Modelling microbiologically influenced marine corrosion of steels

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Outline

- Why corrosion modelling and prediction
- Our overall approach
- Effect of microbiology on steel corrosion
- Importance of nutrient availability
- Examples:

  Accelerated Low Water Corrosion (ALWC)

  Mooring chains for FPSOs

  Water injection pipelines (WIPs)
- Outlook and conclusions

Motivation

- Structural engineers concerned with **safety** of physical infrastructure
- In marine environments: bridges, wharf structures, jetties, sheet-piling, ships, off-shore structures, pipelines ...
- Severe penalties, sanctions if things go seriously wrong….

- Increasing interest in “lifetime” management, durability, economics
- Most structures - life required: 25 - 100 years (typical)
- Nuclear structures, waste containers …. 100,000 years
- Main material: mild/structural steels
- Protective measures: coatings, CP: not always effective or feasible

- Increasing concern with older infrastructure, already corroded
- How ***safe*** is it now? How much ***longer*** will it last? => ***prediction***

Motivation - Prediction

- Anyone can ‘predict’ …. but at what accuracy?

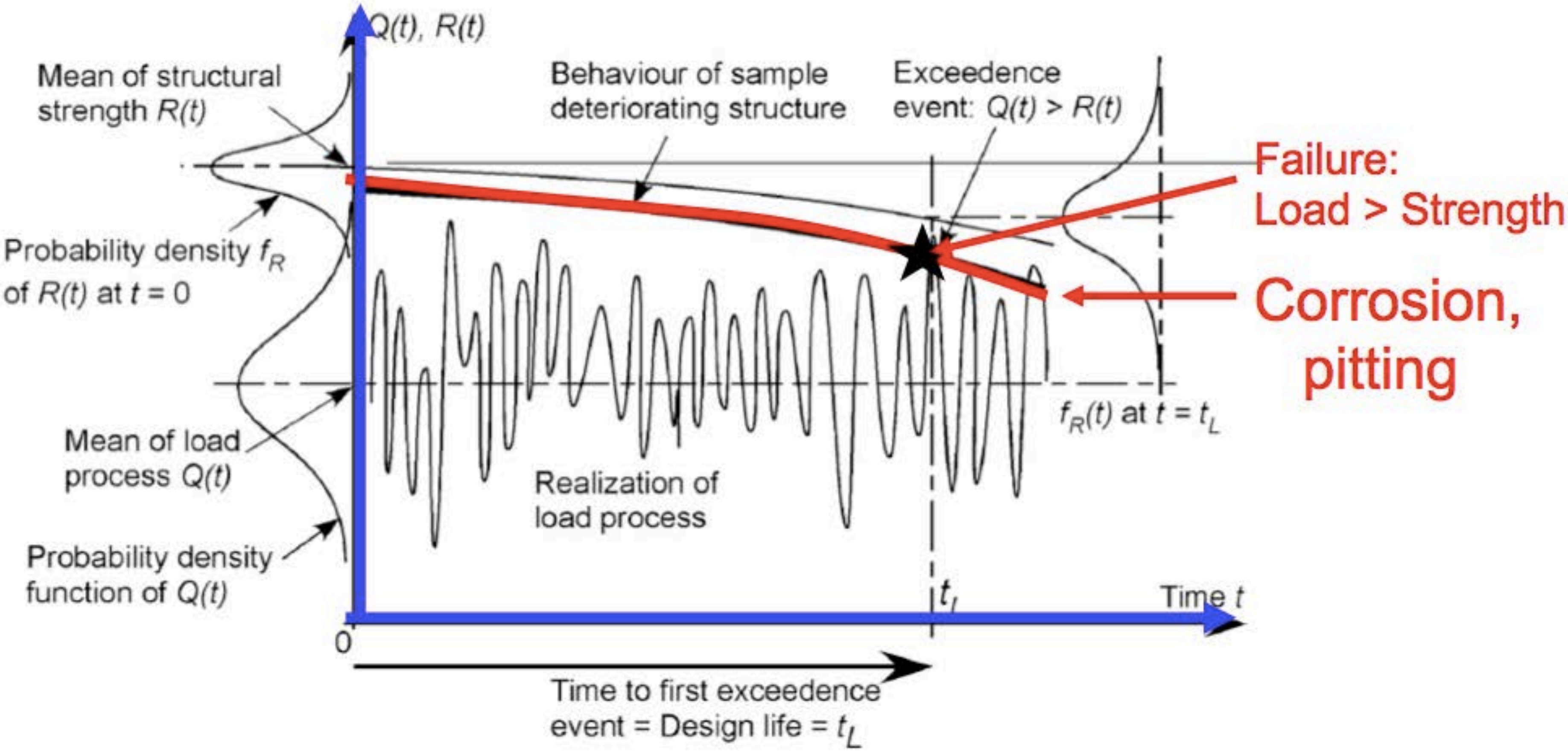
  (how to avoid ' *hocus pocus* '...)
- Engineers rely mainly on ***quantitative*** models (mathematical functions)
- Based on reality, *as currently understood* + calibrated to data
- Long, successful history - includes model up-grading

- Models for loading and demands *Q* ✔
- Models for strengths, capabilities *R* ✔
- Models for ***deterioration*** - e.g. **marine corrosion** ***- in progress***
- Corrosion literature: typically:

  - "high/medium/low" corrosion "risk" .... *means what?*

  - ranking A < B < C etc.
- Not sufficient for structural engineering: need ***quantitative prediction***

Loads, resistances and deterioration



- Need a functional relationship between corrosion $R(t)$ and t and influences => need $c(t)$
- Influences potentially include microbiological influences …

Microbiologically Influenced Corrosion (MIC)

- MIC ***may be*** involved in marine corrosion of steels
- MIC often is the (practitioner's) excuse of “last result”
- Typically because *unexpected severe* corrosion, pitting observed
- Plus bacteria detected in rusts – SRB, IOB, IRB, MOB …..
- Sometimes rusts removed to reveal yellow, black ‘rusts’
- ‘rotten egg’ smell = H_2S
- Usual inference = MIC is occurring…
- ***How much is actually MIC?***



Investigation approaches for MIC

1. Traditional = Tests in small laboratory containers

- Usually a mono-culture + doping with a nutrient – days, weeks, months

2. Electrochemical (laboratory) tests:

- Accelerate rate of Fe dissolution (anodic reaction)
- Cannot accelerate: *diffusion* or *bacterial metabolism*.
- Short-term => Interpretation = problematic

