Corrosion in concrete structures & Ways to enhance the service life

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Courtesy: Some images are sourced from the internet for demonstration purposes

Outline

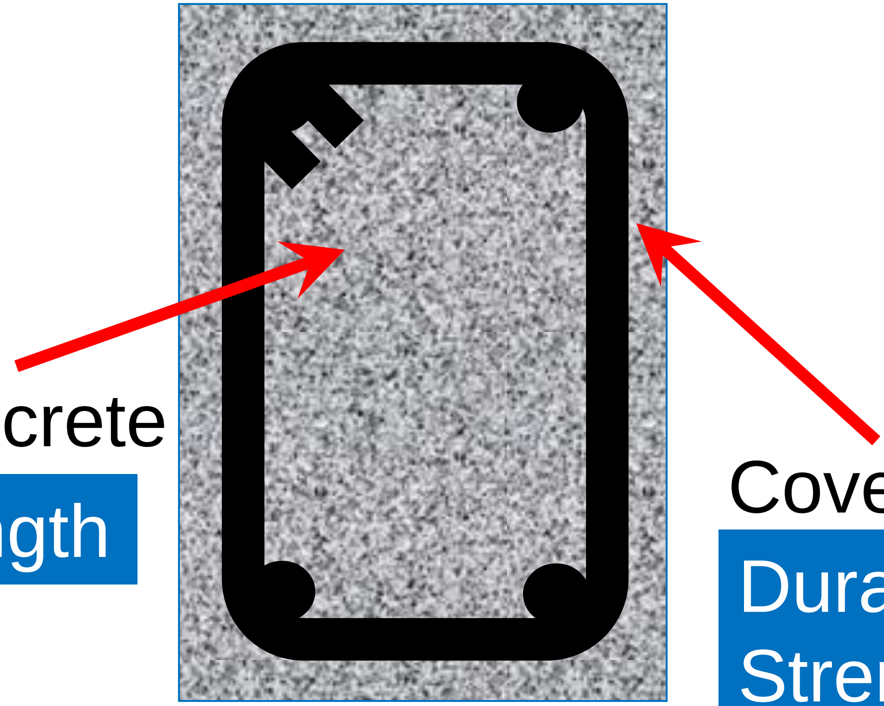
- Corrosion mechanism
- Critical service-life parameters
- Tests/techniques to determine the parameters
  - ✓ Chloride diffusion coefficient of concrete
  - ✓ Critical chloride threshold of steel
- Influence of chemical & mineral admixtures on the key parameters that influence service life

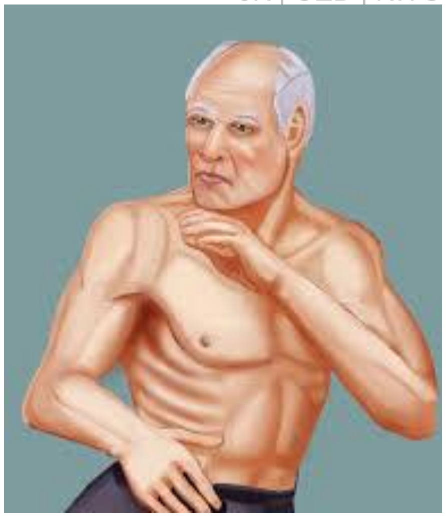
Specify Mx-Dy instead of Mx

- TV with 10K colour, and other features with 5 years warranty
  - ✓ Number of hours of screen time ON
- Why do you need a building with concrete only with M30 on 28th day
  - ✓ What about weathering for 60+ years
  - ✓ No warranty given for civil structures !
- Way forward (example)
  - ✓ Workability: Superplasticizer
  - ✓ Strength: M30 → f_{ck} = 30 MPa
  - ✓ Durability: D2 → 2 x 10^{-12} m^2/s

Build a structure with M30-D2 for achieving your target service life

What is needed to ensure durability?





Heart-crete

Strength

Cover-crete

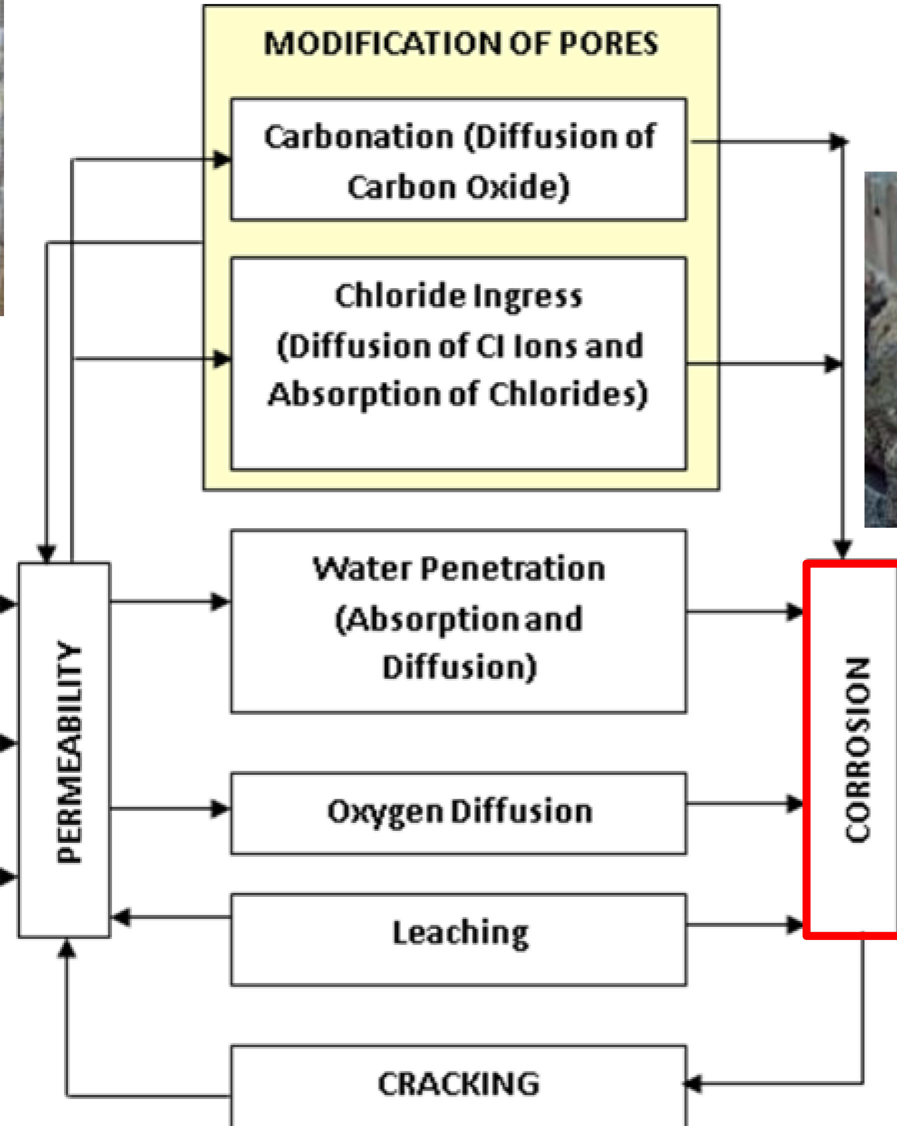
Durability → Strength for long time

Ensure that both heart-crete and cover-crete are highly impermeable

Ballim, 2008

shutterstock

At the end, corrosion of steel is the major problem



Environmental exposure Classification systems

➢

Not specific to the specific deterioration mechanism

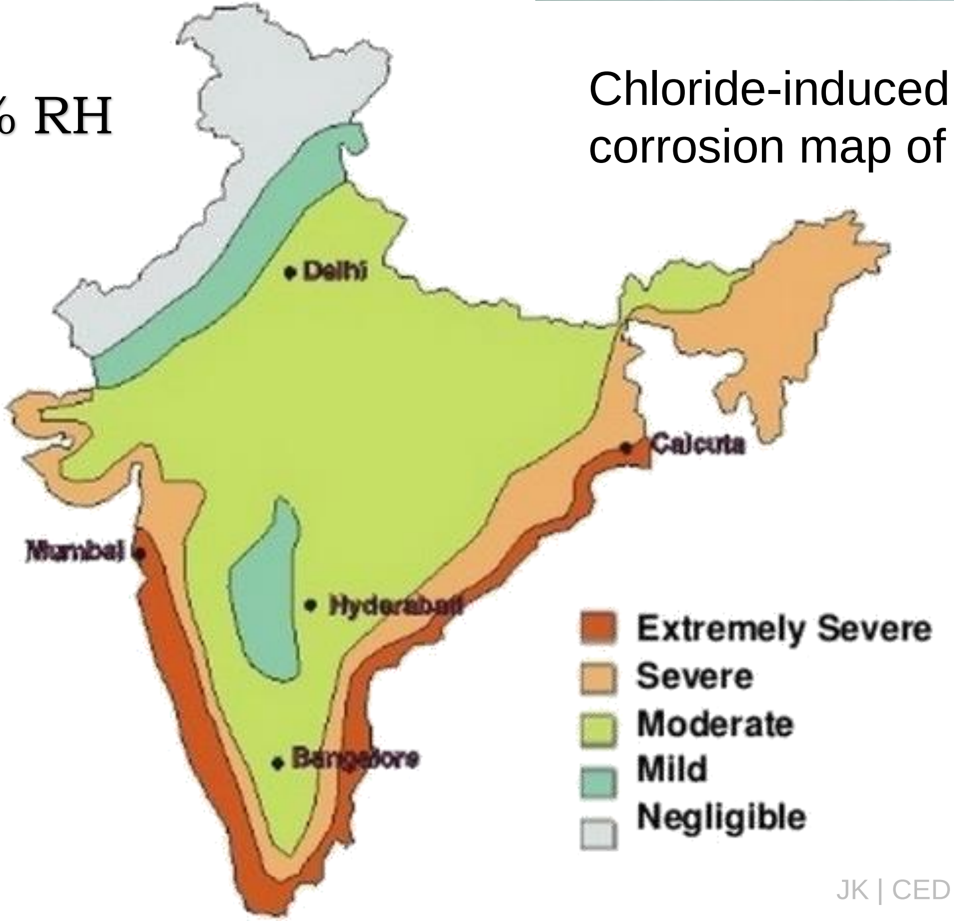
Table 3 Environmental Exposure Conditions

(*Clauses* 8.2.2.1 *and* 35.3.2)

Sl No. (1)	Environment (2)	Exposure Conditions (3)
i)	Mild	Concrete surfaces protected against weather or aggressive conditions, except those situated in coastal area.
ii)	Moderate	Concrete surfaces sheltered from severe rain or freezing whilst wet
		Concrete exposed to condensation and rain
		Concrete continuously under water
		Concrete in contact or buried under non-aggressive soil/ground water
		Concrete surfaces sheltered from saturated salt air in coastal area
iii)	Severe	Concrete surfaces exposed to severe rain, alternate wetting and drying or occasional freezing whilst wet or severe condensation.
		Concrete completely immersed in sea water
		Concrete exposed to coastal environment
iv)	Very severe	Concrete surfaces exposed to sea water spray, corrosive fumes or severe freezing conditions whilst wet
		Concrete in contact with or buried under aggressive sub-soil/ground water
v)	Extreme	Surface of members in tidal zone
		Members in direct contact with liquid/solid aggressive chemicals

Two major types of corrosion

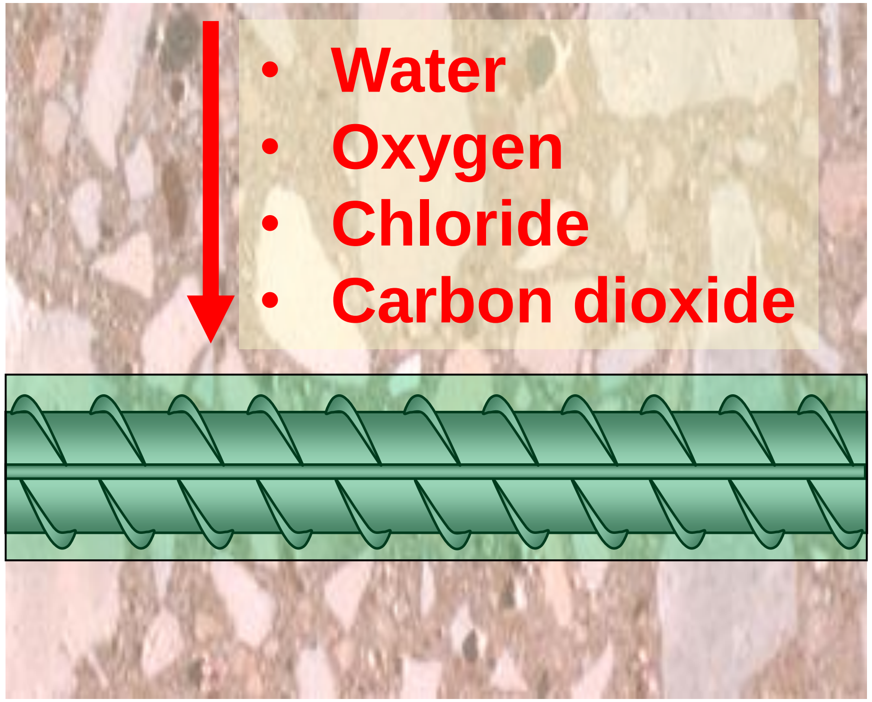
- **Chloride-induced**
  - ✓ **Port cities and coastal zone**
- Carbonation-induced
  - ✓ Cities and inland areas
  - ✓ Or any region with 60-70% RH



Chloride-induced corrosion map of India

Why steel embedded in uncontaminated concrete does not corrode?

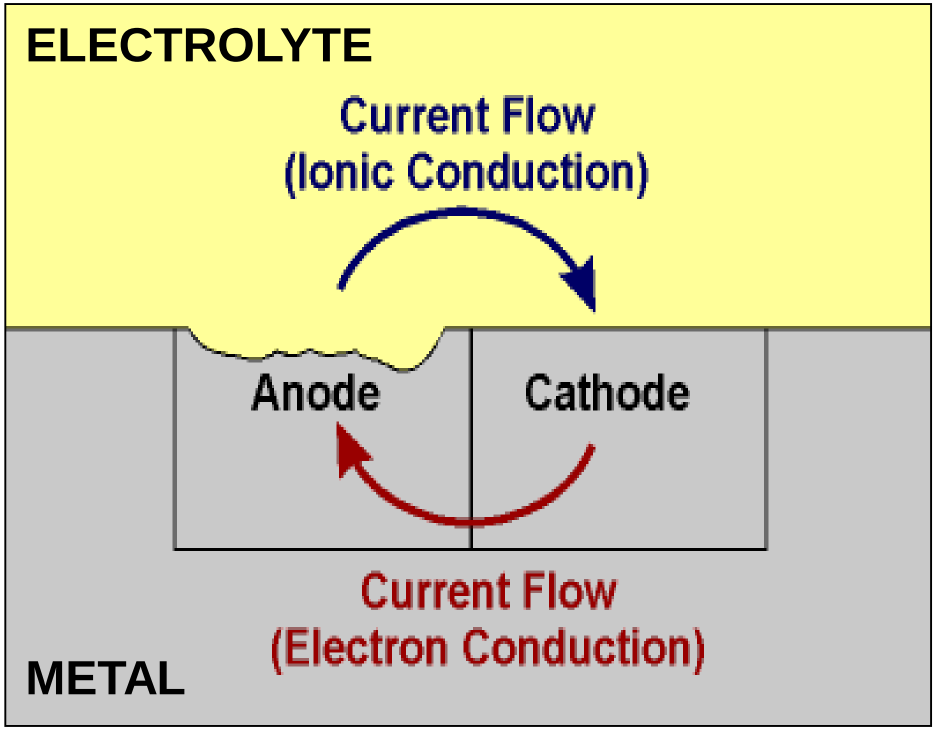
- Steel does not corrode due to high pH of concrete pore solution
- A protective layer ("Passive film") is formed
  - ✓ A thin, invisible, and stable layer of initial corrosion products (i.e., iron oxides and hydroxides).



- However, corrosion can occur when exposed to aggressive conditions

Hoar (1967)

What are the essential parts of a corrosion cell?

