Monitoring of Anti-Corrosive Coatings using Electrochemical Techniques

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What we want to avoid
What we’d like to see more off
Monitoring of external coated structures
Non-Electrochemical Approaches:

- Traditional method: Look at it! ie visual inspection

- Disadvantages: qualitative (not numerical), only tend to see problems well after they have started. No prediction possible

- Thermal Imaging (Infra Red): McNight and Martin, USA. Can it pick up corrosion UNDER a coating? Doing some work on this in lab at moment: need to heat the sample (or structure); if coating has significant thickness (coatings absorbs IR like it absorbs light) have to heat it a lot. Need line of sight Advan could potentially monitor large areas quickly
Conventional Laboratory monitoring eg Panels in immersion test or in salt spray cabinet

- Again visual inspection is very popular (offered job in 1995 in USA excellent salary doing this all day every day) To assist in making visual inspection numerical, might use some sort of rating scale eg ISO 4628, ASTM D610(corrosion), D614(blistering)

- But rarely would the above be employed on site (I would guess!)
Aim of site monitoring

- Main Aim: To be able to assess an organic coating system on any structure and get a numerical indication of its protection ability at that moment in time

- Secondary Aim: Assess how much protection is left on a paint system (by making several measurements over period of time?)
Electrochemical Methods(1)

- Bacon, Smith and Rugg. back in 1948 examined 300 coatings systems in sea water Measured their ionic resistance as a function of time (simple measurement like measuring internal resistance of a battery- NOTE difficult to automate)

- Found:
  - > 100 Megohms/cm² : good protection,
  - 1 megohm-100 megohms : fair,
  - < less than 1 Megohm : poor

- These criteria still essentially the same as those used today
Electrochemical techniques for monitoring coatings in the laboratory

- DC Resistance (similar to BS and R) Keithley electrometer
  Measures to $10^{13}$ ohms
  Advantages: single reading, simple method, difficult to automate – highish voltages

- Electrochemical Impedance Spectroscopy (EIS) – very popular
  Apply sine wave (20mv) from 10,000Hz to 0.01Hz.
  Analyse (Bode and Nyquist plots)
  Alternative AC approach: could make just two measurements, one of resistance (0.1HZ), one for capacitance (1000hz) ($H_2O$ uptake)

- Scanning techniques: SVET, SRET, SKP: Complex, expensive
  Time demanding. Useful in lab for low resistance surfaces ie bare metal checking efficiencies of inhibitors/pre-treatments - less useful where significant resistances (>1E5/cm$^2$) are present

- DC Current interruptor technique; Sykes/Tanabe Promising
  An ISO Standard is being worked on / developed at the moment

- Electrochemical Noise Method (ENM) – now well proven in the lab
  Attempts being made to take it out onto site
The challenge

- To transfer an electrochemical method that works in the laboratory and make it work in the field
- Technique used needs to be non-intrusive, fast, accurate, simple to interpret and leave no indication that any measurement has been made (no change to area)
Site methods

- EIS has been used on Site (Gdansk group) Also some time ago in UK Rowlands and Thomson in sea water Never really caught on though Complicated equipment, complicated circuit analysis. Ok in lab (have available a lecture on this if people are interested!) ISO standard has actually been developed (ISO 16773)

- DC transient/Current Interrupter method This is popular with the Japanese and has been developed to go out on site Apply a 50 mV perturbation to the sample, turn it off, get decay curve, analyse this to obtain resistance of coating etc

- Electrochemical Noise Method (ENM) (going to look at this in most detail!-next 30 or so slides !)
Types of coating

• Going to restrict ourselves to Paints in most of this talk ie an organic system that is built up perhaps with pretreatment layer/ primer/ intermediate coat and colour coat maybe also clear coat

• Note paint might be part of system with metallic coating next to the substrate ie DUPLEX coating – can use electrochemical methods but extra factors come in and the normal “resistance” criteria might not apply in relation to end of life

• Note sometimes Metallic coatings themselves are used If they are operating sacrificially they can be monitored electrochemically using potential measurement. Also potential measurement would give an indication of pin holing where a more noble coating was used : not going to dwell on this

• Also not going to discuss monitoring of non metallic but still total barrier coatings : Vitreous enamels, thick plastics or whatever) Something like a “holiday detector” would be more useful
Background (ENM)

- First used in 1987 by Chen & Skerry to look at protective organic coatings, it has since been used successfully in a number of laboratories (mainly using the Bridge method)
- Gives result for coating resistance very similar to those measured by EIS and DC method
- Data analysis is relatively simple
- Method is relatively fast
- It is an absolutely non-intrusive method
**Development of ENM**

- **Early/ Mid 90s**: range of solvent base coatings examined for US navy at North Dakota State University. Intact coatings in sea water Continuous monitoring, Sextuplicate 50cm²

- **Mid/Late 90’s**: Used at UCN (forerunner of The University of Northampton) to examine water based coatings. Also noise successfully used to monitor *scribe* (Steve Mabbutt : PhD project)

- **Late 90s**: single substrate method developed

- **Early to mid 2000s**: Bridge method used for continuous automated monitoring of a range of coatings to assist a UK paint company to develop a range of lower solvent coatings

- **Mid 2000s**: NOCS method developed

- **Late 2000s to currently**: development of a methodology/instrument to use on site that is effective and user friendly
Experimental requirements Electrochemical Noise Method standard (bridge) arrangement

