Living with Aging Materials – Challenges, and Opportunities

Willis Whitney Award Lecture, AMPP Corrosion 2025

by

Narasi Sridhar

MC Consult LLC

The Ohio State University

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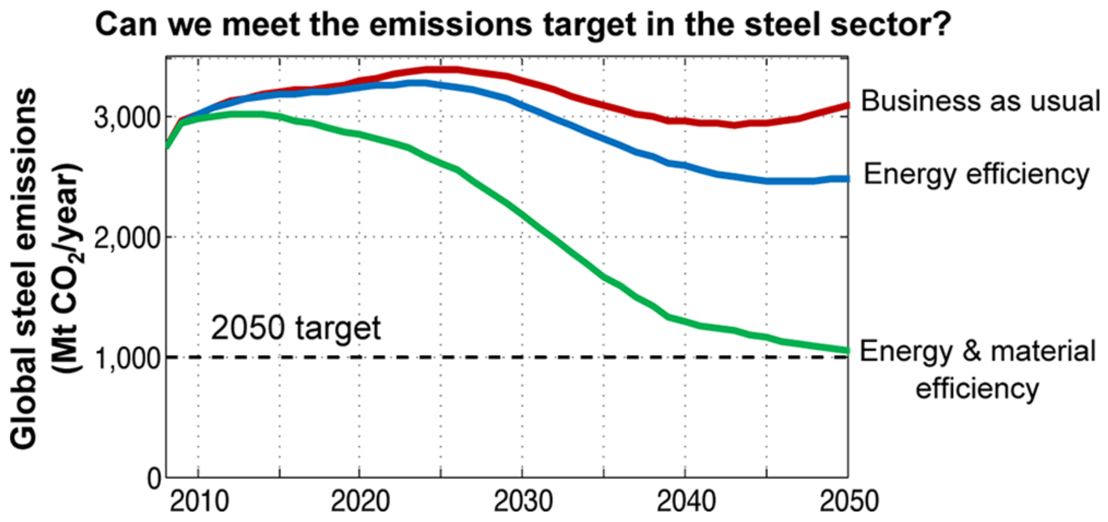
A special appreciation of my mentor and friend, the late Gustavo Cragnolino

Why must we live with aging materials?



- Managing aging materials is critical to safety
- Longer life of materials Improves sustainability (Iannuzzi and Frankel, 2023; Milosev and Scully, 2023)
- Efficient use of materials helps us meet emissions target (Milford et al., 2013)

What is NOT aging

- It is not the calendar time
  - "Ageing is not about how old your equipment is; it is about its condition, and how that is changing over time. Ageing is the effect whereby a component suffers some form of material deterioration and damage (usually, but not necessarily, associated with time in service)....." - UK HSE, www.hse.gov.uk/offshore/ageing.htm.

There is no single, quantitative definition of Aging

Aging Management Approaches focus on lagging indicators

A quantitative definition of aging

Aging is defined as increasing hazard rate

- $Hazard\ rate, h(t) = \frac{f(t)}{(R(t))}$

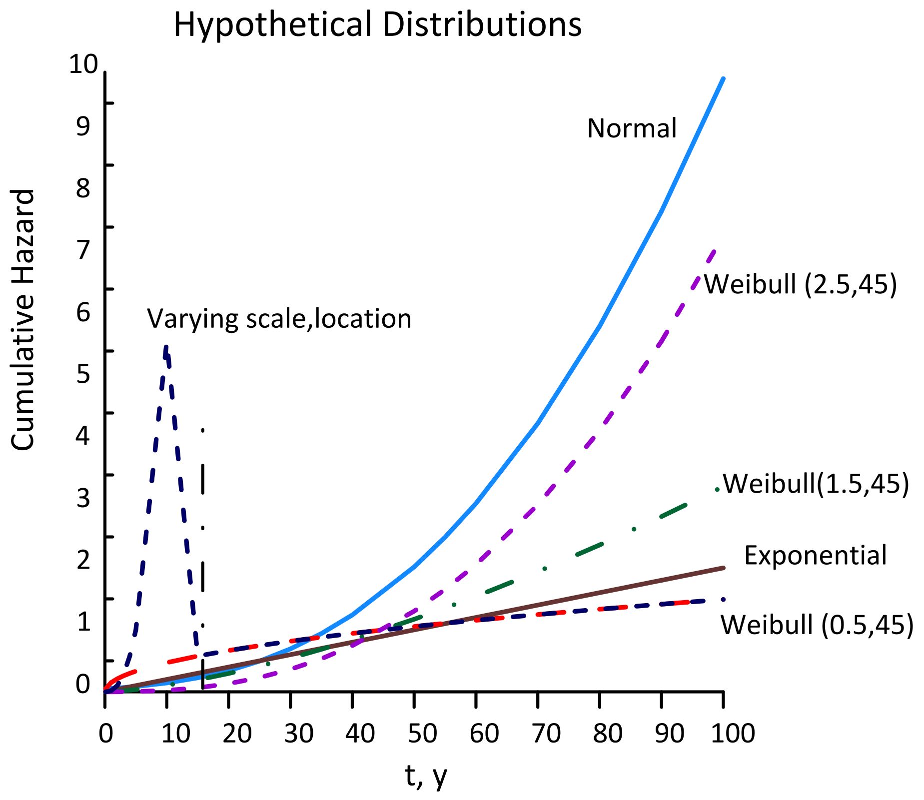
Probability of failure at any time

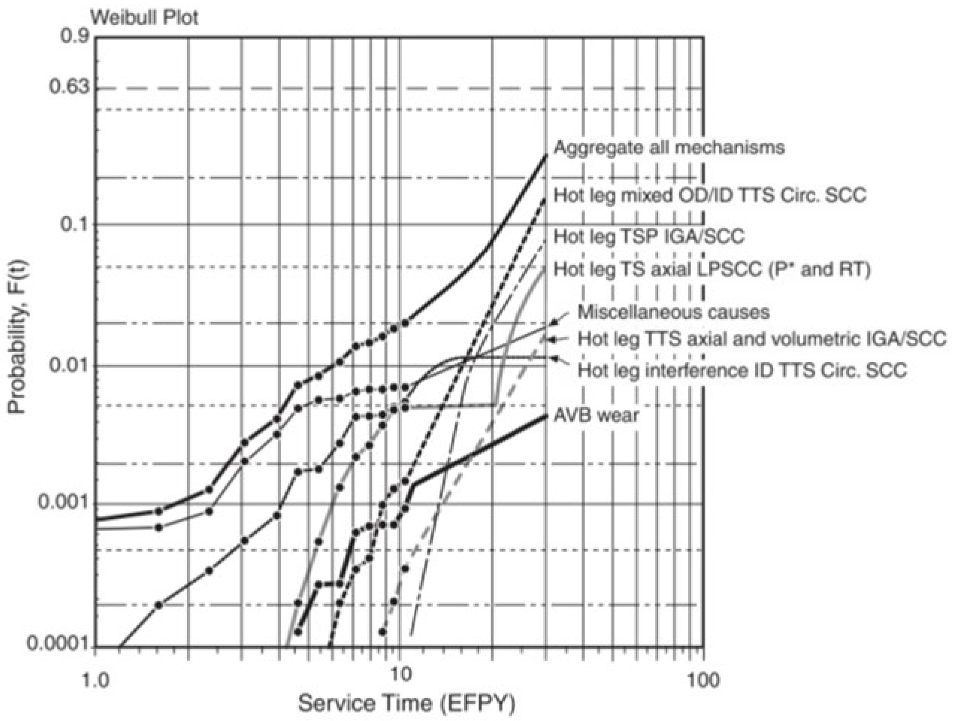
Reliability up to that time $= 1 - \int_0^t f(t)dt$

- Cumulative hazard function, $H(t) = \int_0^t h(t)dt = -Ln\big(R(t)\big)$

- More generally: $\mathrm{H(t)} = \{F(t)|R(t - \Delta t)\} \times R(t - \Delta t)$

Statistical approaches





SCC of MA 600 steam generators

Staehle and Gorman, Corrosion, 59(11), 931-994

If there is no prior failure what distribution should I choose?

If failure mechanism changes how would the distribution change?

Aging of materials is a part of hierarchy of complex systems

Organizations/Nations/Civilizations

Complex social structures of people, organisms and materials

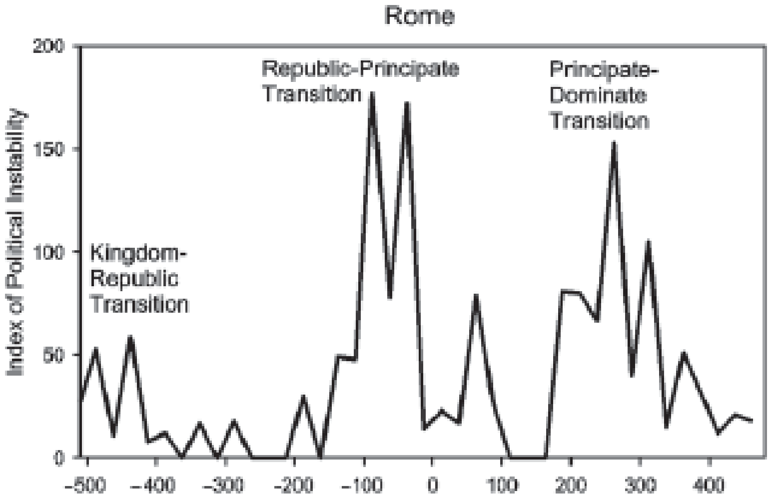
Organisms

Multifunctional assemblages of molecules and materials

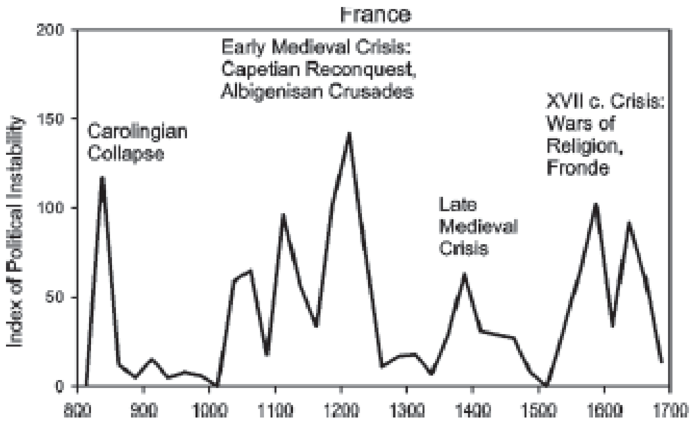
Materials

Complex assemblages of atoms and molecules

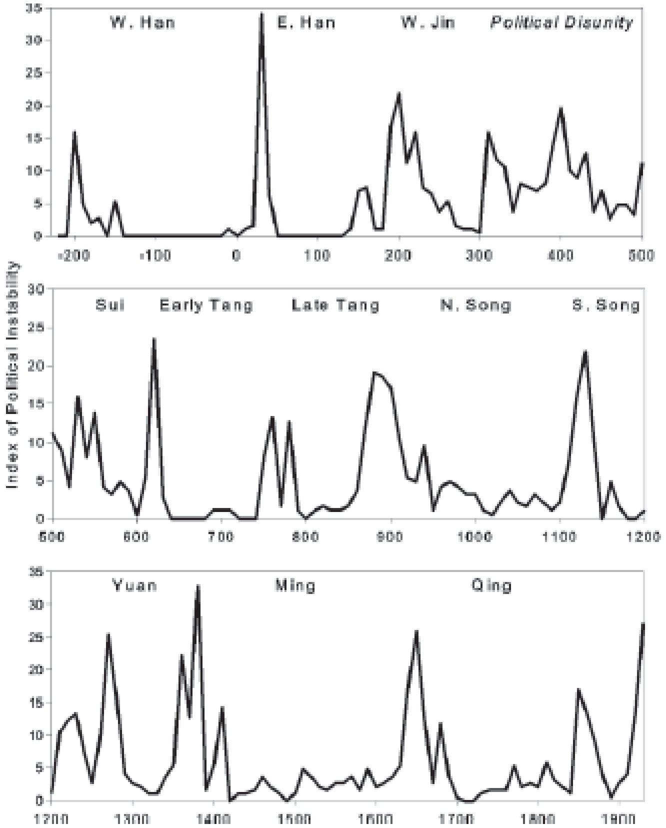
Aging of societies, nations, and civilizations



Rome



France

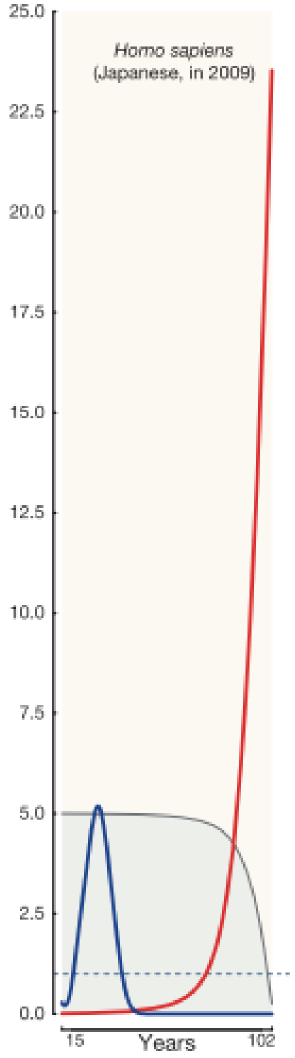


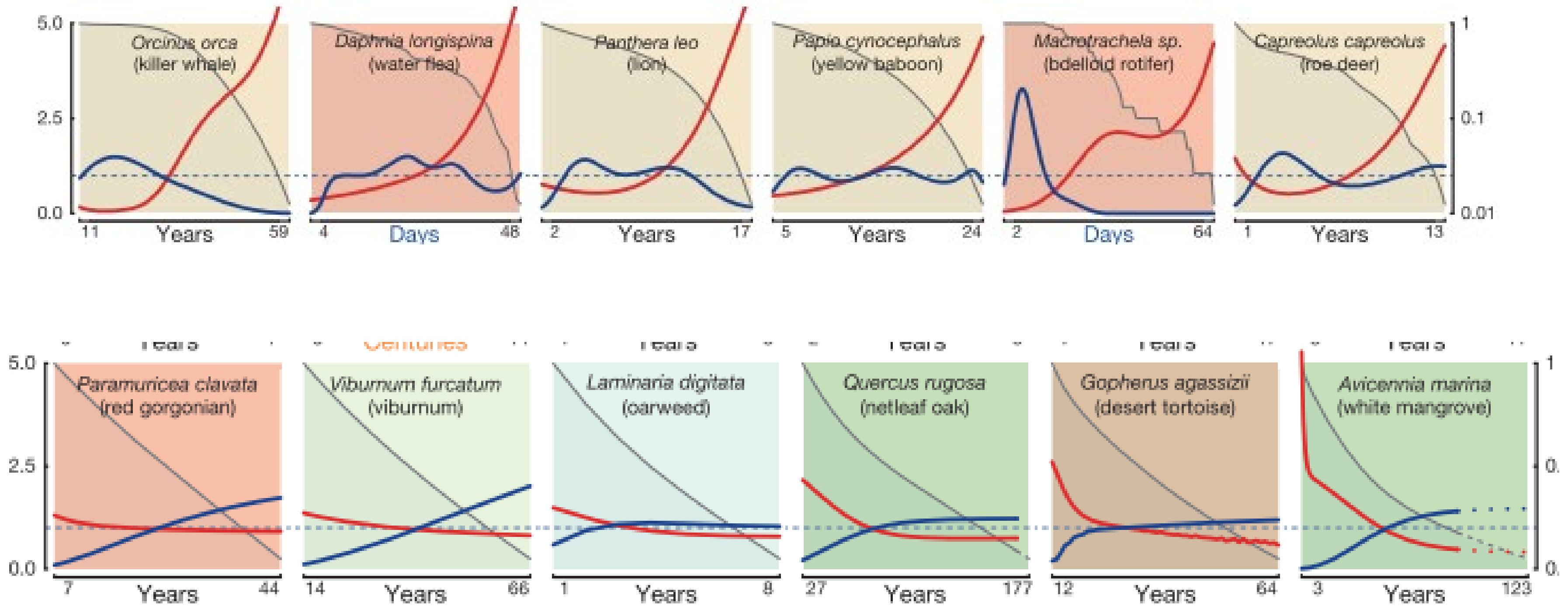
Source: Peter Turchin, Ages of Discord, 2016