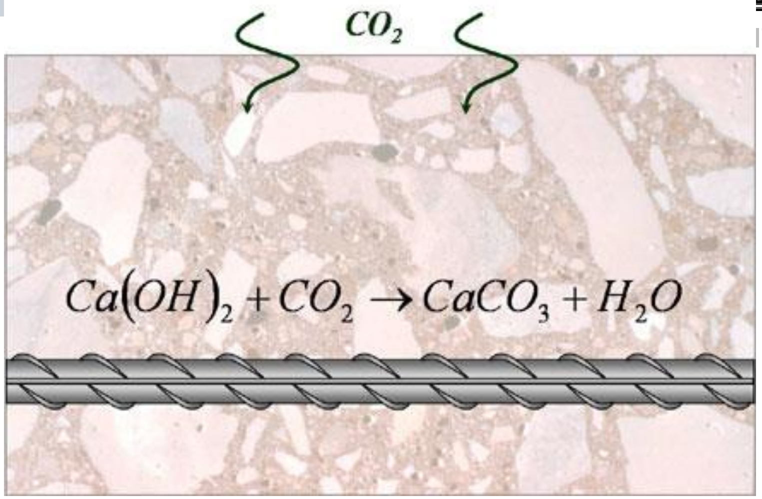


Note: “Current” flows in the opposite direction as the “electrons” move.

http://www.corrosion-club.com/images/corrosioncell.gif

Carbonation induced corrosion

- $CO_2 + H_2O \rightarrow H_2CO_3$ (carbonic acid)
- $H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2 \bullet H_2O$

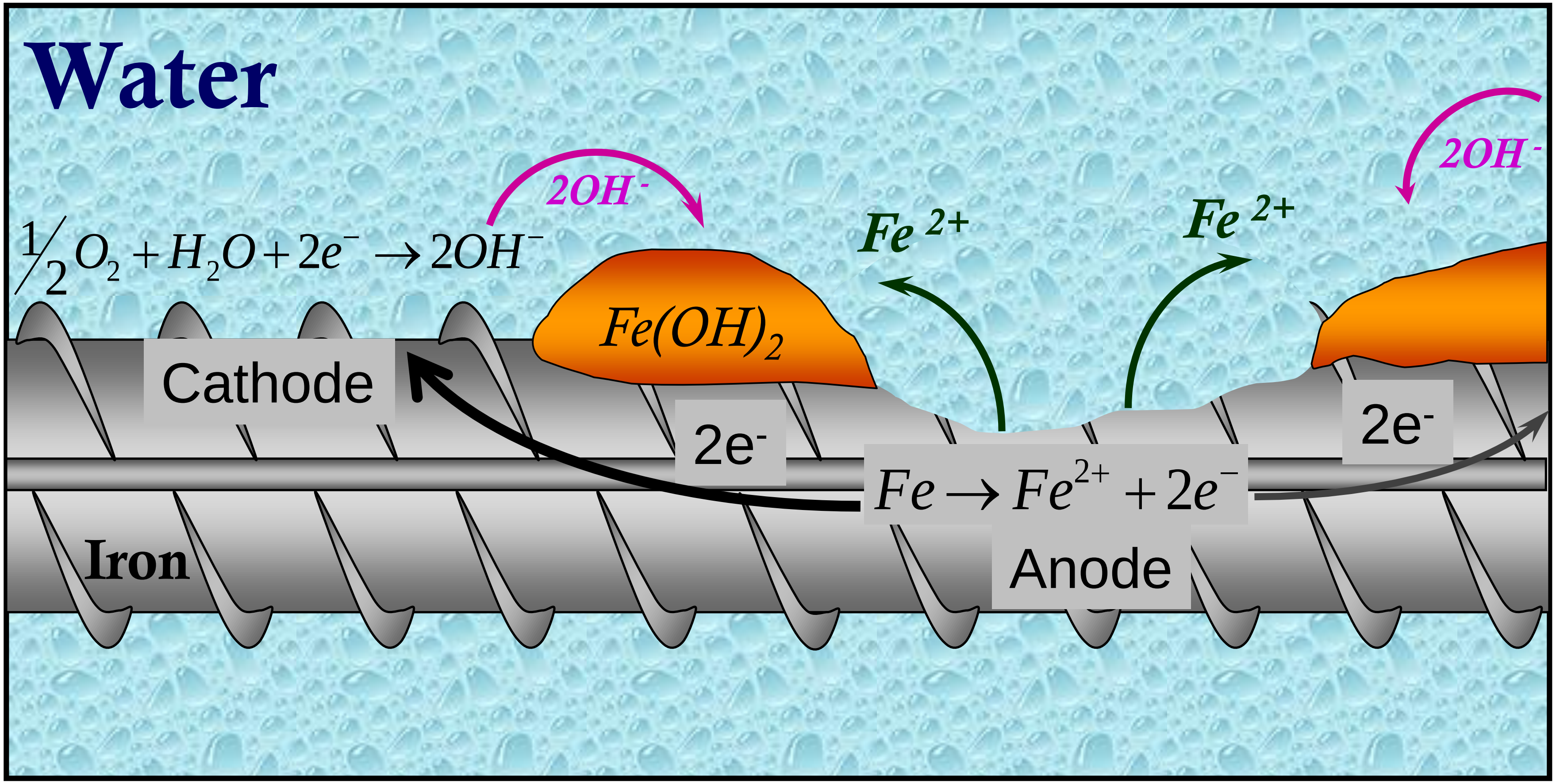


C-S-H will liberate CaO, which will get carbonated

- $H_2CO_3 + CaO \rightarrow CaCO_3 + H_2O$
- Formation of $CaCO_3$ leads to reduced pH at which the passive layer is unstable

http://www.nbmcw.com/articles/concrete/others/493-carbonation-a-durability-threat-for-concrete.html

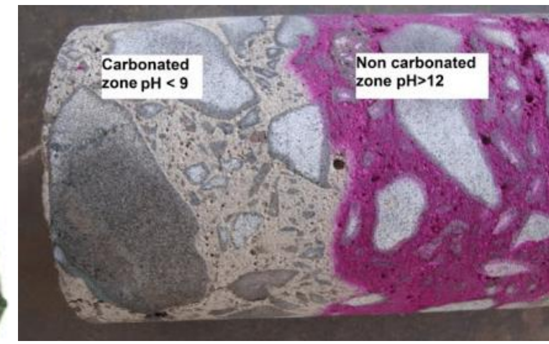
Corrosion of Steel in Water with Oxygen



Anode & cathode coexist on the same piece of metal !

Carbonation: Test / Detection

- Fresh surface (fracture)
- Spray phenolphthalei
  - ✓ pH indicator → colour c



Fractured cross-section of a prism

Deep Purple Indicator

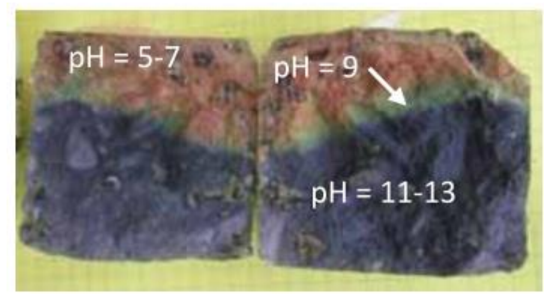
Color:

pH: 8.5 to 9.5

Rainbow Indicator

Color:

pH: 5 7 9 11 13

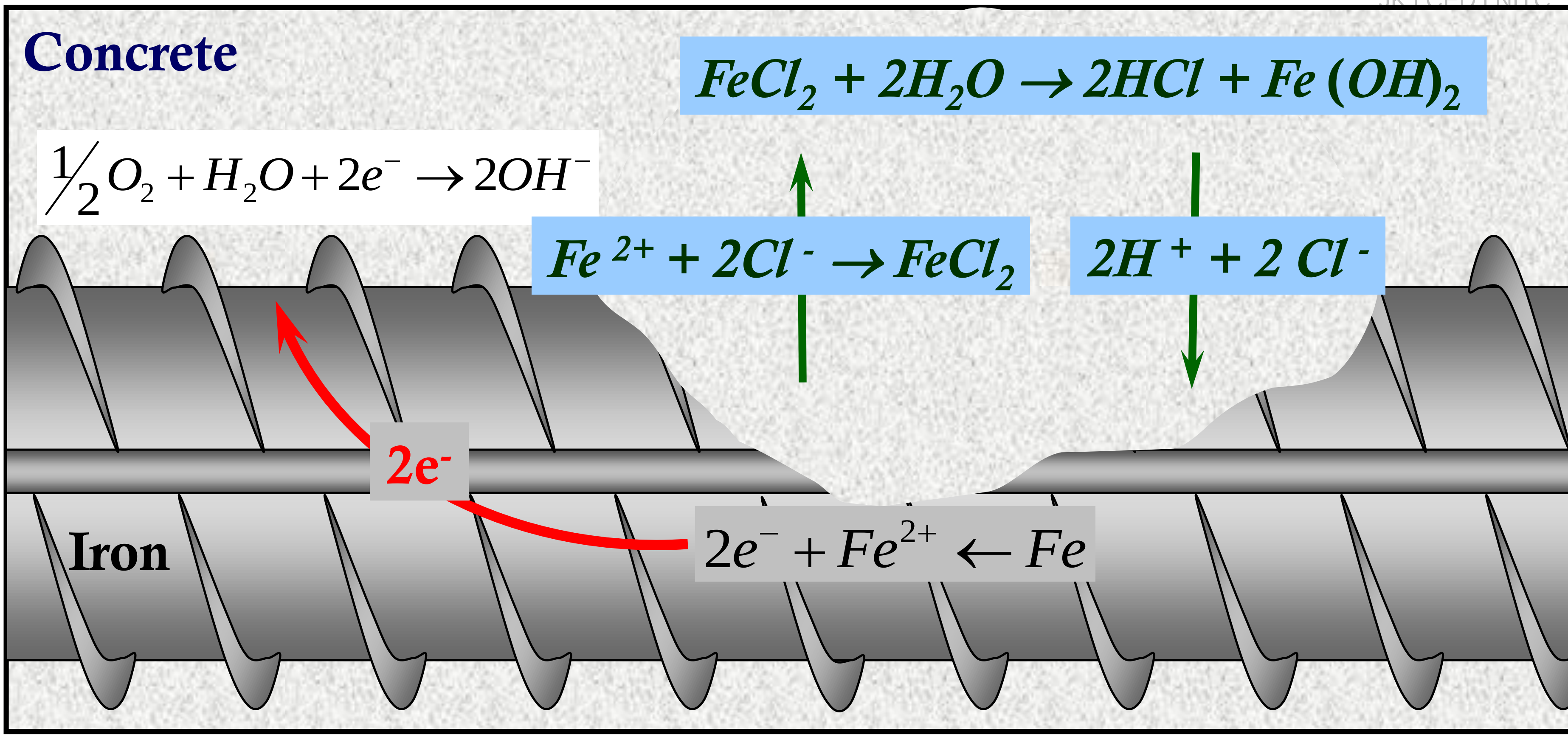


Rainbow Indicator

http://germann.org/

RILEM TC 56 – MHM, 1988

Chloride-induced corrosion

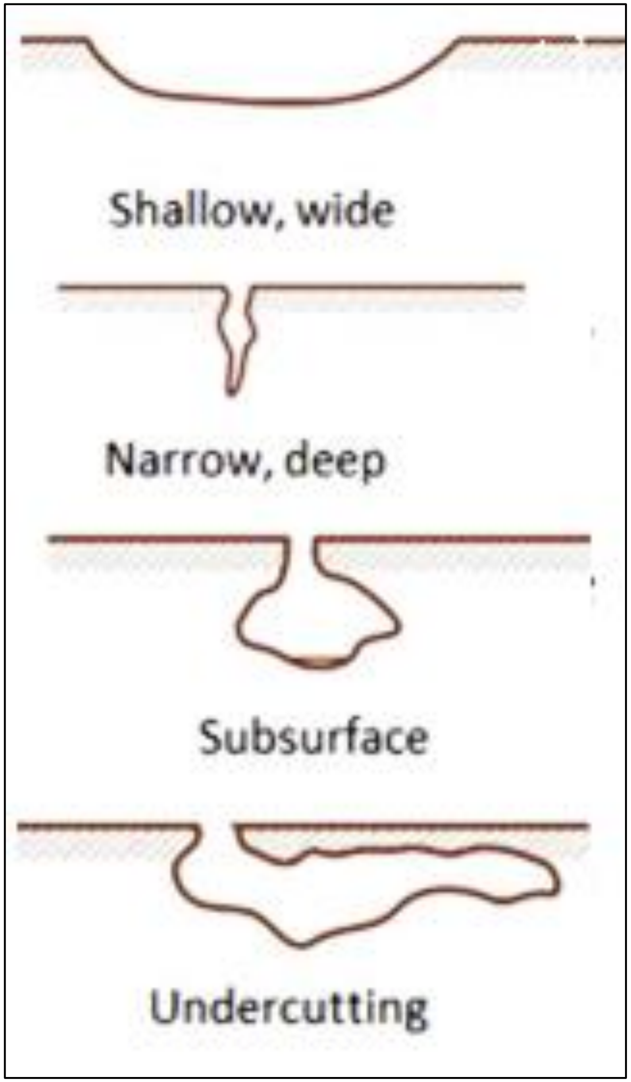


The process is regenerating and instead of spreading along the bar, corrosion continues at local anodes and deep pits are formed.

Pitting corrosion on strands and deformed bars due to chloride attack

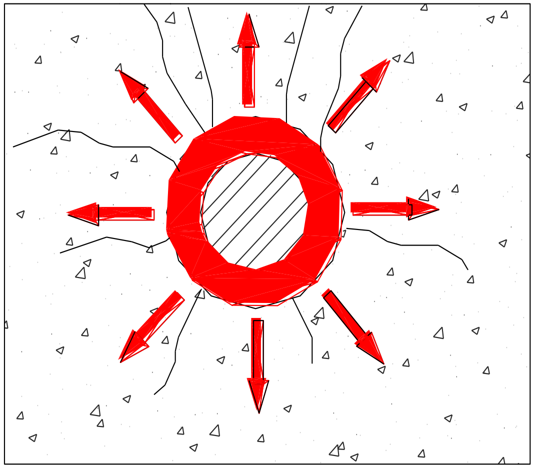
- Deformed bar →

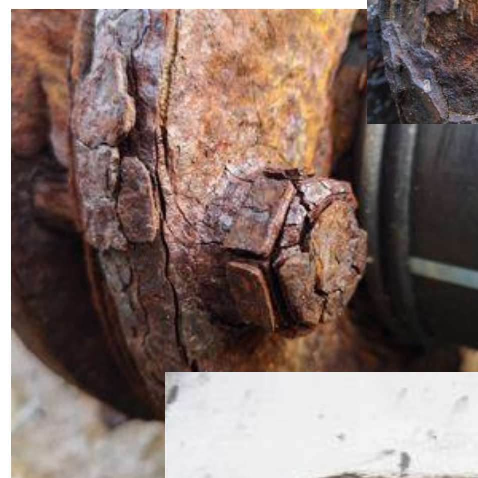
- 7-wire strand →



Why corrosion causes cracking of concrete?

- Fe
- FeO
- Fe_2O_3
- $Fe(OH)_2$
- $Fe(OH)_3$
- $Fe(OH)_3 \cdot 3H_2O$

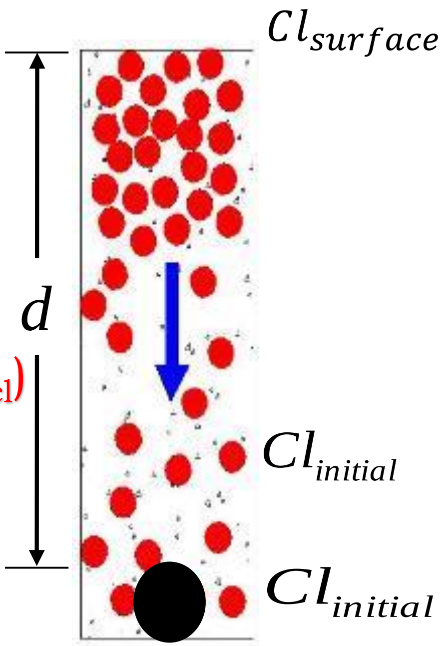


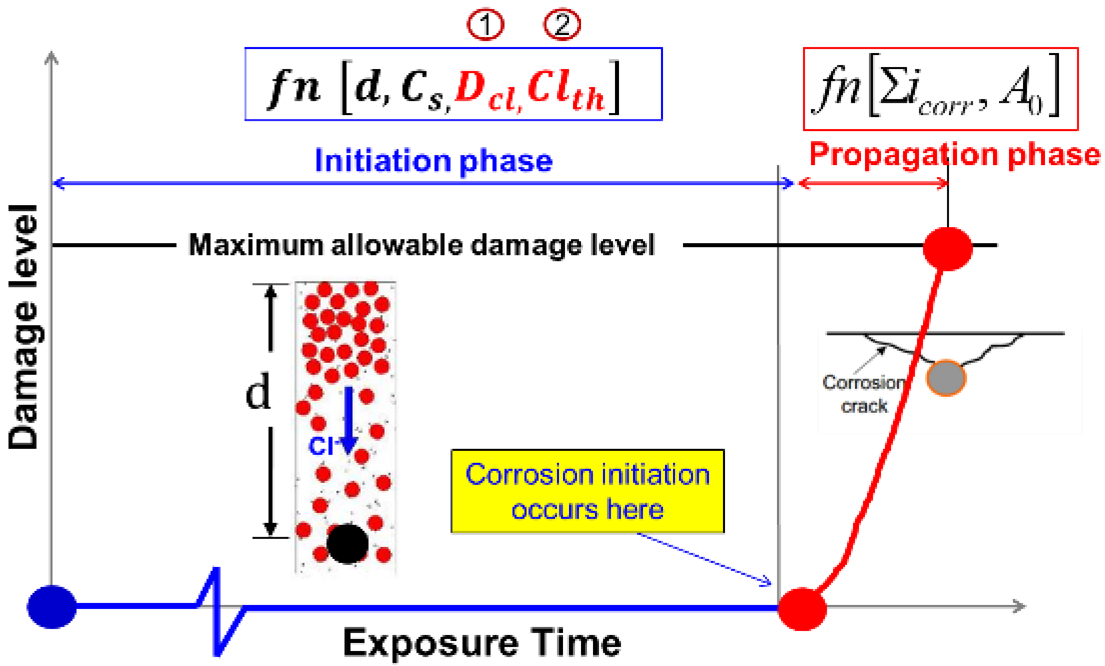


When steel corrodes, its volume increases by approximately 6 times

Critical parameters affecting corrosion initiation time

1. Environmental exposure parameters
   - ✓ Surface chloride build-up rate ($Cl_{surface}$)
2. Design parameters
   - ✓ Cover depth (d)
3. Material parameters of steel and concrete
   - ✓ Apparent chloride diffusion coefficient of concrete (D_{cl})
   - ✓ Critical chloride threshold value (Cl_{th})





Durability Test Methods and parameters

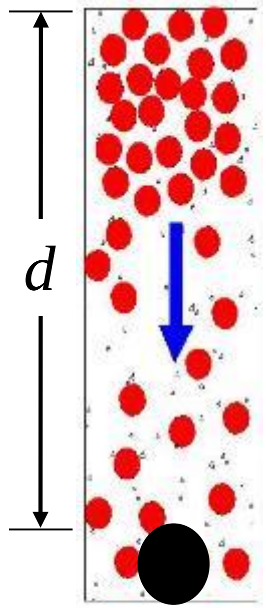
Test method	Standard	Parameter
Wenner 4 Probe Resistivity Test		Surface Resistivity
Rapid Chloride Permeability Test	ASTM C 1202	Total charge passed
Rapid Chloride Migration Test	NT Build 492	Non-steady state diffusion coefficient
Chloride Conductivity Test	SA DI Manual	Chloride Conductivity
Bulk diffusion test	ASTM C 1556	Chloride content
Oxygen Permeability Test	SA DI Manual	Oxygen Permeability Index
Torrent Air Permeability Test		Coefficient of Permeability
Accelerated Carbonation Test		Carbonation depth
Natural Carbonation Test (indoor and outdoor exposure)		Carbonation depth
Sorptivity Test	SA DI Manual	Sorptivity index
Germann water Permeability Test		Surface Permeability

Service life estimation for structures
- Exposed to chlorides

- Step 1: Obtain all the input parameters / assumptions
- Step 2: Determine the initial chloride level in concrete, C_i
- Step 3: Determine the surface chloride concentration, C_s
- Step 4: Determine the chloride diffusion coefficient in concrete, D_{cl}
- Step 6: Determine the chloride threshold at S-C interface, Cl_{th}
- Step 7: Use the Fick's law of diffusion – Non-steady state diffusion
- Step 8: Calculate the probability density function, Pf
- Step 9: Compute the cumulative density function, CDF

Service Life prediction model

- Concrete is a semi-infinite, porous, homogeneous, and isotropic material,
- No reactions occur between the concrete and the diffusing species (chlorides)



Fick's Second Law of Diffusion

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

In case of constant diffusion

$$Cl_{threshold} = Cl_{initial} + (Cl_{surface} - Cl_{initial})\left(1 - erf\left[\frac{x}{\sqrt{4D_{Cl} \times time_{initiation}}}\right]\right)$$

Common equipment required Contd..

