Improving Durability of Reinforced Concrete Structures using Migrating Corrosion Inhibitors as Admixtures

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Objective

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

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

Overview

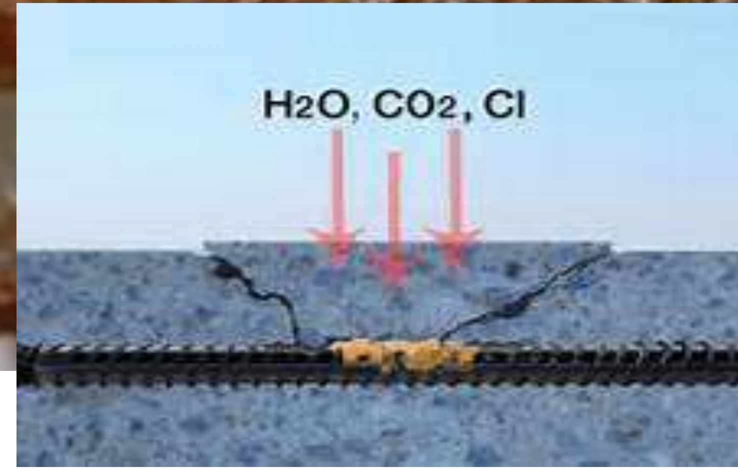
- Corrosion Process
- Testing Procedures
- Sample Preparation
- Results
- Conclusions
- Current Status