China

Certain fundamental mechanisms drive aging of societies that cannot be derived from historical data alone

Aging in the tree of life

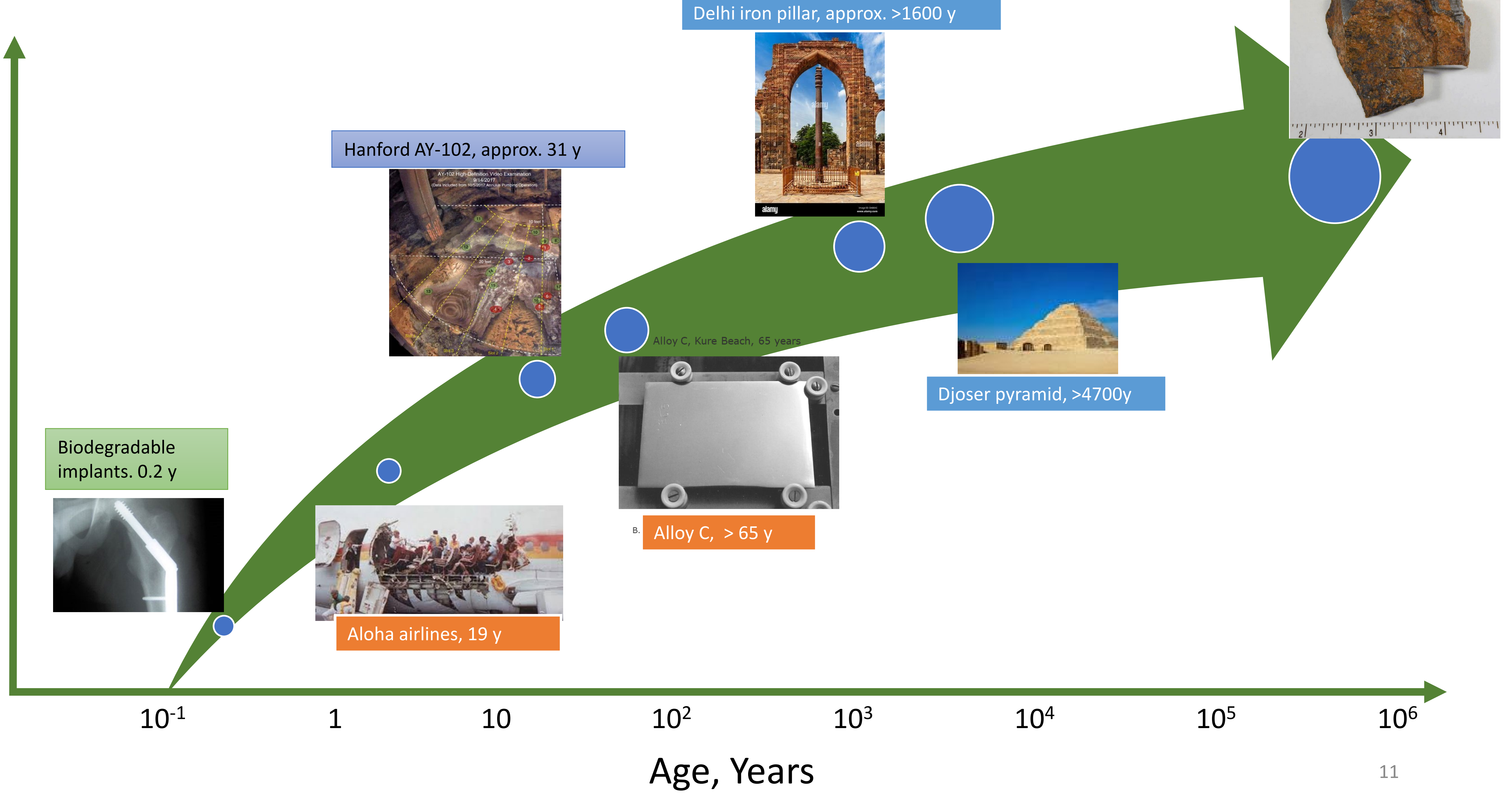




The large diversity in aging rates needs an understanding of fundamental mechanisms

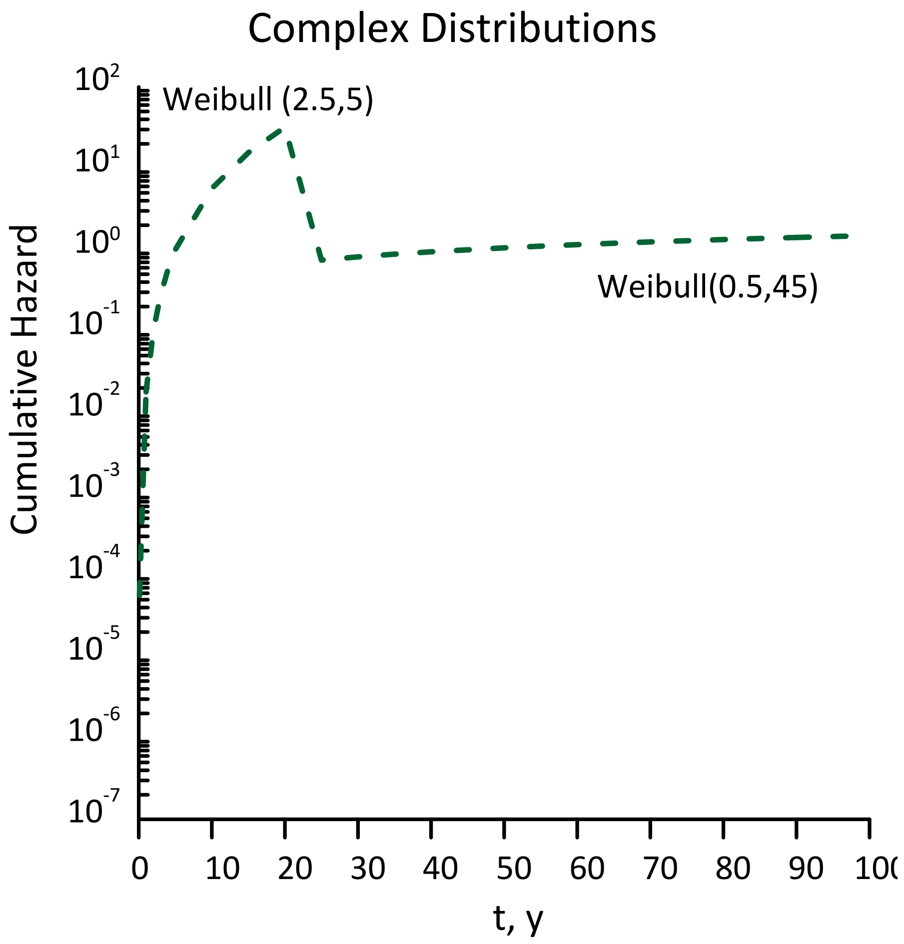
O. R. Jones, et al., Nature, 2014, 505(7482), 169-173.

Corrosion lifetimes



Challenges in predicting aging

- The performance of an aging system depends on its history (probability curve) – lack of knowledge of early history of a structure may lead to failures of currently well-managed systems.
- Predicting aging requires integration across diverse size and time scales and integration across various disciplines.
- Things we don't know that we don't know (unknown unknowns) may affect aging



Two approaches to dealing with time problem

- Model failure rates explicitly (corrosion rate, crack growth rates, etc.)
  - Successful in well constrained systems over limited time periods
  - Works for metal-environment conditions where $pH \leq pH(depassivation)$ – active corrosion
  - Does not work for complex systems or when engineered system interacts with a natural system

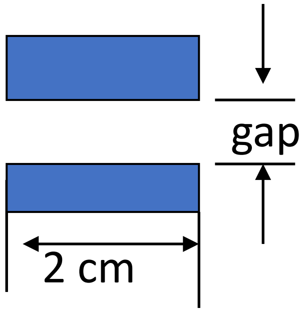
- Give the time problem to somebody else
  - We establish limit states for corrosion/SCC
  - Others determine whether a system exceeds these limit states
  - Allows modeling of complex systems and passive materials

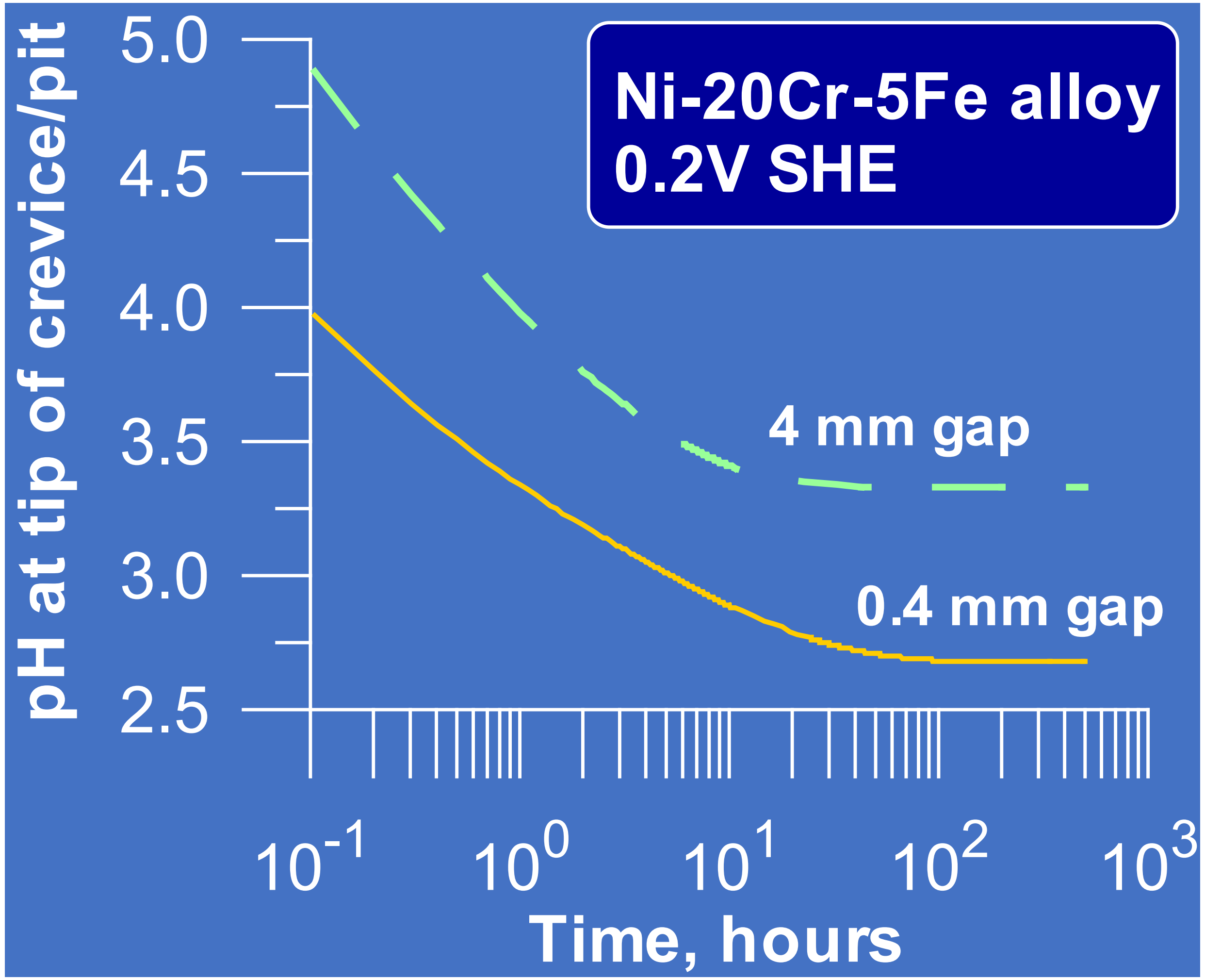
Use of limit states in temporal predictions

- In structural reliability, failure is assumed to occur when load exceeds resistance
  - $P(Failure) = P(m \times Load - n \times Resistance) \geq 0$

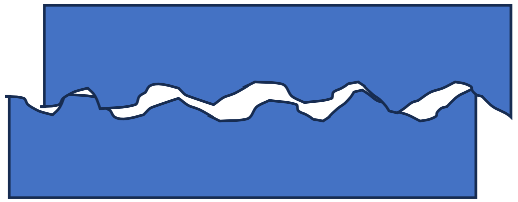
- In corrosion, there may be other limit states:
  - Thermodynamic limit states – Pourbaix diagrams
  - pH $\leq$ Depassivation pH (Galvele, Oldfield-Sutton criteria)
  - Corrosion potential ≥ Repassivation potential
  - Stress intensity factor ≥ Threshold stress intensity factor
  - Temperature ≥ Critical crevice temperature
  - Aggressive species ≥ critical concentration
  - Inhibitors $\leq$ critical concentration