Core cutter

Epoxy resin

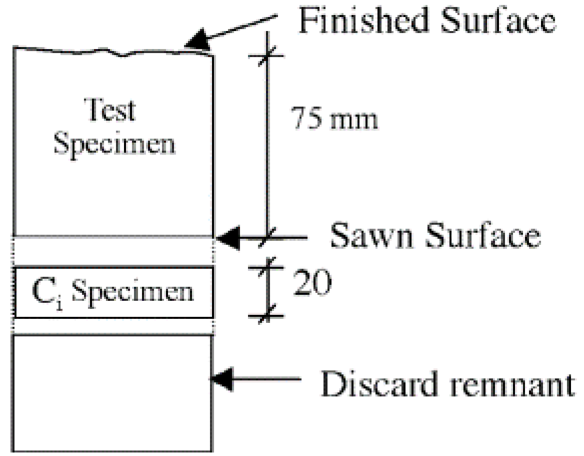
Cylinder mould
200 x 100 ø

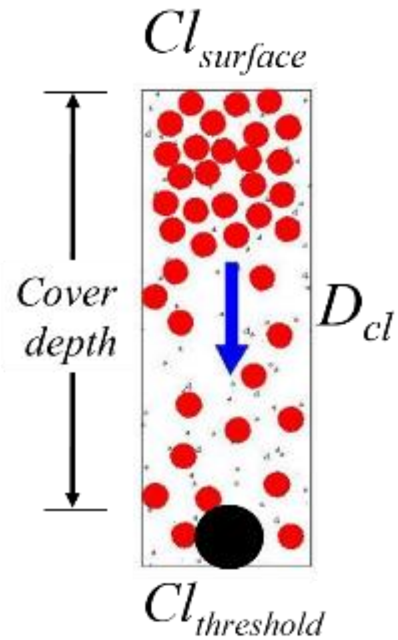
Concrete cutter

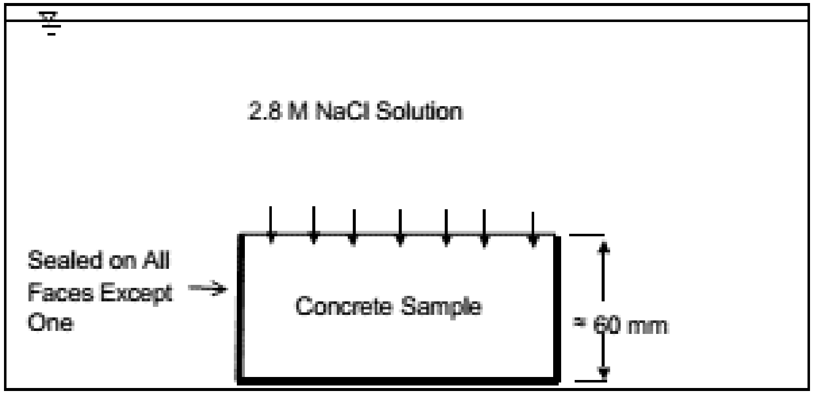
Weighing balance (0.0001 g)

Bulk diffusion test (ASTM C1556)

- Natural diffusion under a very high concentration gradient
- Specimens saturated with saturated lime water is immersed in 3% NaCl solution for 35 days
- Uni-directional diffusion
- Chloride profiling with profile grinder
- Chloride ion concentration determined







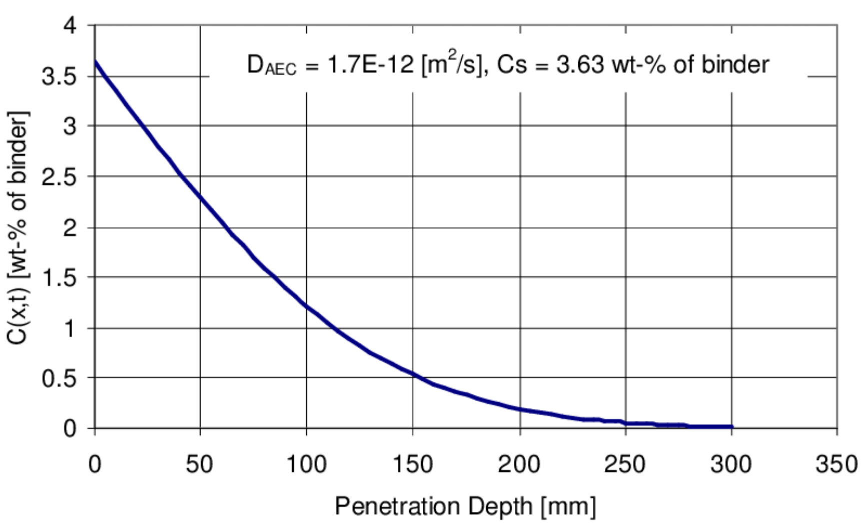
Bulk diffusion test (ASTM C1556)

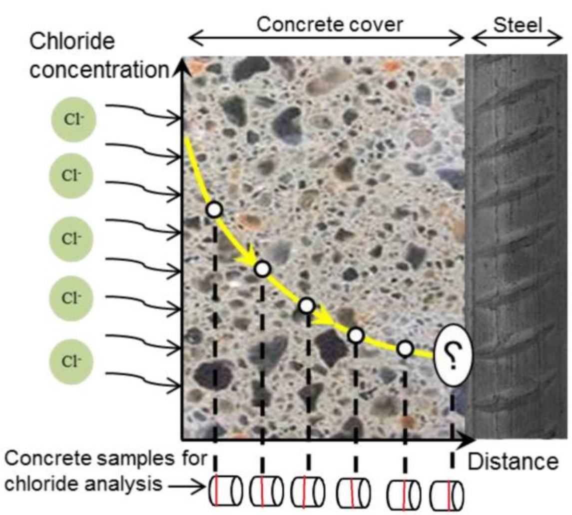
- Recommended Depth Intervals (in mm) for Powder Grinding

w/cm	0.25	0.30	0.35	0.40	0.50	0.60	0.70
Depth 1	0-1	0-1	0-1	0-1	0-1	0-1	0-1
Depth 2	1-2	1-2	1-2	1-3	1-3	1-3	1-5
Depth 3	2-3	2-3	2-3	3-5	3-5	3-6	5-10
Depth 4	3-4	3-4	3-5	5-7	5-8	6-10	10-15
Depth 5	4-5	4-6	5-7	7-10	8-12	10-15	15-20
Depth 6	5-6	6-8	7-9	10-13	12-16	15-20	20-25
Depth 7	6-8	8-10	9-12	13-16	16-20	20-25	25-30
Depth 8	8-10	10-12	12-16	16-20	20-25	25-30	30-35

$$\frac{C_{d,t} - C_i}{C_s - C_i} = 1 - erf\left[\frac{d}{2 \times \sqrt{D_{cl,t}}}\right]$$

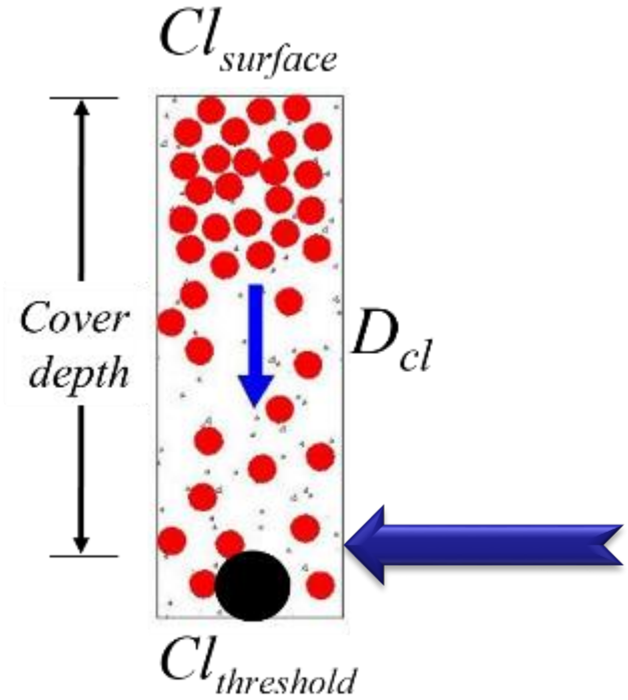
Apparent diffusion coefficient (x 10^{-12} m^2/s)	Resistance to chloride penetration
> 15	Low
10 – 15	Moderate
5 – 10	High
2.5 – 5	Very High
< 2.5	Extremely High





So we have corrosion, now what?

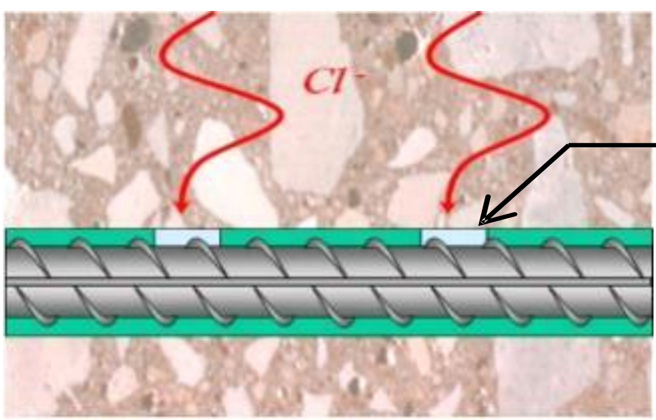
- Evaluate the nature and extent of corrosion.
- What is damage condition: minor/moderate/severe?
- How much corrosion is not yet evident?
- Can we protect / rescue the existing rebar?



What next if chloride reached the steel surface

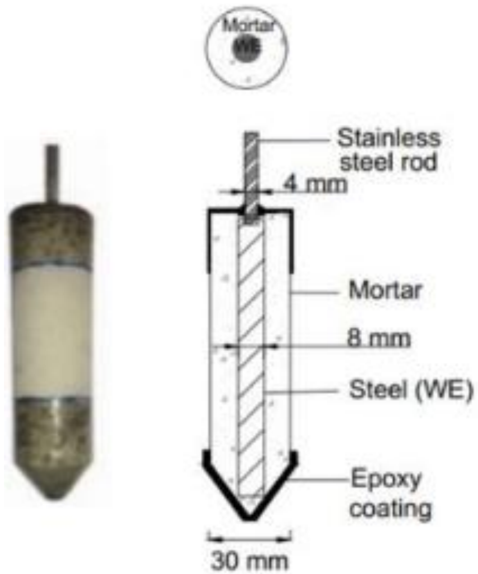
Material parameters of steel and concrete

- **Critical chloride threshold value**
  - ✓ Minimum chloride concentration required, at the steel surface, to initiate "active" corrosion of the embedded steel reinforcement
  - ✓ A competition between the Cl- tending to disrupt and OH- tending to stabilize the passive film
- Corrosion is likely to occur when: $\frac{[Cl^-]}{[OH^-]} > 0.3$
  - ✓ Usually measured in kg/m^3 or **% by weight of binder**

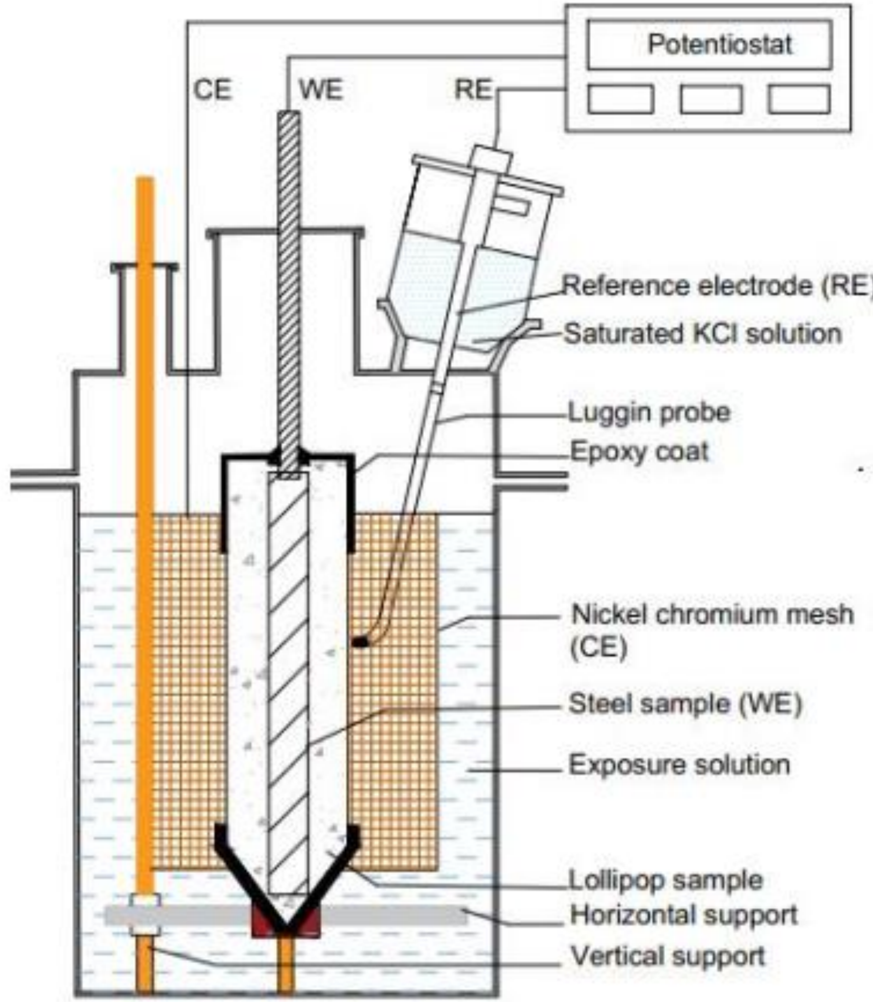


Damaged areas of passive film or corrosion inhibiting layer

Accelerated Chloride Threshold (ACT) test setup



Lollipop test specimen

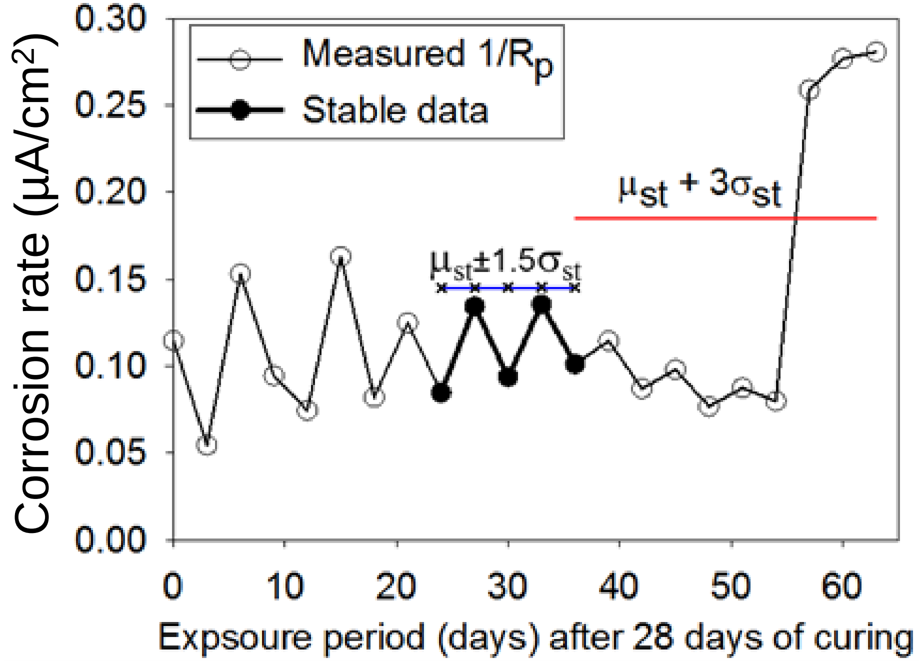


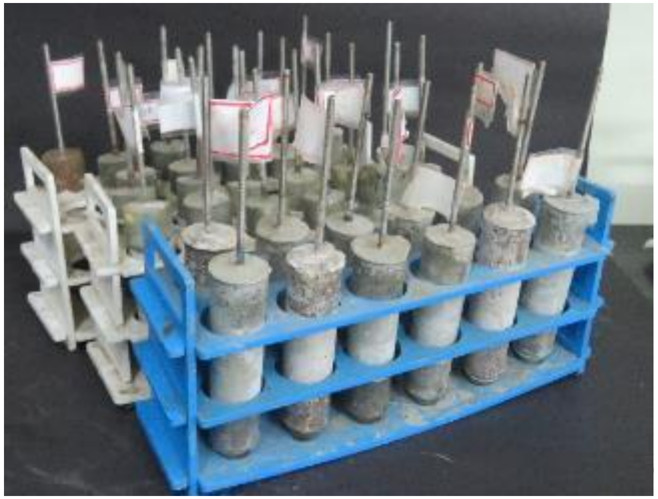
LPR test specimen and setup

(Sripriya and Pillai)

Cyclic exposure and repeated corrosion measurements

- Exposure conditions
  - ✓ 2 days wet and 5 days dry
    - (25 °C, 65% RH)
  - ✓ 3.5% NaCl in Simulated pore solution
- Repeated electrochemical measurements
  - ✓ LPR
    - Scan range: ± 10 mV
    - Scan rate: 0.05 mV/s
  - ✓ EIS
    - AC amplitude : 10 mV
    - Frequency: 10^5 to 0.01 Hz
    - Points per decade: 10
    - DC potential: HCP

