Improving Durability of Reinforced Concrete Structures using Migrating Corrosion Inhibitors

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Advancements in Civil Engineering for a Sustainable, Equitable, and Resilient Infrastructure

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2022 CONFERENCE

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- Projections are that between 2000 and 2050, world population will grow 50%, global economic activity will grow 500%, and global energy and materials use will grow 300%.

- The use of materials challenges the capacity of our plant earth – air, water and land – and many environmental problems.
- This situation fundamentally affects many aspects of our future, such as the economy, energy and climate.
- We need to fulfill our human needs and prosper while using less material, reducing toxics and recycle more.

Sustainable Materials

- **Sustainable Materials** provide environmental, social and economic benefits while protecting public health and environment over their whole life cycle, from the extraction of raw materials until the final disposal.

Three main Goals :

- environmental sustainability
- economic growth
- public welfare

3R "Reduce, Reuse, Recycle" Action Plan,

Group of Eight (G8, July 2008)

Work together to encourage 3Rs on a global scale, through sharing of information and reducing regulatory and trade barriers that inhibit this goal, and collaborate to promote 3Rs capacity in developing countries.

The president's $2 trillion infrastructure bill covers everything from low-income housing to clean energy.

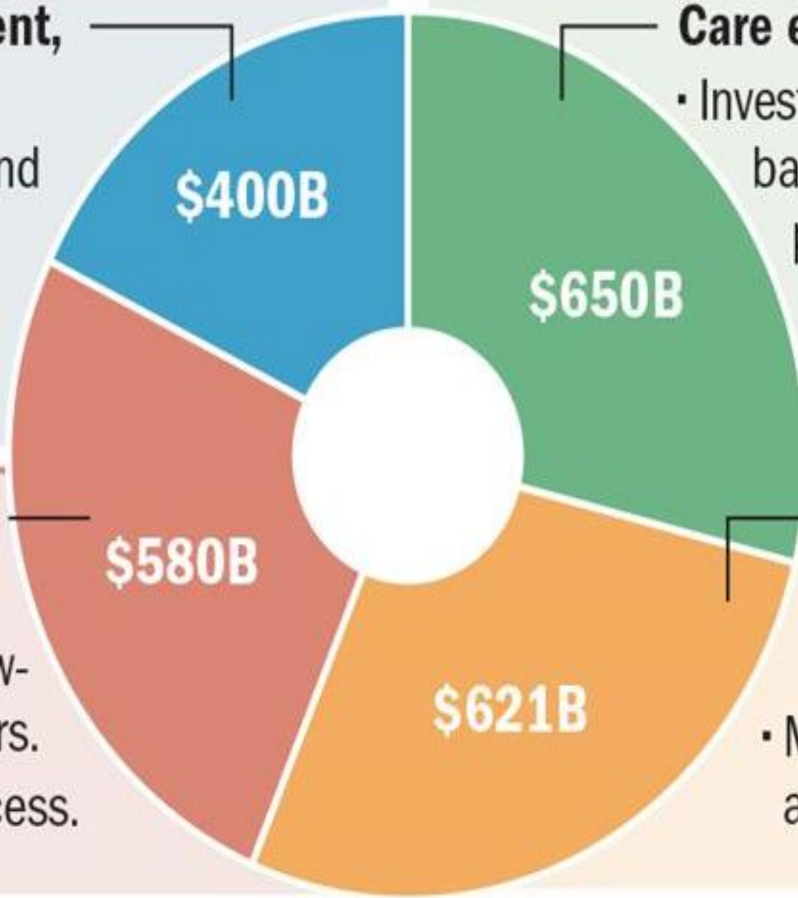
THE AMERICAN JOBS PLAN:

Research and development, manufacturing:

- Focus on clean energy and reducing emissions.
- Invest in more inclusive science/tech workforce.

Care economy:

- Invest in home and community-based care for seniors and people with disabilities.
- Improve benefits, working conditions for caretakers.



'At home' infrastructure:

- Build and renovate affordable housing for low- and middle-income buyers.
- Ramp up broadband access.

Infrastructure:

- Revamp highways, roads and bridges.
- Modernize transit systems, airport terminals.

Source: The Washington Post

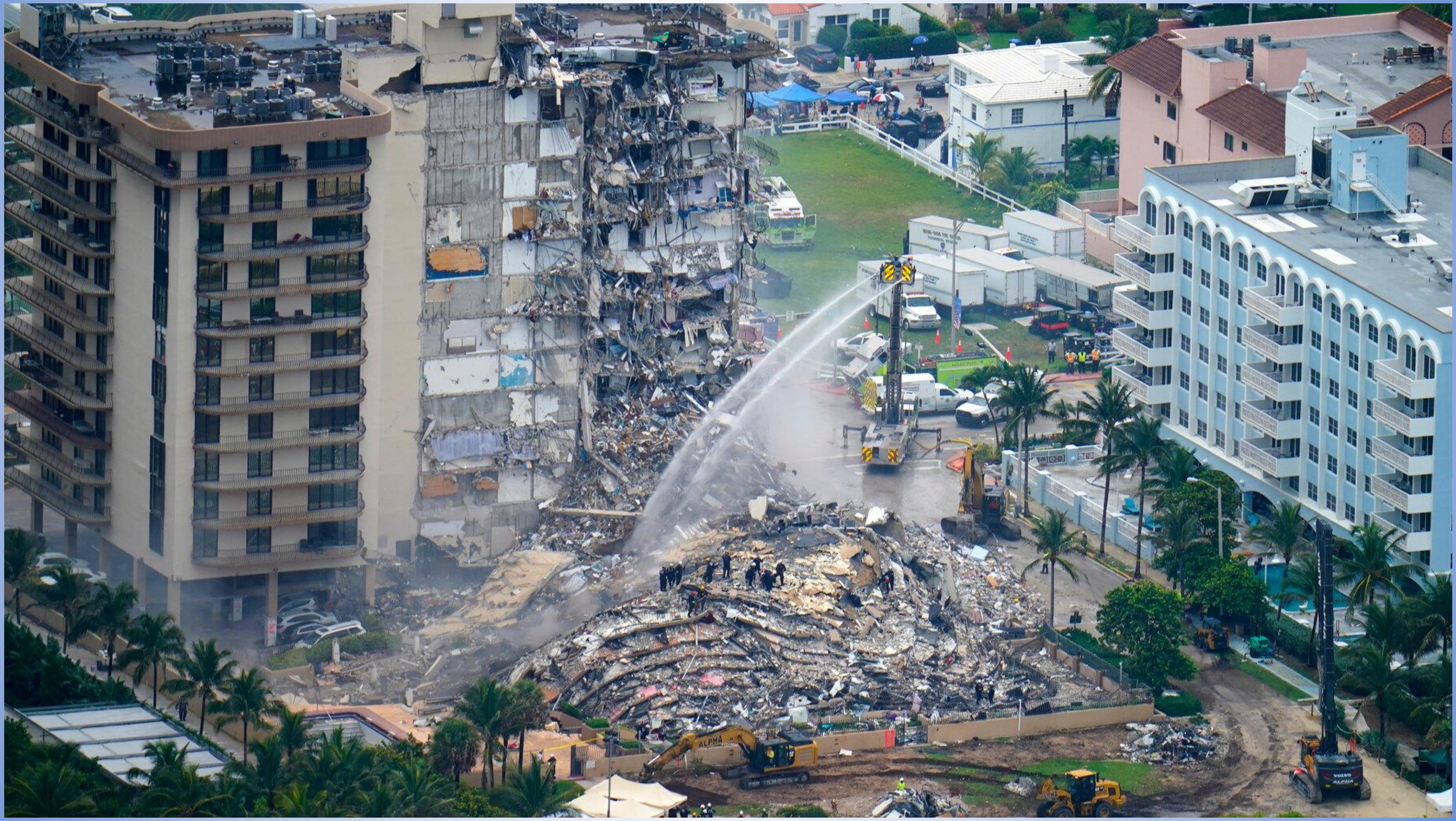
Chance Brinkman-Sull/Post-Gazette

Objective of our research program

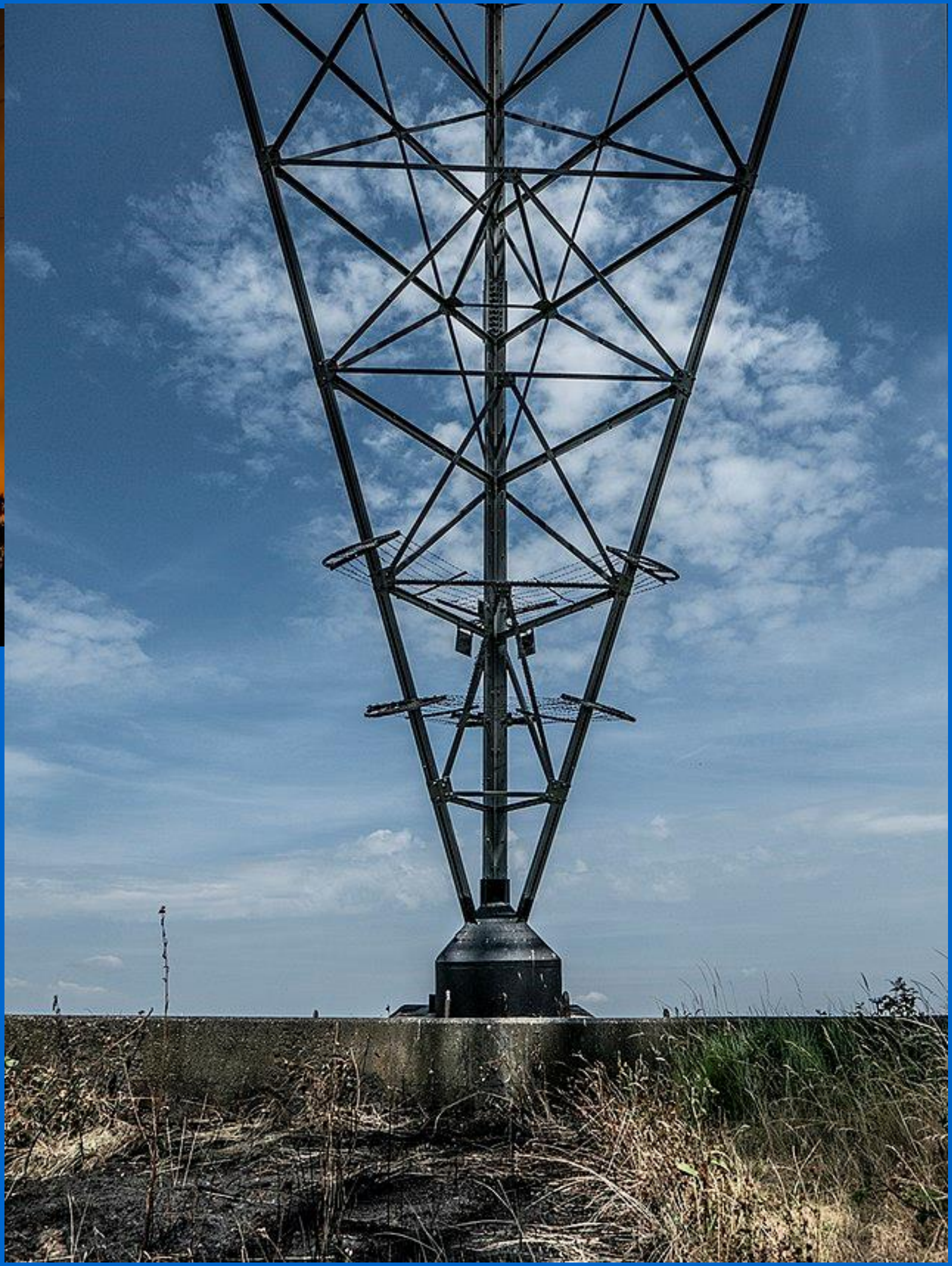
Corrosion is one of the primary concerns in the durability of structures.

Research efforts have been made to find corrosion protection and inhibition processes to prolong the life of existing structures and minimize corrosion damages in new structures.

‘Major Structural Damage’ at Surfside Florida Condo Complex due to corrosion of reinforced concrete, June 24, 2021



The Fern Hollow bridge collapse in Pittsburgh Jan 2022

Overview

- Corrosion Process in Concrete
- Testing Procedures
- Results and Conclusions
- Current Status

Concrete structures Deterioration


Concrete curing reactions

$2(3CaO.SiO_2) + 6H_2O = 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$

(Tricalcium silicate) (Tobermerite gel)

$2(2CaO.SiO_2) + 4H_2O = 3CaO.2SiO_2.3H_2O+Ca(OH)_2$

(Dicalcium silicate) (Tobermerite gel)

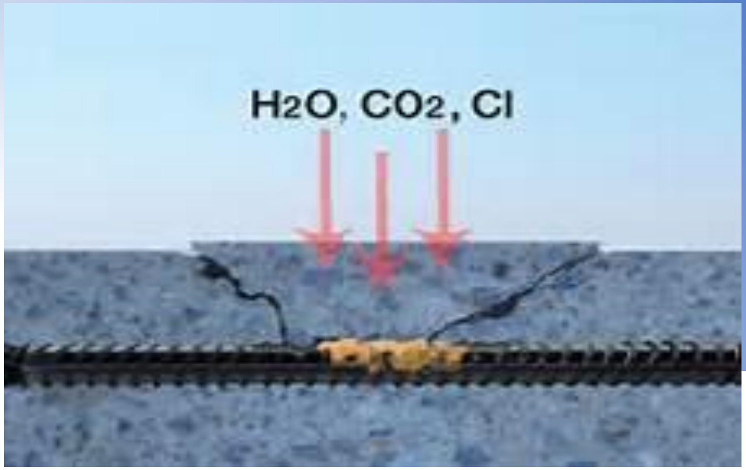
$3CaO.Al_2O_3 + 12H_2O + Ca(OH)_2 = 3CaO.\ Al_2O_3.\ Ca(OH)_2.12H2O$

