Maritime Corrosion – New Insights

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Content

- Reasons for studying marine corrosion
- Corrosion basics
- Models & influencing factors
- Pitting/localized vs. mass loss – some theory
- MIC, Tidal & Atmospheric corrosion
- Corrosion in brackish water
- Importance of localized corrosion in practice
  - Corrosion and protective coatings
  - Corrosion and impressed current Cathodic Protection
- Summary & Conclusion

Motivation

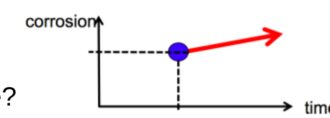
- Corrosion of ships, offshore installations, coastal infrastructure
- Safety, operational, maintenance, replacement costs
- Life-cycle planning and assessment of existing structures
- Need for estimation of likely future deterioration
- Questions for engineers, asset owners: effect of deterioration

  Loss of strength? loss of safety? when? costs? when to repair?
- Wind, wave, etc. loadings, material strengths etc. = well understood.
- Fatigue, wear ... reasonably well understood
- Corrosion:

  Texts: lots of electrochemistry – ***mostly inaccessible to engineers***

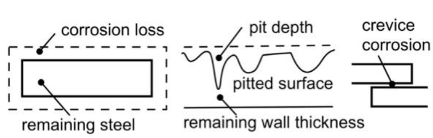
  Handbooks: much information about short-term *observations*
- ***Little fundamental modelling or prediction***
- No answers for:

  how much expected NOW, in the future?



Corrosion basics

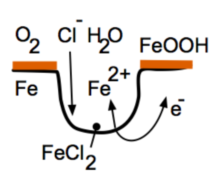
- Text books categorize corrosion as: uniform, pitting, crevice, etc...



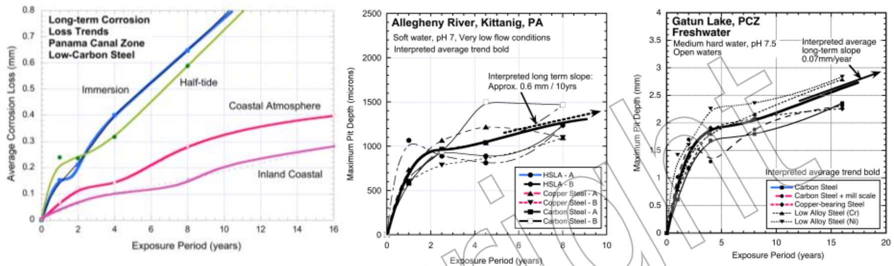
- Description without understanding...
- Fundamental: corrosion = potential differences

  across different parts of a metal surface
- Inclusions (e.g. MnS), grain boundary effects, alloys (incl. some forms of carbon in steels) ...
- => Very small, localized => 'pitting'
- Pitting development:

  initiation, meta-stable pitting, stable pitting, pit growth ..



Field observations – long term exposures

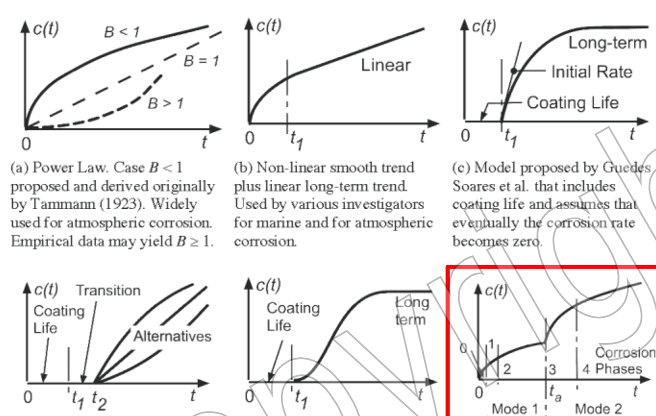


corrosion loss (soft water) max pit depth (hard water)

Tradition

- Constant corrosion '*rate*' = inconsistent with observations
- Similarly for other metals, alloys, other environments
- Several models proposed in 1930-40s: most famous = 'power law'
- $c(t) = A\, t^{B}$ *A, B* 'constants'
- Based on diffusion through rusts, from t = 0 + simplifications to theory.