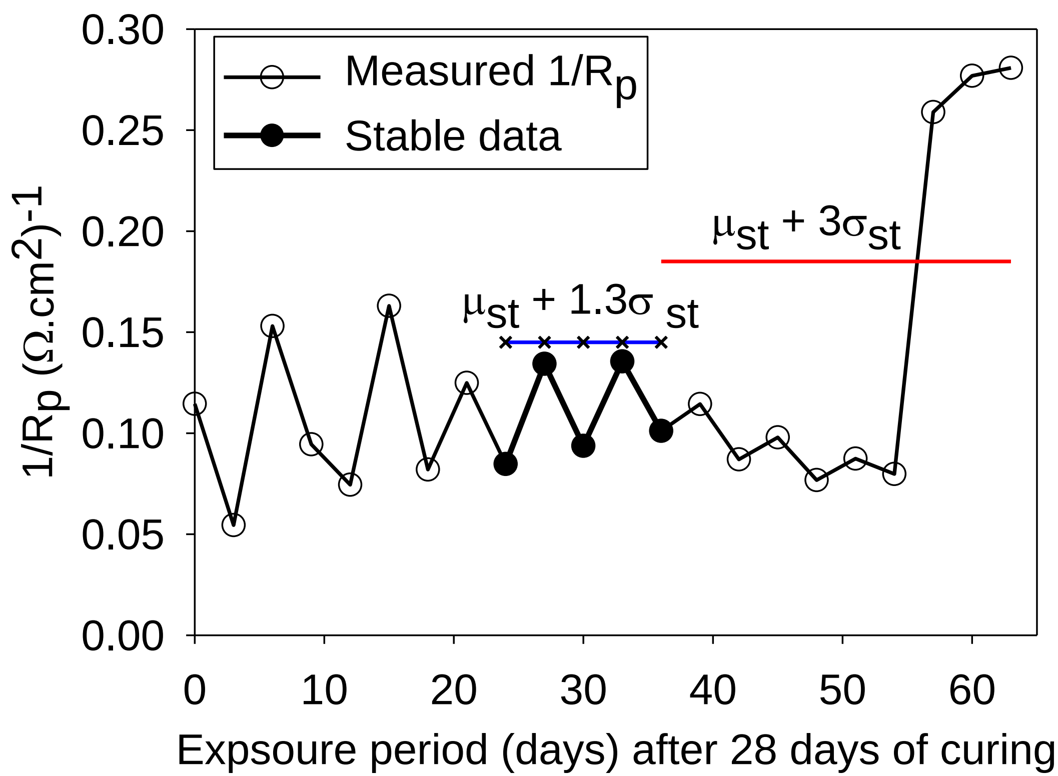


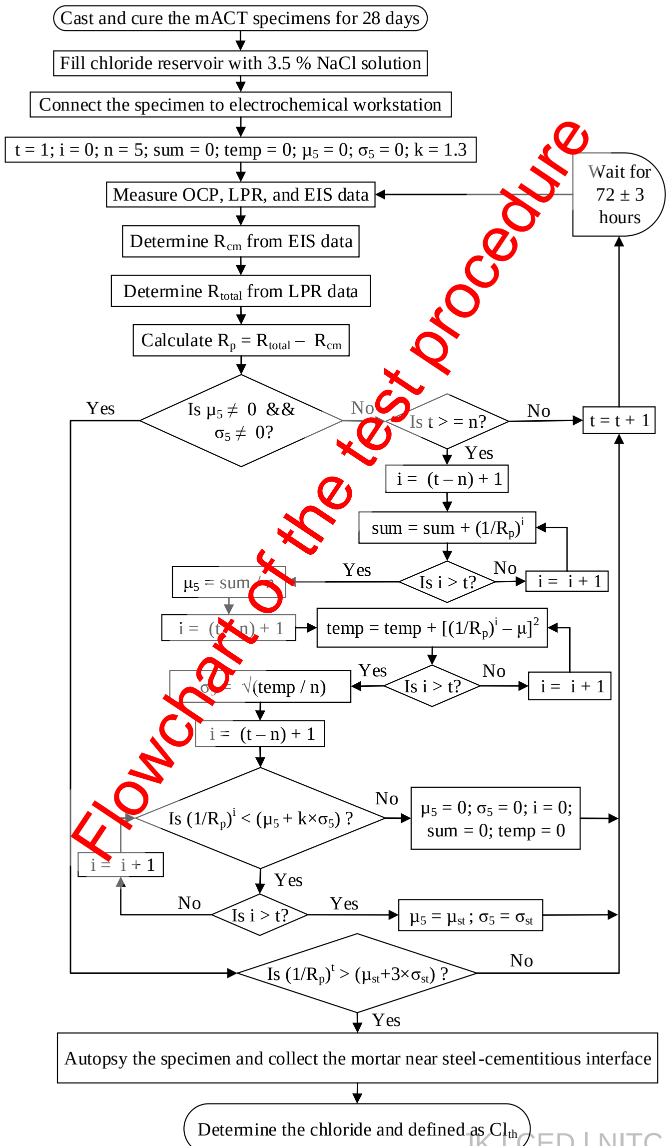


(Sripriya and Pillai)

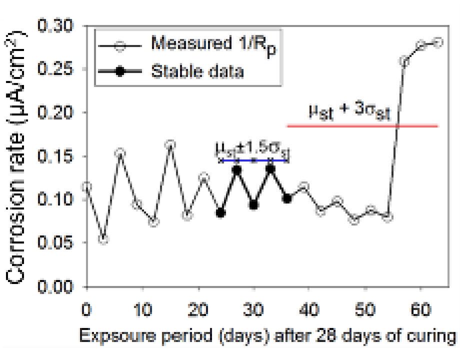
A statistical approach was used to detect the corrosion initiation

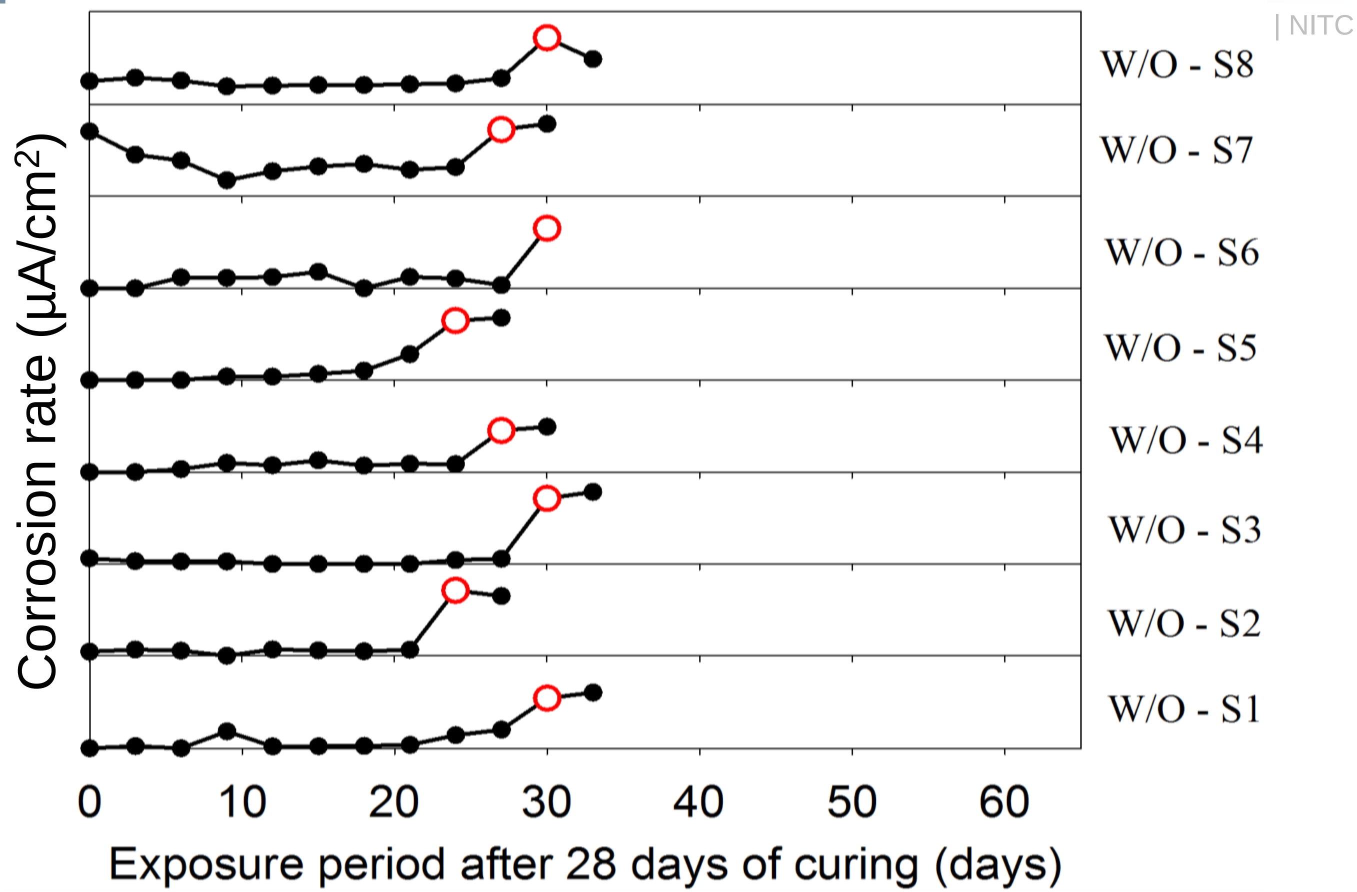
- $(\mu_5 + 1.3\sigma_5)$ → stable data
- $1/R_p > (\mu_{st} + 3\sigma_{st})$ → corrosion initiated





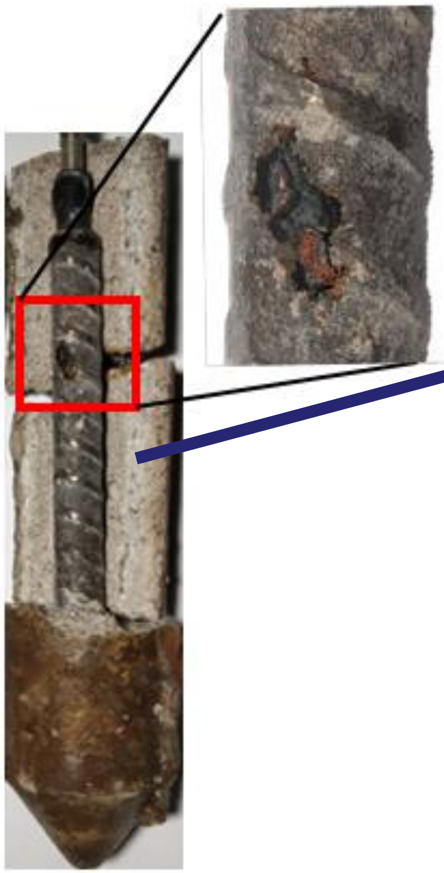
Corrosion rate Vs exposure time





- Corrosion initiation happens in multiple decades.
- The key parameter affecting that is chloride threshold.
- With the hr-ACT test, the chloride threshold can be determined in just about 3 months

Chloride content of the mortar adjacent to the steel specimen was determined



Corroded lollipop specimen

Mortar powder

Test for chloride content

- Short-term tests (about 3 months) are available to determine chloride threshold of CIAs
- Better the inhibitors, it takes longer to test

Types of corrosion inhibiting admixtures (CIAs)

- Based on mechanism of action
  - Anodic inhibitors (Calcium nitrite)
  - Cathodic inhibitors (Amines)
  - **Mixed/Bipolar inhibitors (Calcium nitrite + Amino alcohol + others)**
- Based on method of application
  - Mixed-in or admixed inhibitor
  - Migrating inhibitor
  - Surface coating as water proof / pore blockers
- Based on chemical composition
  - Inorganic inhibitors (Calcium Nitrite, Sodium monofluorophosphates)
  - Organic inhibitors (Alkanolamines, Aminoacids, Amines)

Mechanisms of action of anodic CIAs

- Formation of physical or chemical barrier or layer around the metal
- Passivating the metal surface
- Influencing the surrounding environment of the metal
- Blocking the access of aggressive contaminants into the system

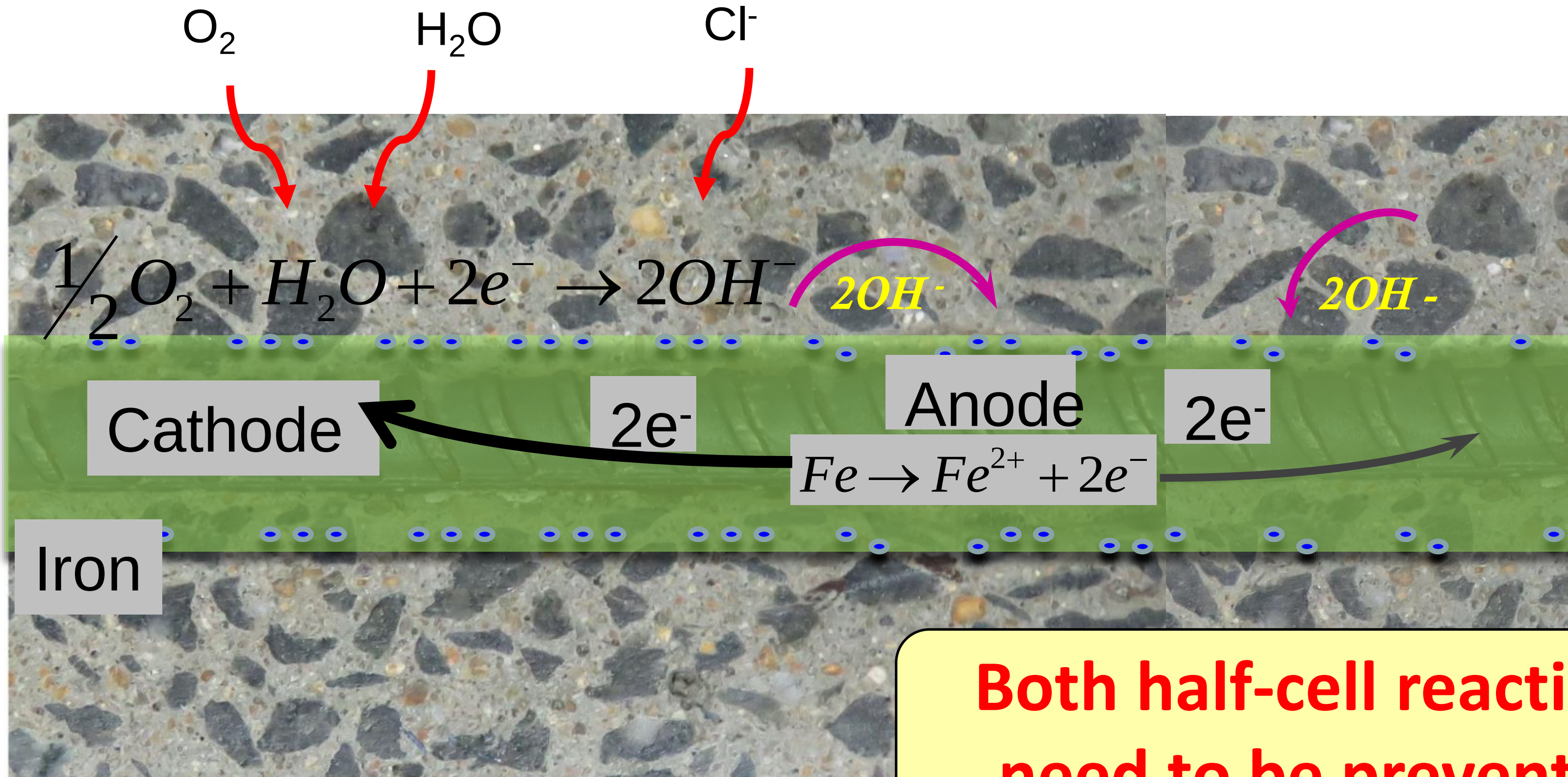
$$Fe^{2+} + (OH)^{-} + (NO_2)^{-} \rightarrow NO + \gamma \cdot FeOOH$$

The nitrite ions help in producing γFeOOH, which is more stable.

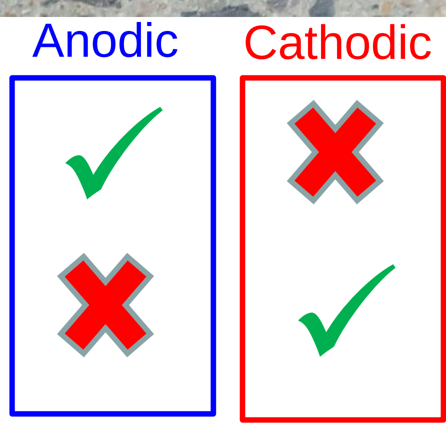
Too little of the corrosion inhibitor fails to protect all anodic sites. Therefore, cathode/anode area ratio increases causing increased corrosion at remaining anodic sites.