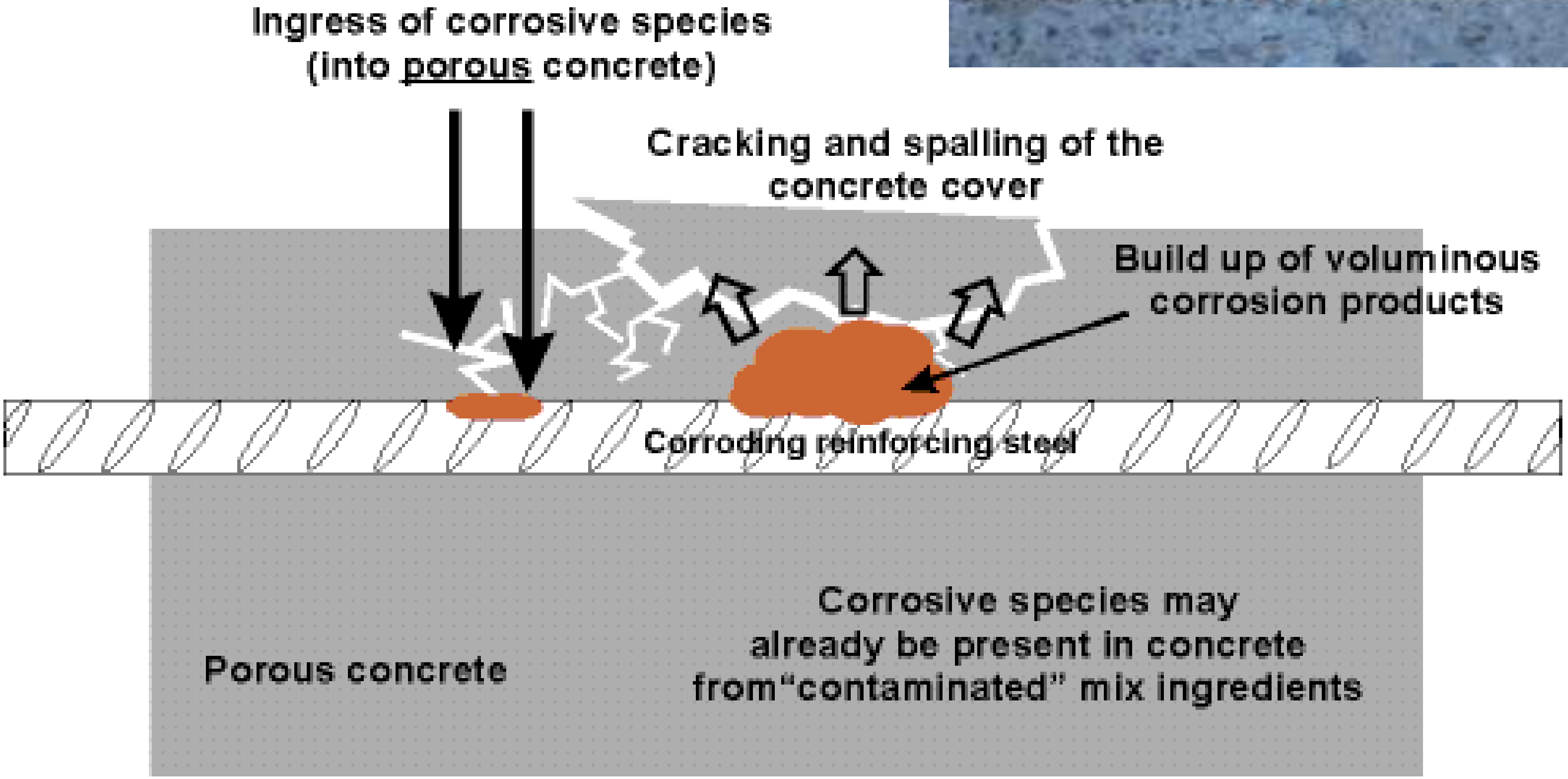
(Tricalcium aluminate) (Tetra-calcium aluminate hydrate)

- C_3S hardens rapidly: responsible for early strength
- C_2S hardens slowly and responsible for strength gain beyond one week

The water quality is critical not to take away any Ca ions from the binding gel otherwise lower concrete strength

Corrosion Damages





Corrosion Reactions of rebar in Concrete

Anodic reactions

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^-$

$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^-$

$Fe + 2H_2O \rightarrow HFeO_2^- + 3H^+ + 2e^-$

$Fe \rightarrow Fe^{++} + 2e^-$

Cathodic reactions

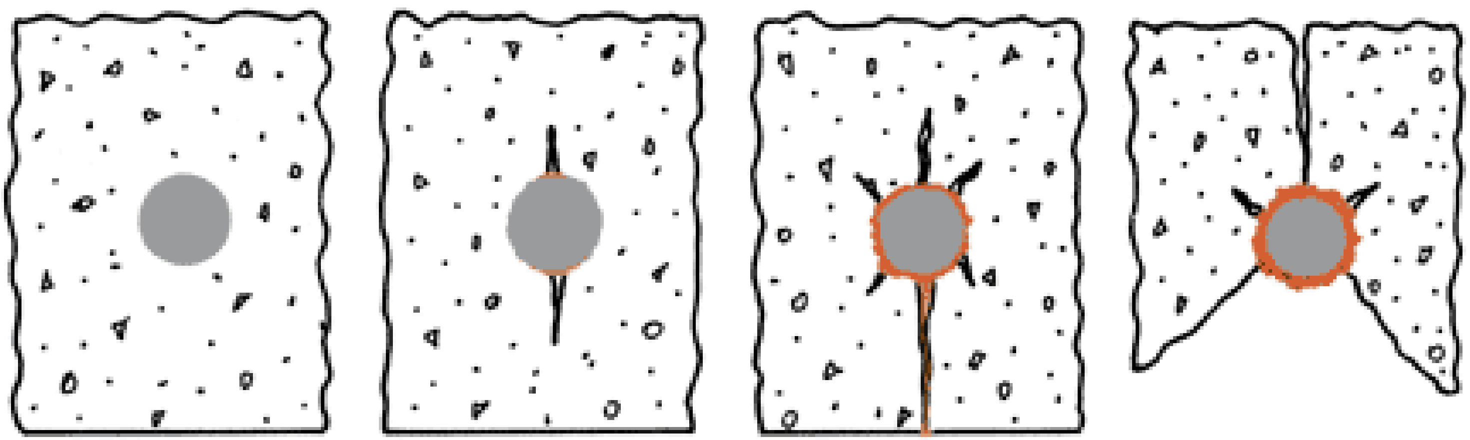
$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

or

$2H^+ + 2e^- \rightarrow H_2$

The anodic reactions result in the transformation of metallic iron (Fe) to rust.

The rust formation on the surface of reinforcement is accompanied by an increase in volume, as large as 6-8 times the volume of Fe, causing the concrete to crack.

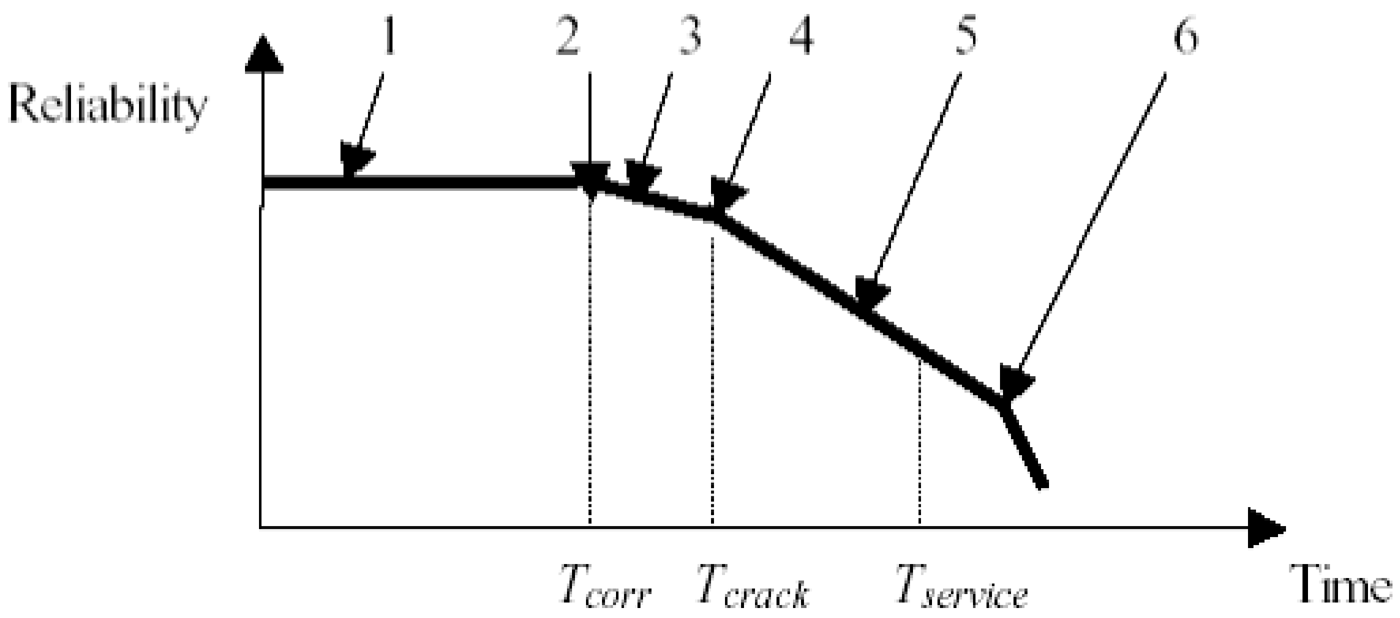


Before Corrosion | Build-up of Corrosion Products | Further Corrosion, Surface Cracks, Stains | Eventual Spalling, Corroded Bar Exposed

The corrosion cycle of uncoated steel rebar begins with the rust expanding on the surface of the bar and causing cracking near the steel/concrete interface. As time marches on, the corrosion products build up and cause more extensive cracking until the concrete breaks away from the bar, eventually causing spalling.

Timeline of Corrosion damages

1. Chloride penetration of the concrete
2. Initiation of the corrosion of the reinforcement
3. Evolution of corrosion of the reinforcement
4. Initial cracking of the concrete
5. Evolution of cracks in the concrete.
6. Spalling



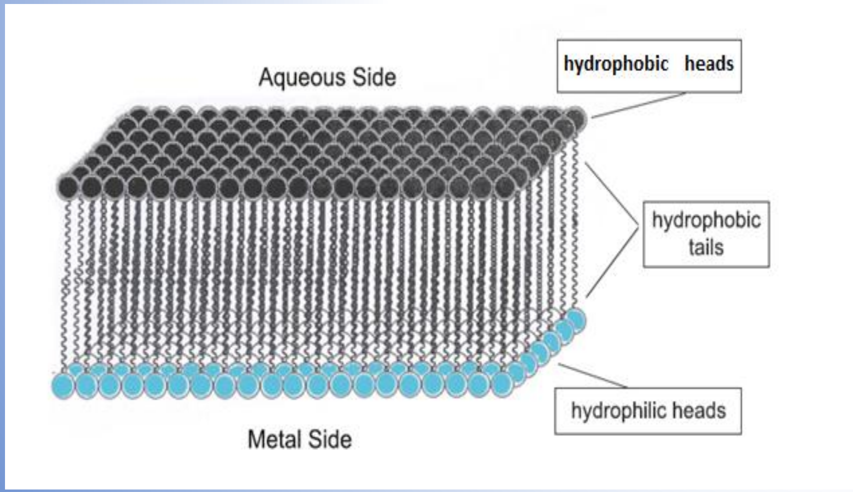
Protection of steel rebar in Concrete

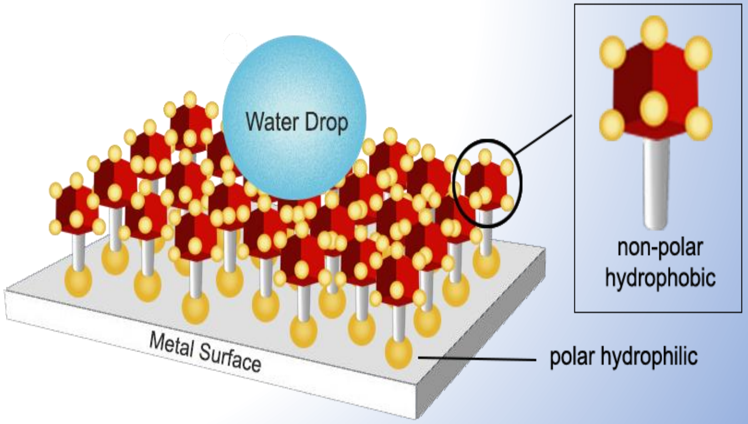
- Clean Concrete
- Cathodic Protection
- Admixtures and Corrosion Inhibitors
- Migrating Corrosion Inhibitors (MCI) or Surface Applied Corrosion Inhibitors(SACI)

How Admixture/Inhibitor works?

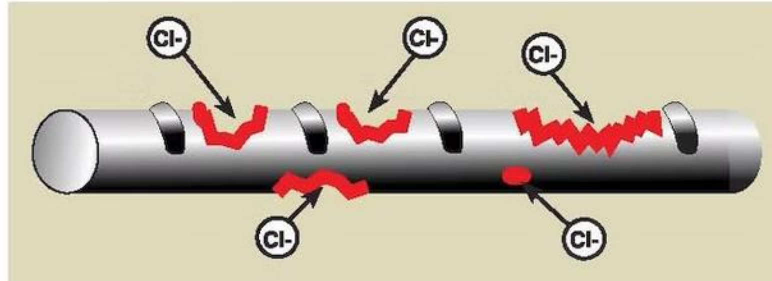
Migrating corrosion inhibitors (MCIs) are developed to protect steel rebar from corrosion in concrete. They were designed to be incorporated as an admixture during concrete batching or used for surface impregnation of existing concrete structures. **Under Chlorine Attack and Carbonatation Attack**

MCI use compounds that work by forming a monomolecular film between the metal and the water. In Film Forming Inhibitors, one end of the molecule is hydrophilic and the other hydrophobic.

