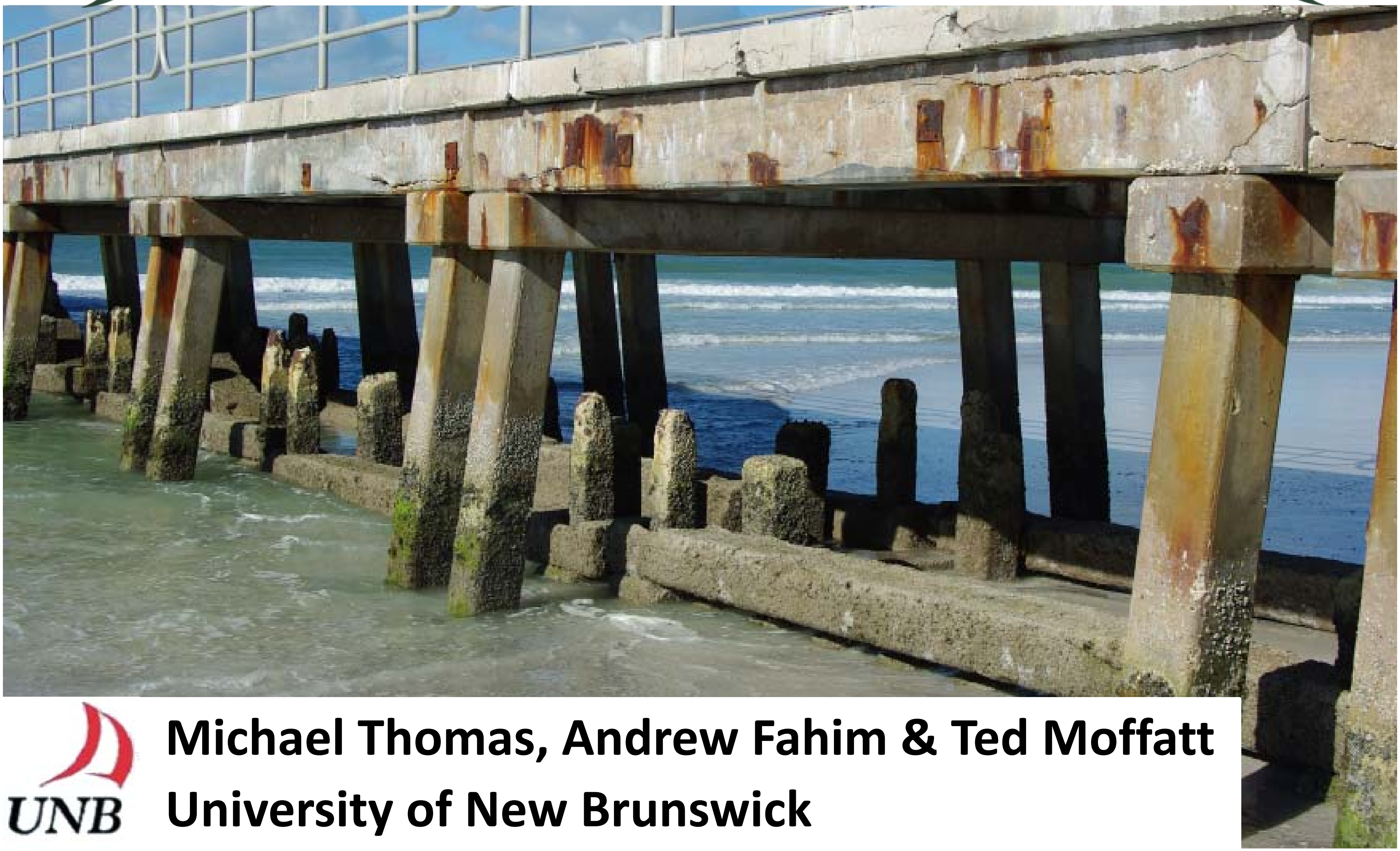
Chemical Attack by Sulfates: Harmonizing Test Methods and Specification Limits

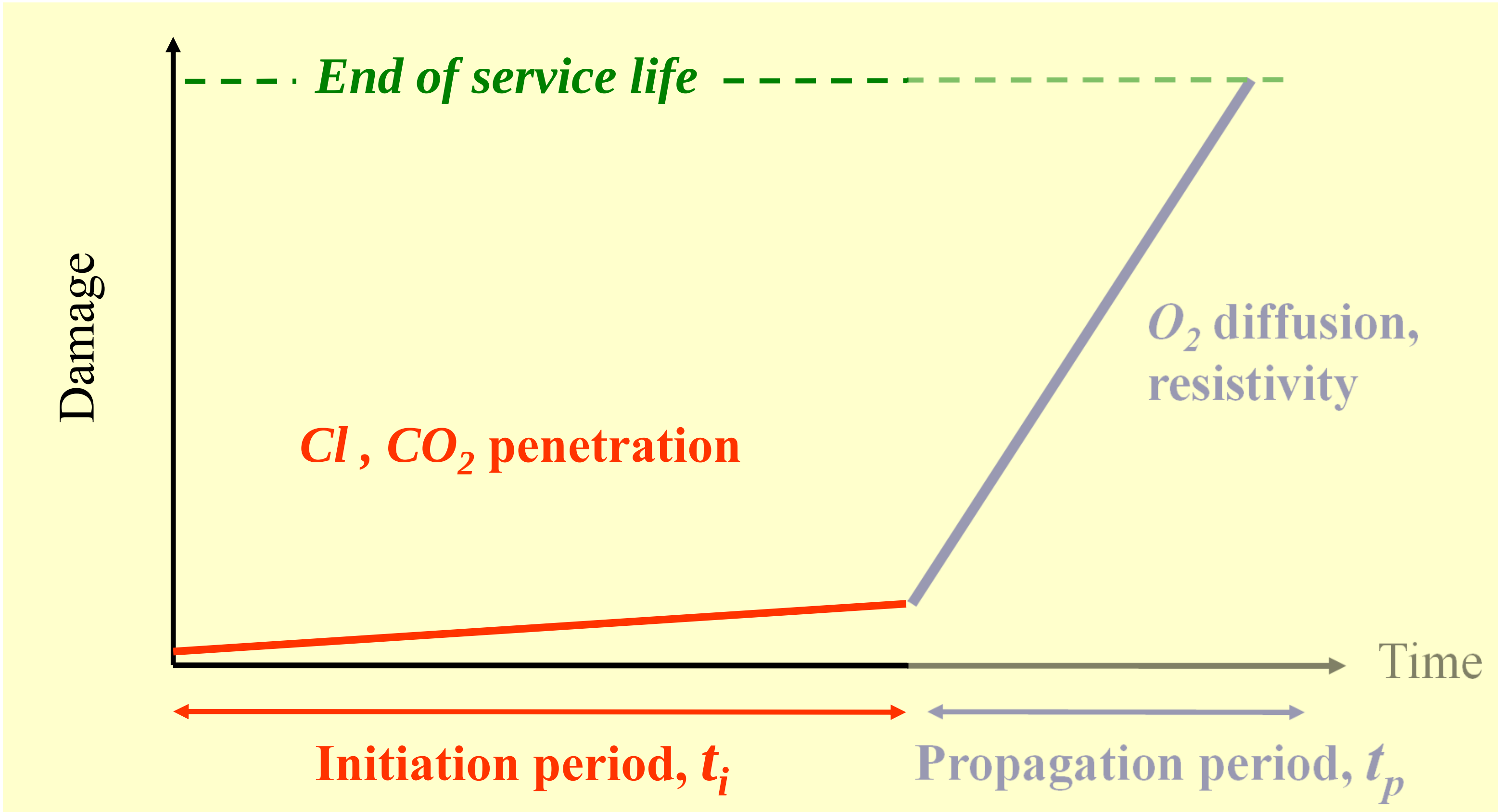
Michael Thomas
University of New Brunswick

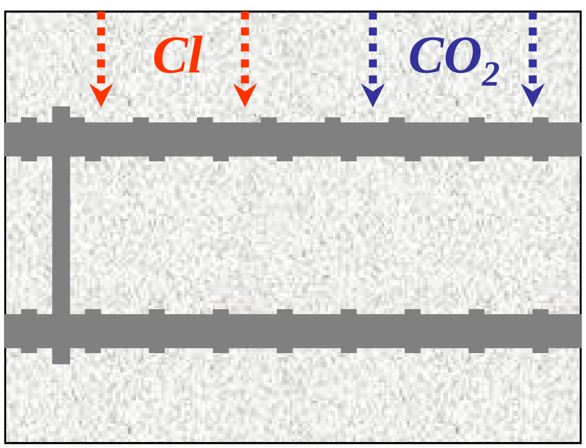
Thano Drimalas
University of Texas

Corrosion Resistance of Concrete Incorporating Supplementary Cementing Materials in a Marine Environment



Michael Thomas, Andrew Fahim & Ted Moffatt
University of New Brunswick



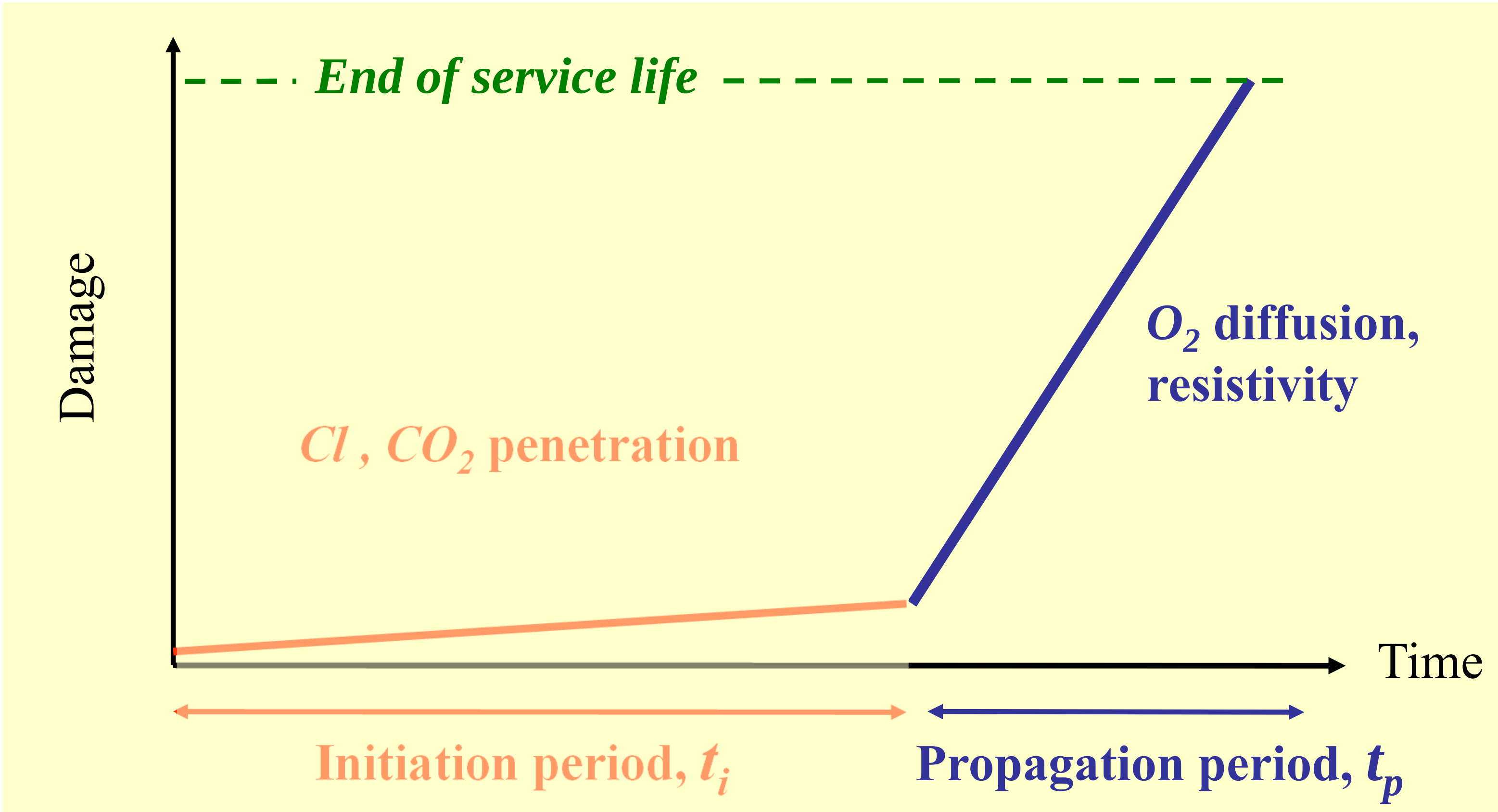


Initiation period depends on:

- Rate of penetration of Cl or CO_2
- Chloride threshold for corrosion

} **Concrete Properties**

- Exposure conditions (Cl^-, T, H_2O & O_2)

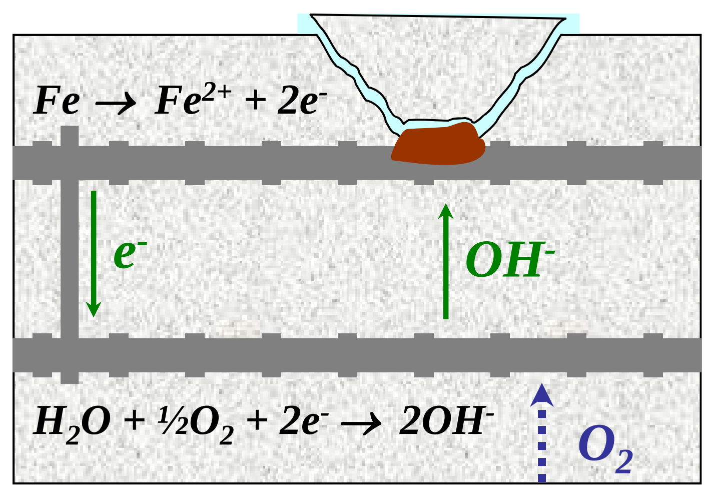


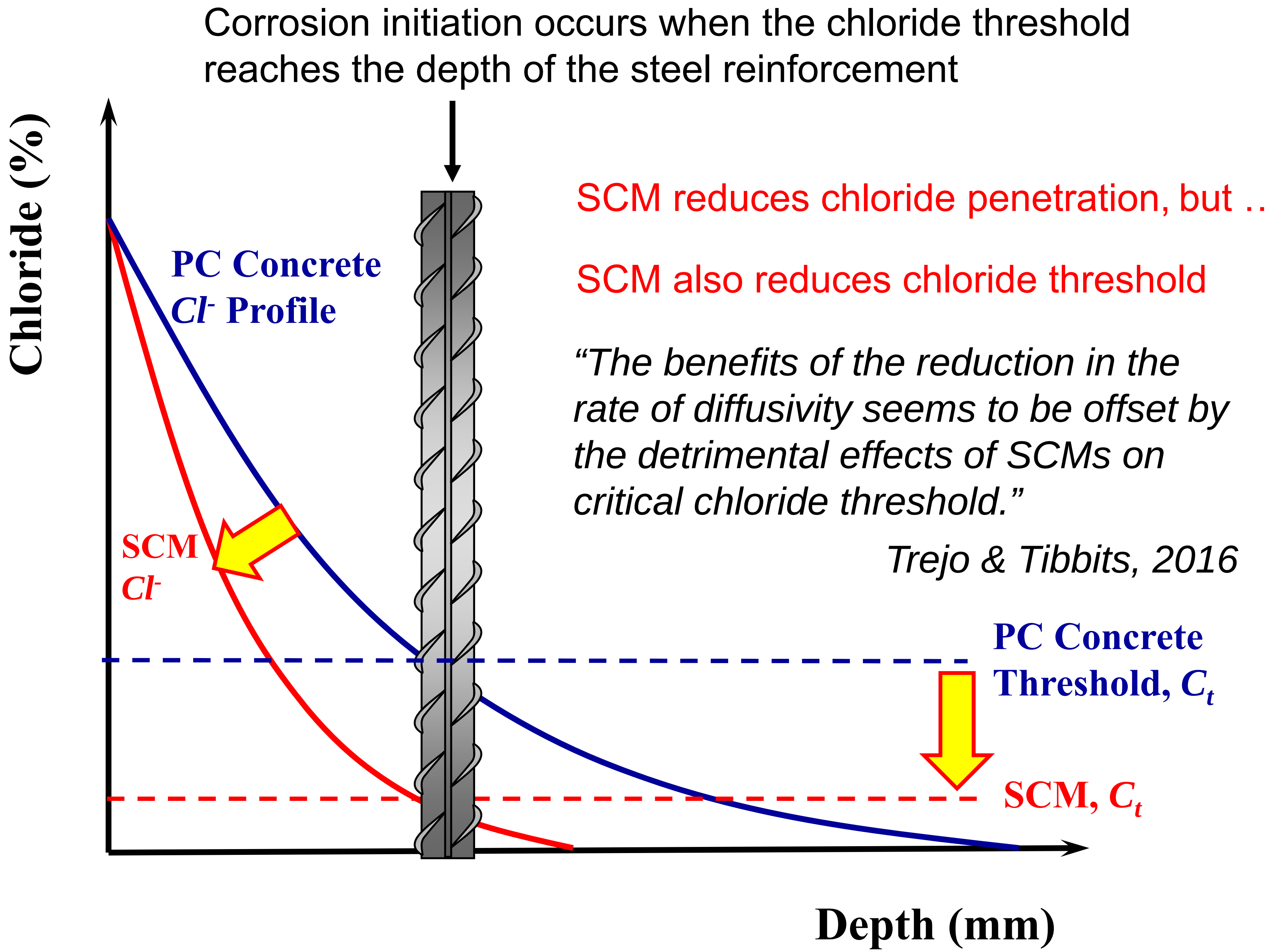
Propagation period depends on:

- Concrete resistivity
- O_2 diffusivity

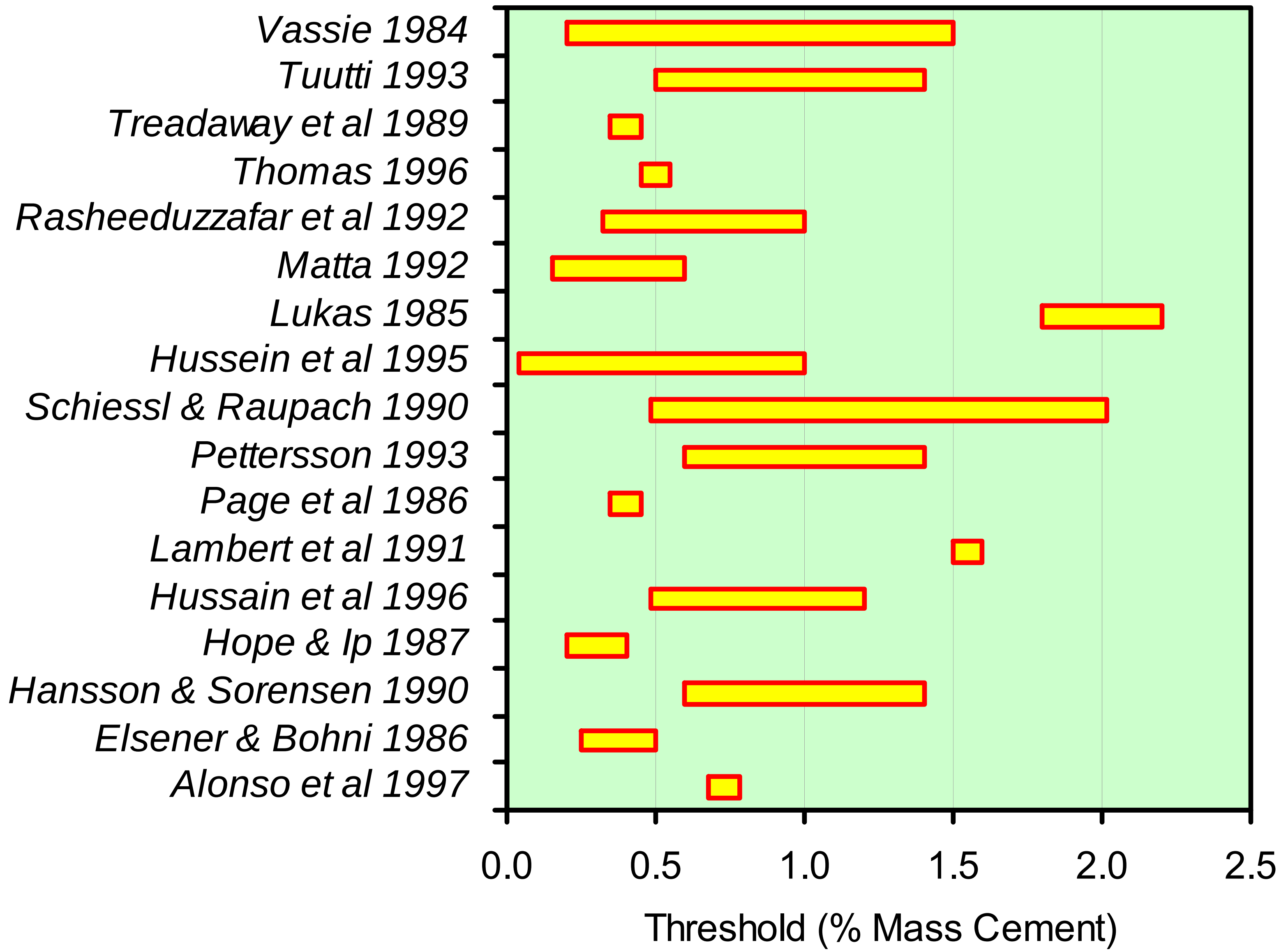
(Concrete resistivity and O_2 diffusivity: **Concrete Properties**)

- Properties of steel (coatings)
- Exposure conditions (*T*, H_2O & O_2)




Corrosion initiation occurs when the chloride threshold reaches the depth of the steel reinforcement
SCM reduces chloride penetration, but …
SCM also reduces chloride threshold
"The benefits of the reduction in the rate of diffusivity seems to be offset by the detrimental effects of SCMs on critical chloride threshold."
Trejo & Tibbits, 2016
Chloride (%)
PC Concrete
Cl- Profile
SCM
Cl-
PC Concrete
Threshold, Ct
SCM, Ct
Depth (mm)

A Summary of Published Chloride Threshold Data for Black Steel (Thomas, 2000)



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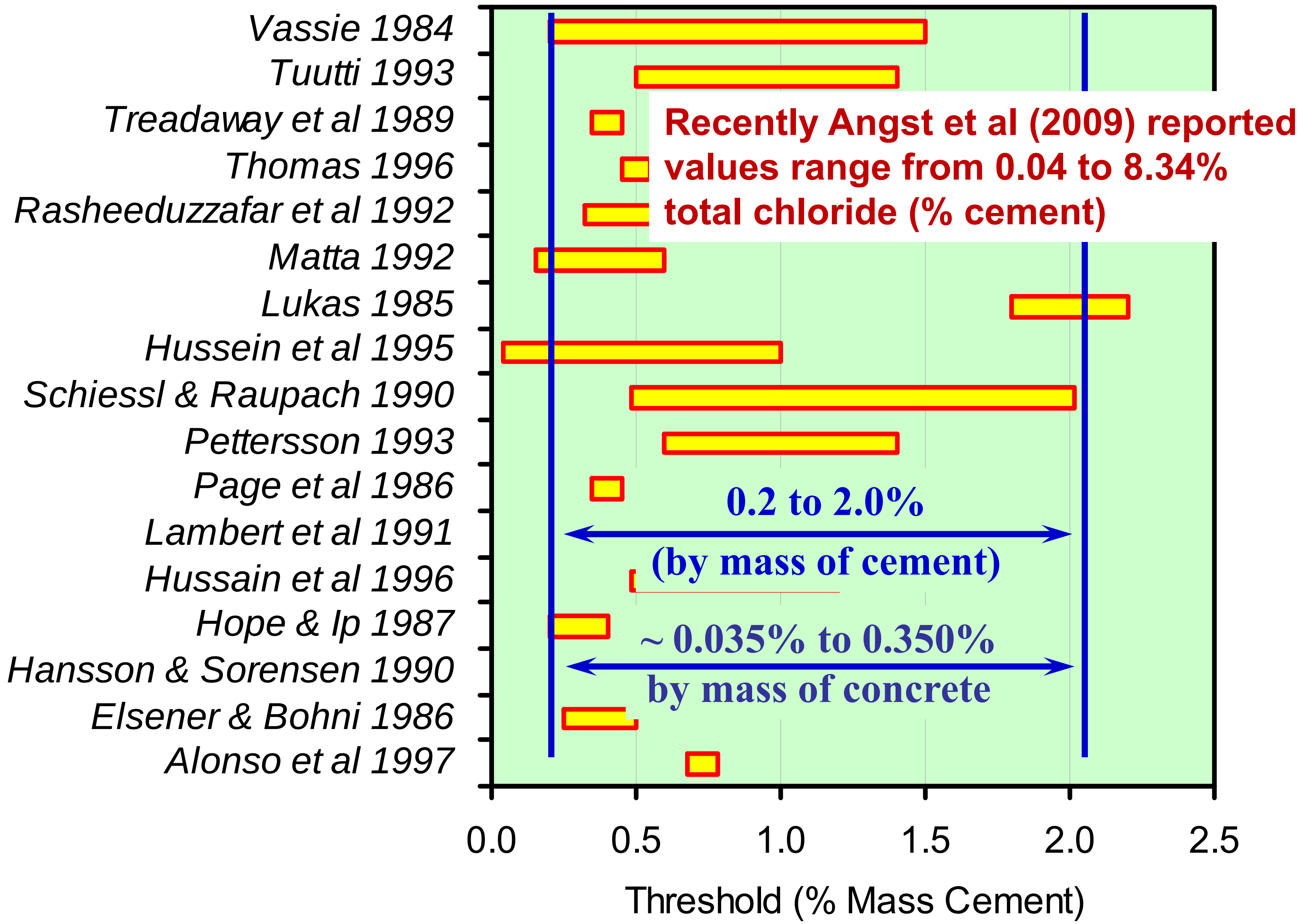
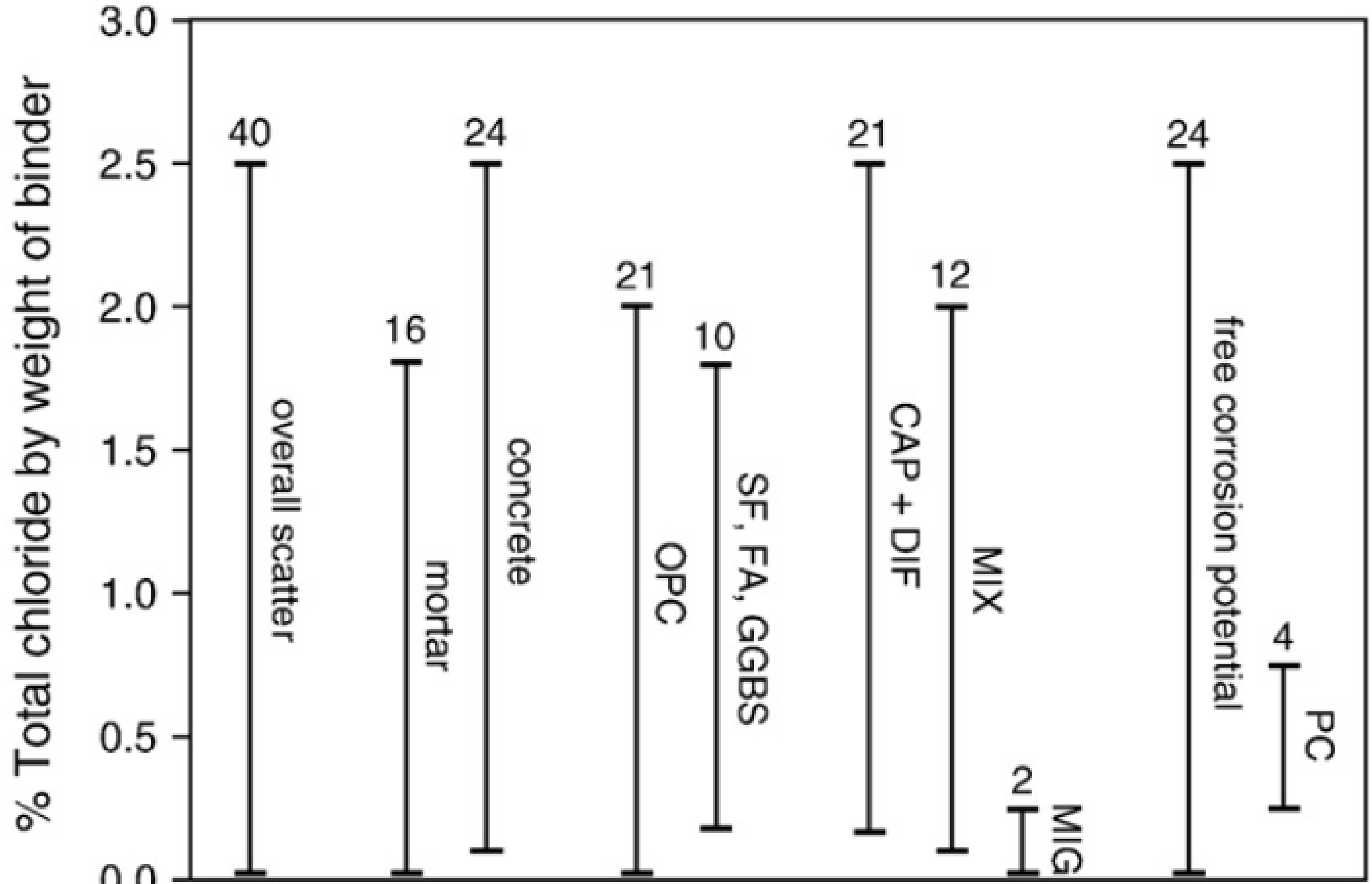
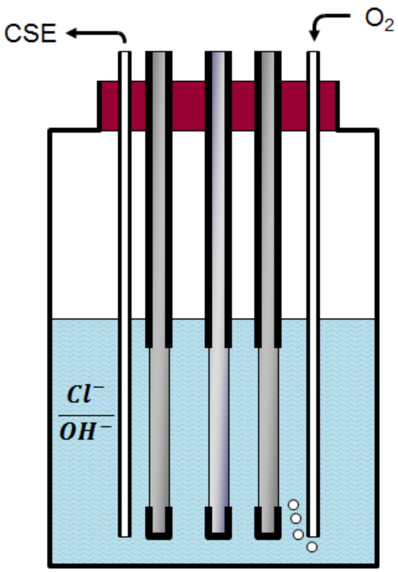


Scatter of Chloride Threshold Values in the Literature

(Angst et al. 2009)

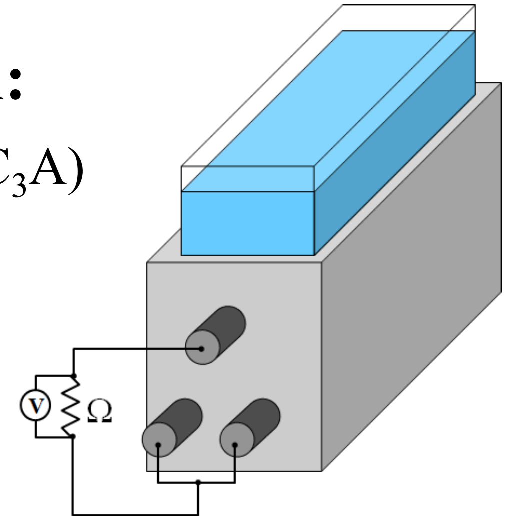


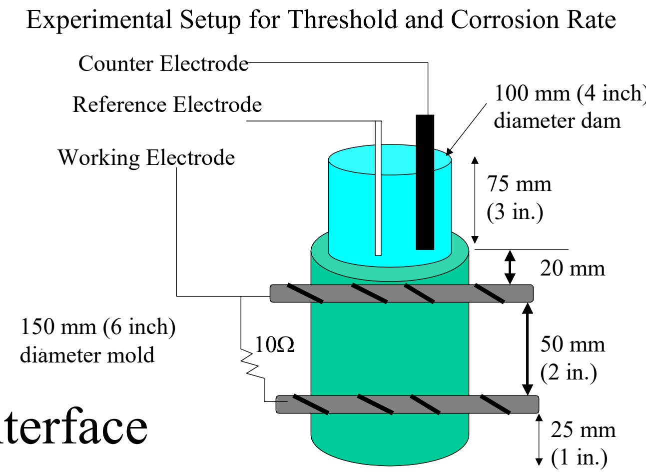
(The numbers above the bars indicate the frequency of occurrence in the literature)



Chloride Threshold Depends on:

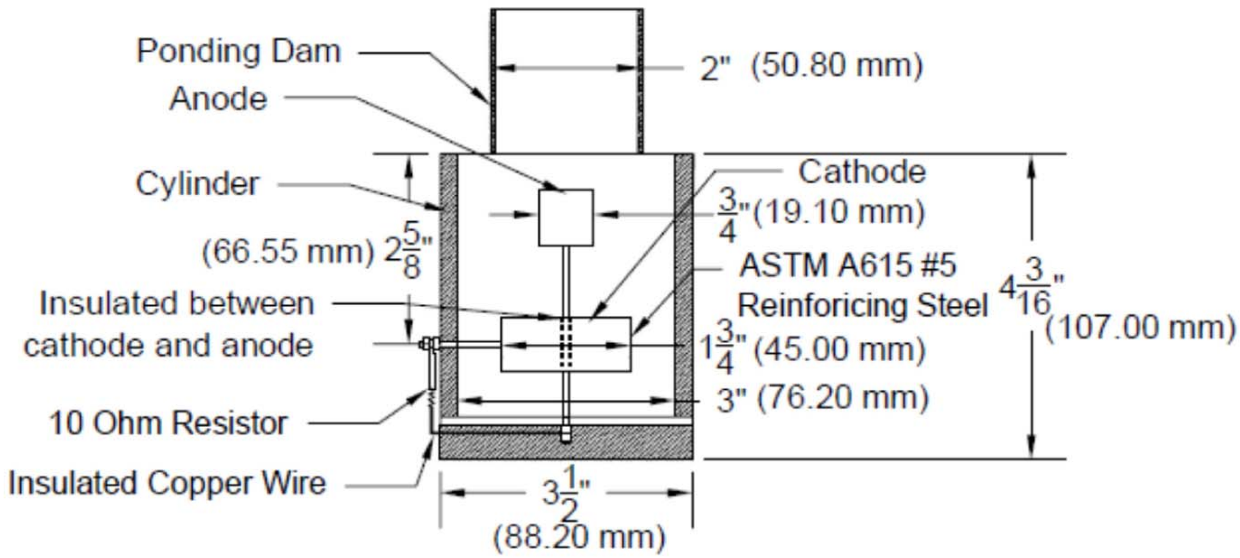
- Composition of the cement (esp. Na_2Oe, C_3A)
- Hydroxyl ion concentration $[OH^-]$
- Presence of pozzolans or slag
- Cement content
- W/CM
- Sulfate content
- Cation type (e.g. Na or Ca)
- Carbonation
- Temperature & humidity
- Steel composition
- Nature of steel surface
- Microstructure at steel/concrete interface





- **Test method**
  - Method of introducing chloride
  - Method of measuring corrosion
  - Method of measuring chloride
  - Type of test – concrete, mortar, solution
  - Other?

