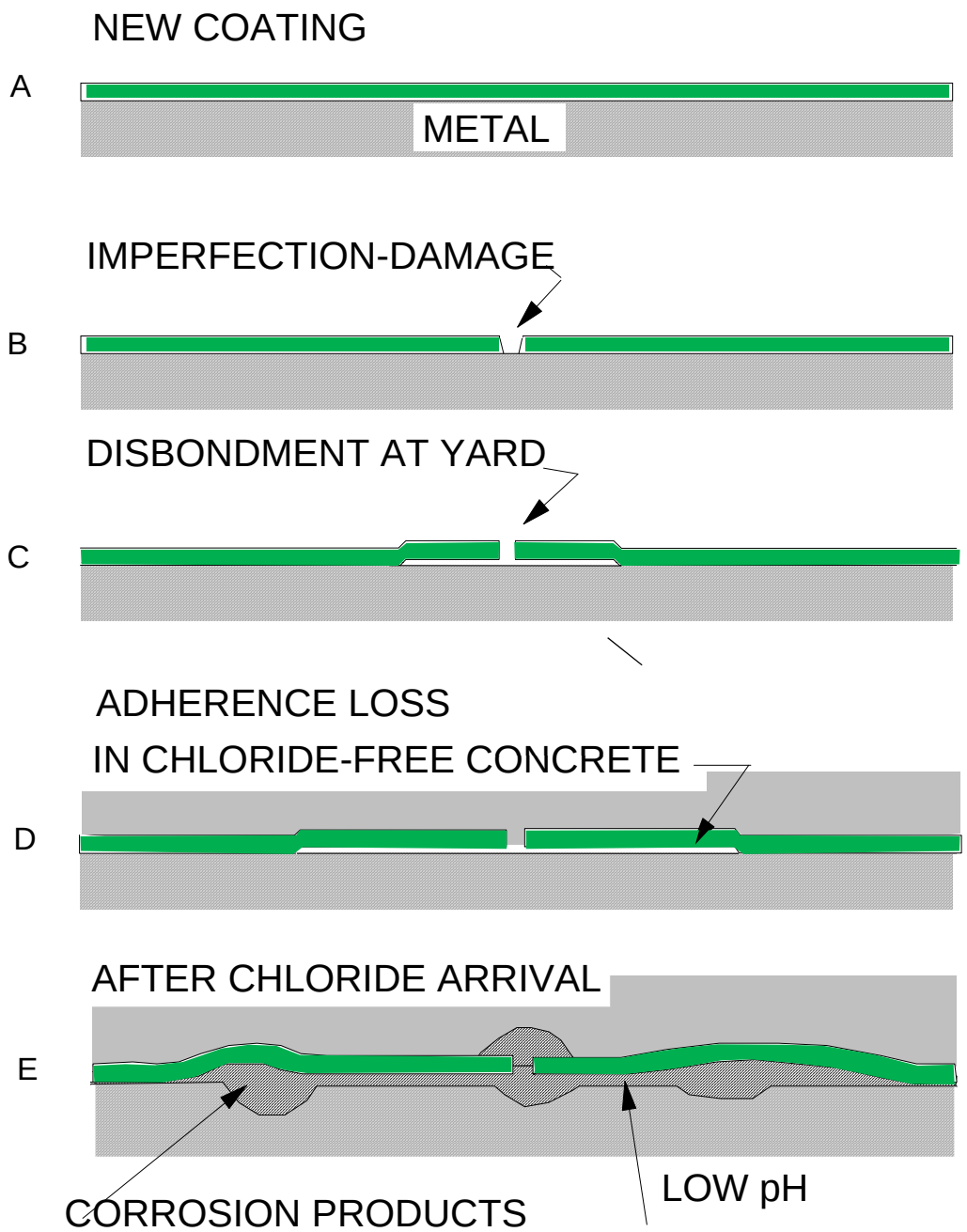
ECR widely used but:

- Subject to severe corrosion in high chloride service – many Florida Bridges affected.
- Corrosion starts at hard-to-avoid coating breaks, continues in disbonded regions.
- It is a form of crevice corrosion with a low pH, high [Cl^-] micro environment.
- Cathodes provided by steel exposed at other breaks.

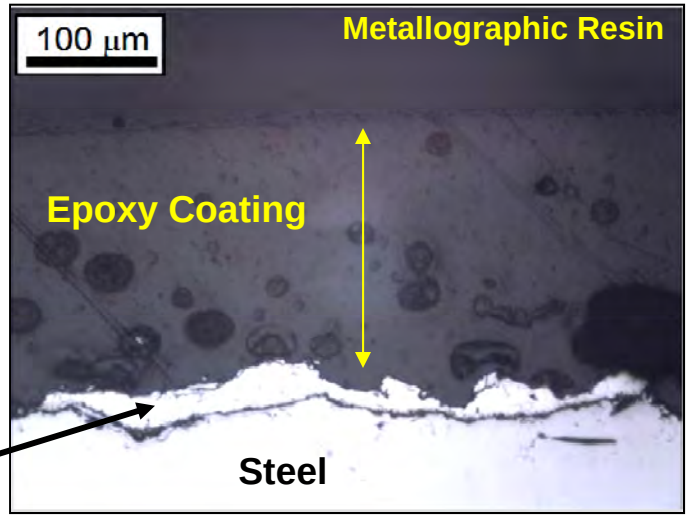




Dual polymer-zinc coated rebar (DCR)

- ~95% pure Zn thermal sprayed to steel surface <0.05mm thick
- Outer epoxy polymer coating ~0.2mm thick.

Zinc Coating
(Epoxy removed)



Expected benefits from a dual coating system

- Recognizes coating breaks inevitable, provides 2nd line of defense
- Zn has higher corrosion threshold than plain steel
- Zn, when passive, has more negative potential than steel thus providing cathodic corrosion prevention to any bare steel exposed at breaks.
- More prevention / protection against steel crevice corrosion provided once Zn begins to corrode.
- Exposed Zn is a lesser cathode than steel – less aggravation of local corrosion.

Initial questions:

- How stable is the polymer to zinc/steel substrate bond?
- Could severe crevice corrosion of Zn take place?
- How much of a cathode is DCR?
- How effective is the galvanic protection / prevention provided?

Investigation*: Test approach

- Distressed DCR and ECR in simulated concrete pore water solutions, accelerating processes with impressed potentials.
  - amount of corrosion
  - disbondment
  - zinc consumption
- DCR and ECR in concrete blocks – no chloride
  - performance as a cathode

* ***Lau et al. Corrosion 65 (2009) 681-694.***
* ***Sagüés et al. Final Report to Gerdau Ameristeel "Mechanistic Issues..." (2010) .***

Tests in simulated concrete pore water

Environments tested

- Simulated pore solution (SPS): ($NaOH + KOH + Ca(OH)_2$, pH 13.3, no Cl^-)
- SPS + 3.5% NaCl (0.6M Cl^-; $[Cl^-]/[OH^-] \sim 2$)

Materials:

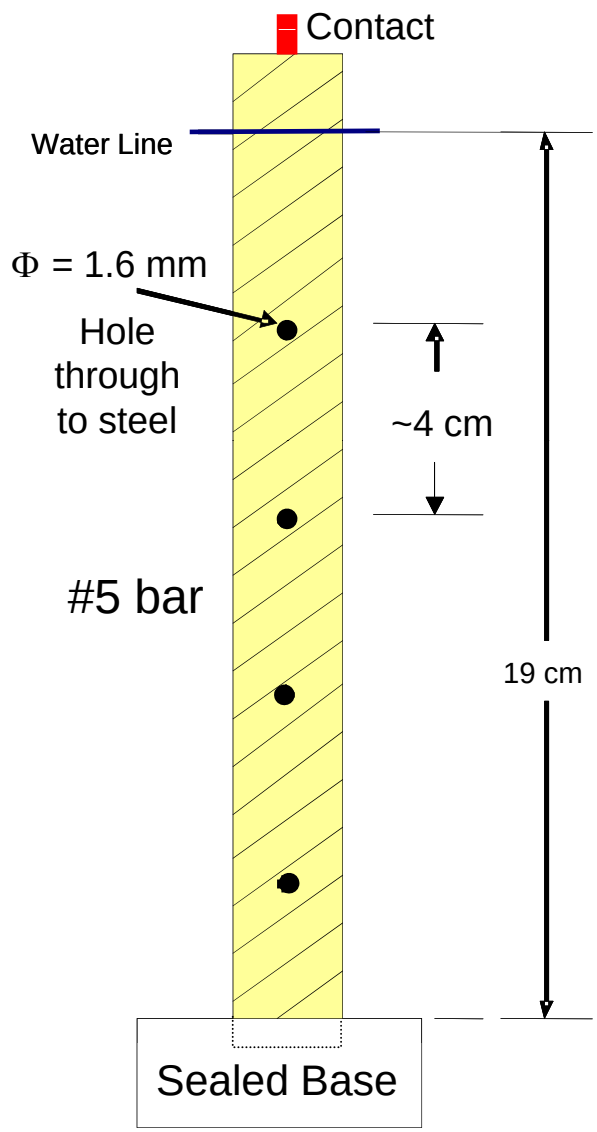
- DCR and ECR

Shape and Condition:

- Steel area exposed ~0.45 cm^2.
- All specimens in duplicate.

30-60 day Polarization (SCE) :

- Open circuit (natural corrosion),
- **+100mV (highly accelerated corrosion)**,
- -500mV (some protection)
- **-1000mV (protect but induce disbondment)**

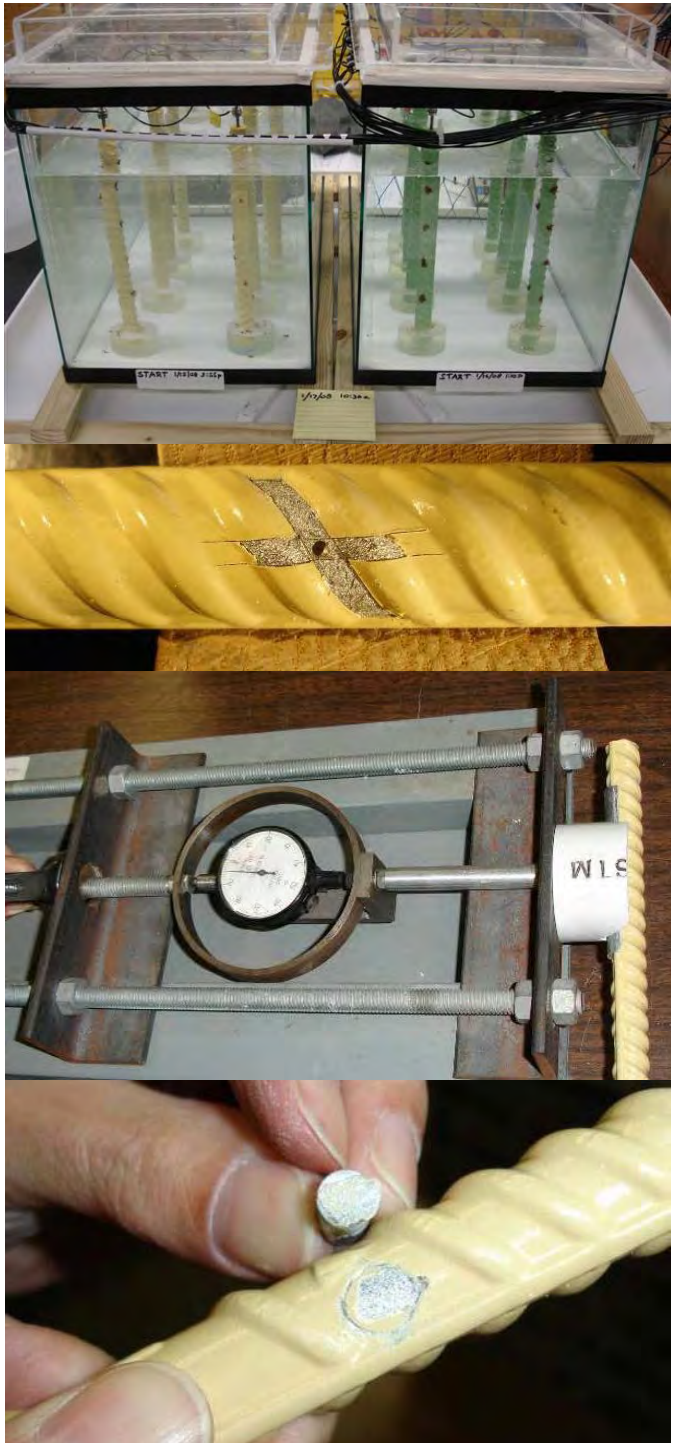


Evaluation during test:

- Current, visual appearance.
- For OC specimens: Potential, Impedance

Post test:

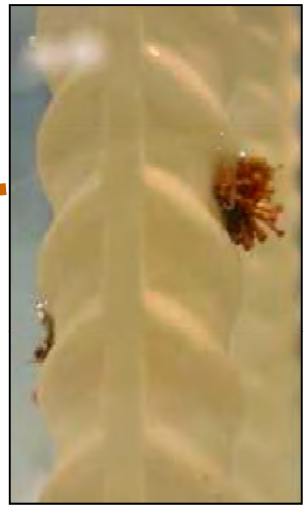
- Disbondment length
- Pull-off strength of coating
- Corrosion product appearance
- Crevice/bulge size
- Crevice fluid pH

