The effect of moisture transport on corrosion protective coatings

or, being careful with accelerated weathering.

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Coatings and Polymeric Materials

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Outline

- Not about corrosion directly
  - But about the protective coatings
  - how they take up water
  - How long they take to respond
- Introduction and Motivation
- Approaches
  - Modeling
  - Experiment
- Conclusions
- Acknowledgment

Importance of Coatings

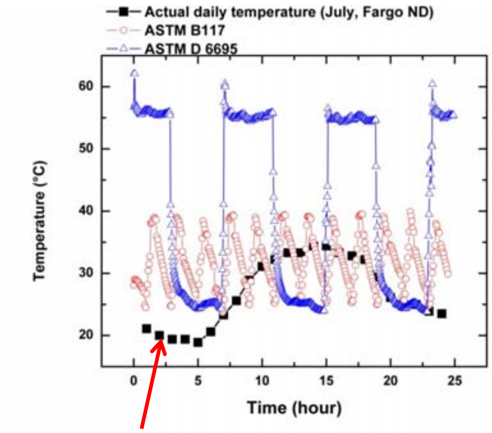
- Principal protection against corrosion

- The end is in sight when the coating is defeated
  - ✓Degradation
  - ✓Cracks
  - ✓Adhesion loss
  - ✓Inhibitor loss

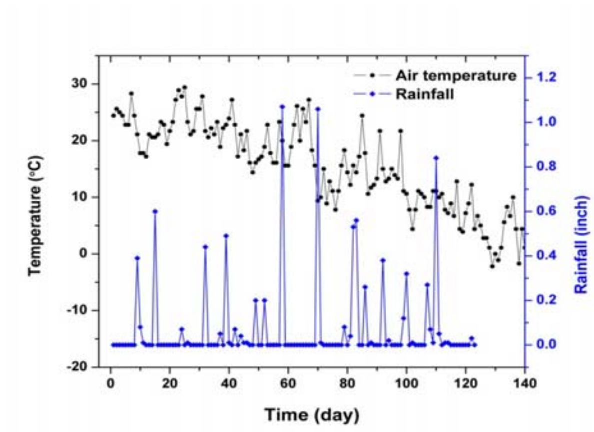
Big Question

- How long will the coating function?
  - How do we find out?
    - » Modeling
    - » Experiment
  - Know and apply basic science
    - » We do this
  - Speed up the failure process
    - » We all do this

How Different Is Natural Weathering?



20-30°C 12-hr cycle
"on average"



The air temperature and precipitation data of July 1st to November 30th, 2007.

- Longer cycle;
- Regular moisture from precipitation and low evaporation rate at low temperature.

www.ndawn.nsdu.nodak.edu/station-info

Degradation – unavoidable variables

Accelerated Exposure and Real life

- Higher temperatures
  - Some locations are hot
  - Chemistry (degradation) goes faster
    - Corrosion
    - Coating degradation
- Ultraviolet Radiation
  - Principal degrading agency
    - Some locations experience more
    - More makes process go faster
- Water
  - Crucial to corrosion
  - Some locations are wetter than others
  - Participates in many coating degradation processes
  - Bad for adhesion
  - Useful coatings absorb water (due to reactivity and polarity)
- Pollution
  - Crucial to corrosion
  - Some places have much more

Modeling

- Based on
  - simple chemical kinetics
  - Time of irradiation
  - Diffusion of water in and out of coatings

Background: Chemical Kinetics

- Zero Order
  - Concentration of any species is not the bottleneck
  - E.g. typical photo-degradation
- First order
  - Progress depends on concentration of one reactant
  - several possibilities
- Second Order
  - Progress depends on $(\text{concentration})^2$ or conc. of two reactants
  - Less common

Focus: Degradation requiring UV + water

- **Humidity shown to impact degradation rate**
  - [Nguyen 2002, Hoffman 1971, Hollande 1999]
- **Degradation events (degraded moieties),** ***N(depth, time)***

$$N(x,t+\Delta t)=N(x,t)-[I_0(x,t)-I_0(x+\Delta x,t)]k(T)_0[H_2O]^{order}\Delta t$$

  - Depending here on intensity of UV and concentration of water
  - Periods of UV and water exposure
  - Temperature implicit in reaction kinetics and rates of diffusion