Trejo & Tibbits, 2016

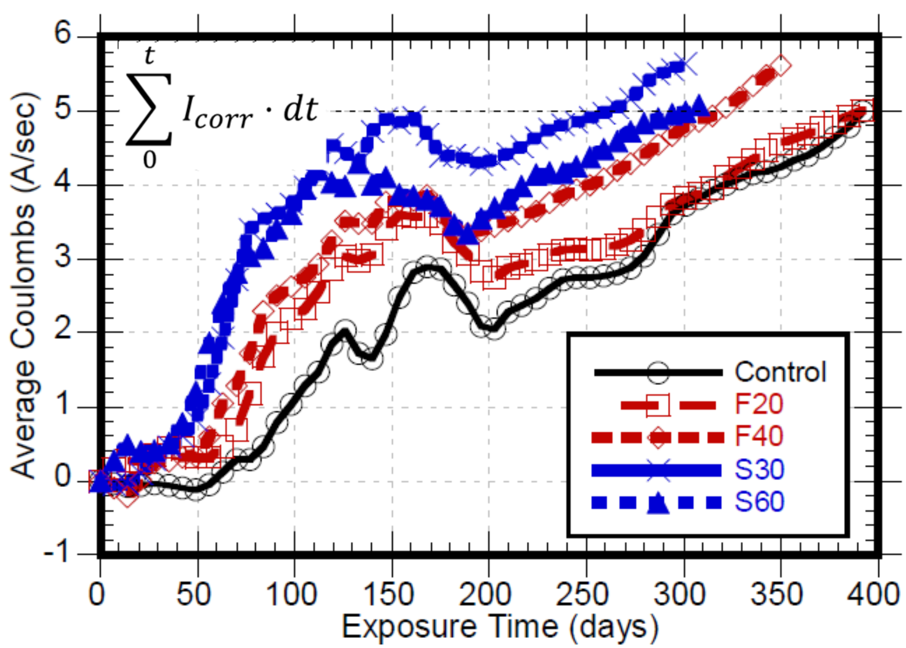


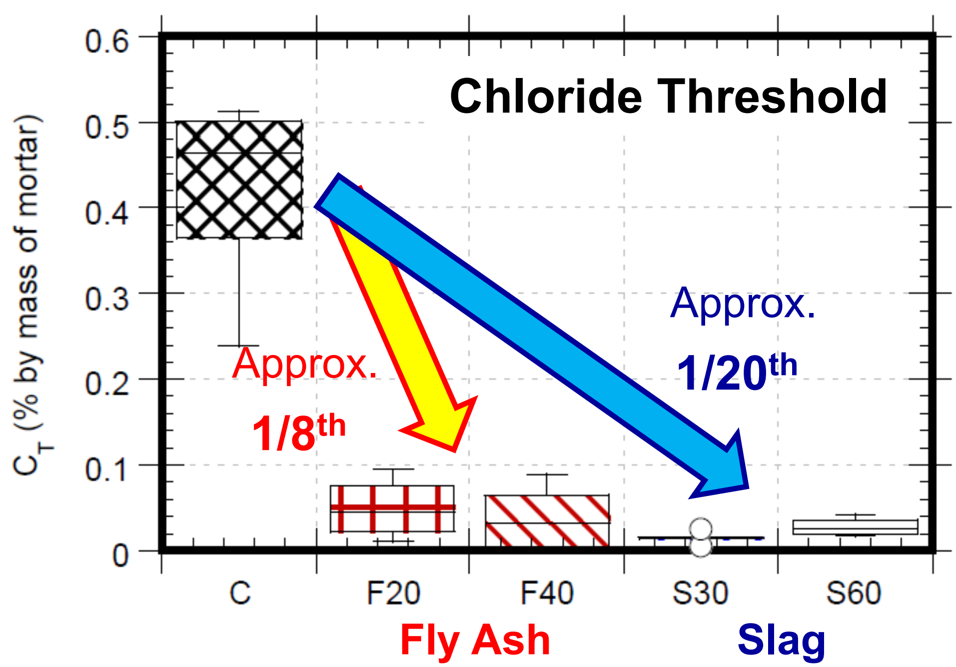
Also D_a determined after:

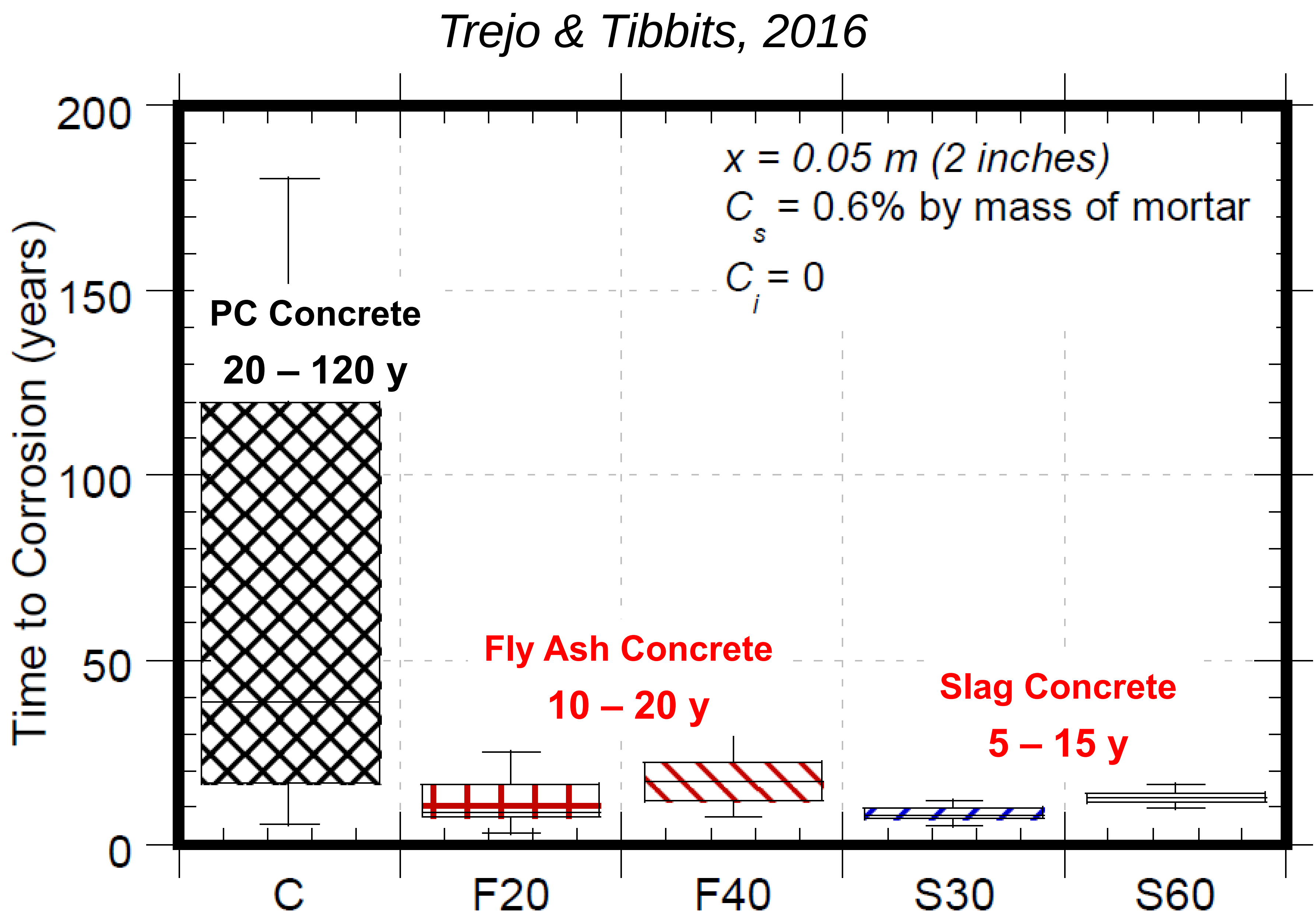
- 28 days
- 56 days

} 56 days in NaCl

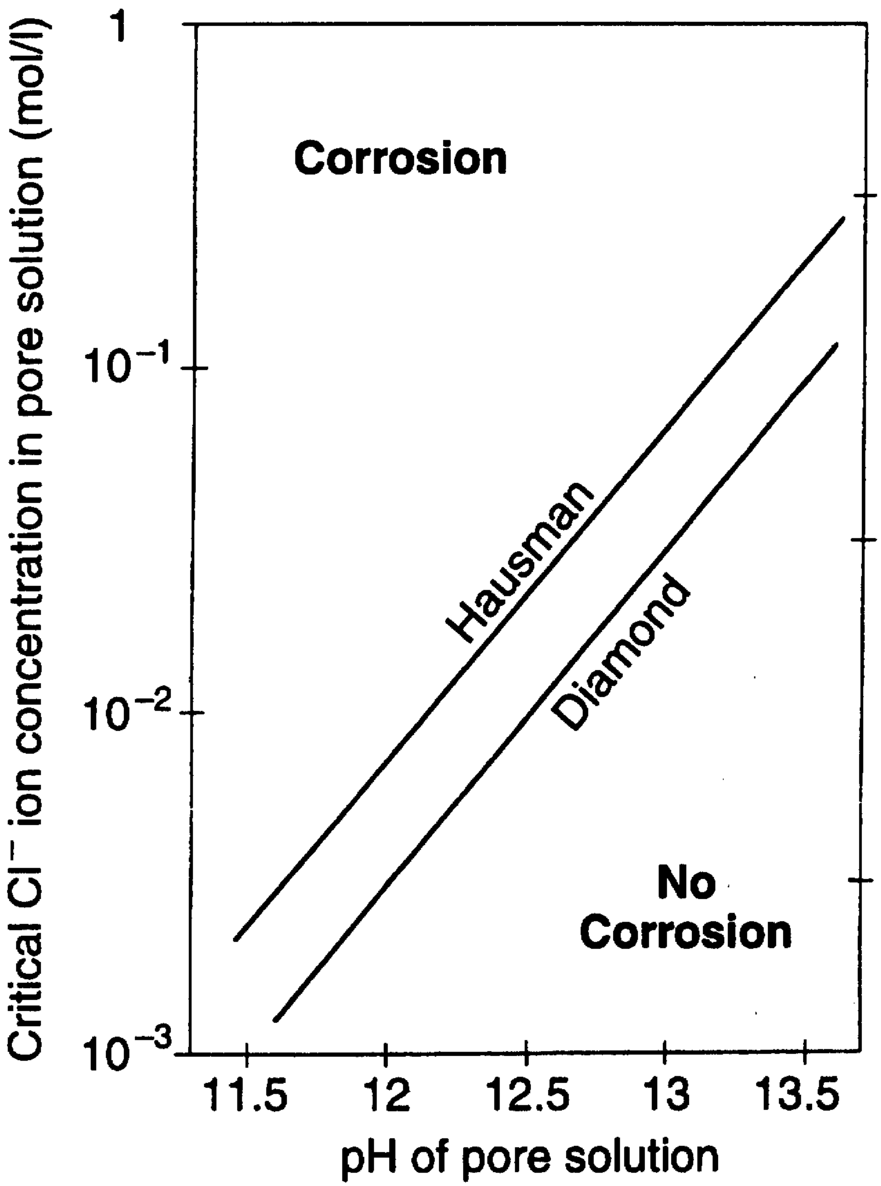
- Using ASTM C 1556 approach






Trejo & Tibbits, 2016
x = 0.05 m (2 inches)
C s = 0.6% by mass of mortar
C i = 0
PC Concrete
20 – 120 y
Fly Ash Concrete
10 – 20 y
Slag Concrete
5 – 15 y
Time to Corrosion (years)
0
50
100
150
200
C
F20
F40
S30
S60

Critical Chloride Concentration



Competition between:

Cl^- which tends to disrupt the passive film

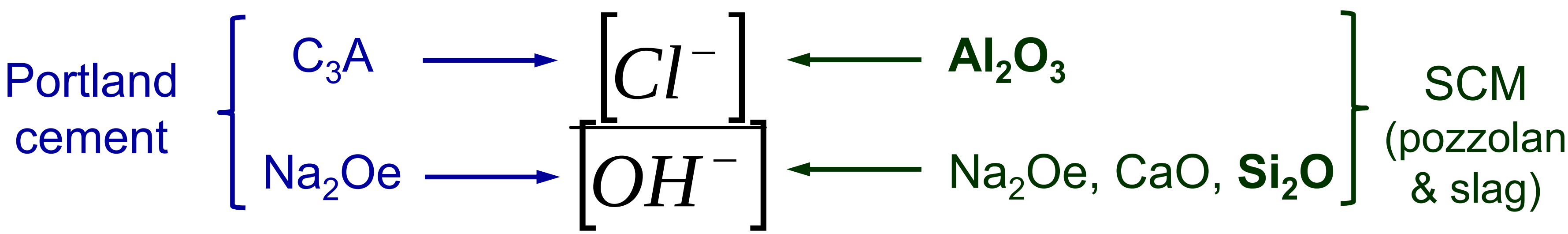
OH^- tending to stabilize the passive film

It has been shown that the molar ratio of chloride ions to hydroxyl ions is the critical factor governing corrosion of steel in concrete. Diamond suggests that corrosion is likely when:

$$\frac{[Cl^-]}{[OH^-]} > 0.3$$

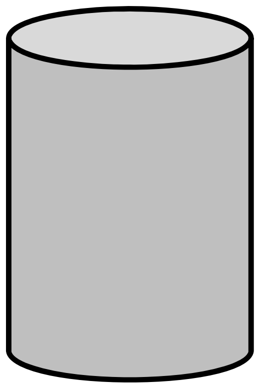
Bentur et al, 1997

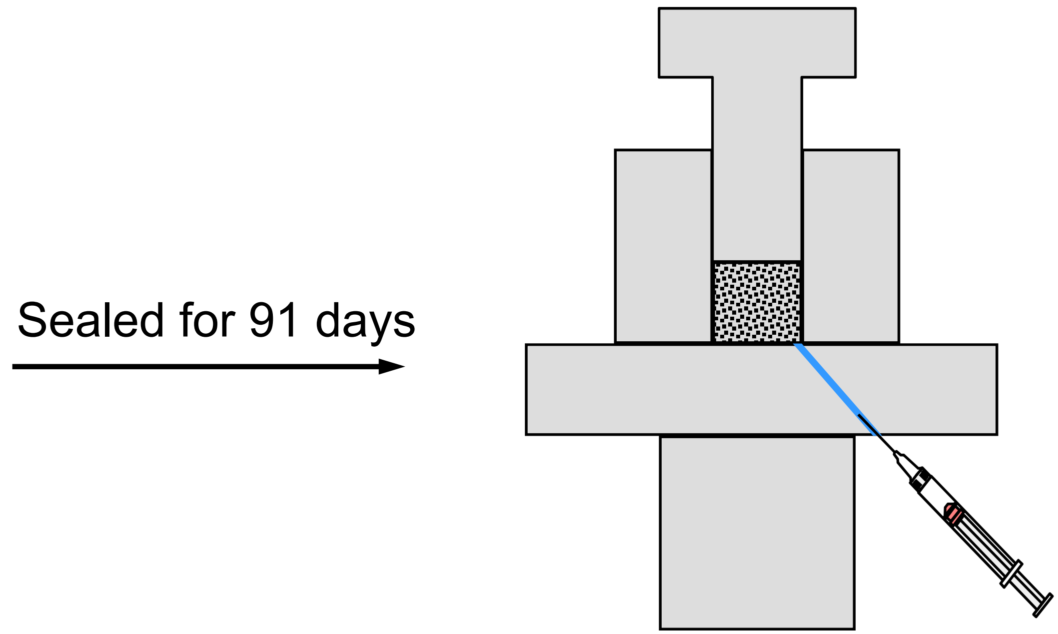
At a given level of chloride (in concrete) the $[Cl^-]/[OH^-]$ of the pore solution will be a function of the amount and composition of the cementing materials (Portland cement + SCM):



- Most SCM's decrease OH concentration of pore solution
- Most SCM's increase Cl binding (not silica fume)
- Page and Havdahl (1985): Cl^-/OH^- is **not** a reliable index.
- For example, silica fume increases Cl^- and decreases OH^- **but** a denser microstructure reduces O_2 content & thus depresses steel potential.
- These effects might compensate for the negative effects on the pore solution chemistry.
- Thus a higher Cl^-/OH^- ratio in the pore solution does **not** necessarily lead to a higher risk of corrosion initiation.

Effect of Fly Ash on Pore Solution Chemistry of Pastes with Admixed Chlorides (Thomas, Matthews & Haynes, 1990)

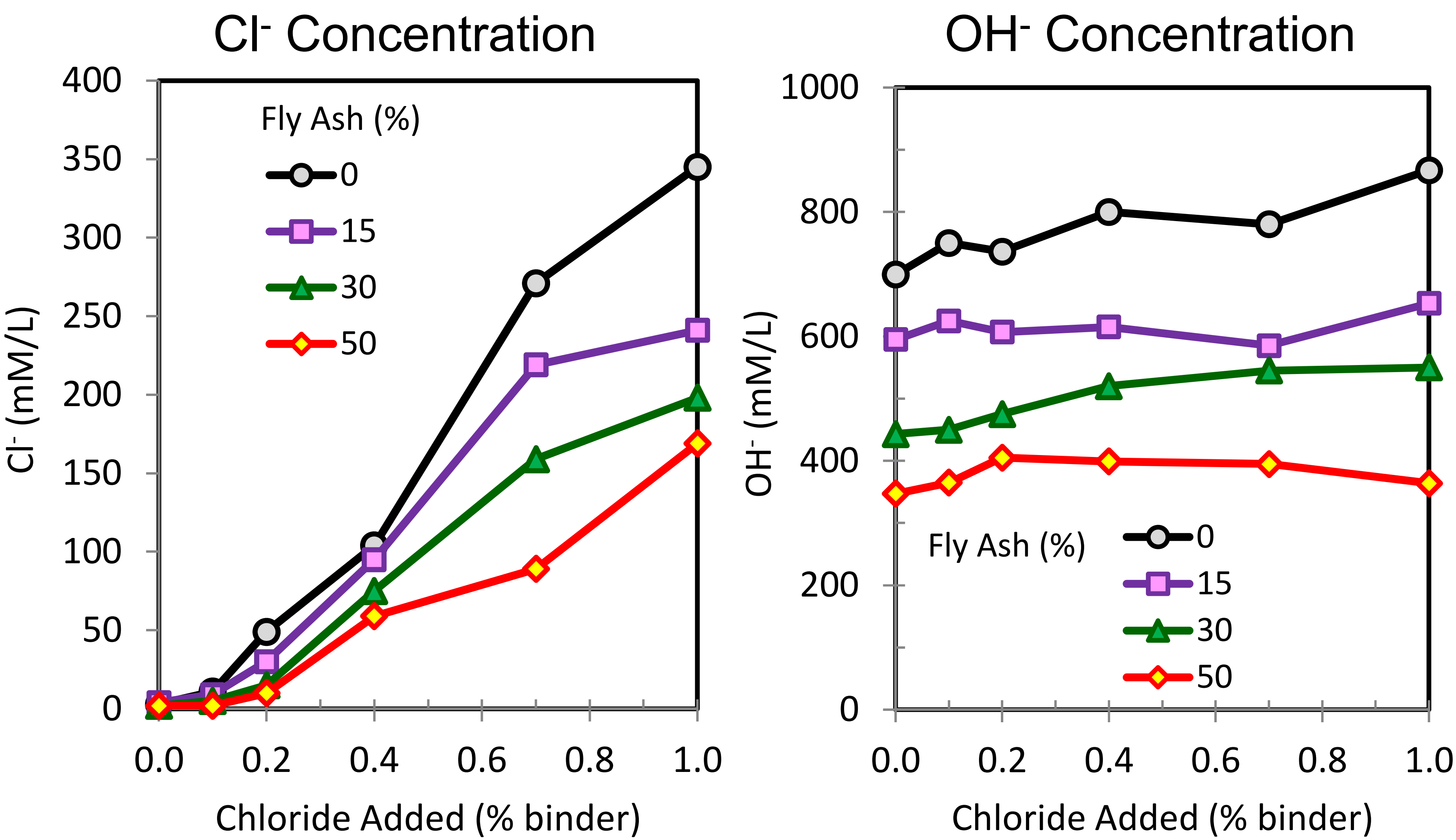




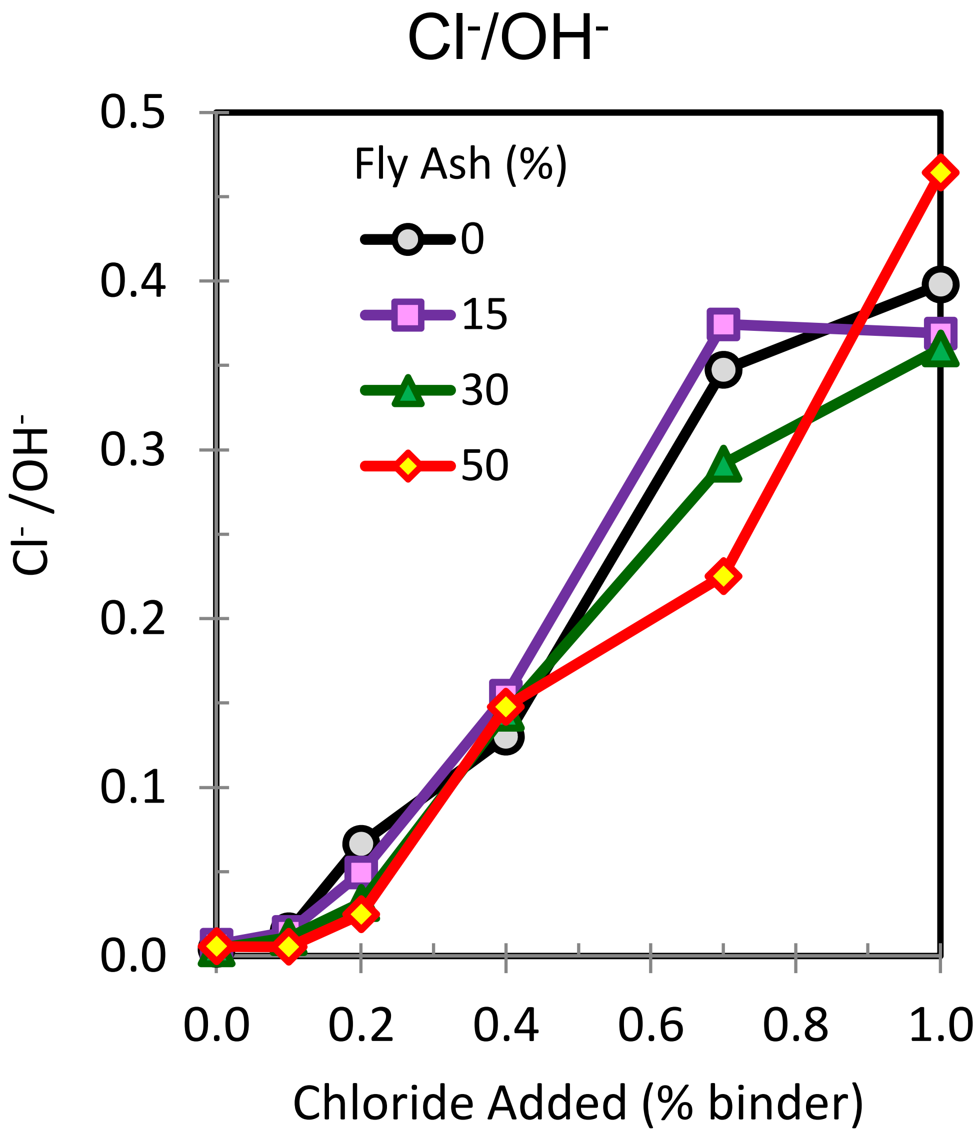
- Pastes: w/cm = 0.50
- PC: 9% C_3A, 0.91% Na_2Oe
- 0, 15, 30 & 50% fly ash
- + NaCl (0, 0.2, 0.4, 0.7, 1.0, 2.0% by mass of PC + FA