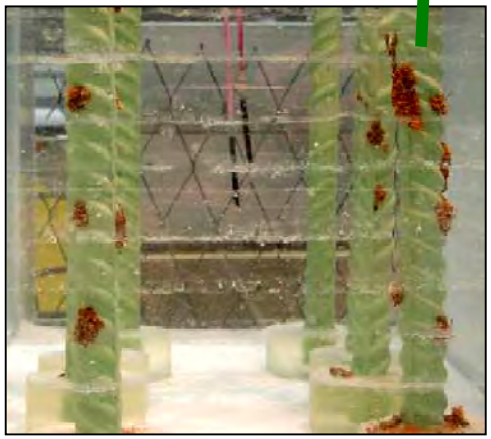


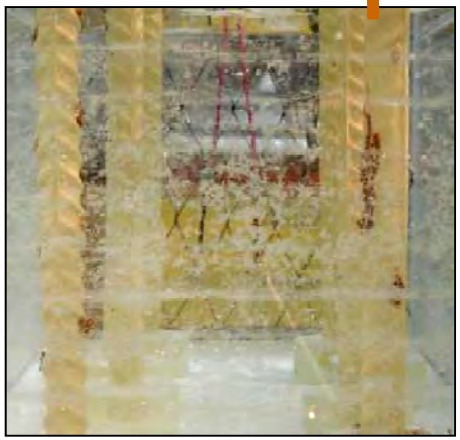
Results shown as Average of Duplicates

External Corrosion Manifestation

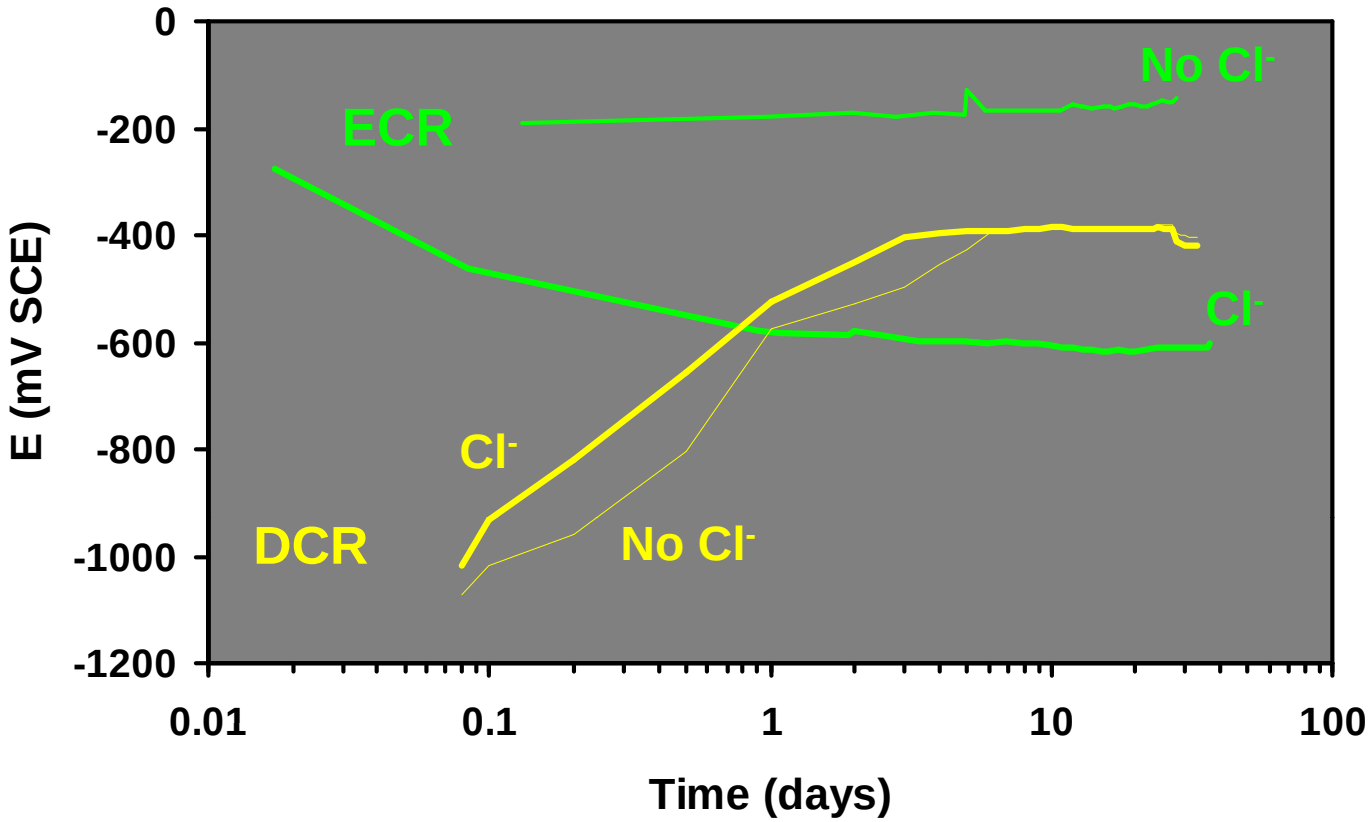
	Potential mV (SCE)	ECR	DCR
No Cl^-	All Cases	No Corrosion	No Corrosion
Cl^-	+100	Start Day 1 Blister Breaks Day 4	Start Day 1 Minor Blistering ~Day 20
	-500	Start Day 3 Blister Breaks Day 11	No Corrosion
	Open Circuit	Start Day 30	No Corrosion
	-1000	No Corrosion	No Corrosion





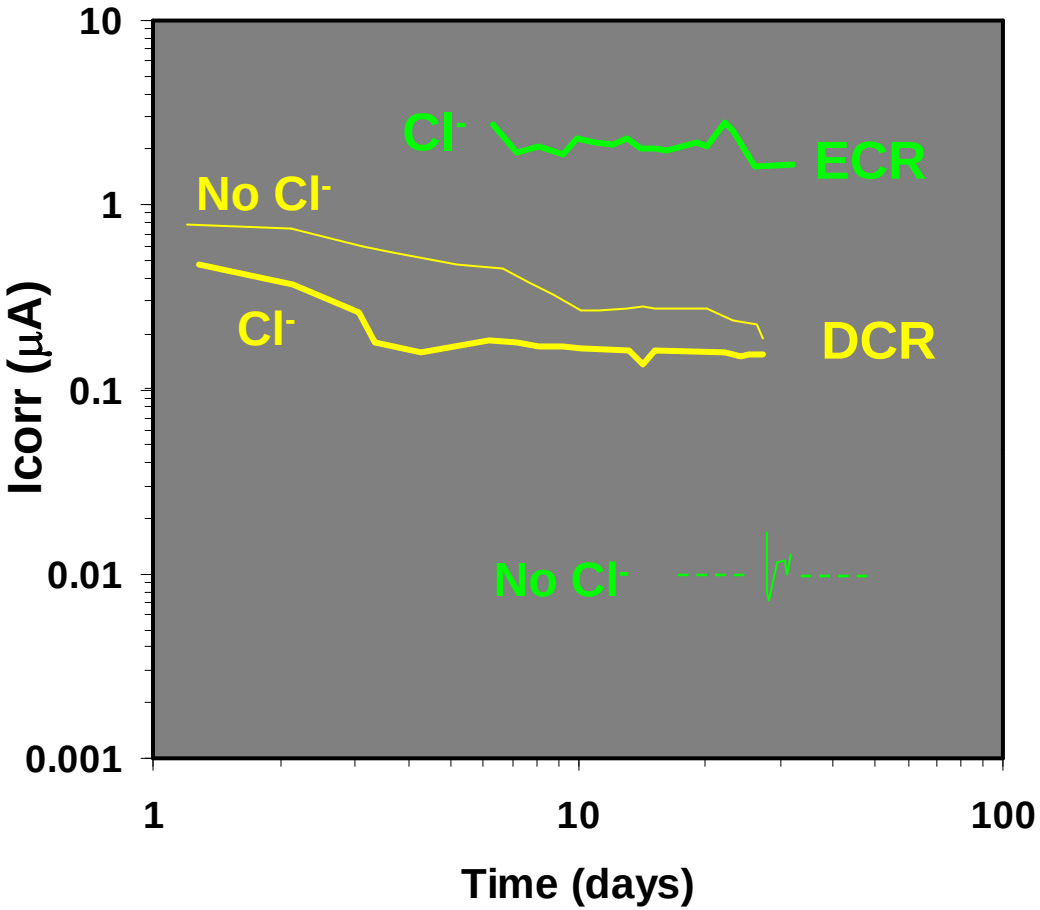


Open Circuit Exposure



- **ECR:**
  - **No Cl^- :** **OCP typical of passive Fe.**
  - **Cl^- :** **Steel corroding.**
- **DCR:**
  - **Both:** **Zn active then passive-like after a few days.**
    Steel not corroding – suggests cathodic prevention.