Limit state pH model

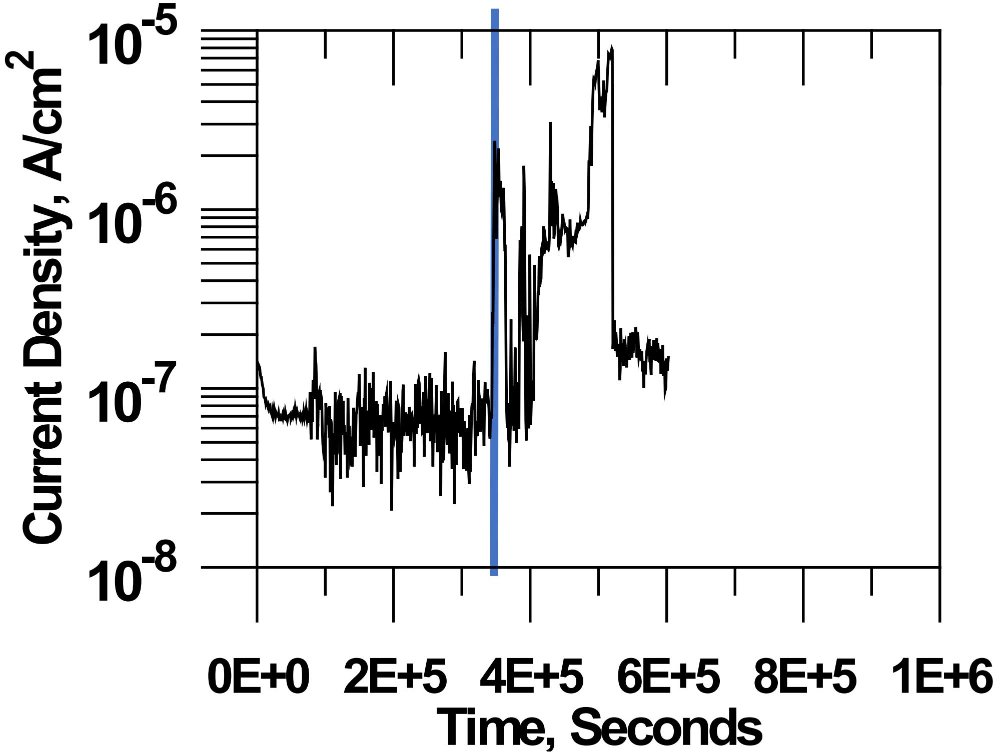


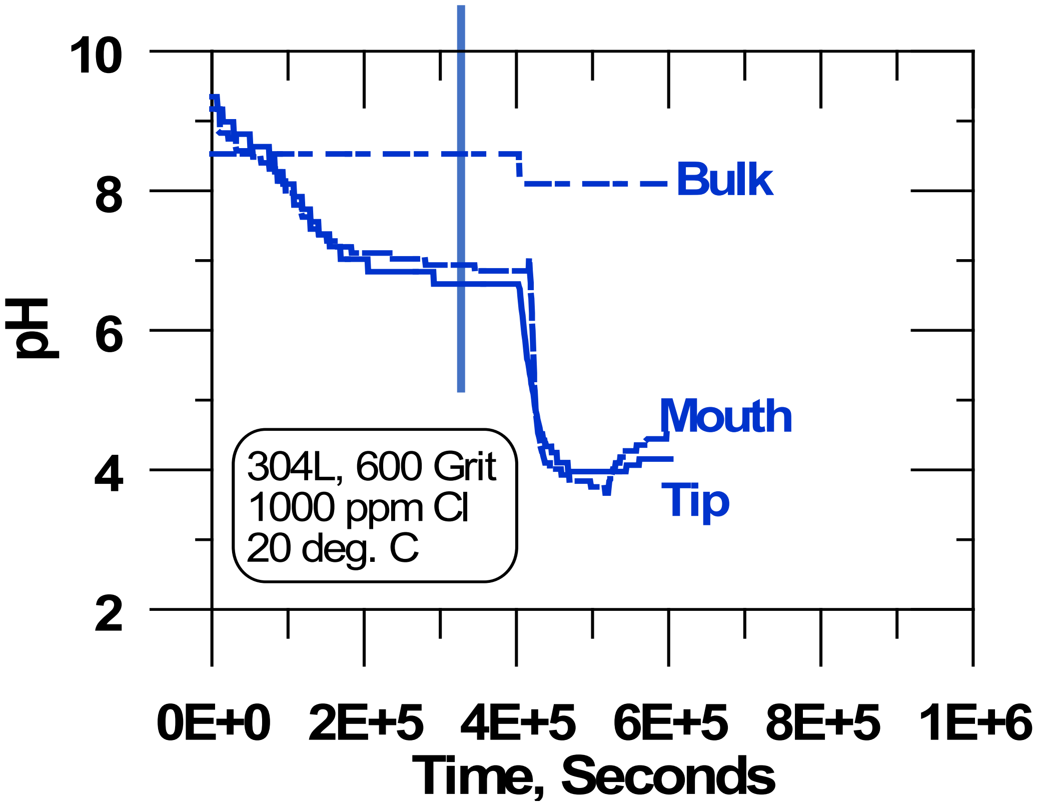


Gaps are stochastic on real mating surfaces



pH vs. Current (304L ss)

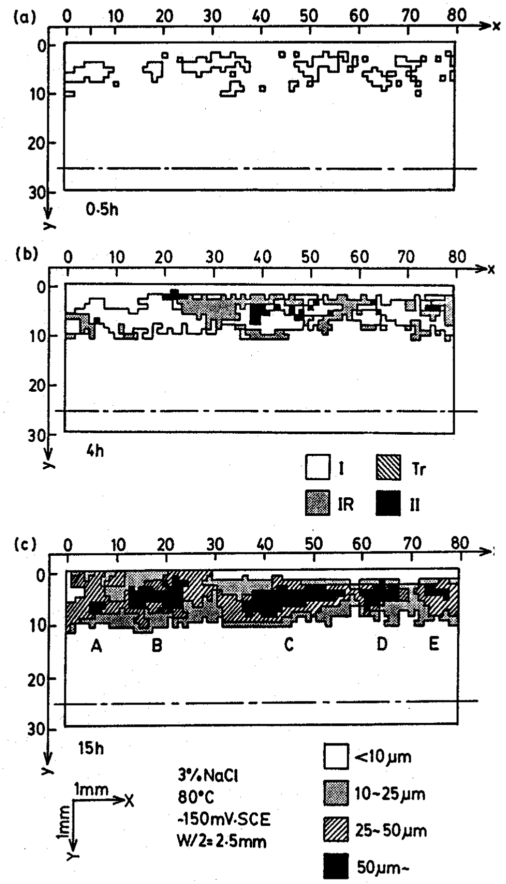


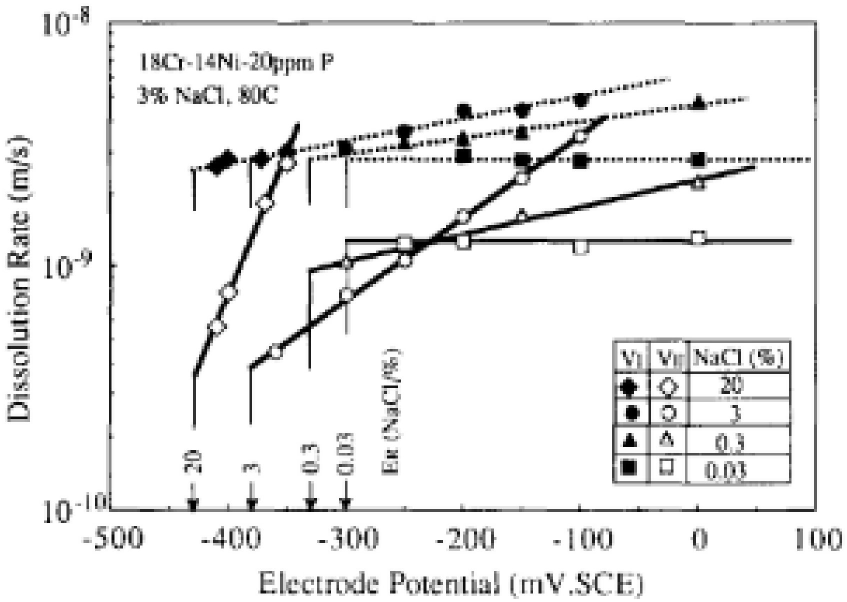


N. Sridhar and D. S. Dunn, Corrosion, 1994, 50(11), 857-872.

- Crevice pH always lags stable current increase

Observation of Corrosion in Crevice

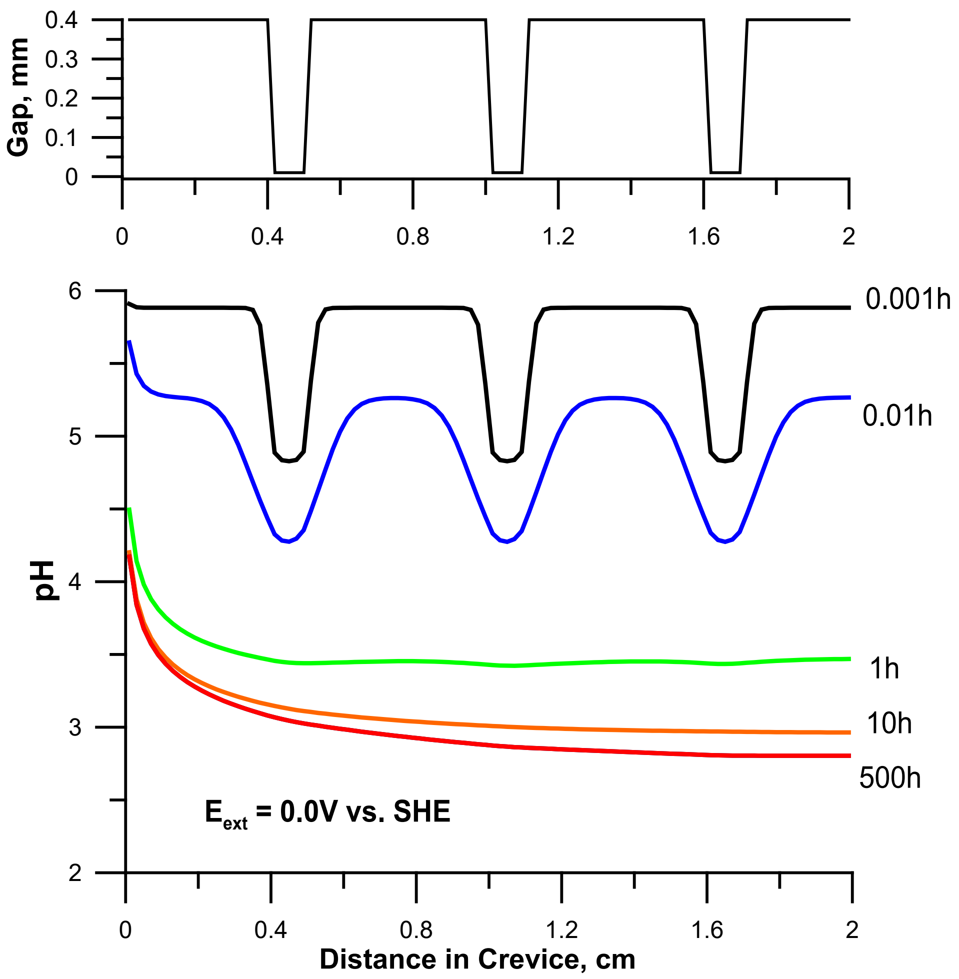


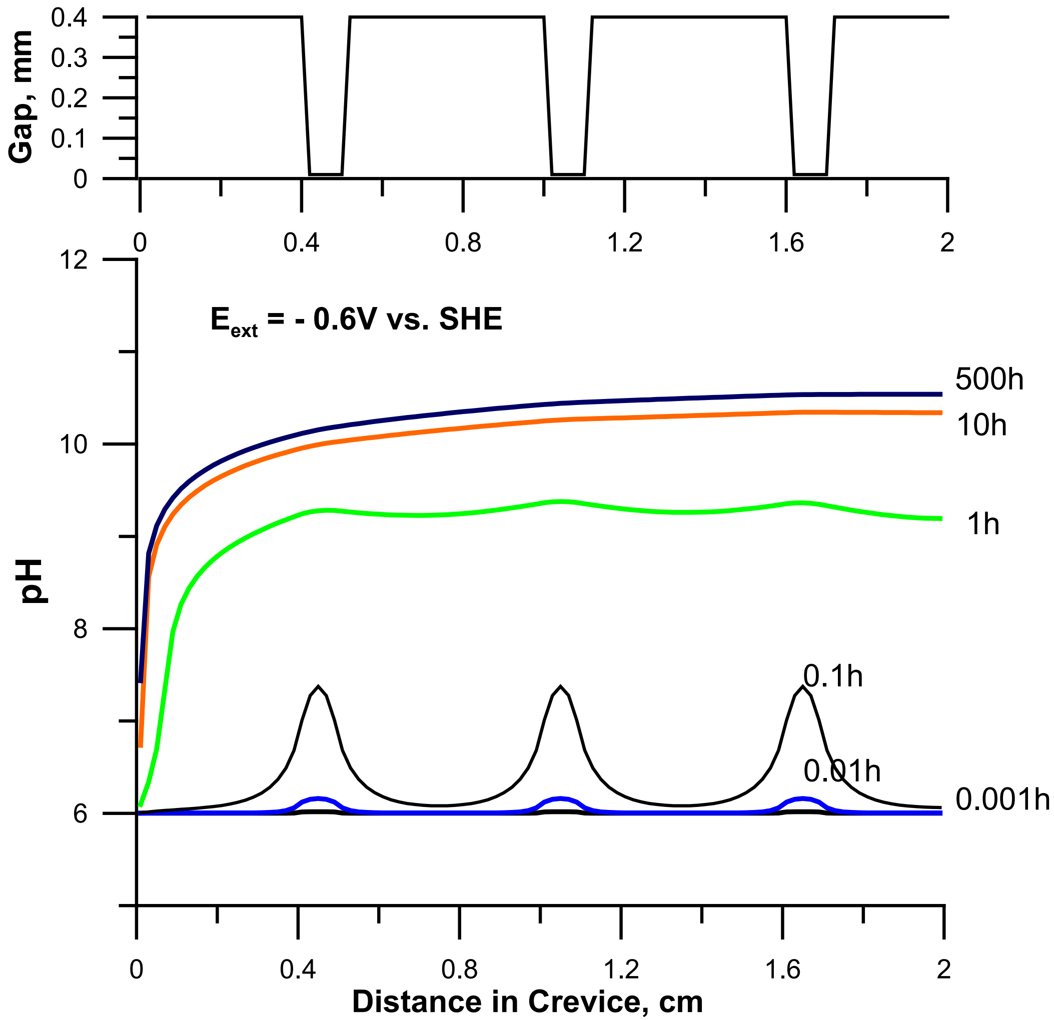


T. Shinohara, N. Mascko, and S. Tsujikawa, Corrosion Science, 1993, 35(1-4), 785-789.

- Moiré fringe measurements under a crevice with plane glass
- Observations of several micro-sites of initiation
- An intermediate distance seems to be favored
- Repassivation potential occurred at a current density of about $3x10^{-1}$ A/m^2 regardless of bulk chloride