Soylev TA, Richardson MG (2006)

Mechanisms of anodic & cathodic CIAs



Both half-cell reactions need to be prevented

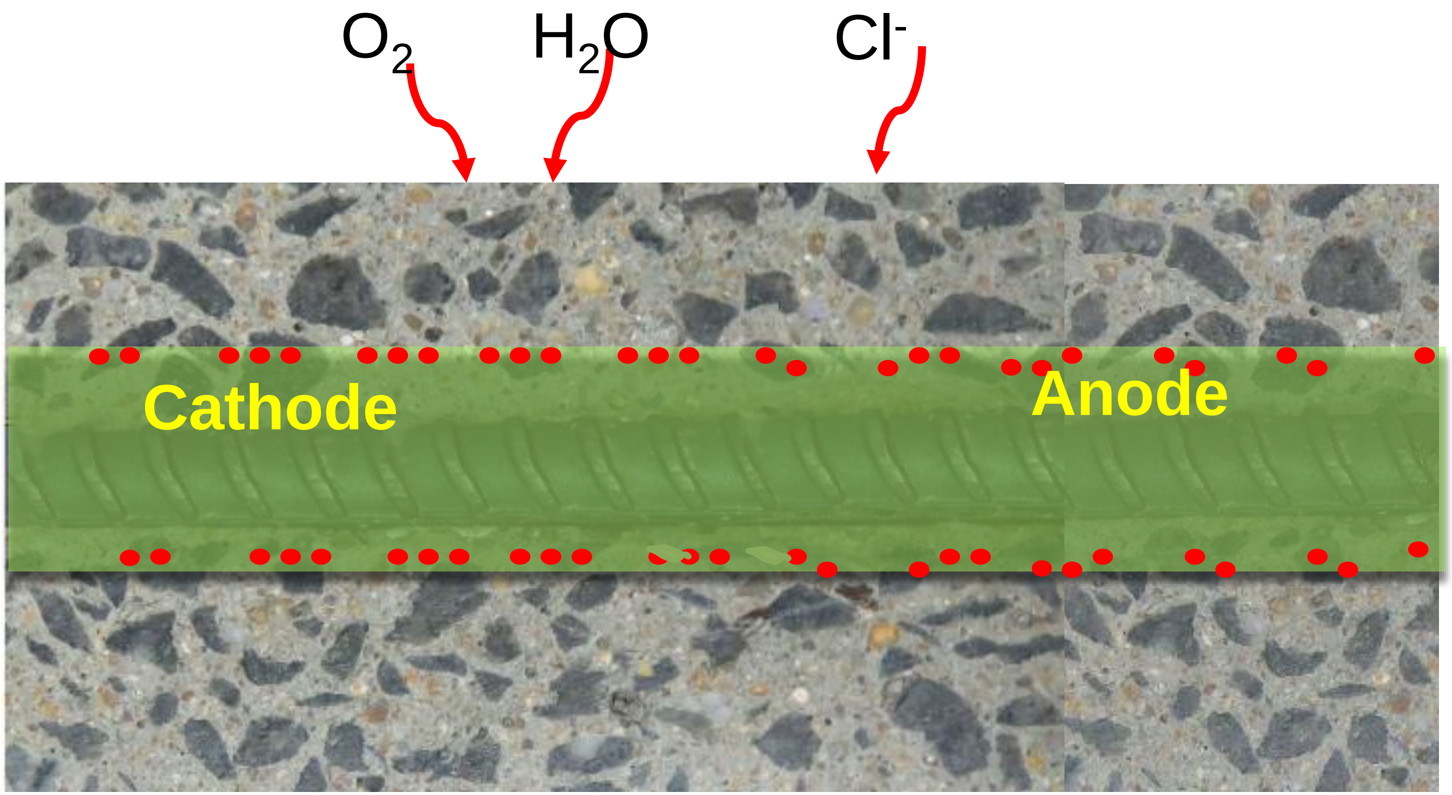


$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$$

Pillai et al. (unpublished work) (Deepak and Pillai)

Mechanism of bipolar inhibitor



Chemical families

- Amino alcohol
- Calcium nitrate and calcium nitrite
- Calcium nitrate, nitrous acid and calcium salt

✓ $$Fe \rightarrow Fe^{2+} + 2e^-$$

✓ $$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$$

Pillai et al. (unpublished work) (Deepak and Pillai)

Commercially available bipolar corrosion inhibitors in the market

Manufacturer	Product
UltraPure	Concare
Sika	FerroGard 901
BASF	MasterLife 222
CAC	Corrobit OCI
CeraChem	Ceraplast CI100
Fosroc	Auramix BCI
Applechemie	AC-Coroguard

Many other equivalent products also exist.

Make sure that they are bipolar in nature.

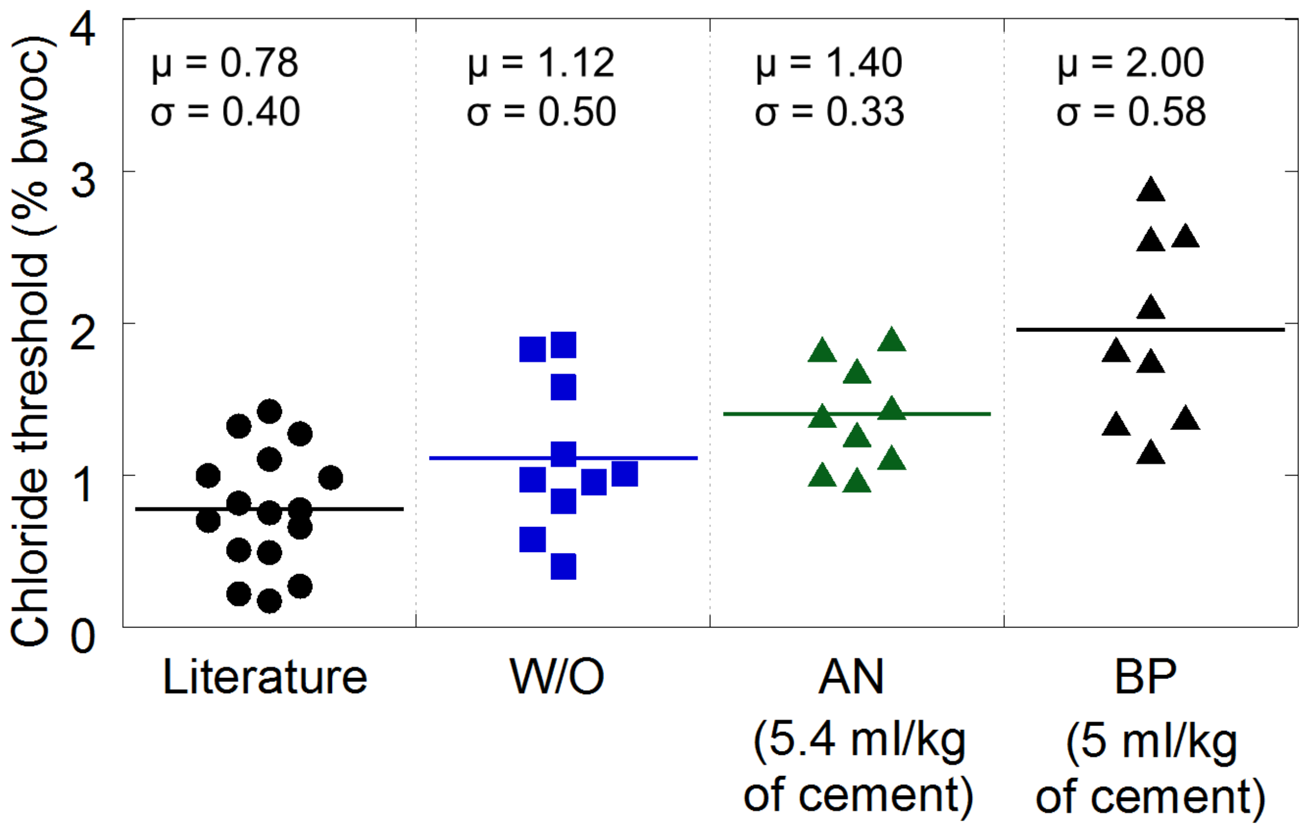
Chemical families

- Amino alcohol
- Calcium nitrate
- Calcium nitrite
- Nitrous acid

Proprietary chemical ingredients

Effect of inhibitors on chloride threshold

- In OPC systems



Cl_{th} ranges from 0.8 to 2 % bwoc with an average of 1.5 %

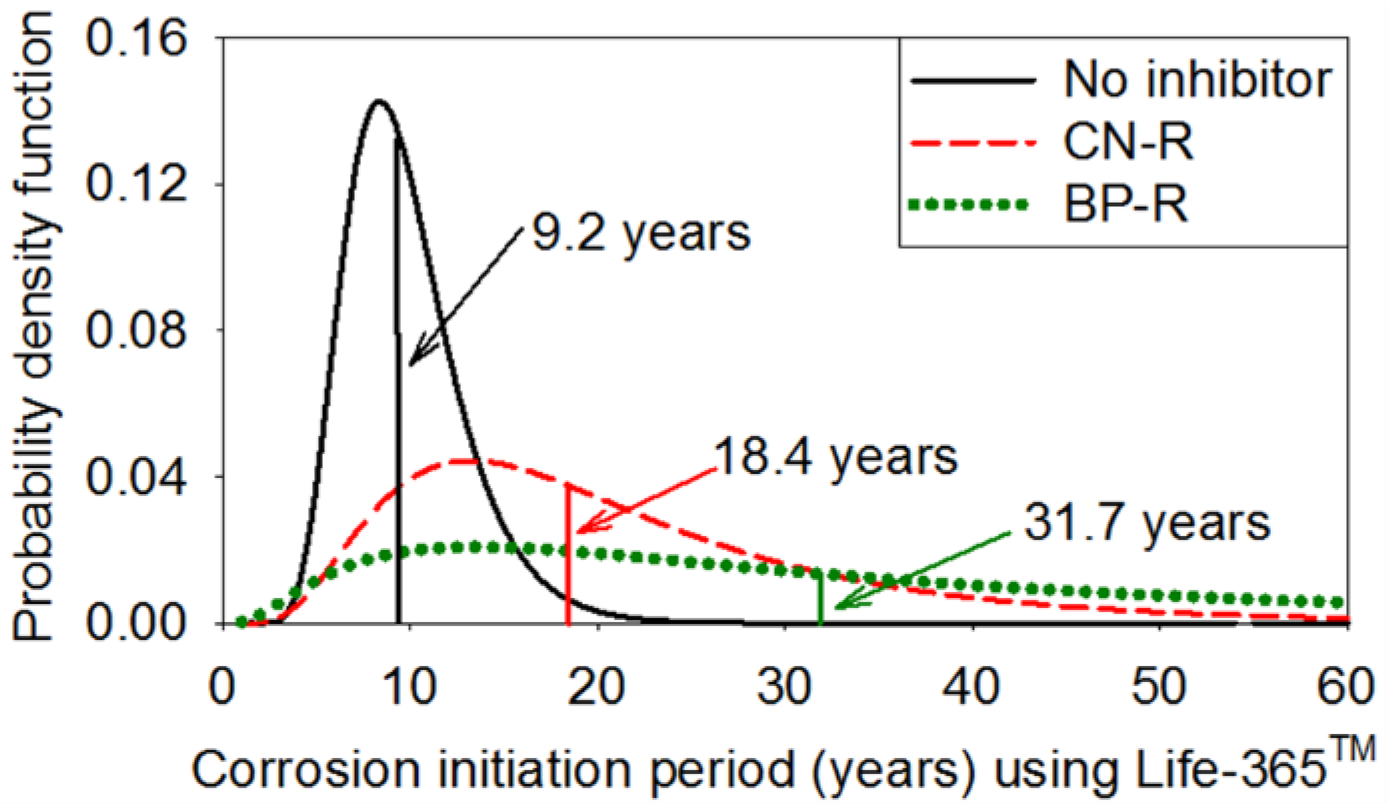
Karupanasamy and Pillai 2014

% bwoc : % by weight of binder

JK | CED | NITC

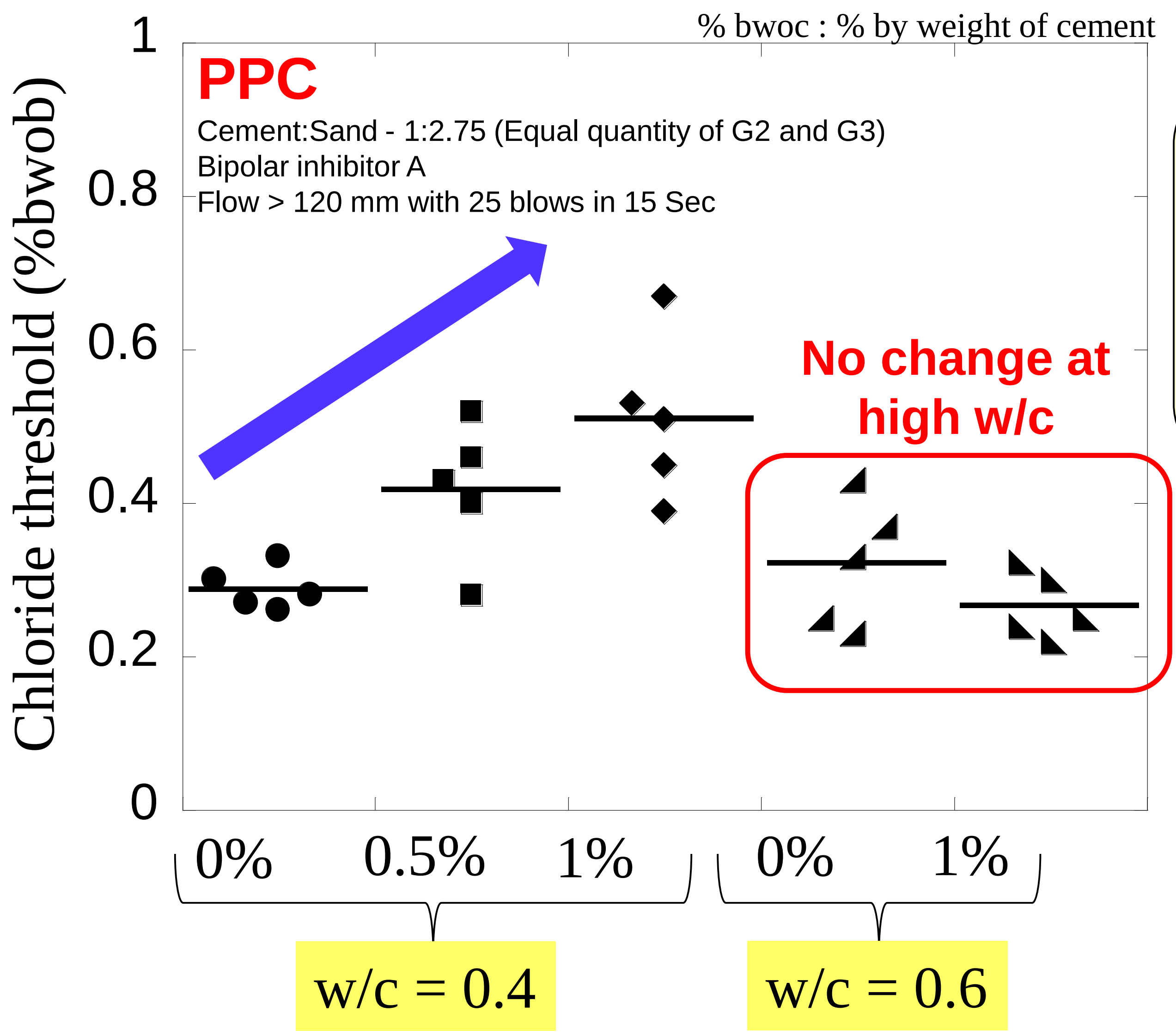
Probabilistic corrosion initiation period (t_i) was estimated using Life-365™

- Assumptions: Concrete with w/b = 0.45, cover depth = 50 mm, & D_{cl} = 8.87E-12



The use of corrosion inhibitors can increase the corrosion initiation time by about 2 to 3 times

Effect of w/c ratio on chloride threshold



Inhibitor A

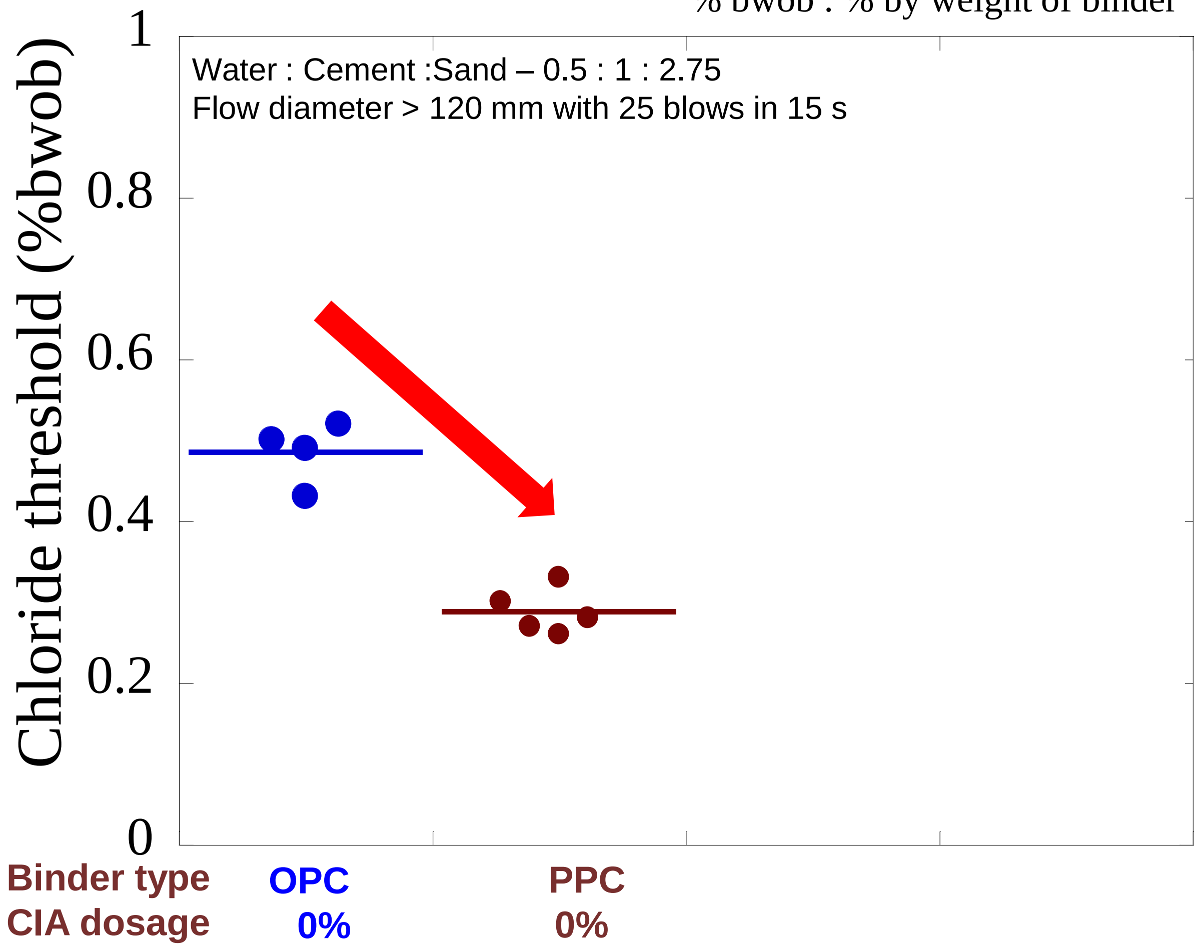
Inhibitors were not effective when used with higher w/c ratio

Pillai et al. (unpublished work)

(Deepak and Pillai)