Review of existing corrosion models



(a) Power Law. Case $B < 1$ proposed and derived originally by Tammann (1923). Widely used for atmospheric corrosion. Empirical data may yield $B \geq 1$.

(b) Non-linear smooth trend plus linear long-term trend. Used by various investigators for marine and for atmospheric corrosion.

(c) Model proposed by Guedes Soares et al. that includes coating life and assumes that eventually the corrosion rate becomes zero.

(d) Model proposed by Paik et al. that includes coating life and non-specific corrosion trends, generally similar to power law.

(e) Model proposed by Qin and Cui that includes coating life and assumes that eventually the corrosion rate becomes zero.

(f) Bi-modal, multi-phase model proposed by Melchers that macro-models corrosion processes including a long-term linear trend.

Towards a more rational model =>

- Issues: Empiricism, Data homogeneity, Different processes, Long term rate

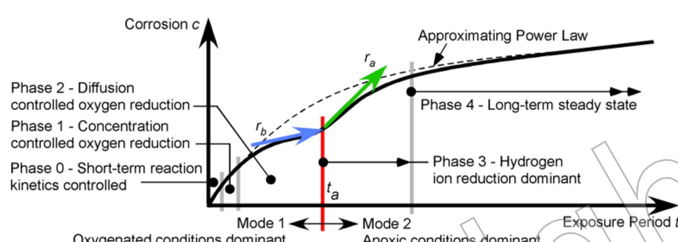
Factors in corrosion - seawater immersion

Oxygen supply, Salinity, pH, Carbon dioxide, Carbonate solubility, Pollutants Temperature, Pressure, Suspended solids, Wave Action, Water velocity, Bacteria, Biomass

Steel composition
Surface roughness
Size
Coupon edge ratio

- Complexity appears daunting
- Engineering approach – reduce complexity!
- Make some reasonable assumptions:
  - mild steel (forget precise composition, surface roughness, size, etc.)
  - unpainted, unprotected
  - 'at-sea' and 'near-surface' exposures
    - ensures high aeration of seawater (i.e. no O_2 restrictions)
    - eliminates most chemical factors and physical factors, except:
- **Average seawater temperature** (T) - governs many processes
- **Biological activity** - function of nutrients / water pollution
- Revisit other factors later

Bi-modal model – general corrosion (2003)



- Phases => different corrosion mechanisms
- *Empirically* shown to hold for:
  - steels (low C, low alloy, weathering, Cr..), cast iron, Cu, Al, Ni alloys
  - environments: immersion, tidal, marine atmos, inland atmos, in soils).
- Bi-modal characteristic = fundamental

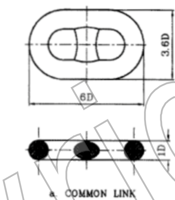
Issues:

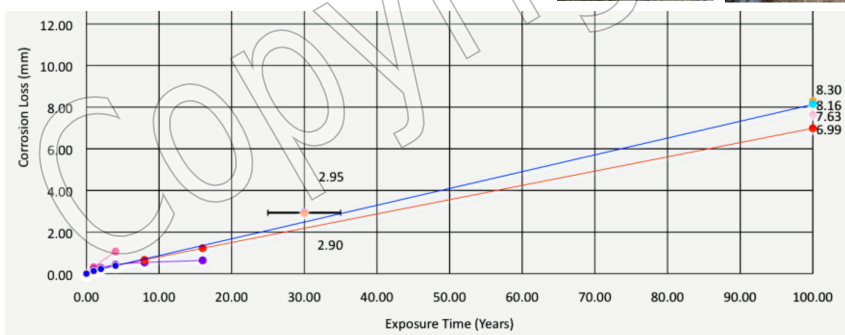
- Is long term corrosion a linear function?
- Model parameters: calibration & influences [revision]
- Why change from r_b to r_a at around t_a?
- Relationship to pitting corrosion?

Long term corrosion - field observations

Immersion in Pacific Ocean – near Newcastle (Aus):

- Mooring chains used for shipping ....
- Chain proportions = key
- Date known => 100 years
- Known replacement @ 30 y
- Multiple calliper readings
- => long term rate = linear
  = 7- 8 mm / 100 years.





