Improving Durability of Reinforced Concrete Structures using Migrating Corrosion Inhibitors

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Lose Angeles Chapter

Concrete 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)

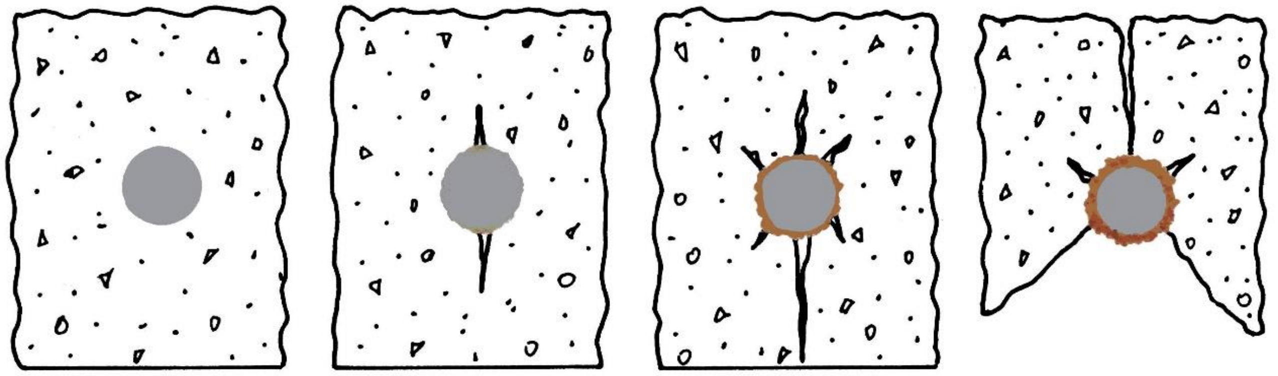
- C_3S hardens rapidly: responsible for early strength
- C_2S hardens slowly and responsible for strength gain beyond one week

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

Effects of different deterioration reactions on Concrete Degradation

Carbonation, Chloride and Sulfate attacks commonly causing damages to concrete structure in forms of :

- Extensive cracking
- Expansion
- Loss of bond between the cement paste and aggregate



Concrete structures Deterioration

Cracking & Spalling


02/27/2008

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

June 24, 2021

Objective of our research program

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

Past 25 years 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.

Research Significance

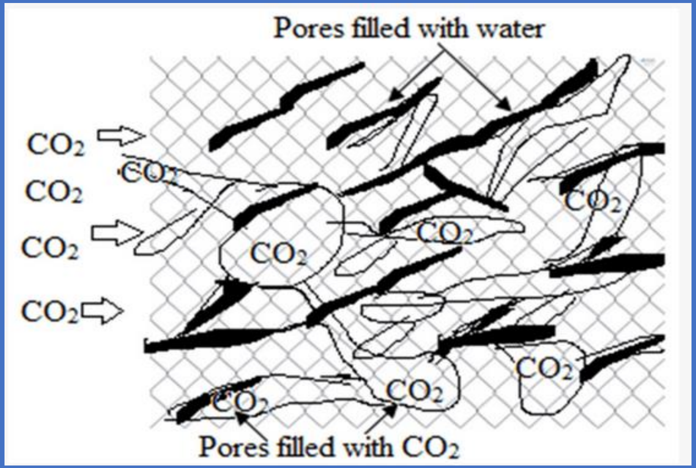
Can we use of admixtures, migrating corrosion inhibitors and surface applied corrosion inhibitors that are very effective in high chloride environment to inhibit MIC?

Carbonation

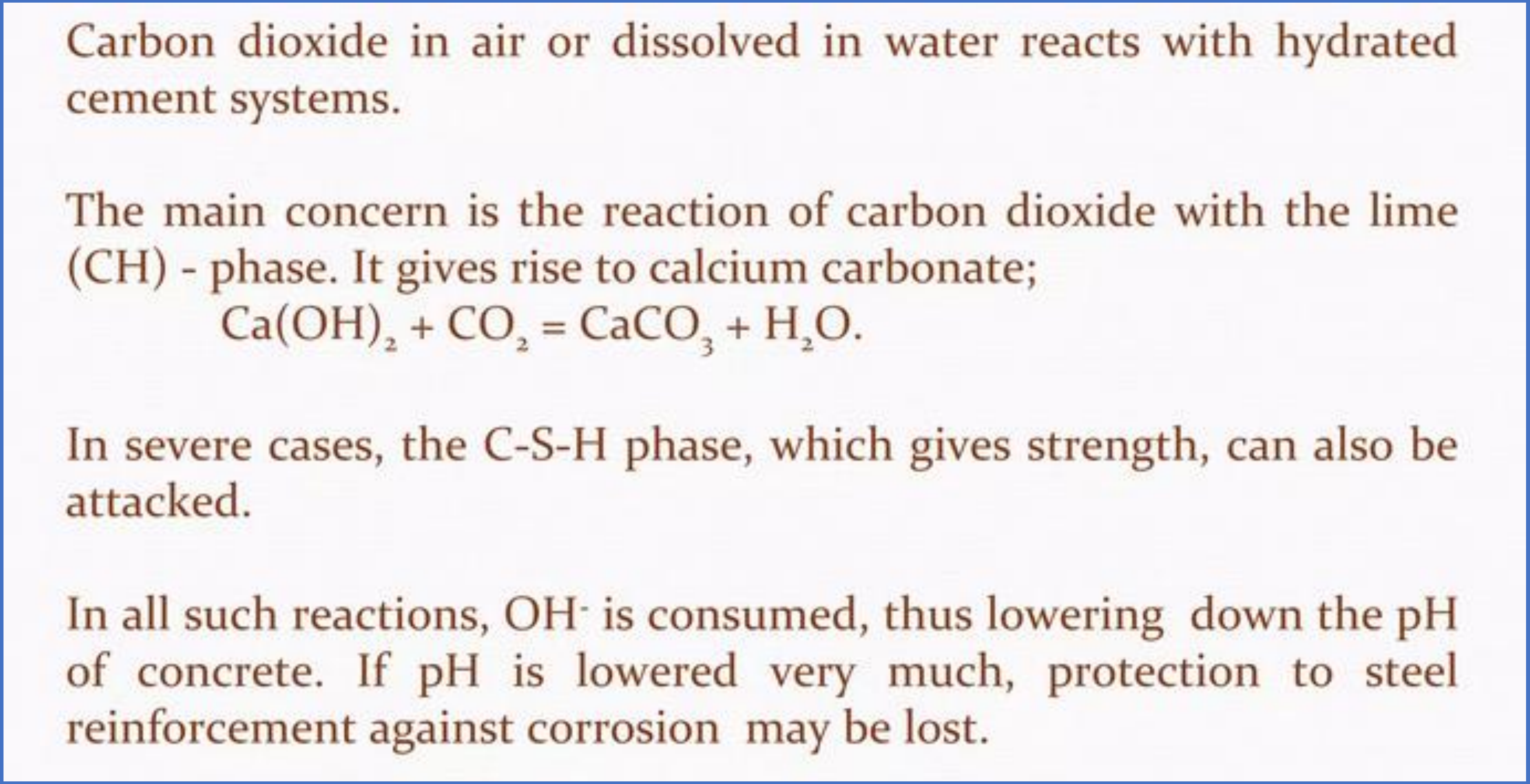
Carbonation-initiated deterioration of concrete by Carbon dioxide (CO_2) from air (~ 400 ppm vol.) and bicarbonate ($HCO^{-}{}_3$) or carbonate ($CO^{2-}{}_3$) anions dissolved in water react with the calcium hydroxide ($Ca(OH)_2$, portlandite) produced by Portland cement hydration in concrete to form calcium carbonate ($CaCO_3$) while releasing a water molecule in the following reaction:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

- Carbonation of concrete is a slow and continuous process of atmospheric CO_2 diffusing from the outer surface of concrete exposed to air into its mass and chemically reacting with the mineral phases of the hydrated cement paste. Carbonation slows down with increasing diffusion depth.



Carbonation Attacks on Concrete



Carbon dioxide in air or dissolved in water reacts with hydrated cement systems.

The main concern is the reaction of carbon dioxide with the lime (CH) - phase. It gives rise to calcium carbonate;

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

In severe cases, the C-S-H phase, which gives strength, can also be attacked.

In all such reactions, OH^- is consumed, thus lowering down the pH of concrete. If pH is lowered very much, protection to steel reinforcement against corrosion may be lost.

Chloride attack

- The main effect of chloride ions on reinforced concrete is to cause localized corrosion of the steel reinforcement bars (rebar). It is a sneaky and dangerous form of localized corrosion because the rebar sections can be decreased to the point that the steel reinforcement are no longer capable to withstand to the tensile efforts they are supposed to resist by design. When the rebar sections are too thin or the rebar are locally broken, the reinforcements are lost and concrete is no longer reinforced concrete.
- Chlorides, particularly calcium chloride, have been used to shorten the setting time of concrete. However, calcium chloride and sodium chloride have been shown to leach calcium hydroxide and cause chemical changes in Portland cement, leading to loss of strength, as well as attacking the steel reinforcement present in most concrete.

$$Ca\,(OH)_2 + 2\,Cl^- \rightleftharpoons CaCl_2 + 2\,OH^- \tag{1}$$

$$Aluminates + CaCl_2 \rightleftharpoons 3\,CaO.\,Al_2\,O_3\,CaCl_2\;10H_2O \tag{2}$$

Sulfate Attacks:

- Sulfates in solution in contact with concrete can cause chemical changes to the cement, causes significant microstructural effects leading to the weakening of the cement binder (chemical sulfate attack).
- Sulfates and sulfites are ubiquitous in the natural environment and are present from many sources, including gypsum (calcium sulfate) often present as an additive in 'blended' cements which include fly ash and other sources of sulfate. Most sulfates are soluble in water. These include acid rain where sulfur dioxide is dissolved in rainfall to produce sulfurous acid. In lightning storms, the dioxide is oxidized to trioxide making the residual sulfuric acid in rainfall even more highly acidic.
- Concrete sewage infrastructure is most commonly attacked by sulfuric acid and sulfate anions arising from the oxidation of sulfide present in the sewage.
- Sulfides are formed when sulfate-reducing bacteria (SRB) present in sewer mains reduce the ubiquitous sulfate ions present in water drains into hydrogen sulfide gas (H_2S). H_2S is volatile and released from water in the sewage atmosphere. It dissolves in a thin film of water condensed onto the wall of the sewer ducts where it is also accompanied by (HS^-) and sulfide (S^{2-}) ions. When H_2S and HS^- anions are further exposed to atmospheric oxygen (SOB: sulfur oxidizing bacteria) or to oxygenated stormwater, they are readily oxidized and produce sulfuric acid (in fact acidic hydrogen ions accompanied by sulfate and bisulfate ions) according to the respective oxidation reactions:

- $H_2S + 2\ O_2 \rightarrow 2\ H^+ + SO2{-}4$

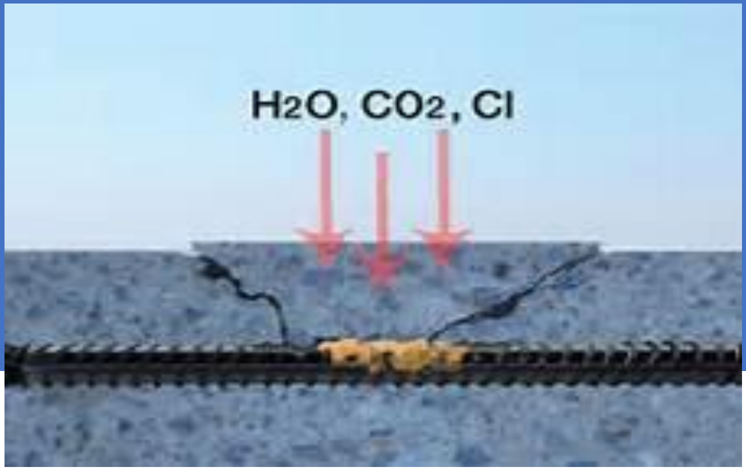
or

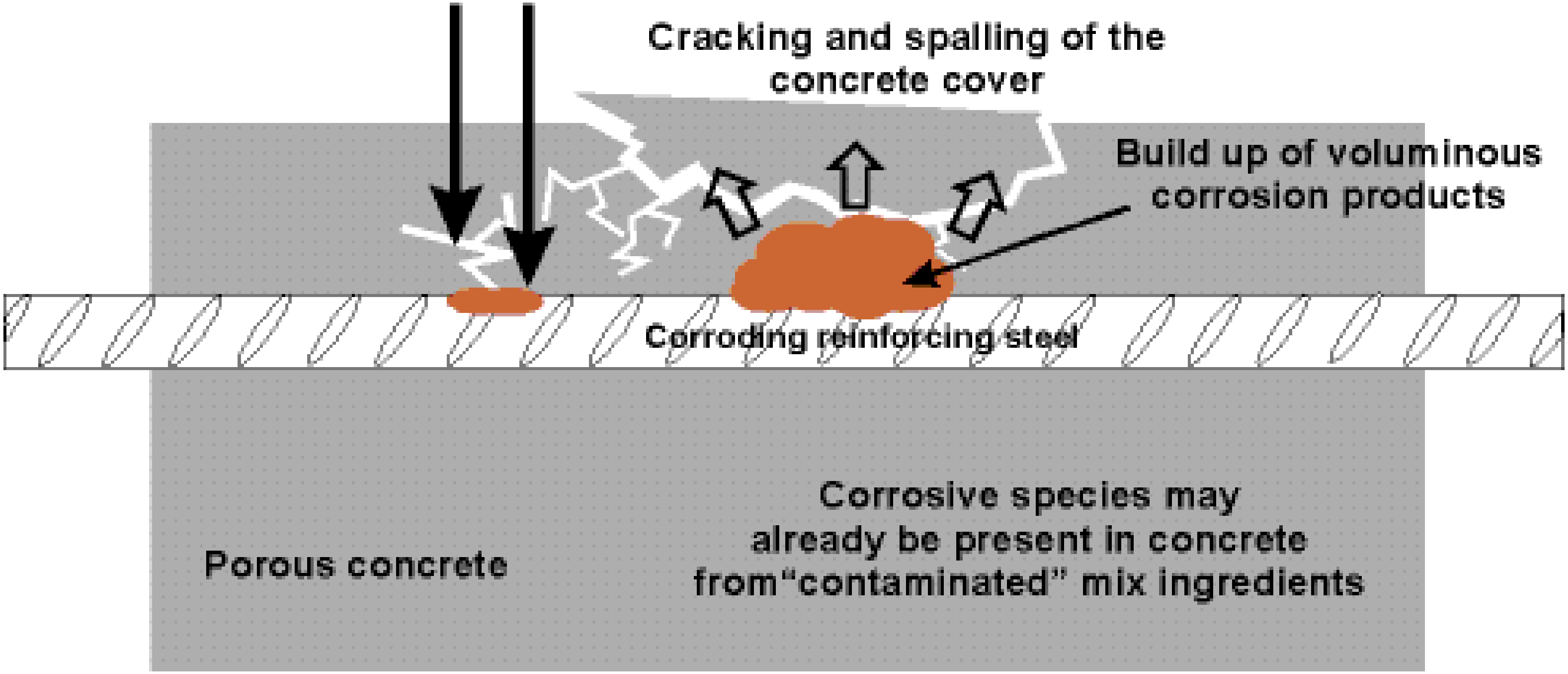
- $HS^- + 2\ O_2 \rightarrow HSO4{-}$

Effects of Bacteria on Concrete

- Bacteria themselves do not have noticeable effect on concrete. But sulfate-reducing bacteria (SRB)and Sulfur Oxidizing Bacteria (SOB) in untreated sewage water tend to produce hydrogen sulfide (H_2S), which is then oxidized in sulfuric acid (H_2SO_4) by atmospheric oxygen and by aerobic bacteria present in biofilm on the concrete surface above the water level.
- The sulfuric acid dissolves the carbonates in the hardened cement paste, calcium hydroxide ($Ca(OH)_2$) and calcium silicate hydrate ($CaO\cdot SiO_2\cdot nH_2O$), and causes strength loss, as well as producing sulfates which are harmful to concrete.
  - $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\ H_2O$
  - $H_2SO_4 + CaO\cdot SiO_2\cdot n\ H_2O \rightarrow CaSO_4 + H_2SiO_3 + n\ H_2O$
- In each case the soft expansive and water soluble corrosion product of gypsum ($CaSO_4$) is formed. Gypsum is easily washed away in wastewater causing a loss of concrete aggregate and exposing fresh material to acid attack.