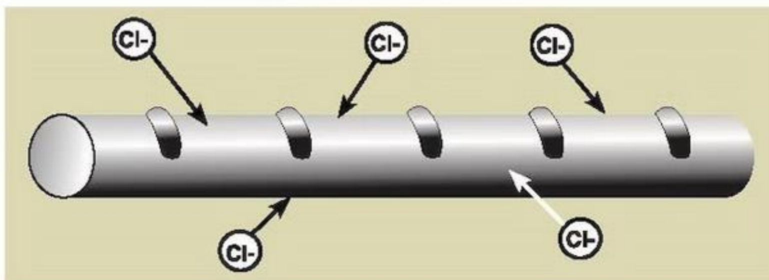




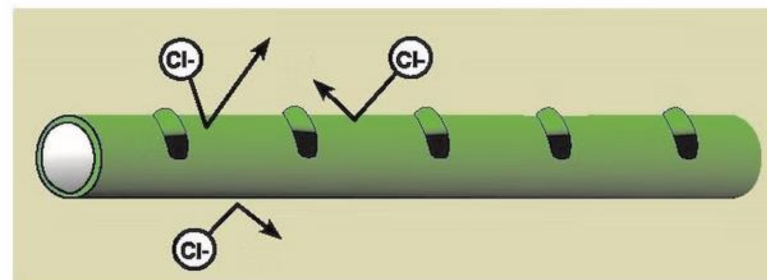
Chloride-Induced Corrosion

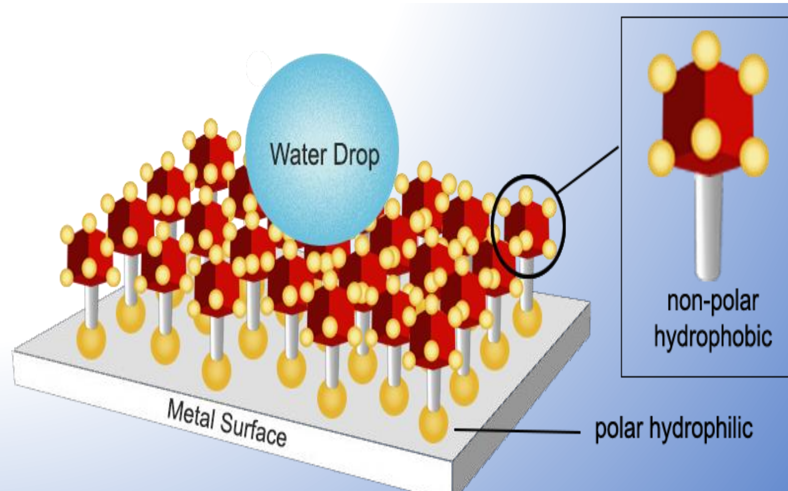


Unprotected Steel



MCI® Protected Steel





Electrochemical Tests

How to evaluate corrosion resistance of concrete:

Due to low conductivity of concrete special test method required to monitor corrosion of Rebar in concrete:

- ASTM G180 "Standard Test Method for Corrosion Inhibiting Admixtures for Steel in Concrete by Polarization Resistance in Cementitious Slurries"
- Electrochemical Impedance test on ASTM G109 samples:
  - Open circuit potentials
  - Polarization Resistance monitoring using EIS Bode plots

Polarization Resistance, Rp

This electrochemical technique enables the measurement of the instantaneous corrosion rate. It quantifies the amount of metal per unit of area being corroding at a particular time.

$$I_{corr} = \frac{B}{R_p \cdot A}$$

Where A is the area of metal surface evenly polarized and B is a constant that may vary from 13 to 52 mV. For steel embedded in concrete, the best fit with parallel gravimetric losses results in B = 26 mV for actively corroding steel , and a value of B = 52 mV, when the steel is passivated.

Typical Polarization Resistance for Steel Rebar in Concrete

Rate of Corrosion	Polarization Resistance	Corrosion Penetration
	R_p (kΩ.cm^2)	p (μm/year)
Very high	$0.25 < R_p < 2.5$	$100 < p < 1000$
High	$2.5 < R_p < 25$	$10 < p < 100$
Low/moderate	$25 < R_p < 250$	$1 < p < 10$
Passive	$250 < R_p$	$p < 1$

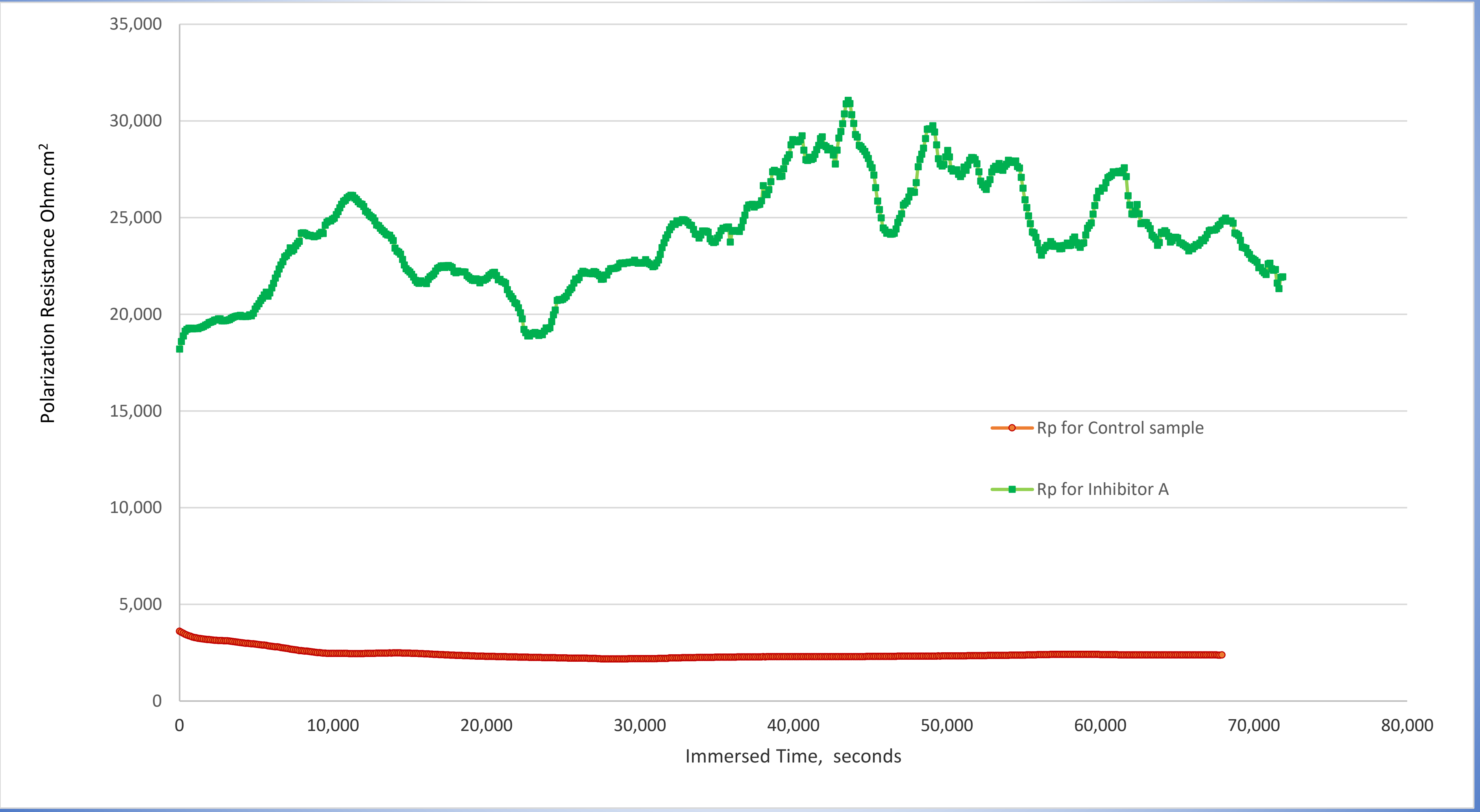
Experiments

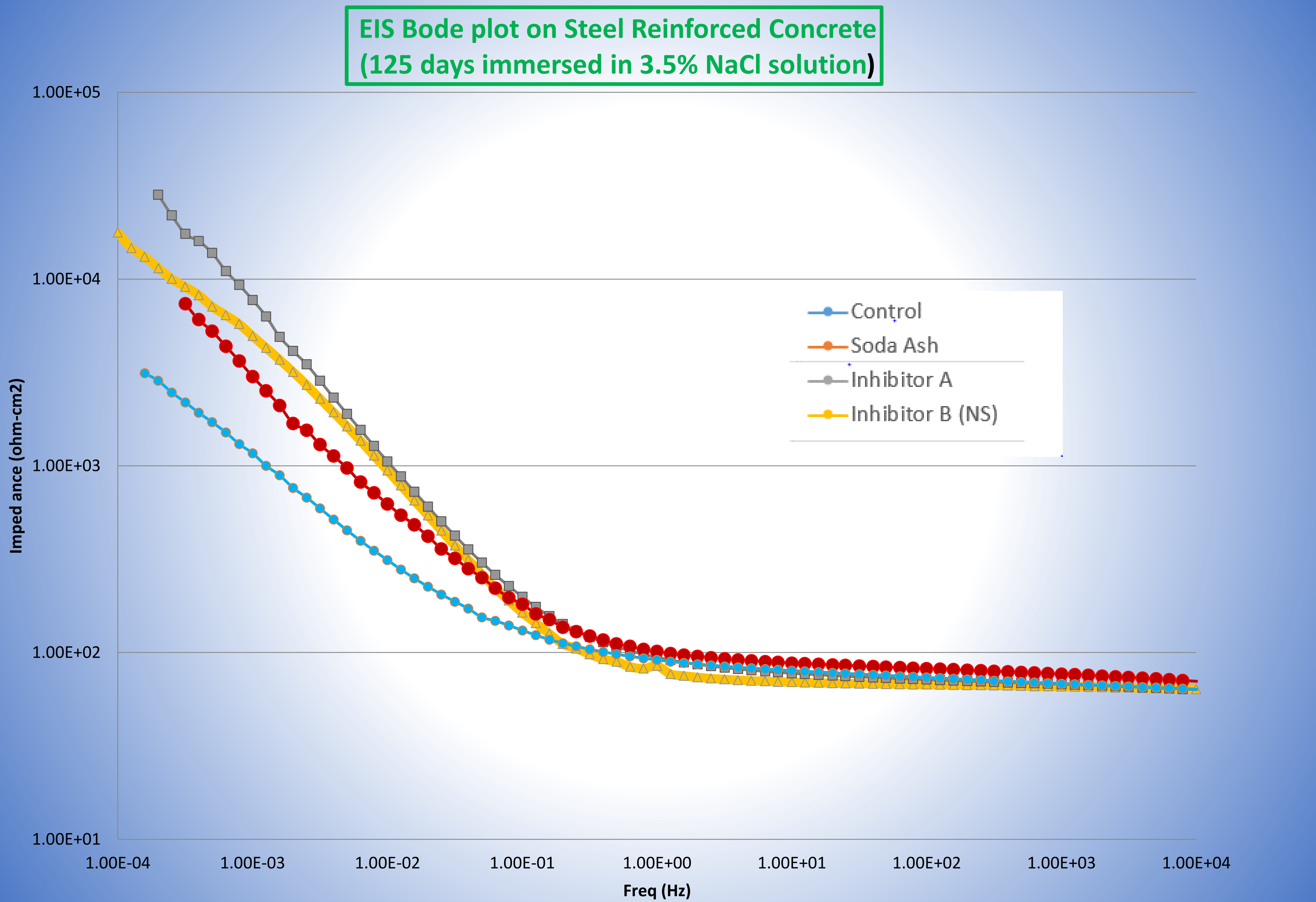
- ASTM G180 test method “Standard Test Method for Corrosion Inhibiting Admixtures for Steel in Concrete by Polarization Resistance in Cementitious Slurries”
- Two inhibitors, A and B, both admixtures of amine carboxylates, added to concrete samples were evaluated using modified G109 standards.
- Eight (8) concrete specimens were prepared with reinforcement placed at 1.9 cm (0.75 inch) concrete coverage, immersed in 3.5% NaCl at ambient temperatures and tested for a period almost five years, using electrochemical impedance spectroscopy (EIS).
- Post experiment visual observation, SEM/EDS and XPS were conducted on steel rebars.