3. Our Approach

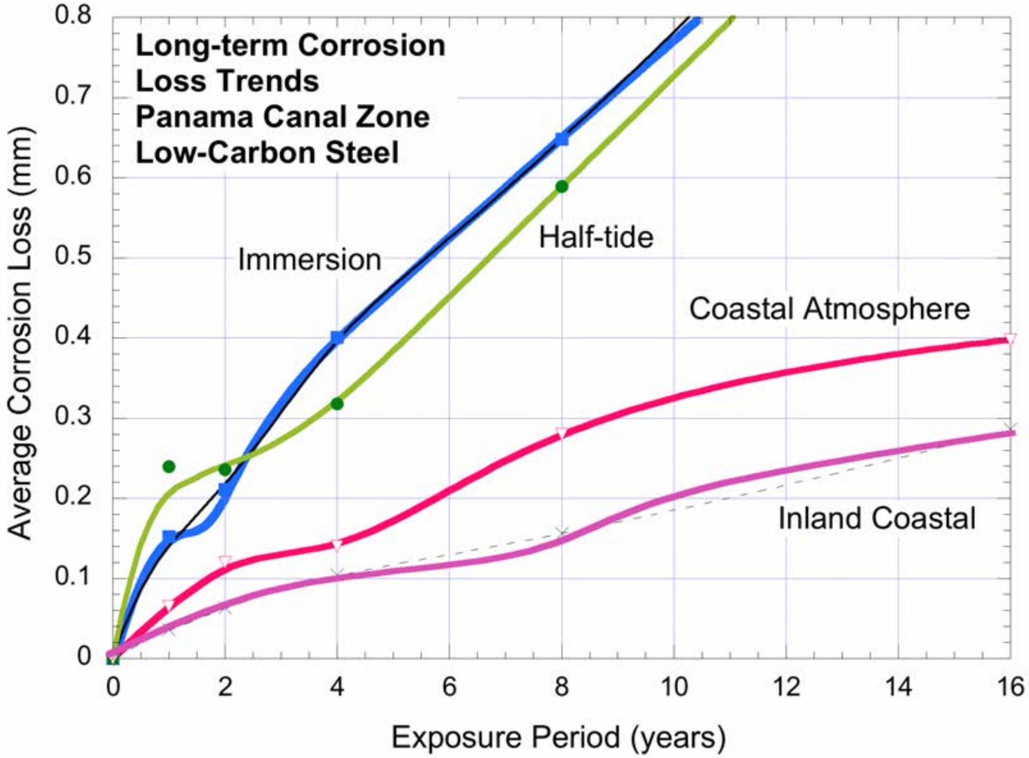
- Build "***environmental input - corrosion output***" relationships
- *By-passing detailed microbiology*
- ***Basic assumption:*** *nutrient availability = rate limiting step*
- Validity?
- How do we build models **including MIC?**

Building models for marine corrosion

- ***Start with observations of what happens in real life …***
- Interested in long-term corrosion – few data sets …

- ***Best set:*** Panama Canal Zone data = Tropics x 16 years
- Immersion, tidal, atmospheric exposure zones
- Mild, low alloy, Cu-bearing,
- weathering, stainless steel
- Many other metals

- **Trends**
- Complex non-linear behaviour
- Not a corrosion 'rate'.
- Rationale for this behaviour?
- Must be consistent with theory



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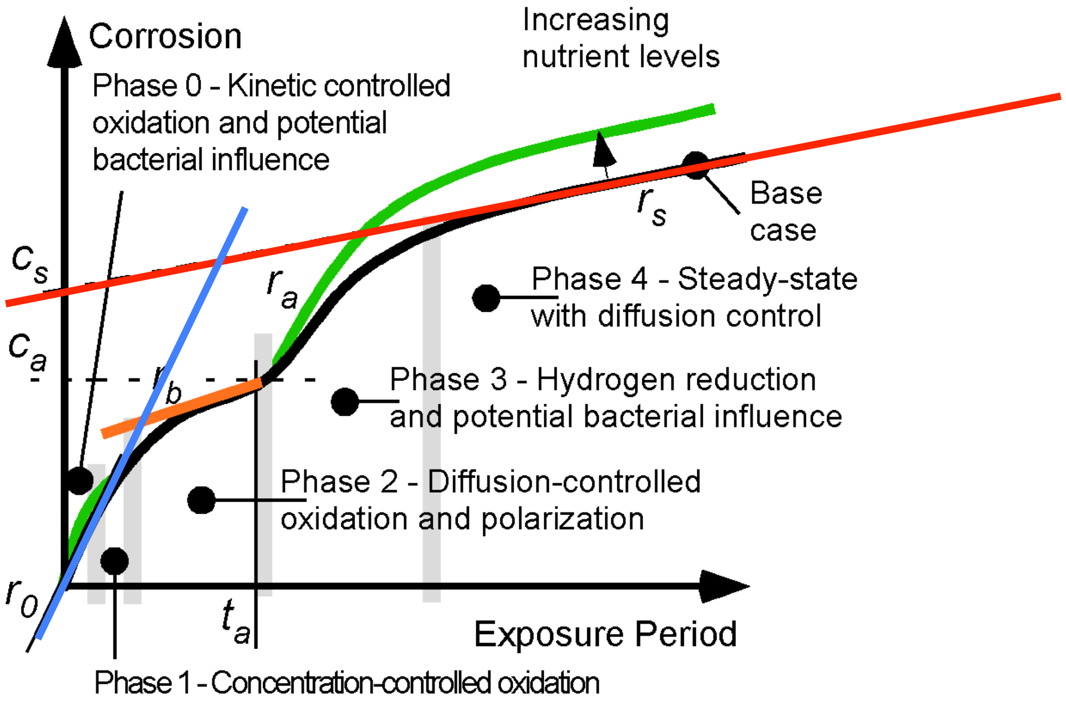
Model for corrosion of steel in seawater (2003)



Long-term corrosion rate defined by c_s and r_s

Initial rate = r_0 (phase 0) - over-predicts

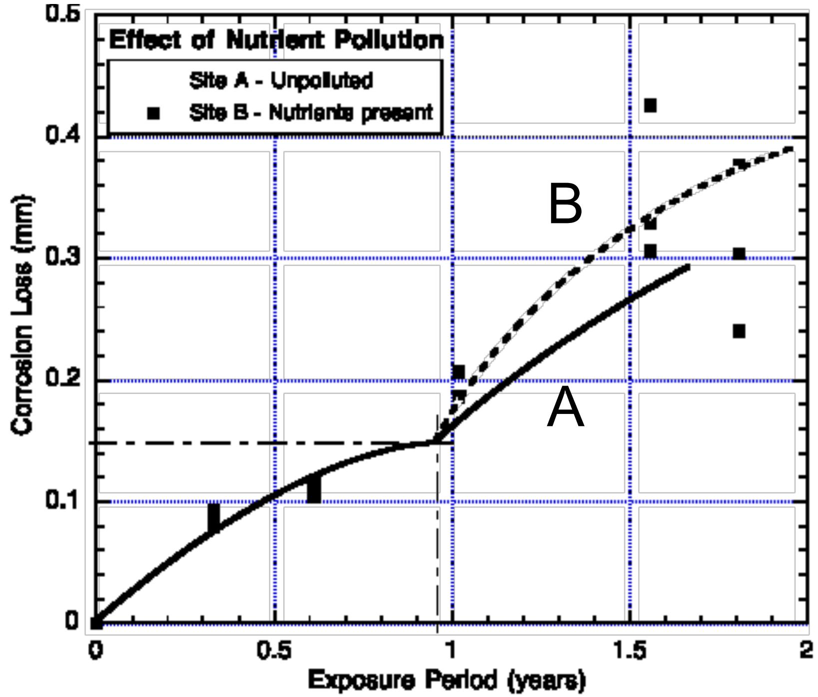
Similar trend for pit depth

- Based mainly on diffusion requirements -> ***mathematics*** ✓
- *Sequential* phases 0 – 4: ***different rate-controlling processes***
- Calibrated to field observations: special new data and literature data
- Factors already considered include oxygen, rust build-up, temperature, salinity, velocity, water depth, alloying, …. *see literature*
- **MIC** – early, but most significant effect in phases 3 & 4 … basis?