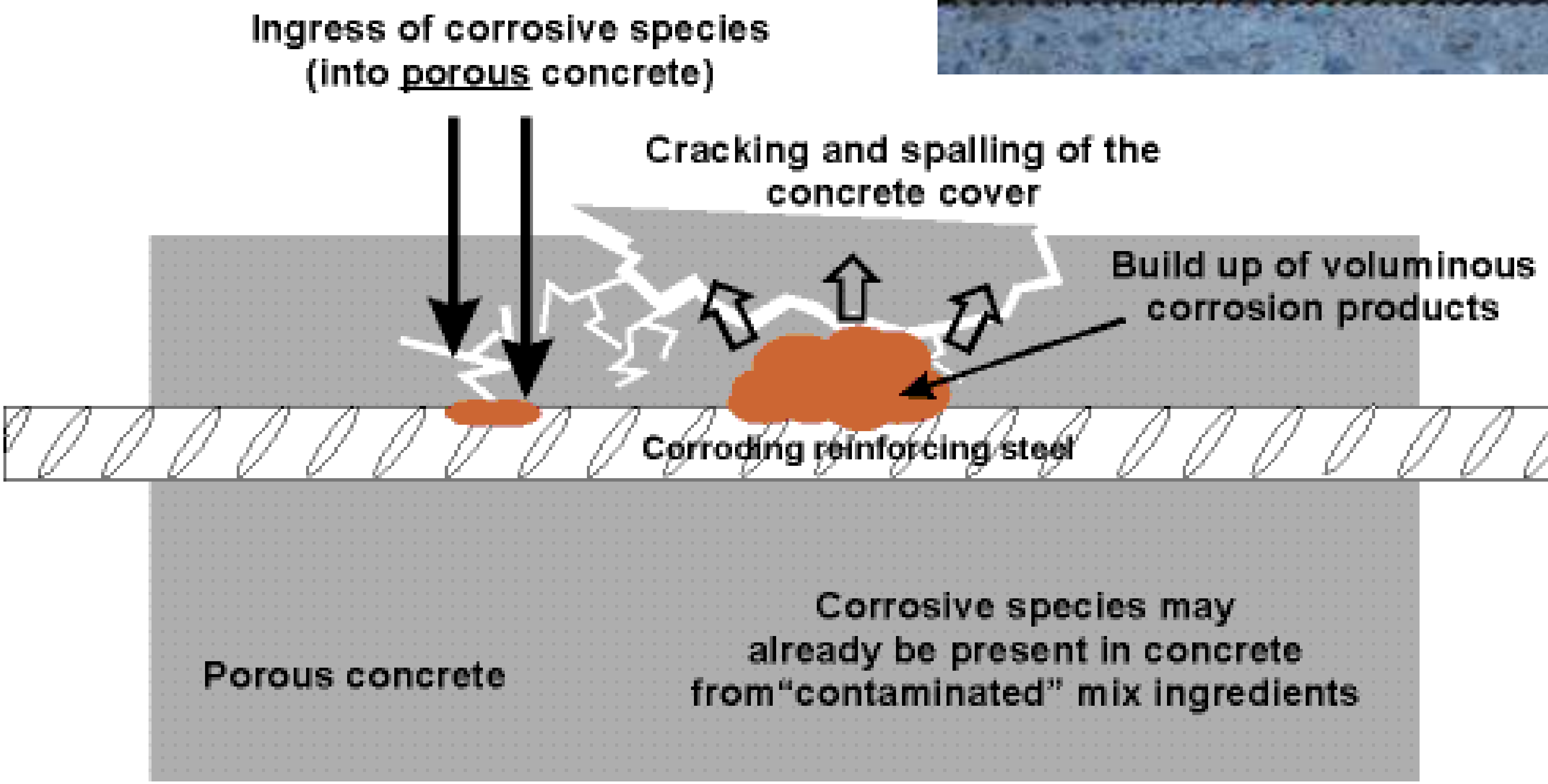

Concrete Damage
and Problems

Concrete structures Deterioration

Cracking & Spalling

Corrosion Damages





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

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

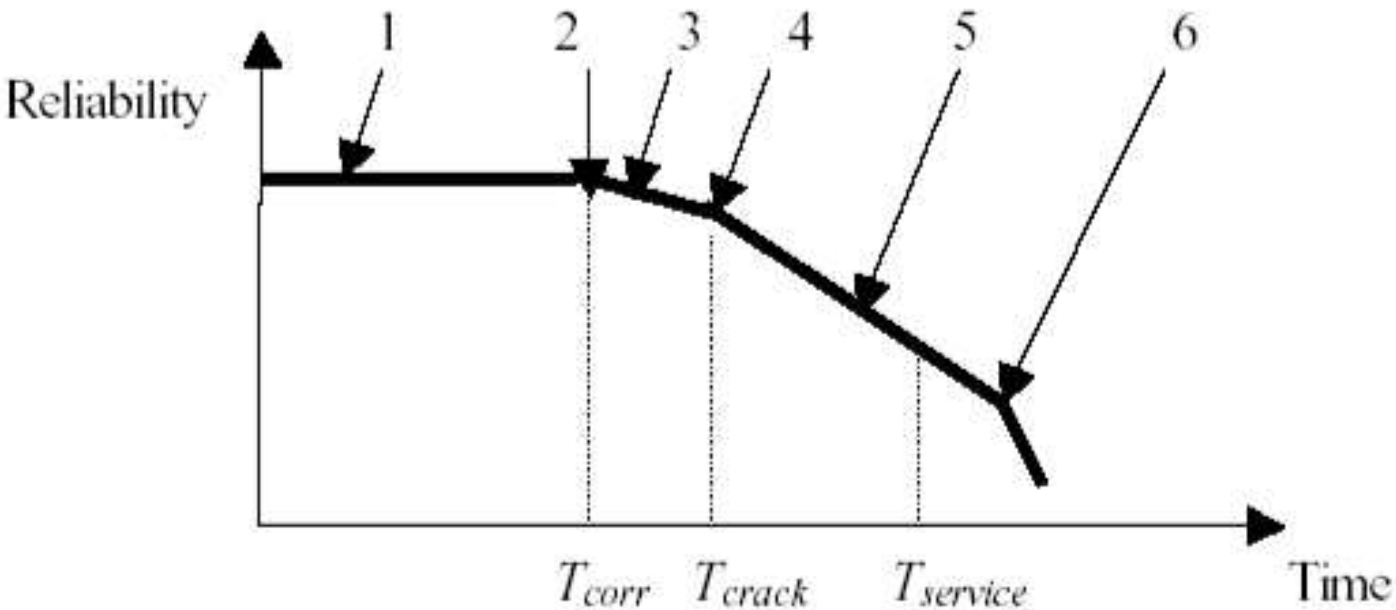
or

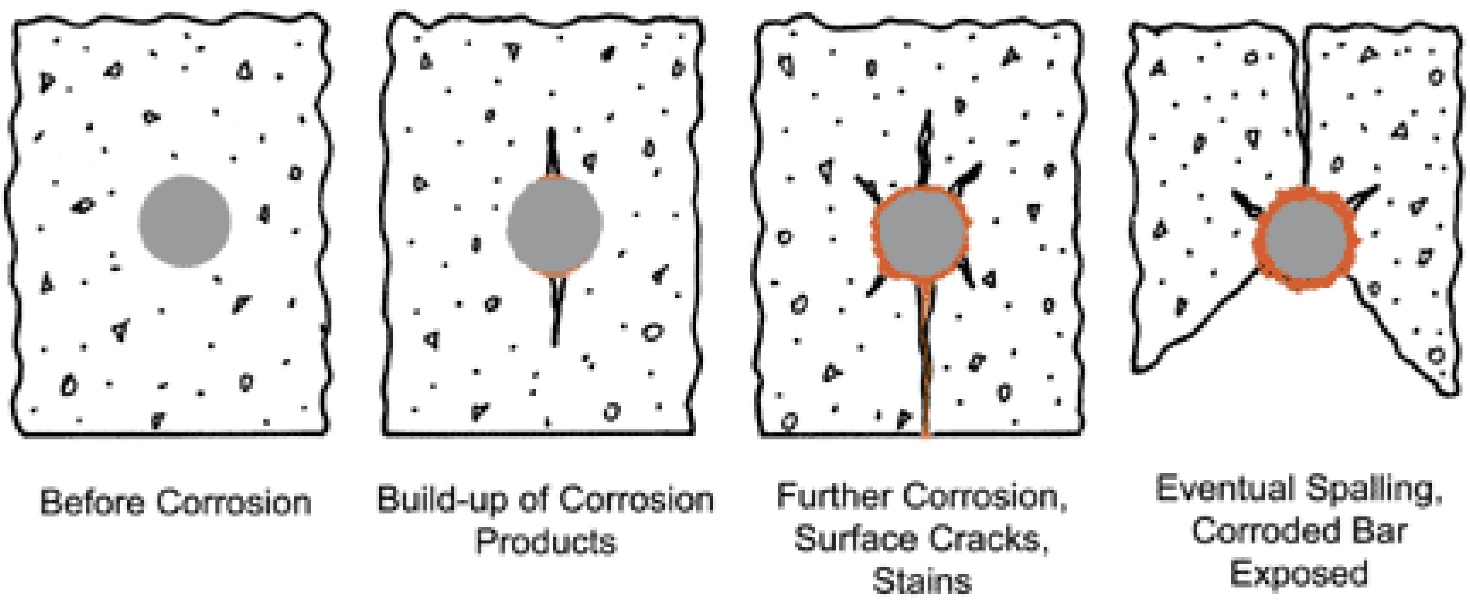
$2H^+ + 2e^- \rightarrow H_2$

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





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.

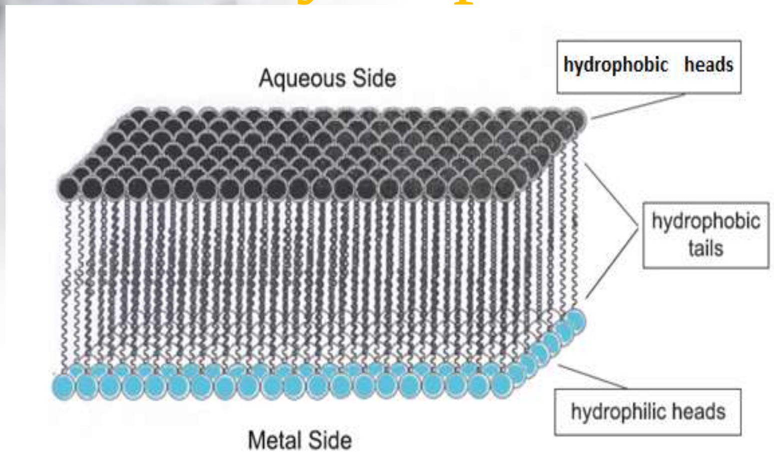
Corrosion control of steel rebar in concrete

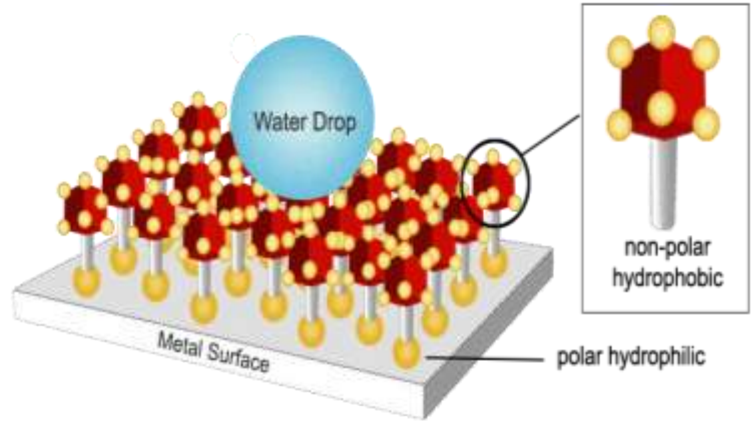
- Good Concrete
- Cathodic Protection
- Admixtures and Inhibitors
- Migrating Corrosion Inhibitors

How MCI Admixture/Inhibitor works?

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.