Concrete Samples Preparation

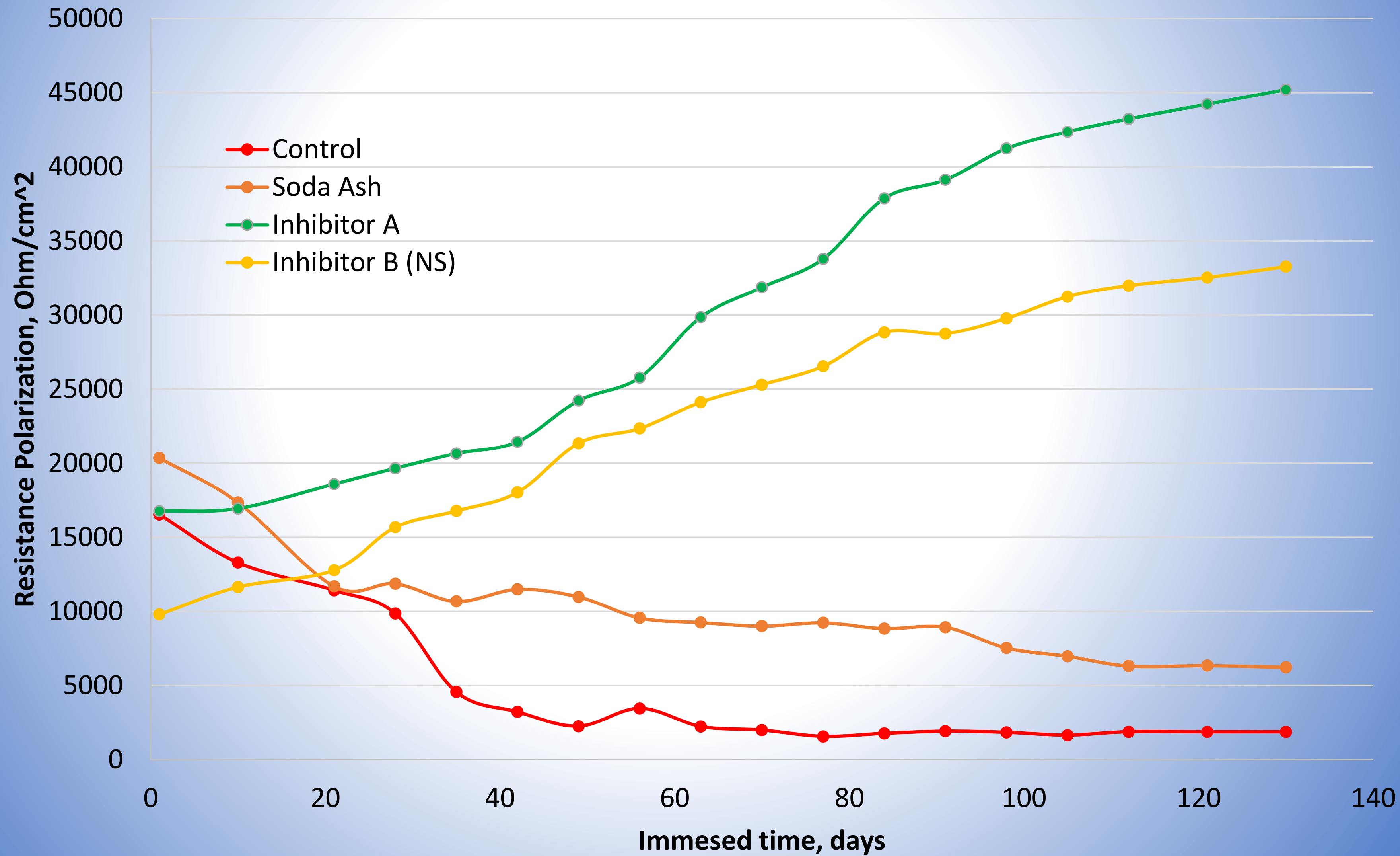
Concrete sample	Density	Water/cement Ratio	Strength, psi (Mpa)	Coverage, inch
Control	2.25 gr/cm3 (133 Ibs/ft3)	0.54	3,950 (27.2)	0.75
Soda Ash	2.27 gr/cm3 (135 Ibs/ft3)	0.53	3,920 (27.0)	0.75
Inhibitor A	2.28 gr/cm3 (135 Ibs/ft3)	0.53	3,880 (26.8)	0.75
Inhbitor B (NS)	2.28 gr/cm3 (135 Ibs/ft3)	0.53	3,910 (26.9)	0.75

Polarization resistance measurements of steel rebar in the solution prepared based on the ASTM G180 test method




EIS Bode plot on Steel Reinforced Concrete
(125 days immersed in 3.5% NaCl solution)
Control
Soda Ash
Inhibitor A
Inhibitor B (NS)
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
Imped ance (ohm-cm2)
1.00E-04
1.00E-03
1.00E-02
1.00E-01
1.00E+00
1.00E+01
1.00E+02
1.00E+03
1.00E+04
Freq (Hz)

Polarization Resistance (R_p) Versus Time; Comparison of Inhibitor treated concrete with Control concrete samples.



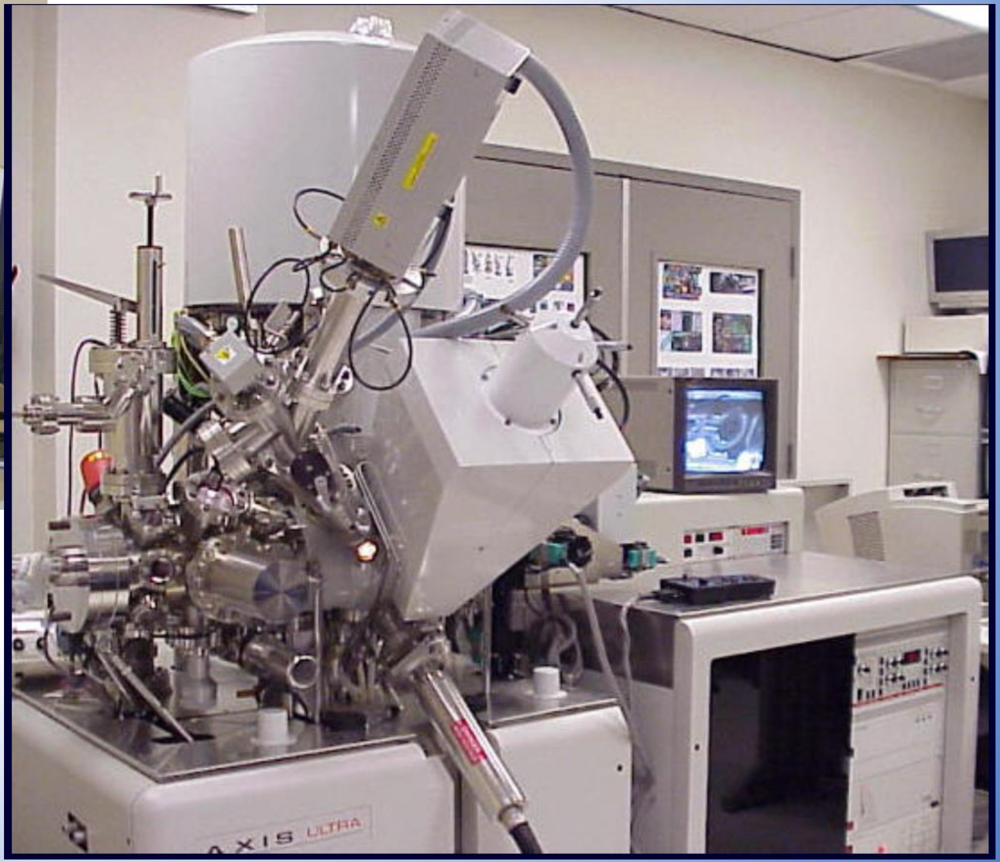
Inhibitor A after 150 days

Control after 150 days

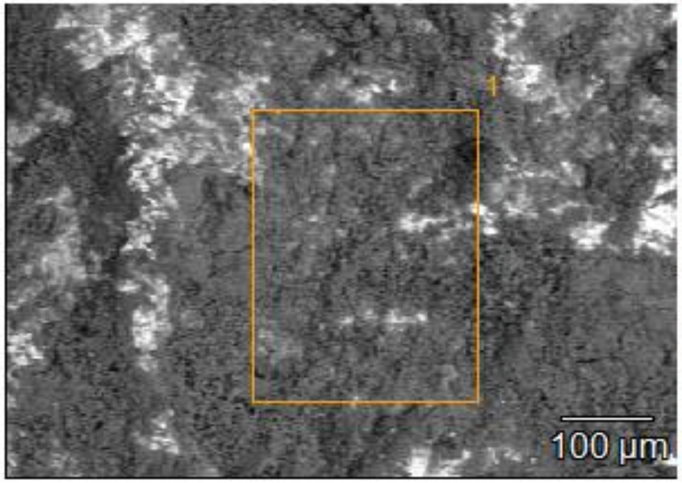
Inhibitor B after 150 days

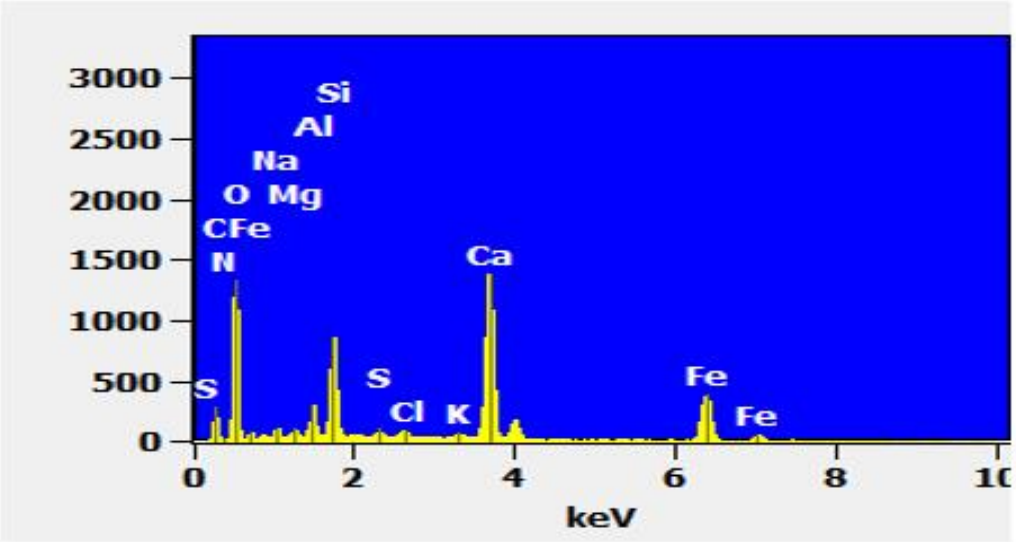
Soda Ash after 150 days

FESEM/EDS and XPS systems for surface analysis



EDS analysis on the Inhibitor A concrete samples.

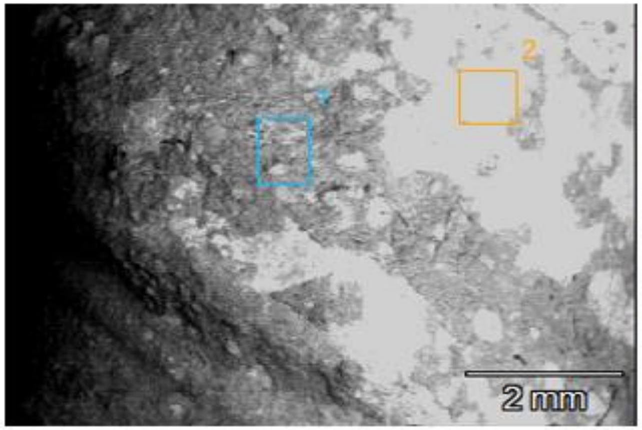


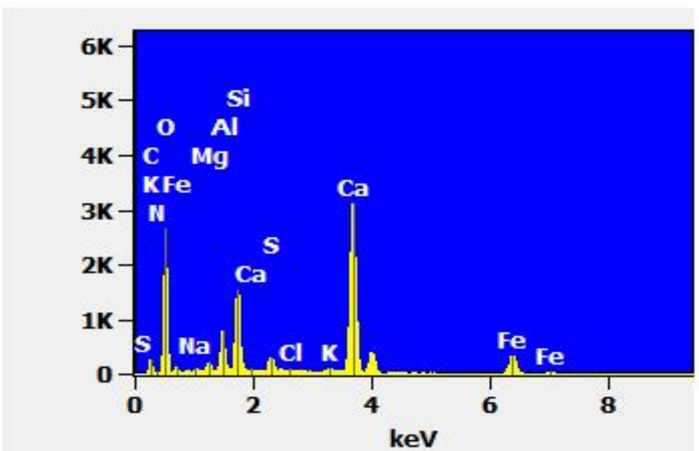


Weight %

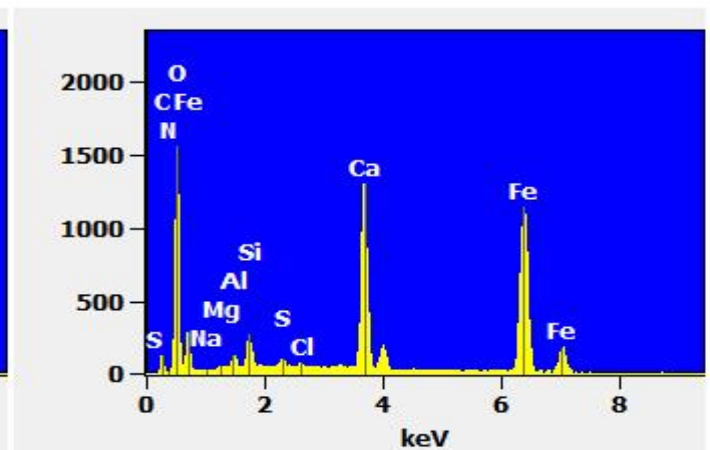
	C	*N*	*O*	*Na*	*Mg*	*Al*	*Si*	*S*	*Cl*	*K*	*Ca*	*Fe*
Inhibitor A_pt1	12.87	0.54	42.85	1.18	0.93	2.25	5.65	0.57	0.72	0.40	17.39	14.68

EDS analysis on the Control concrete samples.





Pt 1

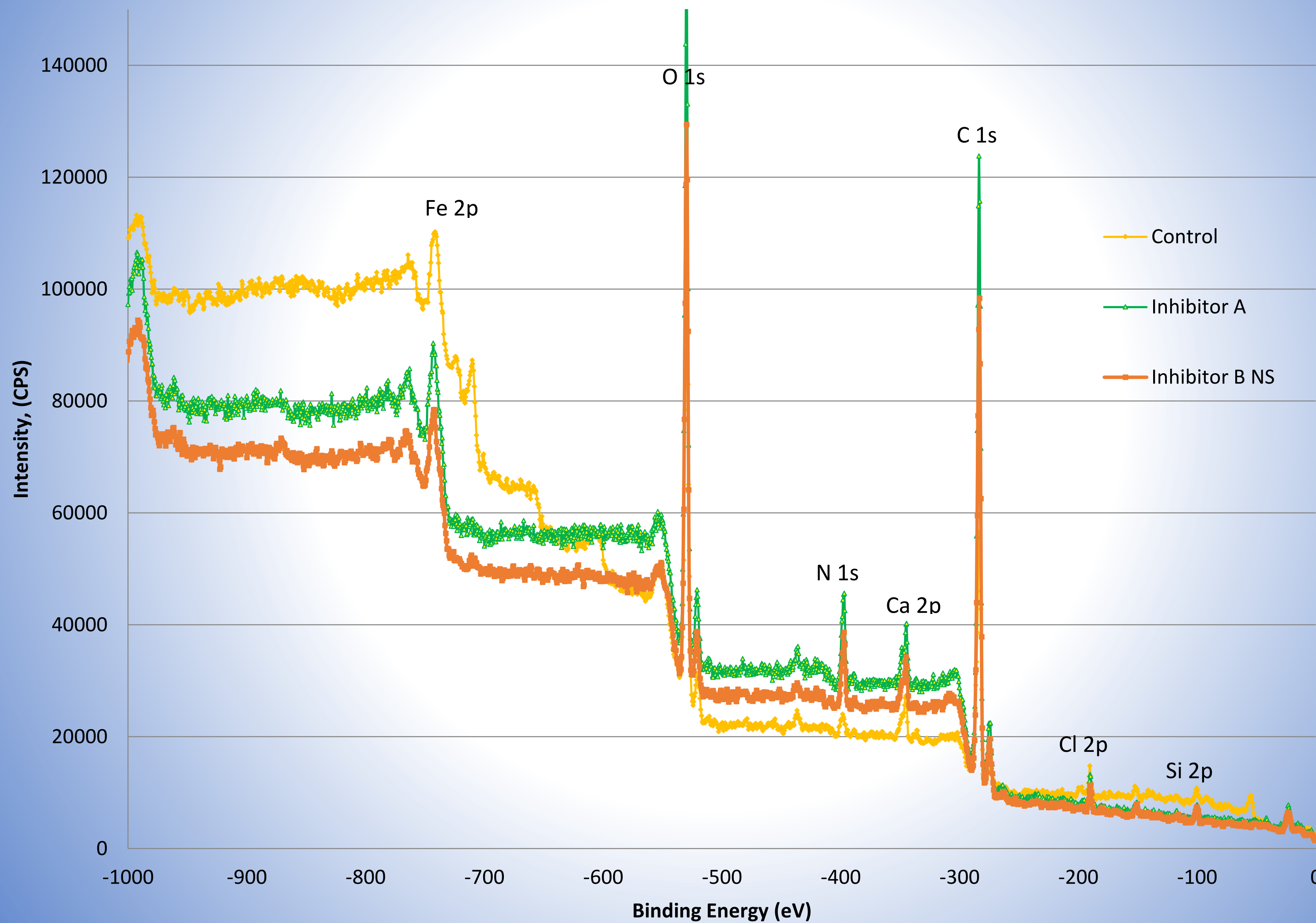


Pt 2

Weight %

	C	N	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
Control (2)_pt1	11.86	0.11	41.15	0.58	0.78	2.23	4.79	1.20	0.63	0.22	20.72	16.47
Control (2)_pt2	11.42	0.22	34.26	0.34	0.66	0.86	1.36	0.55	0.84	0.18	14.06	37.24