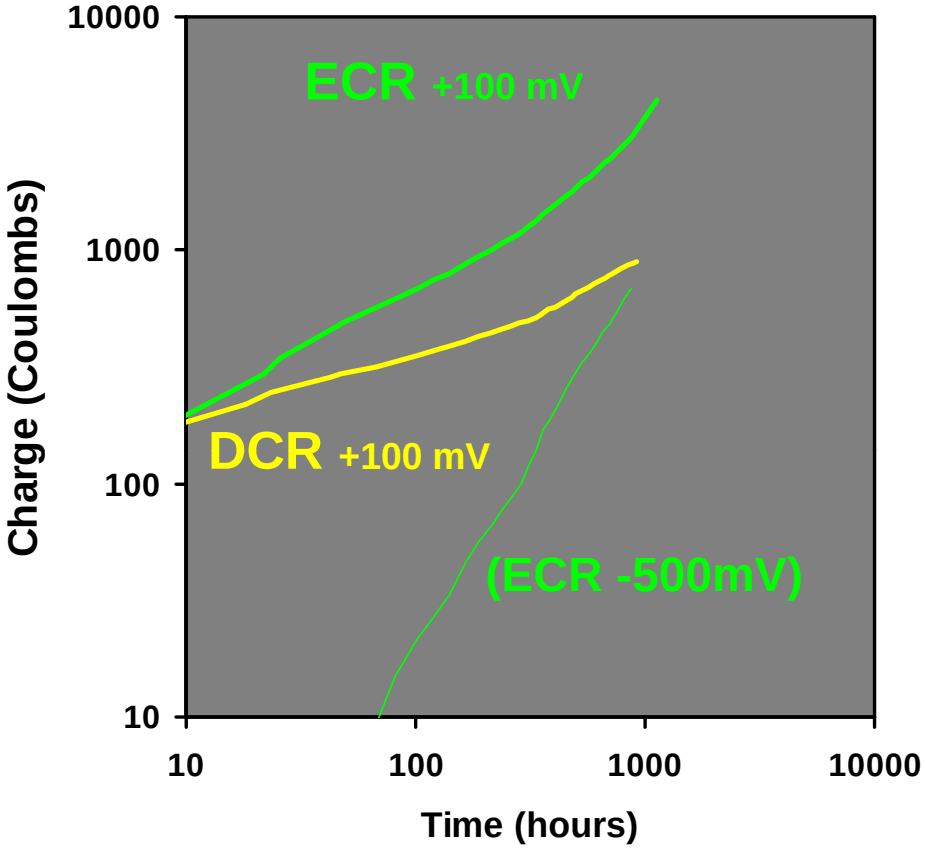
Open Circuit Exposure - Corrosion Rate from EIS



With Chlorides:

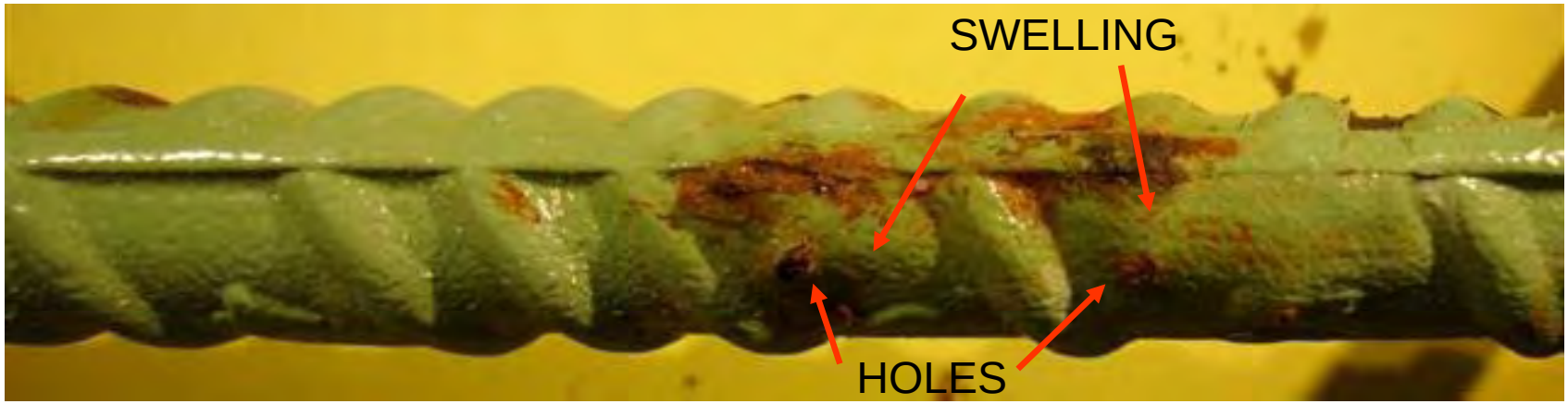
- Active corrosion rate of ECR much higher than for DCR
  - Exposed steel on DCR still passive.
- DCR tends to near passive behavior within few days
  - Consistent with OCP test.

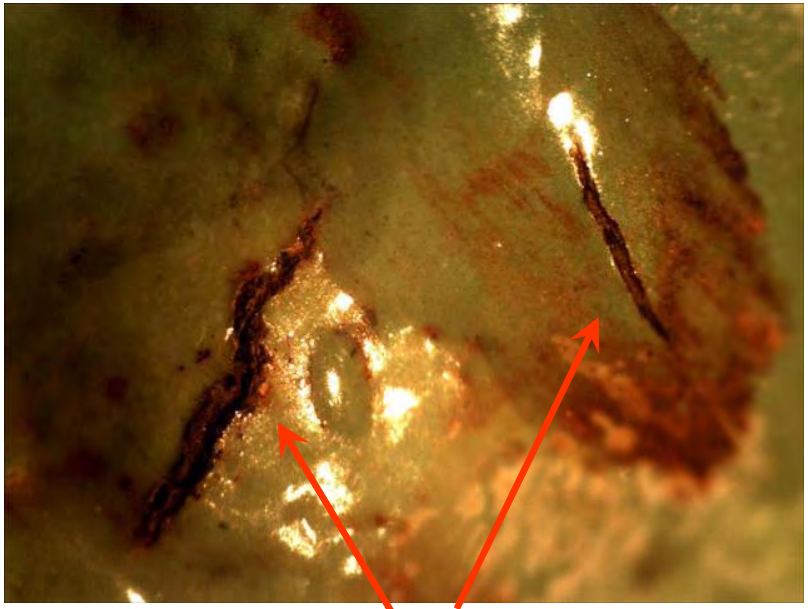
Cumulative Coulombs - Anodic Cases with Cl-