Model calibration – field test data

Field immersion, tidal, splash, atmospheric

Several locations on East coast Australia -

Newcastle Harbour, Swansea Channel, Taylors Beach, Belmont Beach,

Hobart Harbour, Port Arthur, Port Phillip Bay, Jervis Bay, Townsville …

Model parameter calibration

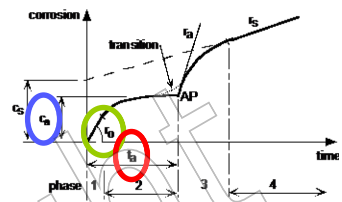
No pollution, no major bacterial influences

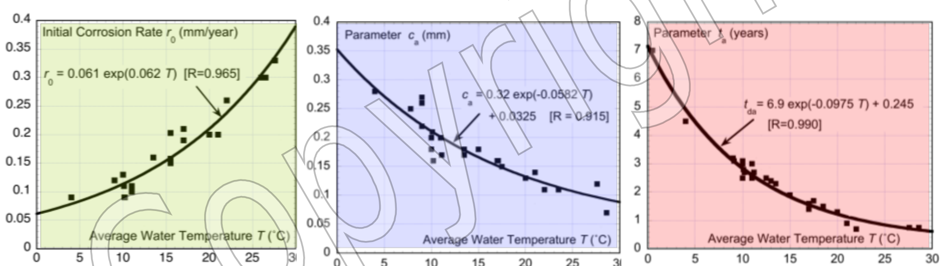
r_0 = early corrosion rate

c_a = corrosion at t_a

t_a = idealized transition time

Function of T = mean temperature





Other parameters similarly

Also: ***estimates for uncertainty / variability/ standard deviations*** …

Models and uncertainty

- Corrosion models must suit applications => uncertain conditions
- Modern trend = *probabilistic* models …
- Corrosion *c* = function of time *t* , various influences **E** …

  $c\,(t, \mathbf{E}) = b.\,fn\,(t, \mathbf{E}) + \varepsilon\,(t, \mathbf{E})$

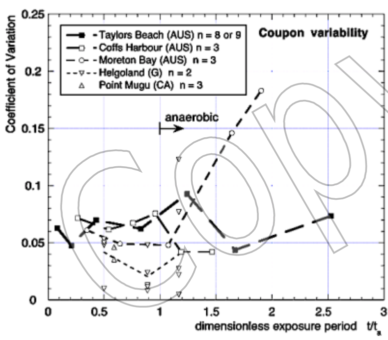
  b = bias factor – should be 1
- Balance between poor quality function *fn ( )* and error term *ε ( )*
- Also quality of **E**
- => understanding of processes, factors and proper modelling of them

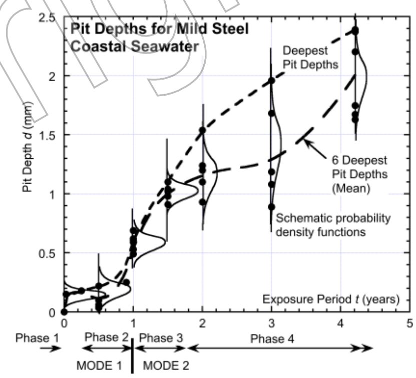
  It is easy to create poor models !

- Corrosion literature is almost devoid of information about *ε ( )*
- Ditto about effects **E**
- For mass loss effects, pit depths…

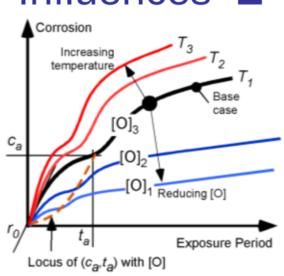
Estimating uncertainty ε(t,T)

- Created data for uncertainty estimate for steel + seawater
- Multiple (9) samples, exposed at Taylors Beach
- For estimating mass loss standard deviations, CoV (bare minimum)
- Multiple pit depth measurements (easier, but need more)
- See literature – mass losses (2003), pit depth statistics (2004++) …