Field observations

Examples:

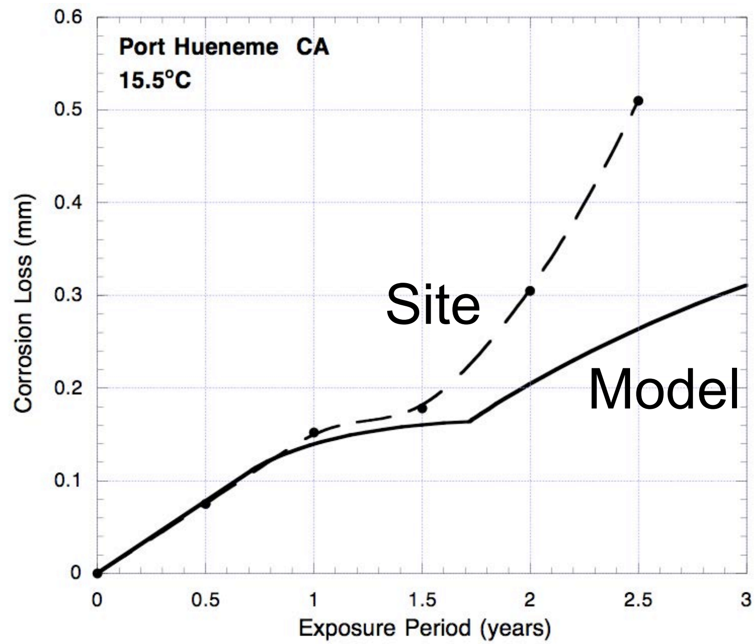
- Two sites on Pacific Ocean, Australia
  - superficially similar, 100 km apart
  - site A – coastal seawater
  - site B – bay: water quality testing - high nitrates and phosphates from nearby *agriculture fertilizer* run-off



- Port Huemene CA.
  - direct evidence of water quality difficult to find but ...
  - anecdotal comments by surf-riders

"…sometimes you have to paddle across filthy water to get out to the line-up' … and 'brown coloured effluent' from a local waste-water treatment plant "

(Wannasurf 2003).



Revision: nutrients for MIC of steel in seawater

Nutrients necessary for bacterial metabolism:

- sulfates - abundant in seawater
- phosphates, phosphorous – abundant, unlikely to be limiting
- organic carbon - almost certainly available in coastal seawater
- ferrous ions (Fe^{2+}) – Micro-nutrient - usually limiting in seawater

  but available from ***corrosion of steel*** $Fe \rightarrow Fe^{2+} + 2e^-$
- ***inorganic*** nitrogen – very limited presence in seawater

  => ***critical nutrient*** (Carlucci 1974, Postgate 1984)

  \- sources: ***nitrate***, nitrite, ammonia (Dissolved Inorganic Nitrogen)

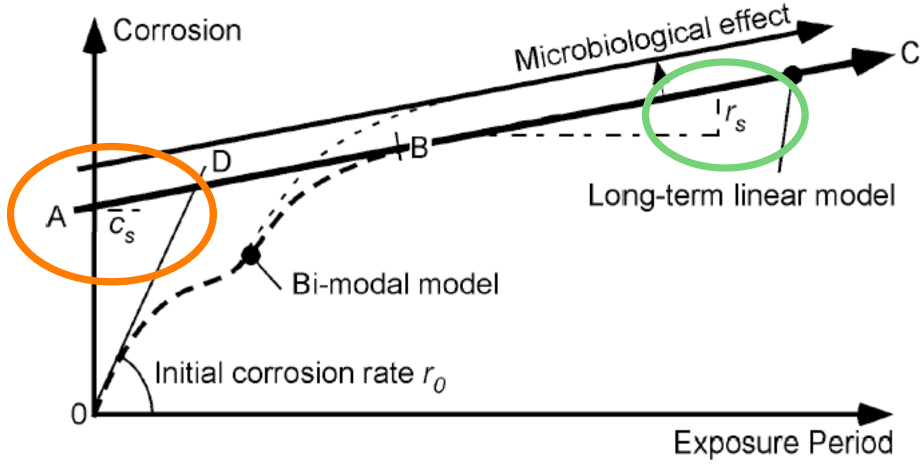
Our approach:

- Compare corrosion (incl. MIC) with availability of critical nutrient - DIN

DIN and long-term corrosion

- Field data from multiple sources
- DIN from water quality reports
- Effect on corrosion: DIN changes model parameters c_s and r_s
- Temperature remains important

See: Corros. Sci. (2014)



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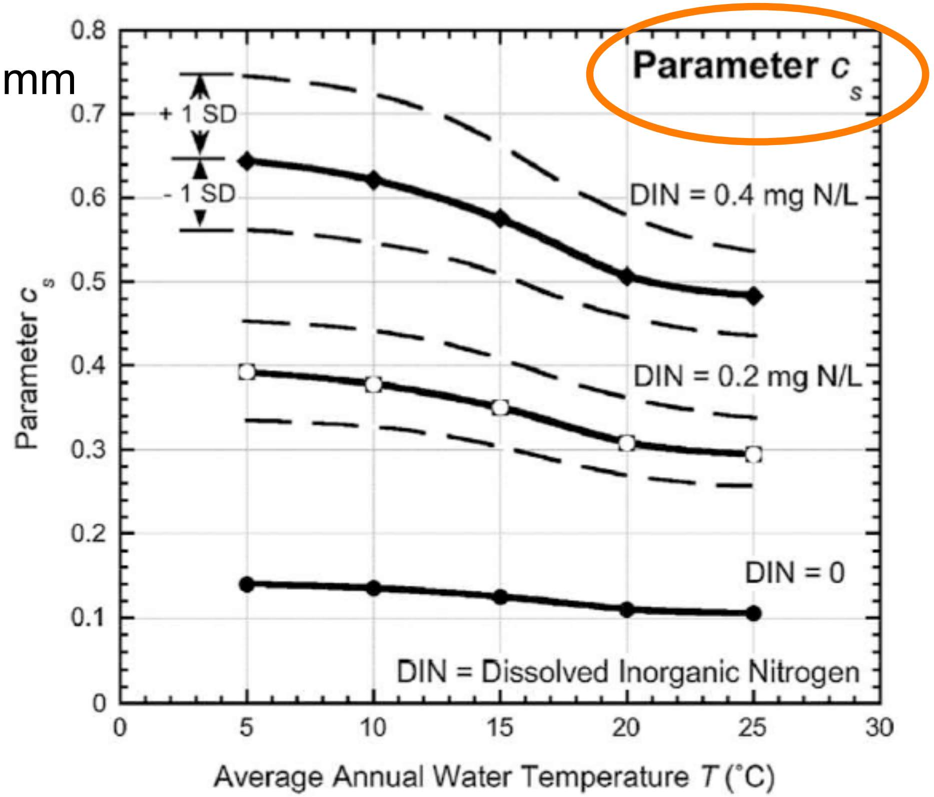