XPS analysis of rebar surface after 150 days in 3.5% NaCl



XPS analysis of on Rebar in concrete after 150 days, Mass Concentration %

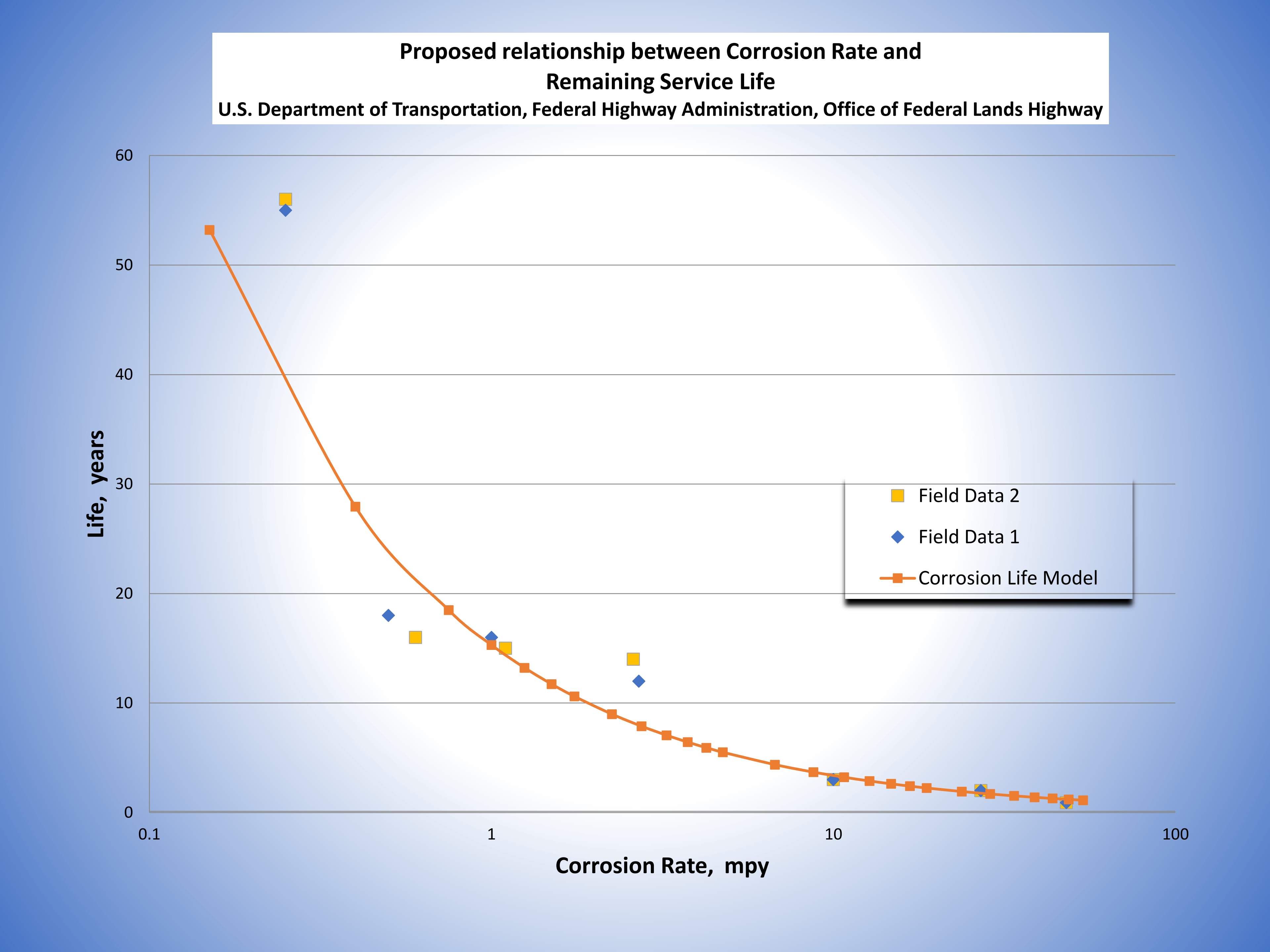
XPS Depth Profile (Ar at 4 kV, 15 mA)

	Binding Energy	710 eV	532 eV	284 eV	399 eV	200 eV	347 eV	99 eV
Sample	Etching Time (seconds)	Fe 2p	O 1s	C 1s	N 1s	Cl 2p	Ca 2p	Si 2p
Control	0	10.25	40.71	27.37	0.39	2.12	14.19	4.97
Control	120	13.6	39.43	22.08	0.34	2.16	17.2	5.19
Control	240	14.3	38.77	22.35	0.31	2.05	17.13	5.03
Inhibitor A	0	2.3	41.22	29.9	1.76	1.72	17.61	5.26
Inhibitor A	120	2.53	43.01	25.32	1.80	1.74	18.84	6.52
Inhibitor A	240	2.56	42.85	23.95	1.73	1.64	20.16	6.62
Inhibitor B (NS)	0	3.02	36.06	37.05	1.62	1.70	14.54	5.53
Inhibitor B (NS)	120	3.22	39.74	32.63	1.62	1.71	14.31	6.32
Inhibitor B (NS)	240	3.82	40.61	30.99	1.58	1.67	14.71	6.01

Life Predication based on Corrosion Rate

Sample	Rp, ohm/cm2	Corrosion Rate, UA/cm2	Life Expancy, yrs
Inhibitor A	48,400	0.23	>50
Inhibitor B NS	38,800	0.39	>50
Soda Ash	7,180	1.56	~10-12
Control	2,030	5.51	~ 5-6

Icorr ($\mu A/cm^2$)	Severity of Damage
<0.5	no corrosion damage expected
0.5-2.7	corrosion damage possible in 10 to 15 years
2.7-27	corrosion damage expected in 2 to 10 years
>27	corrosion damage expected in 2 years or less


Proposed relationship between Corrosion Rate and
Remaining Service Life
U.S. Department of Transportation, Federal Highway Administration, Office of Federal Lands Highway
Life, years
Corrosion Rate, mpy
0
10
20
30
40
50
60
0.1
1
10
100
Field Data 2
Field Data 1
Corrosion Life Model

Summary

- Amine carboxylate based migrating inhibitors Can successfully inhibit corrosion of rebar and prolong the life of reinforced concrete structures as demonstrated using ASTM G180 and ASTM G109 test method. Rp increased from 2,300 to 48,000 Ohm.cm^2 when Admixtures and SACI are used.
- Inhibitor protected samples showed an average corrosion rate of 0.23 $\mu A/cm^2$ (with a reducing trend) compared to untreated samples that were 5.5 $\mu A/cm^2$ based on the EIS test results. This will increase the life expectancy by more than ~50-60 years.
- XPS analysis demonstrated the presence of the amine carboxylate based inhibitor on the steel rebar surface indicating migration through the concrete.
- Depth profiling showed a ~50-60 nm layer of amine-rich compounds and chloride ions on the rebar surface, but neutralizing effects of the inhibitor assured satisfactory corrosion resistance even in the presence of corrosive chloride ions.
- Adding soda ash can maintain a high pH, but unable to stop corrosion attacks.