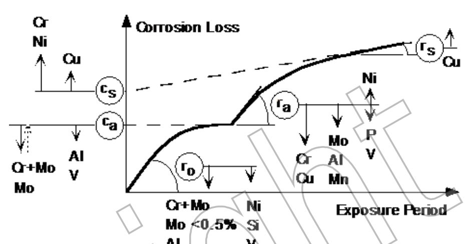




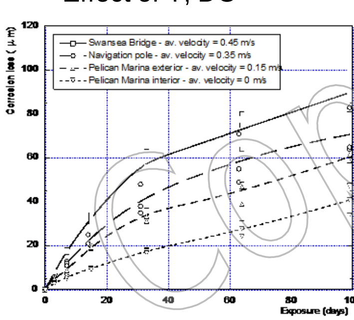
Influences **E**



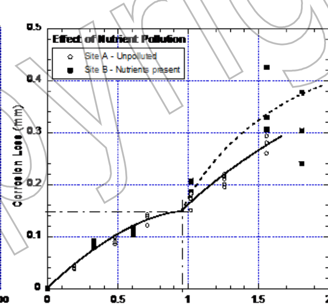
Effect of T, DO



Alloying



Water velocity

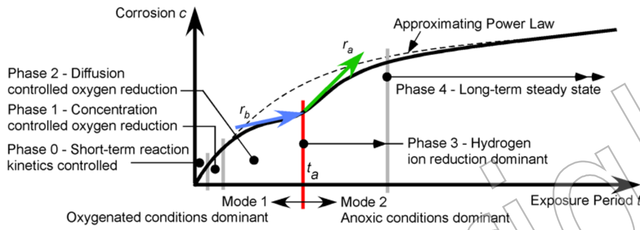


Nutrients (DIN)

Deep water – effects from temperature, DO, nutrient levels, velocity – see literature

Salinity – see literature & later

r_b to r_a change – from mode 1 to mode 2



At around t_a corrosion rate changes gradually from r_b to r_a

- Just before t_a
  - corrosion predominantly under inward oxygen *diffusion* controlled by thickness/permeability of rust layers
  - O_2 consumed by cathodic reaction

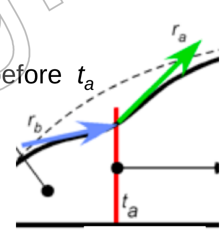
- Just after t_a
  - corrosion predominantly under anoxic conditions
  - rate controlled by outward *diffusion* of H_2 generated in corrosion pits
  - through *essentially same* corrosion product layer

Transport through magnetite layer

- Hydrogen, oxygen *diffuse* through the ***thin*** porous magnetite layer
- Oxygen inwards, hydrogen outwards

- Diffusion through a thin membrane … Graham's law:
- Rate of diffusion depends on 1 / √ (molecular mass)
- For ratio $O_2 : H_2$ => 1/√(16x2) : 1/√2 = 1:4

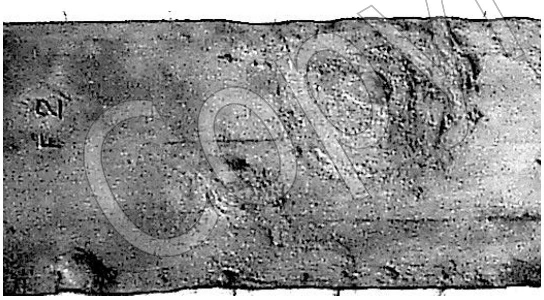
- **Observed ratio**: slope r_a after t_a vs. slope r_b before t_a = approx. 4 in many cases



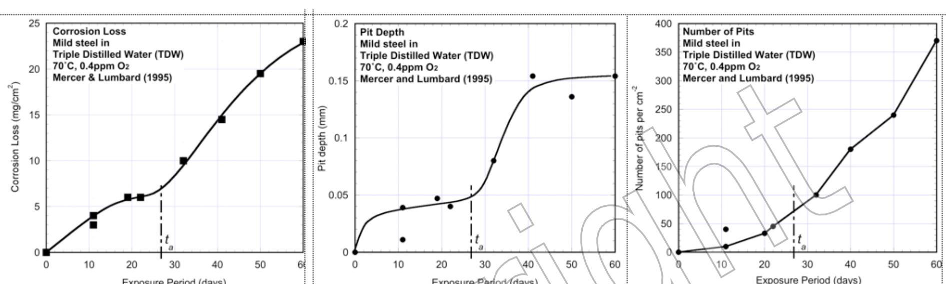
- Observed for:
  steels, aluminium alloys, copper alloys

