INSTITUTE OF CORROSION

Assessment of Anti-Corrosive Organic Coatings and Inhibitors by Electro-Chemical Techniques; particularly Electrochemical Noise

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Outline of Talk

- PART 1 Assessing coatings
- 1) Background
- 2) Experimental
- 3) Info on ISO Standard (TR 5604)
- 4) The Electrochemical Noise Method
- 5) Different Configuration of ENM
- 6) Original work : aims and objectives
- 7) Experimental work
- 8) Results
- 9) Conclusions
- 10) A practical application
- PART 2 Inhibitors

Part one: Coatings.Background to work

- Late 80's : ENM (Electrochemical Noise Method) first used to look at protective organic coatings by Brian Skerry (Sherwin Williams) & David Eden (UMIST/CAPCIS)

- Early/ Mid 90's : ENM used to examine solvent-borne Navy coatings at North Dakota State University (Bierwagen's group) – standard laboratory ("bridge or beaker") arrangement of ENM.

- Late 90's : A new arrangement of ENM called "Single Substrate" invented by Steve Mabbutt and Douglas Mills at The University of Northampton and developed to practical use (also ENM successfully applied to a wider range of coatings eg waterborne)

- Mid 2000's :Even more practical arrangement of ENM called "NOCS" (No Connection to the Substrate) invented by Chris Woodcock and Douglas Mills

Background (Organic Coatings)

2010s to now : Work at University of Northampton (grant from Sherwin Williams) development of a DEDICATED Instrument and suitable electrodes (probes) for practical application of ENM to coated structures. Commercial instrument produced (ProCoMeter).

Much academic work has been published (see Appendix of ISO TR 5604).

Little work published on the Practical Application. But it was covered in part of a paper by DaHai Xia et al. Electrochemical measurements used for assessment of corrosion and protection of metallic materials in the field: A critical review DaHai Xia ,ChengMan Deng, Digby Macdonald, Sina Jamali, Douglas Mills, JingLi Luo, Michael G. Strebl, Mehdi Amiri, Weixian Ji, Shizhe Song, Wenbin Hu ; Journal of Materials Science & Technology 112 (2022) 151–183.

There is also an ISO Technical Report which has been voted on and accepted
ISO/TS 5604:2023(E) ISO TC 35/SC 9 Secretariat: BSI

- **Test method for assessment of protection of metal by organic coatings using electrochemical noise measurements.**

Contents of TR ISO 5604

Introduction

ENM – a technique which can be used to assess the protectiveness of organic coatings.

Advantages:

- ✓ Non-intrusive
- ✓ Quick
- ✓ Easy to operate
- ✓ Interpretation of gathered data is not complicated.

NOTE: The first part of this talk is derived from work done by Lidia Mularczyk which was presented at EMCR 2012 (Maragogi, Brazil) and published in Electrochimica Acta in 2014

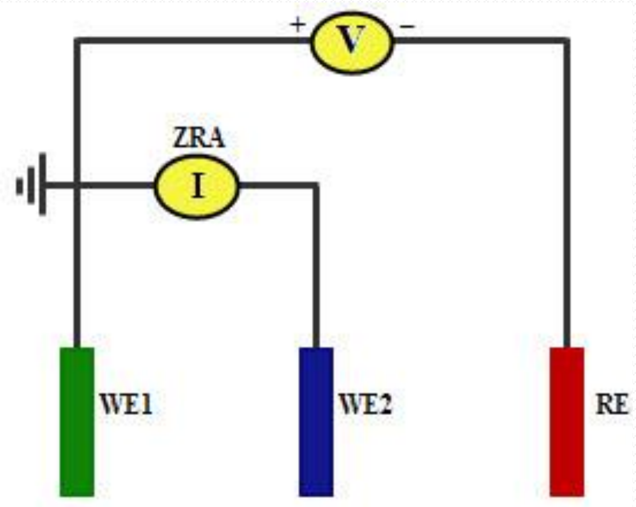
THE MAIN PURPOSE OF ENM - to obtain a single result: **the Noise Resistance** (***R_n***) which relates to Protective ability