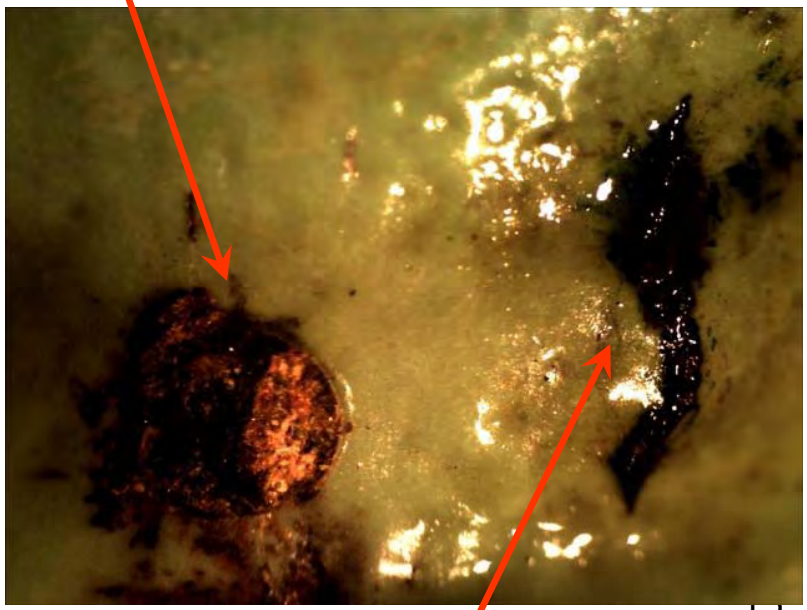


- Both corrode at highly accelerated +100 mV regime, but DCR much less.
- Only ECR corrodes at -500 mV
- Bend upward on ECR trend reflects strong in-crevice blistering.
- Lesser effect on DCR: suggests Zn resulted in tighter or plugged crevice

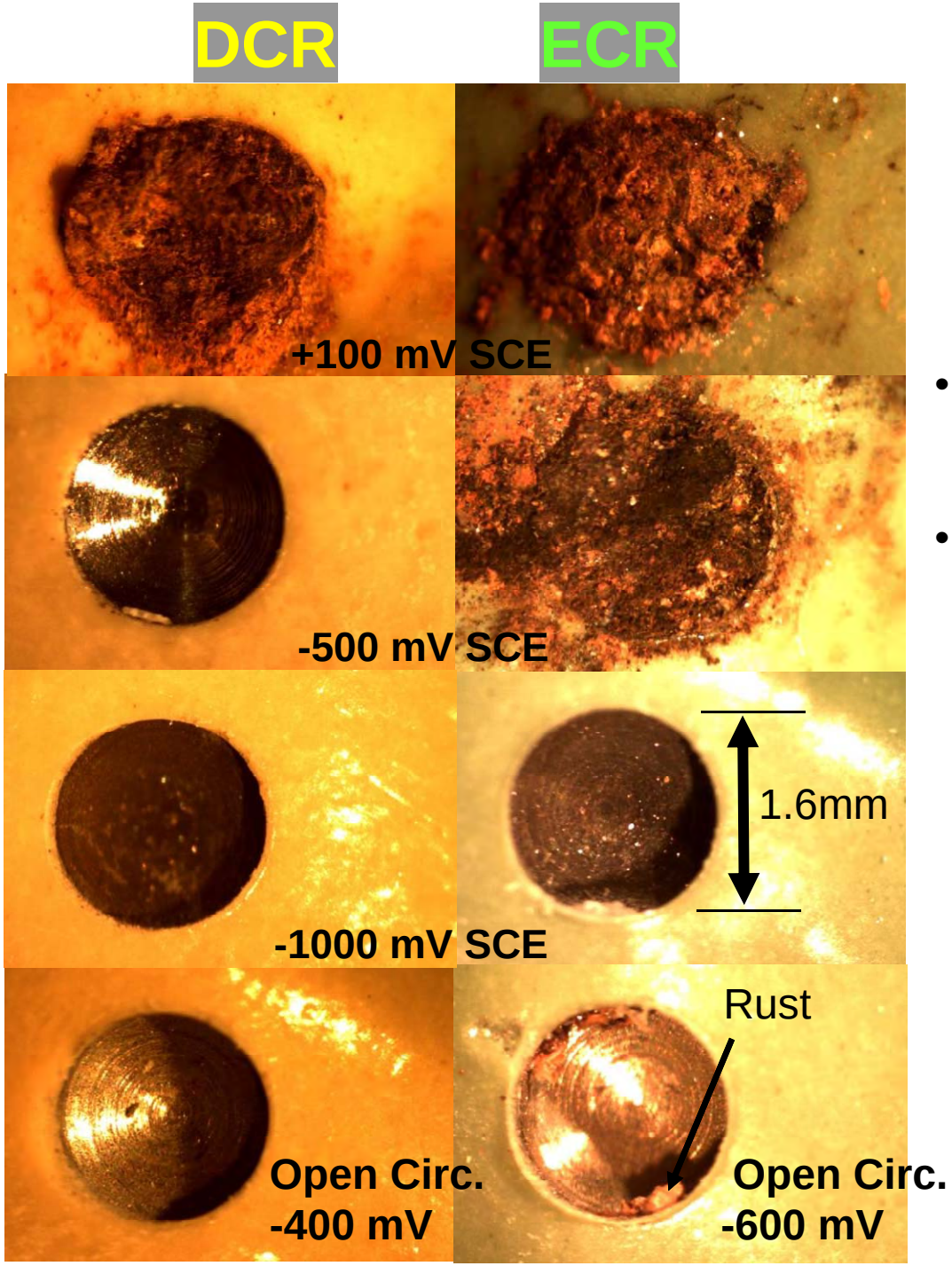
- ECR in SPS with Cl^-: Blistering / epoxy cracking from corrosion product and electrolyte buildup in crevice around holes.
- Significantly less swelling for DCR.





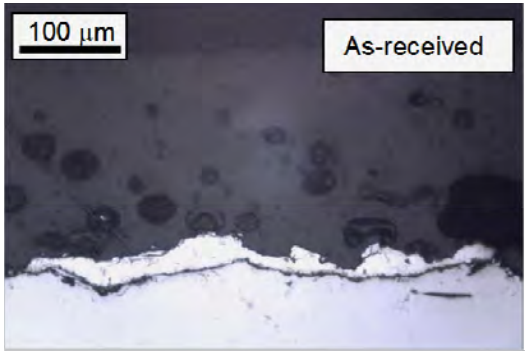


EPOXY CRACKS ON SWOLEN REGIONS



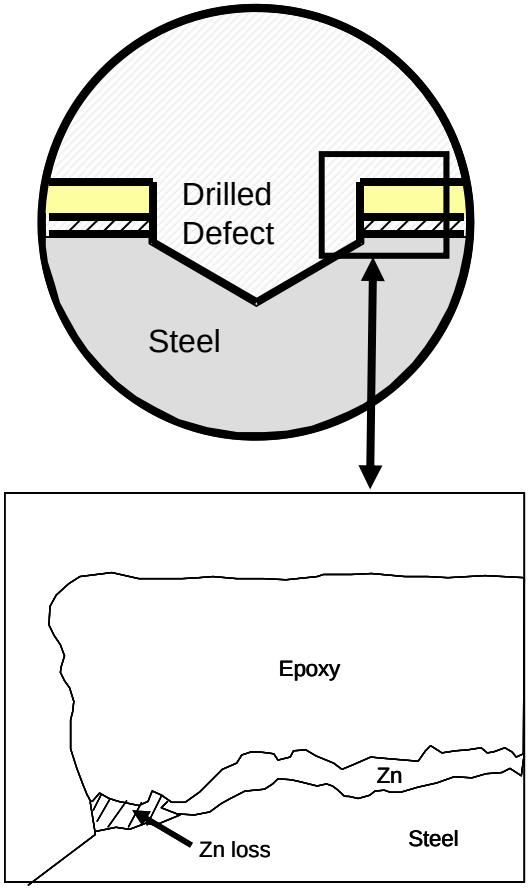
Drilled defect after exposure to SPS with chloride for 40-60 days.