- Pore solution expressed (~ 450 MPa) at 91 days
- Analyzed for Na & K by flame photometry and OH & Cl by titration

Effect of Fly Ash on Pore Solution Chemistry of Pastes with Admixed Chlorides (Thomas, Matthews & Haynes, 1996)



Effect of Fly Ash on Pore Solution Chemistry of Pastes with Admixed Chlorides (Thomas, Matthews & Haynes, 1996)



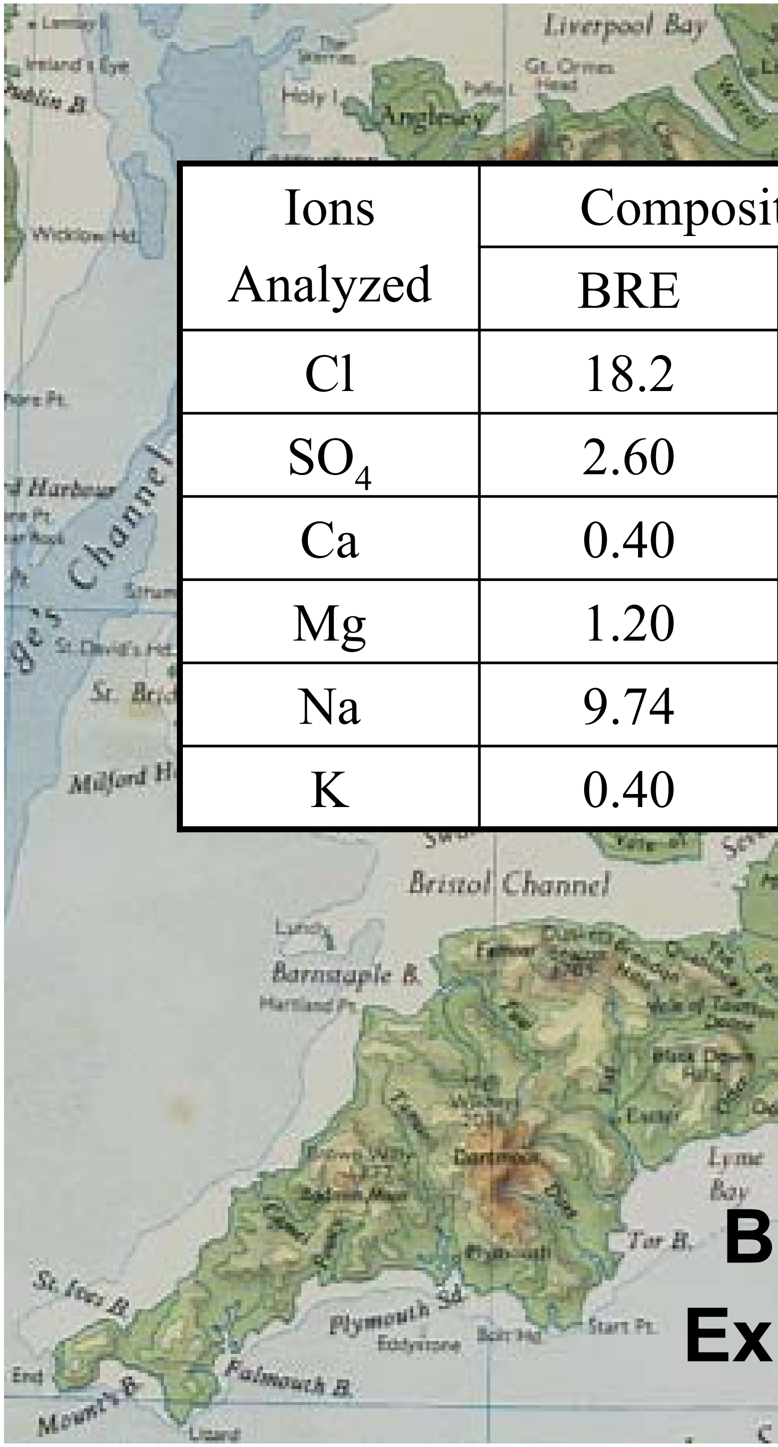
- Fly ash reduced both Cl^- & OH^- concentrations of the pore solution
- No consistent trend observed in the Cl^-/OH^- ratio with fly ash content
- At 0.4% chloride (by mass of binder) there is essentially no difference in the Cl^-/OH^- ratio regardless of fly ash content

Condition of Reinforced Prisms after 10 Years' Exposure Outdoors

Chloride (% PC + FA)	Fly Ash Content (% mass of total cementing materials)			
	0 (Control)	15	30	50
0.0	No evidence of corrosion on any specimens.			
0.4				
0.7				
1.0	Rust staining over all bars. Cracks > 1mm over bars with 10-mm cover. Cracks < 1mm over bars with 20-mm cover	Rust staining with hairline cracks (< 1mm) over bars with 10-mm cover only.	Minor rust staining over bars with 10-mm cover only. No cracking.	

No corrosion when Cl ≤ 0.70% by mass of binder

Plan to examine specimens again in May ~~2015~~ 2018

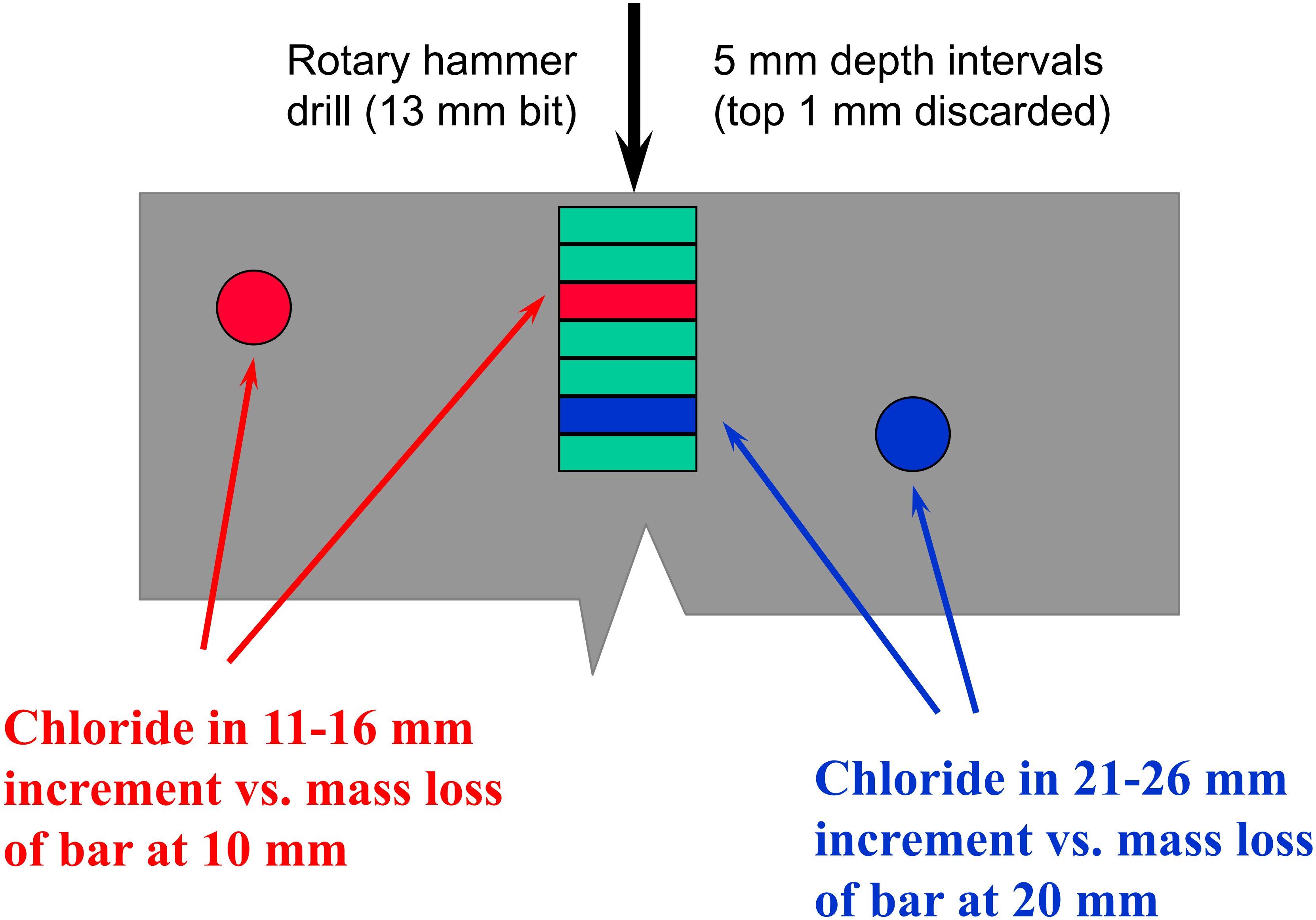


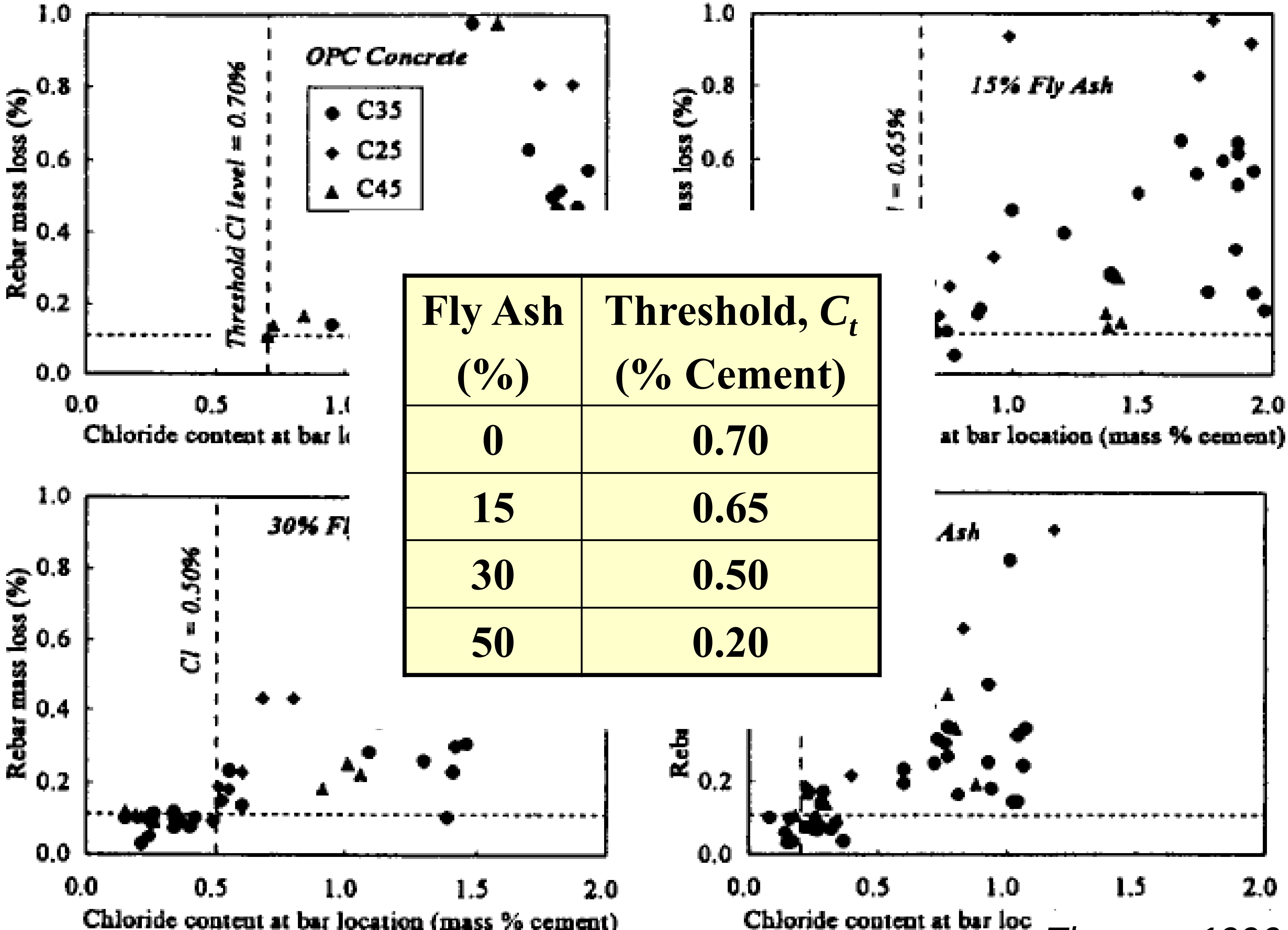
Ions Analyzed	Composit
	BRE
Cl	18.2
SO_4	2.60
Ca	0.40
Mg	1.20
Na	9.74
K	0.40