Electrochemical Tests

- **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: (Test Duration:150 days)
  - Open circuit potentials
  - Rp monitoring using Bode plots

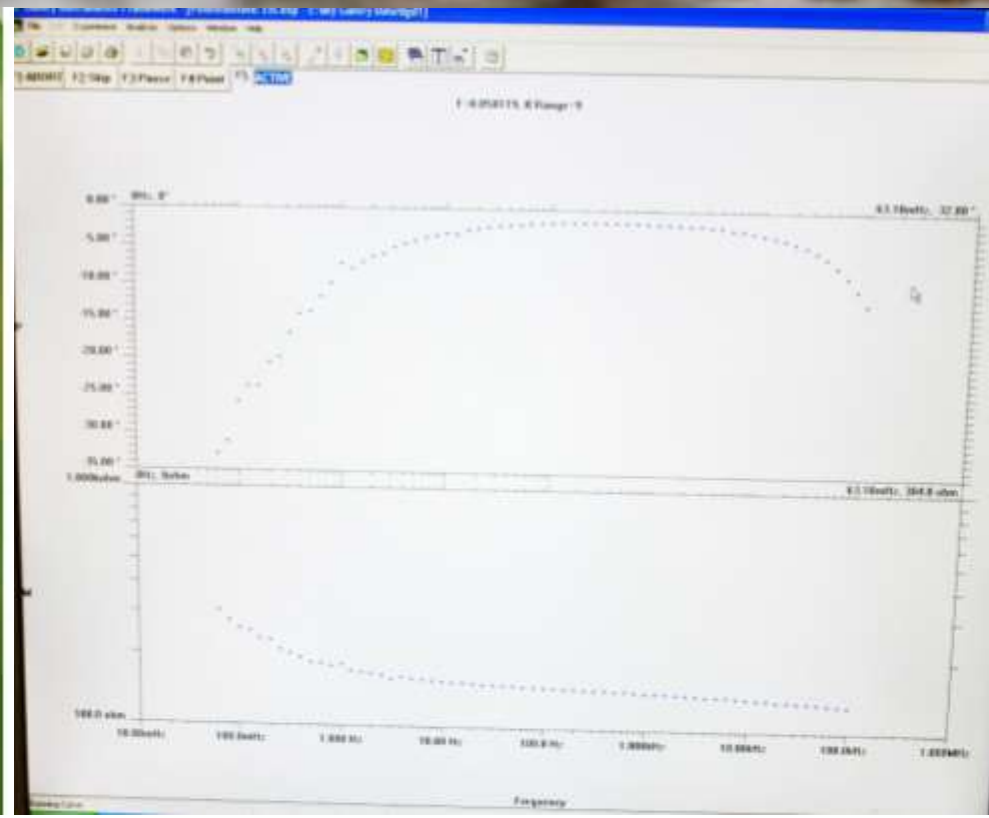
Experiments

- 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 of 150 days, using electrochemical impedance spectroscopy (EIS).
- Post experiment visual observation, SEM/EDAX 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

EIS on ASTM G109 Modified sample,
Constant Immersion



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

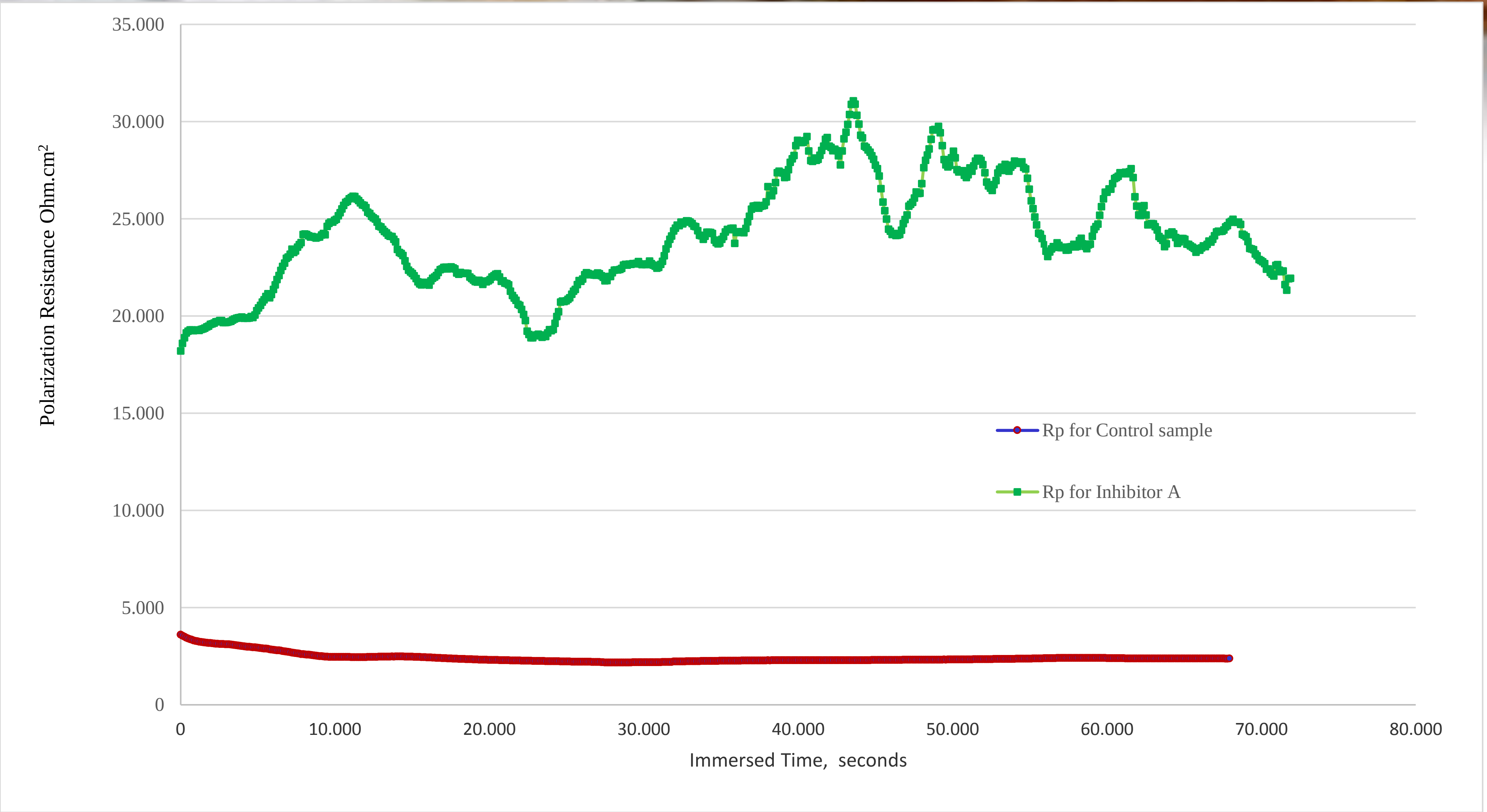
Rate of Corrosion	Polarization Resistance	Corrosion Penetration
	R_p (kΩ.cm^2)	p (μm/year)
Very high	$0.25 < R_p < 2.5$	$100 < p < 1000$
High	$2.5 < R_p < 25$	$10 < p < 100$
Low/moderate	$25 < R_p < 250$	$1 < p < 10$
Passive	$250 < R_p$	$p < 1$