Effect of binder type on chloride threshold

% bwob : % by weight of binder

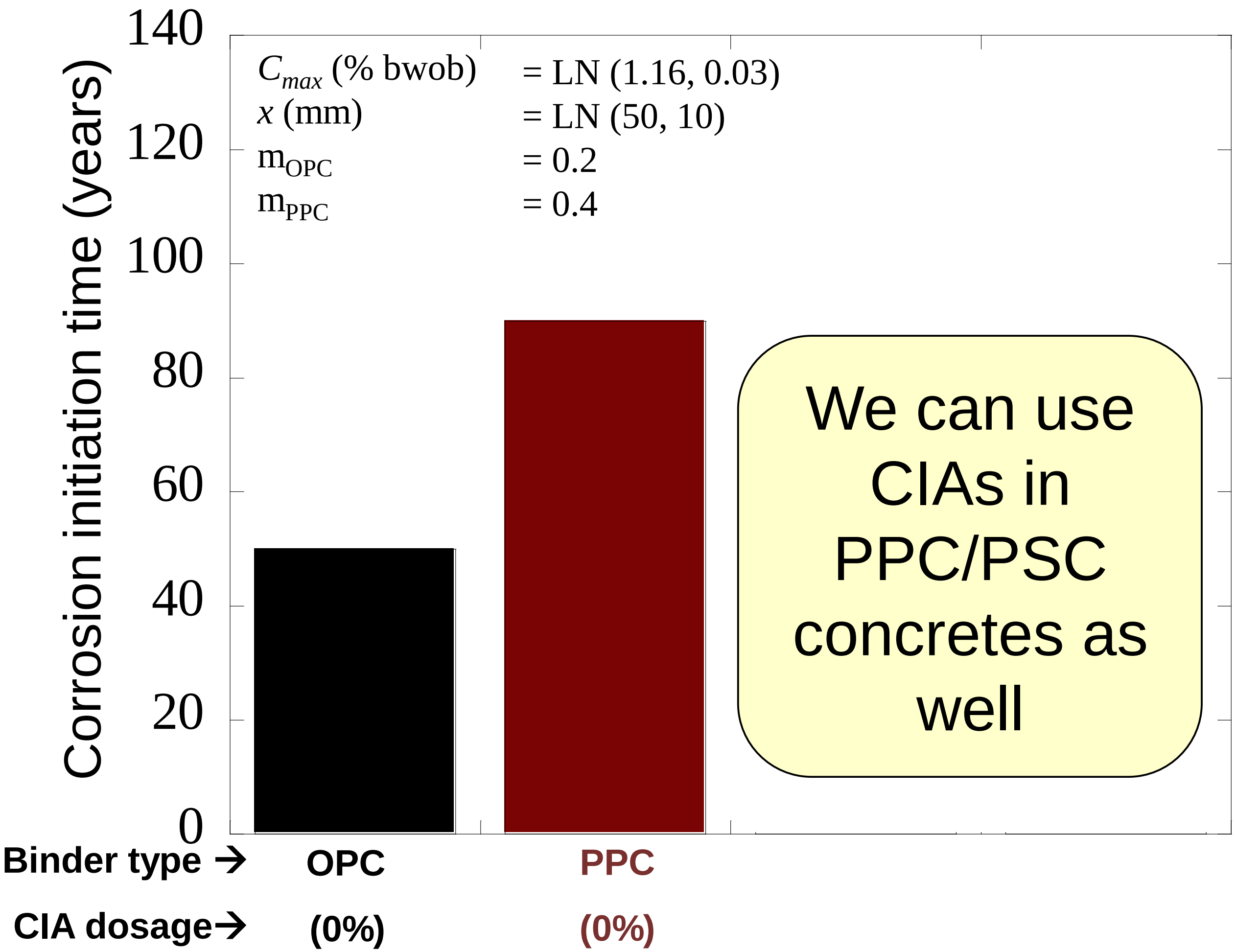


- Although the Cl_{th} may be less for PPC systems, because of the low D_{Cl}, the service life of PPC systems can be high
- Synergistic effects of Cl_{th} and D_{Cl} on service life must be calculated

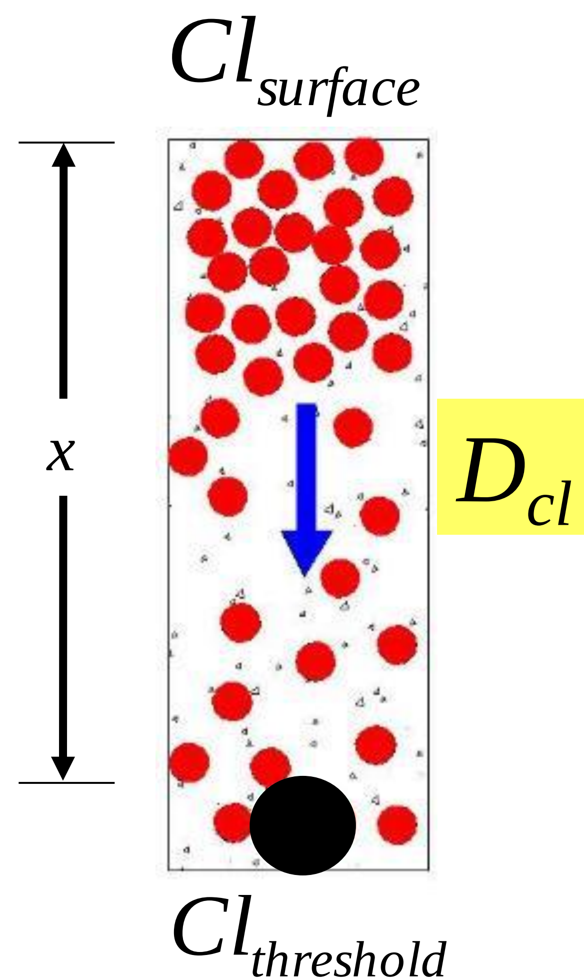
Pillai et al. (unpublished work)

(Deepak and Pillai)

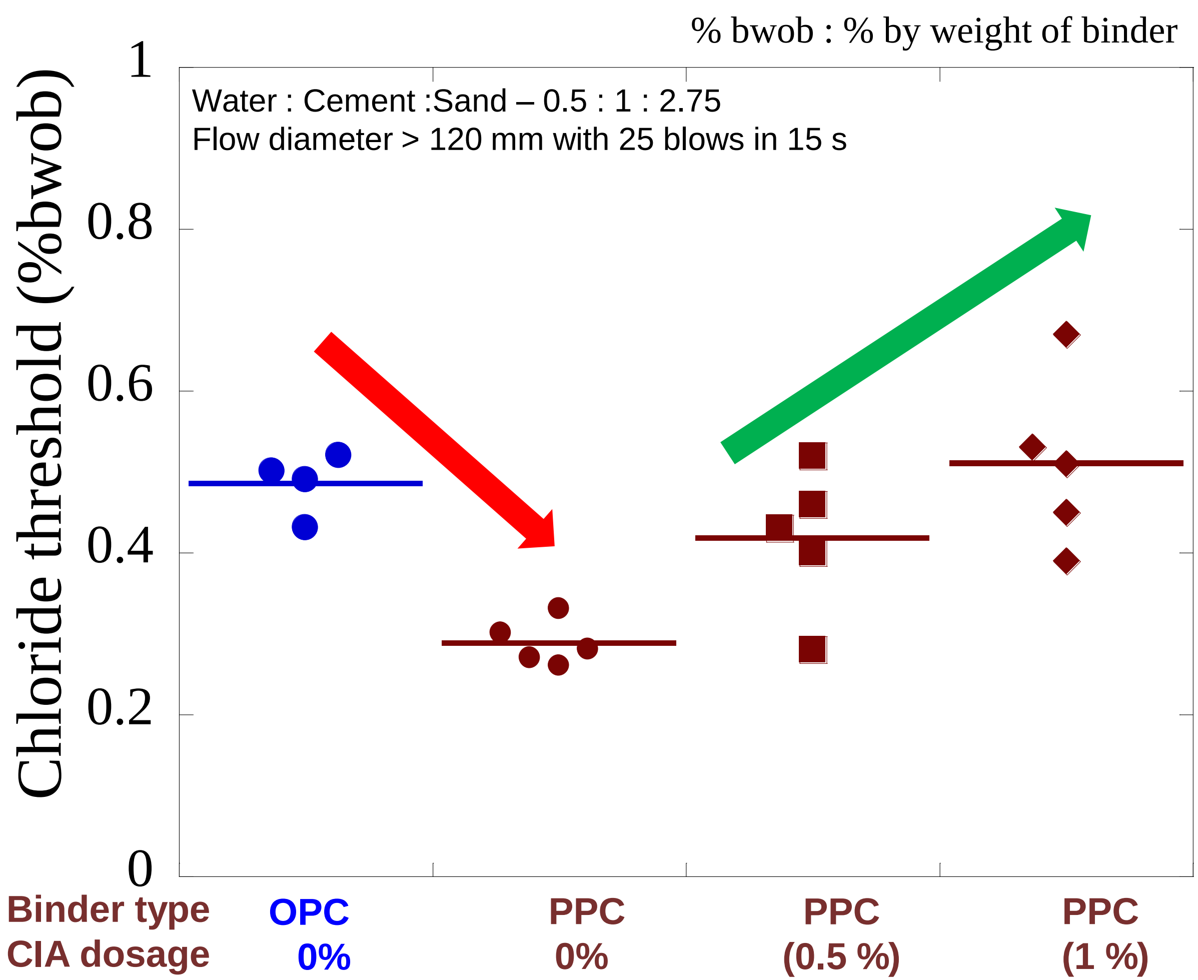
Service life = Function of D_{cl} & Cl_{th}



We can use CIAs in PPC/PSC concretes as well



Effect of binder type on chloride threshold



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- Synergistic effects of Cl_{th} and D_{Cl} on service life must be calculated
- Reduction in Cl_{th} due to SCMs can be compensated by inhibitors

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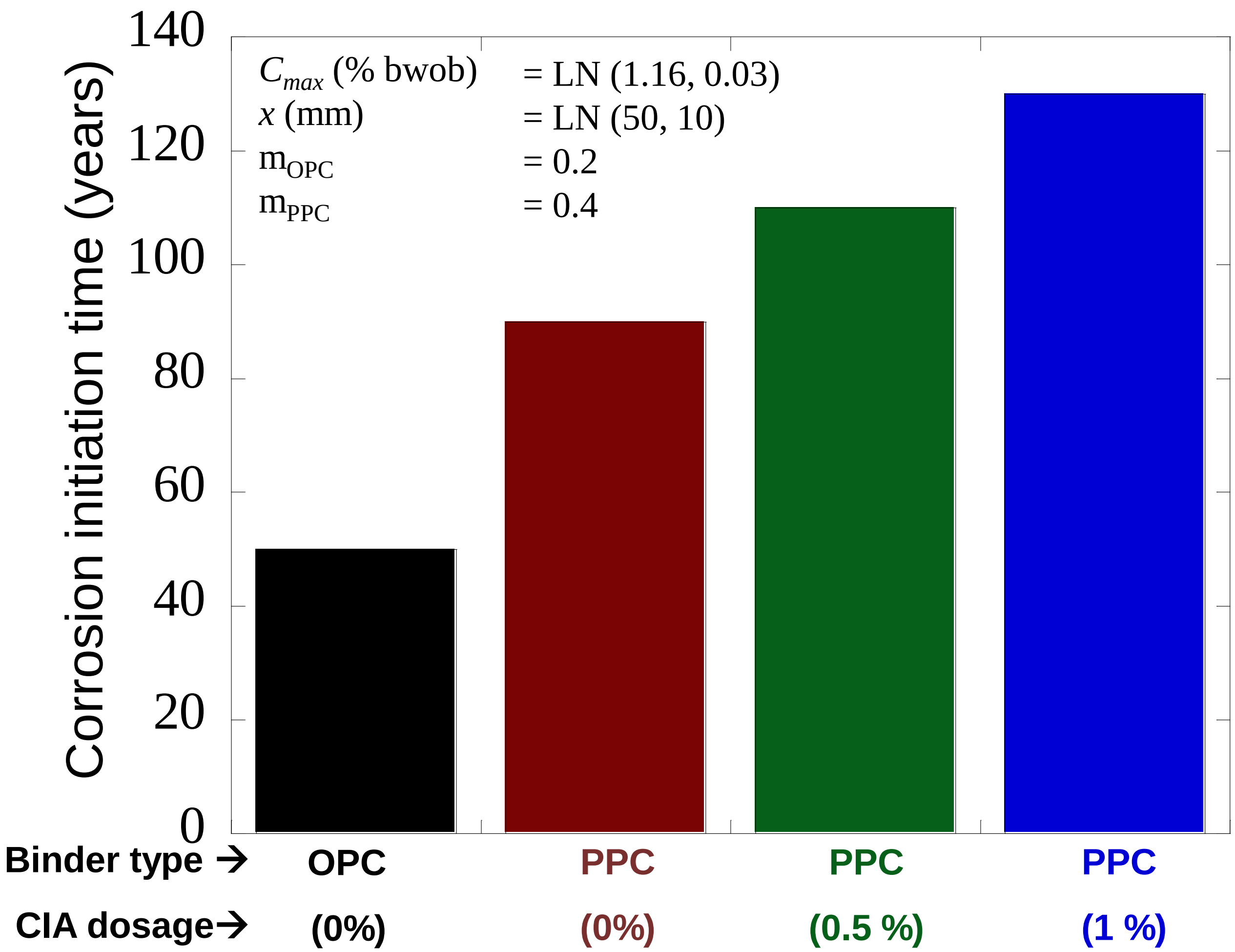
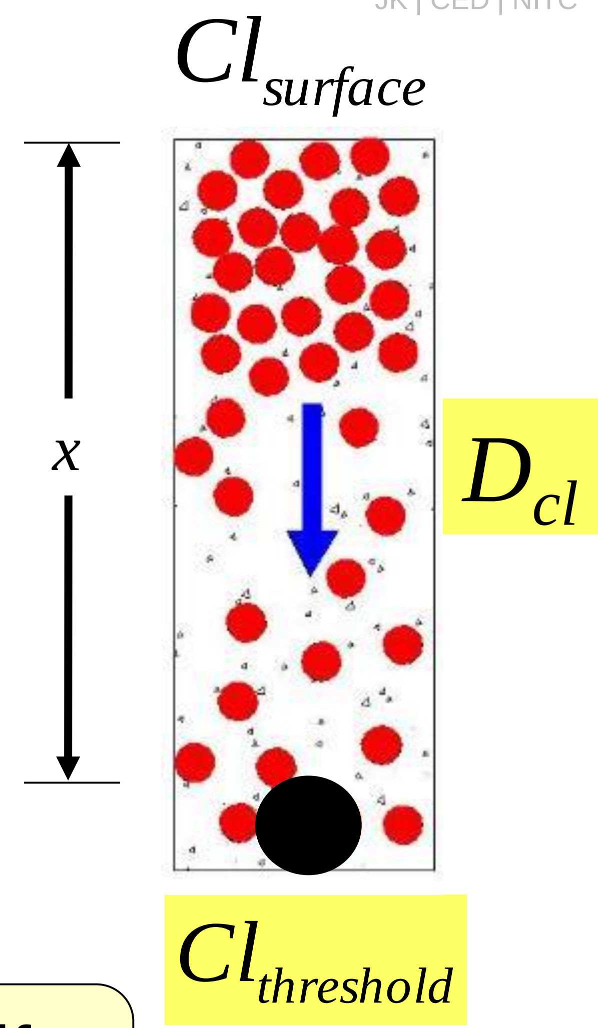
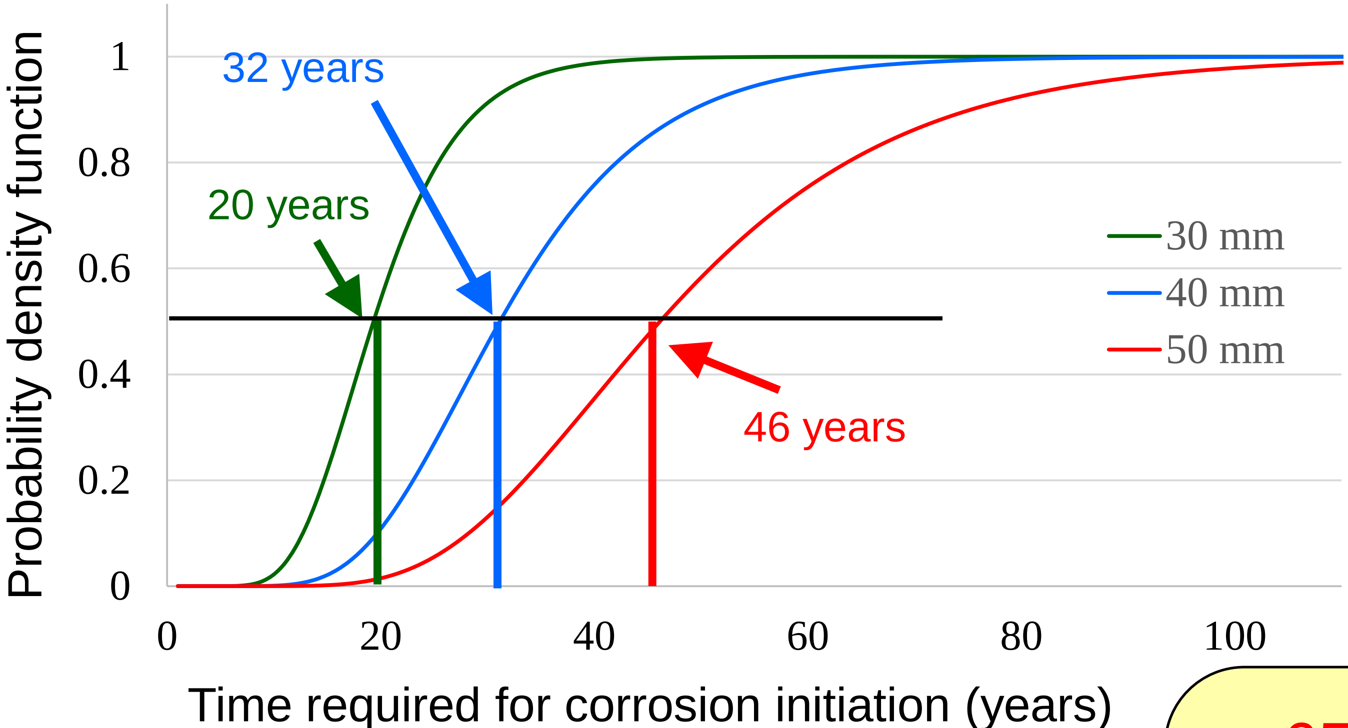




Inhibitors could enhance the service life of RC structure by about 30%.