Trends in pit depths and corrosion loss

- Pitting *does occur* for carbon steels (e.g. Butler, et al. 1972)
- Occurs quickly – within days – 'near-circular' pits
- Pit depth is constrained by ***electrochemical potential***
- – long history + experimental results + theory.
- Pits surrounded by cathodic region = alkaline (Evans 1960)
- Eventually …. rusts over pit mouth (Wranglen 1971)
- New pits close to original pit (Butler et al. 1972)



Laboratory evidence (Mercer & Lumbard 1995)



- Lab. data for mild steel tubular samples
- Rotated (to speed up reactions)
- Triply distilled water + low DO + 70˚C (to speed up reactions)
- **Mass loss** = bi-modal
- **Pit depth** = occurs in steps …..
- **Number of pits** increases …. influences mass loss

Field evidence

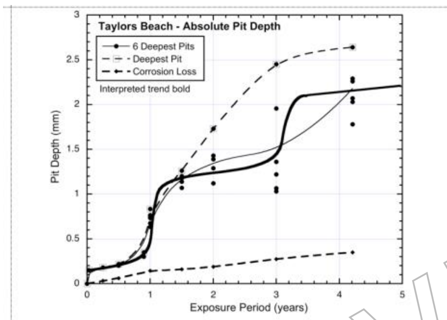


Figure 3. Data and trends for natural seawater immersion corrosion as a function of exposure time for mild steel exposed at Taylors Beach (a) mass loss and (b) maximum pit depth and also the interpreted trend (bold) through the 6 deepest pits.

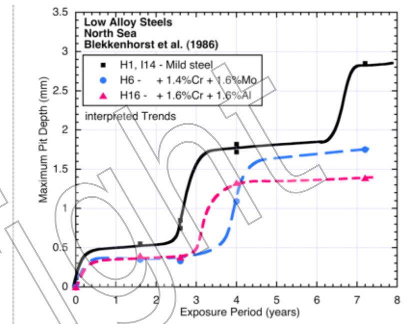


Figure 5. Data and trends for maximum pit depth of 3 low alloy steels exposed in the North Sea, showing that the step-wise interpretation of the data (Data from Blekkenhorst et al. 1986).

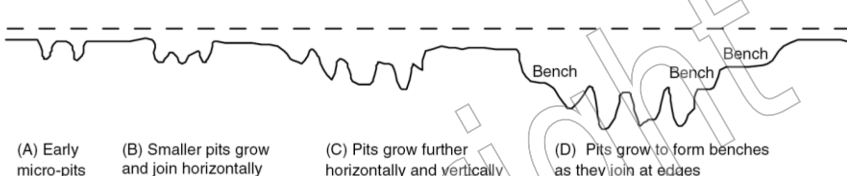
Taylors Beach - pit depths

North Sea - pit depths

•Generally similar observations - up to 8 years
•Number of pits – increases with mass loss
•Consistent with laboratory observations

Development of pitting corrosion

- Consider only propagation of pitting (assume starts at imperfections, inclusions etc. - schematic process:



- Requires local *close-spaced* pitting => cathodic areas somewhat removed. Observed in practice…
- Coalescence of close-spaced pitting, also observed in practice (Gainer & Wallwork 1979, Jeffrey & Melchers 2007)
- Physicochemical modelling … (Sharland & Tasker 1988)
- Downward 'migration' of magnetite Fe_3O_4 'layer' (Evans & Taylor 1972)

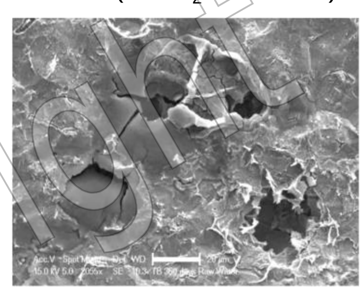
Supporting observations

- Plateaued corrosion pits =>
- Closely spaced pits
- Magnetite layer visible under outer rusts
- New pits on the plateaus
- Evidence of amalgamations to form a new, lower plateau
- Indicates cycling pattern of pit depth development.