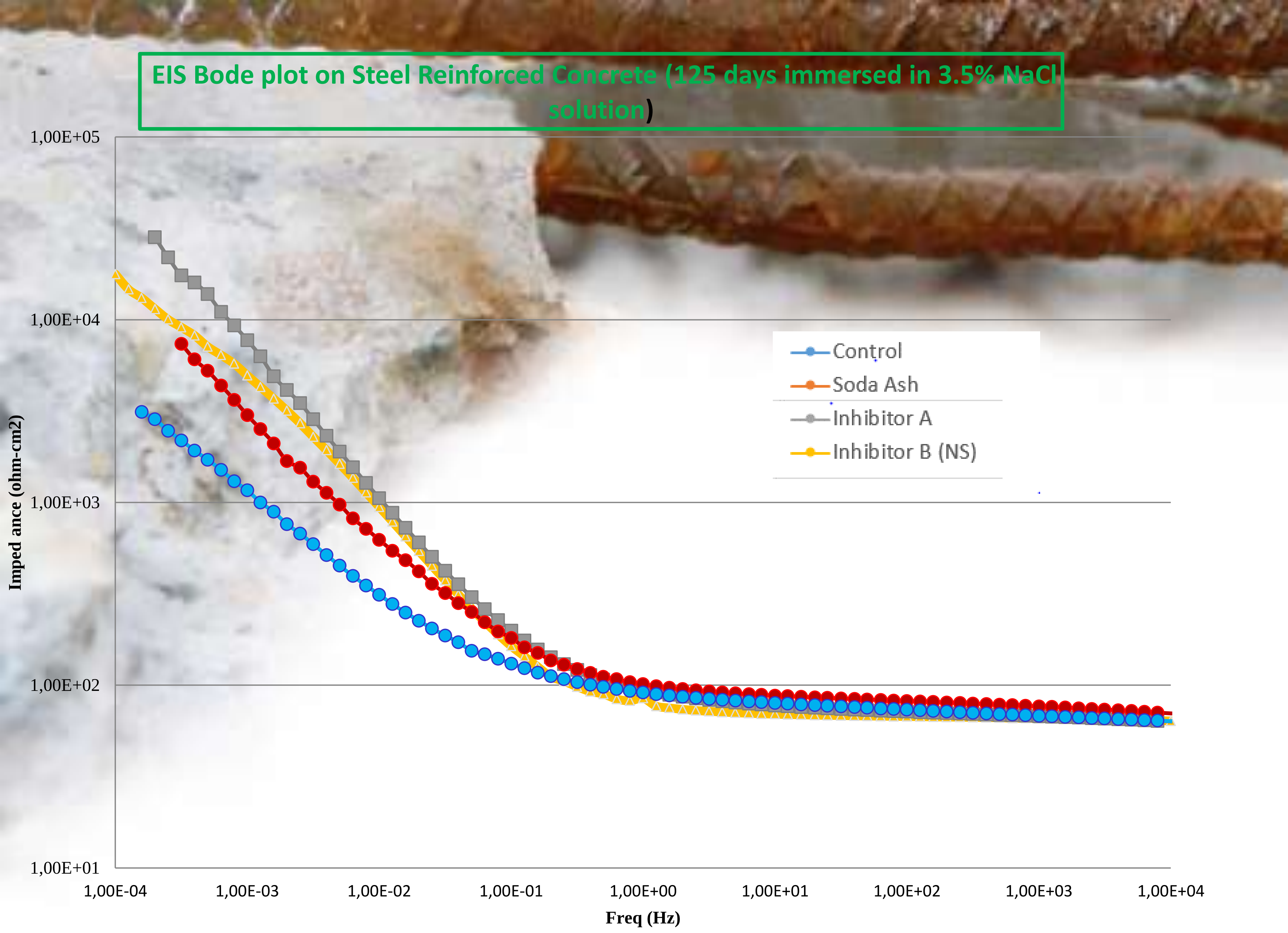
Proposed Relationship between Corrosion Rate and Remaining Service Life