BRE Marine Exposure Site


MT 30
Marine Exposure
10 yrs.
MT 31

Threshold Chloride Content

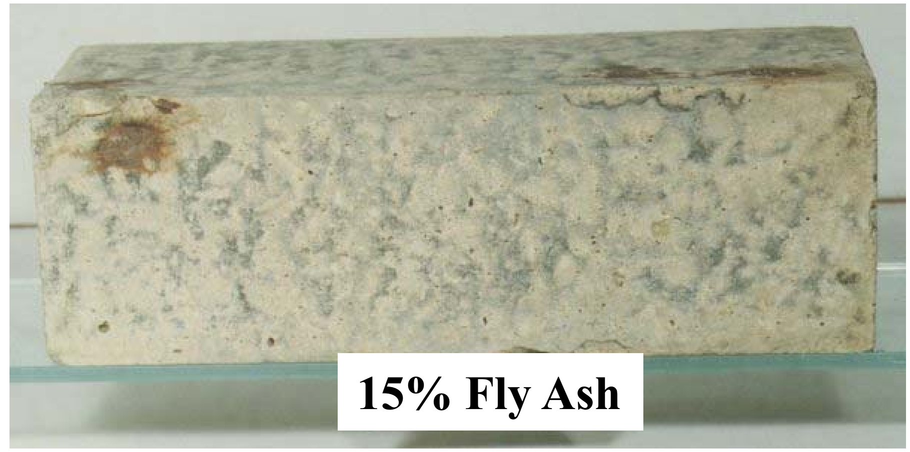




Fly Ash (%)	Threshold, C_t (% Cement)
0	0.70
15	0.65
30	0.50
50	0.20

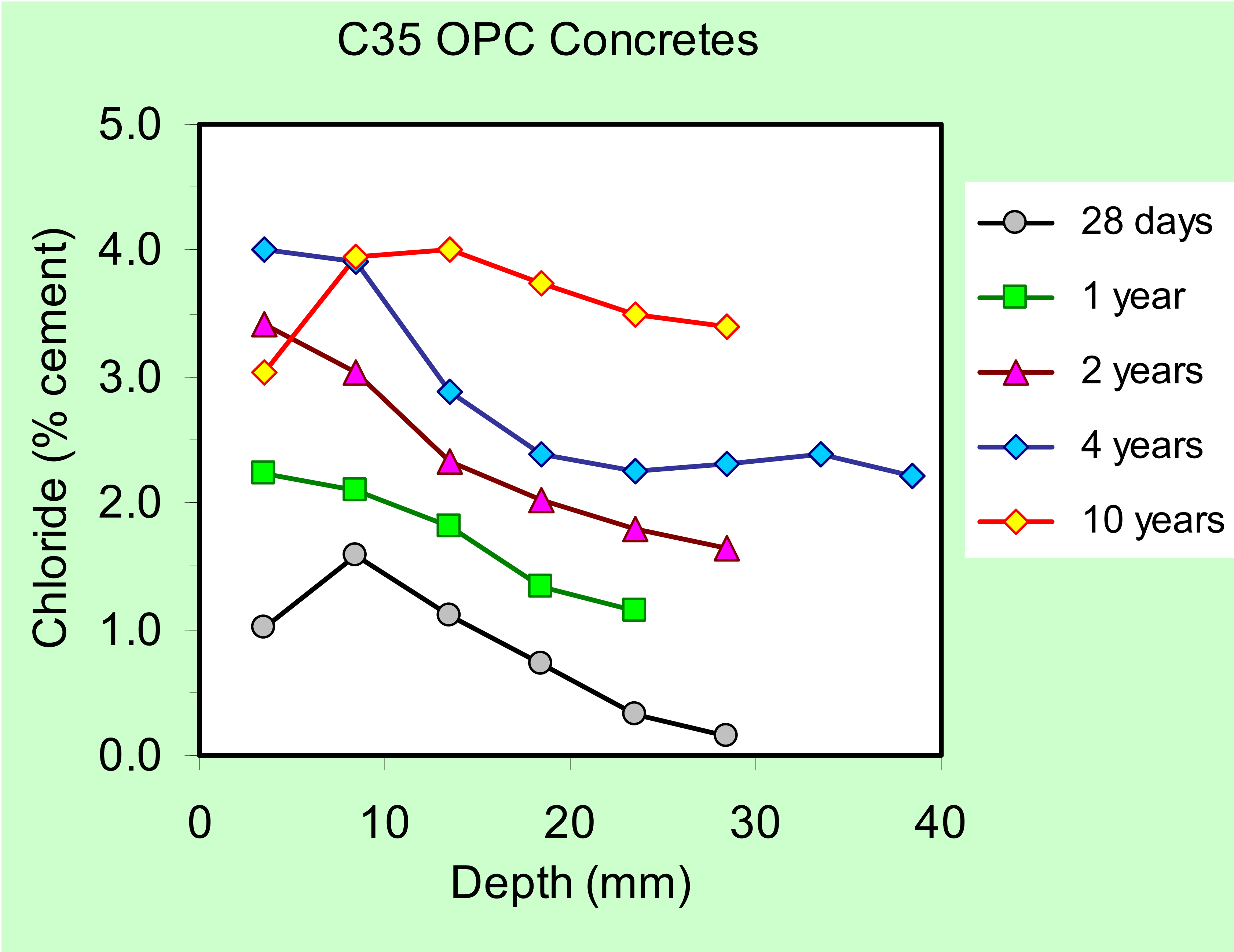
Thomas, 1996

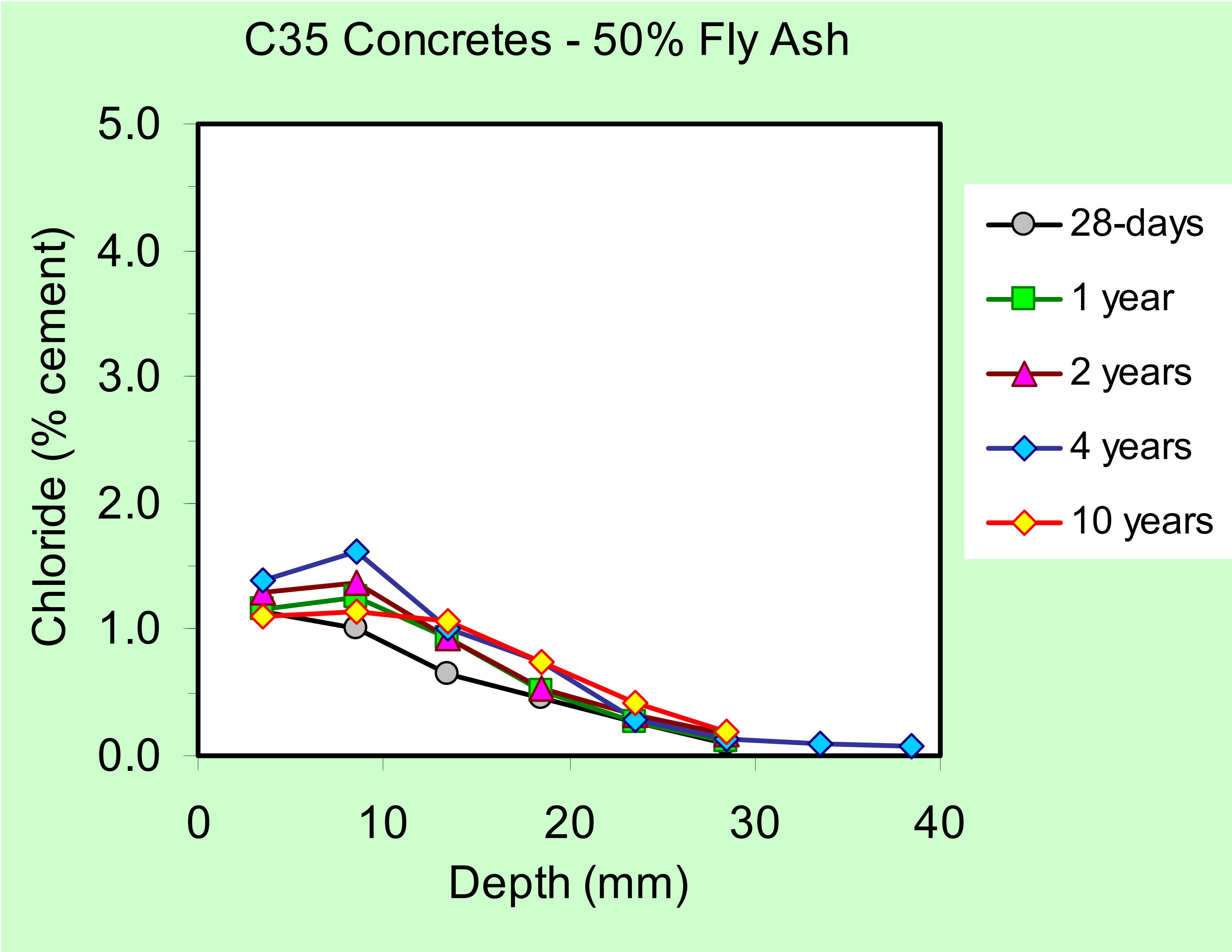
Condition of Reinforced Prisms after 10 Years' Exposure Outdoors



PC Concrete – significant corrosion of all rebar (with 10-mm & 20-mm cover) in all concrete samples

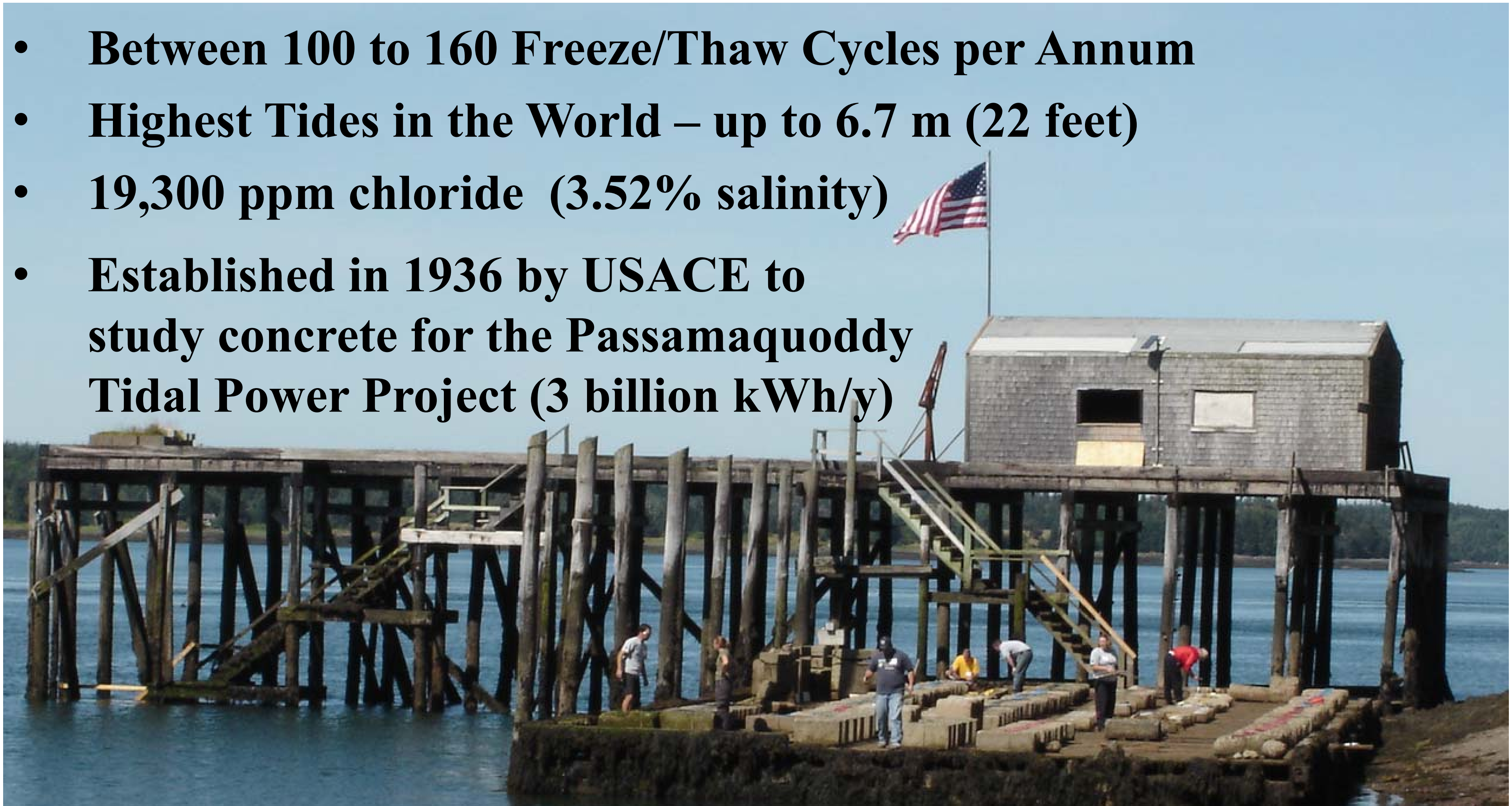
FA Concrete – minor corrosion signs but **only** for steel with 10-mm cover – no signs of corrosion for steel at 20 mm

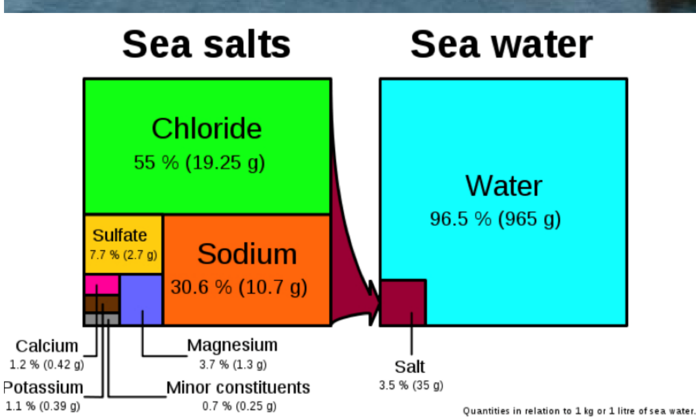

C35 OPC Concretes
Chloride (% cement)
0.0
1.0
2.0
3.0
4.0
5.0
0
10
20
30
40
Depth (mm)
28 days
1 year
2 years
4 years
10 years



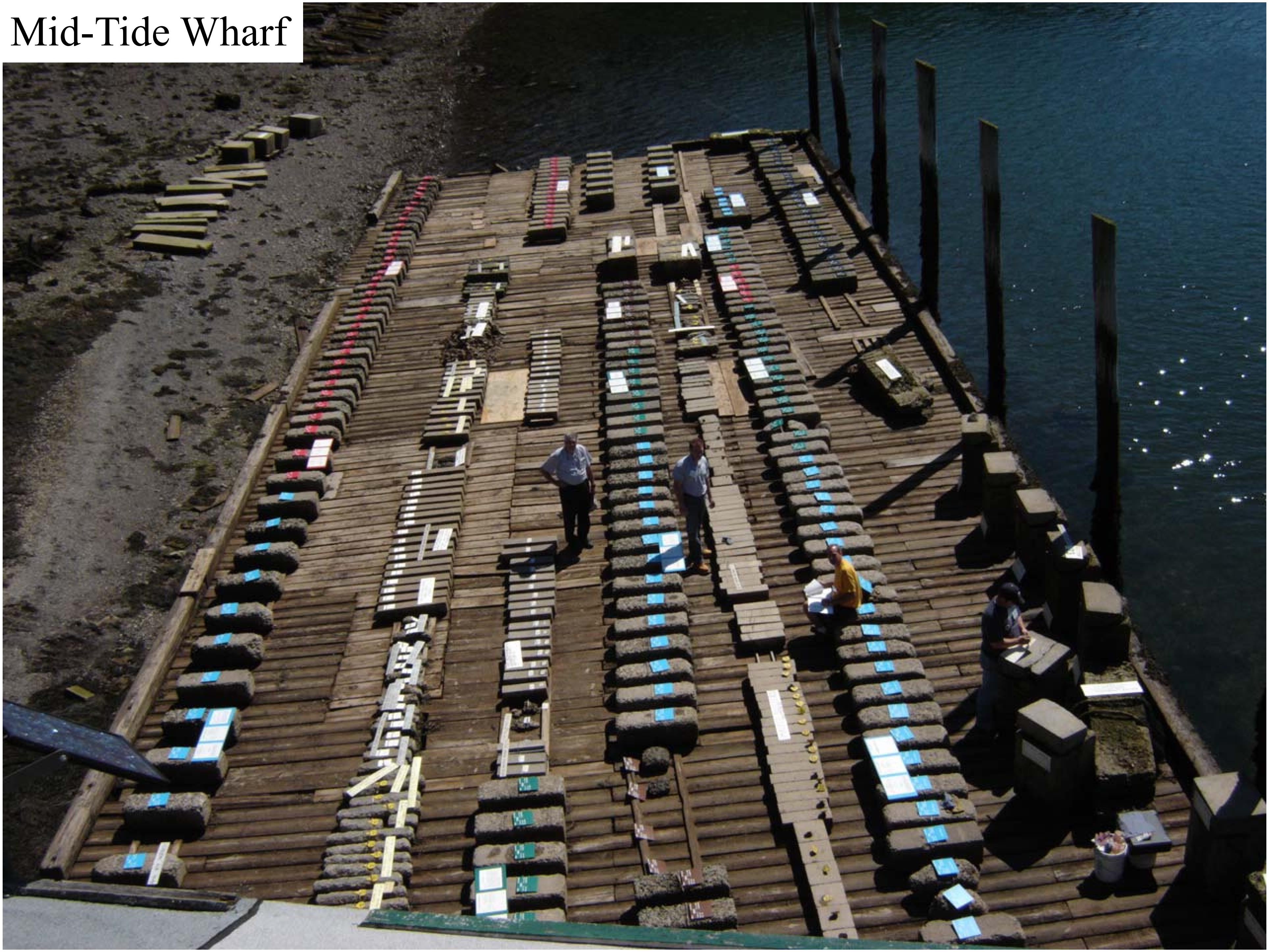
C35 Concretes - 50% Fly Ash
Chloride (% cement)
5.0
4.0
3.0
2.0
1.0
0.0
0
10
20
30
40
Depth (mm)
28-days
1 year
2 years
4 years
10 years

- **Between 100 to 160 Freeze/Thaw Cycles per Annum**
- **Highest Tides in the World – up to 6.7 m (22 feet)**
- **19,300 ppm chloride (3.52% salinity)**
- **Established in 1936 by USACE to study concrete for the Passamaquoddy Tidal Power Project (3 billion kWh/y)**





Mid-Tide Wharf



Over 80 years studies have included:

- fibre-reinforcement
- polymer-impregnation
- supplementary cementing materials
- portland-limestone cement
- sulfur concrete
- high-alumina cement
- ettringite-based rapid-set binders
- w/cm and strength
- ultra-high-performance concrete
- corrosion-resistant reinforcement
- impact of load and cracking
- “mechanical air-entrainment”
- corrosion-inhibiting admixtures
- alkali-aggregate reaction


SECTION 112 - 2006
PERMEABLE CONCRETE BASE
R3

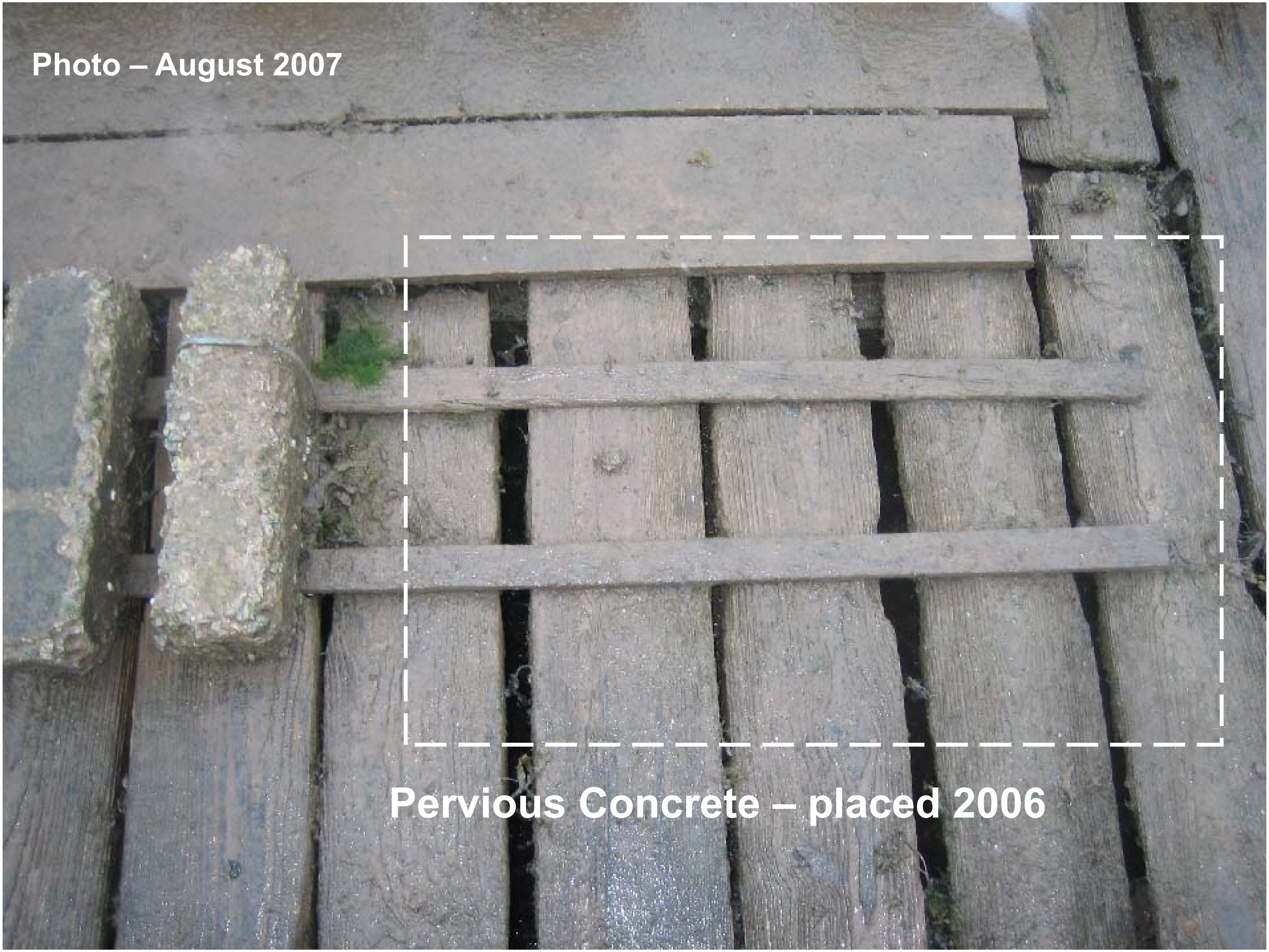


Photo – August 2007
Pervious Concrete – placed 2006


CM 1 3 5 7
INCH 1 2 3

In Summer 2003: Started to retrieve blocks with a wide range of SCM as they reached an age of 25 years.