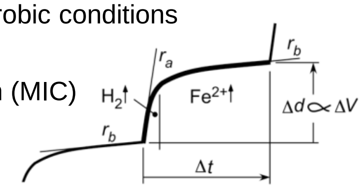
Figure 10. Broad pit revealed after removal of loose rusts by mechanical impact. Dimpled bright steel at floor of plateau partly covered with magnetite. The whole oxidized within 1-2 hours after exposure.

Pit depth development & mass loss

- Above shows cycling of pit and plateau processes
- Pitting = process for progression of *corrosion mass-loss*
- May occur in later part of mode 1 and in mode 2 (low O_2 conditions)
- Second mode is rate controlled initially by hydrogen bubbling out of pits, through magnetite layer =>
- Consistent with observations hydrogen evolving from inside walls of corrosion pits….



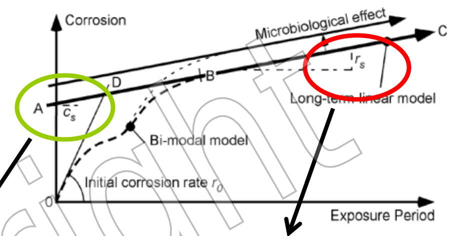
- Unifies various observations
- Shows importance of pitting under anaerobic conditions
- Has practical implications
  - Microbiologically Influenced Corrosion (MIC)
  - Coatings and CP

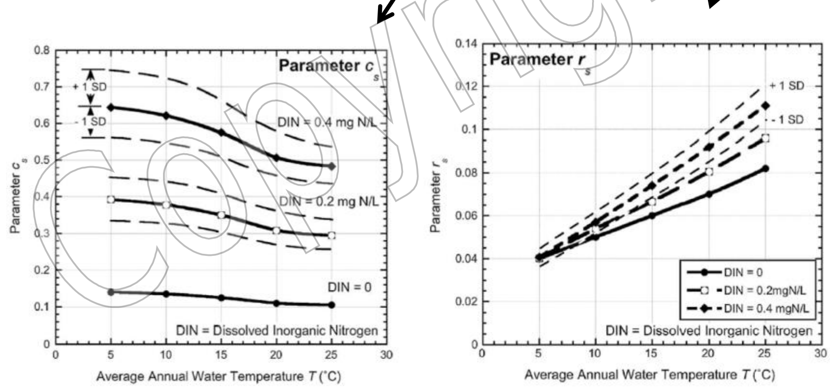


MIC - Effect of Dissolved Inorganic Nitrogen

- DIN affects c_s and r_s in simplified corrosion model
- Long-term => anaerobic part
- => MIC effect - mainly pitting
- Field data
- Calibration

(Corros. Sci. 2014)





Accelerated Low Water Corrosion

UK – 1980s - High corrosion just below Low Tide level – major concern

•MIC suspected ...

•Bacteria both affected and unaffected cases => prediction?

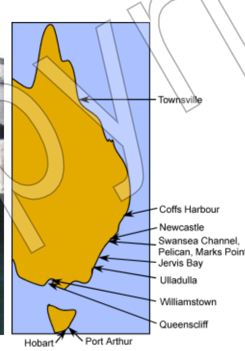
Australian research project:

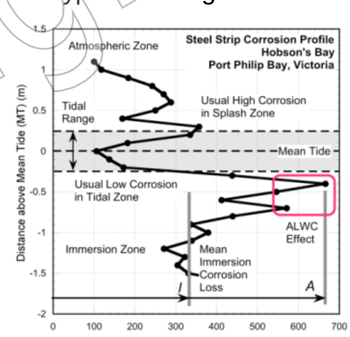
•Based on: *nutrients are critical* - Microbial identification ignored

•Steel strips 3, 6m long, 50 x 3mm - Exposures at 13 locations

•Exposed for up to 3 years - **DIN measured in-situ**.