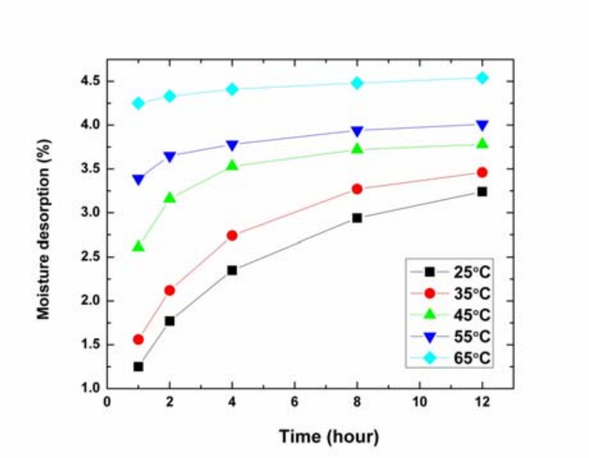
Water + UV degradation

- **Compare:**
  - Miami, Florida
  - Whittmann, Arizona
  - modified ASTM D6695-03b(Q-Sun, Xenon arc)
  - ASTM D4587-05 cycle 2 (QUV, fluorescent)

Protocol	Wet hours	Wet Temp.	Dry hours	Dry Temp.	Relative humidity, %	Irradiation Intensity, W/m^2
Modified ASTM D6695-03b	4	25C	4	58 C		0.55
ASTM D4587-05 cycle 2	4	50C	4	60 C		0.89
Miami, Florida*	16	24C	8	24 C	81	0.43
Whittmann, Arizona*	16	22C	8	22 C	39	0.35

Diffusion of water out of a coating: drying

Coating: typical epoxy
Water loss by weighing.



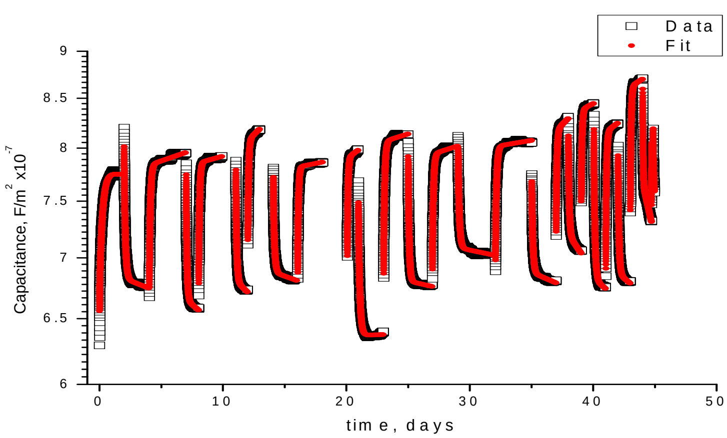
Time scale – much longer than accelerated weathering cycles.

Water content can build up over several cycles.

Diffusion Coefficient of Water in Coatings Measured by EIS

Room Temperature
Ionic Liquids as external electrolyte

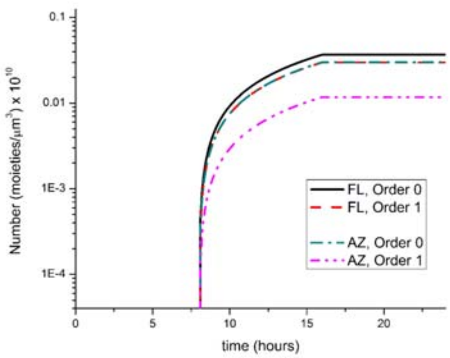
Single Frequency Electro-Chemical Impedance Spectroscopy: alternate wetting and drying cycles:



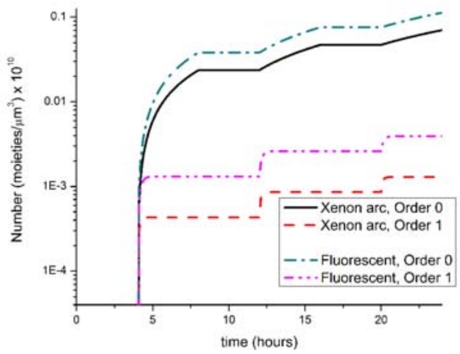
Capacitance gives water content.
Fit to time trend gives diffusion coeff.
Done at different temperatures so we can deduce activation energy.