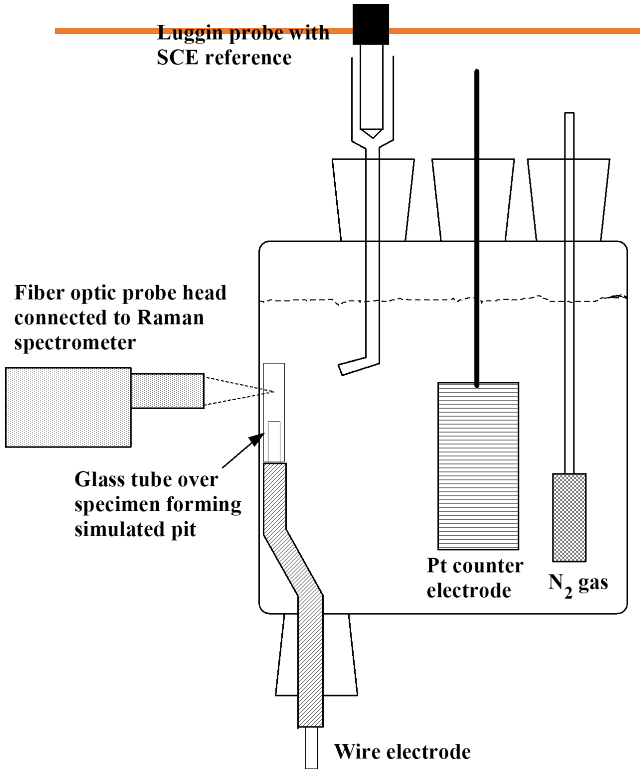
Importance of potential as limit state

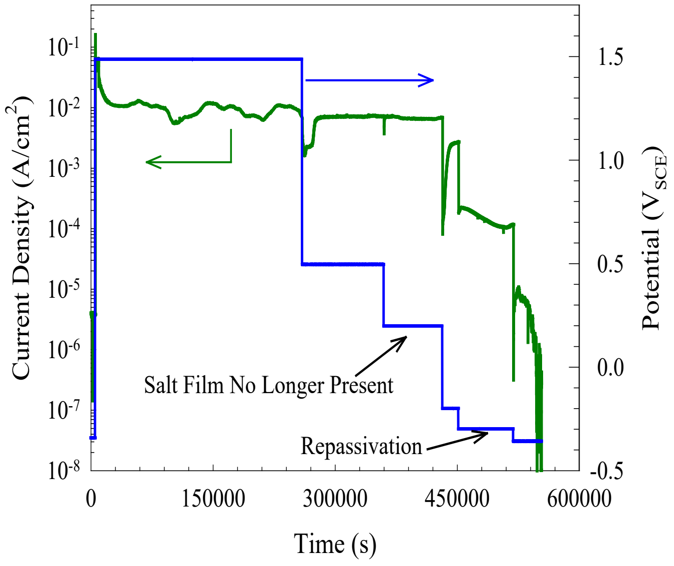


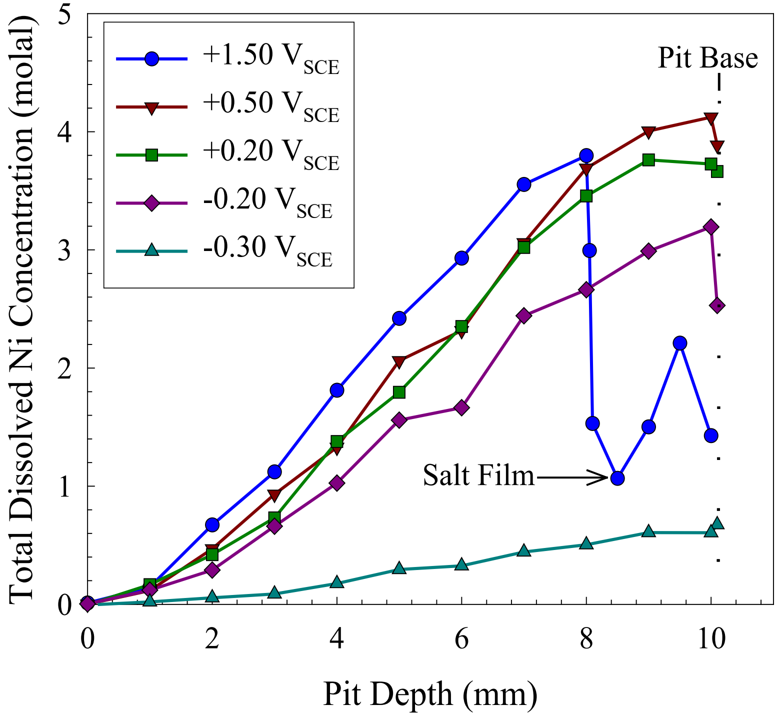


N. Sridhar, *Corrosion, 2016, **73(1), 18-30.***

The role of salt film on repassivation



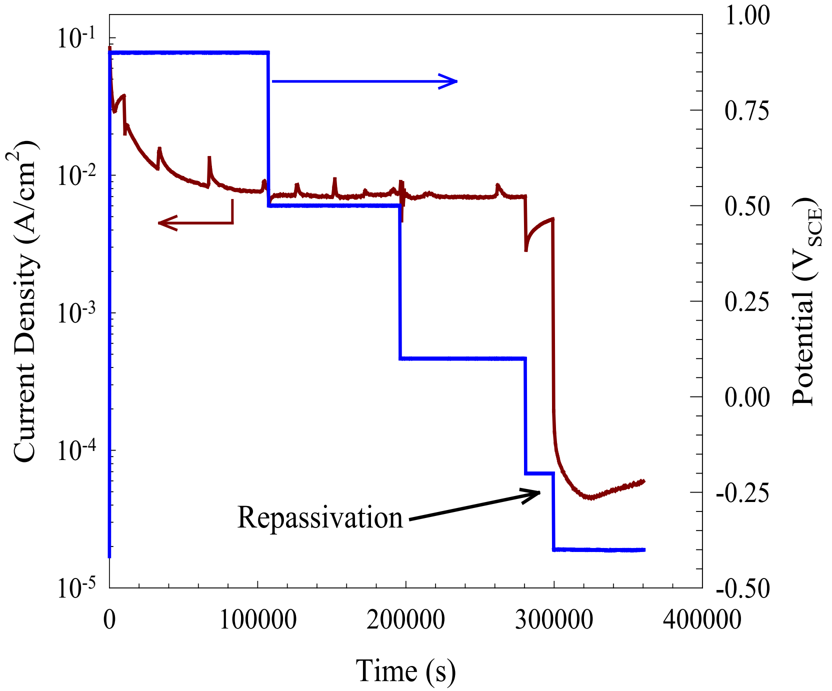


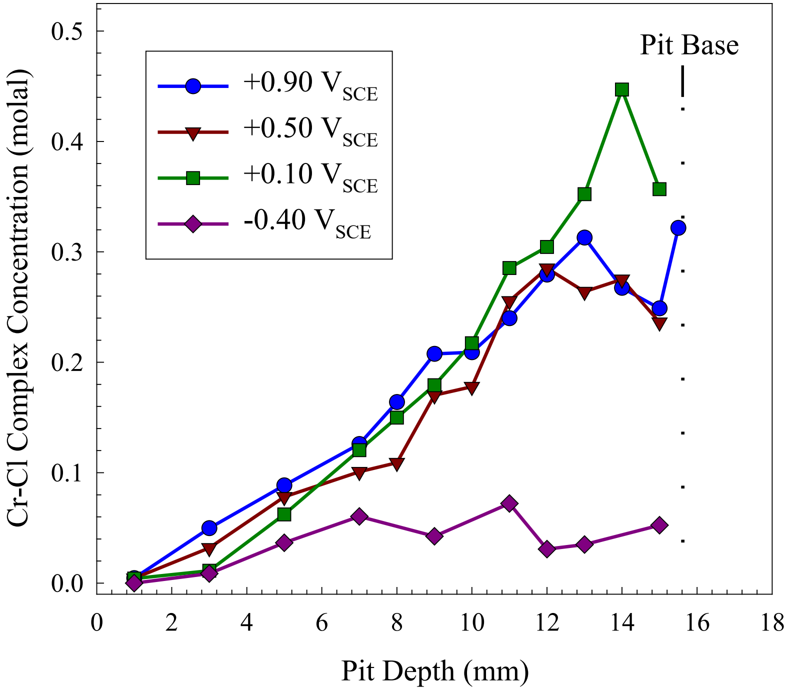


- Concentrated metal-chloride solutions affect repassivation of pits

N. Sridhar and D. S. Dunn, *Journal of the Electrochemical Society, 1997,* ***144(12), 4243-4253.***

Experimental Results - 308SS

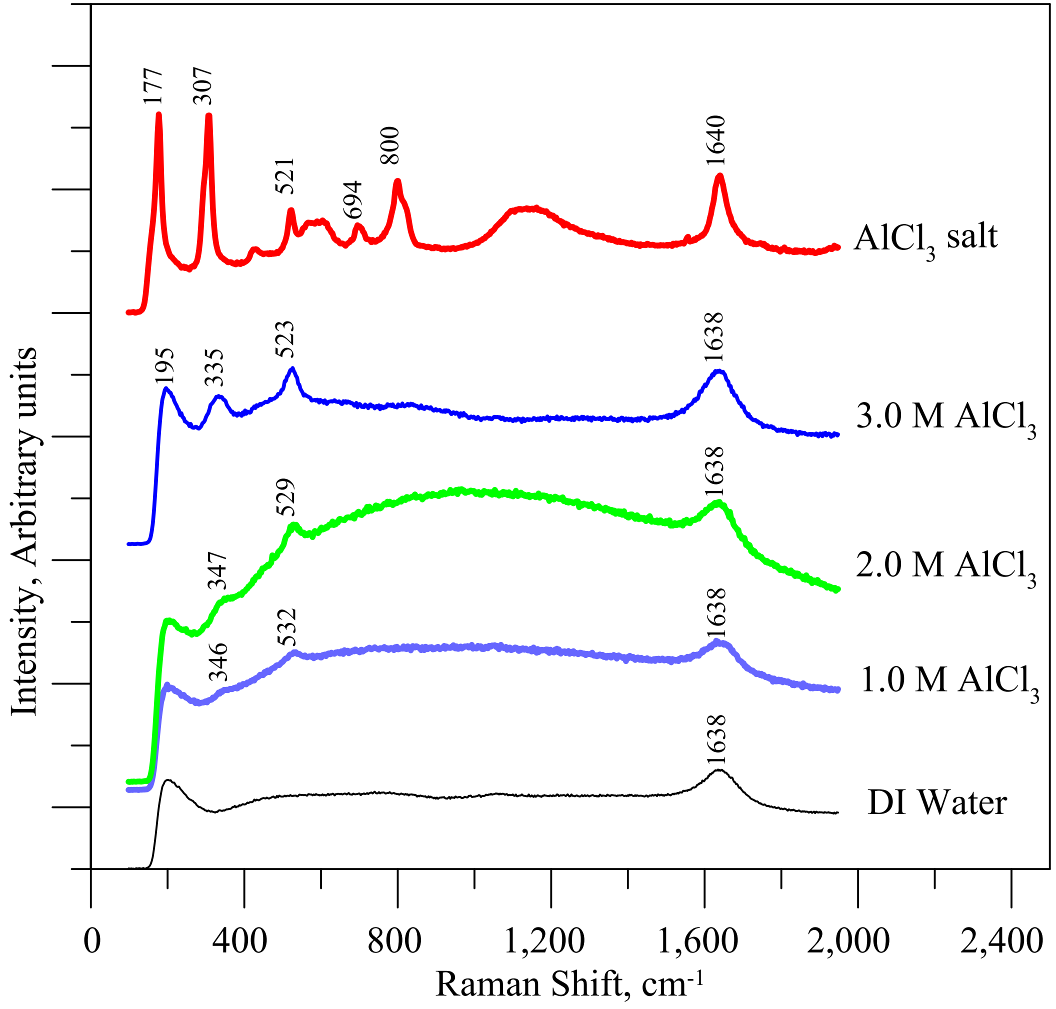


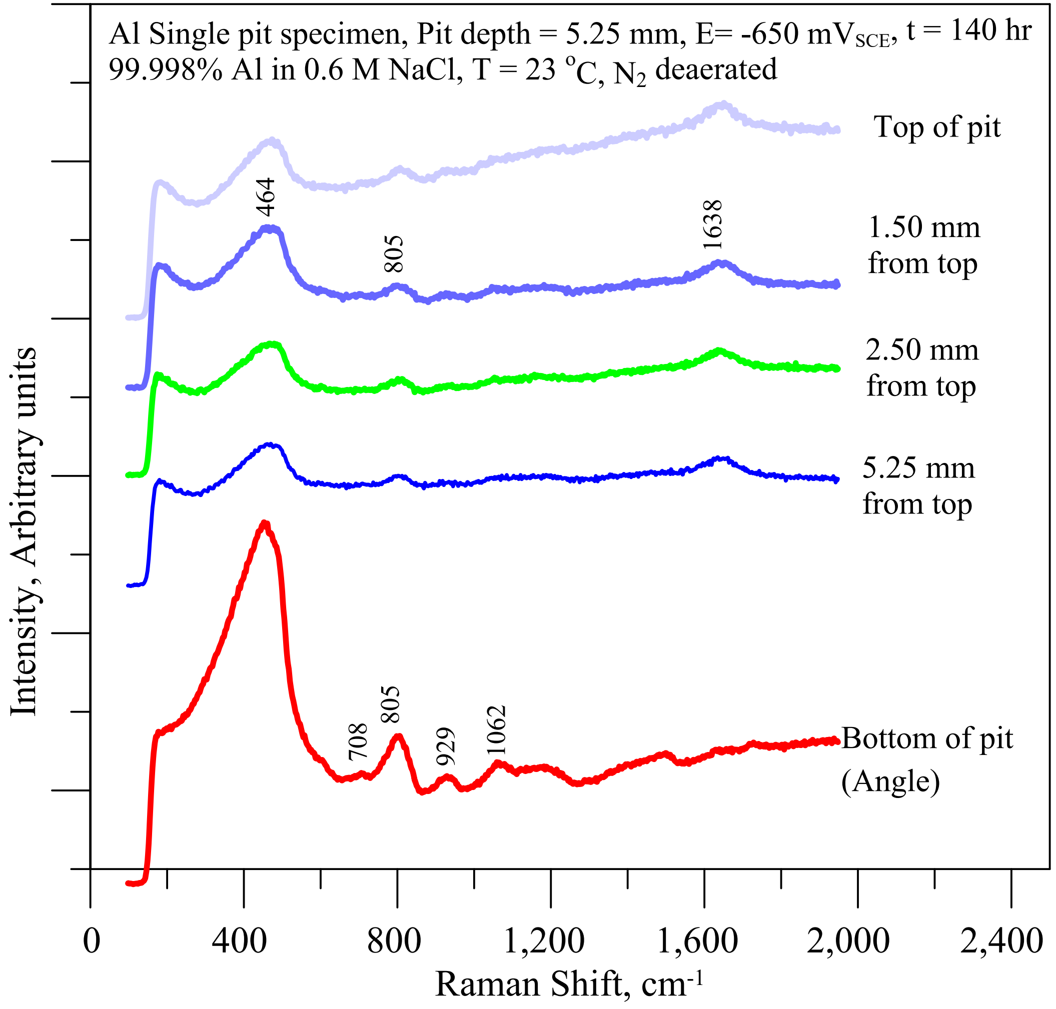


Brossia et al., ECS, 1998

- Dissolution rate still high even at -0.20 V_{SCE}
- Observed relationship between Cr-Cl concentration and dissolution rate -- similar to Ni