$$R_n = \sigma_v / \sigma_i$$

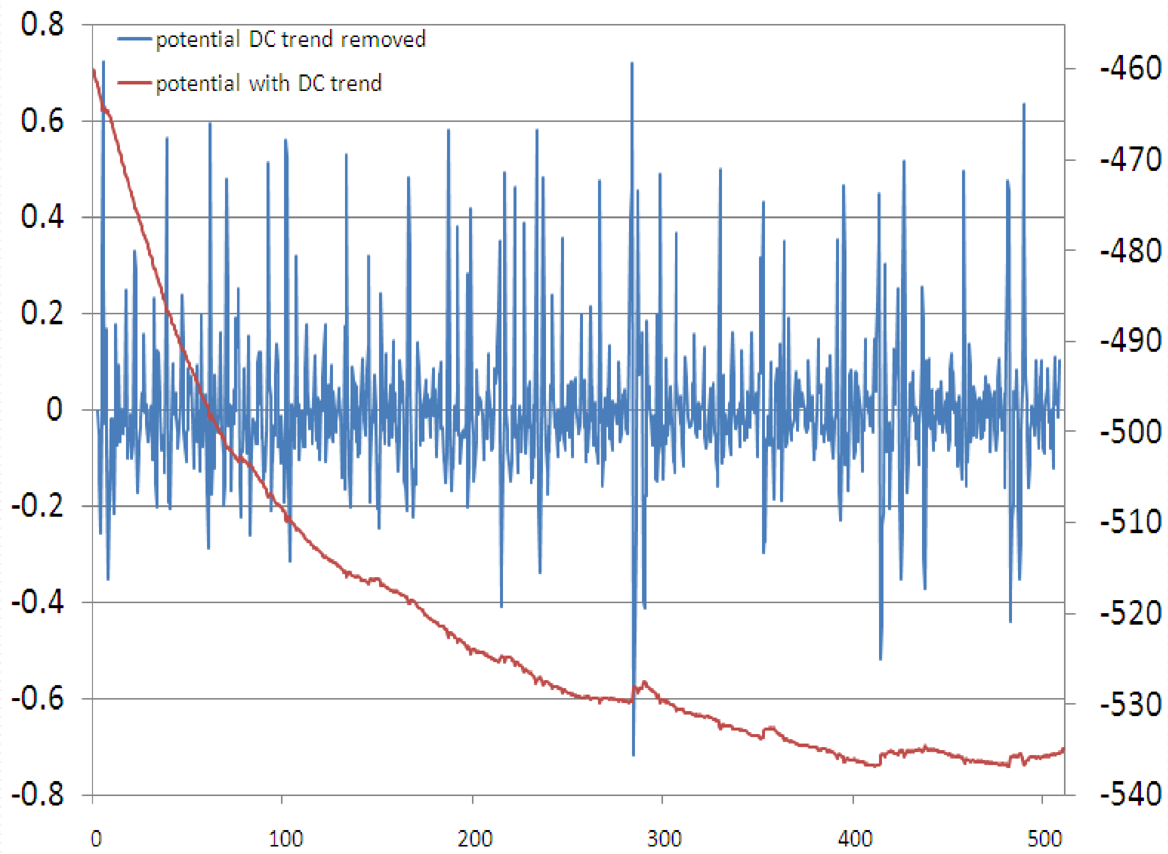
σ_v - standard deviation of the potential data series
σ_i - standard deviation of the current data series

*HOW TO GET THE **R_N** VALUE?*

- 3 electrodes are required – two Nominally identical working electrodes (WE1 and WE2) and one reference (Re)
- Measure natural fluctuations of voltage (potential noise) between WE and RE
- AT THE SAME TIME measure natural fluctuations of current (current noise) between the two WE
- Data gathered typically over about 4 mins at 0.5 sec intervals (512 data points) Repeat run