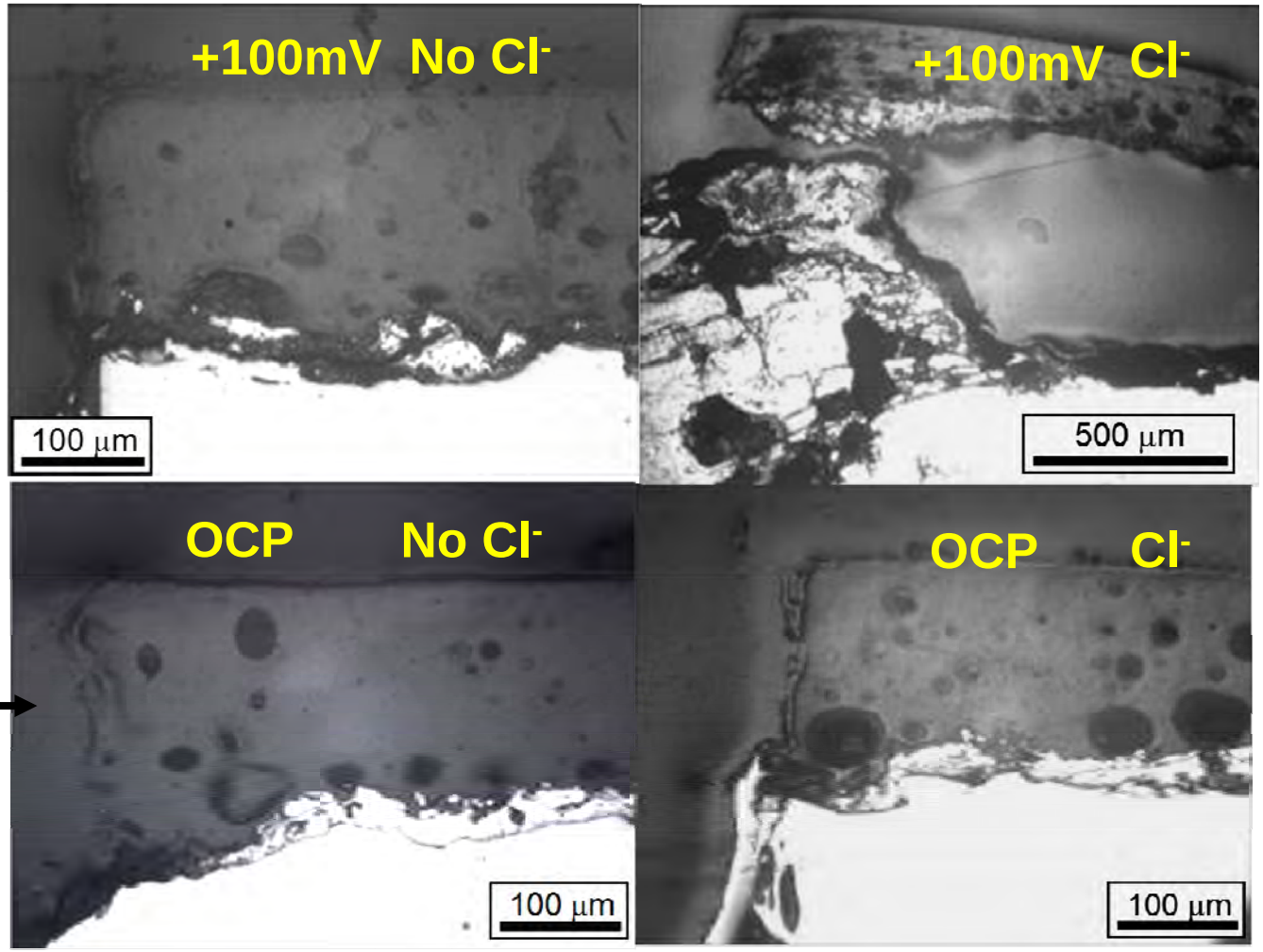
- **Cathodic prevention effect in DCR.**
- **Steel on DCR at Open Circ. shows only minor discoloration. ECR shows some rust on hole edge (crevice corrosion seen around hole when lifting coating).**