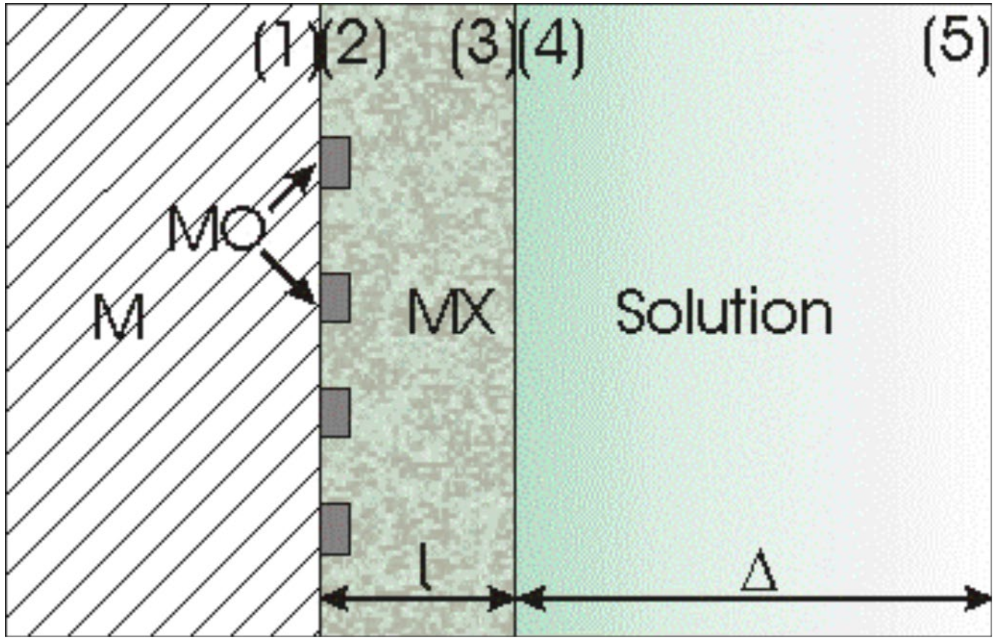
Single pit in Al





D. Dunn et al., unpublished

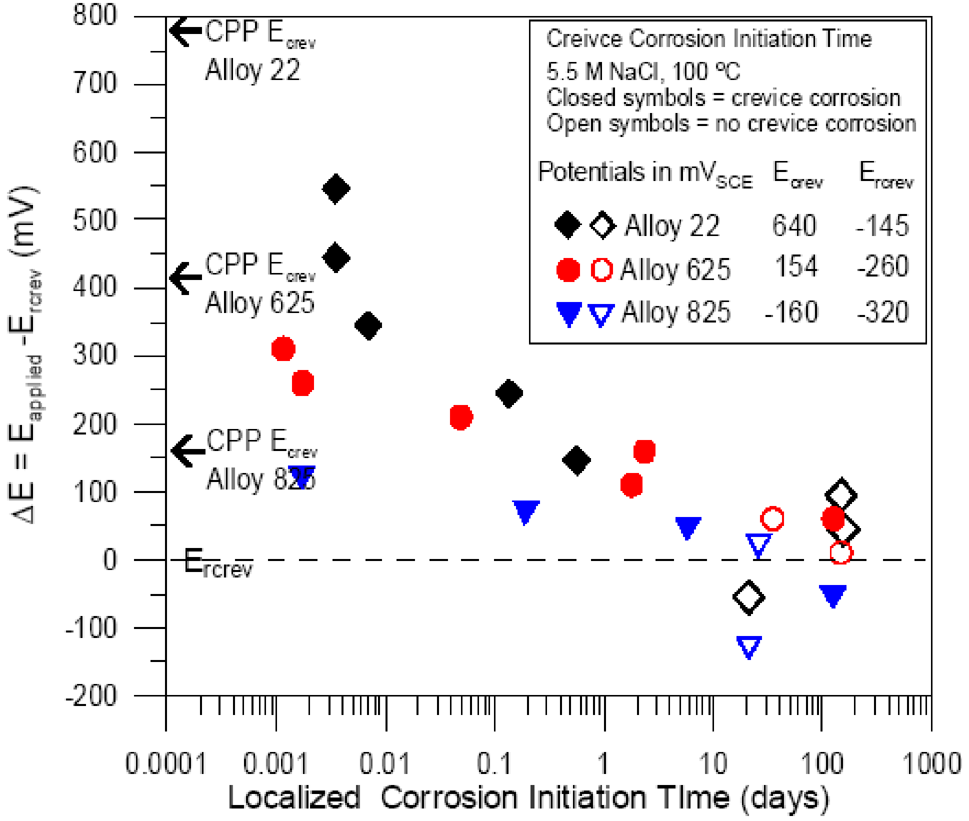
Repassivation Potential Model:
Limiting Behavior as Repassivation is Approached



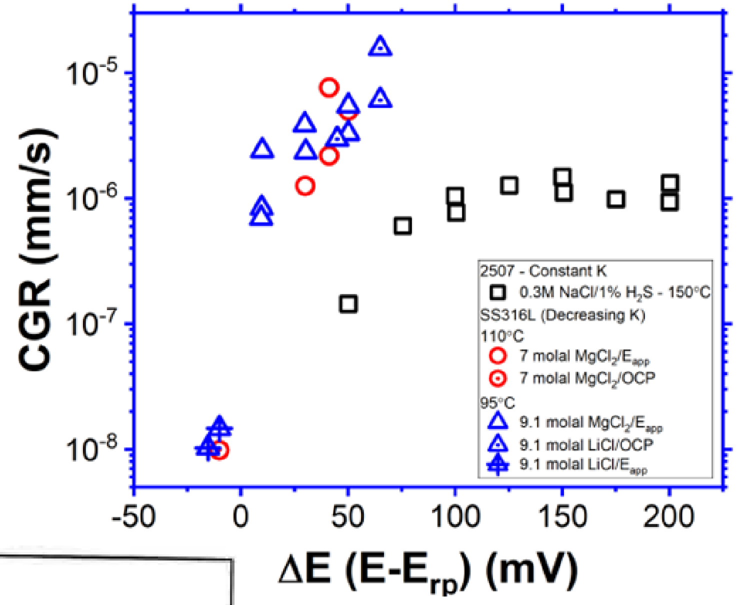
- The expressions can be solved in the limit E -> E_{rp}

A. Anderko, N. Sridhar and D.S. Dunn, *Corrosion Science*, 46 (2004) 1583

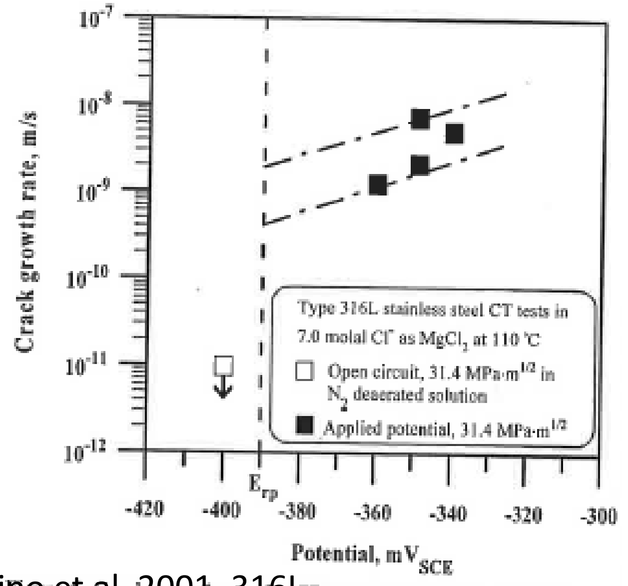
Modeling long-term performance using limit states