Data treatment
Figure below shows detrending



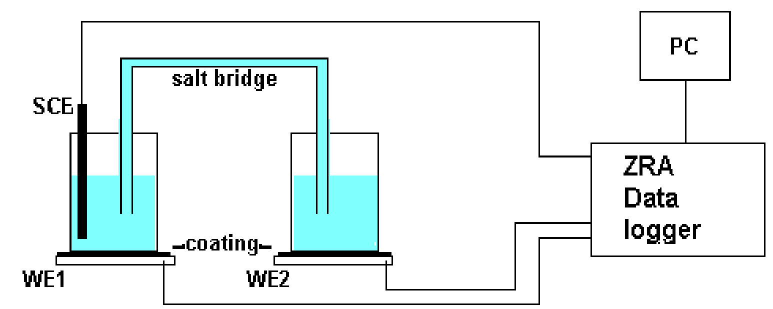
Values of R_n

BACON, SMITH AND RUGG CRITERIA (1948) :

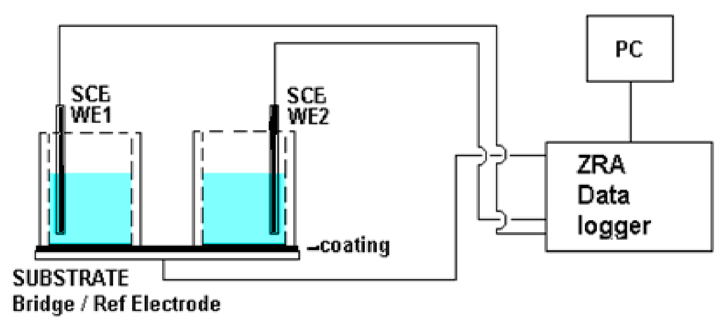
- less than 10^6 Ωcm^2 - poor corrosion protection,
- between 10^6 Ωcm^2 and 10^8 Ωcm^2 - intermediate level of corrosion protection
- more than 10^8 Ωcm^2 - good corrosion protection.

Different Configurations of ENM

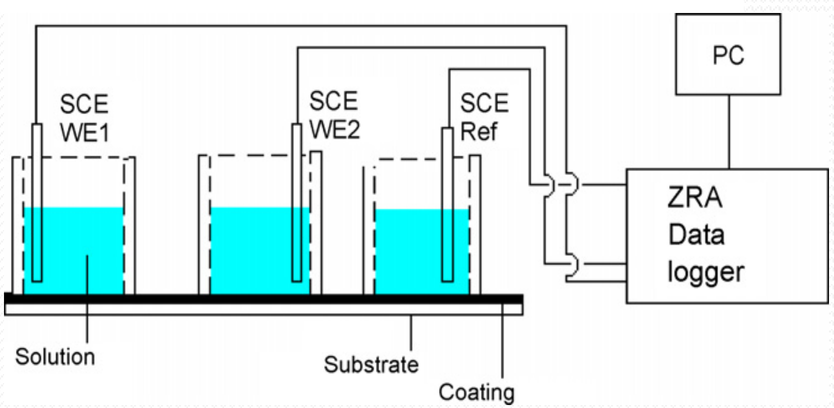
1. **Bridge (standard method)** **(can be an actual bridge between cells of the solution itself provides the bridge)**



2. **Single Substrate**



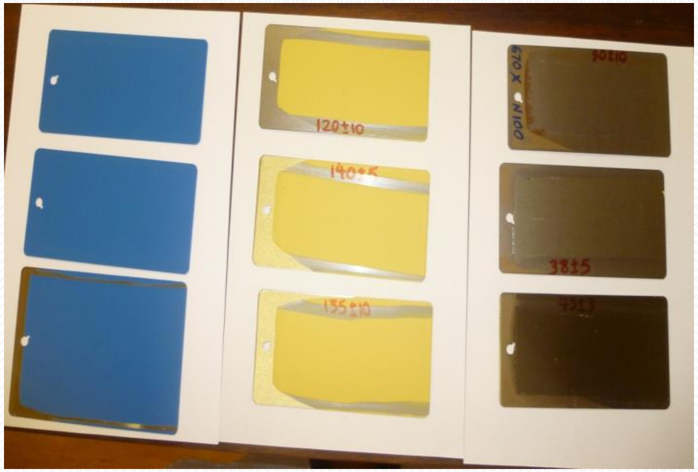
2. **NOCS (No connection to the substrate)**



Original work: aims and objectives

1. Examination of different arrangements of ENM on a range of coated samples and comparison between them.
2. Checking the reproducibility of results + considering the more practical application of this technique in the field.
3. Investigation of NOCS arrangement of ENM.