Corrosion Damages to Rebars





Ingress of corrosive species
(into porous concrete)

Cracking and spalling of the
concrete cover

Build up of voluminous
corrosion products

Corroding reinforcing steel

Porous concrete

Corrosive species may
already be present in concrete
from "contaminated" mix ingredients

Anodic and Cathodic Reactions

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

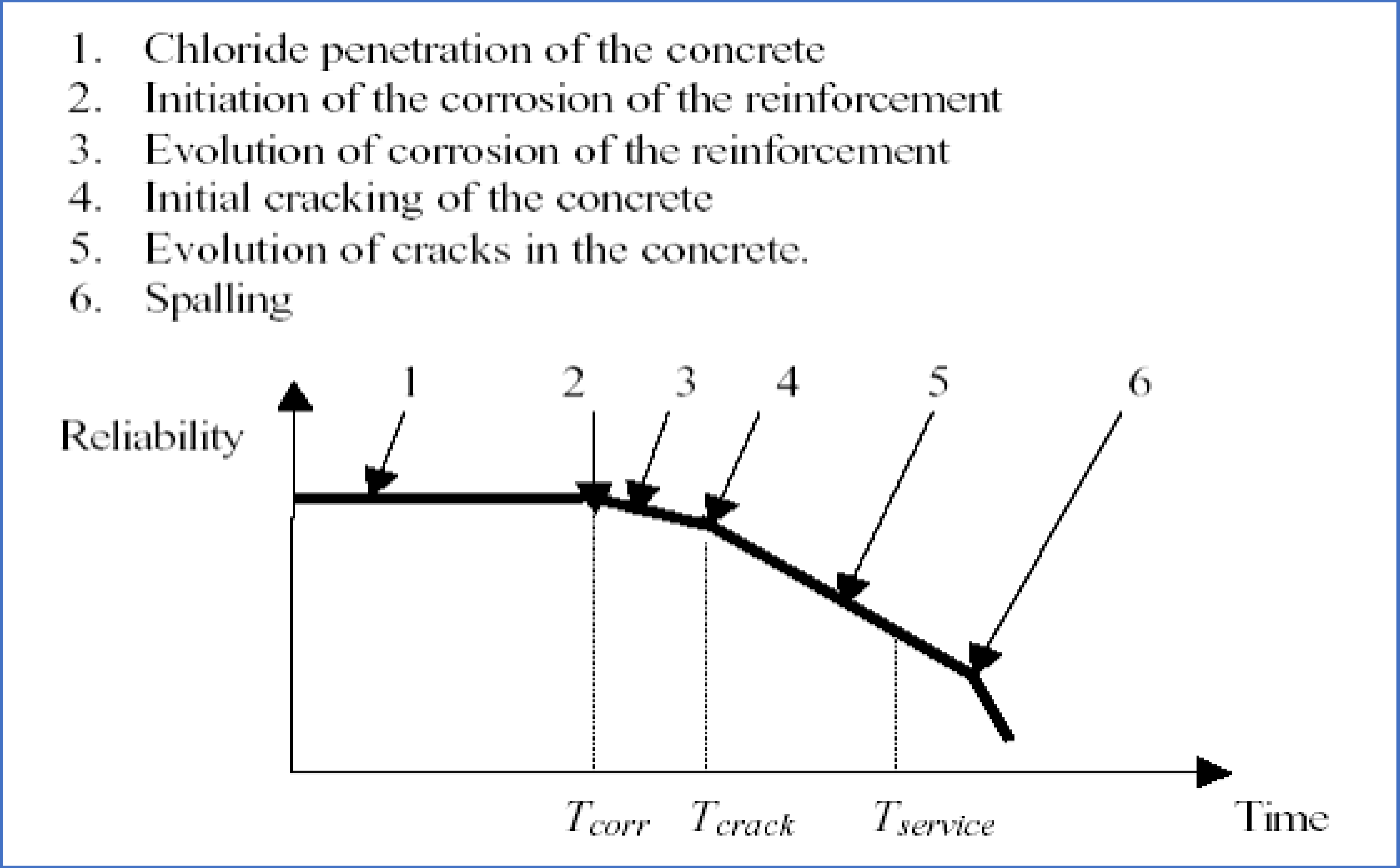
$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

or

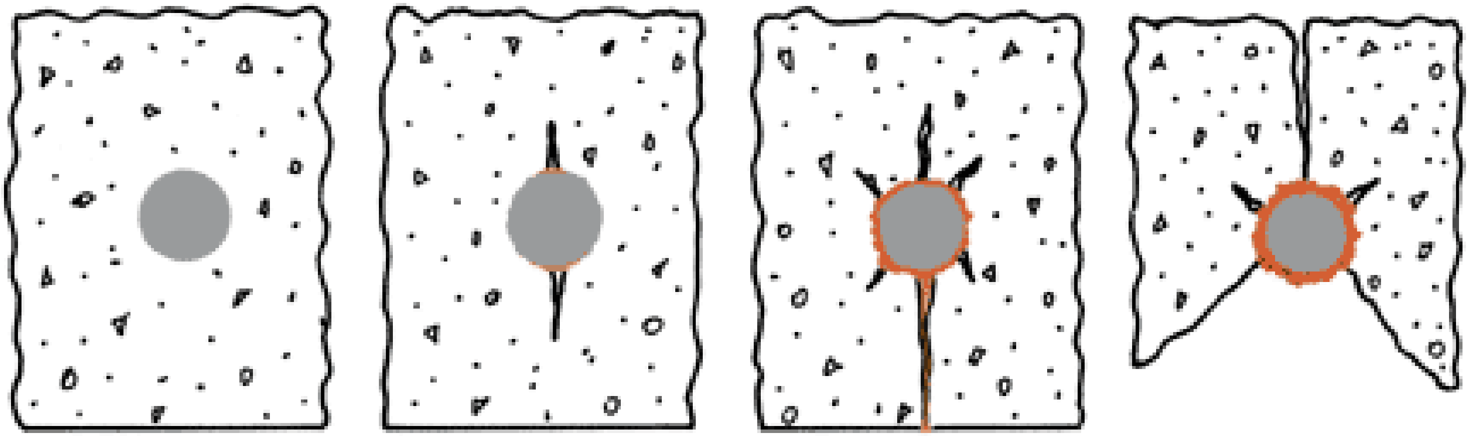
$2H^+ + 2e^- \rightarrow H_2$

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.

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



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.

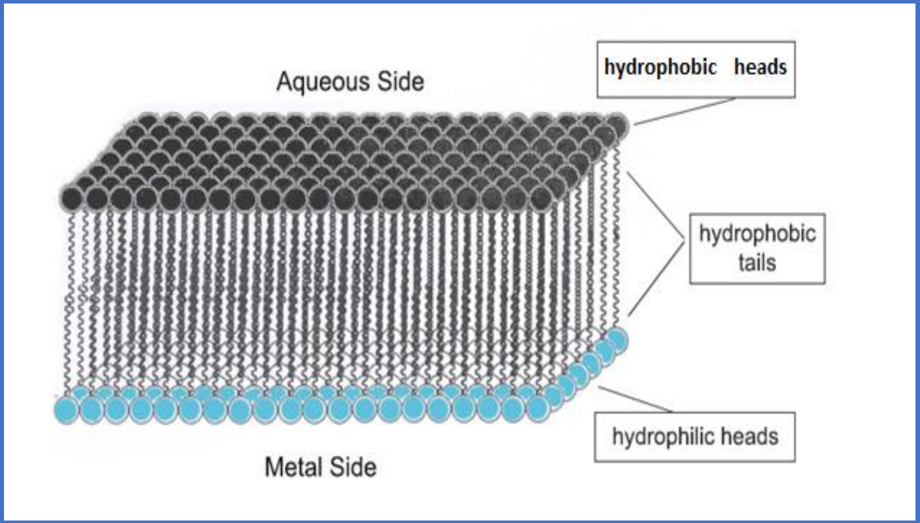
Protection of steel rebar in Concrete

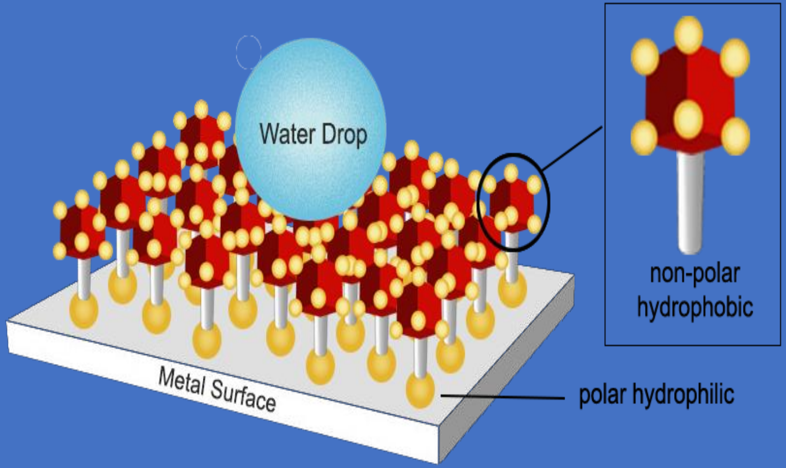
- Clean Concrete
- Cathodic Protection of Reinforcements (rebars)
- Admixtures and Corrosion Inhibitors
- Migrating Corrosion Inhibitors (MCI) or Surface Applied Corrosion Inhibitors(SACI)

How Admixture/Inhibitor works?

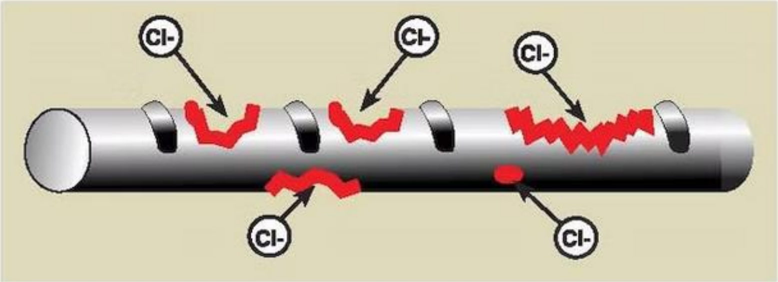
Migrating corrosion inhibitors (MCIs) are developed to protect steel rebar from corrosion in concrete. They were designed to be incorporated as an admixture during concrete batching or used for surface impregnation of existing concrete structures. **Under Chlorine Attack and Carbonatation Attack**

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.