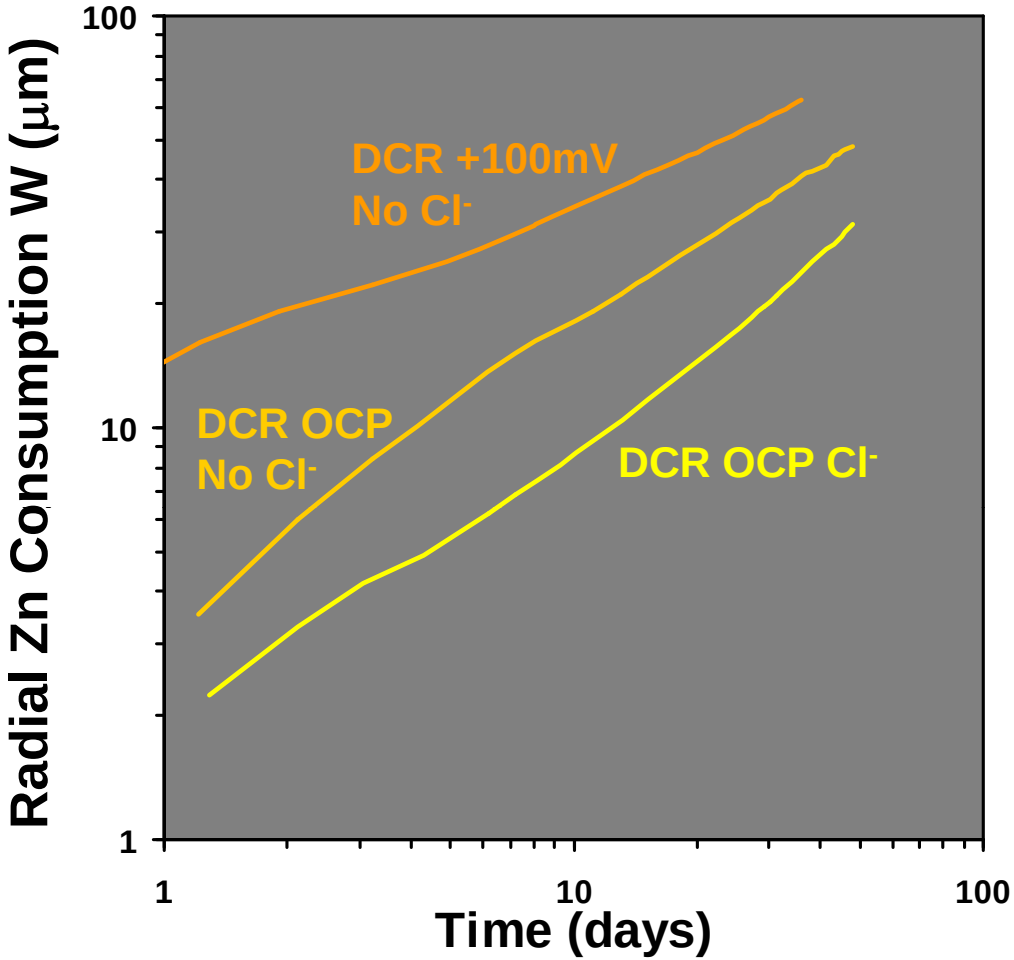
Zinc Coating Durability

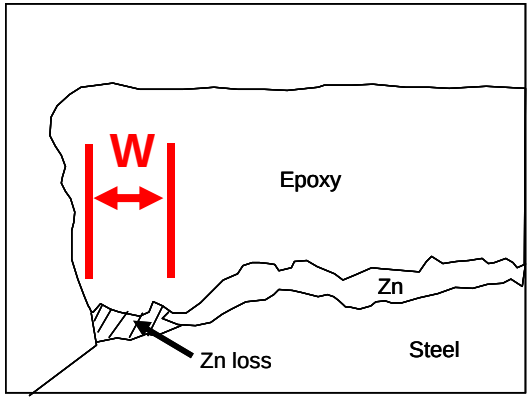
- **Metallographic observation of DCR zinc corrosion.**





Zinc Coating Durability Estimate: OCP and No Cl^- Anodic.





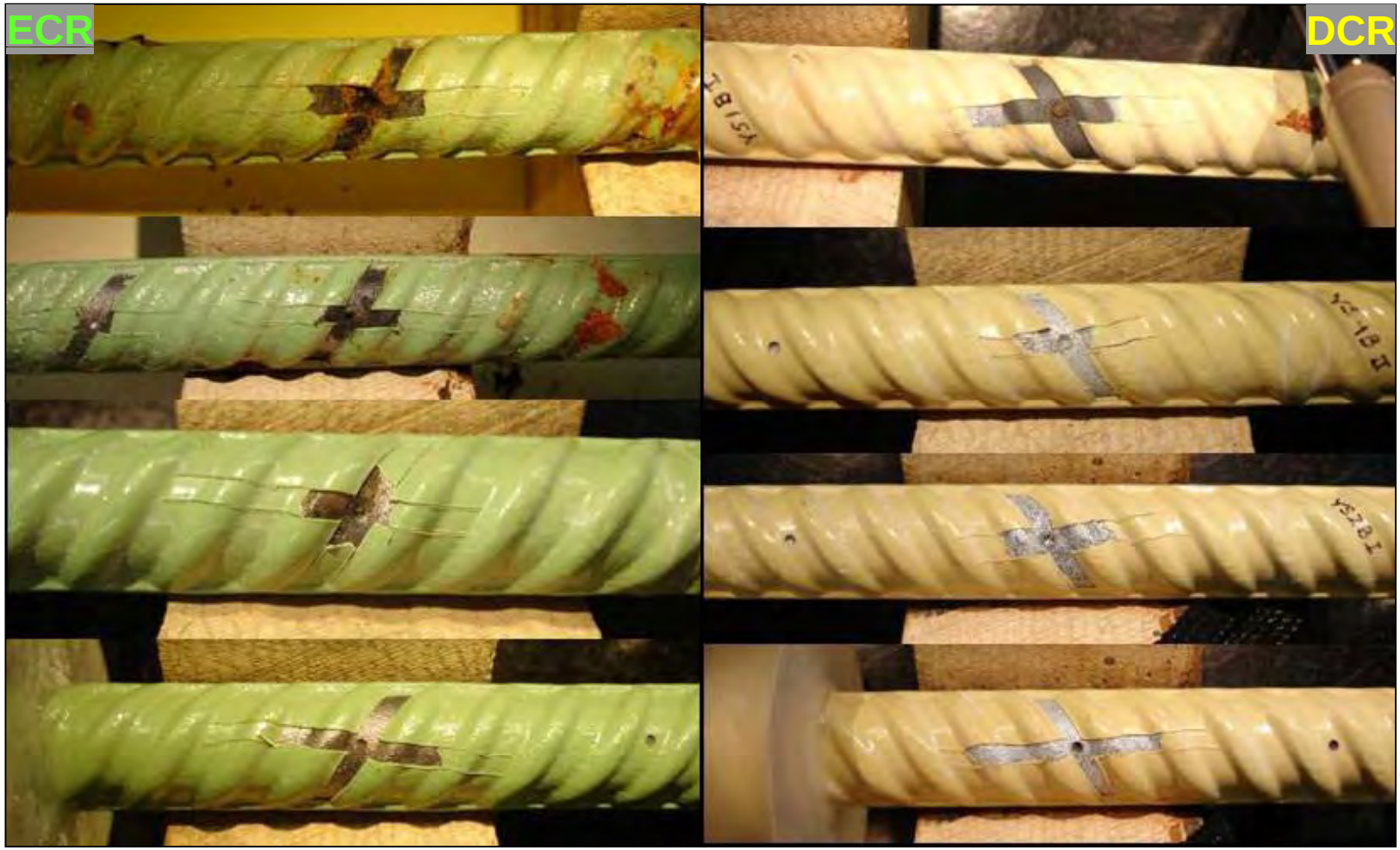
- Estimated from EIS and current data.
- Consistent with metallography.

- DCR at OCP: ~ 20-40 μm Zn consumed after 30 days. $W \alpha t^n$ with n<1.
- DCR at $+100mV_{SCE}$: Twice as much as for No Cl- cases.
- **Extrapolation: Long time (decades?) at Open Circ. for Zn loss to reach distances in the order of bar diameter.**

Extent of Disbondment
No Chlorides

- ECR trends follow well established pattern - more disbondment at more negative potentials.
- DCR disbondment seems no worse and less potential dependent.