Experimental work



Samples preparation:

Mild steel Q-panels were coated with appropriate coating in the laboratory by spreader bar.

Types of coating used in ENM experiments:

- ***Polyurethane*** (in 1., 2., 3. experimental parts) – transparent,
- ***Alkyd*** (in 1. experimental part) – blue, (at two different thicknesses)
- ***Waterborne epoxy*** (in 1. experimental part) – yellow.

Experimental work (for aims 1 and 3)

- Exposure to the corrosive solution :

  Plastic tubes stuck on coated substrate and filled with 3% NaCl solution.

  The area exposed to electrolyte was 4 cm^2 (each cell).

- Electrode(s):

  Ref. is Saturated Calomel Electrode(s)

  Original Work : ACM equipment (Copper pad electrodes)

  Recent work (with ProCoMeter) Ag/AgCl electrodes Exposed area 5cm^2

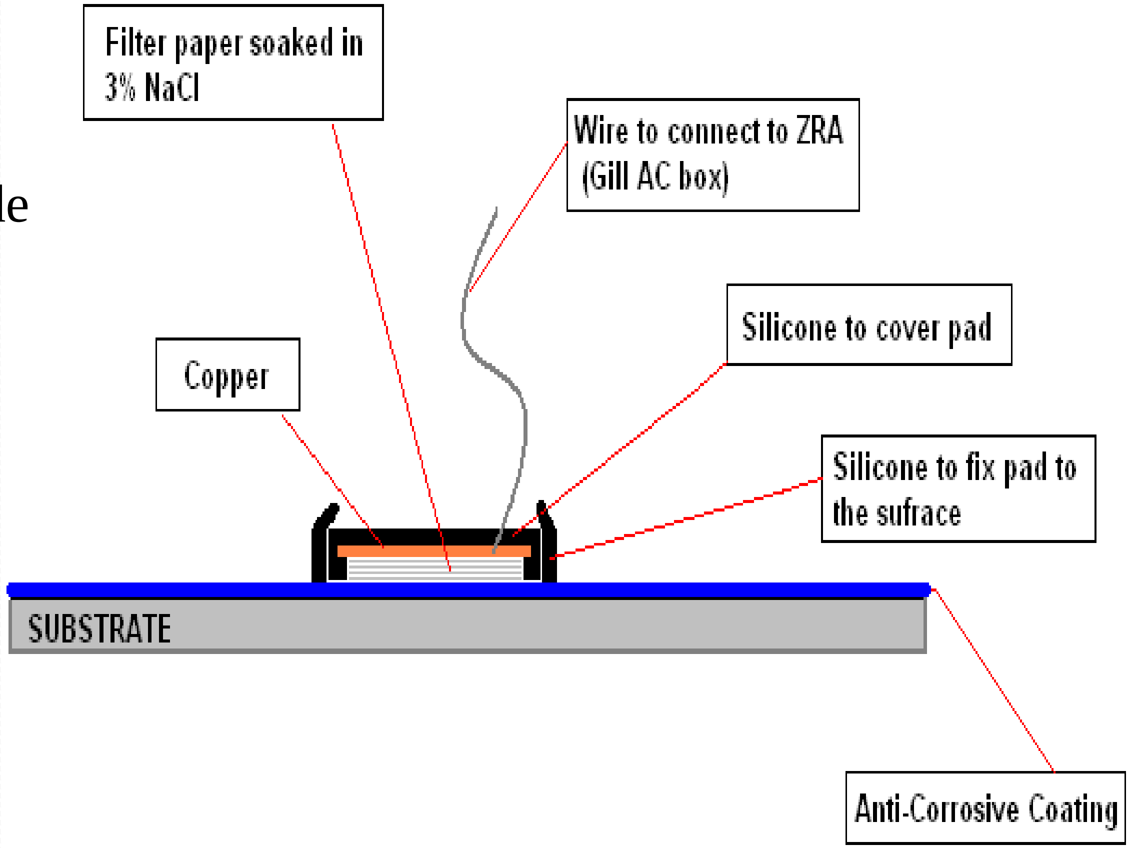
EXPERIMENTAL WORK(field work/aim2)

- <u>Original Work</u>: Exposure to the corrosive solution : coated panels immersed in 3% NaCl in a beaker, taken out from the solution and dried to perform a measurement, then put back.