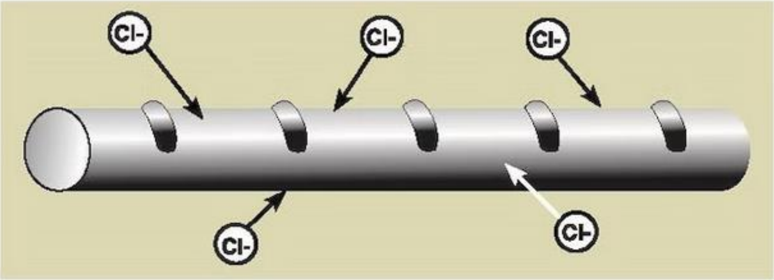




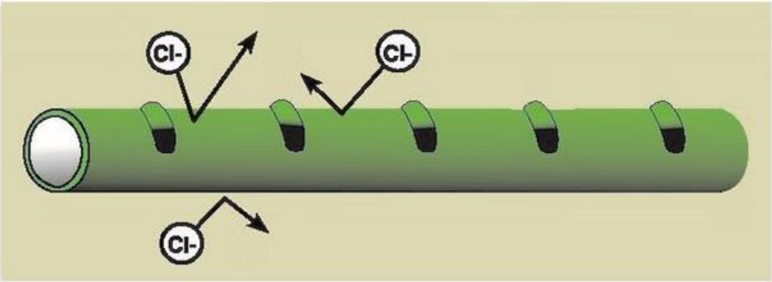
Chloride-Induced Corrosion

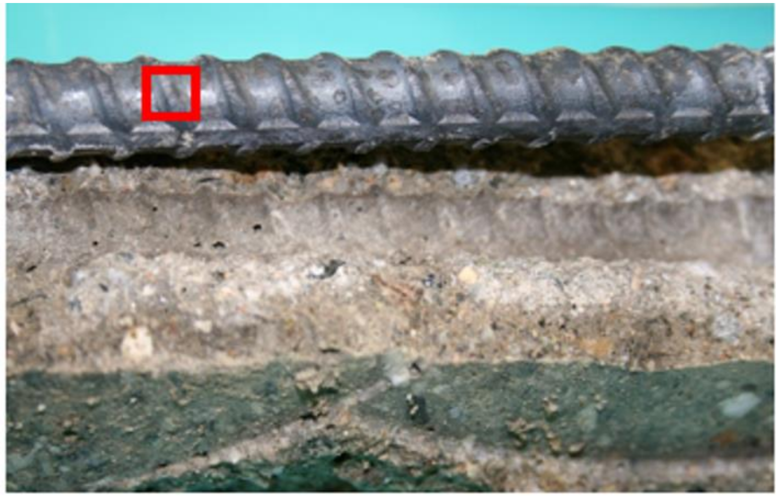


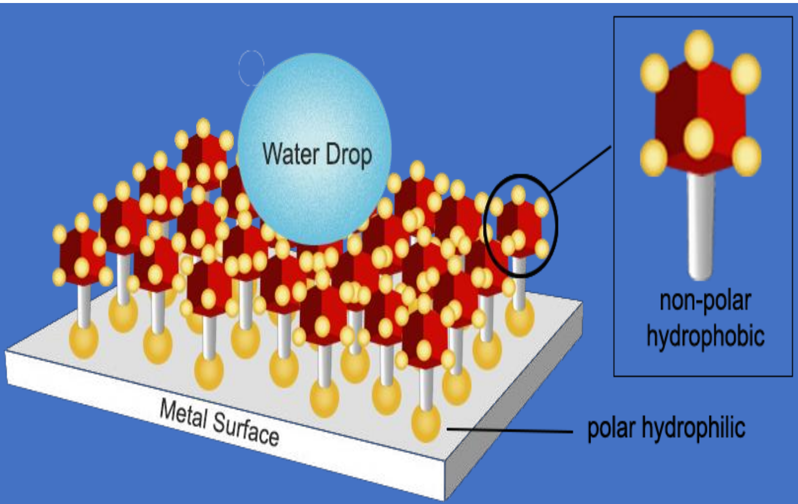
Unprotected Steel



MCI® Protected Steel







Electrochemical Tests

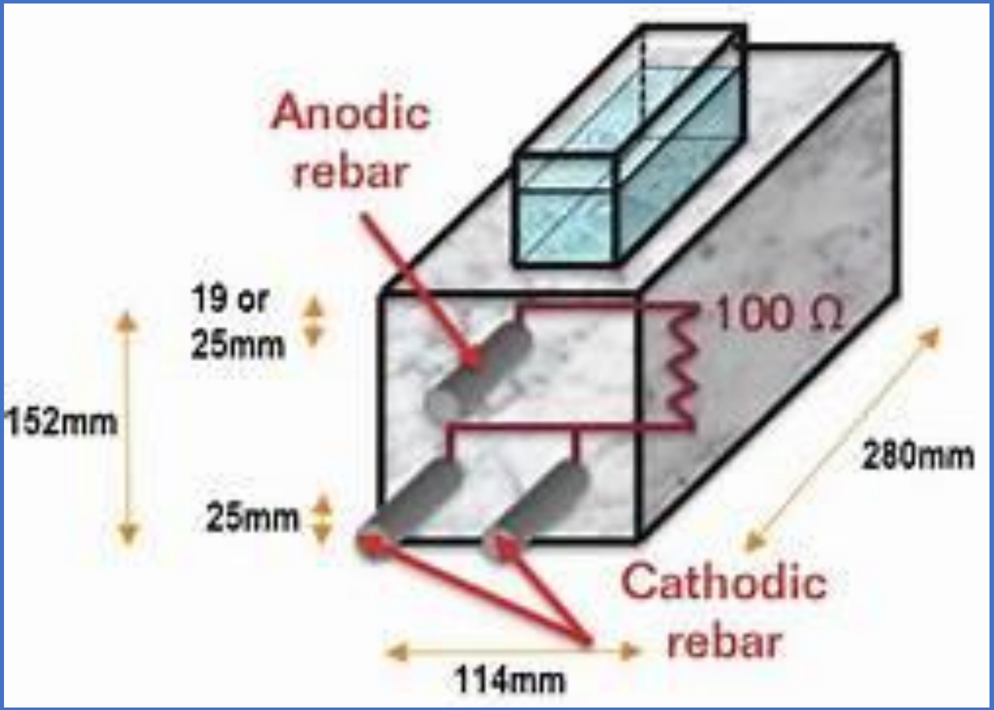
How to evaluate corrosion resistance of concrete:

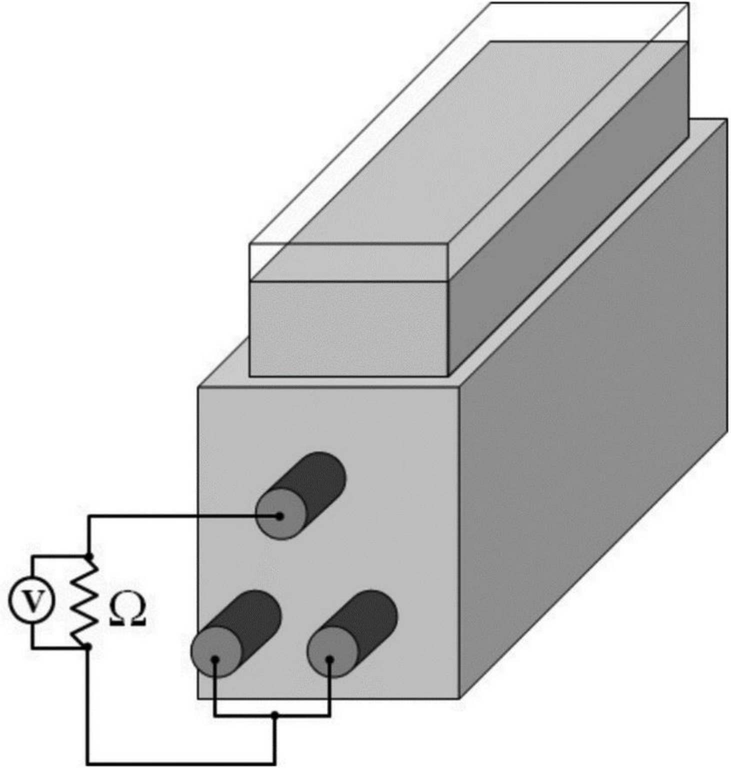
Due to low conductivity of concrete special test method required to monitor corrosion of rebar in concrete:

- 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

ASTM G109


Anodic rebar
19 or 25mm
100 Ω
152mm
280mm
25mm
Cathodic rebar
114mm


V
Ω

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	$0.25 < R_p < 2.5$	$100 < p < 1000$ (4 to 40 mils)
High	$2.5 < R_p < 25$	$10 < p < 100$ (0.4 to 4.0 mils)
Low/moderate	$25 < R_p < 250$	$1 < p < 10$ (0.04 to 0.4 mils)
Passive	$250 < R_p$	$p < 1$ (<0.04 mils)

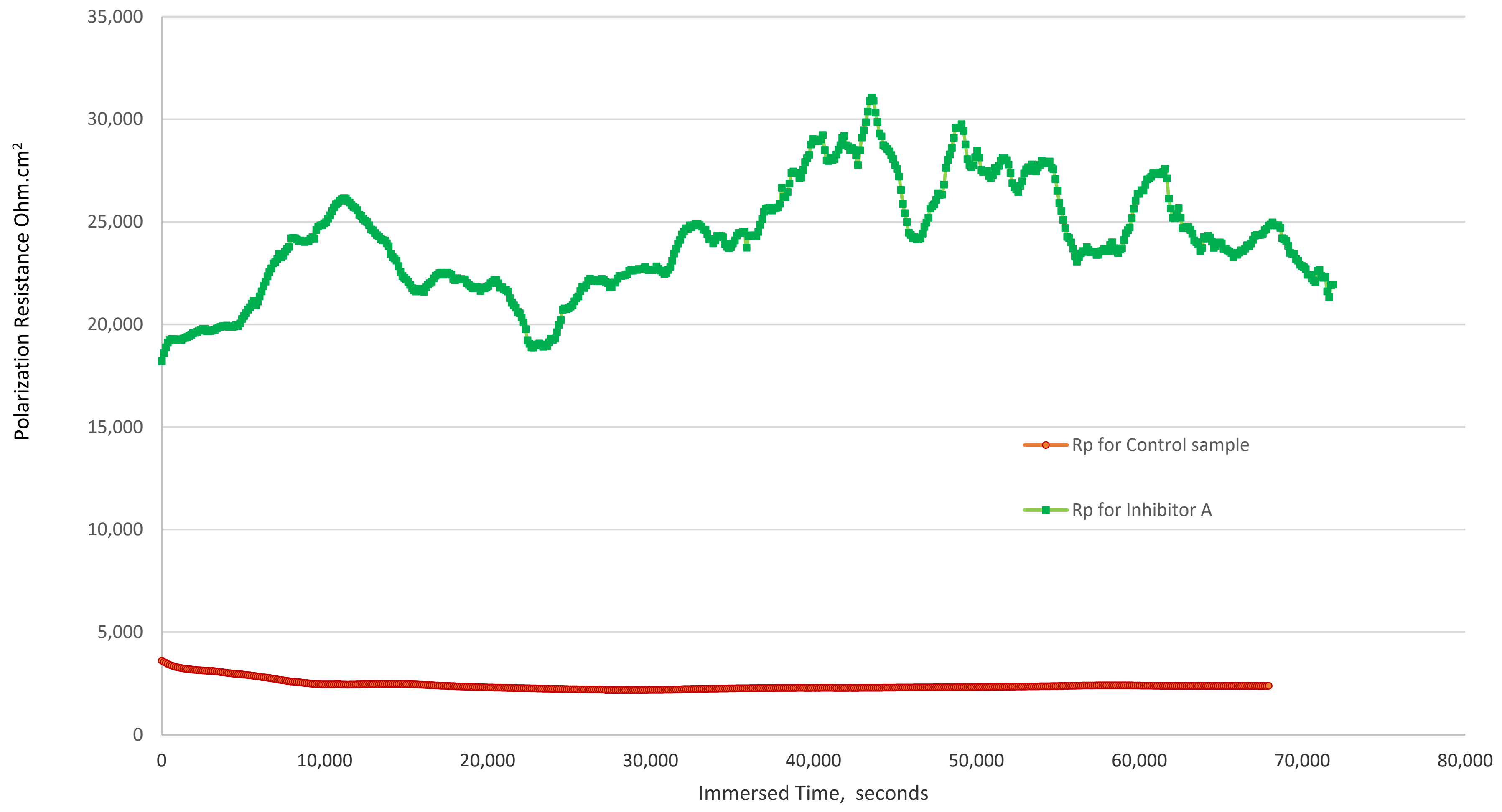
Experiments

- 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.