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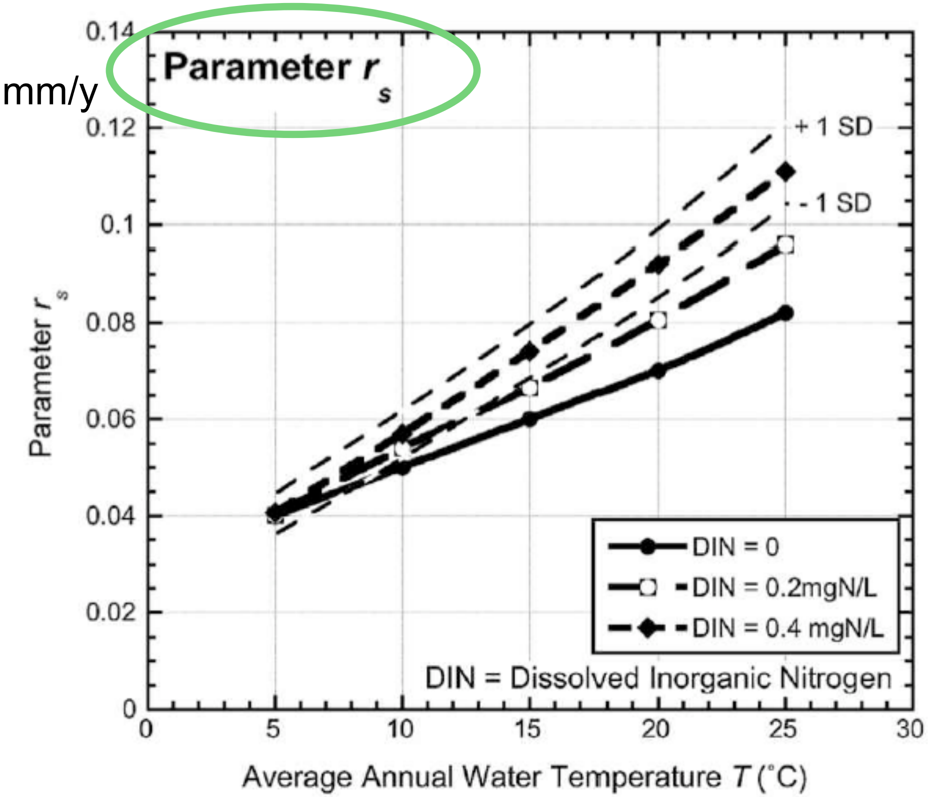


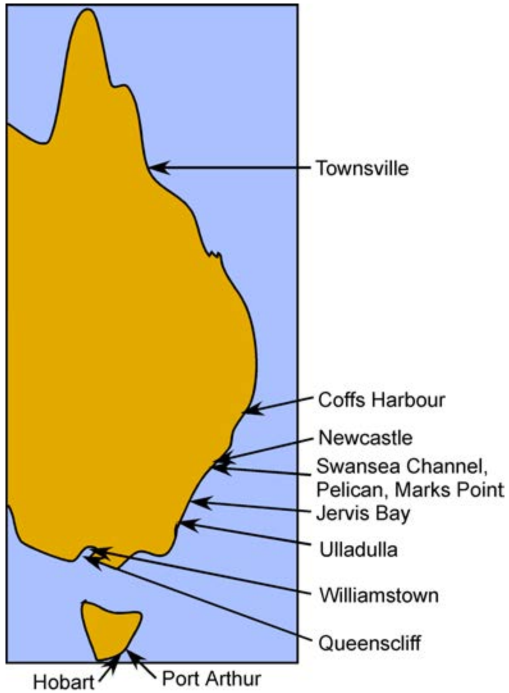
Examples

Accelerated Low Water Corrosion

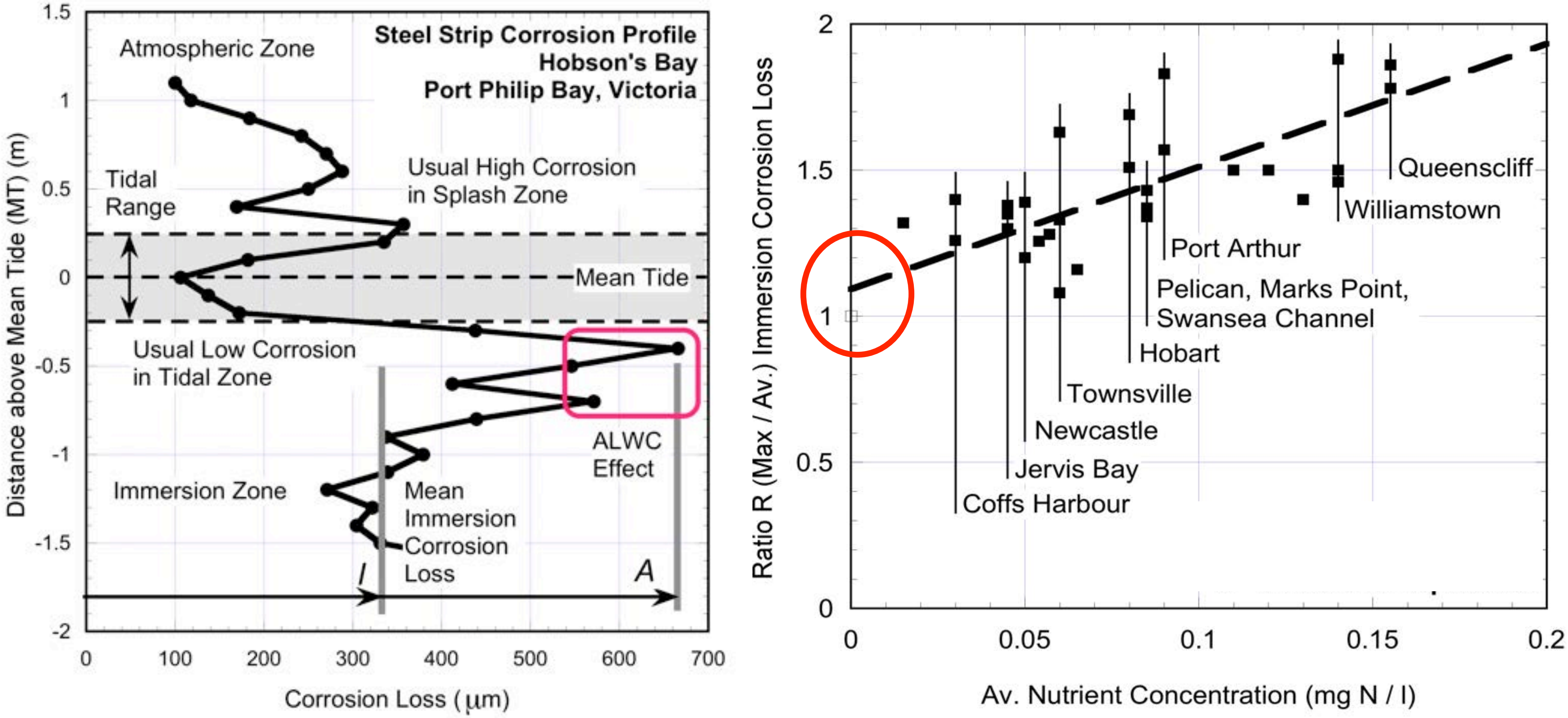
- High local corrosion just below Low Tide level
- Can affect steel sheet and other piling in harbours
- Detected in 1980s -> major concerns
- Earlier observations did not raise alarm
- MIC suspected ... 1980s ++
- Evidence of bacteria ✔
- *Affected and unaffected* piling - similar bacteria
- => no prediction capability