- 3 electrodes – two WE and one Ref
- Voltage (between WE and ref) and Current (bet’n the two WE) Data gathered over say 5mins at 0.5 sec intervals
- Need ZRA and computer- commercially available equipment eg ACM, Gamry, CML
- Can be battery operated - take out on site
Data gathering

- Potential Noise = Spontaneous perturbation of voltage between working electrodes and Reference electrode
- Current Noise = Spontaneous perturbation of current between working electrode 1 and working electrode 2
Data Analysis
Data Analysis

Noise Resistance (Rn) = \frac{\text{Standard Deviation of Potential Noise}}{\text{Standard Deviation of Current Noise}}
Salt Bridge arrangement

- Traditional arrangement but not practically useable in the field
Single Substrate arrangement(1)

- Established in 1998 and has been successfully used for in-situ measurements
- More practical No need for two separated working electrodes
- Needs an electrical connection to the substrate
Single Substrate arrangement(2)
Results of using single substrate method

Comparison of SS and Bridge Method using CM epoxy on Fe in 10% Harrison’s solution
No Connection to Substrate(1)

• First proposed and initially developed by Woodcock
• Needs no electrical connection to the substrate
• Needs three isolated areas
• Ambiguity in measuring between three cells
No Connection to Substrate(2)
Choice of best ENM arrangement for external monitoring of structures

- Where electrical connection can be made to the metal, single substrate arrangement is preferred. In fact SS ENM has been developed and tested to the point that it is essentially “ready to go” for site work (summary of some of this work follows)

- NOCS would be preferred where there is no easy connection to the metal possible (But further lab work is needed to buttress this method)
General Requirements for Site work using Electrochemical Measurements

- Battery Operation
- Minimal measurement time
- Confidence that equilibrium has been reached (note: paint surface may be wet / may be dry)
- Way of connecting to substrate – needs to deal with different shapes and orientations, be inexpensive and robust, work on any metal
Method of Connection to Substrate

Filter paper soaked in dilute Harrisons solution

Copper

Wire to connect to AutoZRA

Tape to cover/stick/seal pad

Anti-corrosive coating
Solutions

- 3% NaCl - OK in salty, sea air environment
- To simulate inland situations use dilute Harrison’s Solution (0.35% ammonium sulphate, 0.05% sodium chloride)
Time to Equilibrium

- Depends on prior wetness and resistance of coating
- Lab Results obtained here using DC Resistance. Field tests would use ENM. Need to log (ie record) the data until values have flattened off (could this be done automatically?) Typically might use a thirty minute exposure
Results (time to equilibrium) Pad versus cell(electrode) and demin water versus Harrison’s
Results (Time to equilibrium) AMP

![Graph showing AMP Time to Settle with time (minutes) on the x-axis and resistance (Ohms) on the y-axis. The graph shows a decrease in resistance over time, approaching an equilibrium.]
Results Time to equilibrium (DSP)
ENM – can measurement time be reduced?

- Standard method takes nearly 5 mins (256 seconds) to make measurement- normally repeated twice ie 10 mins
- Data gathered at 2Hz (every 0.5sec) Could data be gathered eg at 10HZ? Also could fewer data points be gathered?
- Mabbutt (in PhD) investigated effect of frequency - published Proc. 1997 ACPOC
- Some further work done here NOTE samples used had been in solution for several weeks and thus resistance would have reached a constant value
Effect of Frequency on $R_n$ (512 data points in all cases)-alkyd primer

Light Red Sample Single Coat

<table>
<thead>
<tr>
<th>Frequency/Hz</th>
<th>Rn1/Logs</th>
<th>Rn2/Logs</th>
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<tr>
<td>1</td>
<td>1.00E+05</td>
<td>1.00E+05</td>
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<tr>
<td>10</td>
<td>1.00E+09</td>
<td>1.00E+09</td>
</tr>
</tbody>
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Preparation for field work - set up in Lab
Preliminary site work-general view showing pipe and bracket
Preliminary Field Work (close up of connection)
Preliminary Field Work (close Up –vertical section of bracket )
Preliminary Field work (drainpipe outside leather centre)  April 07
Results (preliminary site work)

Values of Rn (2Hz-average of two values) were consistent with appearance

Horizontal Bracket : 4E5 - visible corrosion

Vertical Bracket (same thickness/type of paint as Horiz?) 4E6 - minor blistering

Vertical Rounded Pipe : 7E8 - excellent paint condition
Conclusion-lab work on effect of frequency

- No obvious disadvantage in using 10Hz measurement compared with 2 Hz. The two paints (red alkyd and two coat PU/Epoxy) are clearly differentiated at both frequencies and scatter is similar.

- If use 10Hz and make two measurements (512 points each), this will cut measurement time down to 2 minutes per sample area.
General Conclusions

- Filter paper pads backed with 4x4 cm copper foil are excellent way of connecting temporarily to a structure.
- Time to equilibrium typically 30 minutes.
- Looks promising that can use higher frequency of measurement than 2Hz eg 10Hz and still get accurate result.
- Single substrate method with battery operation works satisfactorily in the field.
Further Work

• Try system on further structures (Bridges etc)
• Programme computer to decide how long pad needs to be left in place
• If use salt, develop simple method of removing it (e.g. leach out again by swabbing with water)
• Develop dedicated, small, portable Coatings testing Instrument
Re first further work item, still some challenges ahead!
eg how do you select the areas to measure on this?
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THANKS FOR YOUR ATTENTION