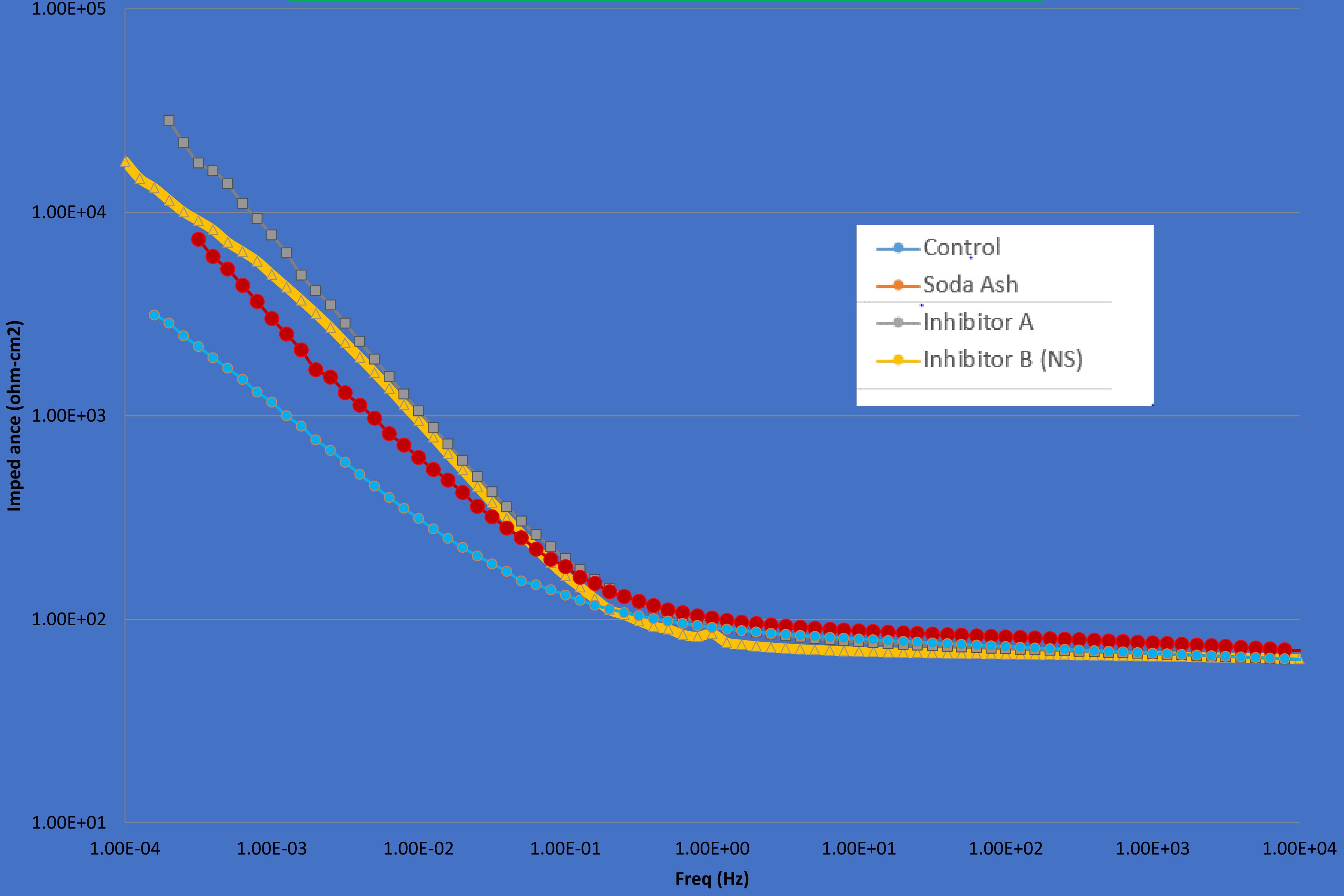
Concrete Samples Preparation

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

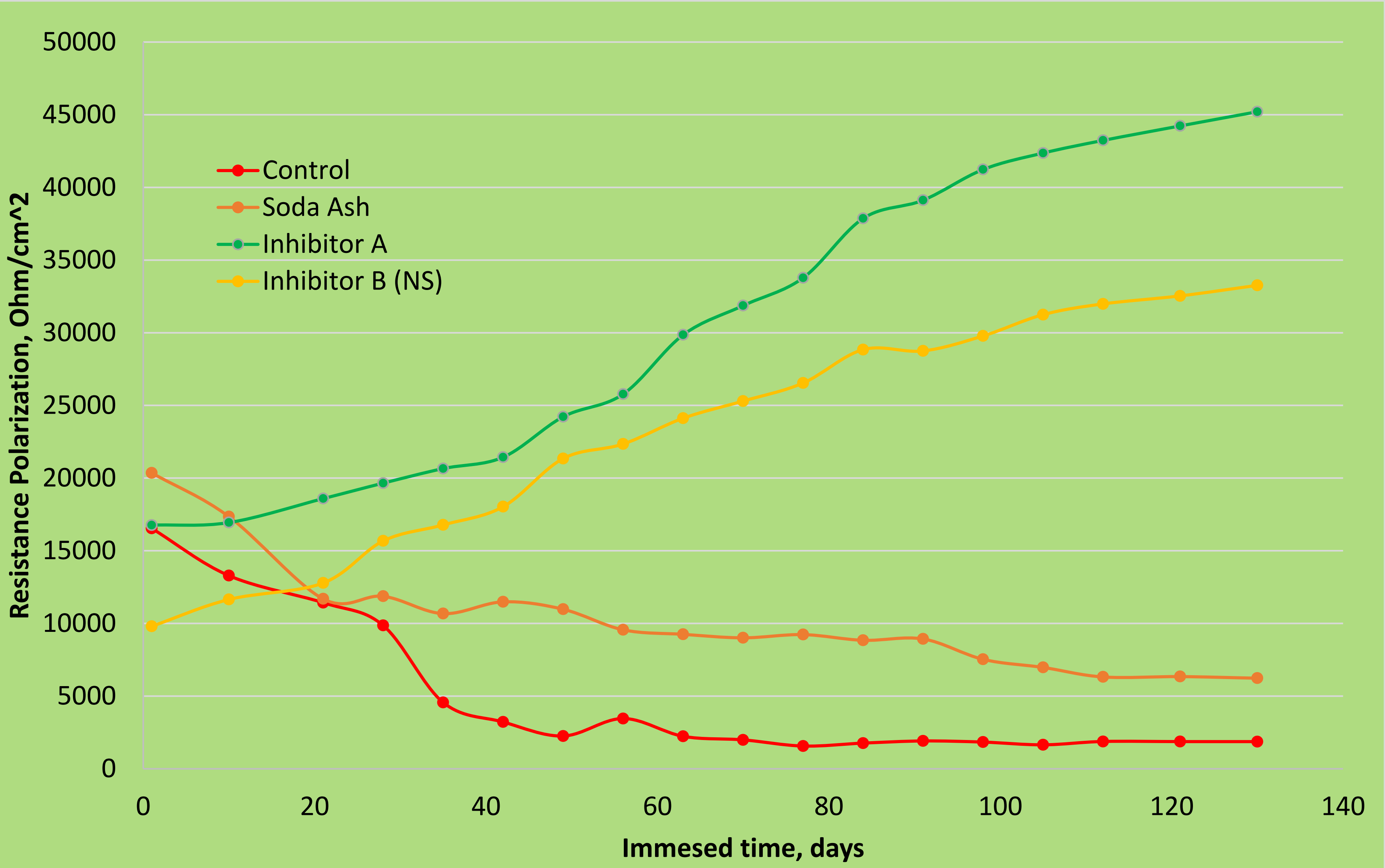
Polarization resistance measurements of steel rebar in the solution prepared based on the ASTM G180 test method



EIS Bode plot on Steel Reinforced Concrete
(125 days immersed in 3.5% NaCl solution), ASTM G109



Polarization Resistance (R_p) Versus Time; Comparison of Inhibitor treated concrete with Control concrete samples, ASTM G180.

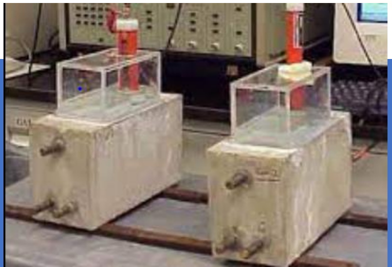


Inhibitor A after 150 days

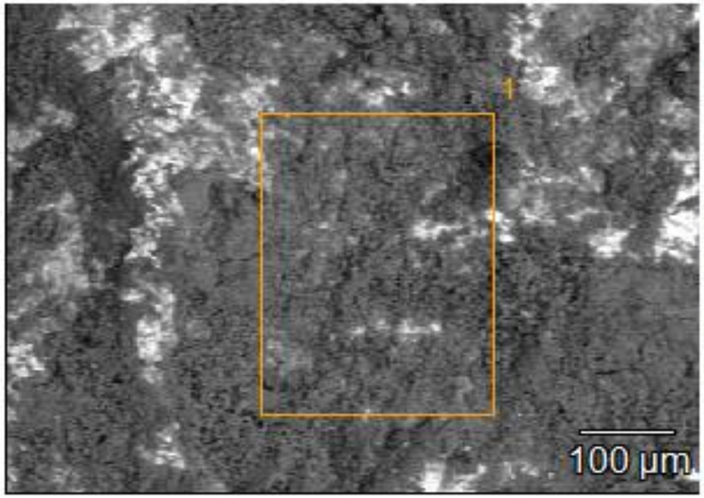
Control after 150 days

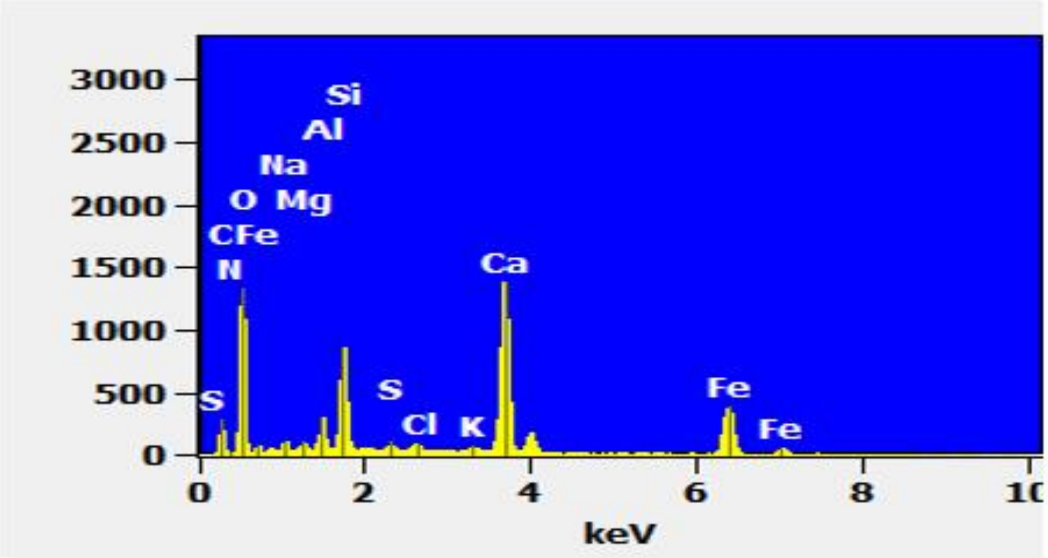
Inhibitor B after 150 days

Soda Ash after 150 days



EDS analysis on the Inhibitor A (MCI 2005) concrete samples.

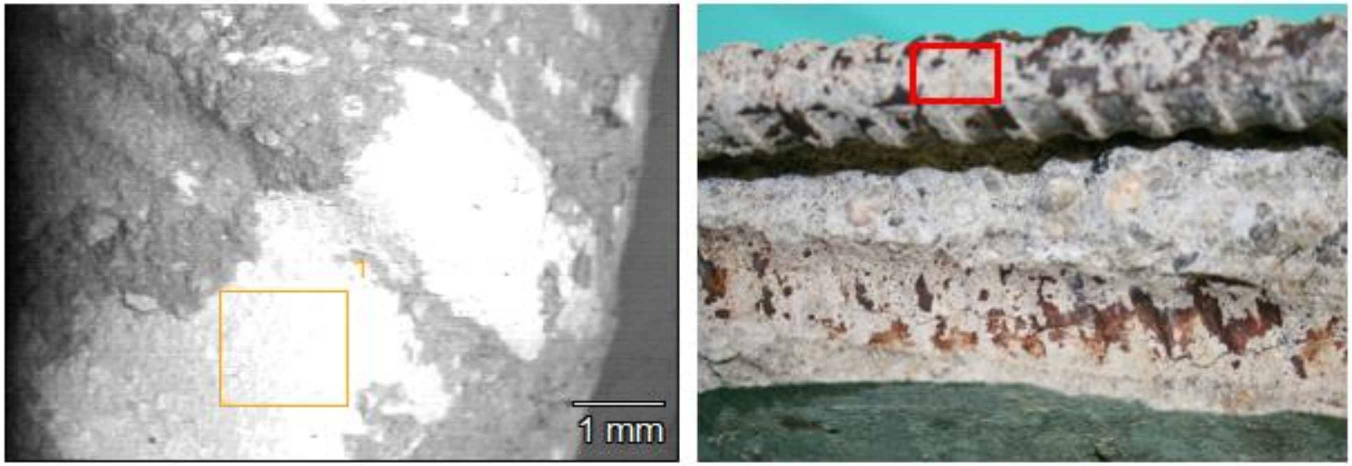


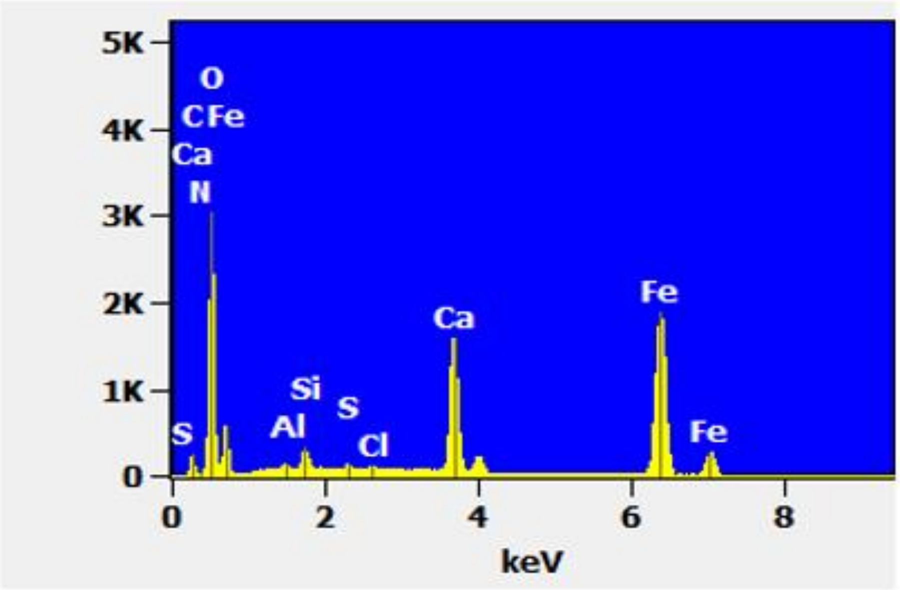


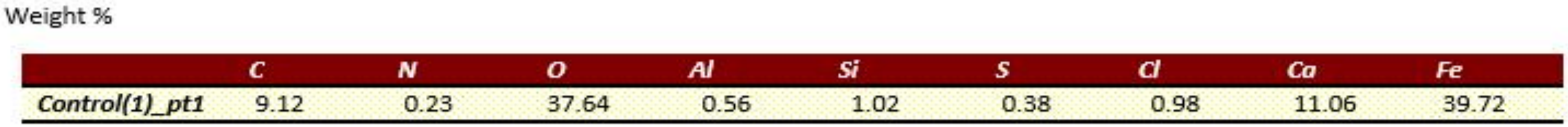
Weight %

	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.