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

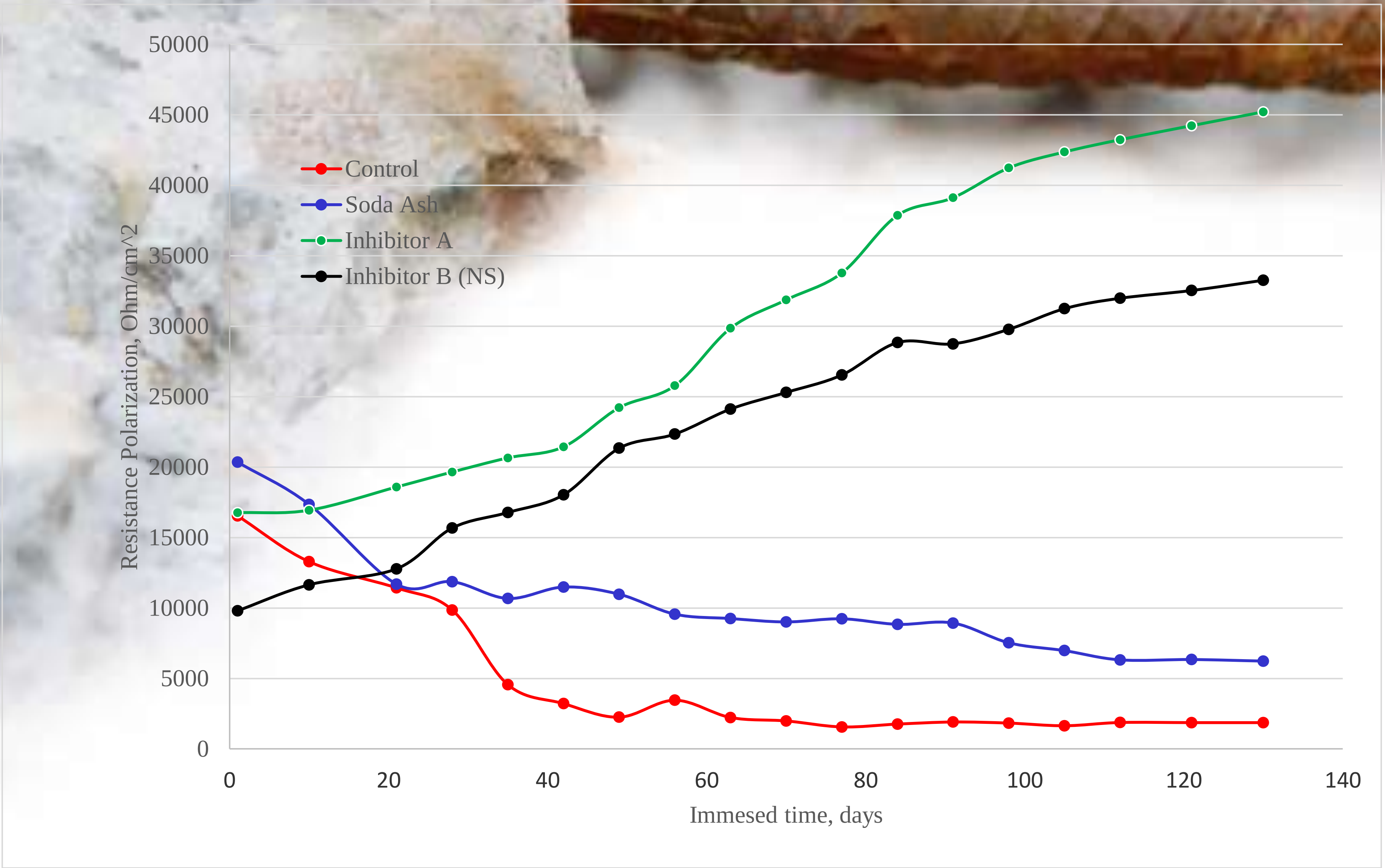
Test Results

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)
Imped ance (ohm-cm2)
1,00E+05
1,00E+04
1,00E+03
1,00E+02
1,00E+01
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)
Control
Soda Ash
Inhibitor A
Inhibitor B (NS)

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



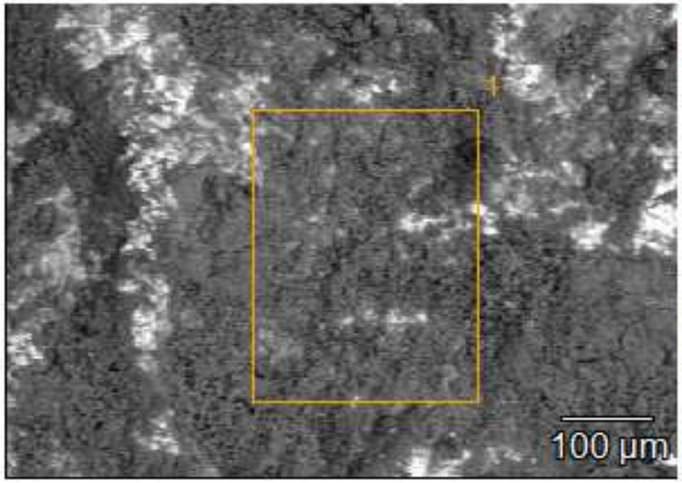
Inhibitor A after 150 days

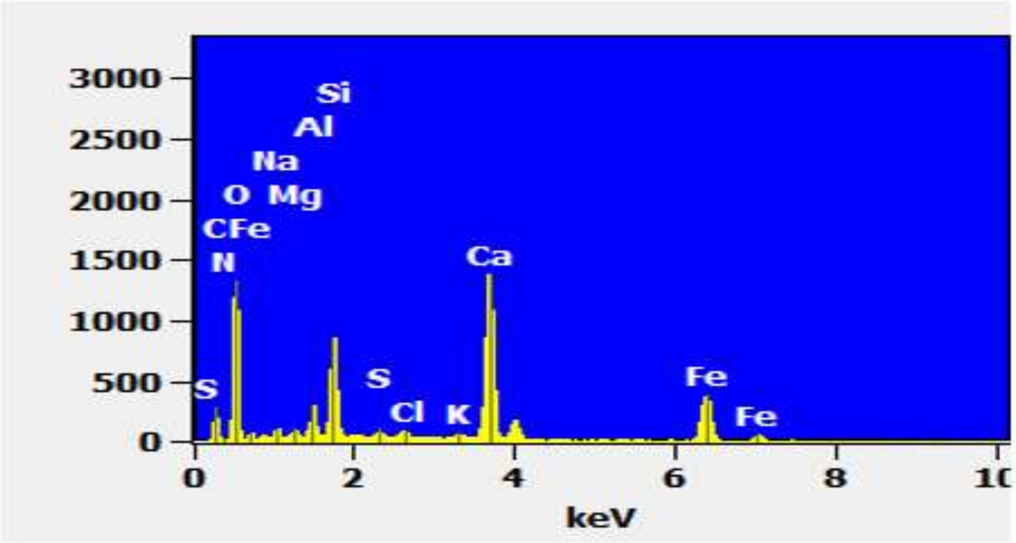
Control after 150 days

Inhibitor B after 150 days

Soda Ash after 150 days

EDS analysis on the Inhibitor A concrete samples.

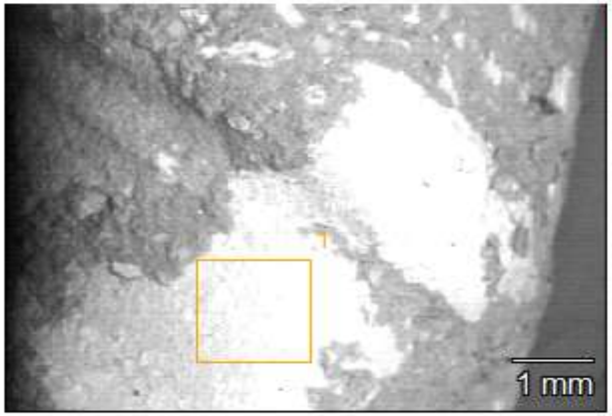


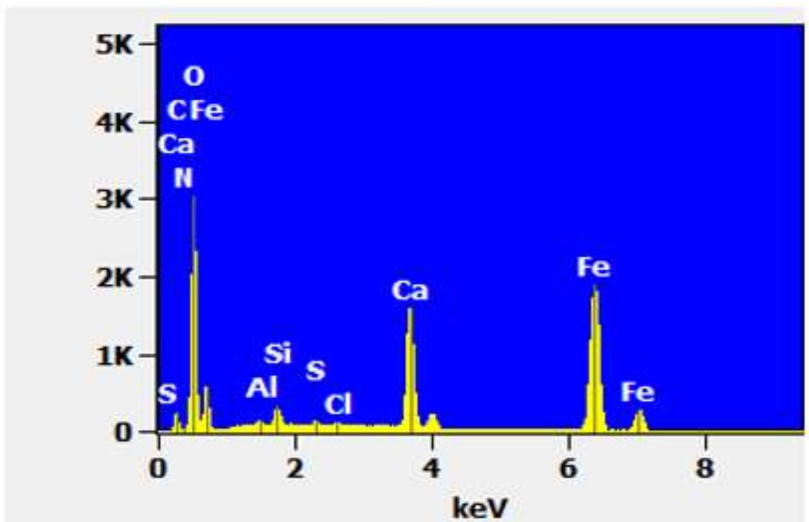


Weight %

	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.