Typical finding



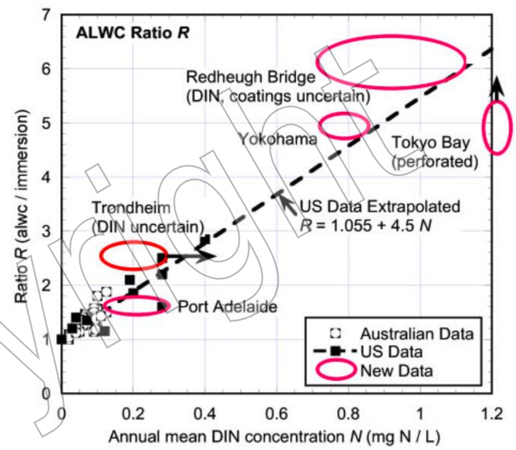


ALWC: 25+ years data, higher DIN …

- Australian data + US Navy steel piling corrosion data (25 years) re-analysed +
- US EPA Environmental data
- Other ' long-term data
- Correlation extends to much longer exposure periods
- Higher DIN (5x earlier DIN)
- ***Same trends*** for *R = A / I*

Conclusion:

- Use concentration of DIN to predict *R*
- Use short term tests to predict *R*



Marine atmospheric corrosion

5 years

Belmont Beach. Rated as Australia's most severe atmospheric exposure test site. Major 5 year test program

Marine atmospheric corrosion 2

- Practical observations – **Catherine Hill Bay**
- Pacific Ocean exposure
- Jetty with steel piles
- About 40 years exposure after painting
- Blisters, relative low corrosion
- On-going project

- cf. chain 100 years =>

Marine atmospheric corrosion 3

Coastal Newcastle – Pacific Ocean =>

•6-7 years old
•Painted over galvanised steel
•Delamination, rust staining ($FeCl_2$)

•316 SS
•Overall in very good condition
•Except at some welded joints
•Those with rough weld region =>

Reconciliation of these various observations
•On-going project

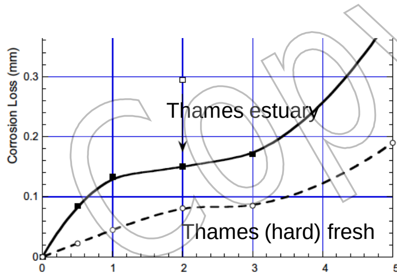
Ships and offshore vessels - interior corrosion

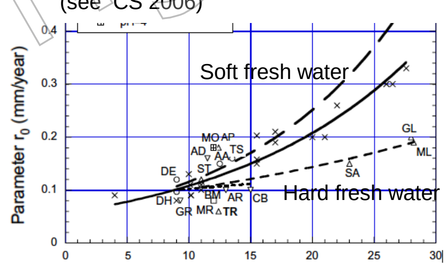
- On-going project (2017-) Aust Research Council Linkage grant
- Effect of corrosion and fatigue on sea-keeping behaviour
- Major FEA of seawater wave motion + structure
- Note: Corrosion often occurs at welds, sharp edges
- Also bilges, areas of deposits

Brackish water - Effect of salinity

- Salinity is lower in coastal, estuarine waters
- Lower salinity does ***not*** always mean lower corrosion
- Depends on *hardness of freshwater* entering seawater
- Water hardness = $CaCO_3$, $MgCO_3$ - measured in various ways ….
- Seawater is 'very hard' – supersaturated with $CaCO_3$, $MgCO_3$
- ***Hard*** fresh water (river water, ground water) inflow increases pH or saturation => $CaCO_3$, $MgCO_3$ *deposition*…=> increases the diffusion barrier / reduces permeability => ***less*** corrosion
- ***Soft*** fresh water => lower pH => less protection => more corrosive

(see CS 2006)





Protective coatings

- Not always feasible - e.g. bulk carrier holds, chains...
- Require maintenance !
- A certain degree of 'black magic' (– driven by service providers?)