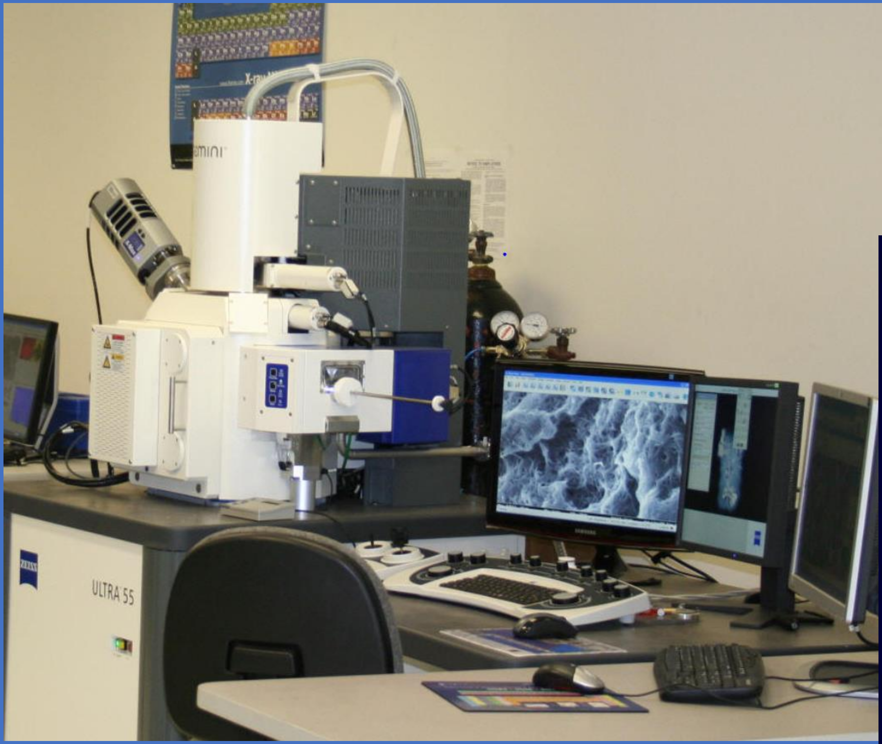


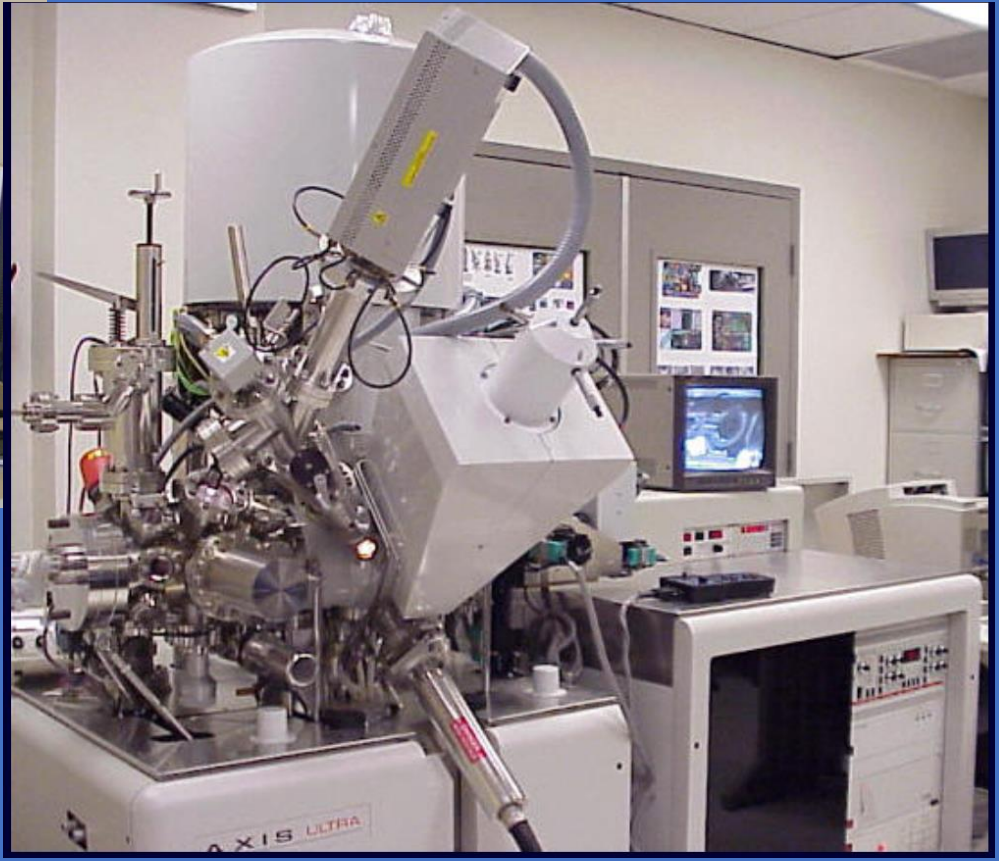


Weight %

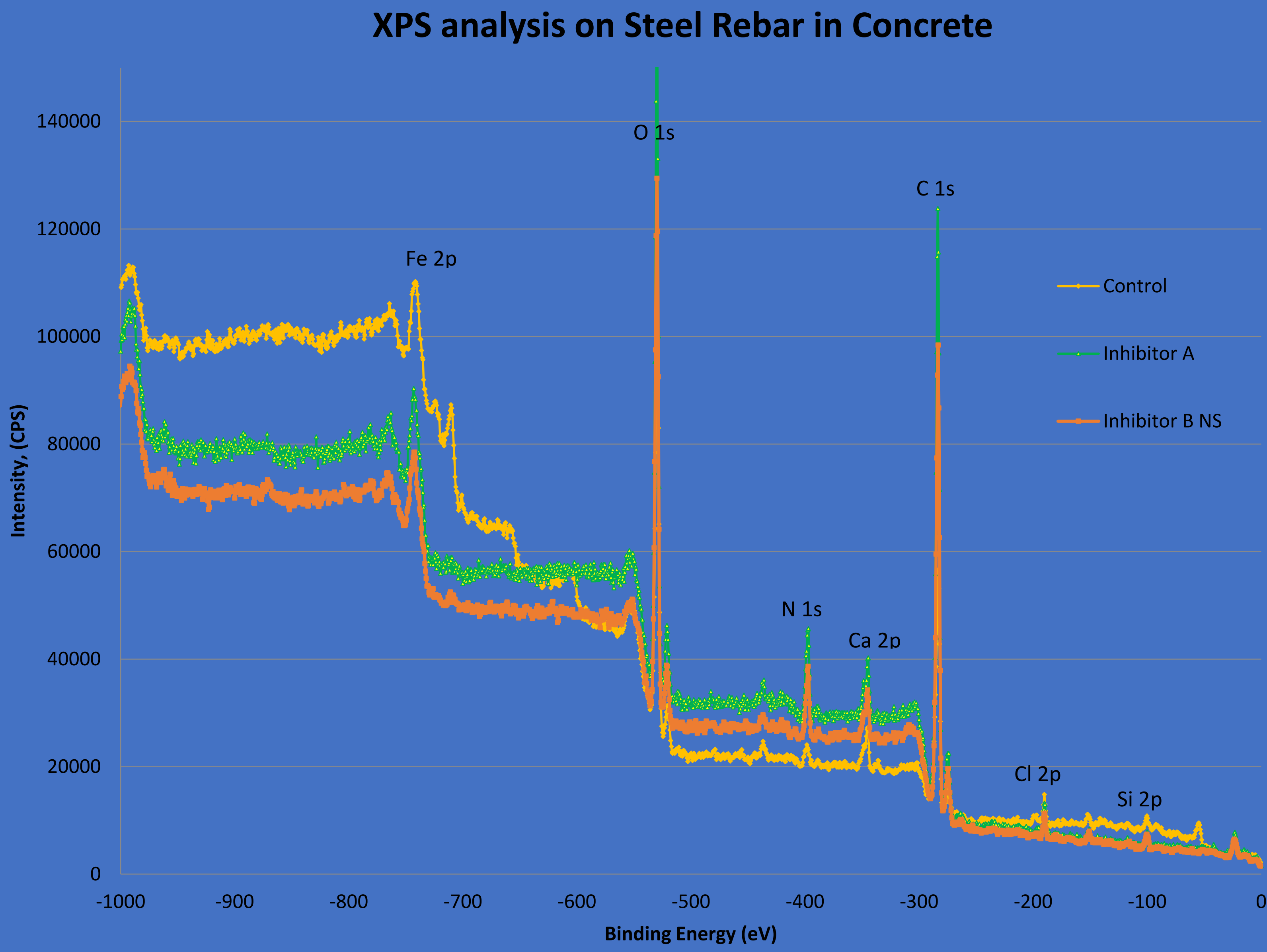
	C	N	O	Al	Si	S	Cl	Ca	Fe
Control(1)_pt1	9.12	0.23	37.64	0.56	1.02	0.38	0.98	11.06	39.72

FESEM/EDS and XPS systems for surface analysis





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

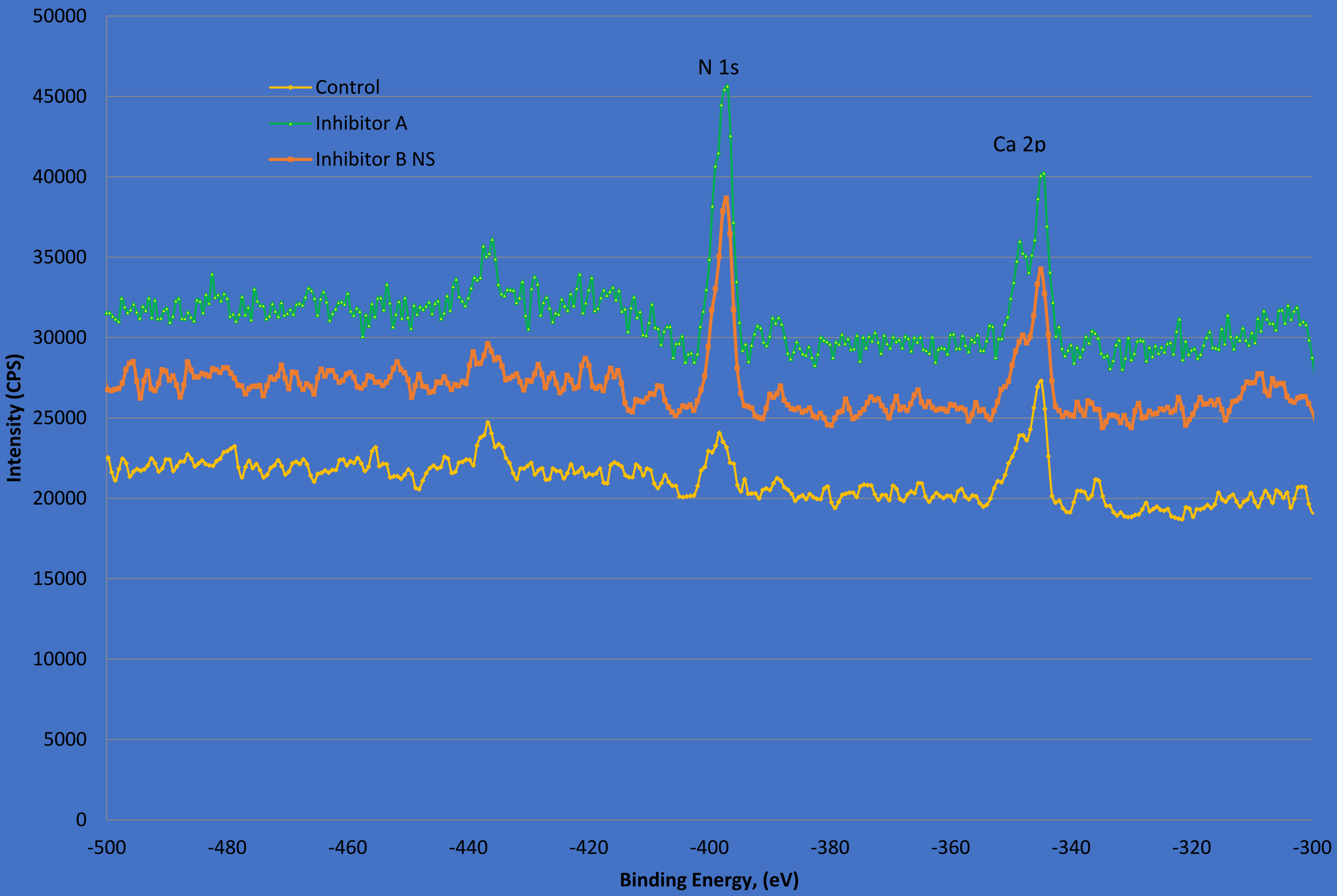


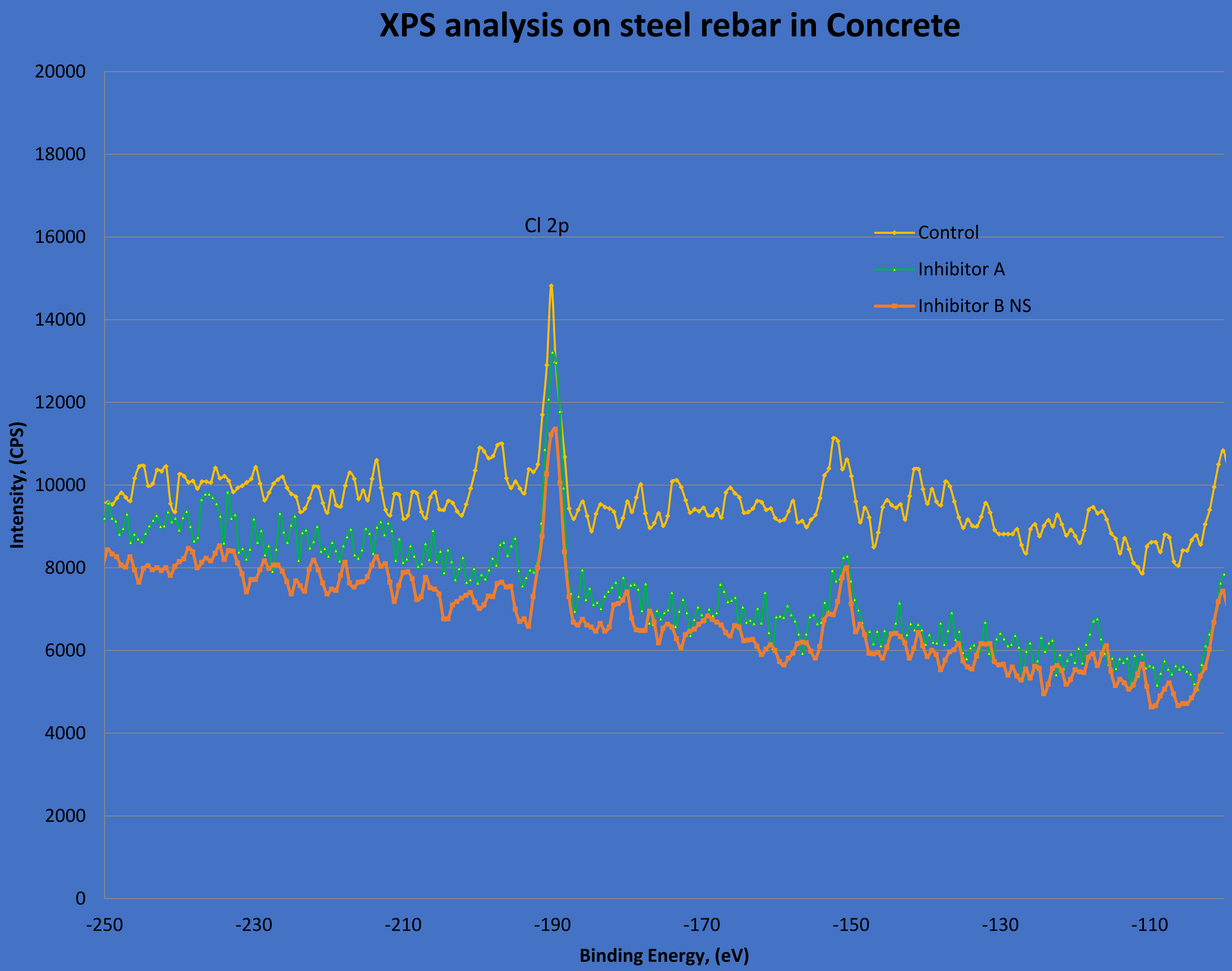
XPS analysis of on Rebar in concrete after 150 days, Mass Concentration %

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

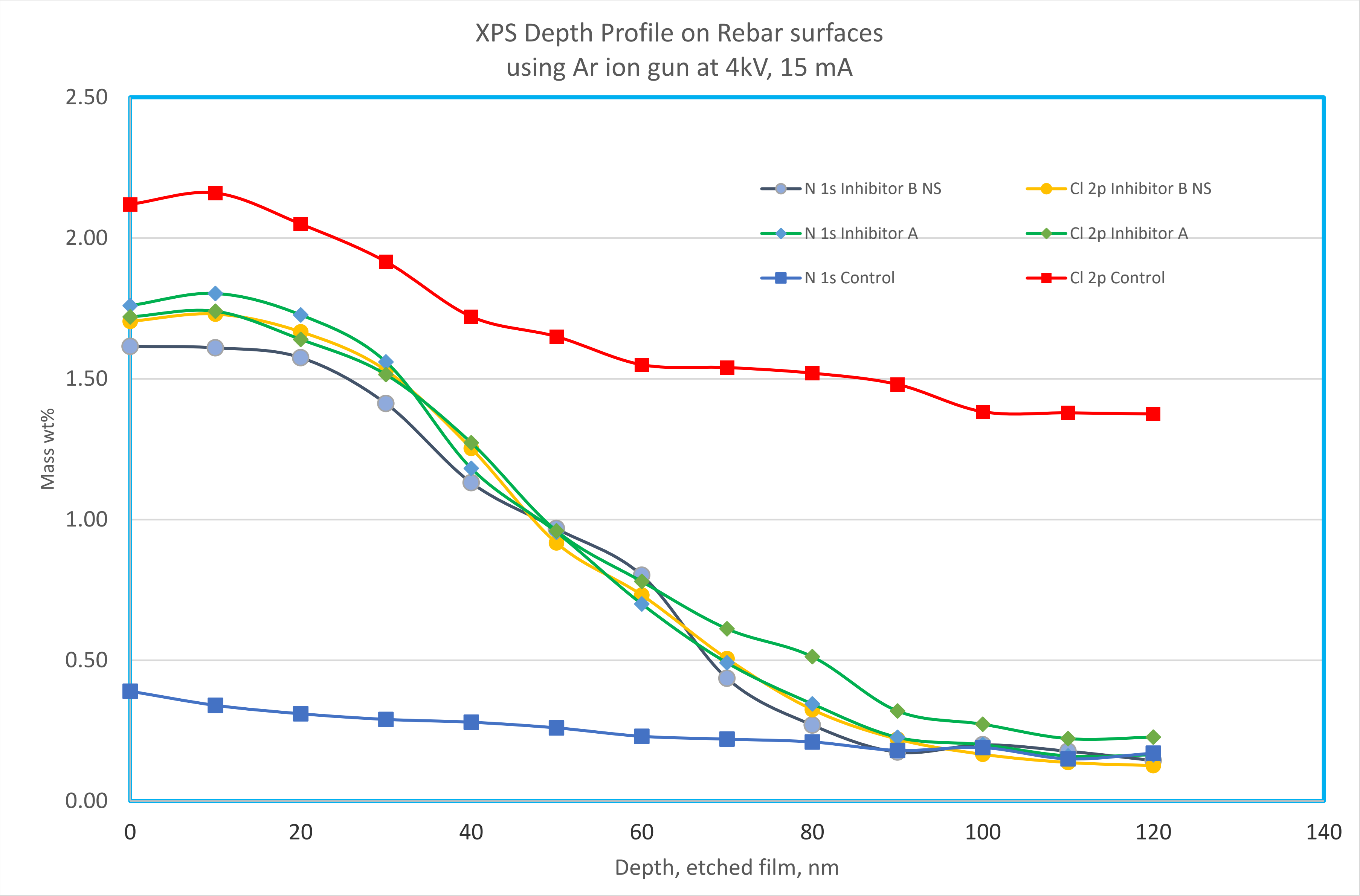
	Binding Energy	710 eV	532 eV	284 eV	399 eV	200 eV	347 eV	99 eV
Sample	Etching Time (seconds)	Fe 2p	O 1s	C 1s	N 1s	Cl 2p	Ca 2p	Si 2p
Control	0	10.25	40.71	27.37	0.39	2.12	14.19	4.97
Control	120	13.6	39.43	22.08	0.34	2.16	17.2	5.19
Control	240	14.3	38.77	22.35	0.31	2.05	17.13	5.03
Inhibitor A	0	2.3	41.22	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