CANMET Test Program at Treat Island

Phases I to VII (1978 – 1986)

Phase I	1978	✓	0 to 65% Slag
Phase II	1979	✓	Binary blends with Fly Ash Ternary blends with Fly Ash & Slag
Phase III	1980	✓	0 to 65% Slag with LWA
Phase IV	1981	✓	0 to 25% Fly Ash
Phase V	1982	✓	0 to 80% Slag 0 to 20% Silica Fume (AE & Non-AE)
Phase VI	1985	✓	Ternary blends with Silica Fume & Fly Ash with & without fibers
Phase VII	1986	✓	Silica Fume with LWA (Truck Mixed)

✓ = specimens retrieved and tested

Malhotra & Bremner, 1996

CANMET Test Program at Treat Island

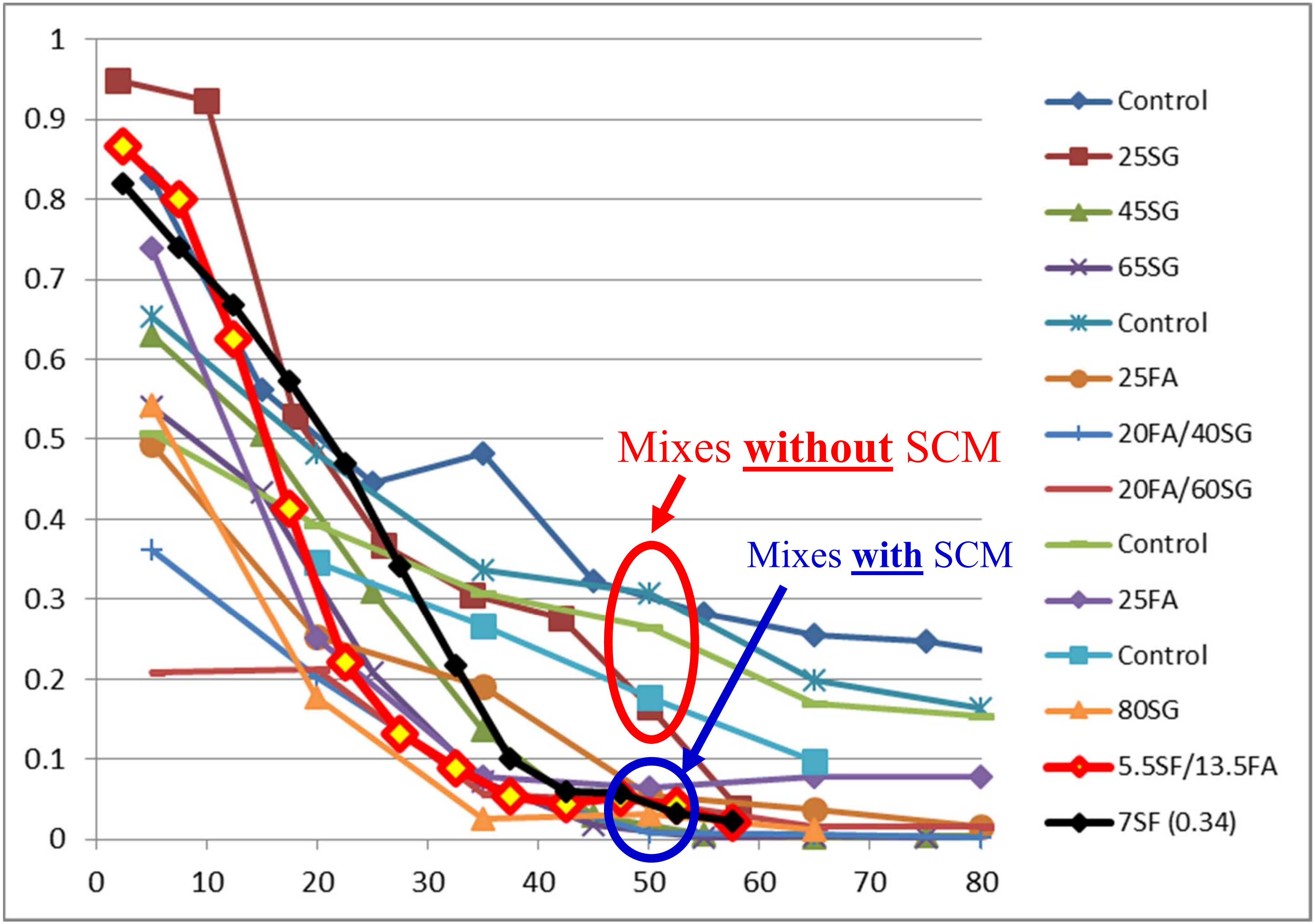
Phases VIII to XIV (1987 – 1994)

Phase VIII	1987 ✓	High-Volume Fly Ash Concrete (56% FA)
Phase IX	1988 ✓	Steel reinforced concrete with Fly Ash, Slag & Silica Fume
Phase X	1989 ✓	Silica Fume with LWA (3 sources)
Phase XI	1990 ✓	HVFA Concrete with LWA (3 sources)
Phase XII	1991 ✓	Uncoated and epoxy-coated steel
Phase XIII	1992 ✓	HVFA Concrete – 8 fly ash sources
Phase XIV	1994	ASR prevention with fly ash and silica fume

✓ = specimens retrieved and tested

Malhotra & Bremner, 1996

25-Year Profiles: All Mixes (with W/CM = 0.40)



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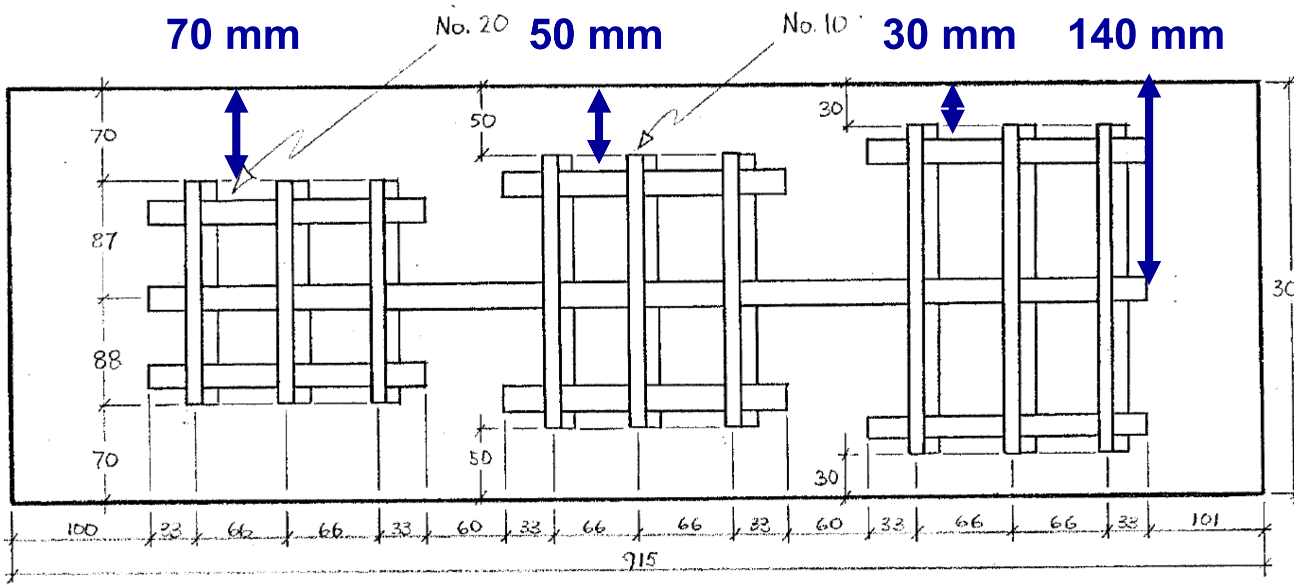
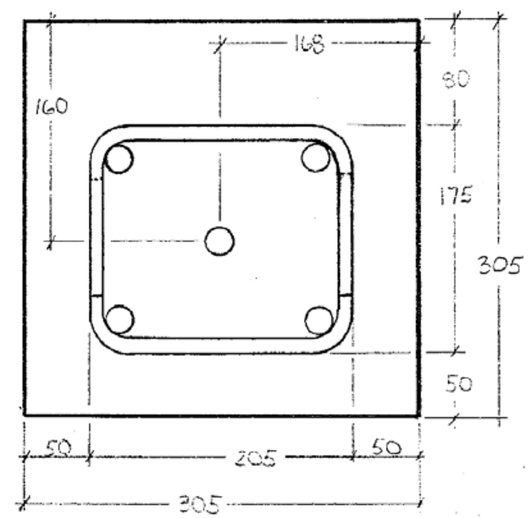
Acknowledgements

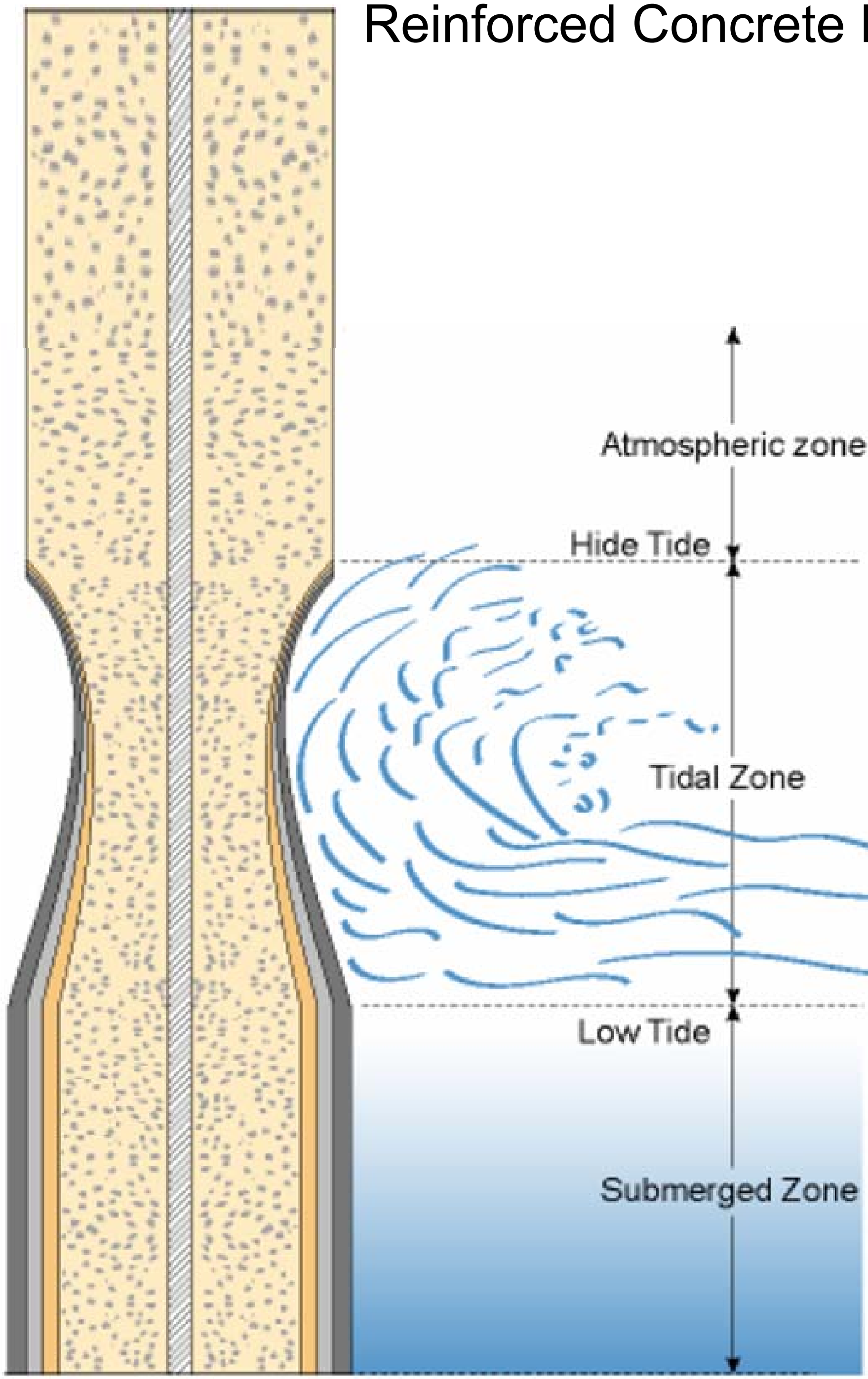
Reinforced-Concrete Samples placed in 1987

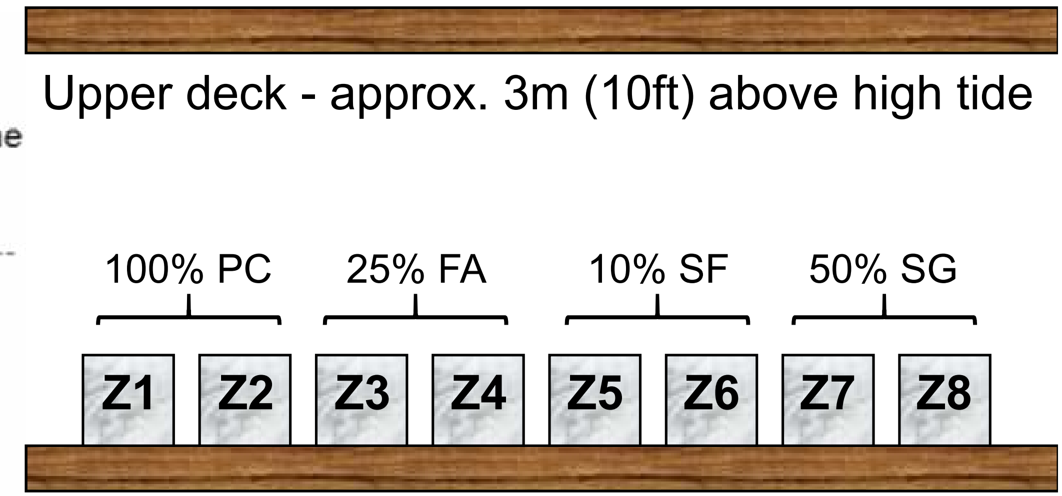




- Four concrete mixes
  - 100% Portland Cement (PC)
  - 25% Fly Ash (FA)
  - 10% Silica Fume (SF)
  - 50% Slag (SG)
- Steel bars with cover depths of:
  - 30, 50 & 70 mm
  - And 140 mm !
- W/CM = 0.50, Air = 6 to 7%, Slump = 75 ± 25 mm

Reinforced Concrete Blocks at Treat Island (CANMET Phase X)





- 1987 – 8 blocks placed at mid-tide
  - 100% Portland Cement (PC)
  - 25% Fly Ash (FA)
  - 10% Silica Fume (SF)
  - 50% Slag (SG)
  - W/CM = 0.50, Air = 6 to 7%