(Deepak and Pillai)

Effect of concrete cover depth on corrosion initiation



Assumptions

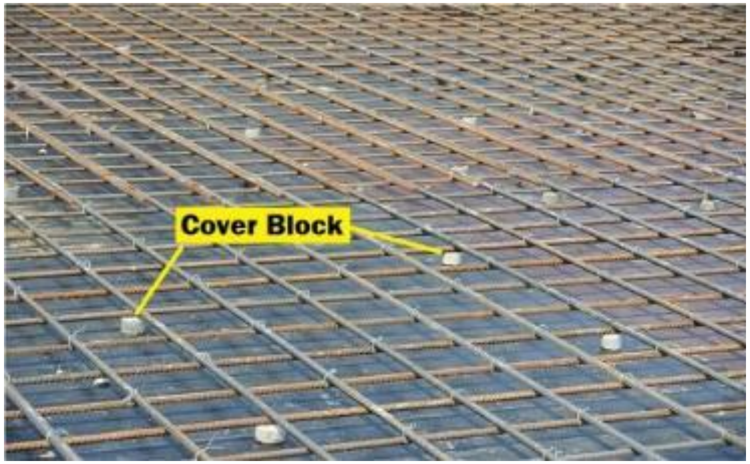
- Concrete with w/b = 0.45
- Cover depth = 30, 40 & 50 mm
- **D_{cl} = 1.35E-12 m^2/s**

- ~65% increase with every 10 mm cover
- Ensuring adequate cover is extremely important

Provide good quality cover blocks

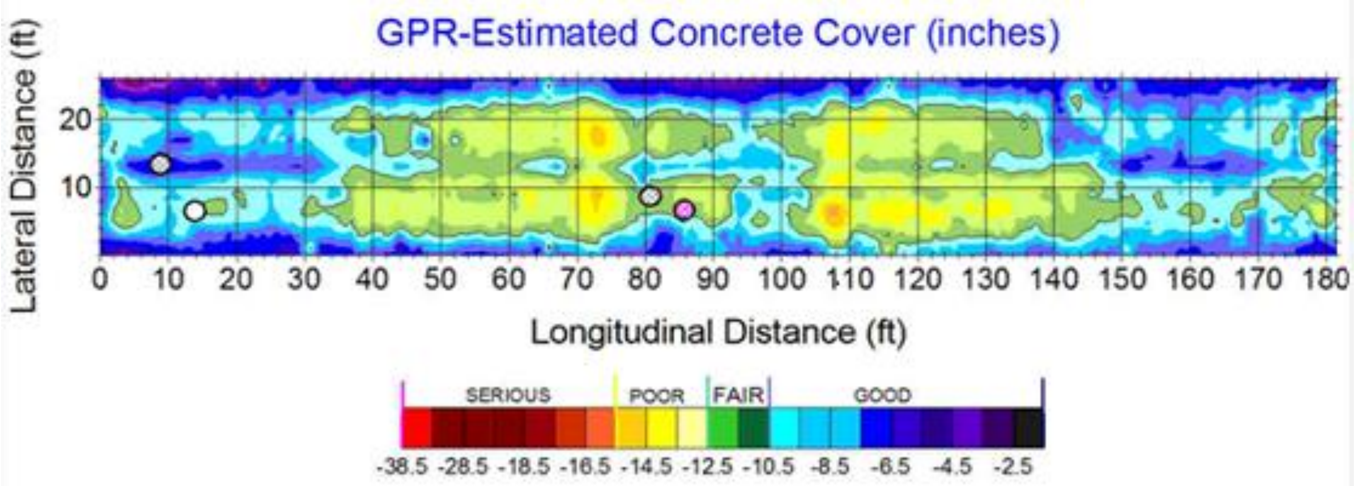
- Transport properties of cover block is very important
  - ✓DO NOT use brick pieces → localized corrosion of steel
  - ✓Do NOT use plastic products → localized corrosion of steel
- Use concrete with similar transport properties as of parent concrete

?



Enforce concrete depth mapping after construction

- Performance specification
  - ✓ Any region with less than the recommended cover → penalty



Contour plot of cover depth

Check cover depth after removal of formwork or as soon as possible and take necessary action

https://fhwaapps.fhwa.dot.gov/ndep/DisplayTechnology.aspx?tech_id=9https://fhwaapps.fhwa.dot.gov/ndep/DisplayTechnology.aspx?tech_id=9

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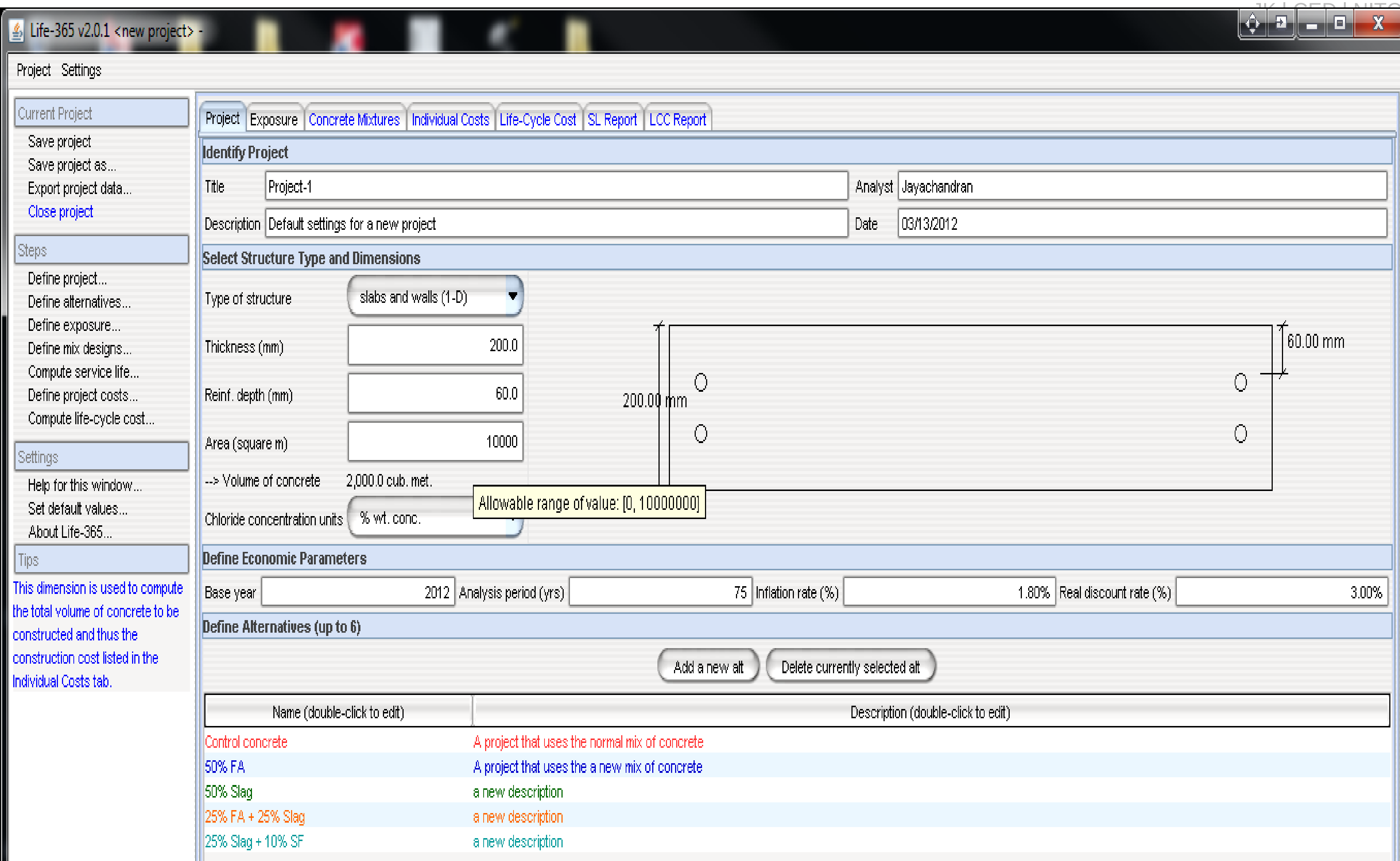
Tool to estimate the service life of concretes with various w/b, inhibitors, steels, SCM’s & EXPOSURE