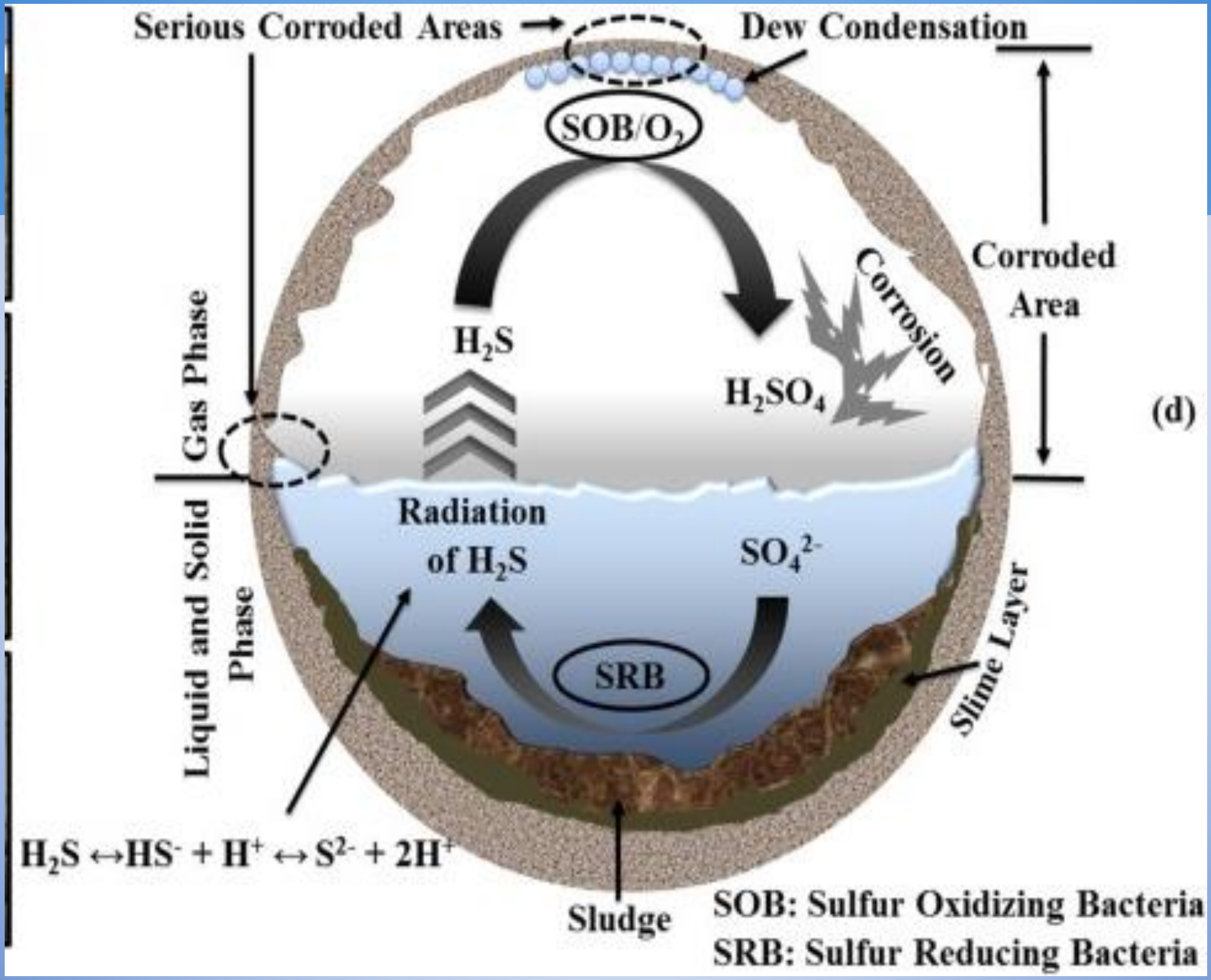
 

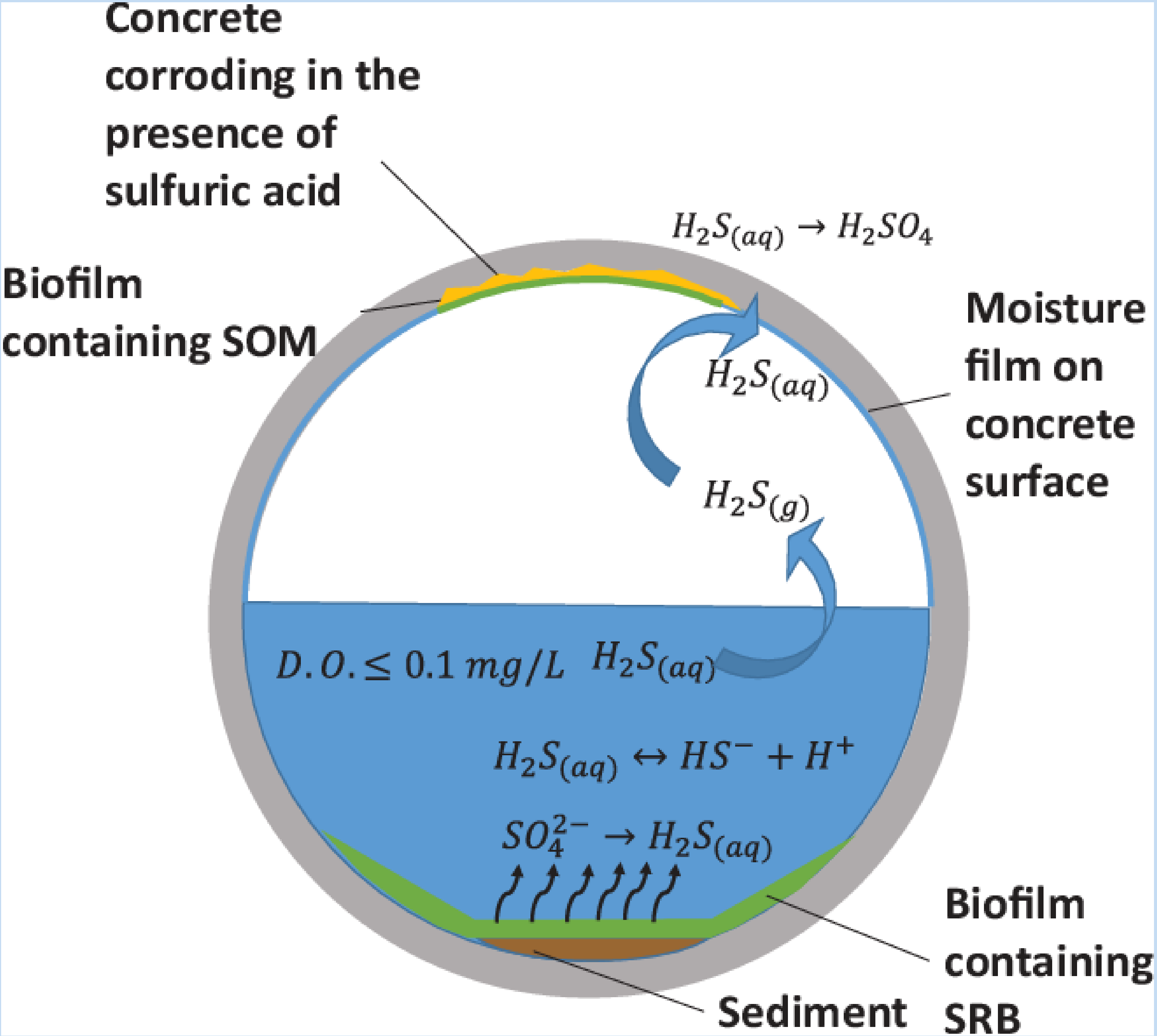
The Peljesac Bridge Croatia’s Adriatic coastline.

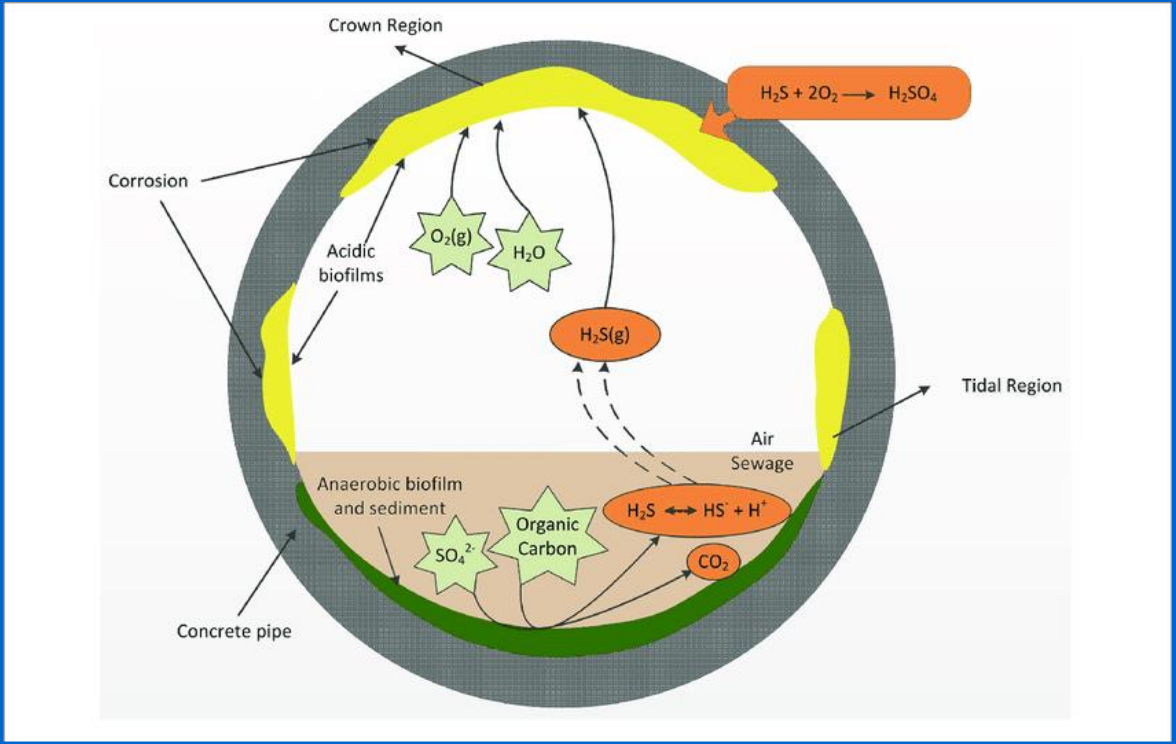
The USD $500M, 2.4-kilometre beam and cable-stayed structure, protected by MCI 2018 Surface Applied Corrosion inhibitor and MCI 2005 admixture.

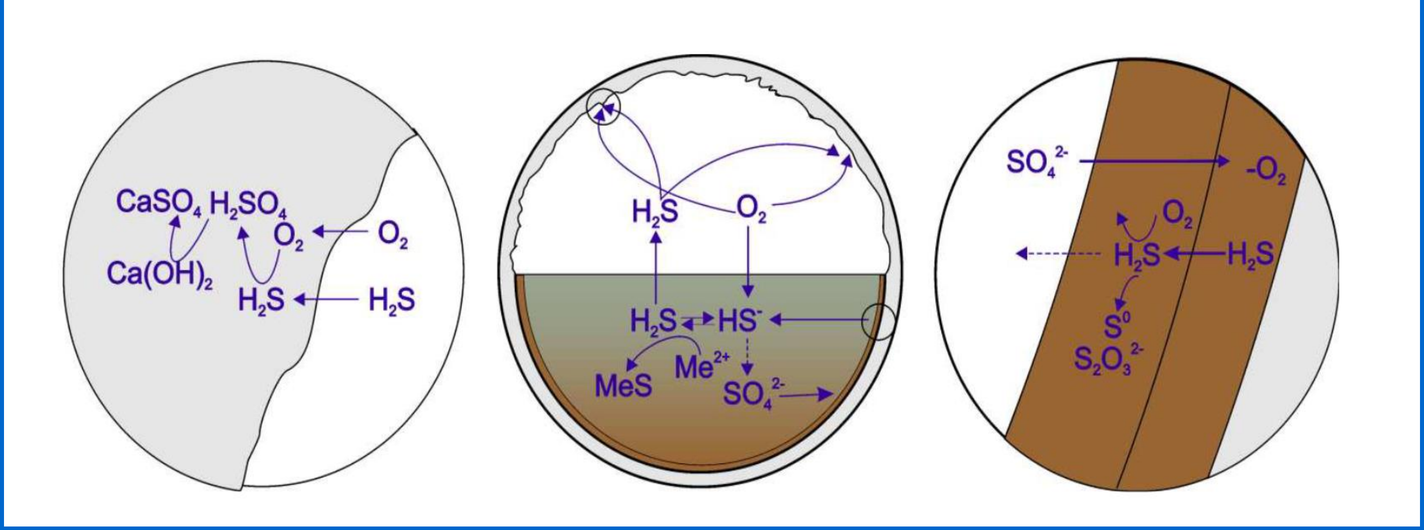
Current Research Project

Microbially-induced corrosion of Concrete Structures




Concrete corroding in the presence of sulfuric acid
$H_2S_{(aq)} \rightarrow H_2SO_4$
Biofilm containing SOM
Moisture film on concrete surface
$H_2S_{(aq)}$
$H_2S_{(g)}$
$D.O. \leq 0.1\, mg/L$
$H_2S_{(aq)}$
$H_2S_{(aq)} \leftrightarrow HS^- + H^+$
$SO_4^{2-} \rightarrow H_2S_{(aq)}$
Biofilm containing SRB
Sediment


Crown Region
H2S + 2O2 → H2SO4
Corrosion
Acidic biofilms
O2(g)
H2O
H2S(g)
Tidal Region
Air
Sewage
Anaerobic biofilm and sediment
Organic Carbon
SO4 2-
H2S ↔ HS- + H+
CO2
Concrete pipe


CaSO4 H2SO4
O2
O2
Ca(OH)2
H2S
H2S
H2S
O2
H2S HS-
MeS
Me2+
SO4 2-
SO4 2-
-O2
O2
H2S
H2S
S0
S2O3 2-

MIC effects: Production of hydrogen sulfide and concrete-destroying sulfuric acid, SRB (Sulfate Reducing Bacteria)

$SO4^{=} + 2\ H^{+} + 4\ H2 \rightarrow H2S\uparrow\ (H+/HS-) + 4\ H2O$

Formation of gypsum is an expansive reactions (white powdery deposites) , lower concrete strength, overstressing, cracking and spalling, mainly due to SOB reactions

$$H_2SO_4 + CaOSiO_2.2H_2O \rightarrow CaSO_4 + Si(OH)_4 + H_2O \quad (1)$$

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2CO_3 \quad (2)$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O \quad (3)$$

$$3CaSO_4 + 3CaO.Al_2O_3.6H_2O + 2H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.31H_2O \quad (4)$$

Sewer system Rehabilitation cost ~ $4 billion for LA County

Worst-Case Scenario for Sulfate attacks in sewer systems

- The conditions that lead to excessively high sulfide/sulfate production are listed below :

- Warm annual sewage temperatures (Average > 70 ^{o}F)
- Long force mains and/or flat sewers with debris
- High BOD, (biochemical oxygen demand) wastewater (> 250 mg/L)
- High sulfate wastewater concentrations (> 50 mg/L)

Deterioration of reinforced concrete in sewer environments

- Billions of dollars are being spent worldwide on the repair and maintenance of sewer systems and wastewater treatment plants. Microbially-induced corrosion causes damage via micro-organisms. Deterioration is caused by acid excretion which etches the surface of concrete, penetrating the mortar surface, especially in sewer systems. The mechanisms of concrete and reinforcement deterioration in sewer environments and microbially-induced corrosion (MIC) is very complex.

The role of hydrogen sulfide and micro-organisms(SRB and SOB) in the deterioration of concrete in sewer environments and of repair and rehabilitation measures, including the following preventative measures:

(a) modification of the materials used in construction of sewer pipes;

(b) coatings;

(c) sewer treatments.

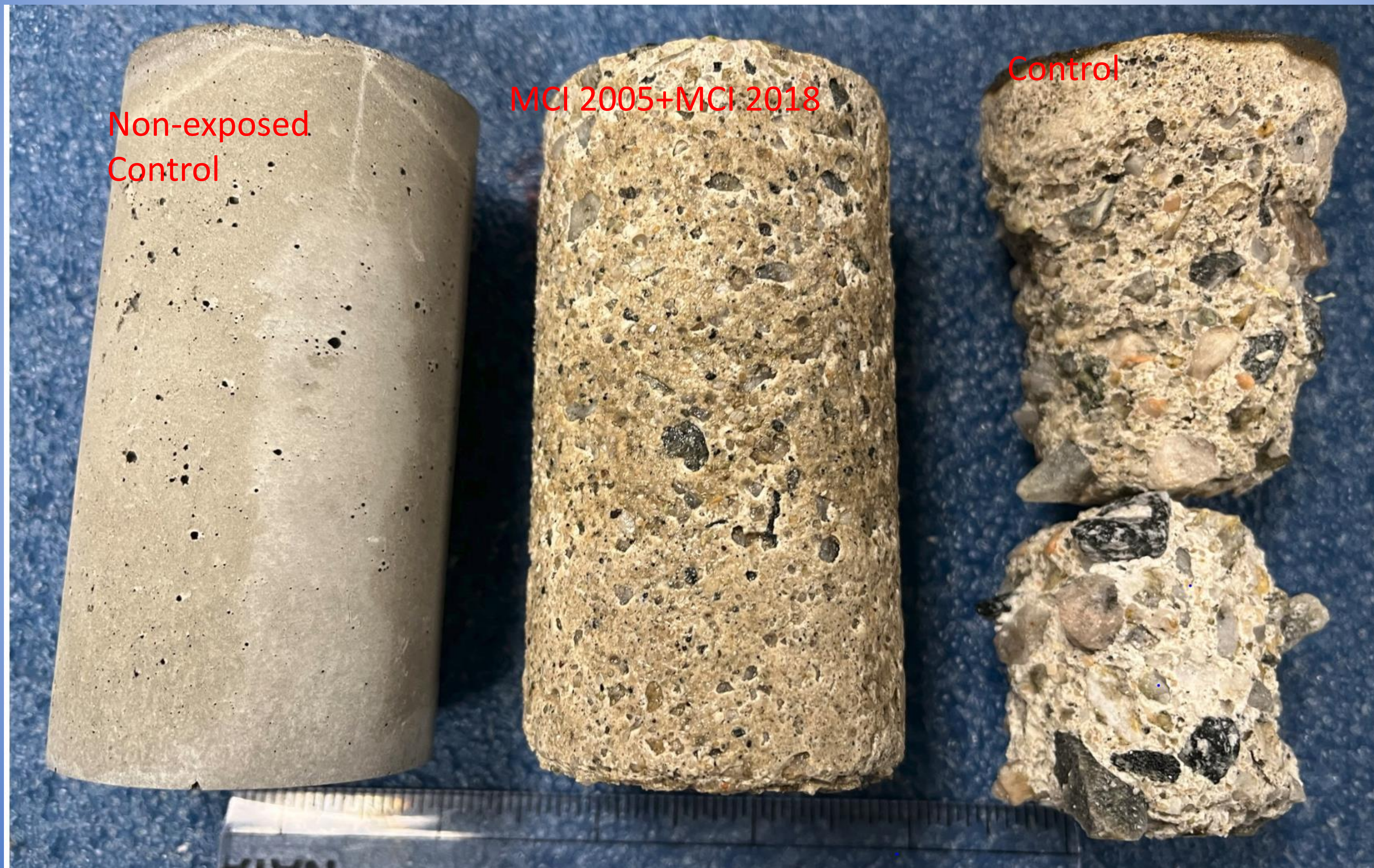
How to protect concrete against MIC?