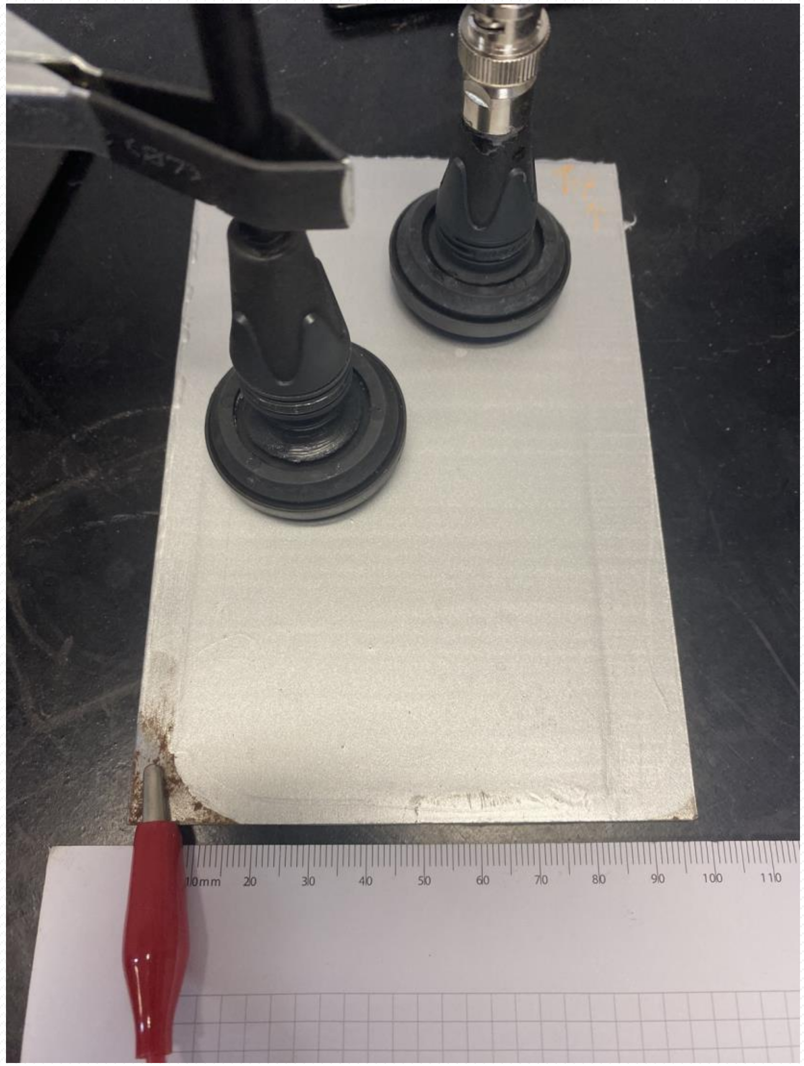
- <u>Electrode(s):</u>

  Original type of electrode "copper pad"