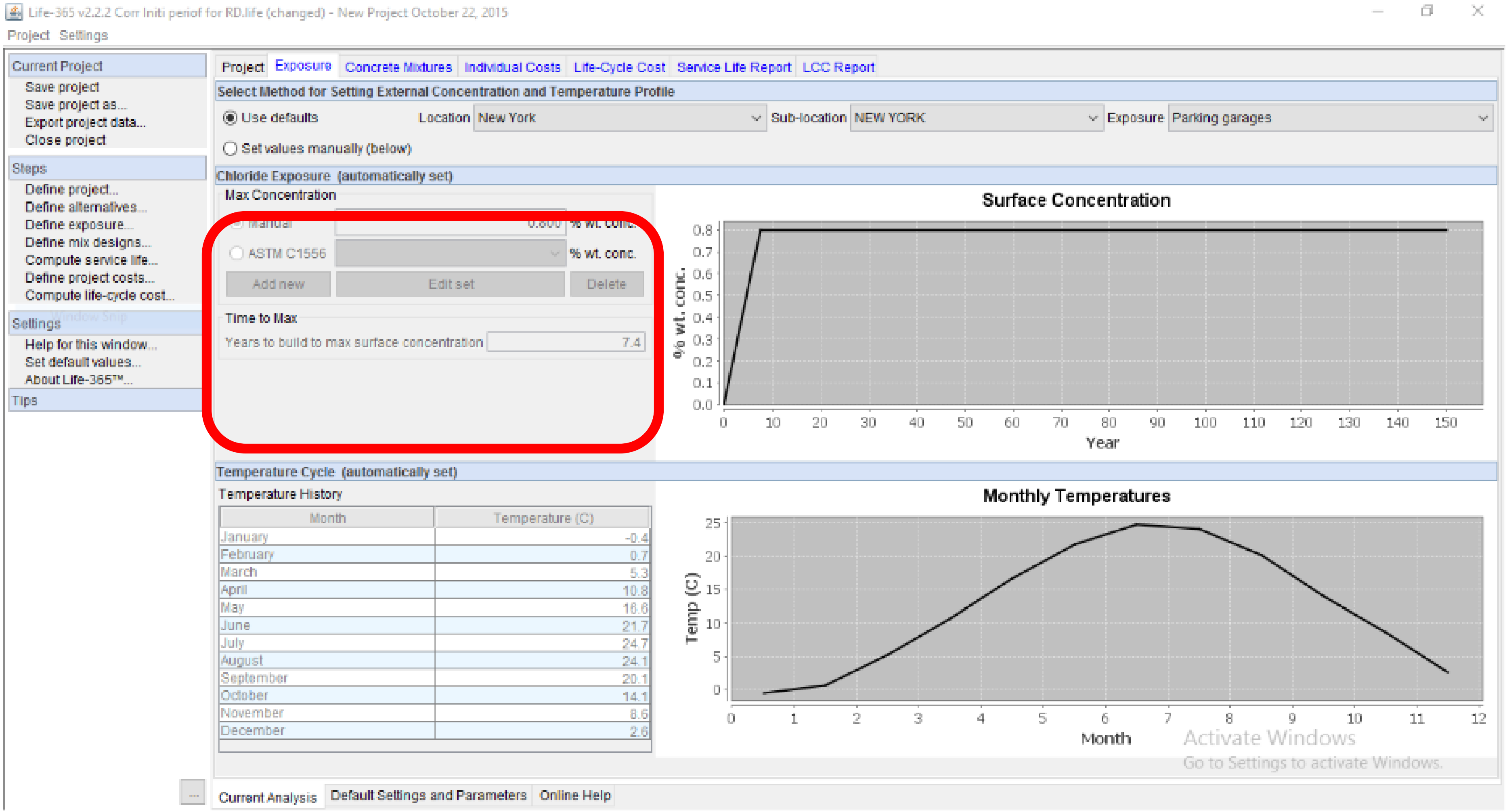
www.life-365.org

Life-365™ – User interface

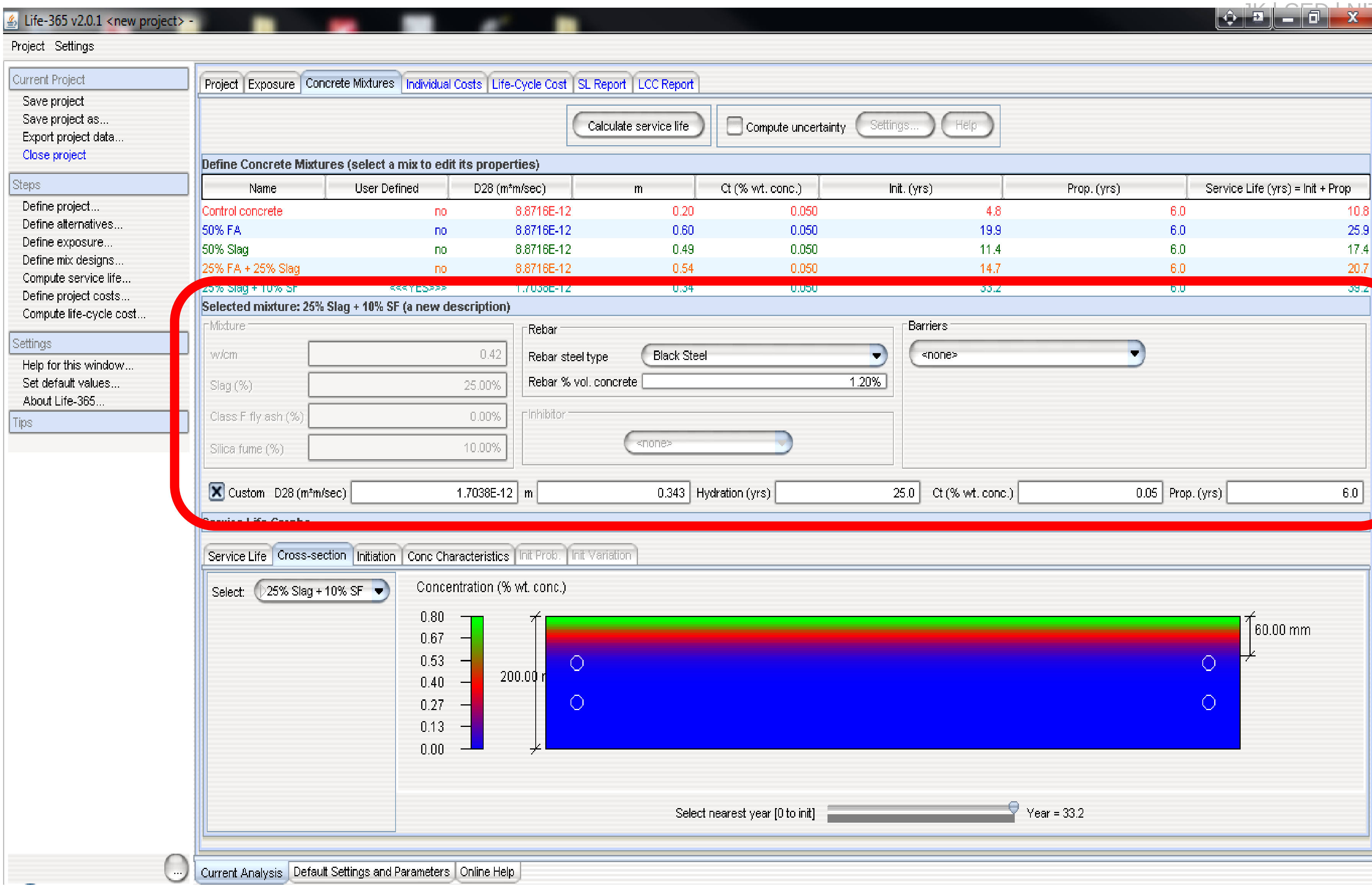
Life-365™ – Element geometry



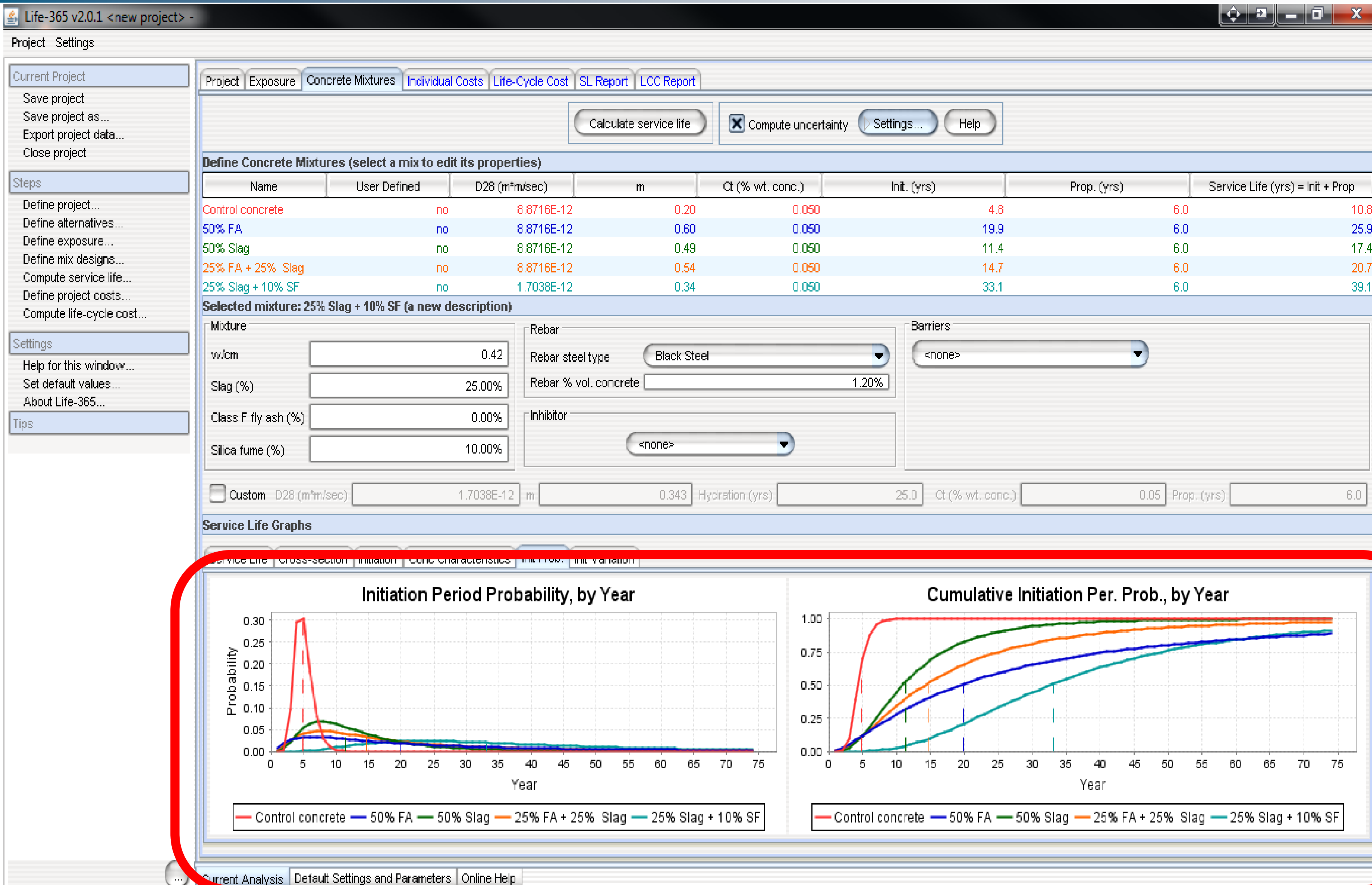
Life-365™ – Exposure conditions



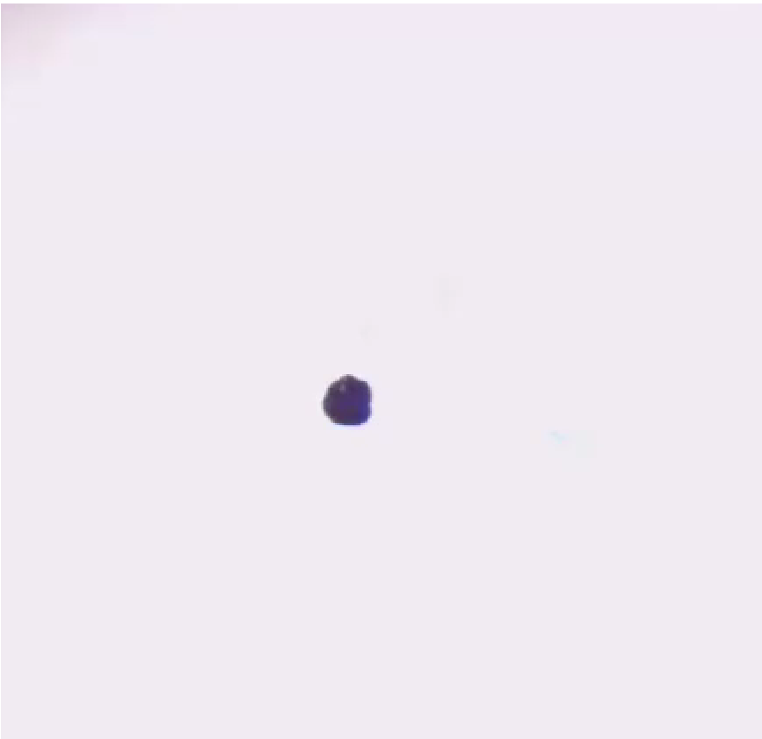
Life-365™ – Mix proportion and material properties



Life-365 software - Probability of corrosion initiation



Rebars with discontinuities were observed… (Short videos of the test)



POOR

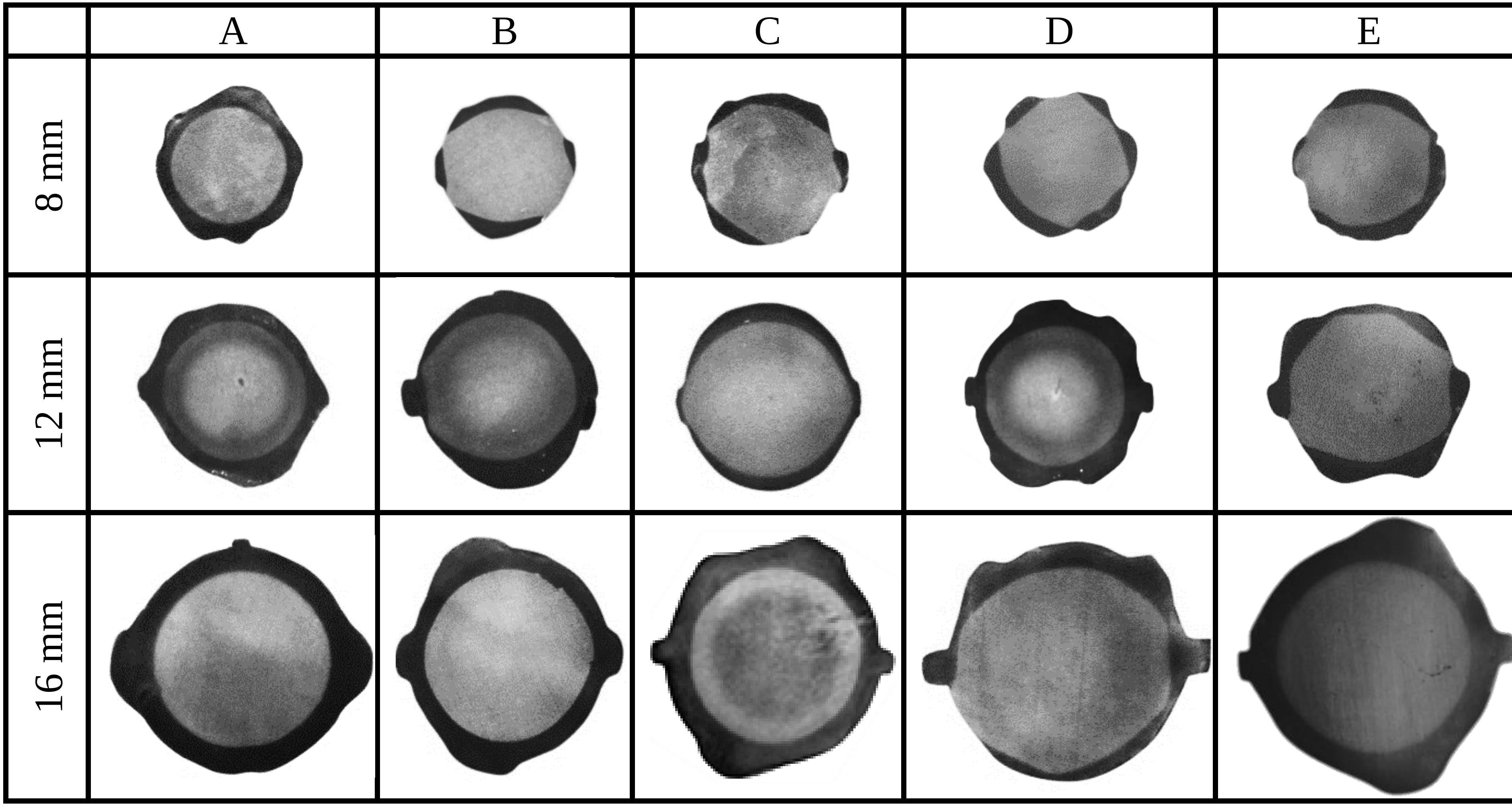
GOOD

Nital test

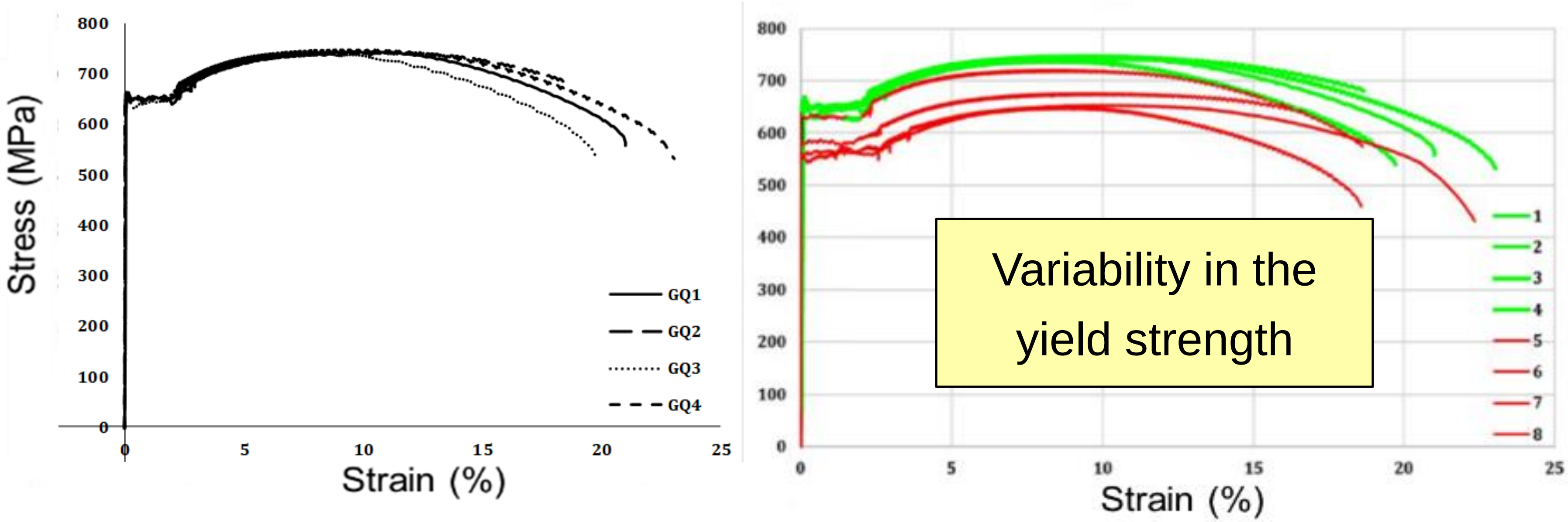
QST rebars cut and polished, cold mounted in 25mm moulds and Etched using a 5% Nital solution (Nitric acid in ethanol)

Courtesy: **Sooraj A.O, 2016**

Rebars with discontinuities observed predominantly in 8 and 12 mm diameter rebars (stirrups)



Corrosion and mechanical performance of some of the TMT/QST rebars in the market

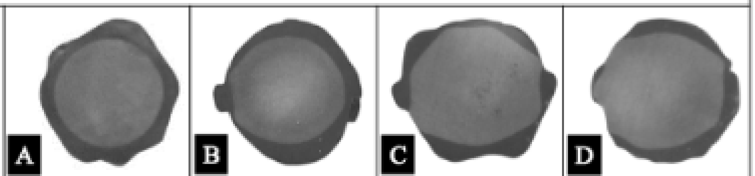


"TM-Ring" test – A quality control test for TMT/QST steel rebars

JK | NITC

Data sheet for "TM-Ring test"

REFERENCE CASES



	A	B	C	D
L1	Y Y Y Y	Y Y N N	Y N N N	Y N N N
L2	Y Y	-	-	-
	Accepted	Rejected	Rejected	Rejected

LEVEL 1 (L1) ACCEPTANCE CRITERIA

No.	Question	Answer (circle one)
1	Is a dark grey peripheral region and light grey core seen?	Yes / No
2	Does the dark grey peripheral region form a continuous outer ring?	Yes / No
3	Are the dark grey peripheral region and light grey core concentric?	Yes / No
4	Is the thickness of the dark grey peripheral region uniform?	Yes / No

Decision

If all the answers are 'Yes', then accept the rebar lot

If any one or more answers are 'No', then reject the rebar lot

LEVEL 2 (L2) ACCEPTANCE CRITERIA

No.	Observations	in mm
1	Diameter of rebar, D	
2	Measured thickness of TM, t_{TM}	

No.	Question	Answer (circle one)
1	Is $t_{TM} \geq 0.07$ D ?	Yes / No
2	Is $t_{TM} \leq 0.10$ D ?	Yes / No

Decision

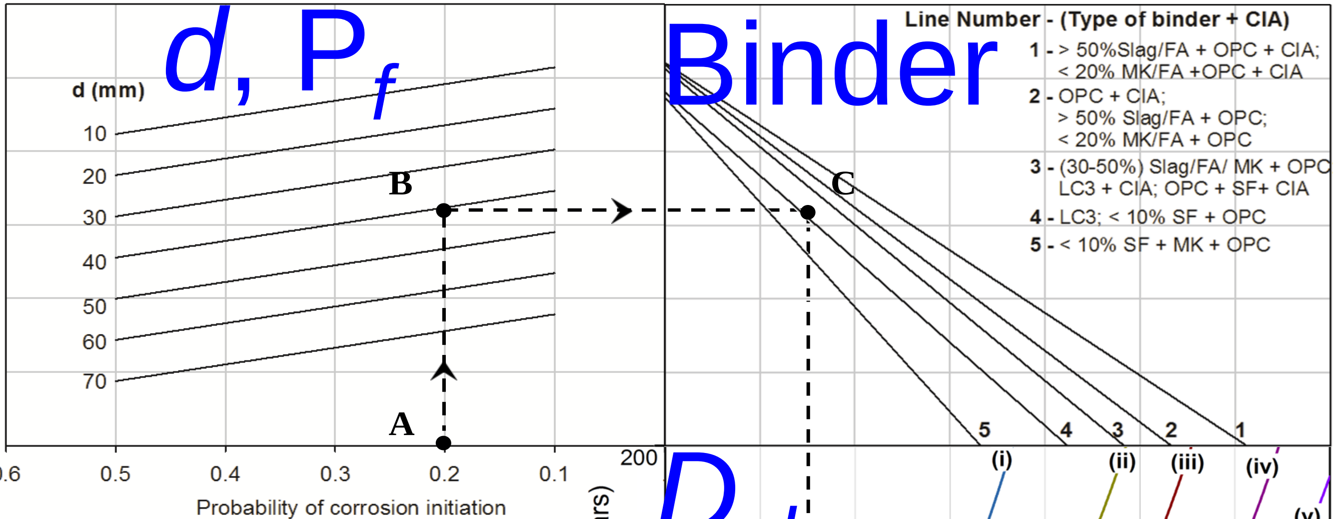
If all the answers are 'Yes', then accept the rebar lot

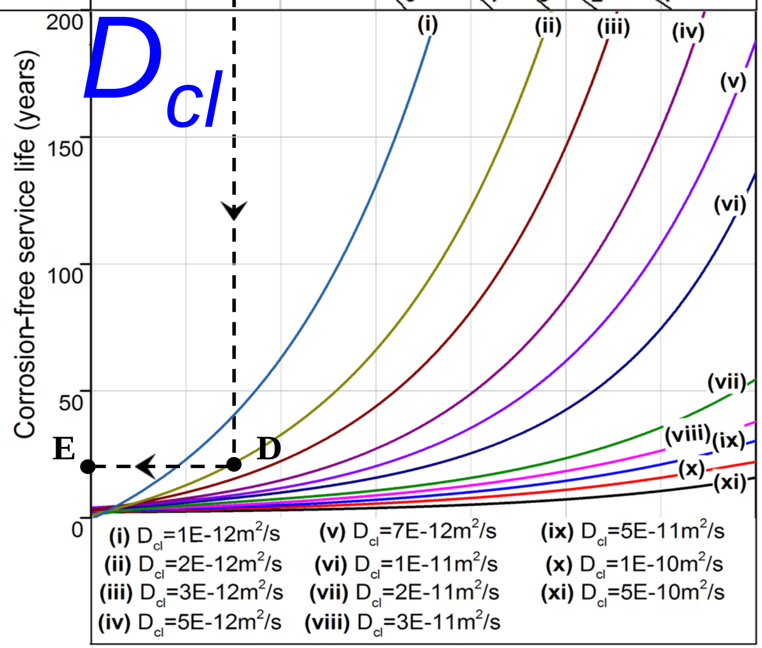
If any one or more answers are 'No', then reject the rebar lot

Sometimes it becomes necessary to determine if a particular reinforcing bar/wire, or lot, has undergone proper heat treatment or is only a mild steel deformed bar. Because the two cannot be distinguished visually, the following field test may be used for purposes of identification. A small piece (about 12 mm long) can be cut and the transverse face lightly ground flat on progressively finer emery papers up to '0' size. The sample can be macroetched with nital (5 percent nitric acid in alcohol) at ambient temperature for a few seconds which should then reveal a darker annular region corresponding to martensite/bainite microstructure and a lighter core region. However, this test is not to be regarded as a criterion for rejection. The material conforming to the requirements of this standard for chemical and physical properties shall be considered acceptable.

What about the $Cl_{threshold}$ of TMT steel rebars, especially when embedded in systems with corrosion inhibitors?

Nomograms are available to estimate the service life





Steps

1) Assume probability of corrosion initiation (A)
2) Choose cover and find the intercept (B)
3) Traverse right from B; choose binder property (C)
4) From C, move down and choose D_{Cl} (D)
5) Traverse left from D and navigate to y axis (E)
6) E is the corrosion-free service life for the chosen parameters

Assumptions

1) Chloride build-up rate = 0.04% bwoc
2) Max. surface Cl$^-$ concentration = 0.6% bwoc
3) Duration of hydration = 2 years

CIA - Corrosion inhibiting admixture
d - Cover depth
D_{Cl} - Diffusion co-efficient
FA - Fly ash
LC3 - Limestone calcined clay cement
MK - Metakaolin
OPC - Ordinary portland cement
SF - Silica fume

Synergistic effect of various parameters on service life must be considered while selecting materials

Specify Mx-Dy instead of Mx

Rengaraju, S. (2019), PhD Thesis, IITM

Summary

- Critical material, design, and environmental parameters for predicting service life
- Inhibitor mechanisms, Bipolar inhibitors are recommended
- Test methods to determine chloride threshold & results
- Optimal dosage is important (strength and durability)
- Reduction in Cl_{th} due to the use of SCMs can be compensated by inhibitors
- Ensuring cover depth is very important

Acknowledgement

- Prof. Radhakrishna G. Pillai, IIT Madras
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- Prof. Mark G. Alexander, University of Cape Town
- Prof. David Trejo, Oregon State University
- BTCM Corrosion Research Group, IIT Madras

Corrosion in concrete structures & Ways to enhance the service life

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Courtesy: Some images are sourced from the internet for demonstration purposes