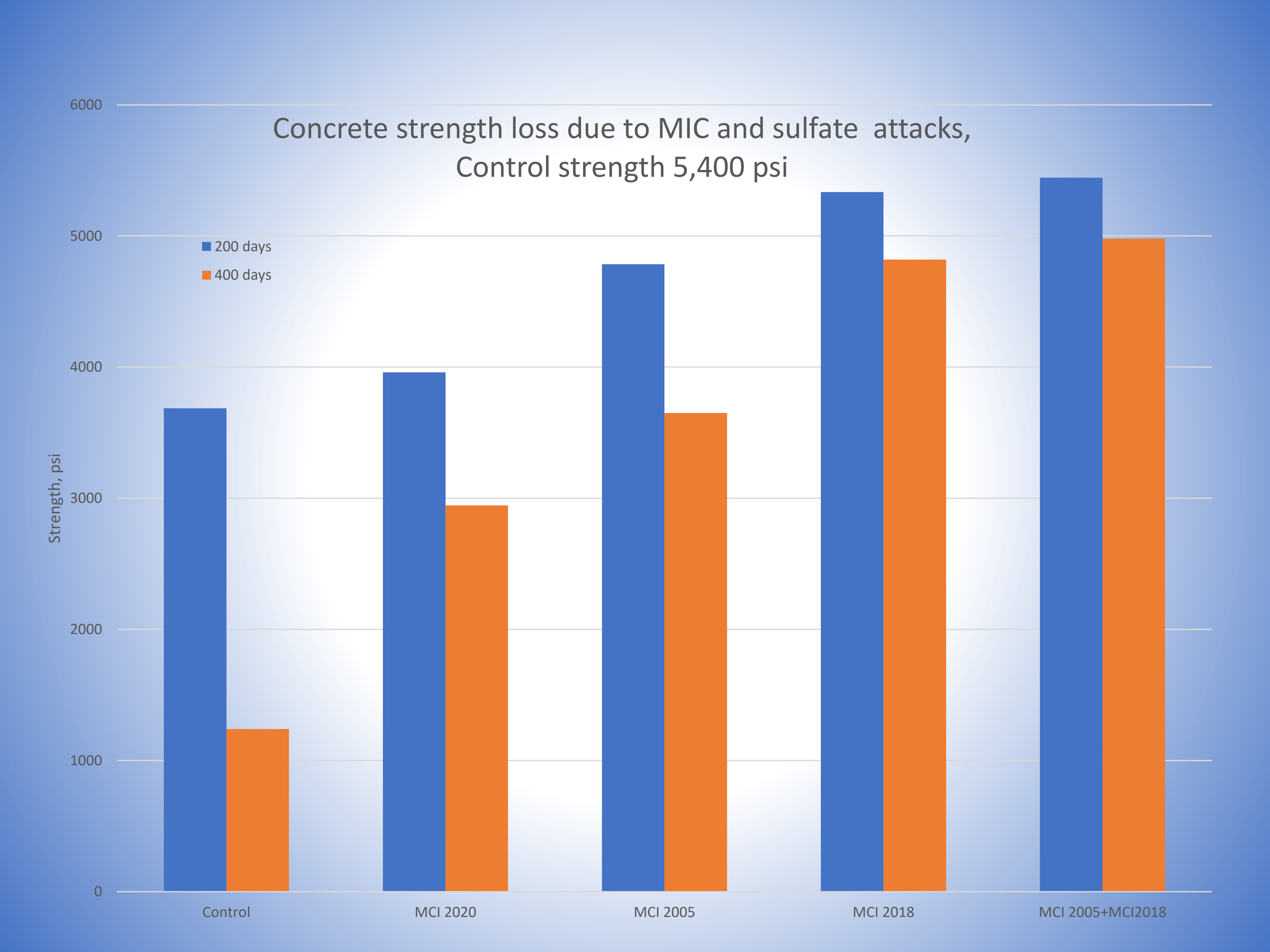
- Chlorine compounds such as bleach, sodium hypochlorite, calcium hypochlorite and ferric chloride and calcium nitrate salt are examples of chemicals that are effective in controlling H2S in wastewater collection systems and used by municipalities to control hydrogen sulfide-related odors and corrosion on a daily basis. However, chloride rich compounds can promote corrosion of reinforcement rebars.
- Migrating corrosion inhibitors and Surface applied Corrosion inhibitors appear to be a better alternative than nitrate and chloride rich compounds and more environmentally friendly chemical.
- In this research project, MCI 2020, MCI 2018 and Admixture MCI 2005 have been evaluated.

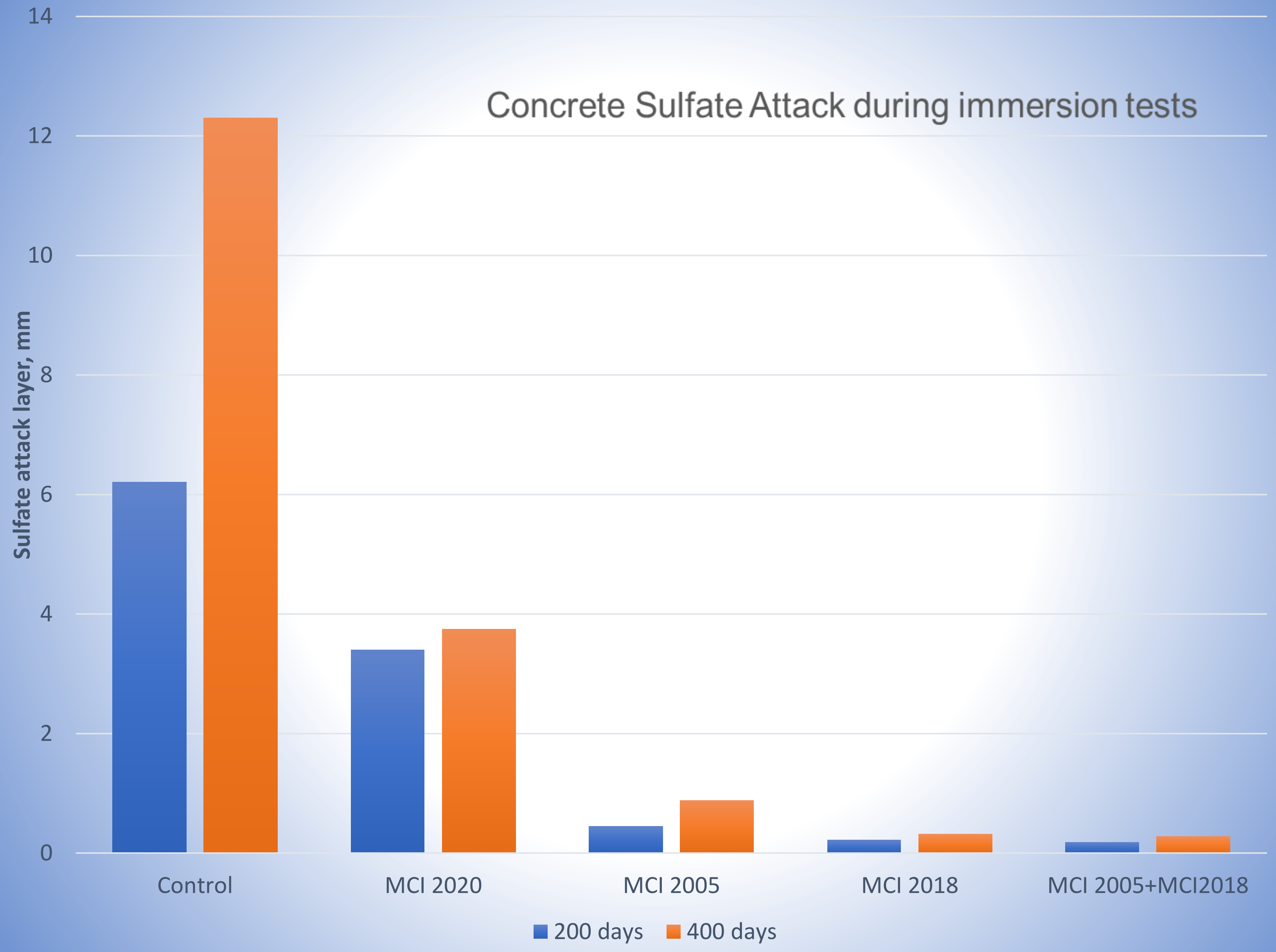
Application of MCI to fight MIC

- MCI 2020M +MCI 2022 is proven technology and shown to be very effective in high Chloride environment.
- MCI-2018 is water repellant product which is silane-base + MCI, showed to be an effective surface applied corrosion inihibitor.
- Admixtures MCI-2005/2005 NS.
- MCI-2018 (SACI) + Admixtures MCI-2005/2005 NS

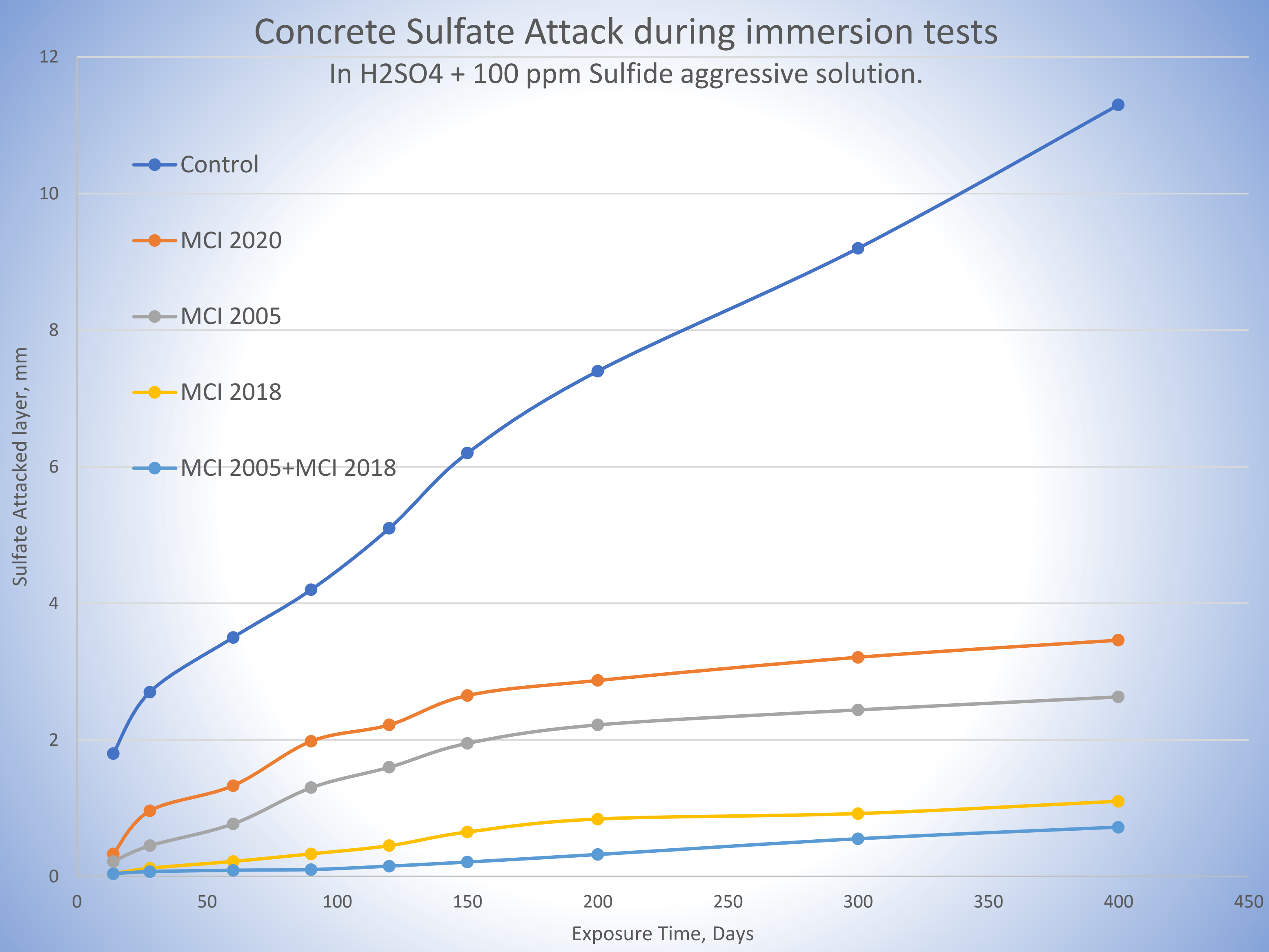
Concrete samples immersed to H2SO4 + 100 ppm Sulfide aggressive solution. pH 2, 72 oF after 400 days




Concrete strength loss due to MIC and sulfate attacks,
Control strength 5,400 psi
200 days
400 days
Strength, psi
6000
5000
4000
3000
2000
1000
0
Control
MCI 2020
MCI 2005
MCI 2018
MCI 2005+MCI2018