Dunn et al., Corrosion/2005

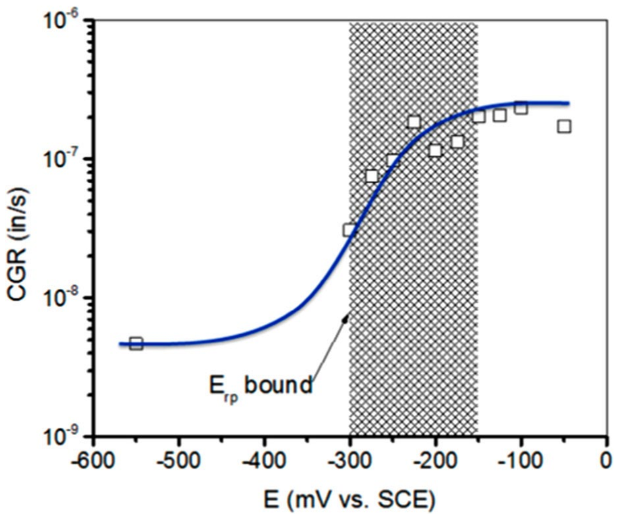


Gui et al. 2016

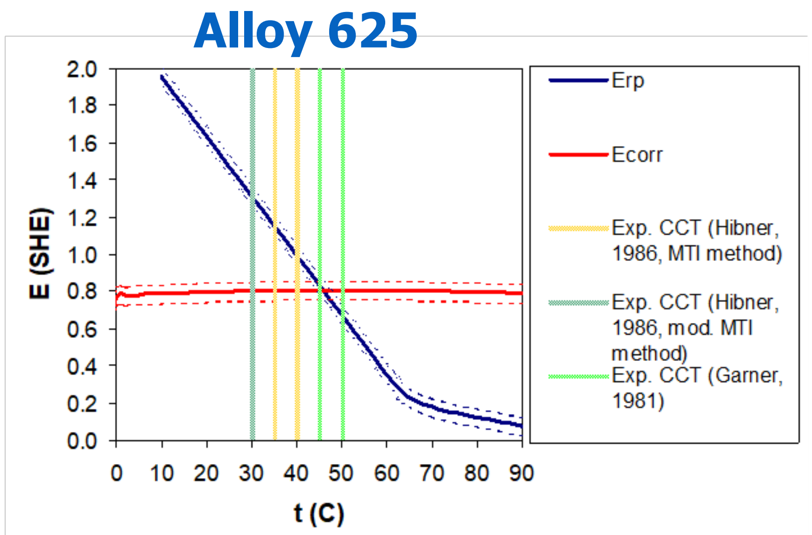


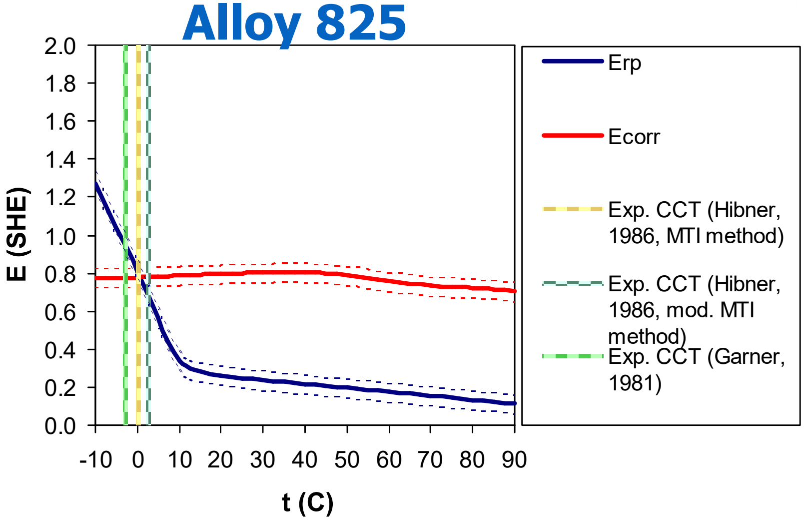
Cragnolino et al. 2001, 316L

Sridhar et al., 2017, 13Cr

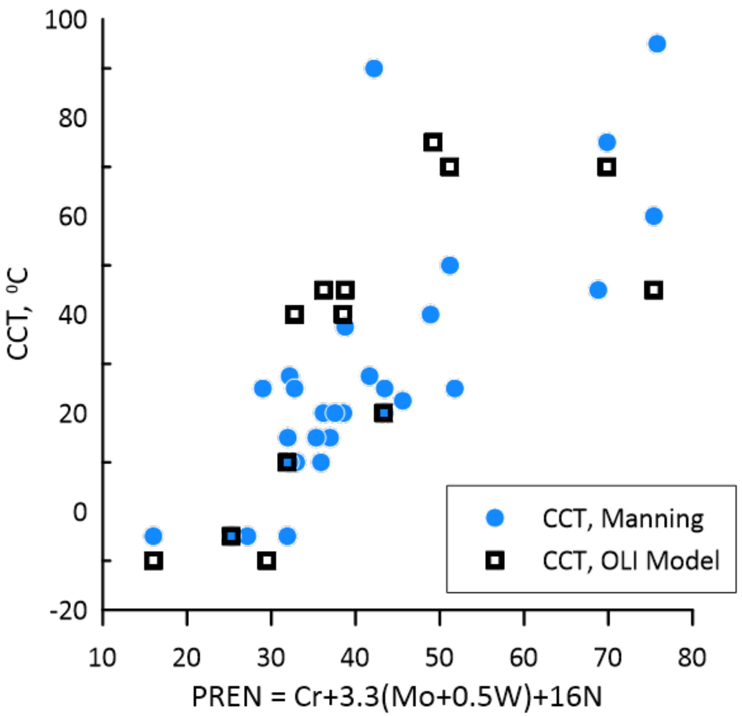


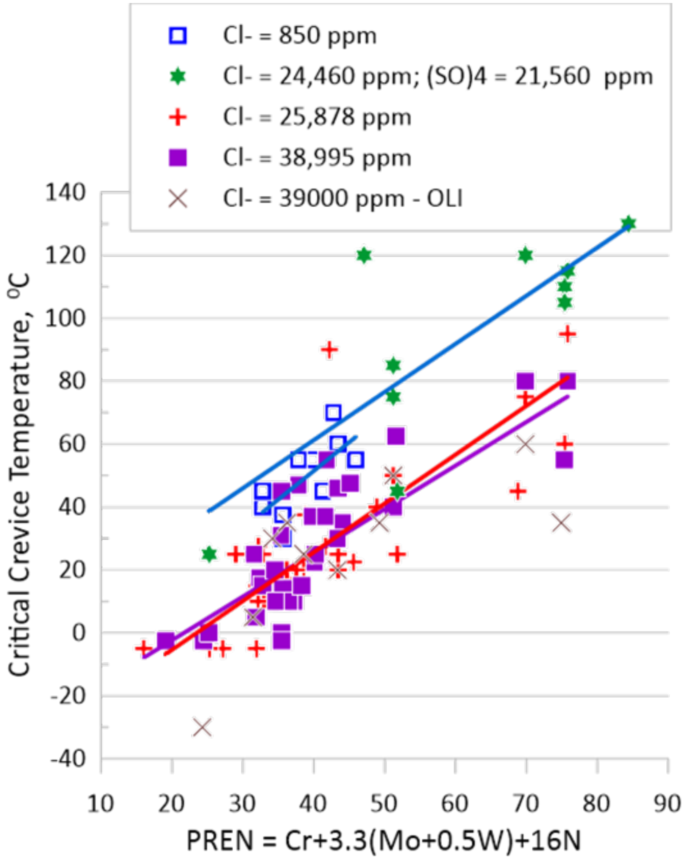
Relationship between limit states





Anderko et al., Corrosion/2005, Paper 05053



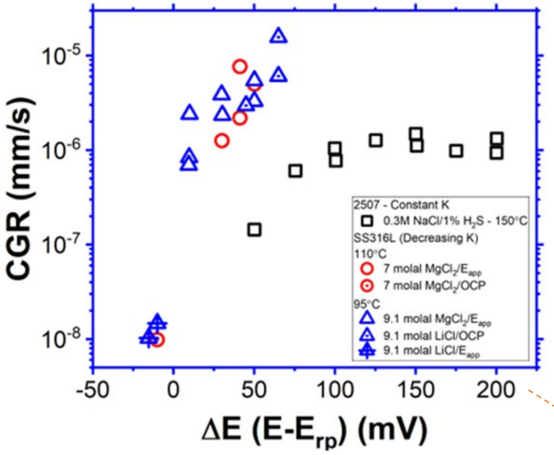


Sridhar et al., JES, 2023

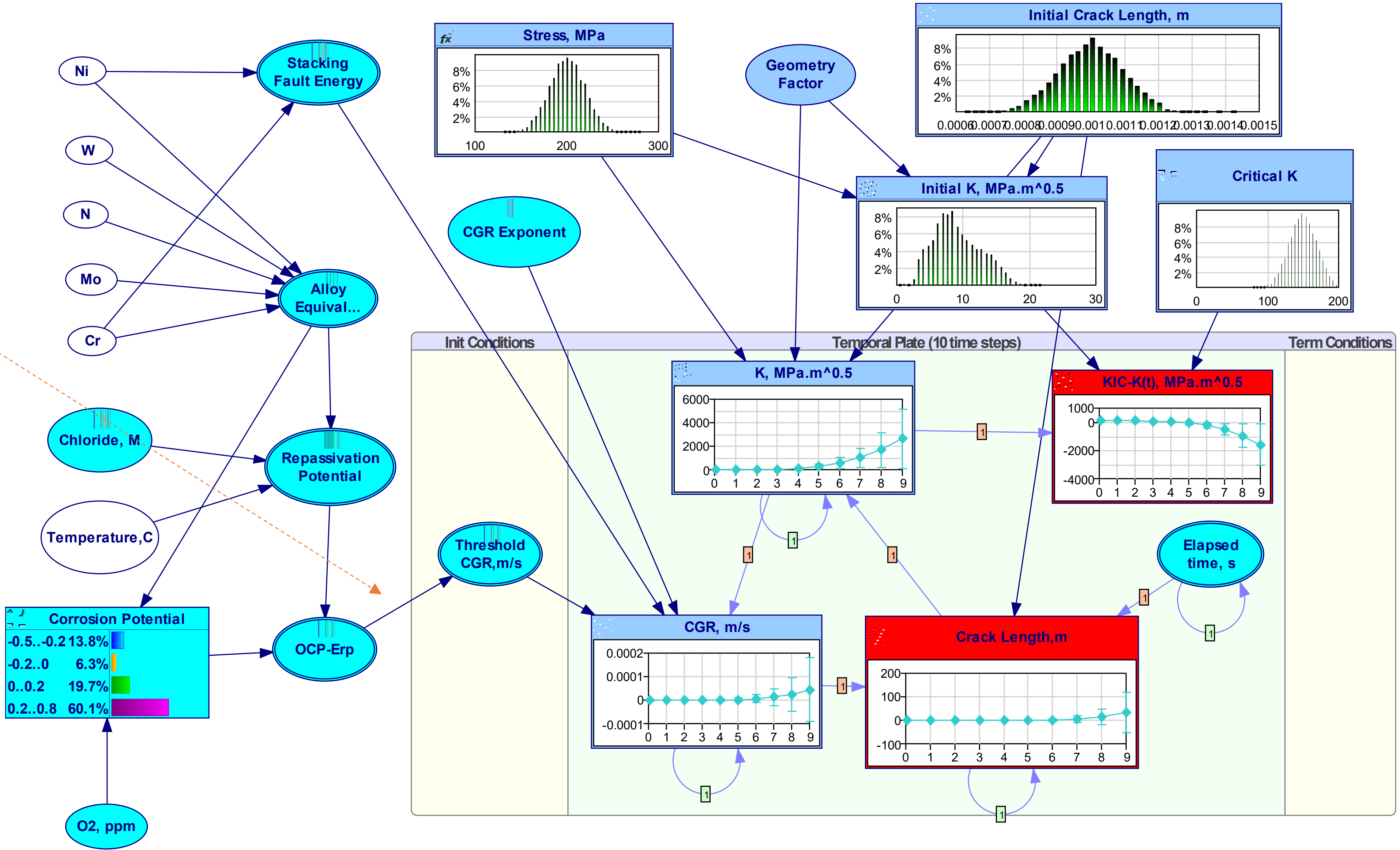
Predicting hazard rate from limit states

Current and future work

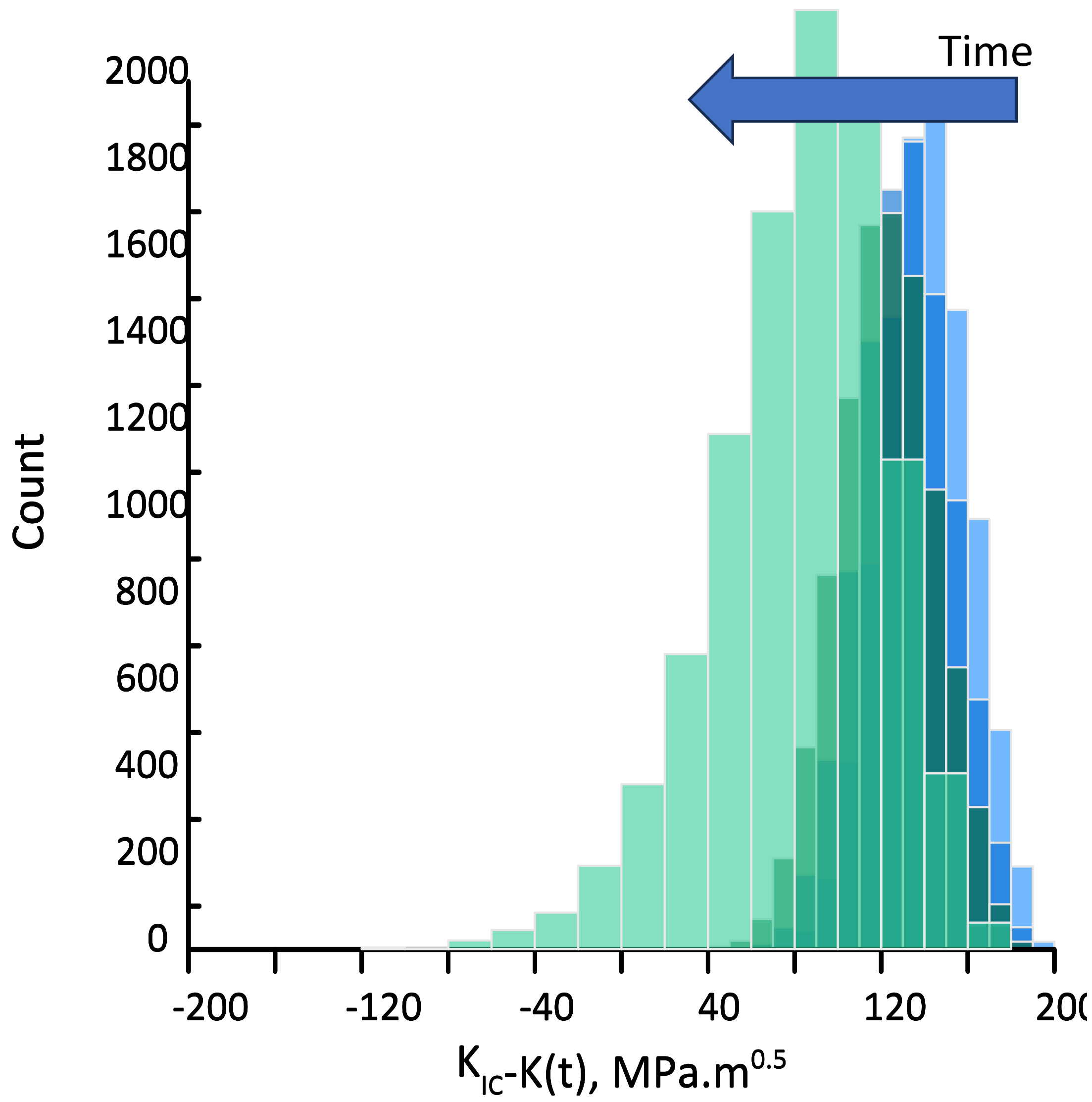
Probability of SCC vs. Time using limit states

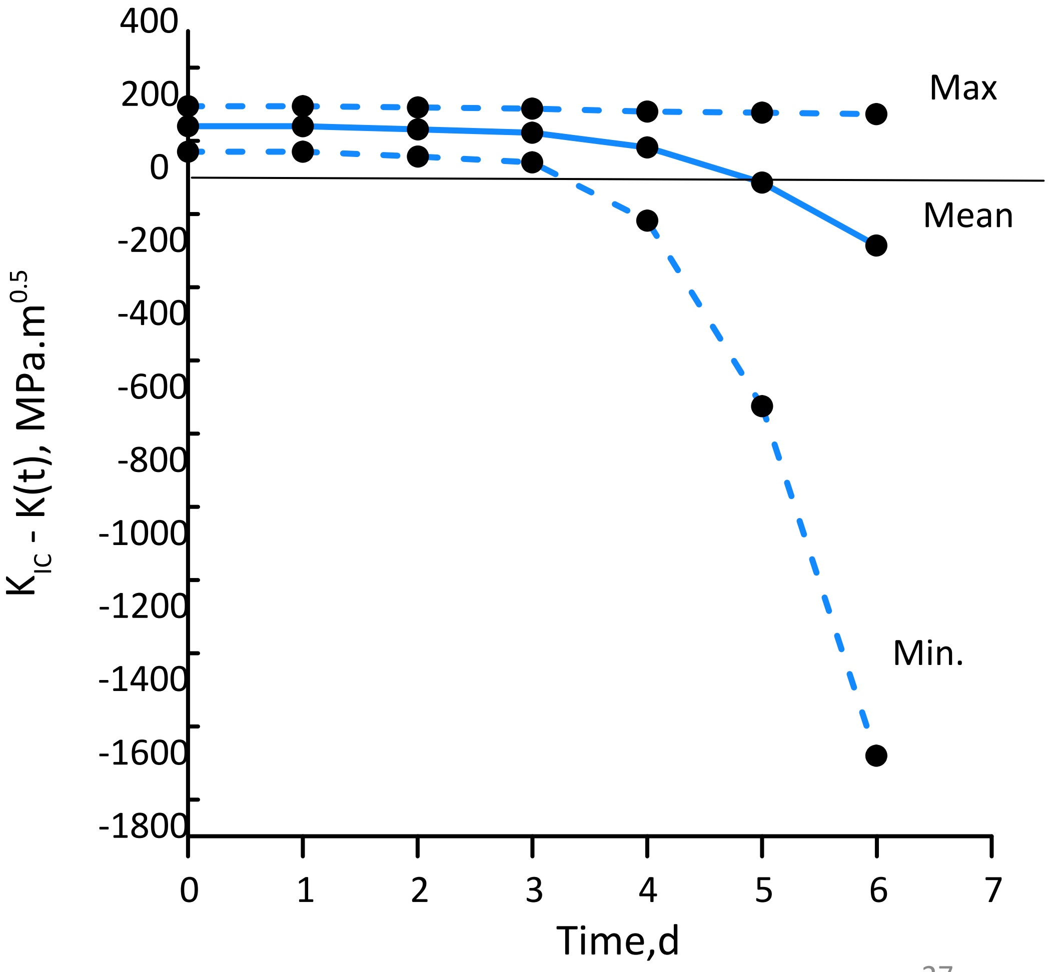


The concept of repassivation governing SCC in chloride environments is used in defining threshold K