Our research project:

- Field exposures at 13 locations
- Steel strips 3, 6m long, 50 x 3 mm
- Exposed for up to 3 years
- Microbial ID ignored
- Nutrient levels measured in-situ.



Effect of DIN on ALWC



[See: Corrosion Science, 65:26-36.]

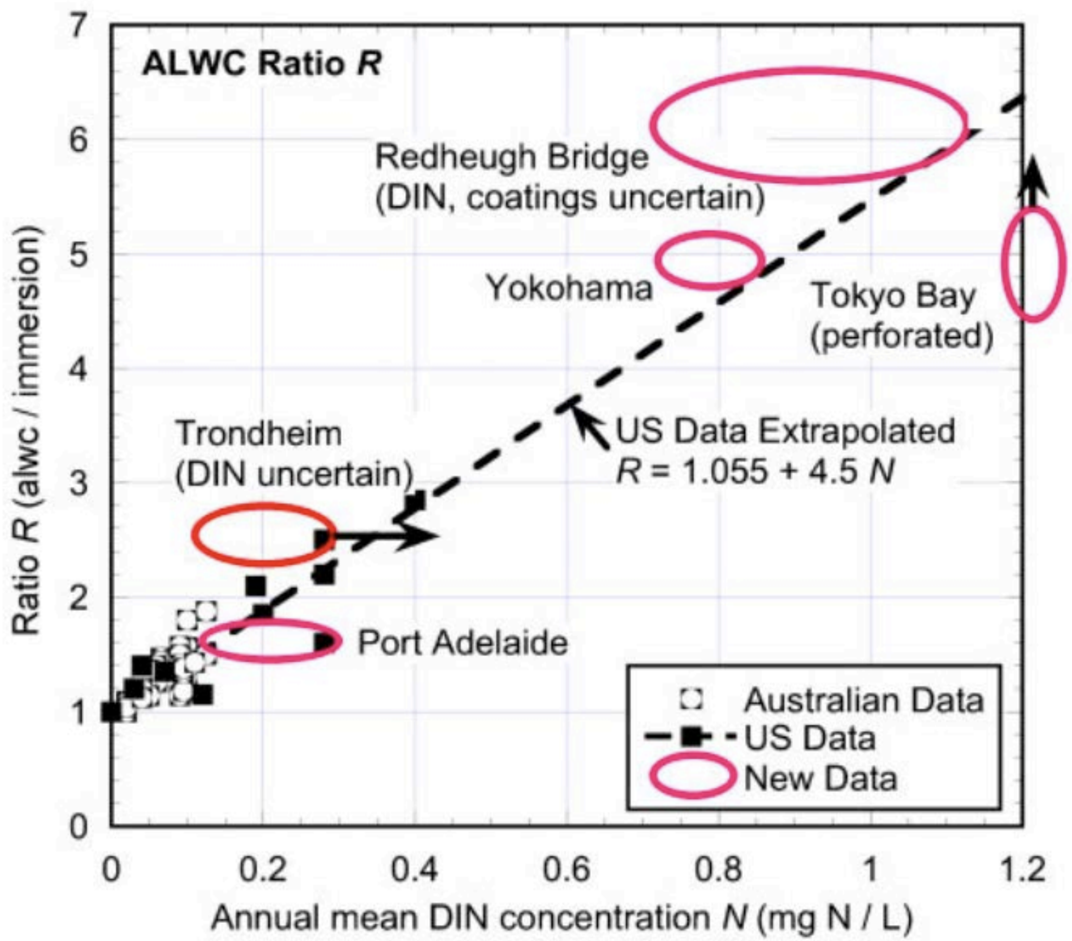
- Correlates ALWC effect with DIN concentration (N)
- ***Research outcome:*** can estimate likelihood of ALWC from:
  - ‘short-term’ field tests (1-3 years)
  - Dissolved Inorganic Nitrogen (av.) concentration (N) in local seawater.

Testing the hypothesis: 25+ years data …

- Re-analysed steel piling corrosion data (25 years) for US Navy base sites
- Environmental data from US EPA etc.
- Same trend for $R = A / I$
- Also 'other' various long-term data

Conclusion: correlation extends to:

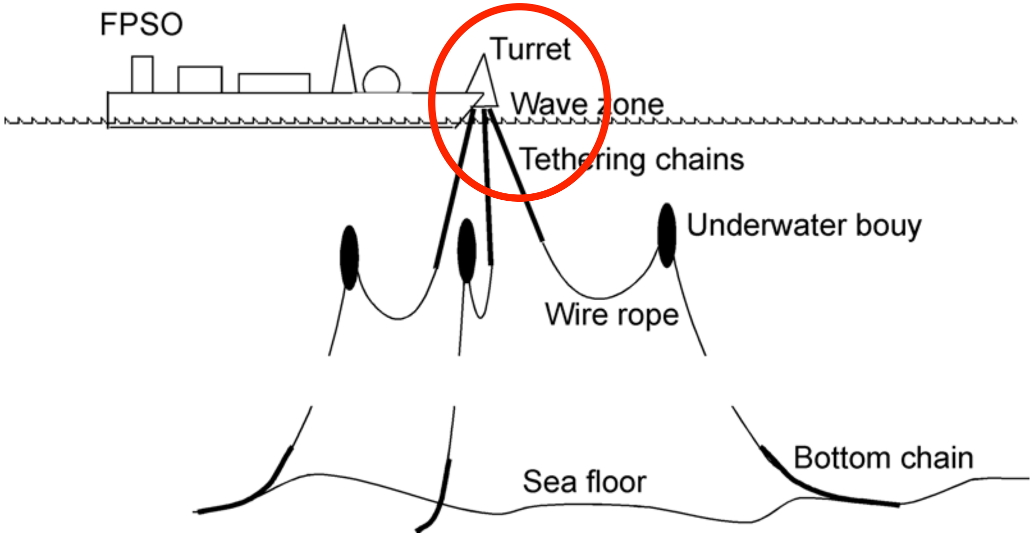
- much longer exposure periods
- higher DIN (5x earlier DIN)