- Protective coatings are not impermeable
- – provide ***additional diffusion barrier*** – for O_2, … DIN …
- - also 'protection' against MIC
- Slows rate of corrosion
- Most coating deteriorate with time
- – dry film thickness criterion (wrappings, much thicker, just take longer)

- Surface preparation is important – poor surface preparation accounts for most failures
- Key to understanding effectiveness of coatings is ***pitting corrosion***
- Removal of all rusts important – pitting can continue inside pits, aggressively, under very low O_2 conditions (mode 2 of bi-modal model)

Cathodic 'protection'

- (a) sacrificial anodes (b) impressed current
- Both can offer protection but care required
- (even more 'black magic'?)

Impressed Current systems:

- For new surfaces need simply a potential to prevent corrosion initiation (which is by pitting!) – around 850mV. - see Pourbaix.
- Conventional wisdom = need greater potential when MIC is involved (+100mV -> 950mV) – no real logic presented…. - why? Biofilm potential? Why – it occurs in seawater even without MIC.
- Note: MIC is an *active* corrosion process

- Possible reason for extra potential is to allow for *poor surface conditions* – already pre-existing pits (which is not unusual…)
  – may be worse under initial MIC activity.
- Impressed current => calcareous coating to the steel surface …

Impressed current CP

Calcareous coating - builds up with time

•Current raises surface pH to around 10 = alkaline

•Calcium carbonates extracted from seawater

•pH = 10 sufficient to inhibit initiation of general corrosion (see Pourbaix)

•Some pitting may occur (high Cl^-) but build-up of calcareous layers reduces O_2 access & increases pH => pitting stops (see Pourbaix).

Kure Beach experience (Humble 1949):

•Steel piles with CP in Atlantic Ocean

•Turned off the current, and nothing happened – for months!

•Corrosion when calcareous layers disintegrated under wave action…

•*Calcareous layer adds diffusion barrier for nutrients*

•Thus affects proneness to MIC.

Conclusions

- Localised corrosion (pitting) is key to what is observed, including for mass loss (corrosion loss).
- Pit growth is episodic.
- Mode 2 of bi-modal model is the result of much growth of pitting, severe under anaerobic conditions
- Microorganisms may make this worse, provided nutrients (and energy) are available

- Marine atmospheric corrosion requires much more work yet to untangle effects of shelter, coatings, MIC.
- Brackish waters may be less or more corrosive than seawater - depends on the hardness of the diluting waters.
- Pitting, surface preparation and MIC => major effects on protective systems.

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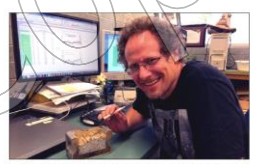
The University of Newcastle, Australia

Port Arthur Heritage, NSW Fisheries Taylors Beach + many coastal site owners

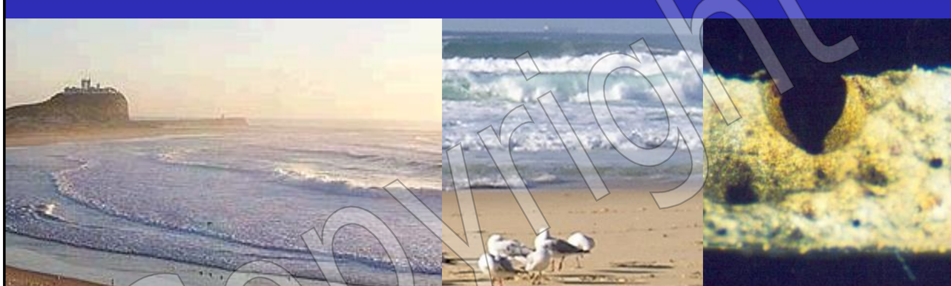
Plus - A great team of colleagues, **research associates**, research students + laboratory staff …



Tony Wells with a sectioned, very heavily corroded concrete surface of one sample of the many coupons exposed for up to 7 years in working sewers.

Igor Chaves examining some of the concrete samples used in the reinforcement corrosion study.

Robert Petersen with one of his experimental samples for the study of clay soil corrosivity.



Thank you

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