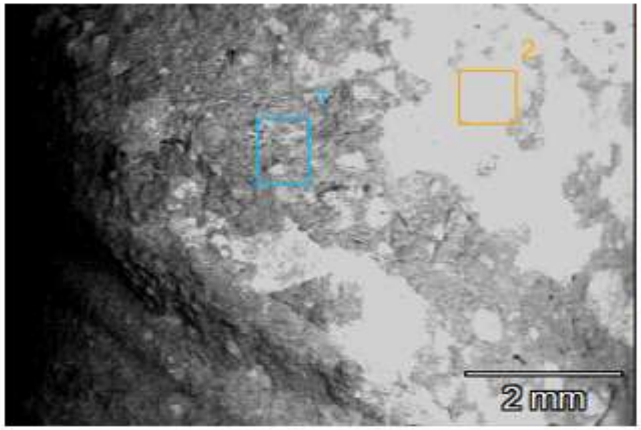


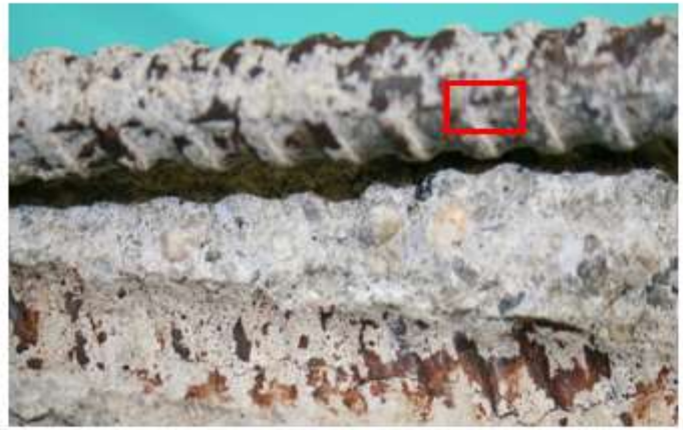


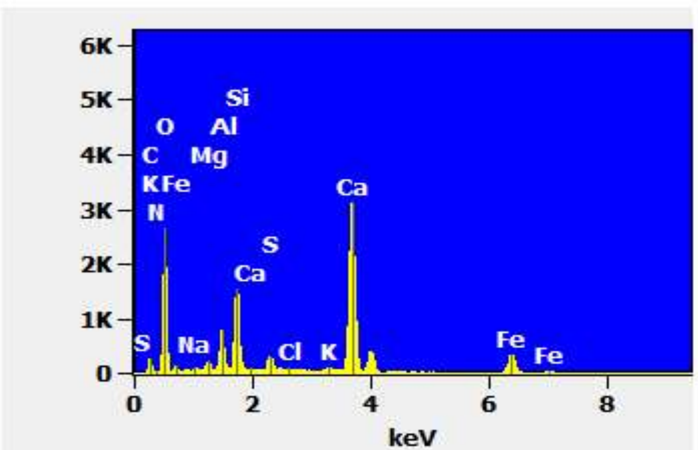
Weight %

	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

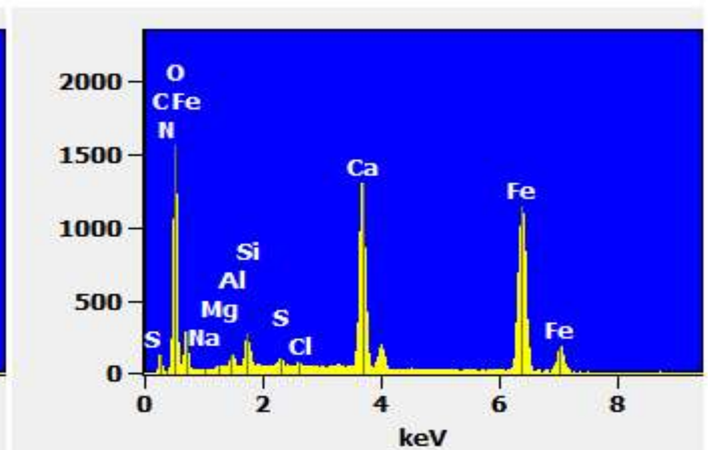
EDS analysis on the Control concrete samples.