Extent of Disbondment
With Chlorides

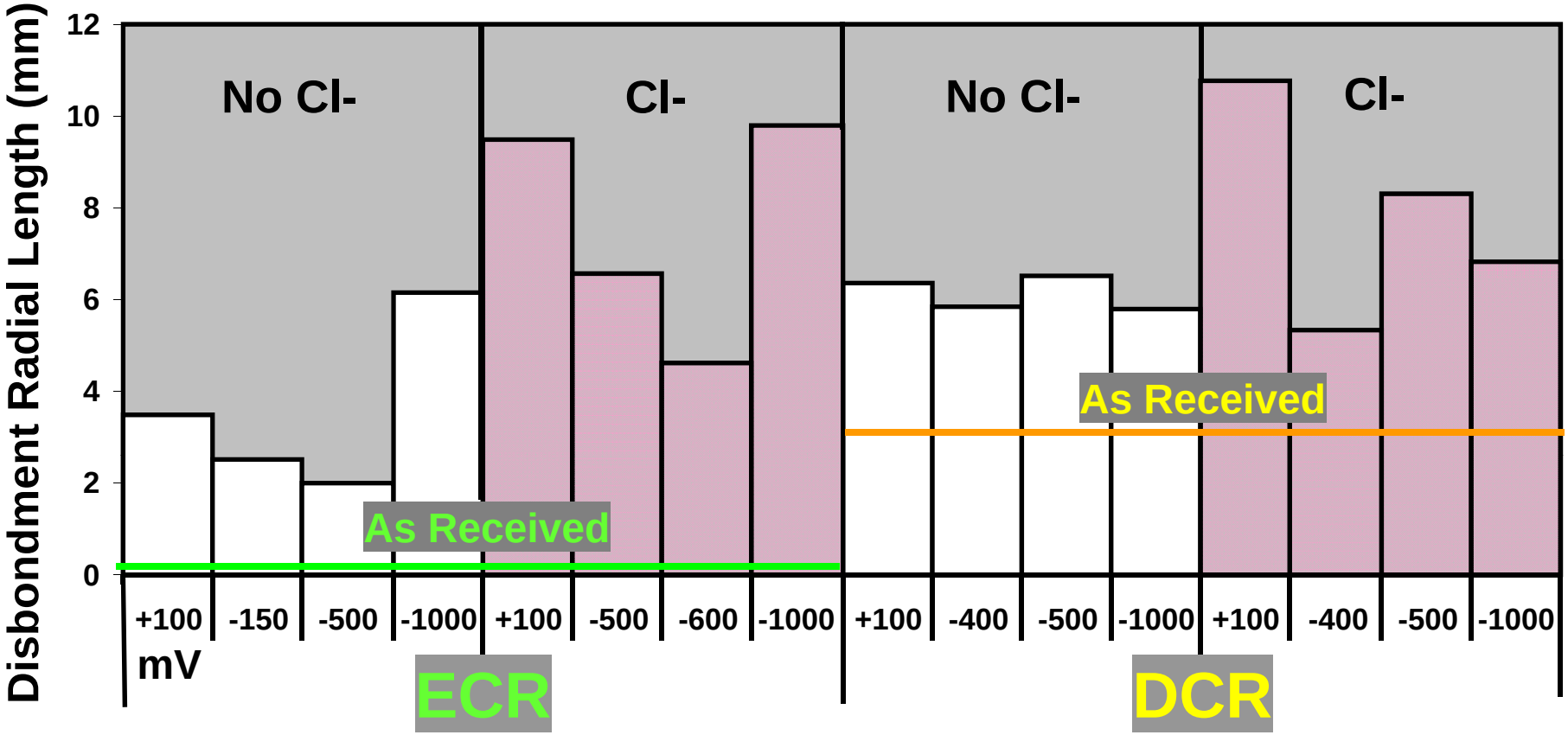


+100
-500
OC
-600
-1000

+100
OC
-400
-500
-1000

- ECR and DCR: Both cathodic and anodic disbondment.
- DCR: Zinc loss around anodic spot, much less corrosion than for ECR.
- DCR: Little discoloration all other cases, including Open Circ.
- ECR: Corrosion at Open Circuit conditions.

Disbondment Radius



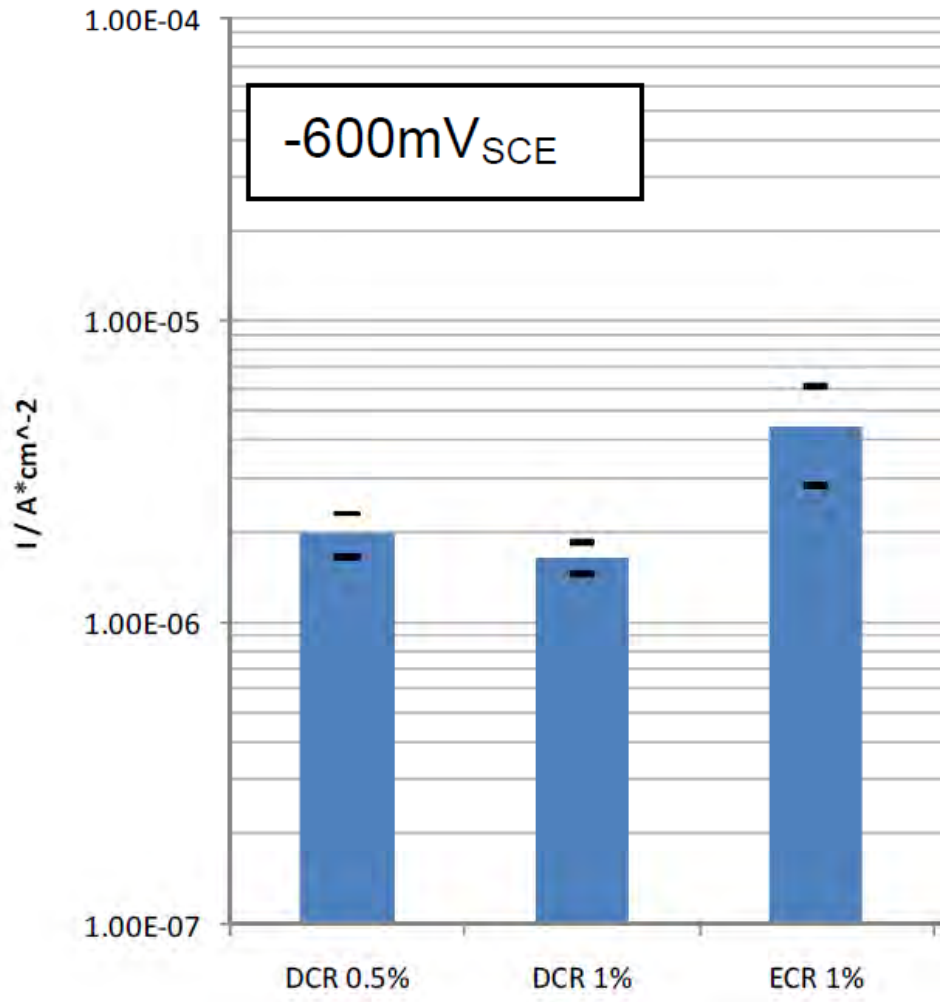
- Baseline disbond radius for DCR reflects native cohesive strength of sprayed Zn.
- Cathodic disbondment for DCR (relative to baseline) **similar / less than ECR's.**
- Anodic disbondment for DCR (relative to baseline) **comparable to ECR's.**

Cathodic Strength in Concrete

No Cl^-; w/c 0.5; cured 2 mo.; kept @ 75% RH

Breaks exposing indicated fraction of total surface.
Current density normalized to break area.

- DCR cathodic current density 2-3 times smaller than for ECR.
- Model projects corresponding ~X2 reduction in corrosion rates.
- Effect disappears if Zn is consumed.



Conclusions

- Both DCR and ECR had severe corrosion under strong anodic polarization in simulated pore solution with Cl^-, but DCR less than ECR.
- For open circuit DCR (with and without Cl^-), after initial surge Zn wastage at defect rim was very slow and OCP stabilized to ~-400 mV_{SCE} . Exposed steel remained free of corrosion.
- In contrast, steel exposed at open circuit in ECR showed significant corrosion.
- Steel corrosion mitigation in DCR at the OCP possibly due to prevention (threshold elevation) by galvanic coupling with corroding zinc exposed at the defect rim.

Conclusions (continued)

- Coating adhesion of DCR limited by cohesive strength of sprayed zinc. Bond degradation of DCR relative to as-received condition generally comparable/less than for ECR.
- Without Cl^- and under medium to strong cathodic polarization, DCR had cathodic current (and hence an ability to support corrosion macrocells) no greater than for ECR. Before Zn consumption cathodic strength was 2-3 times less than for ECR,