Diffusion coeff. Used to calculate damage progress, $N(x,t)$

Natural weathering: starts in morning, builds for rest of daylight



Accelerated weathering, showing start and several 4 hour cycles

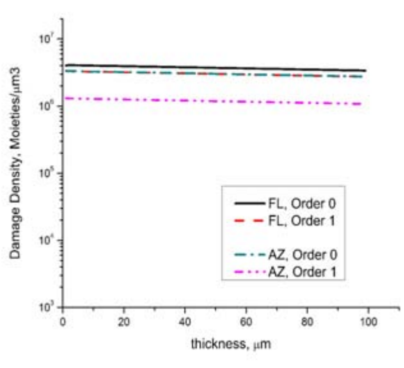


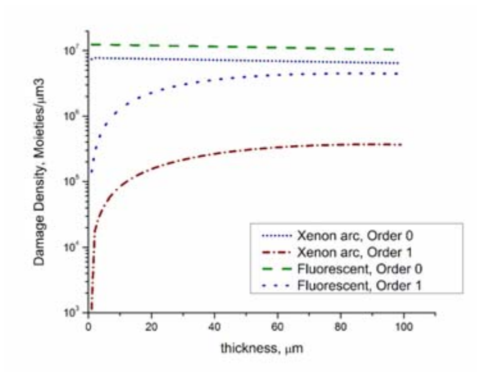
The creation of photolytic products for two simulated natural environments (AZ and FL) and two accelerated weathering protocols.

Damage rate varies: depends on exposure and chemical kinetics.

Natural environment correlates, except for 1st order in AZ.

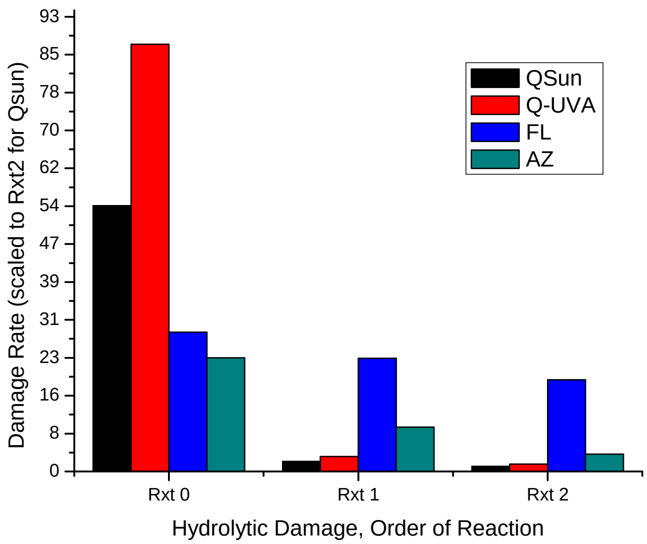
Damage Concentration with depth, $N(x,t)$ Depends on how far water can diffuse in or dry out.





- Natural environments (AZ and FL) and two accelerated weathering protocols.
- Again, 1st order kinetics is where correlation breaks down and more complicated situations are worse
  - more damage at depth, not near surface
- If water cannot dry during cycle, then water collects (near substrate) and adhesive failure may also happen in one type of exposure (not the other).

Degradation (UV + hydrolysis) Note how ranking changes with chemical kinetics and exposure



2nd order included here.

Need to understand degradation chemistry before use of accelerated exposure to predict natural.

Cannot compare different chemistries (we knew that!)

Protective Properties depend on mechanical properties

- Corrosion protection
  - Resistance to cracking
- Abrasion Resistance
  - Brittleness

- Mechanical properties depend on time intrinsically
  - Relaxation times
  - Structural relaxation
- and water content
  - plasticization

Effects also determined by Diffusion time, Temperature

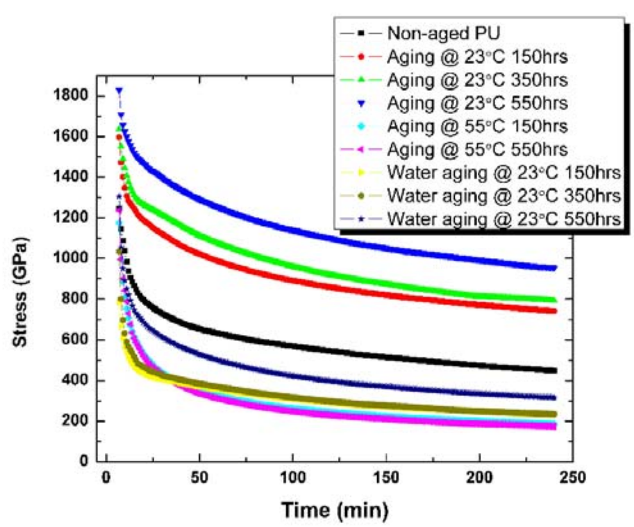
Mechanical Properties

- Saturated water content may be 1-5%
- Water plasticizes epoxies and polyurethanes
- Relaxation goes faster when water is present
- Dry coatings tend to be more brittle
- Water content leads to swelling and stress

More variables!