Pt 1

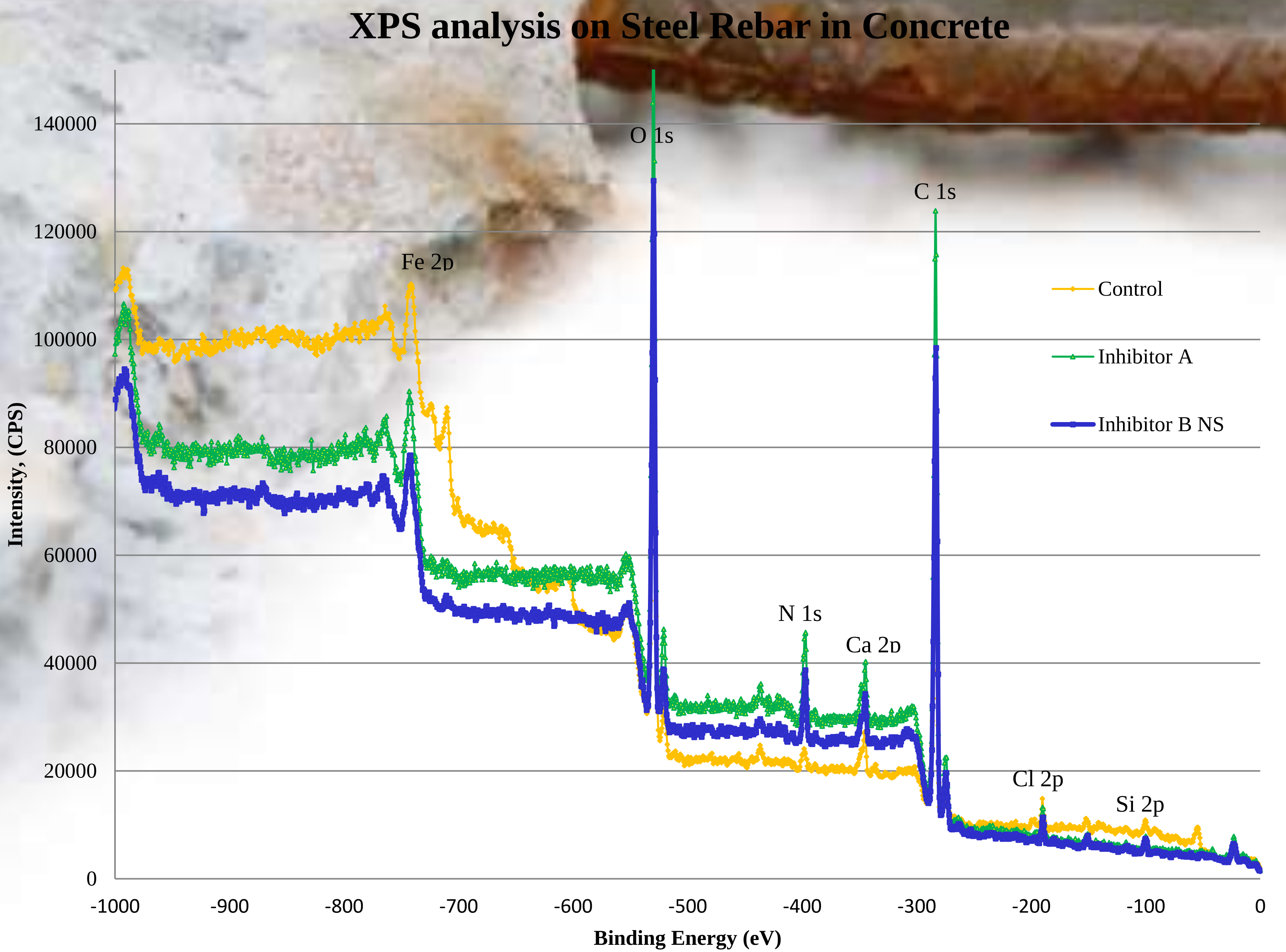


Pt 2

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

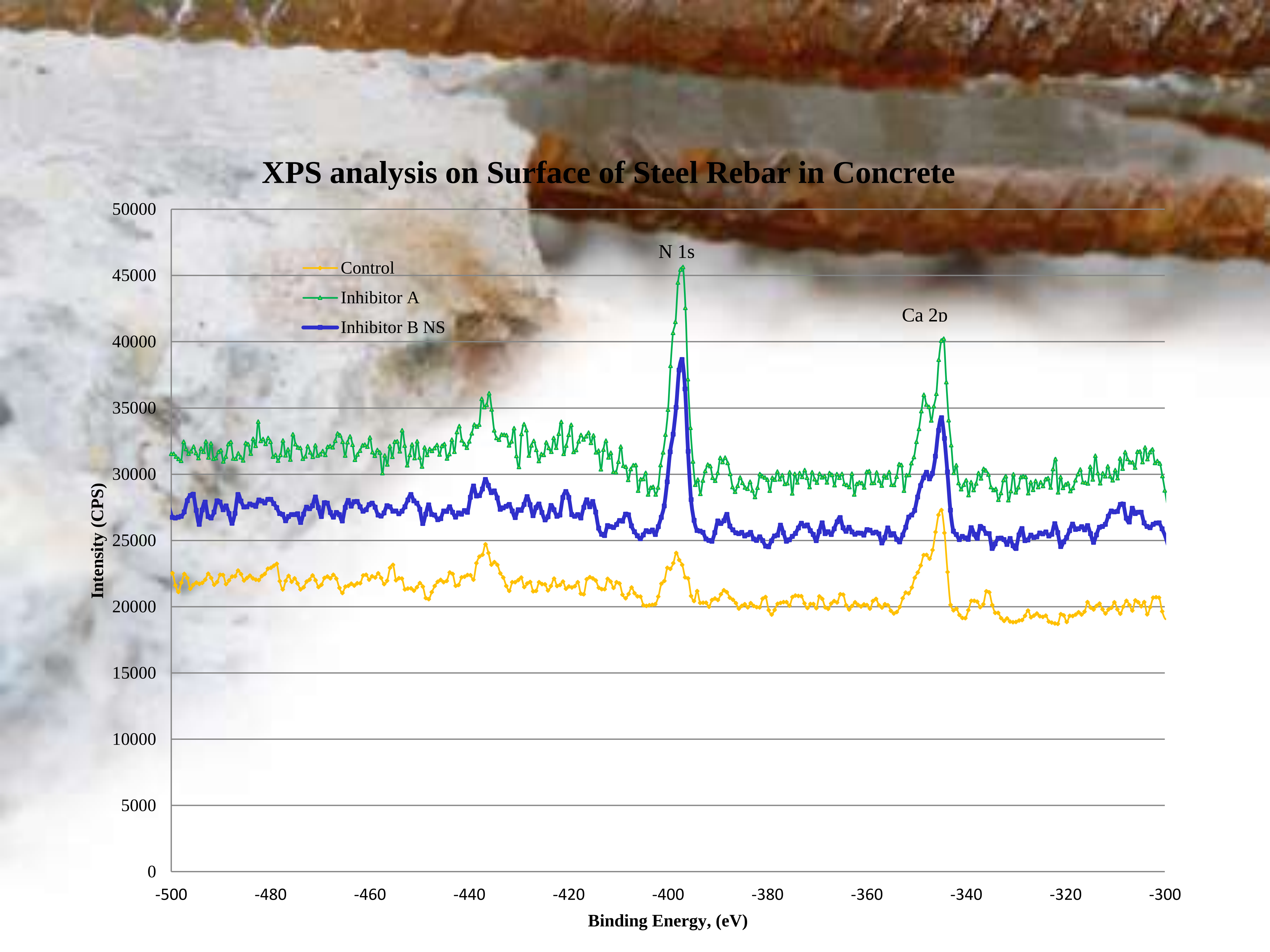
XPS analysis of rebar surface after 150 days in 3.5% NaCl