Mooring chains for oil and gas FPSOs

FPSO = Floating Production, Storage and Offloading vessels

- Oil & gas exploitation moving into deeper waters - 2-3 km deep
- Specially built vessels, or converted oil tankers
- Remaining "on-station" = critical



FPSO Moorings in the Tropics

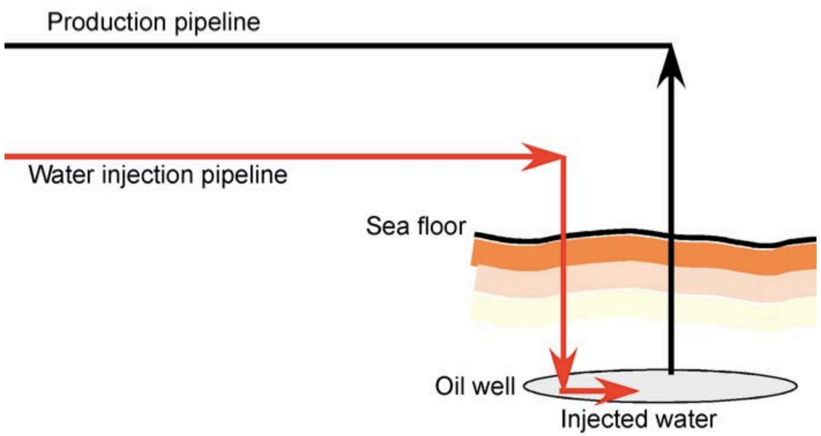
- Very deep "pitting" observed in Tropical waters - off the coast of West Africa, in Timor Sea
- >> than expected from temperature

- Detailed field investigations – incl. water quality
- Very high DIN in ***local*** seawater >> any in harbours, etc.
- Chain links scanned -> pit depths:
- Consistent with steel piling trends extrapolated

75 mm diam. steel.
20+ mm pitting in
about 8-10y

Water injection pipeline corrosion

- Water injection pipelines used in offshore oil / gas extraction



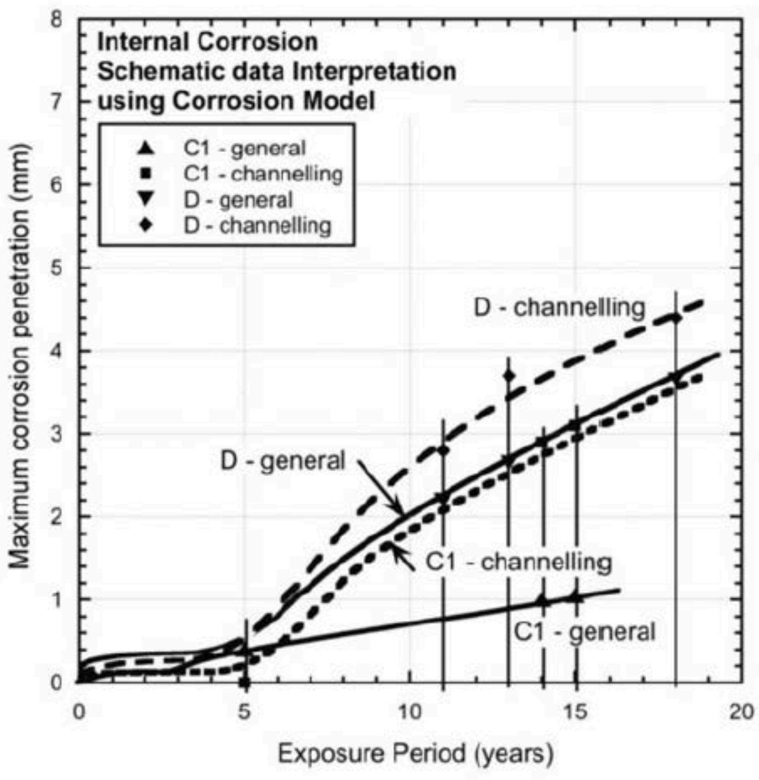
Heidersbach and Roodselaar 2012, used with permission

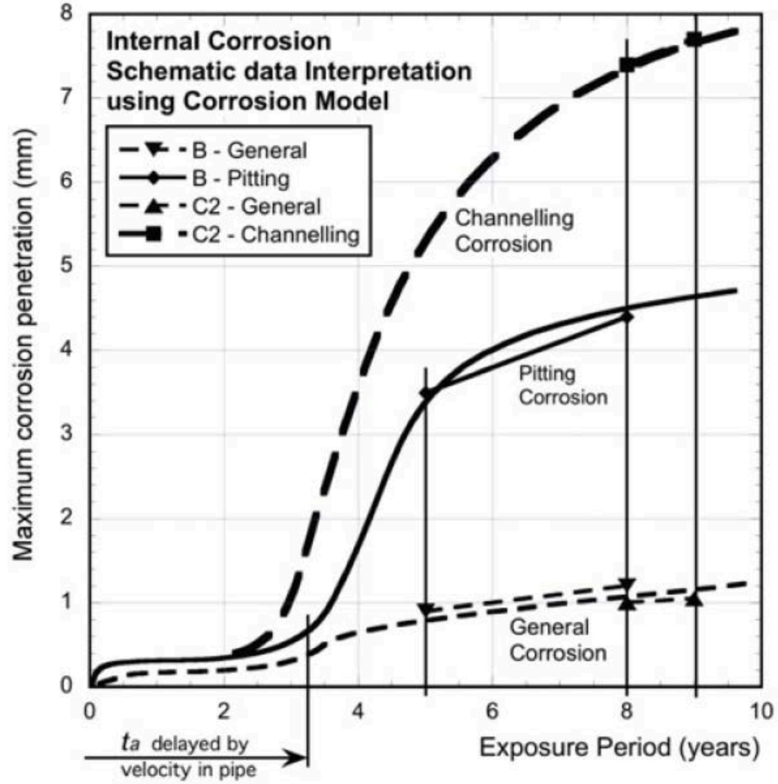
- A big issue = channelling corrosion

- Investigation: EU – BIOCOR funded + Swerea-KIMAB, Statoil
- Industry: MIC suspected – tests show range of bacteria (on pipe wall)
  additives used to try to control bacterial populations, numbers
- Nitrate injection - to let (hope that) NRB outcompete SRB inside wells (to try control H_2S generation)
- De-oxygenated water used: <80 ppm O_2 to suppress corrosion
- ***Only some*** pipelines show channelling corrosion, others not – ***why?***

Corrosion model applied to WIP data

- Examined bio. sampling results, pigging results, water quality, corrosion
- No clear outcomes initially….
- 5 pipelines investigated in much detail and data + corrosion compared
- Intelligent pigging data also became available
- 'Fitted' to corrosion model - for general, pitting, channelling corrosion





Pipes with: lower nitrate injection higher nitrate injection

Water injection pipeline corrosion

Previous work => nitrate addition should affect corrosion inside WIPs

•But why, ***not all around the pipeline walls***?