  Later electrodes : silver/ silver chloride, but same Basic arrangement

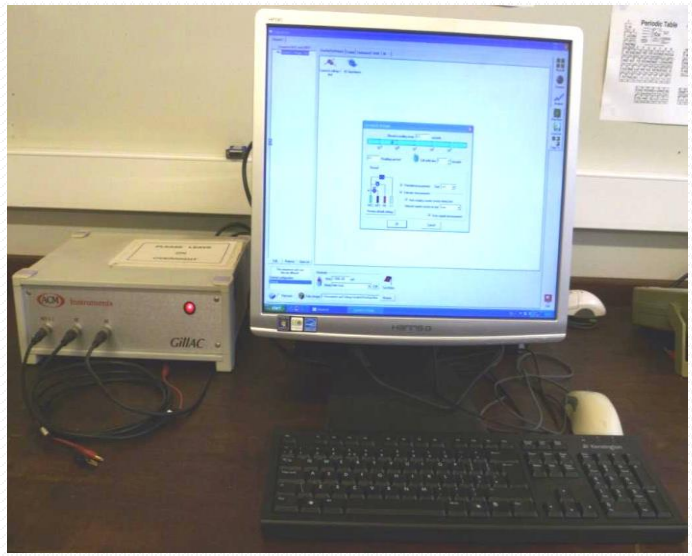


Silver/Silver Chloride electrodes in use

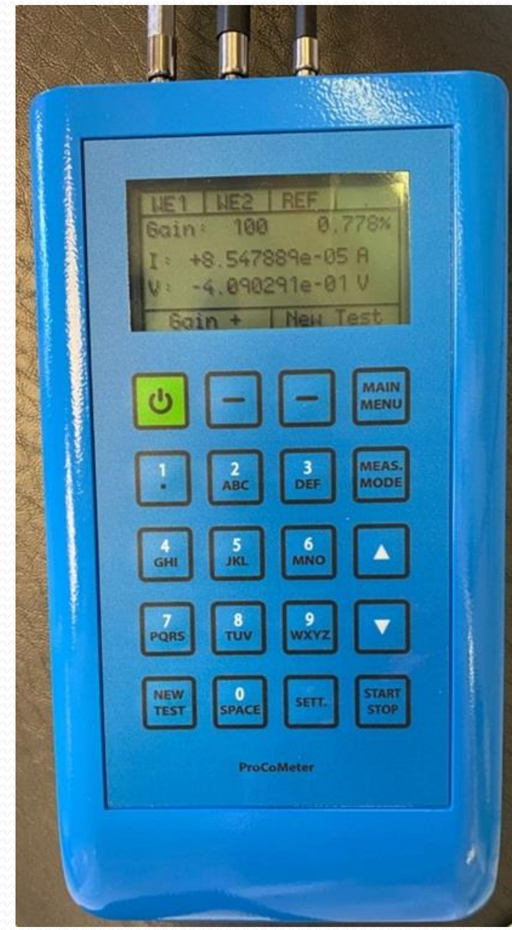


Experimental work
test equipment for ENM

- ACM Instrument works well, but not portable



- ProCoMeter portable data gatherer. Plugged into computer to download.



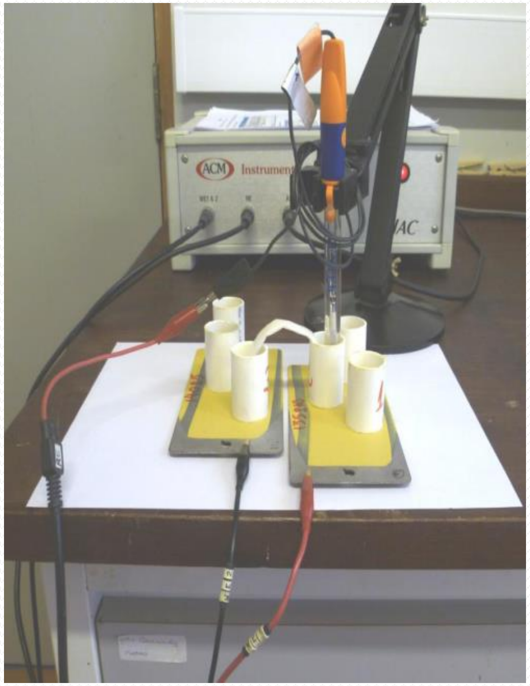
Experimental work – data treatment and control measurement

- Original Work “ENANALIZ” software by R Cottis, in order to treat the noise data
- Recent Work ProCoMeter (DCVG software detrending And brushing by eye)

- Used Electrometer (Keithley 610) to make DC measurements - to compare Rn values obtained using ENM with DC resistance value