XPS analysis on Surface of Steel Rebar in Concrete





XPS analysis on steel rebar in Concrete


XPS Depth Profile on Rebar surfaces
using Ar ion gun at 4kV, 15 mA
Mass wt%
2.50
2.00
1.50
1.00
0.50
0.00
0
20
40
60
80
100
120
140
Depth, etched film, nm
N 1s Inhibitor B NS
Cl 2p Inhibitor B NS
N 1s Inhibitor A
Cl 2p Inhibitor A
N 1s Control
Cl 2p Control

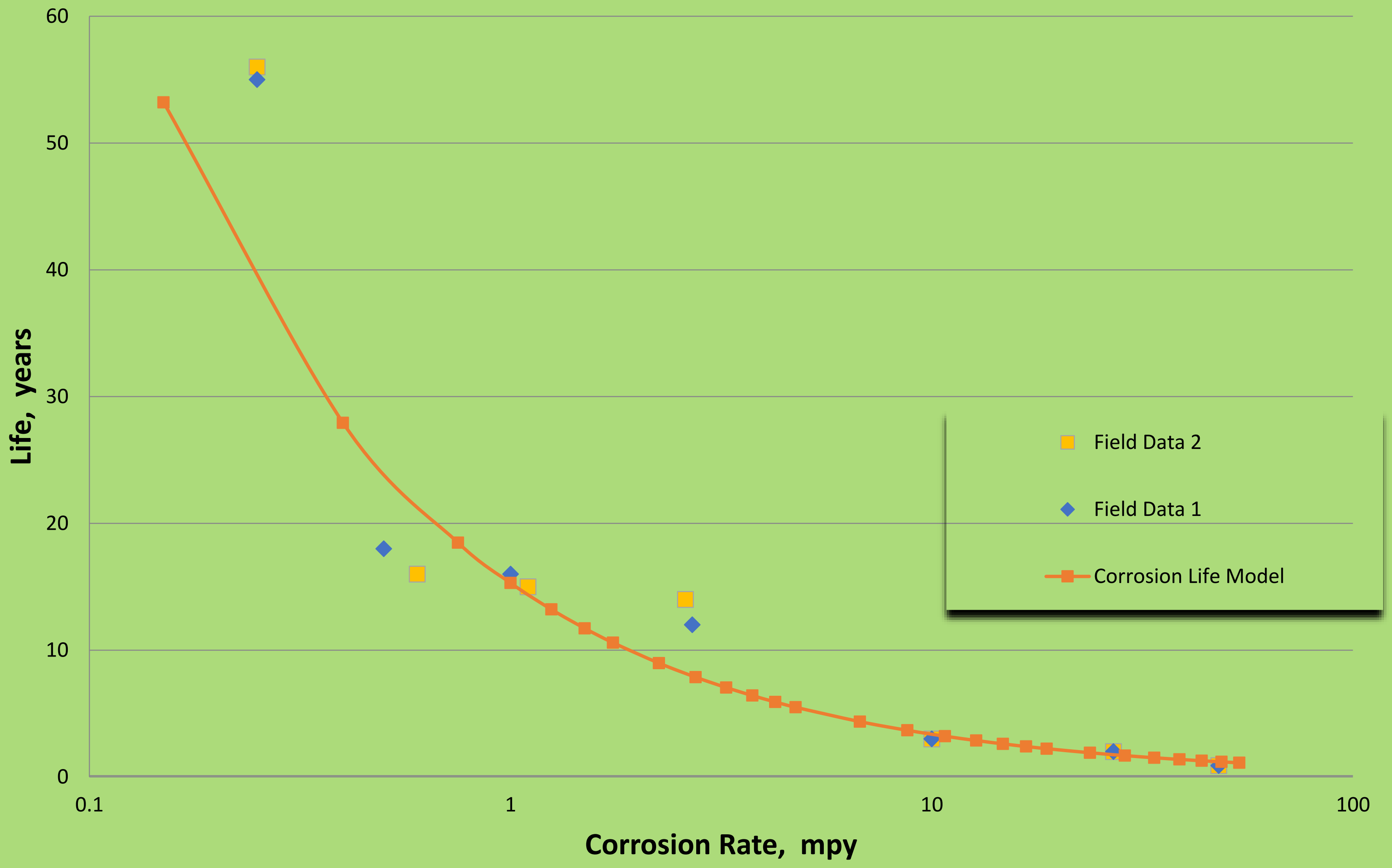
Life Predication based on Corrosion Rate

Sample	Rp, ohm/cm2	Corrosion Rate, UA/cm2	Life Expancy, yrs
Inhibitor A	39,400	0.28	>50
Inhibitor B NS	28,800	0.39	>50
Soda Ash	7,180	1.56	~10-12
Control	2,030	5.51	~ 5-6

Icorr (μA/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

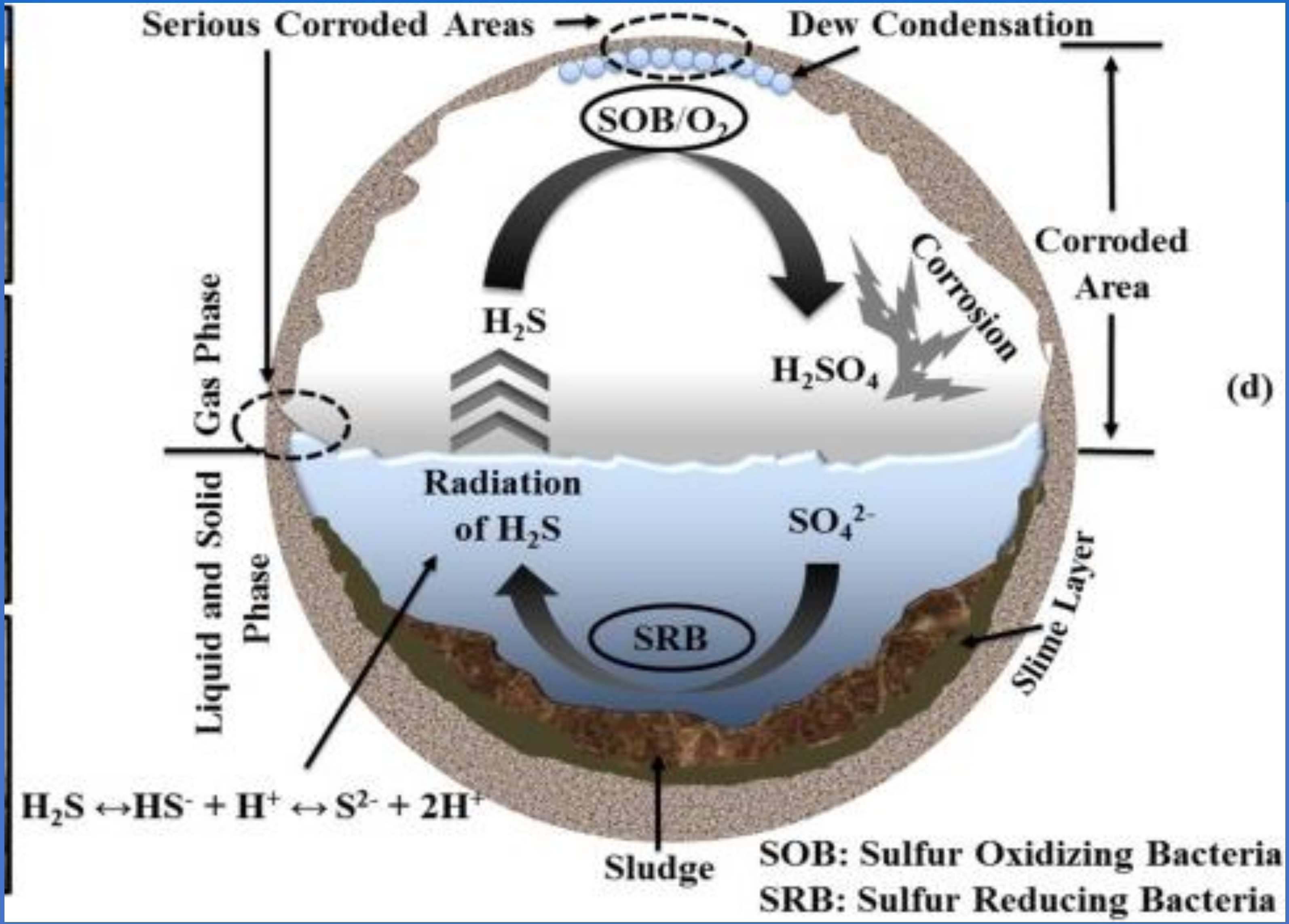
Proposed relationship between Corrosion Rate and Remaining Service Life

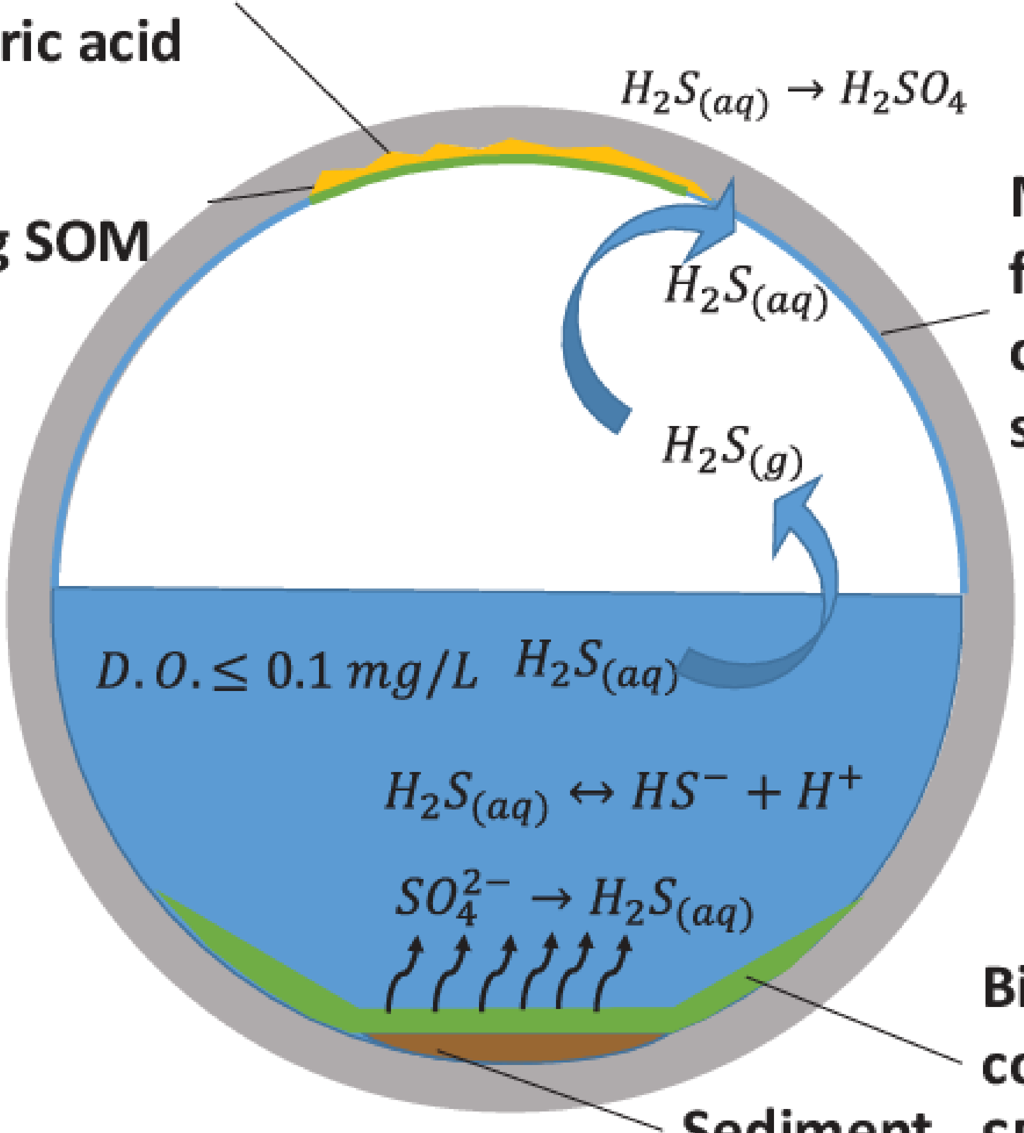
U.S. Department of Transportation, Federal Highway Administration, Office of Federal Lands Highway