•Why only the severe channelling corrosion?

More investigation:

•Operational reports showed internal deposition of rust / debris

•Removed by periodic (?) pigging (a "cleaning" process)

•Question: how is deposition inside the pipes possible since operational pipelines have: *high to very high* water velocities

Further investigations showed " maintenance periods "

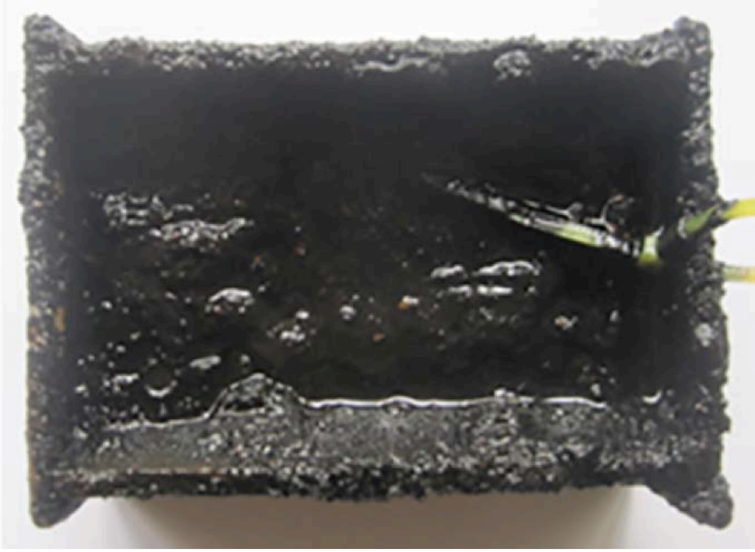
•i.e. water flow is very low or stopped.

•Allows ***deposition*** – what effect does nitrate then have?

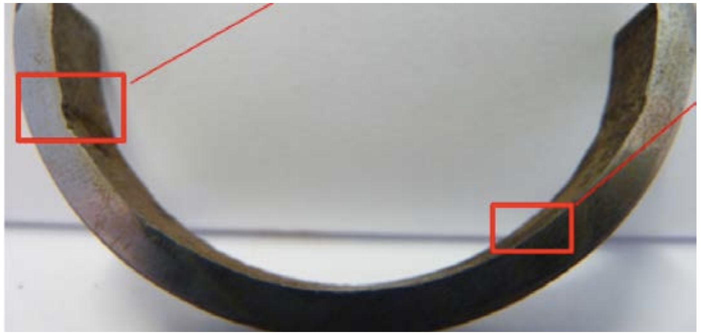
•=> Laboratory studies … of ***under-deposit*** corrosion

Laboratory studies

- Model pipes 90mm long 60 mm diam, epoxy coated, external, not inside
- Deposits (magnetite, calcium carbonate, sea sand)
- Stagnant seawater, heated 30˚C
- Deoxygenated with $NaHSO_3$ = industry standard
- Nitrate source = Calcium nitrate $Ca(NO_3)_2$ = industry standard



Plan view

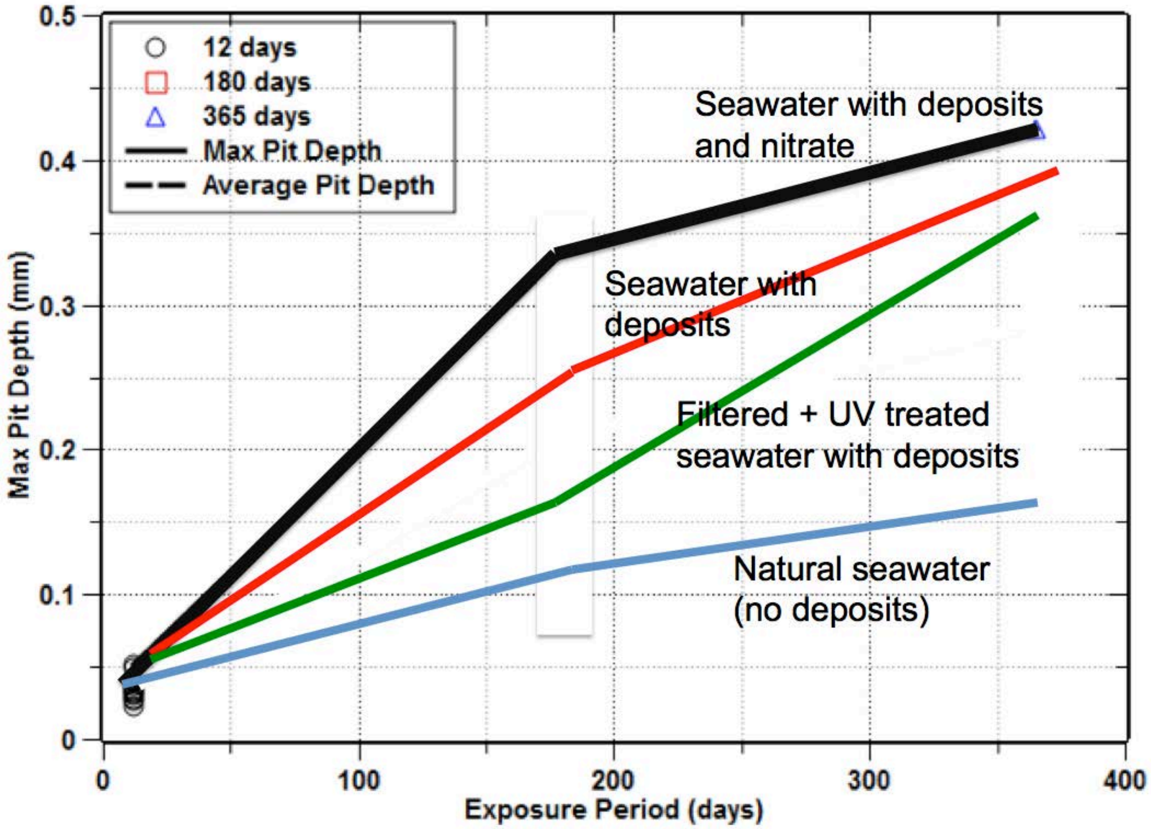


Cross-section

Four different test environments:

1) no deposits + natural seawater
2) deposits + filtered & UV treated seawater
3) deposits + natural seawater
4) deposits + natural seawater + **nitrate addition**