Water plasticization affects level and relaxation rate of stress

- Clear Polyurethane
- Absorbs only 1.4% water
- Note differences in relaxation rate and stress level
  - (yellow & brown vs. green and red)
- Water content is important



More on time scales: degradation defects

- ✓ Produced by UV (Hg lamp)
- ✓ Measurements done by AFM
- ✓ Degradation scales with scan size;
  - sampling effect;
- ✓ Increase of roughness with exposure;
  - RMS height

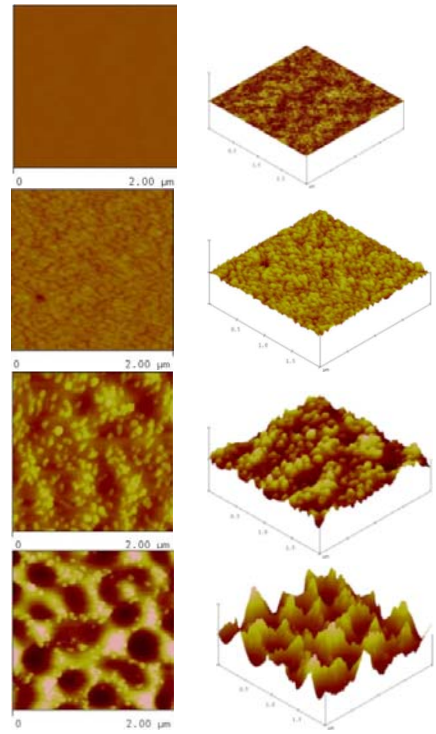
Irradiation time

0-hr

6-hr

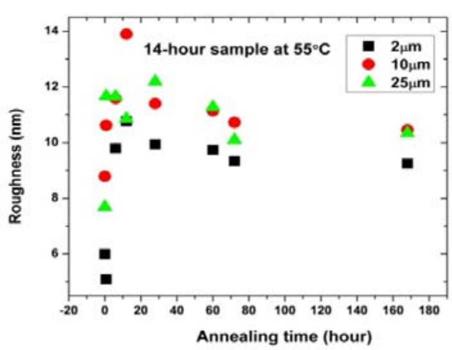
14-hr

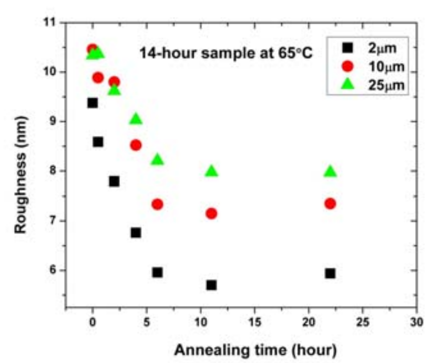
22-hr



Degradation defects recover with time

- Relaxation of the defect size competes with new defect formation or enlargement processes
- Note the time scale
  - Recovery over many hours, depending on temperature, even at 55 ºC & 65 ºC here





Summary

- Presence of water is crucial to performance of coating
  - By itself
    - Degradation chemistry
    - Mechanical, protective properties
- Time scales of water ingress and egress are long compared to typical accelerated exposure cycle
  - Periodicity becomes a variable
- Different exposures may provoke different types of failure
  - Water may gather near substrate if drying is slow compared to cycle length
    - Degradation may be worst at substrate
    - Adhesion failure?
    - May not be characteristic of real life
  - Photodegradation may otherwise progress from outside inwards

Summary Accelerated vs. Natural Weathering

- Materials that only suffer simple degradation processes may correlate, e.g. if they only experience zero order kinetics
- Correlation is more likely if the exposures reach the same equilibrium distribution of water etc.
  - After each cycle
  - Or, after a number of cycles

Modeling allows understanding of difficult situations.

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QUESTIONS?