Growth of fracture limit distribution over time

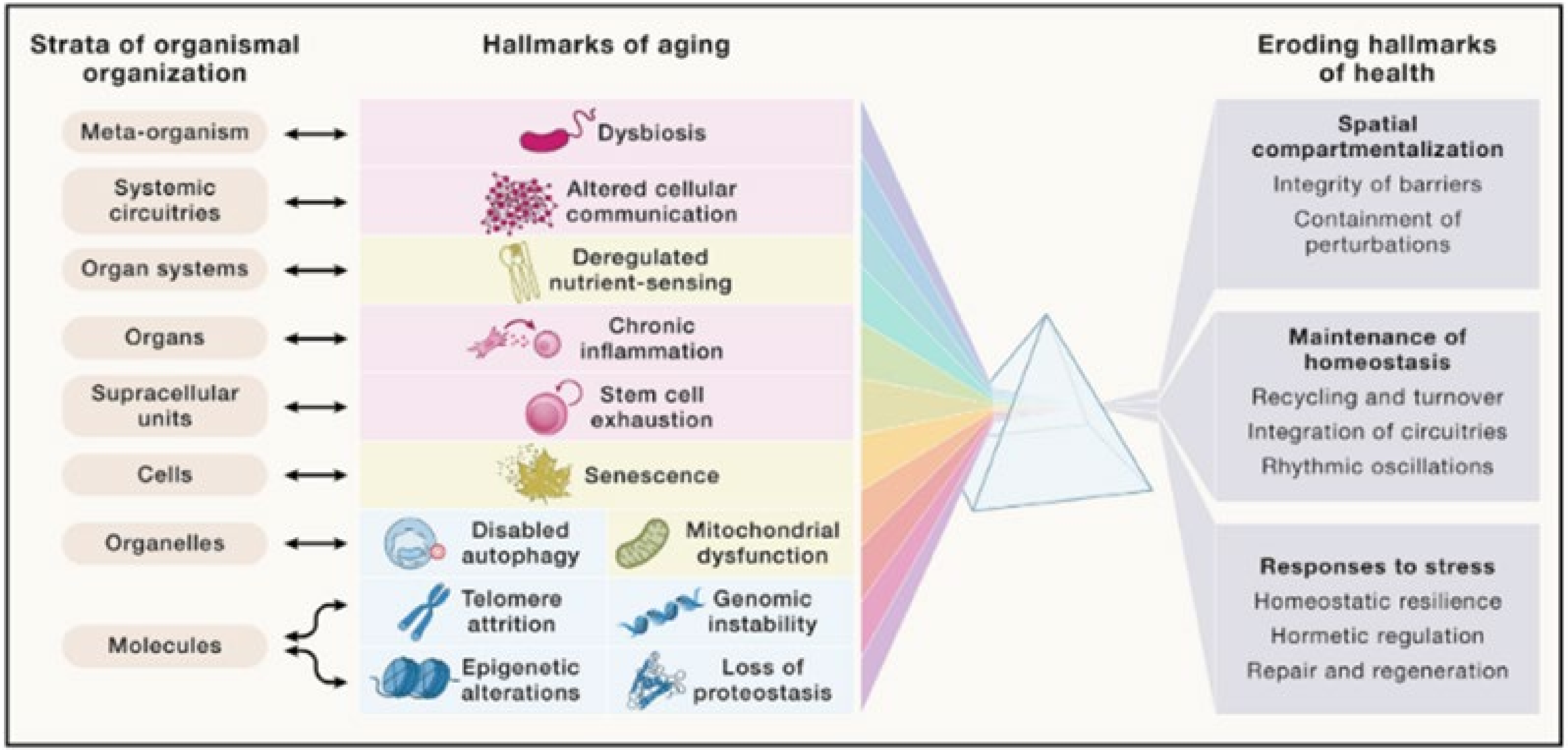




Hallmarks of Aging

Leading indicators

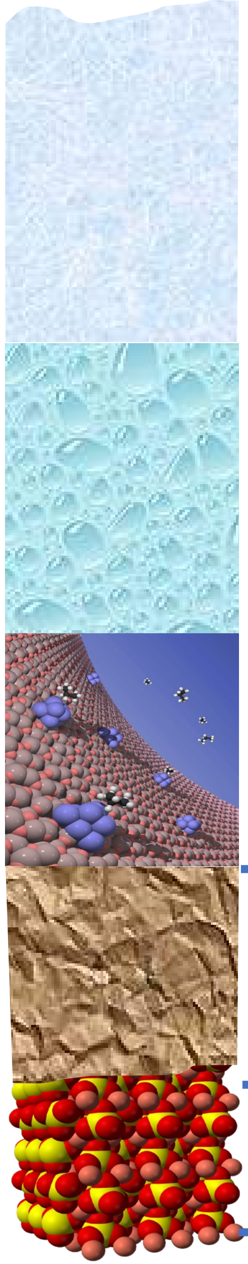
Hallmarks of aging in biological systems



C. Lopez-Otin et al., Cell, 2023, 186(2), 243-278

Can we identify hallmarks of aging for materials?

Domains



Factors and Events

External Environment
- Temperature
- Pressure
- Gas-liquid reactions
- Deliquescence
- Speciation, ion exchange, micellization
- Radiolysis
- Microbiological colonies
- Flow/erosion
- Stress/Strain rates

Local Environment
- Alkalinization at cathodes
- Acidification from hydrolysis
- Biofilm environment
- Inclusion reactions
- Chemistry change - % saturation
- Scaling
- Evaporative concentration

Surface
- Adsorption/desorption
- Passivity/depassivation
- Slip steps/fresh metal
- Point defect generation and transport
- Segregation
- Dealloying

Bulk Microstructure
- Alloying element depletion
- Anti-phase domains/coherent phase – planar slip
- Deformation mode/ twinning
- Dislocation pileup at boundaries
- Trapping

Nanostructure
- Point defect generation and transport
- Nanovoid formation

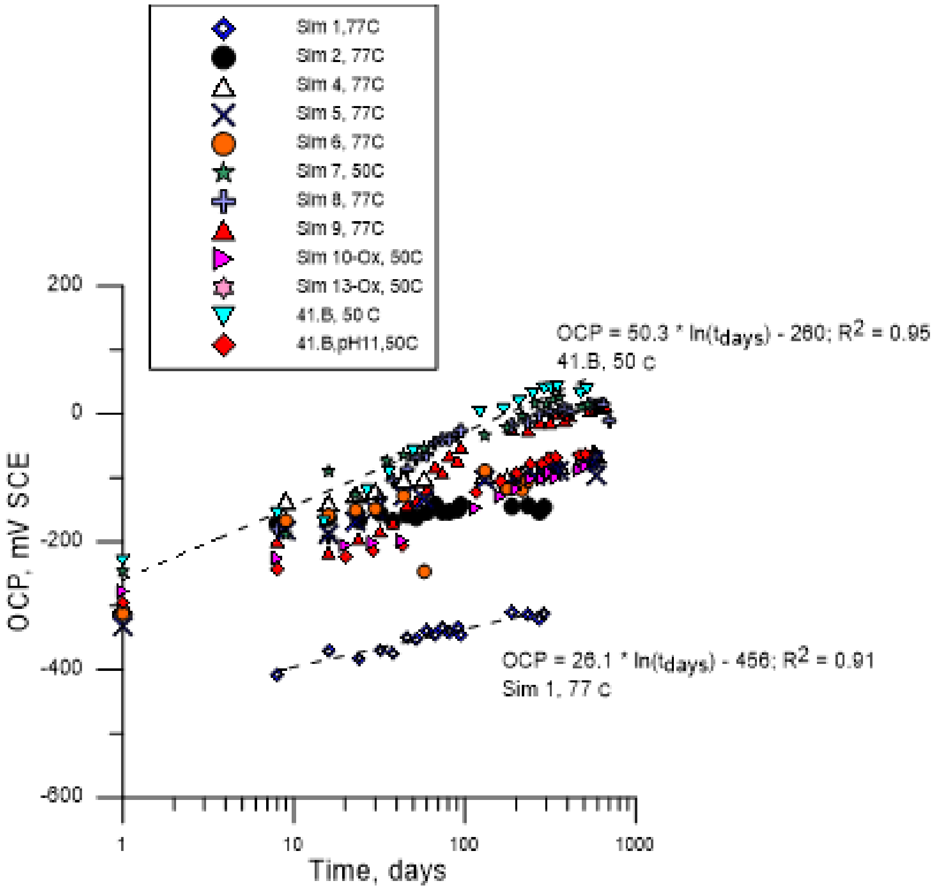
Hallmarks of Aging

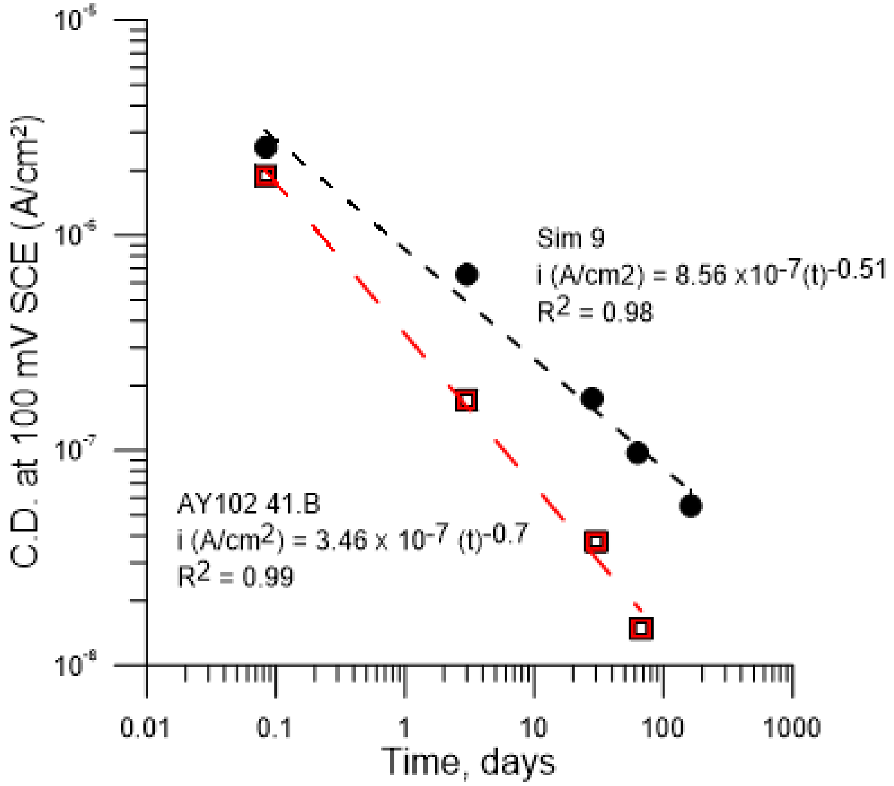
- Changes in corrosion (open-circuit) potential
- Increase in corrosion products
- Rapid changes in electrochemical impedance
- Increase in current variations between nominally identical electrodes
- Increase in hydrogen uptake
- Crack colonies increase and link up
- Increasing segregation of alloying elements
- Changes in surface composition and element distribution
- Increase in macro or microhardness and decrease in toughness
- Increase in precipitates or second phase formation
- Acceleration of increase in strain rate or decrease in load
- Grain boundary void formation/depletion

Failure Modes

- Large area nonuniform corrosion
- Pitting
- Crevice corrosion
- Stress corrosion cracking
- Hydrogen stress cracking
- Hydrogen Induced Cracking
- Hydrogen reaction cracking
- Corrosion fatigue
- Embrittlement

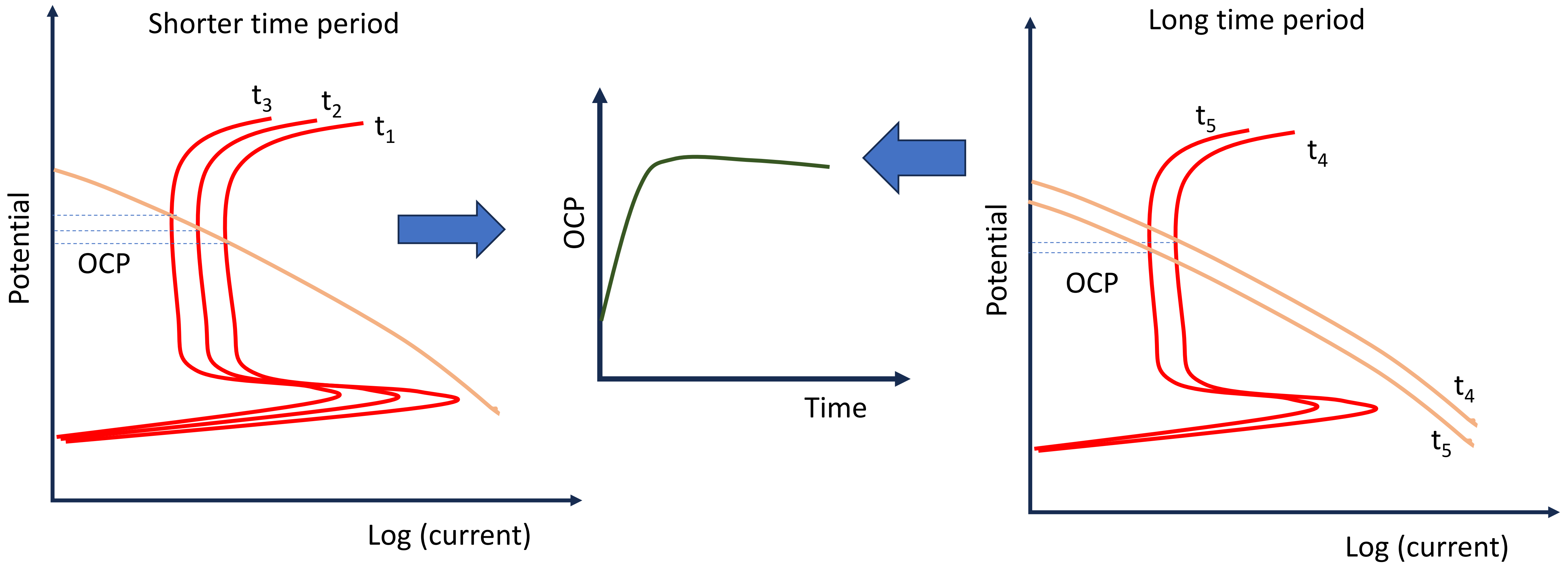
Corrosion potential vs. time (Carbon steel – nitrate-nitrite solutions)