Laboratory studies – results



1) no deposits + natural seawater – least corrosion pitting

2) deposits + filtered & UV treated seawater – somewhat greater pitting

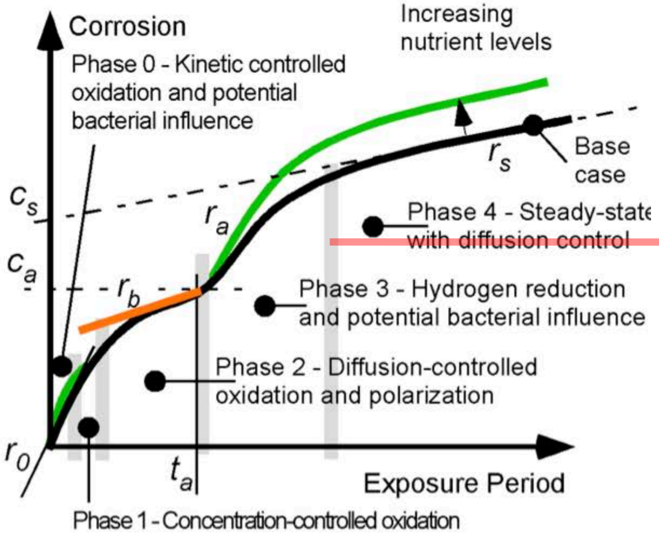
3) deposits + natural seawater – ***deep pitting***

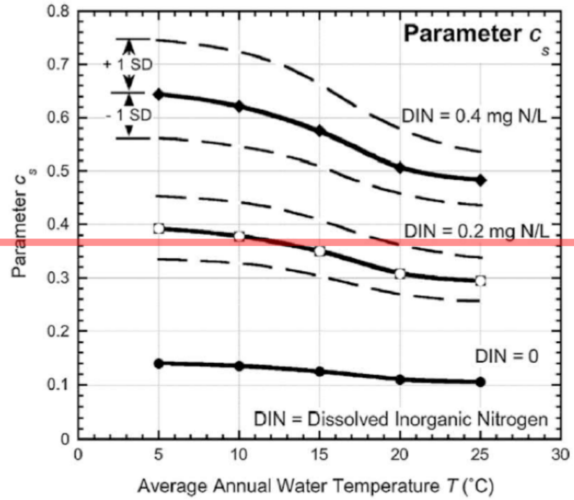
4) deposits + natural seawater + **nitrate addition –> *deepest pitting***

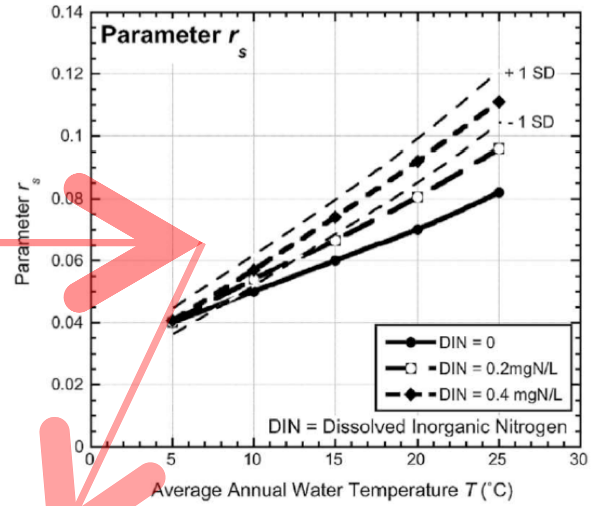
This effect is for *Mode 1* of bi-modal behaviour

Modelling for prediction

- From bi-modal model behaviour expect similar (worse) effect also later



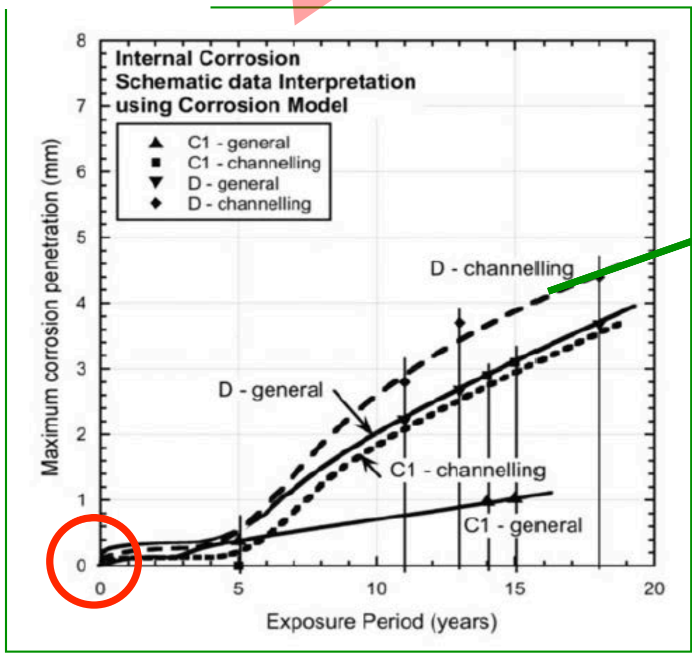




- Bi-modal model enables:
  quantitative ***extrapolation*** = ***prediction***

Present approach:

- demands focus on practical outcomes
- demands quantitative information
- provides focus for further research



Conclusion and outlook

- Mathematical modelling provides for quantitative prediction and extrapolation – corrosion, pitting
- Necessary in 'hard' decision regimes (e.g. for infrastructure)
- In principle, modelling can be applied at various 'levels of abstraction'
- Need good understanding at that level + quality data
- We have used an '*input – output*' approach
- Based on recent correlation of severe long-term marine corrosion (pitting) with elevated levels of DIN
- ***Corrosion is not a simple function*** - short-term data may not reveal long-term effects (cf. bi-modal model)
- ***Severe localized corrosion not necessarily only MIC*** – also can have severe (abiotic) under-deposit corrosion !
- ‘who does what?‘ is still a major microbiological research challenge…

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The University of Newcastle, Australia

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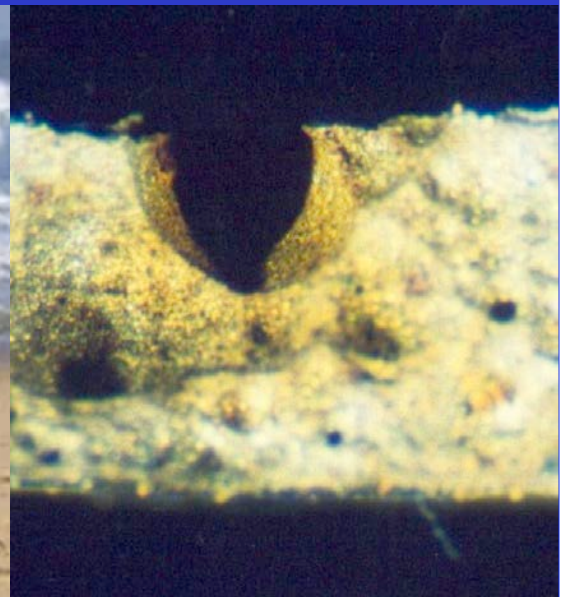

Thank you

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