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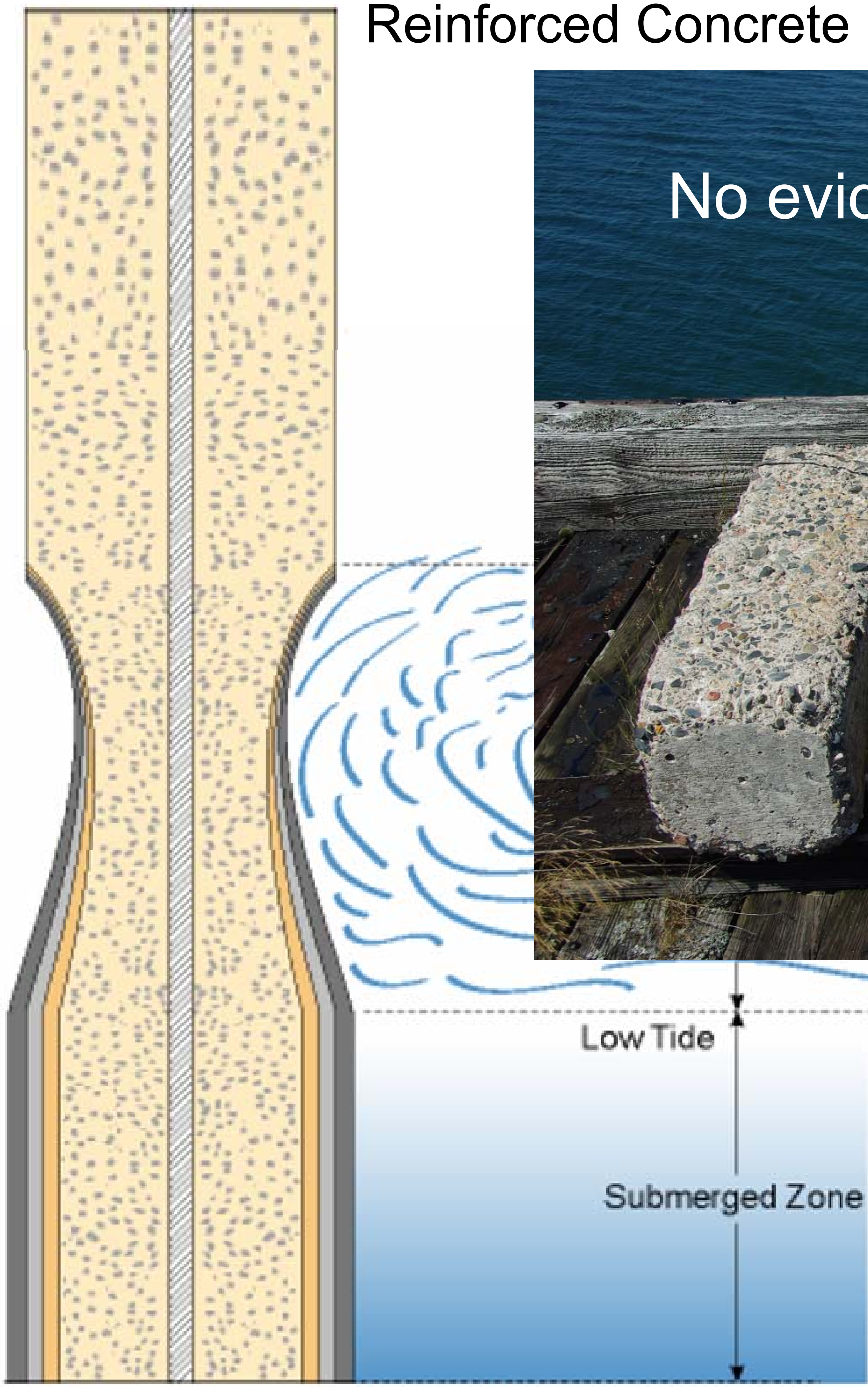
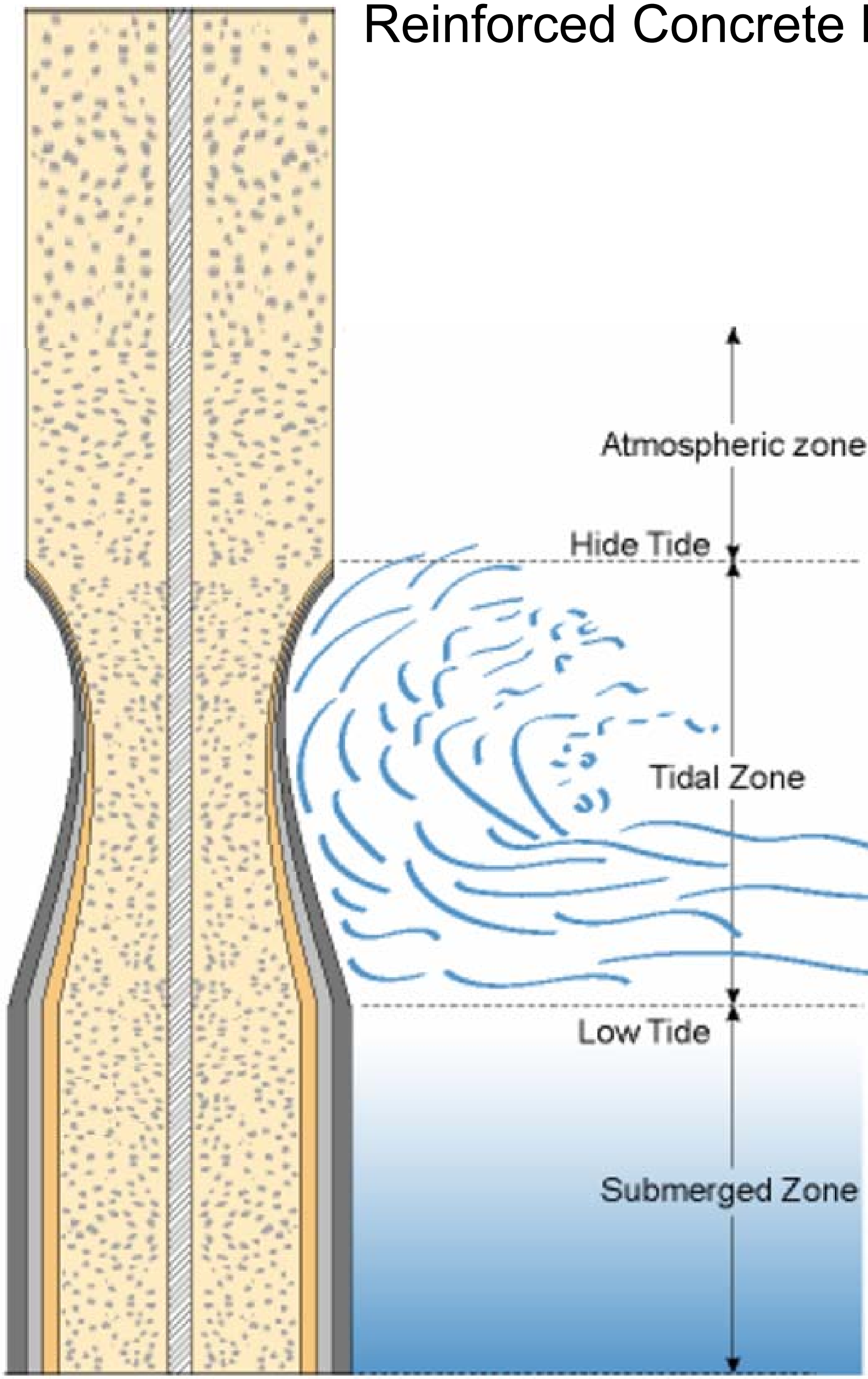
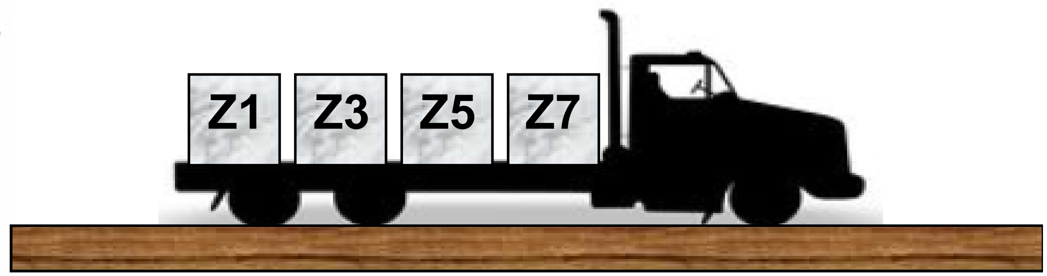


- 2007 – 4 blocks moved to upper deck

Reinforced Concrete Blocks at Treat Island (CANMET Phase X)



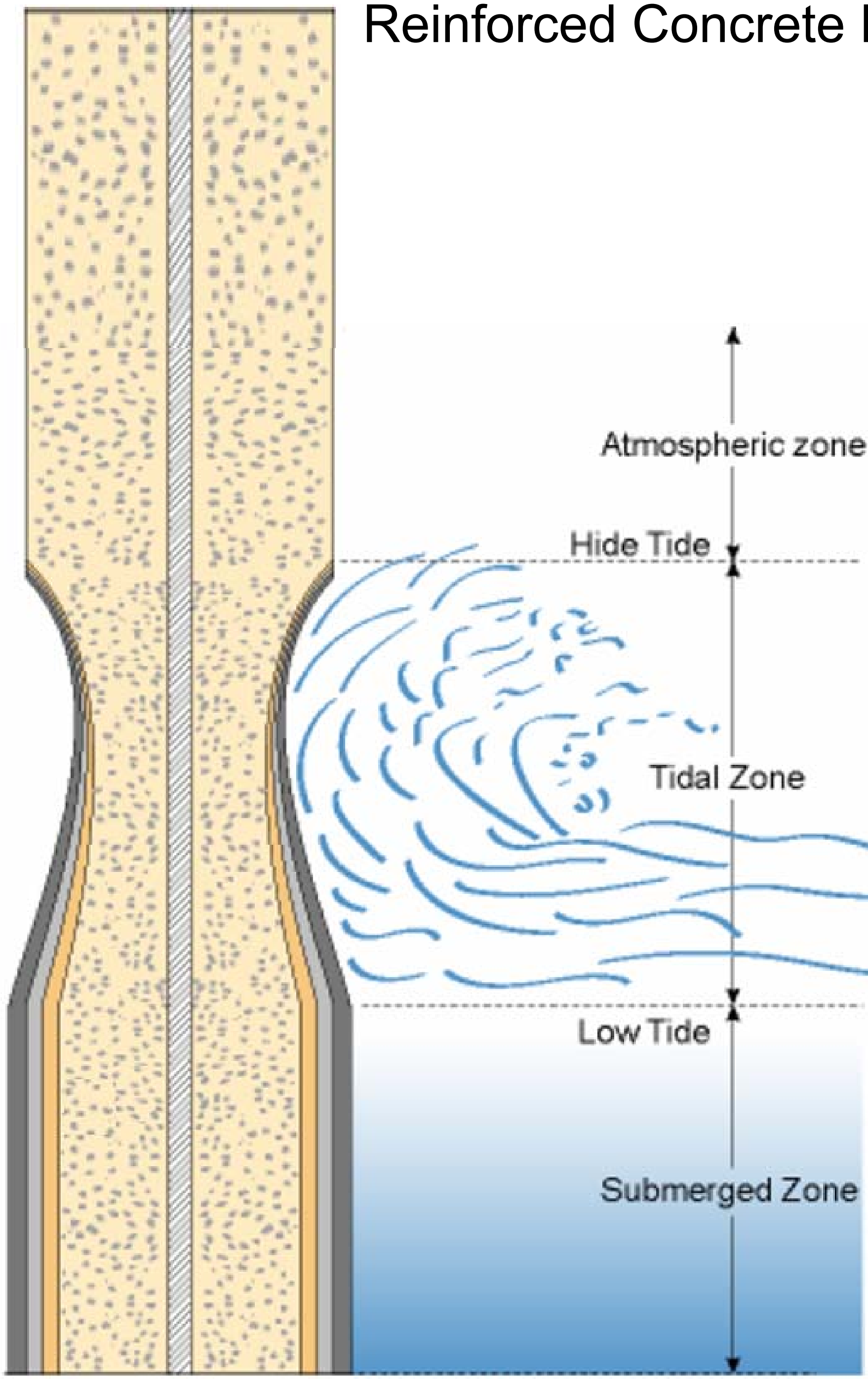
Upper deck - approx. 3m (10ft) above high tide

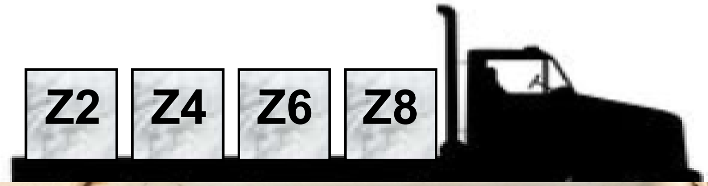


Mid-tide wharf

- 1987 – 8 blocks placed at mid-tide
- 2007 – 4 blocks moved to upper deck
- 2012 – blocks at mid-tide to UNB for chloride profiling

Reinforced Concrete Blocks at Treat Island (CANMET Phase X)



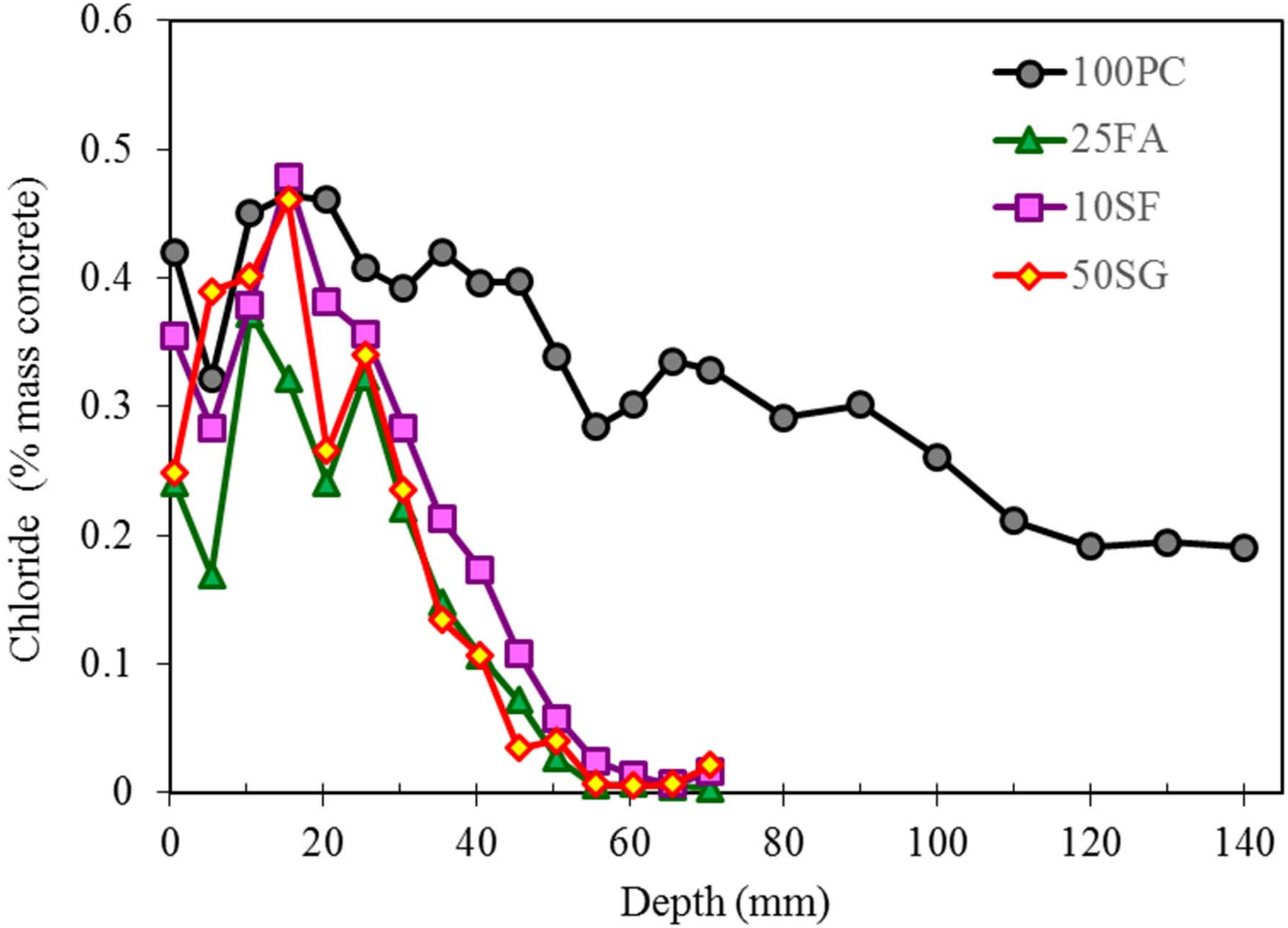


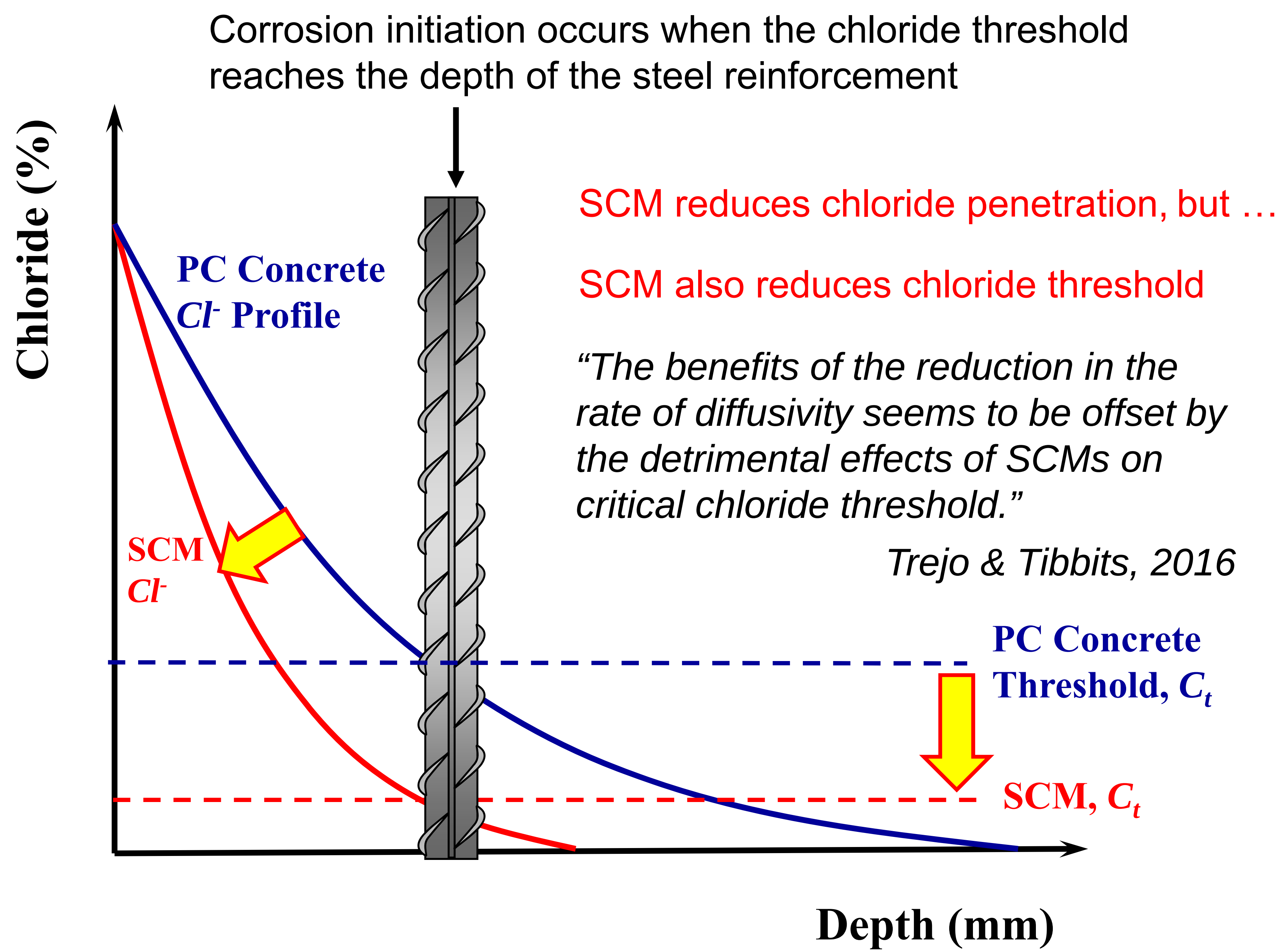
Uppe ... tide

Mid-

- 19
- 20 ... eck
- 20
- 20 ... UNB for corrosion measurements

Chloride Profiles after 25 Years in Marine Tidal Zone





Corrosion initiation occurs when the chloride threshold reaches the depth of the steel reinforcement
Chloride (%)
PC Concrete
Cl- Profile
SCM
Cl-
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"The benefits of the reduction in the rate of diffusivity seems to be offset by the detrimental effects of SCMs on critical chloride threshold."
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PC Concrete
Threshold, Ct
SCM, Ct
Depth (mm)