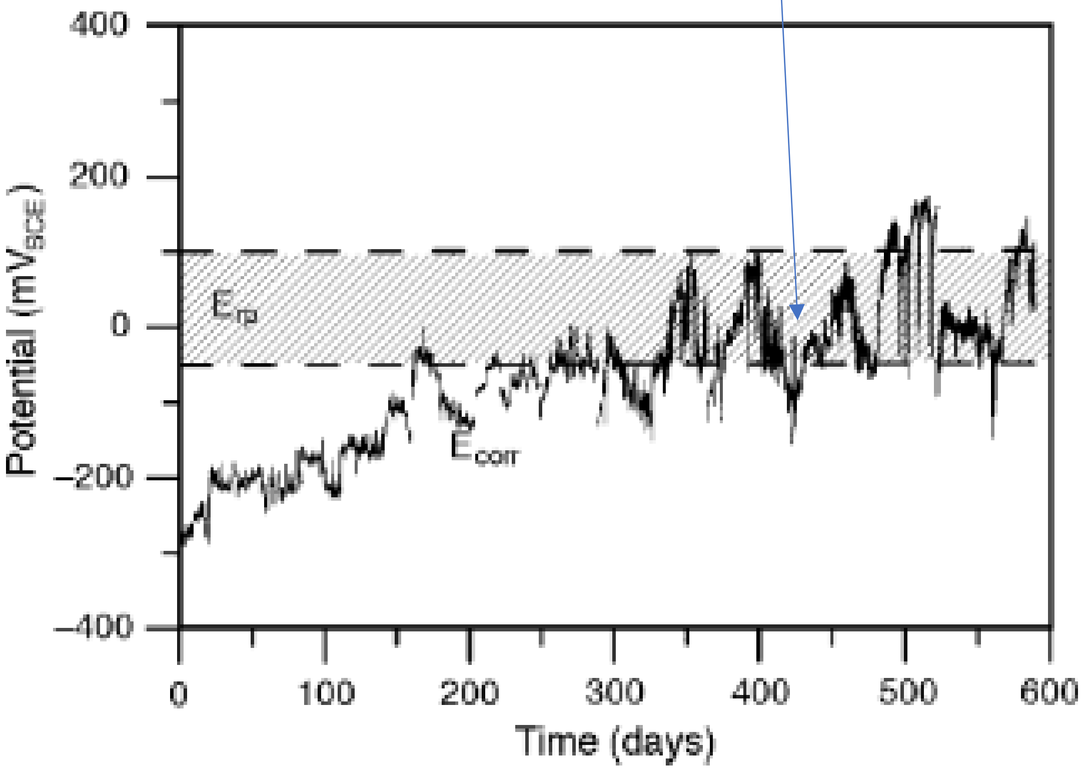
K. Evans, N. Sridhar, B. Rollins, S. Chawla, J. Beavers, and J. Page, Corrosion, 2019, 75(1), 106-119.

Corrosion potential vs. time



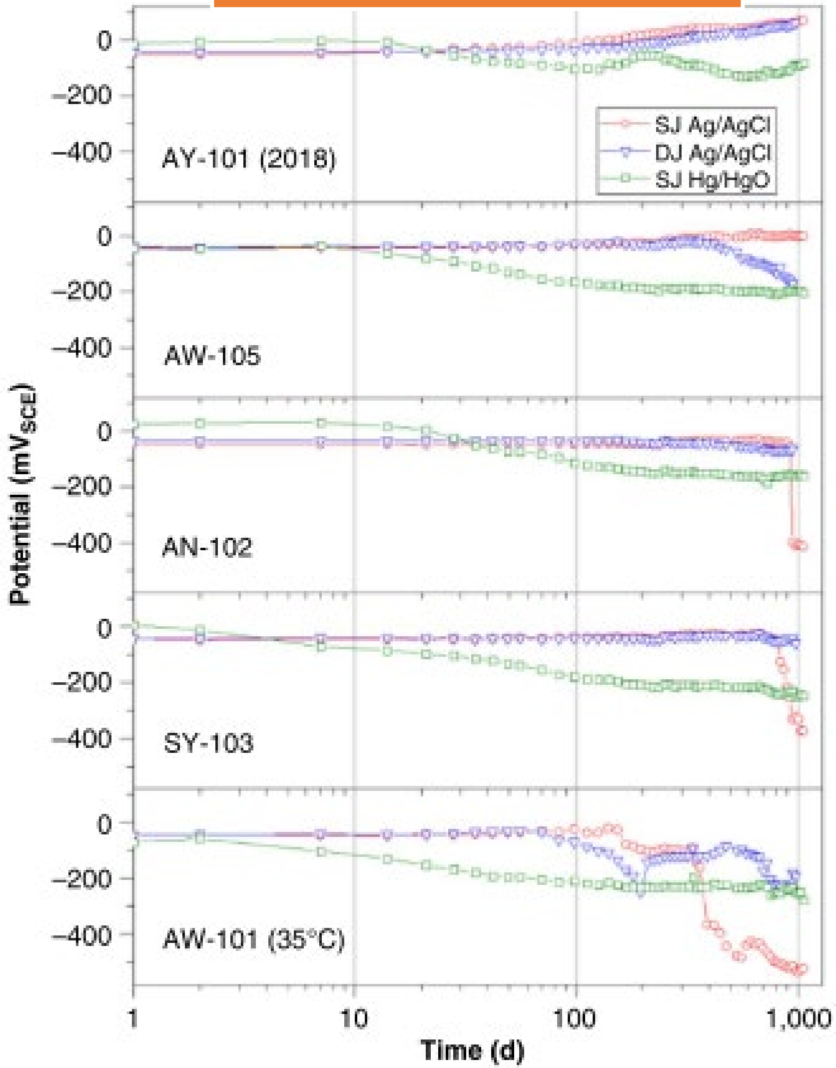
Interpretation of corrosion potential must be done carefully

Crevice corrosion



D. S. Dunn, G. A. Cragnolino, and N. Sridhar, Corrosion, 2000, 56(1), 90-104.

Reference electrode drift

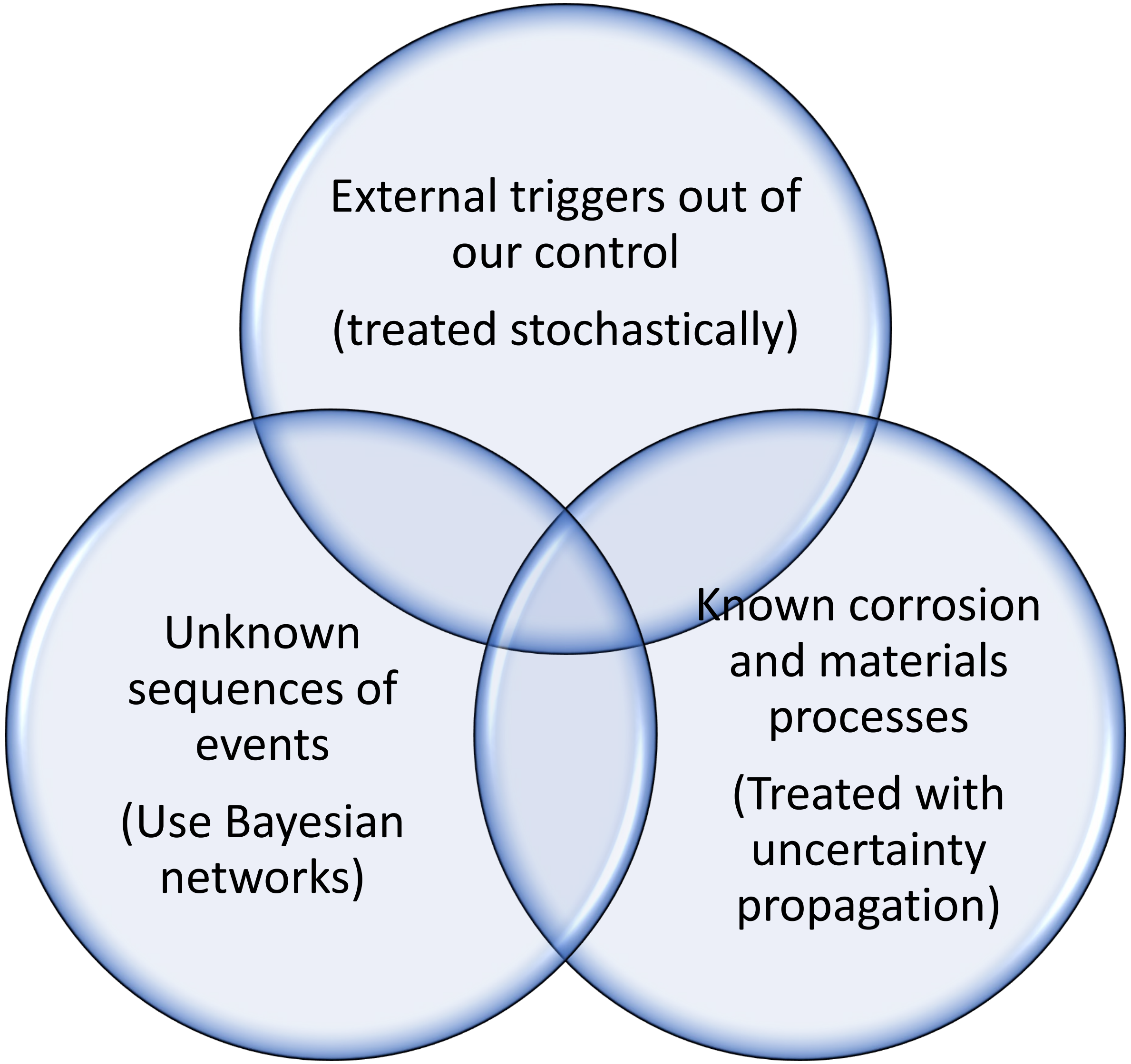


S. Chawla, K. Evans, S. Feng, and N. Sridhar, Corrosion, 2024, 80(5), 472-488.

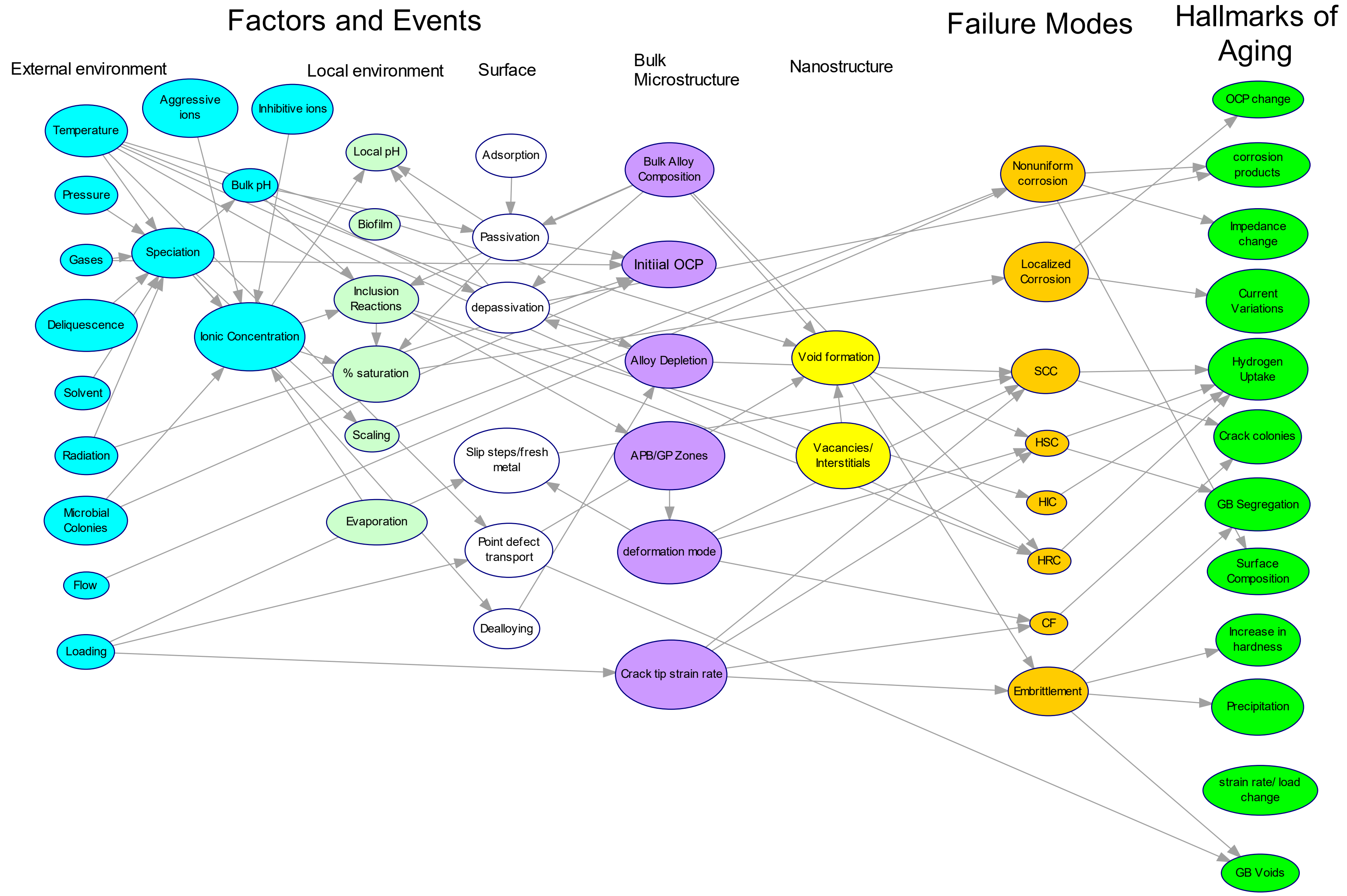
Unknown unknowns

“Thus, the category of scenarios not yet thought of may be handled by the same process as any other scenario category: The relevant evidence is assembled and quantitatively assessed using Bayes’ theorem.” – Kaplan and Garrick

Unknown unknowns



Event sequences



Summary

- Aging involves increasing hazard rate – but hazard rates cannot be predicted using only data-based models
- Our knowledge is the key to our ability to predict future performance of aging systems
- Predicting the behavior of aging systems should involve an understanding of fundamental mechanisms – aggregate data should be used to validate predictions, but not as inputs
- Limit state models provide us flexibility in considering a variety of materials and systems
- A complete identification of hallmarks of materials aging will be beneficial in monitoring aging systems proactively
- Unknown unknowns can be represented as unknown sequences of events governed by known laws of corrosion

Narasi Sridhar, Ph.D.
CEO

MC Consult LLC

Materials & Corrosion Consulting

31510 Sweetwater Circle
Temecula, CA 92591
USA
(614) 787-8249
Nsridhar@mcconsultco.com
www.mcconsultco.com