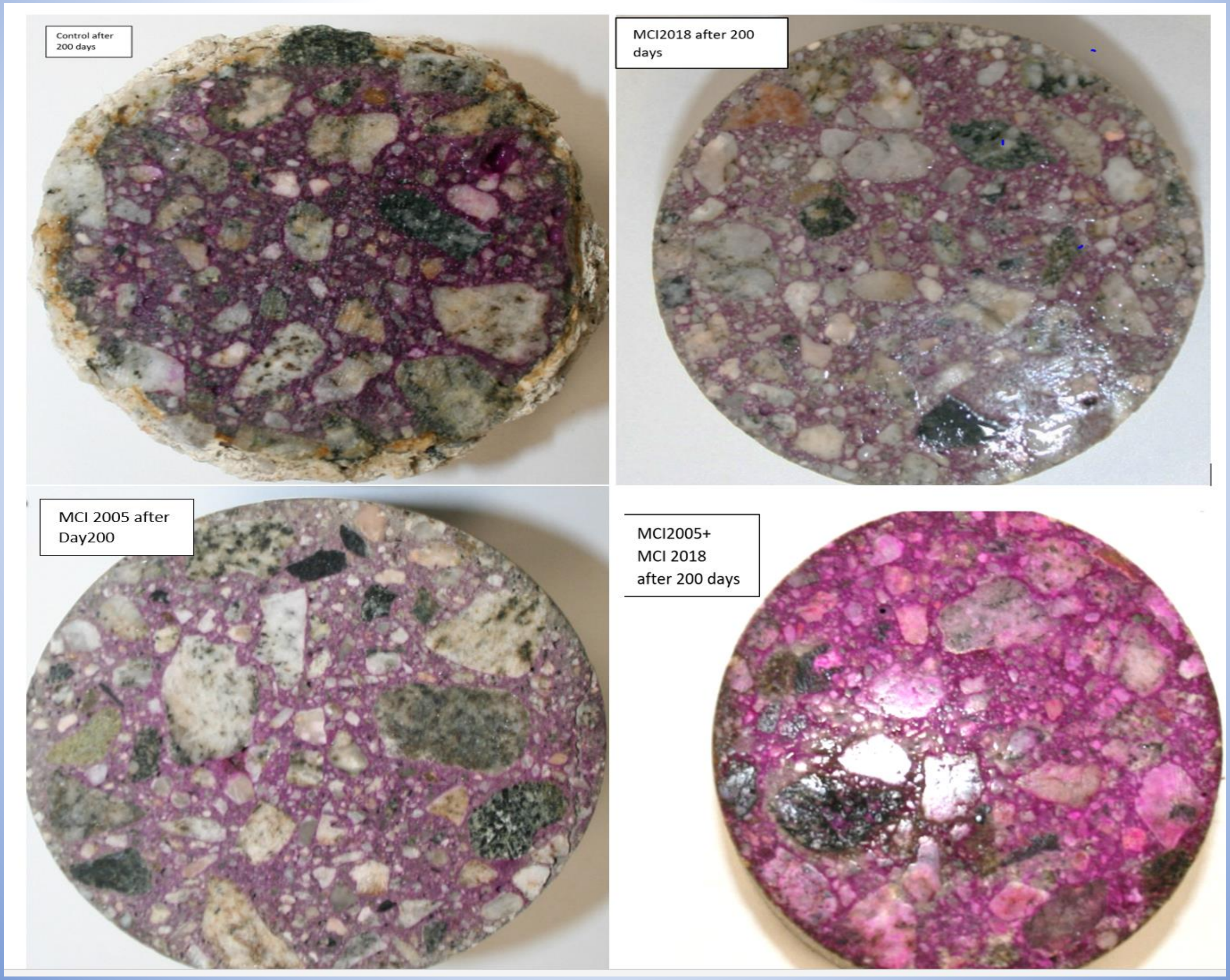


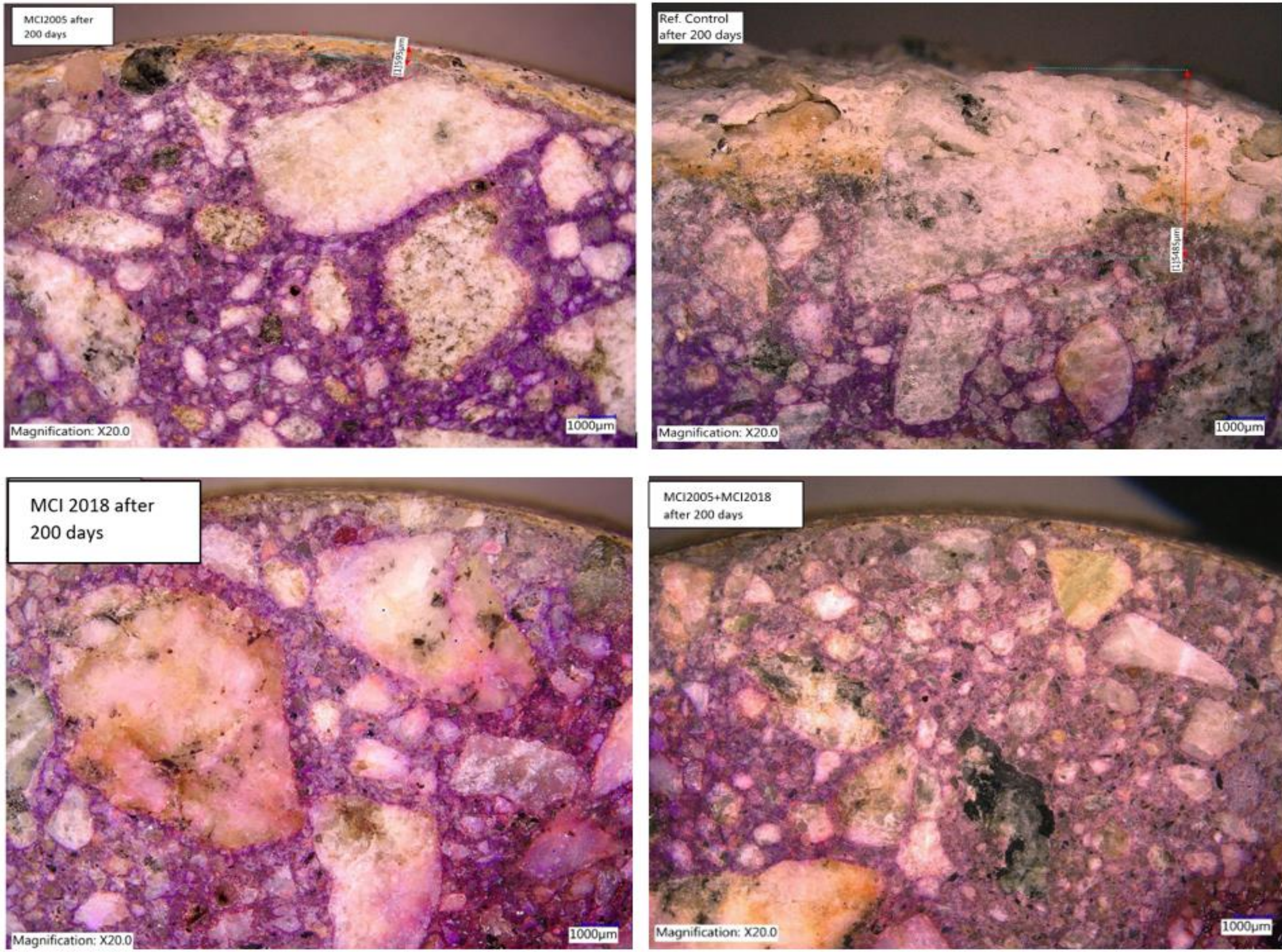
Concrete Sulfate Attack during immersion tests
Sulfate attack layer, mm
14
12
10
8
6
4
2
0
Control
MCI 2020
MCI 2005
MCI 2018
MCI 2005+MCI2018
200 days
400 days

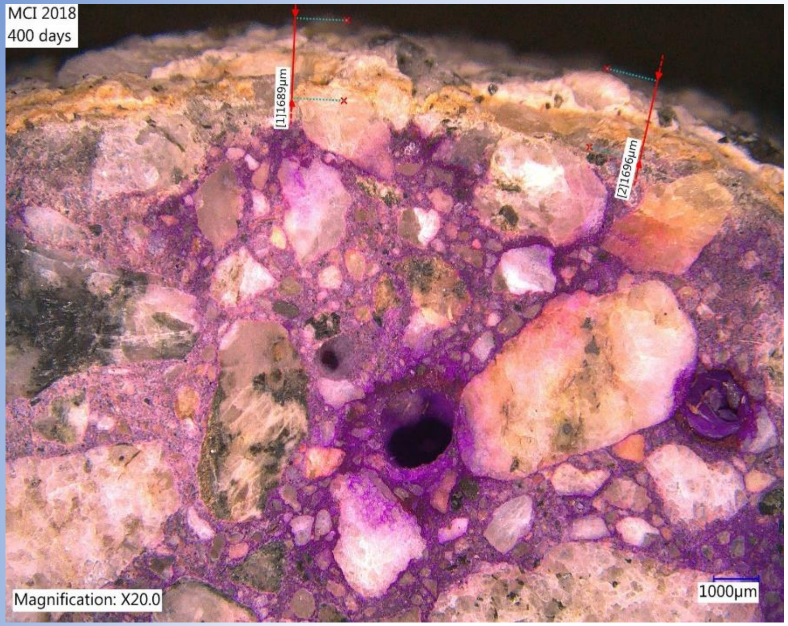


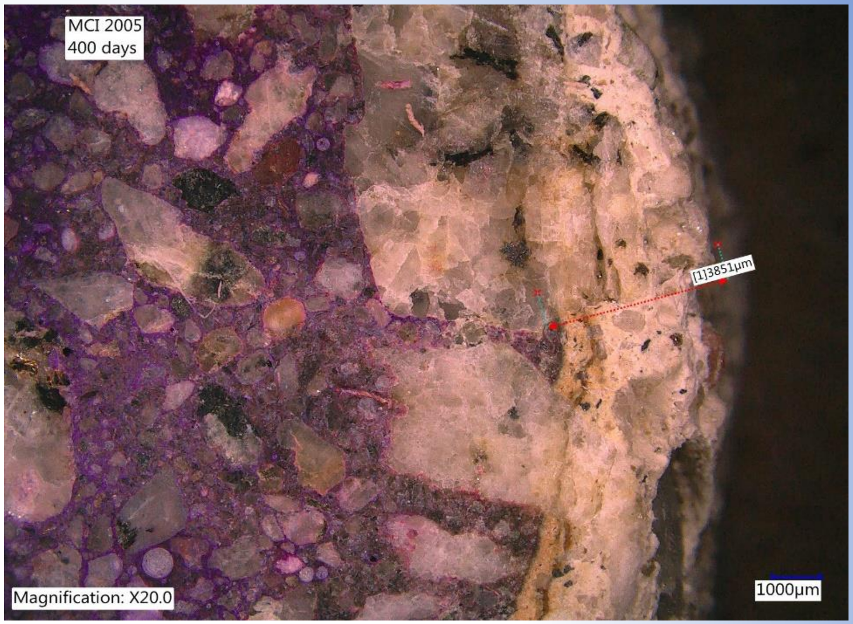
Concrete Sulfate Attack during immersion tests
In H2SO4 + 100 ppm Sulfide aggressive solution.
Control
MCI 2020
MCI 2005
MCI 2018
MCI 2005+MCI 2018
Sulfate Attacked layer, mm
0
2
4
6
8
10
12
0
50
100
150
200
250
300
350
400
450
Exposure Time, Days

Concrete sections were polished and etched with phenolphthalein to measure the sulfate attacked layer thickness.
Both MCI 2005 and MCI 2018 are very effective to improve sulfate attack resistance.

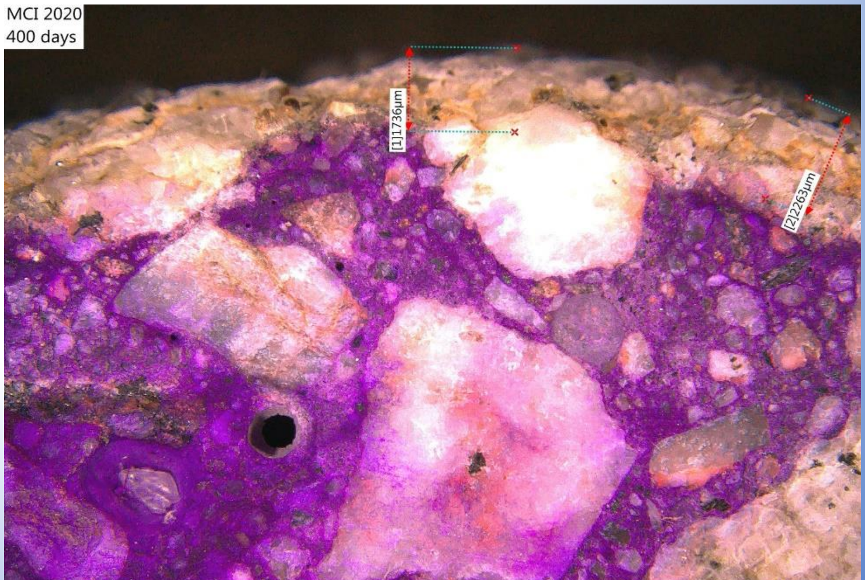



MCI2005 after 200 days
[1]595µm
Magnification: X20.0
1000µm
Ref. Control after 200 days
[1]5485µm
Magnification: X20.0
1000µm
MCI 2018 after 200 days
Magnification: X20.0
1000µm
MCI2005+MCI2018 after 200 days
Magnification: X20.0
1000µm


MCI 2018
400 days
[1]1689µm
[2]1696µm
Magnification: X20.0
1000µm


MCI 2005
400 days
[1]3851µm
Magnification: X20.0
1000µm


MCI 2005
400 days
[1]3851µm
Magnification: X20.0
1000µm


MCI 2020
400 days
[1]1736µm
[2]2263µm

Summary

- Application of MCI Inhibitor protected concrete samples showed lower sulfate attacks
- Sulfate attacked layer were measured in ~ 1mm for MCI protected concrete samples while control samples showed more than 12 mm Sulfate attacked layer and significant strength loss, after 400 days of exposure to pH 2 (adjusted using H_2SO_4) + 100 ppm Sulfide aggressive solution.
- A combination of MCI 2005 (admixture) + MCI 2018 (Surface applied corrosion inhibitor) showed to be very effective to lower sulfate attacks on concrete.

Current Engineering efforts to address deteriorations of our Infrastructures

- **Bridge Corrosion Prevention and Repair Act by**

AMPP (the Association for Materials Protection and Performance)

AMPP (NACE International) Recently introduced legislation

(H.R. 8033) would further advance our infrastructures industry.

- **First Monday of June is designated as “Corrosion Day” at Congress.**

- **Introduction of new proven technologies in the advanced concrete courses (application of admixture, corrosion inhibitors and nanomaterials) that next generation of civil engineers will be ready for the near future complex challenges.**