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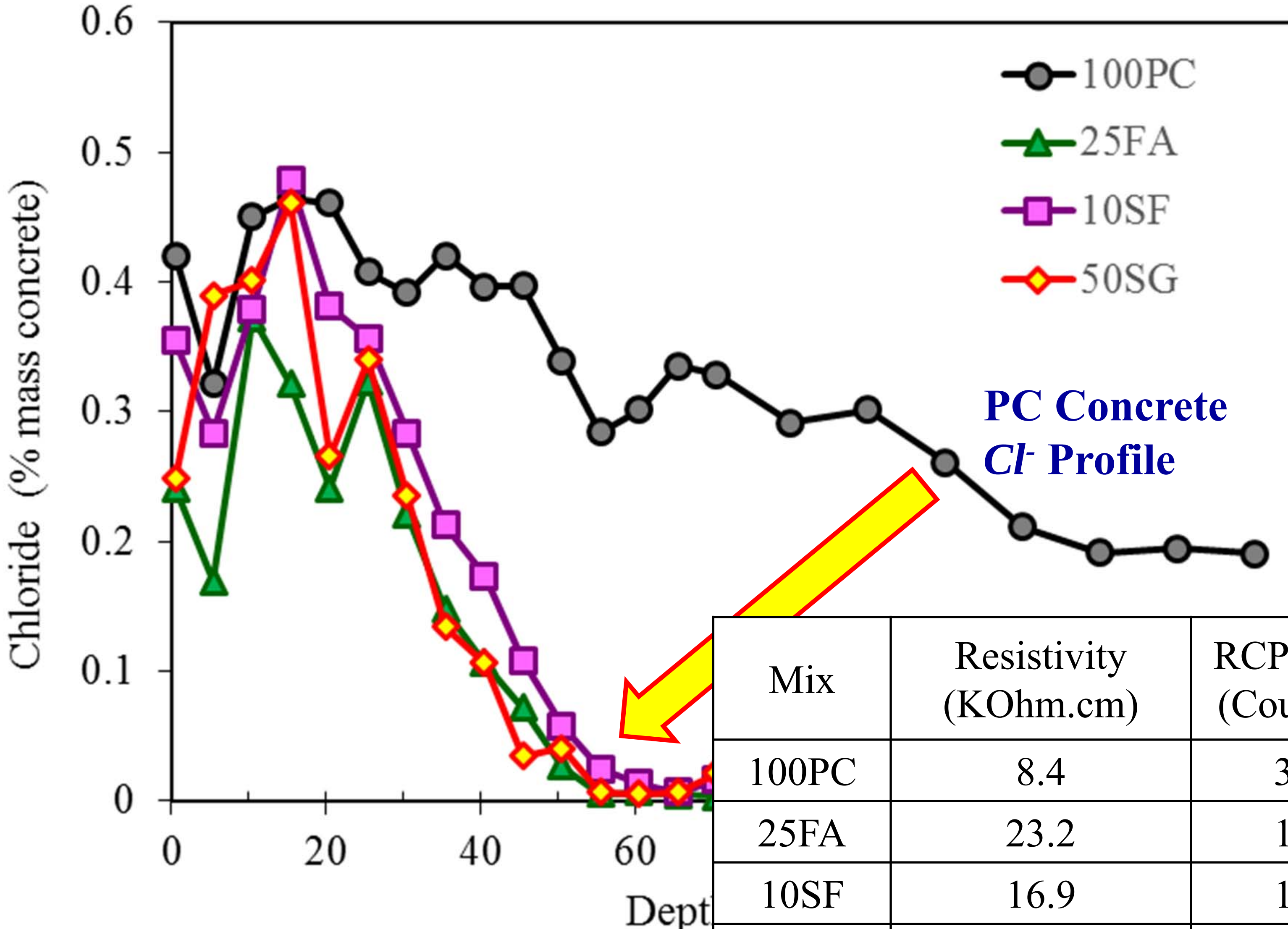
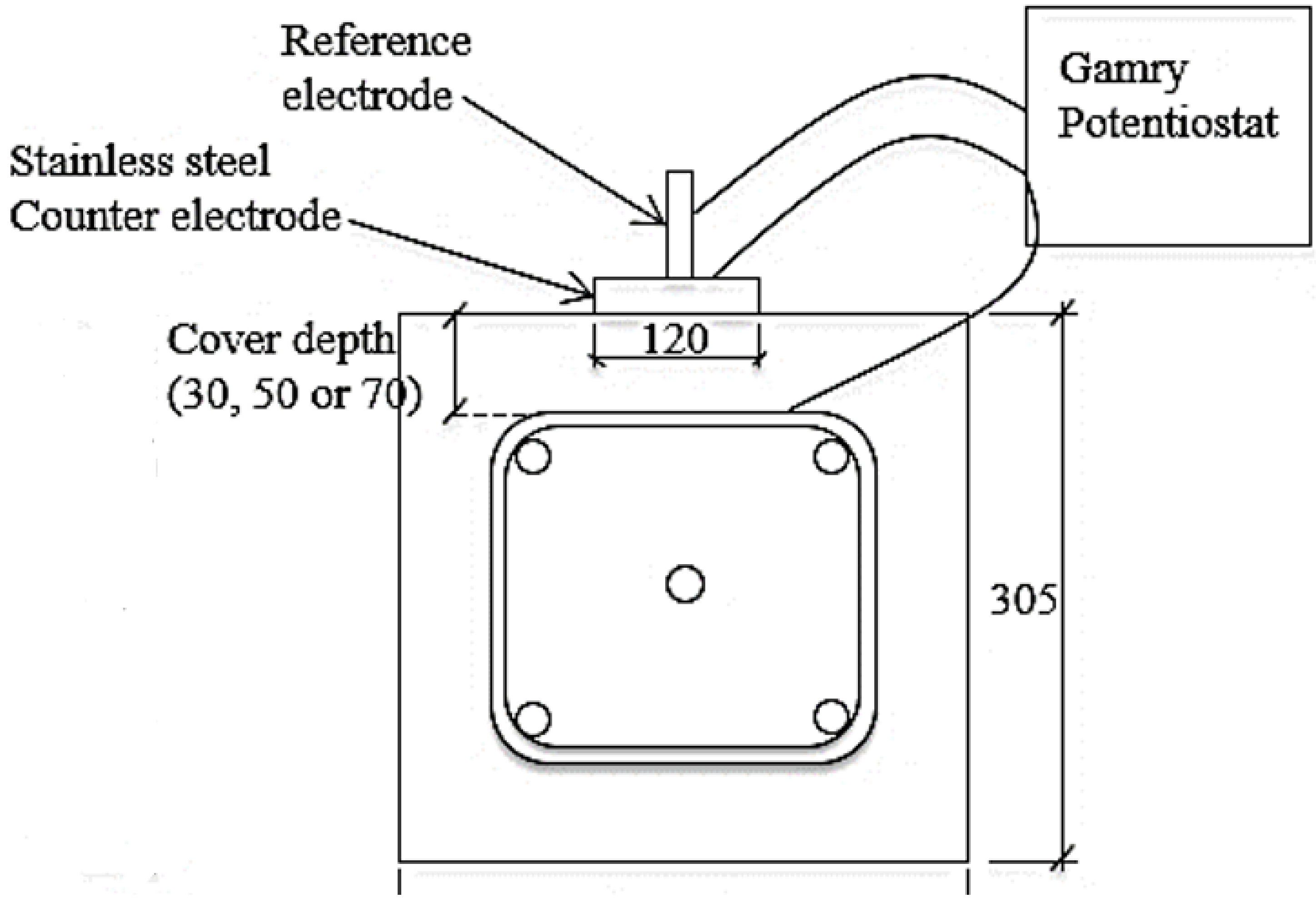
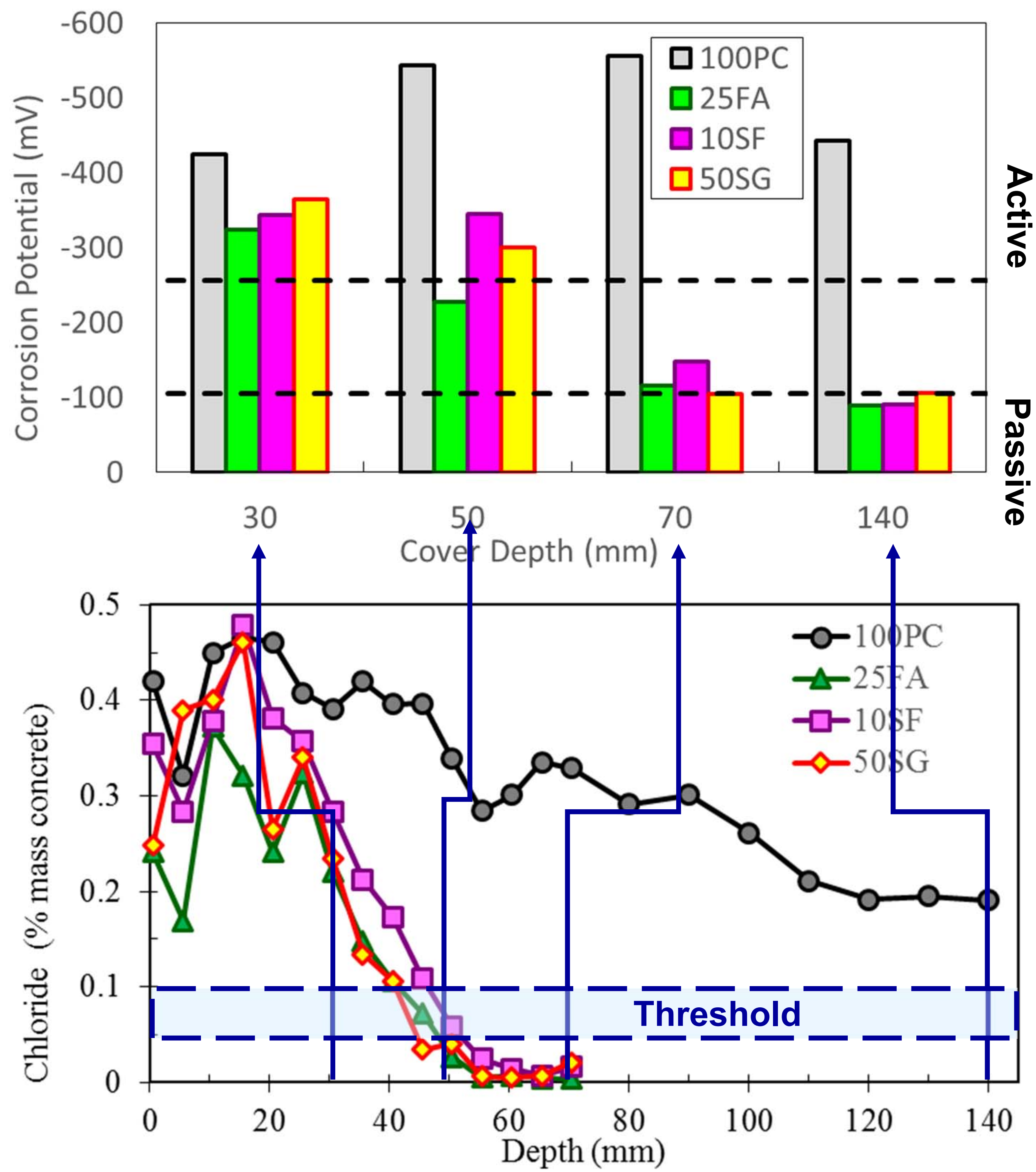


Mix	Resistivity (KOhm.cm)	RCPT Value (Coulombs)
100PC	8.4	3050
25FA	23.2	1230
10SF	16.9	1650
50SG	29.7	900


Reference
electrode
Stainless steel
Counter electrode
Gamry
Potentiostat
Cover depth
(30, 50 or 70)
120
305

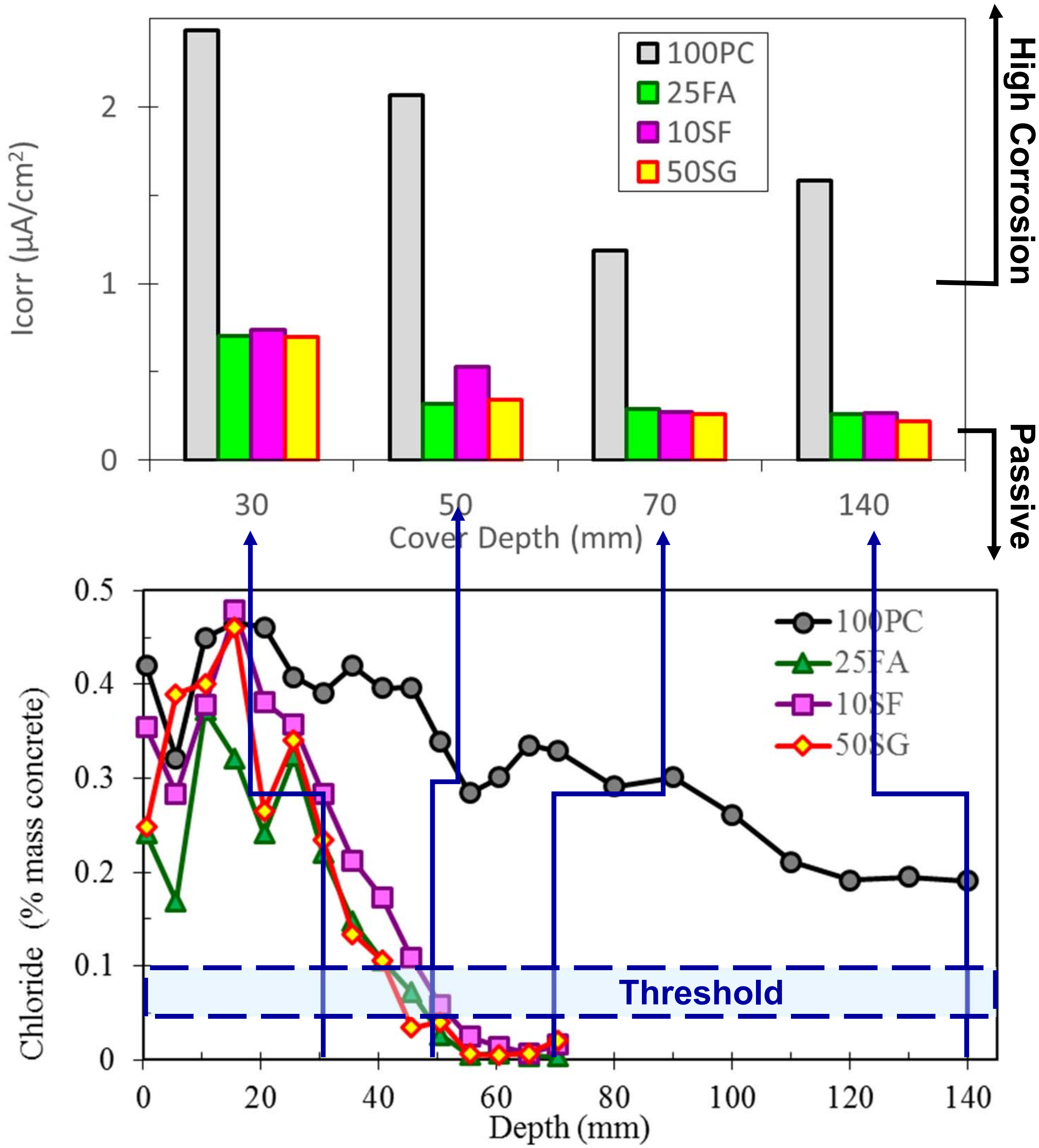
Half-Cell Potentials

Chloride Profiles

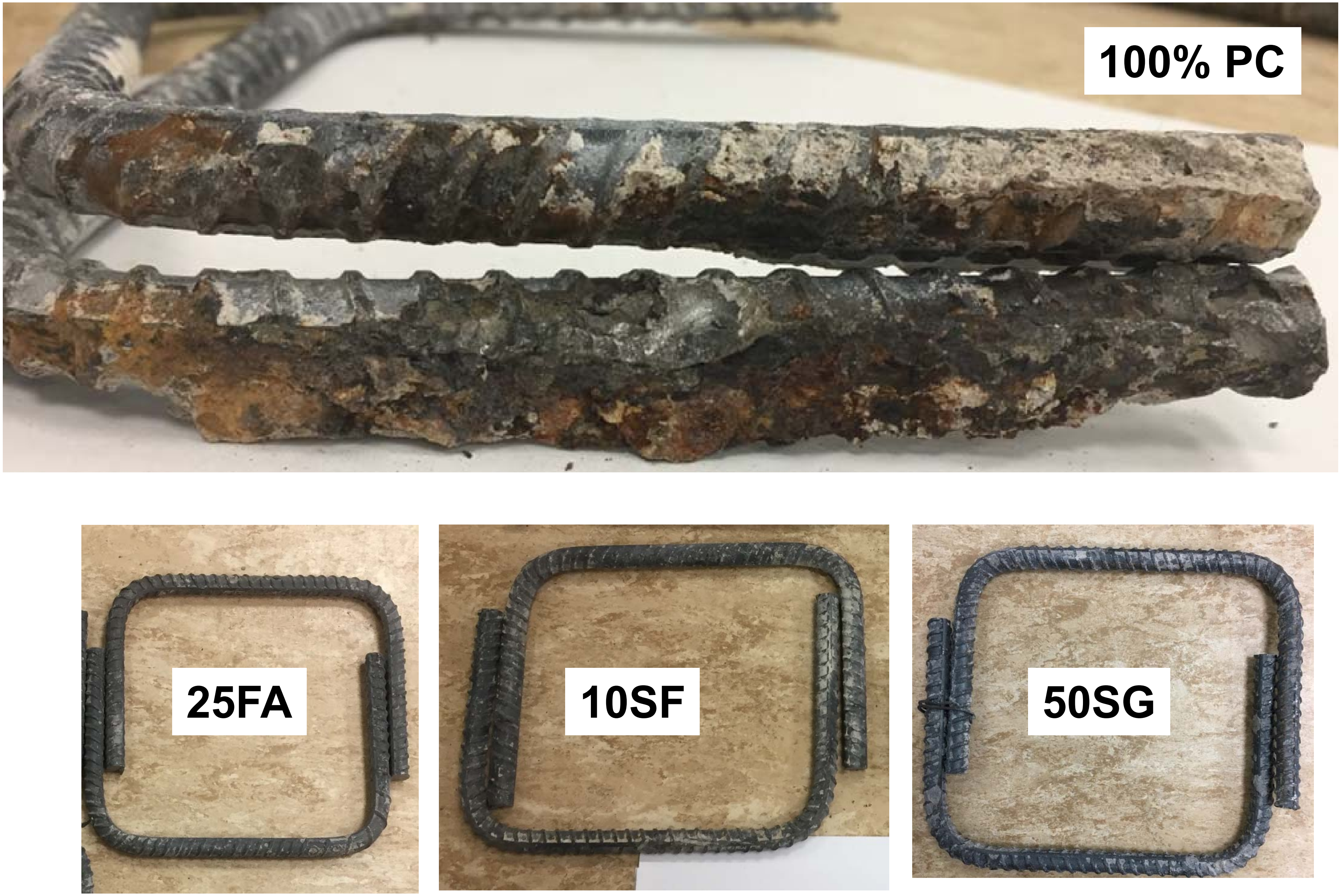


Linear Polarization Resistance

Chloride Profiles



Visual Condition of Steel with 70-mm Cover at 27 Years



Conclusions

- Data from long-term natural field exposure studies indicate that the **beneficial** effect of SCM's increasing chloride resistance substantially outweighs any detrimental effect of reducing the chloride threshold for corrosion.
- SCM's influence both the Cl^- and the OH^- concentration of the pore solution (generally reducing both) – the actual Cl^-/OH^- ratio may not be affected to any significant extent (similar differences in the ratio may be encountered with Portland cements of varying composition).
- Measuring transport coefficients and chloride thresholds at early ages in accelerated tests negates the long-term effects of SCM and likely leads to erroneous results
- Establishing realistic chloride concentration thresholds is critical for meaningful service life predictions. Need to develop appropriate methodology for determining chloride thresholds


Questions?

The  End