Current Research Project

Microbially-induced corrosion of Concrete Structures





Concrete corroding in the presence of sulfuric acid

Biofilm containing SOM

$H_2S_{(aq)} \rightarrow H_2SO_4$

Moisture film on concrete surface

$H_2S_{(aq)}$

$H_2S_{(g)}$

$D.O. \leq 0.1\, mg/L$ $H_2S_{(aq)}$

$H_2S_{(aq)} \leftrightarrow HS^- + H^+$

$SO_4^{2-} \rightarrow H_2S_{(aq)}$

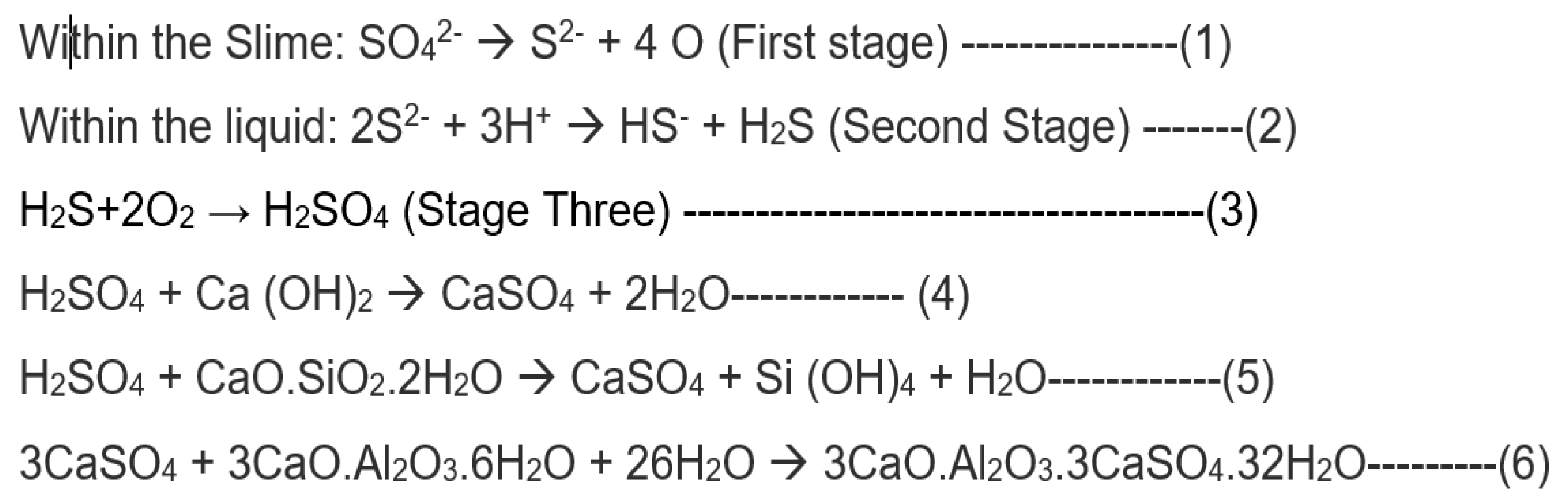
Biofilm containing SRB

Sediment

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

$$SO_4^{=} + 2\ H^{+} + 4\ H_2 \rightarrow H_2S\uparrow\ \ (H^{+}/HS^{-}) + 4\ H_2O$$

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



Within the Slime: $SO_4^{2-} \rightarrow S^{2-} + 4\ O$ (First stage) ---------------(1)

Within the liquid: $2S^{2-} + 3H^+ \rightarrow HS^- + H_2S$ (Second Stage) -------(2)

$H_2S+2O_2 \rightarrow H_2SO_4$ (Stage Three) -----------------------------------(3)

$H_2SO_4 + Ca\,(OH)_2 \rightarrow CaSO_4 + 2H_2O$------------ (4)

$H_2SO_4 + CaO.SiO_2.2H_2O \rightarrow CaSO_4 + Si\,(OH)_4 + H_2O$------------(5)

$3CaSO_4 + 3CaO.Al_2O_3.6H_2O + 26H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$---------(6)

Sewer system Rehabilitation cost ~ few $ 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 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 by sewer treatments?

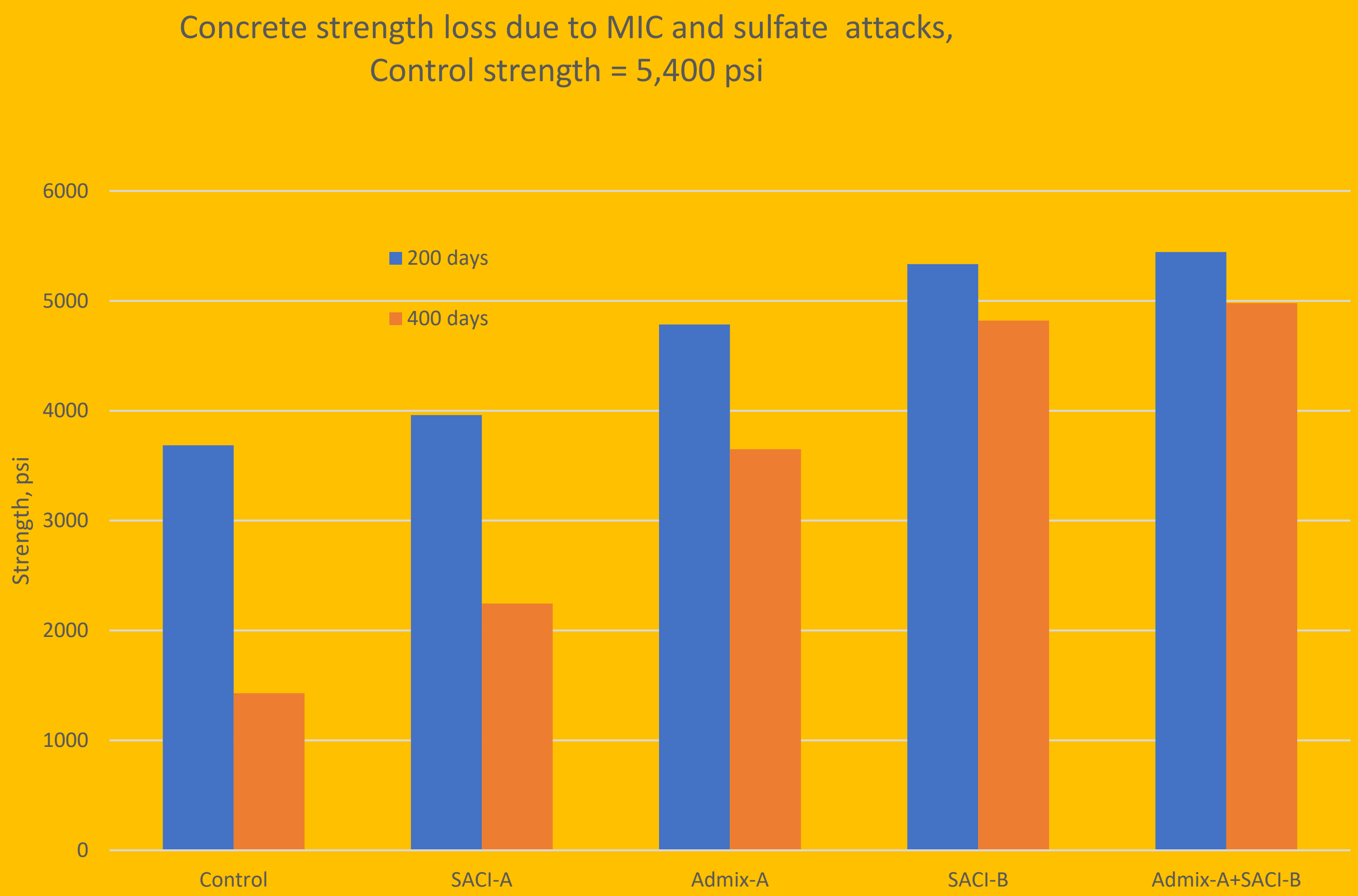
- Chlorine compounds such as bleach, sodium hypochlorite, calcium hypochlorite and ferric chloride and calcium nitrate salt are examples of chemicals that are effective in controlling H2S in wastewater collection systems and used by municipalities to control hydrogen sulfide-related odors and corrosion 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.
- Objective of this research project: Recommend commercially available Inhibitors and Admixture were evaluated.

EXPERIMENTAL PROCEDURE

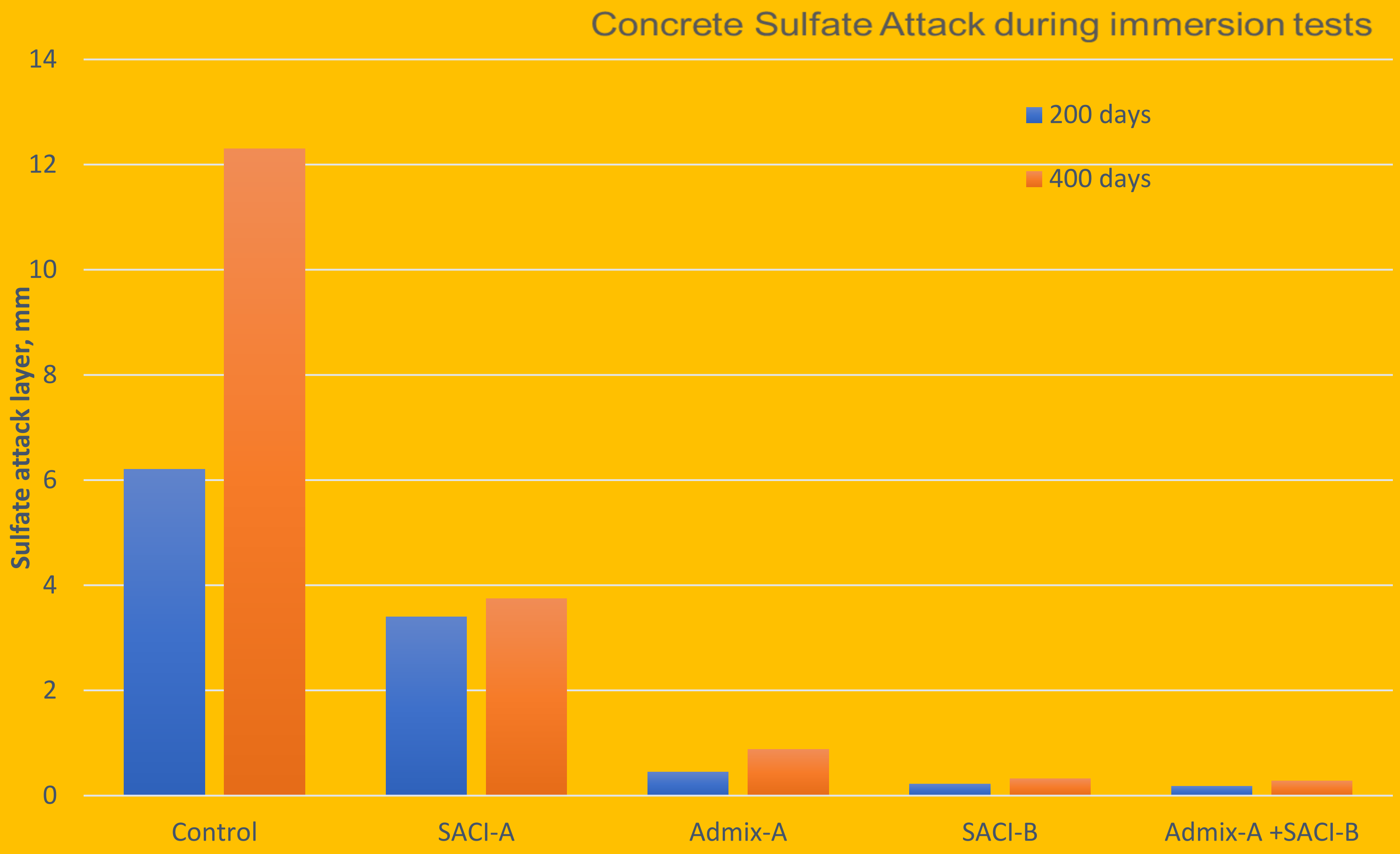
- A concrete mixture (4 Aggregate: 2 Sand: 1 Portland Cement type II with moderate sulphate resistant hydraulic cement) was used to make the concrete (0.5 W/C ratio). The premixed concrete was used to cast 2 inch x 4 inch cylinders. Curing and compression tests were done per ASTM C31 and ASTM C39 standards, the compressive strength was on average 5,400 psi after four weeks of curing.
- Four types of samples were prepared: 1) samples surface coated with migrating corrosion inhibitor; 2) samples made with admixtures; 3) samples made with 5% admixtures and coated with surface applied migrating corrosion inhibitors; and 4) control samples (no admixtures, no corrosion inhibitor coatings).
- Three layers of the surface applied migrating corrosion inhibitor (SACI-A and SACI-B) were applied to the cylindrical samples after curing and prior to the immersion corrosion tests.

Sulfate attack layer thickness after 400 days exposure to highly acidic solution shows that Admix-A+SACI-B have the lowest sulfate reactions

Sulfate attack layer thickness after 750 days exposure to highly acidic solution shows that Admix-A+SACI-B and SACI-B still maintained their strength

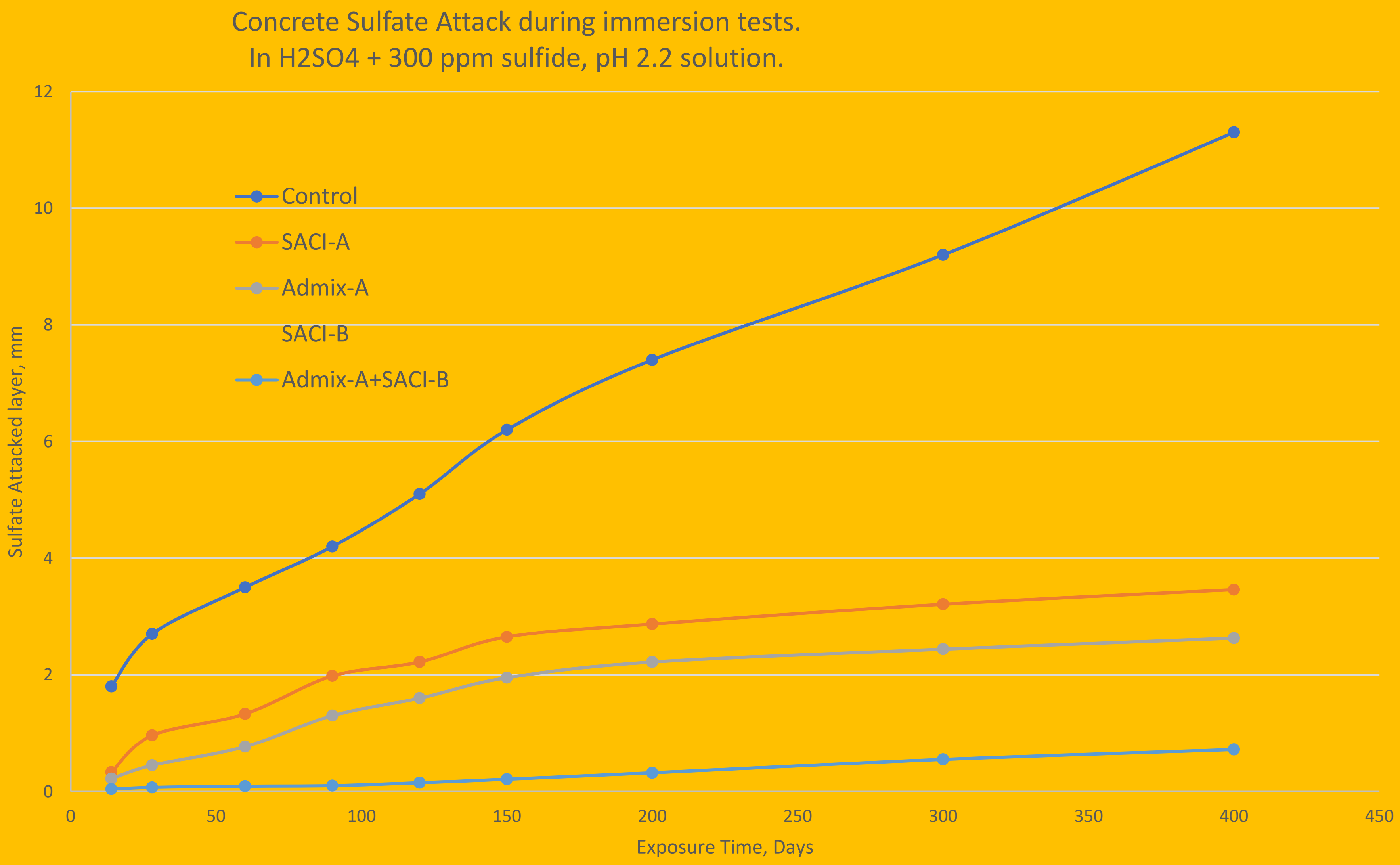

Concrete strength loss due to MIC and sulfate attacks,
Control strength = 5,400 psi

Comparison of compressive behavior for concrete samples after 400 days of immersion tests. The combination of Admix-A (MCI 2005)+SACI-B(MCI 2018) had the best performance in highly acidic solution.