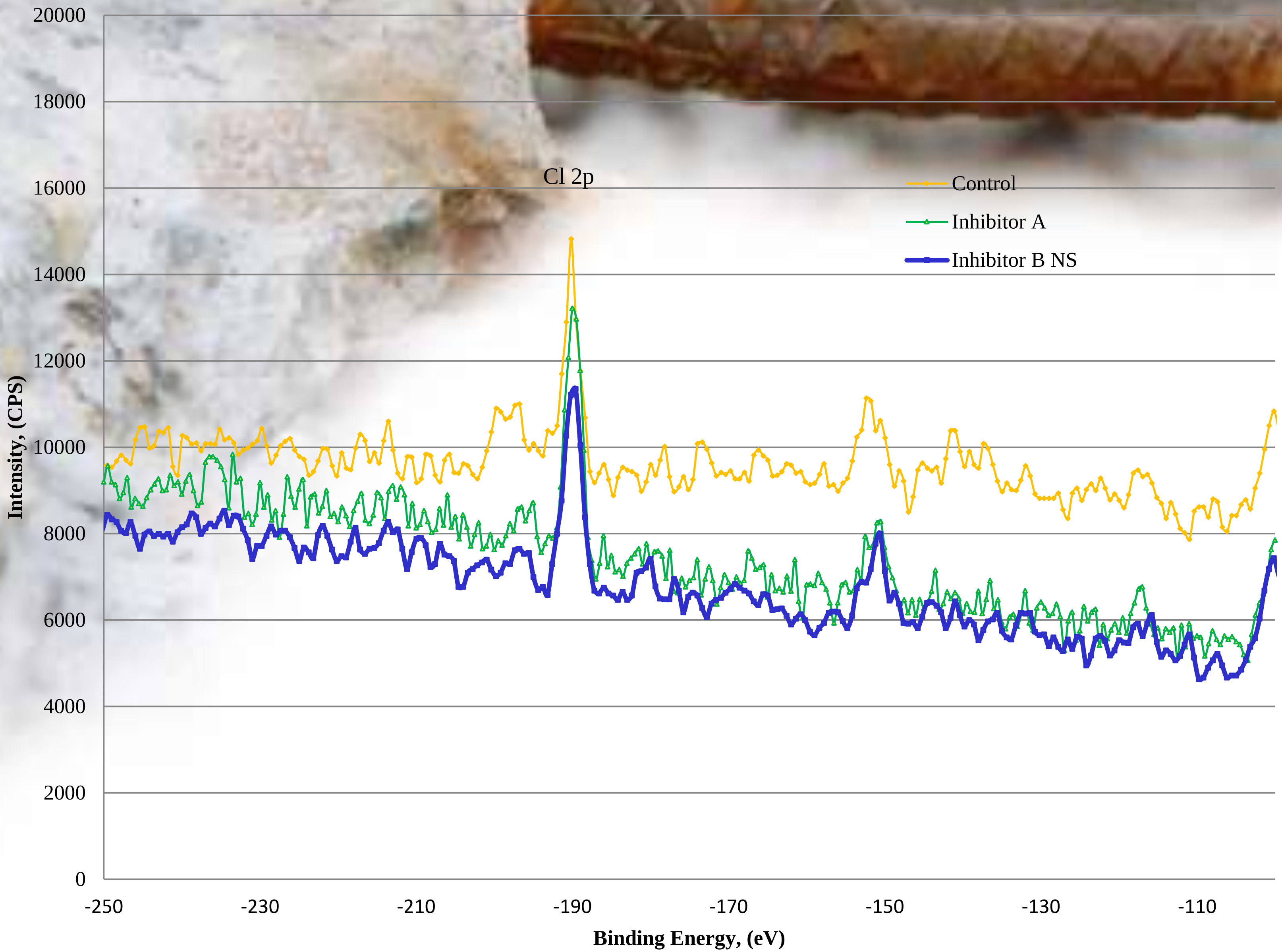
XPS analysis of on Rebar in concrete after 150 days, Mass Concentration %

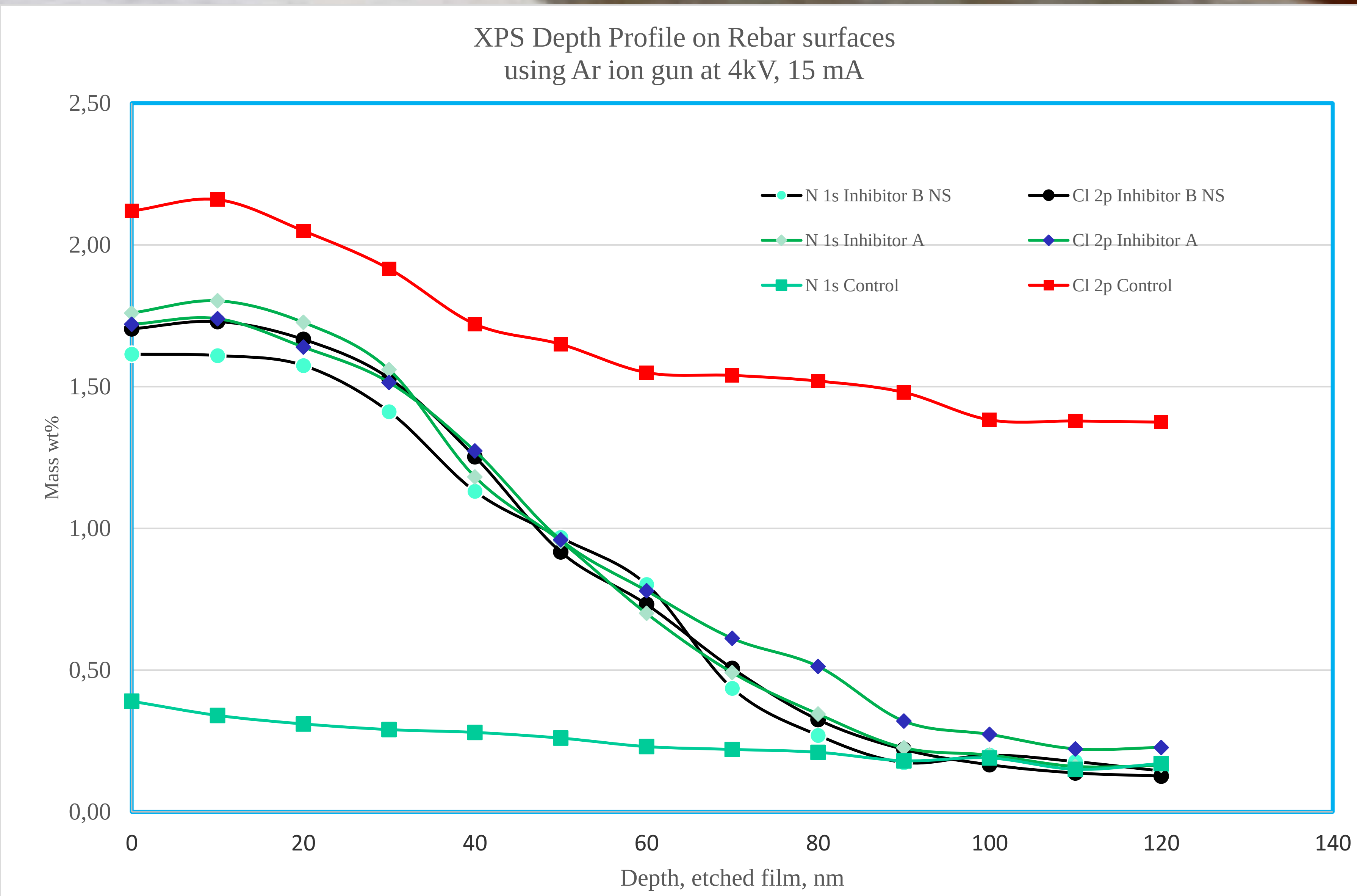
XPS Depth Profile (Ar at 4 kV, 15 mA)

	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


XPS analysis on Surface of Steel Rebar in Concrete
Control
Inhibitor A
Inhibitor B NS
N 1s
Ca 2p
Intensity (CPS)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-500
-480
-460
-440
-420
-400
-380
-360
-340
-320
-300
Binding Energy, (eV)

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 ($\mu A/cm^2$)	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

Conclusions

- Amine carboxylate based migrating inhibitors Can successfully inhibit corrosion of rebar and prolong the life of reinforced concrete structures as demonstrated using ASTM G180 test method. Rp increased from 2,300 to 31,000 $Ohm.cm^2$ when Admixtures were added to concrete.
- Inhibitor protected samples showed an average corrosion rate of 0.28 $\mu A/cm^2$ (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.

Questions?