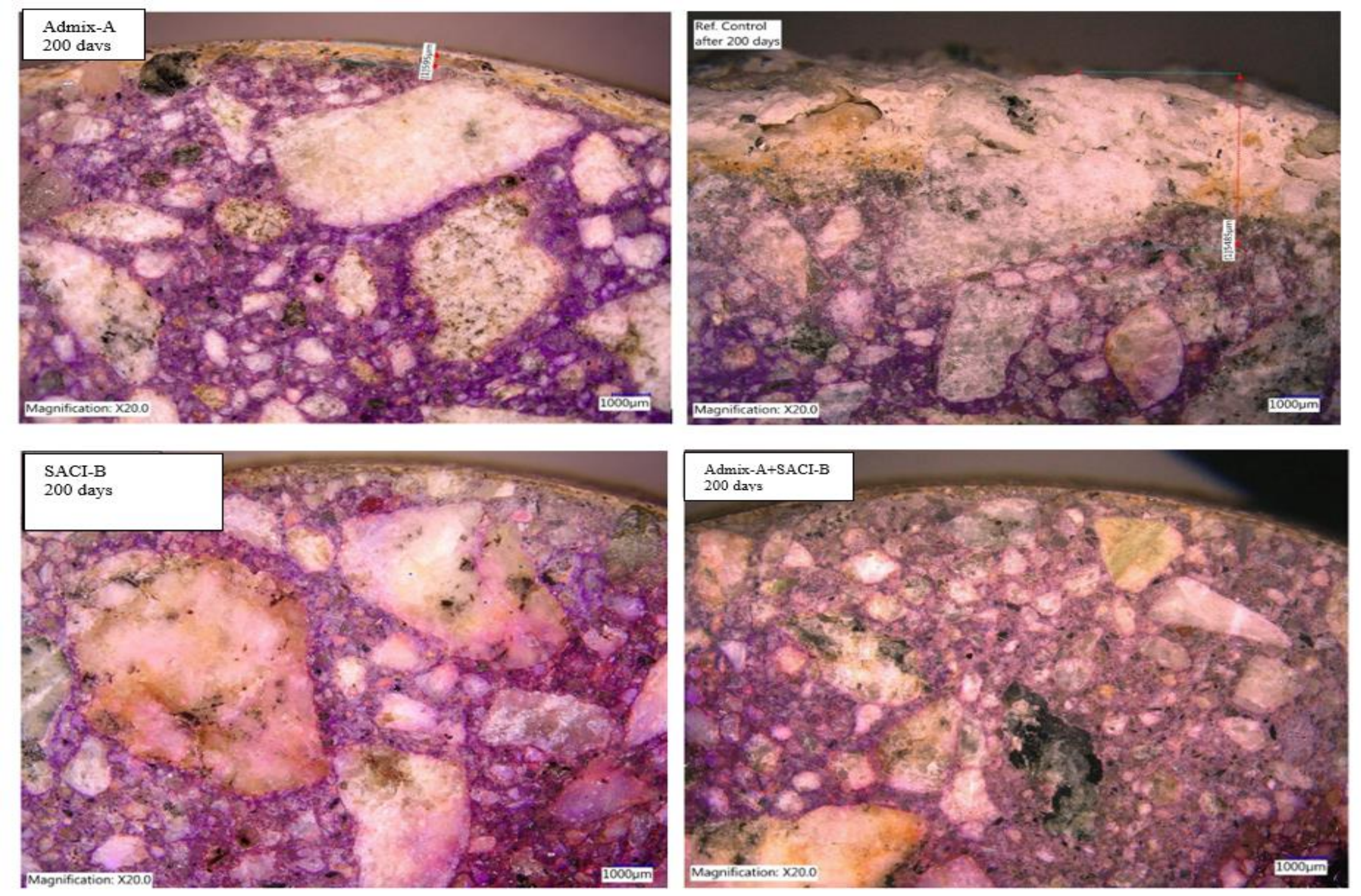


Comparison of sulfate attacks for 200 and 400 days exposure to highly acidic solution. SACI-B and Admix-A have the lowest sulfate attack reactions.

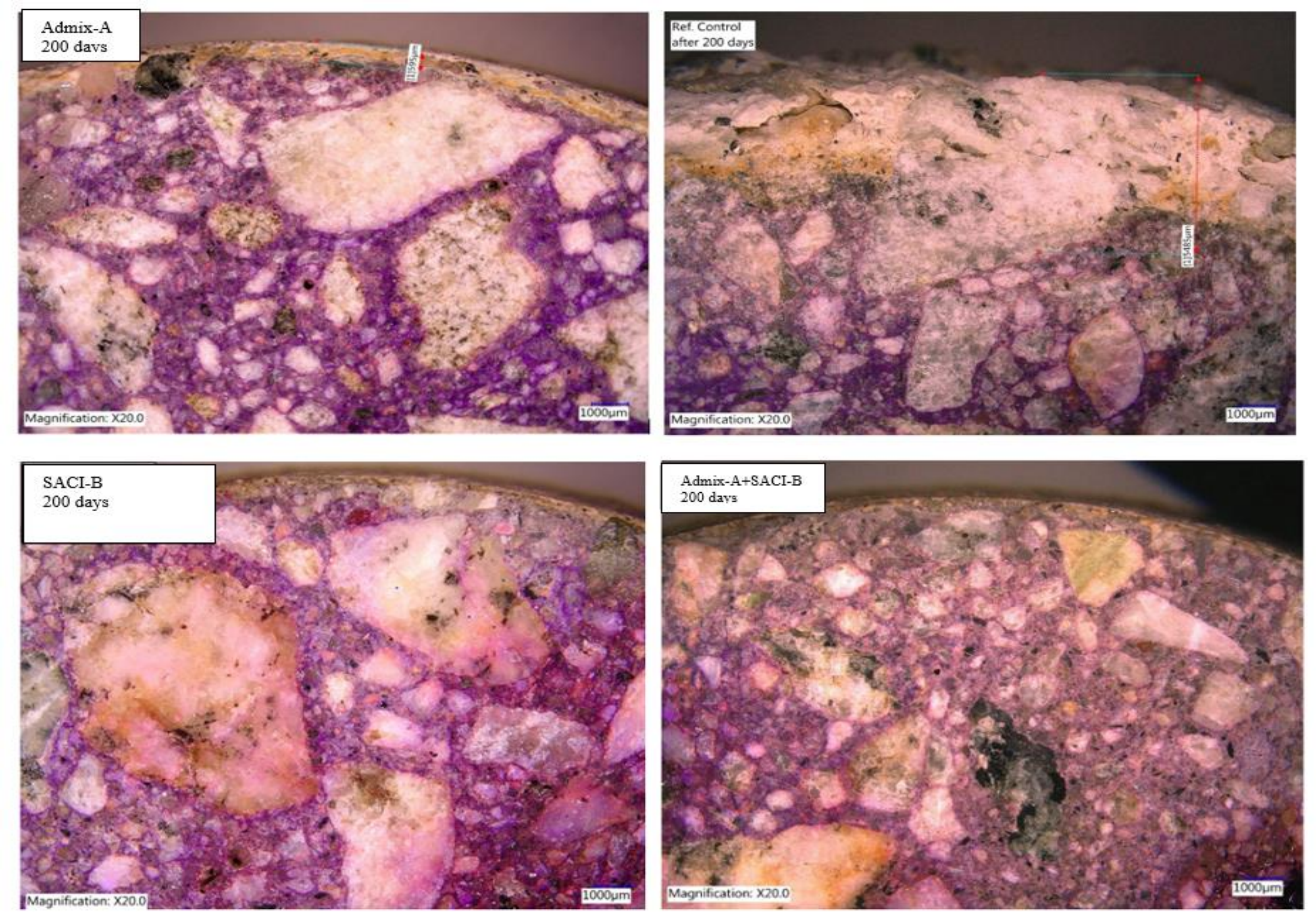
Sulfate attack layer thickness after 400 days exposure to highly acidic solution



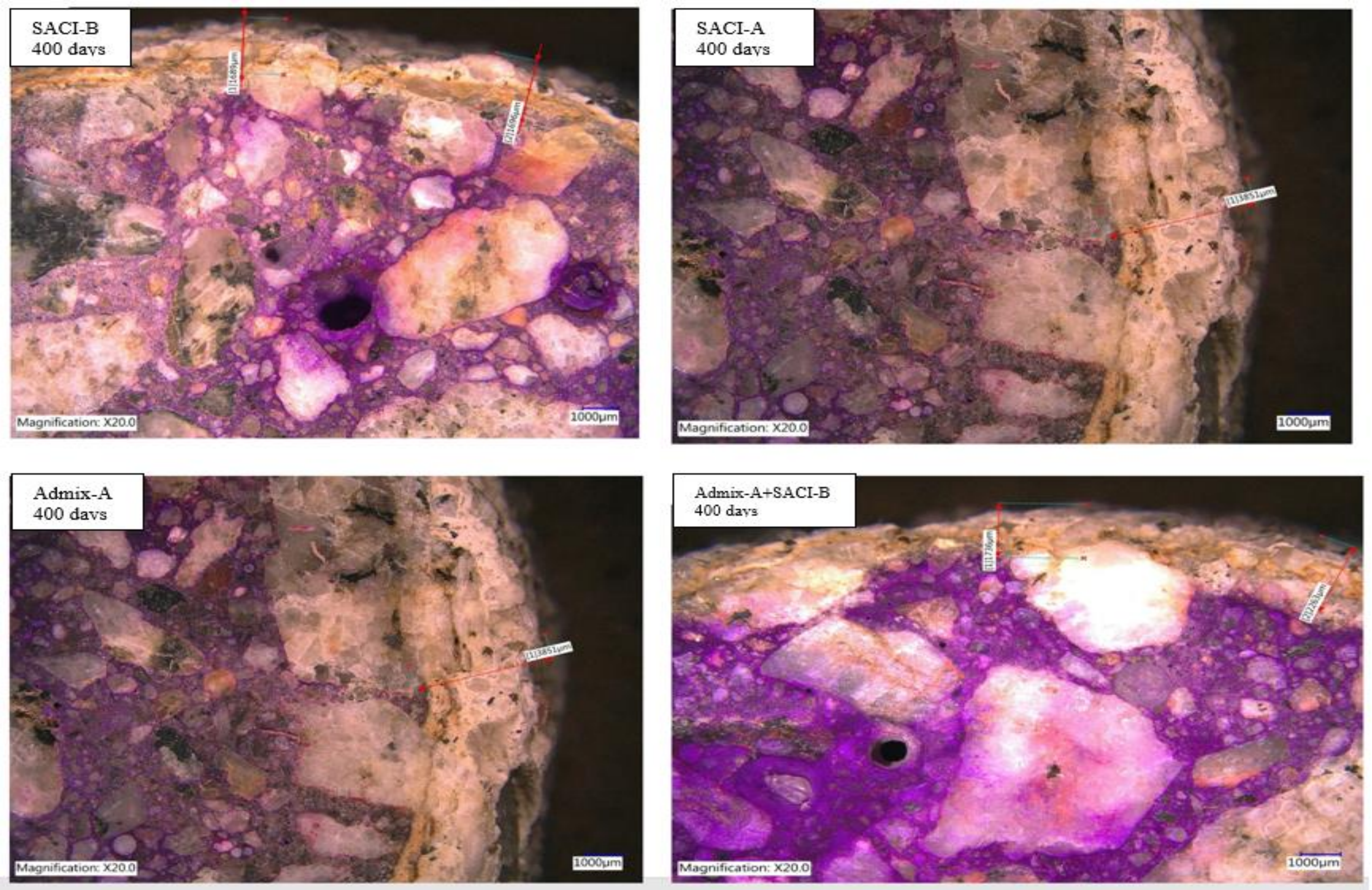
Etched micrographs of the concrete control samples after immersion for 200 days, shows severe sulfate attacks and cracking of the concrete due to severe chemical MIC attacks.



Comparison of concrete sections used to measure the sulfate attack layer thickness after 200 days, both Admix-A and SACI-B are very effective resisting sulfate attack. The control sample showed more than 24.5% thickness, (etched with Phenolphthalein).



Comparison of Concrete sections used to measure the sulfate attack layer thickness after 400 days.



Summary

- Microbiologically influenced corrosion of concrete was investigated in a highly acidic solution +300 sulfide (similar to SRB and SOB attacks) for more than 750 day. The concrete control samples suffered severe corrosion attack, presenting with a very thick sulfate layer, surface etching, disintegration of concrete (more than 12.0 mm) and significant loss of compressive strength, more than 78% after 750 days exposure
- Admixture-A and surface applied SACI-B, a super hydrophobic corrosion inhibitor, showed excellent protection for the concrete samples without any loss of strength and a very thin layer of sulfate attack (~0.1-0.5 mm) for 200 day immersion tests. After 750 day immersion tests the strength loss for these samples was less than 8%.
- Admixture-A and surface applied SACI-B has showed a minimum chemical attacks (deterioration), still maintained ~90% of concrete strength after 750 days
- SACI-A showed some improvement and protection in the short term, however, due to its low surface adhesion, ultimately, the concrete samples showed some strength loss due to the sulfate attack after 150 days of exposure tests.

In summary, to assure a satisfactory performance for concrete structures (such as manhole, channels and pipes) in aggressive (sulfate rich) waste water systems, a combination of admixture-A (MCI 2005) and surface applied (highly hydrophobic) SACI-B, MCI 2018) is recommended.

The Peljesac Bridge Croatia’s Adriatic coastline. In service since July 2022 The USD $500M, 2.4-kilometre beam and cable-stayed structure, protected by Surface Applied Corrosion inhibitor (MCI 2018) and Migrating Corrosion Inhibitor admixture (MCI 2005).

Questions?