Results(1): Original work

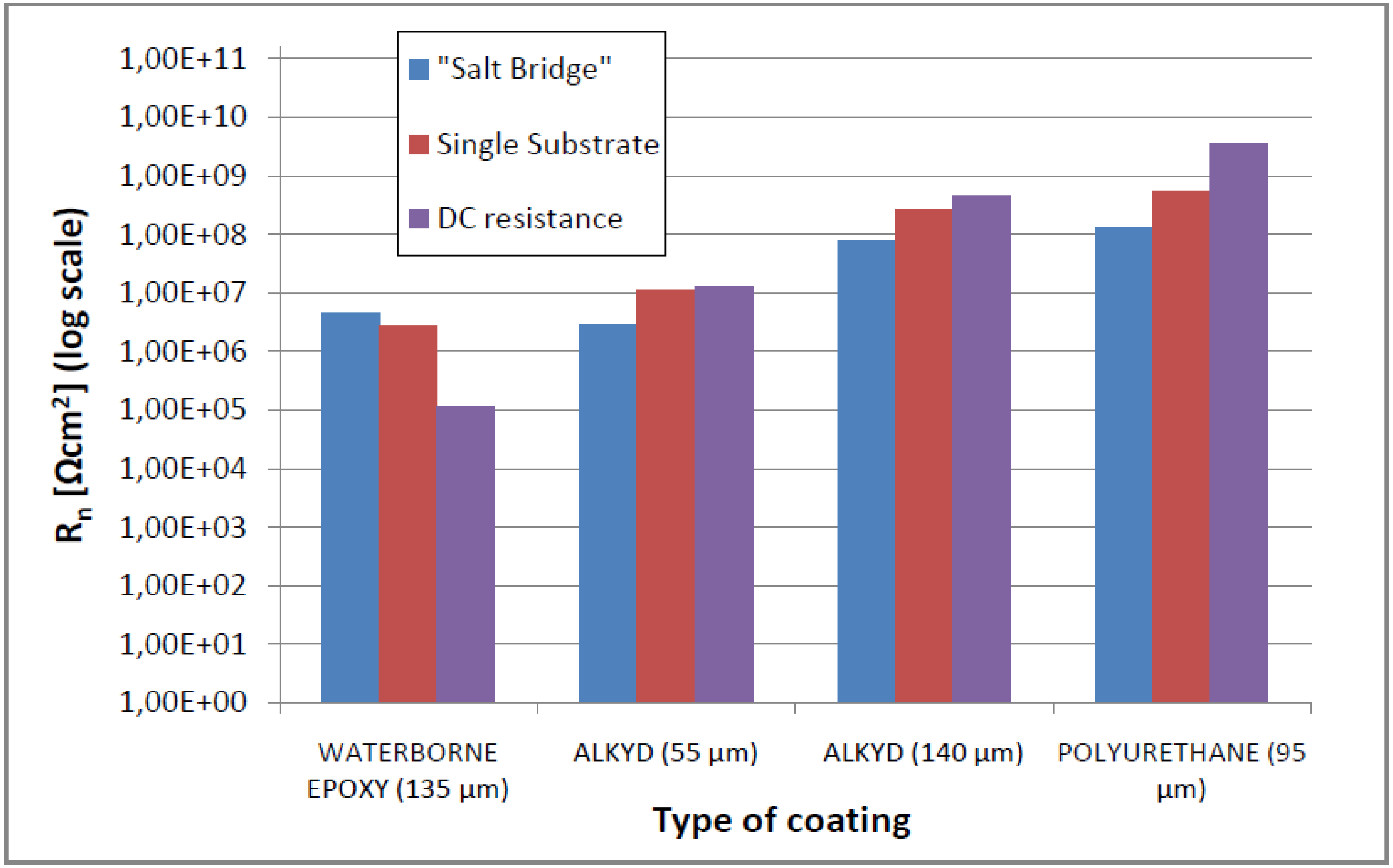
Measurements for a range of samples in **Bridge** and **Single Substrate** arrangement of ENM and the measurements of DC as a comparative method for ENM



Salt Bridge

Single Substrate

DC Resistance



Comparison of two arrangements of ENM and the DC resistance method for four coatings after 168 hours of exposure.

Results (2)

REPRODUCIBILITY EXPERIMENTS

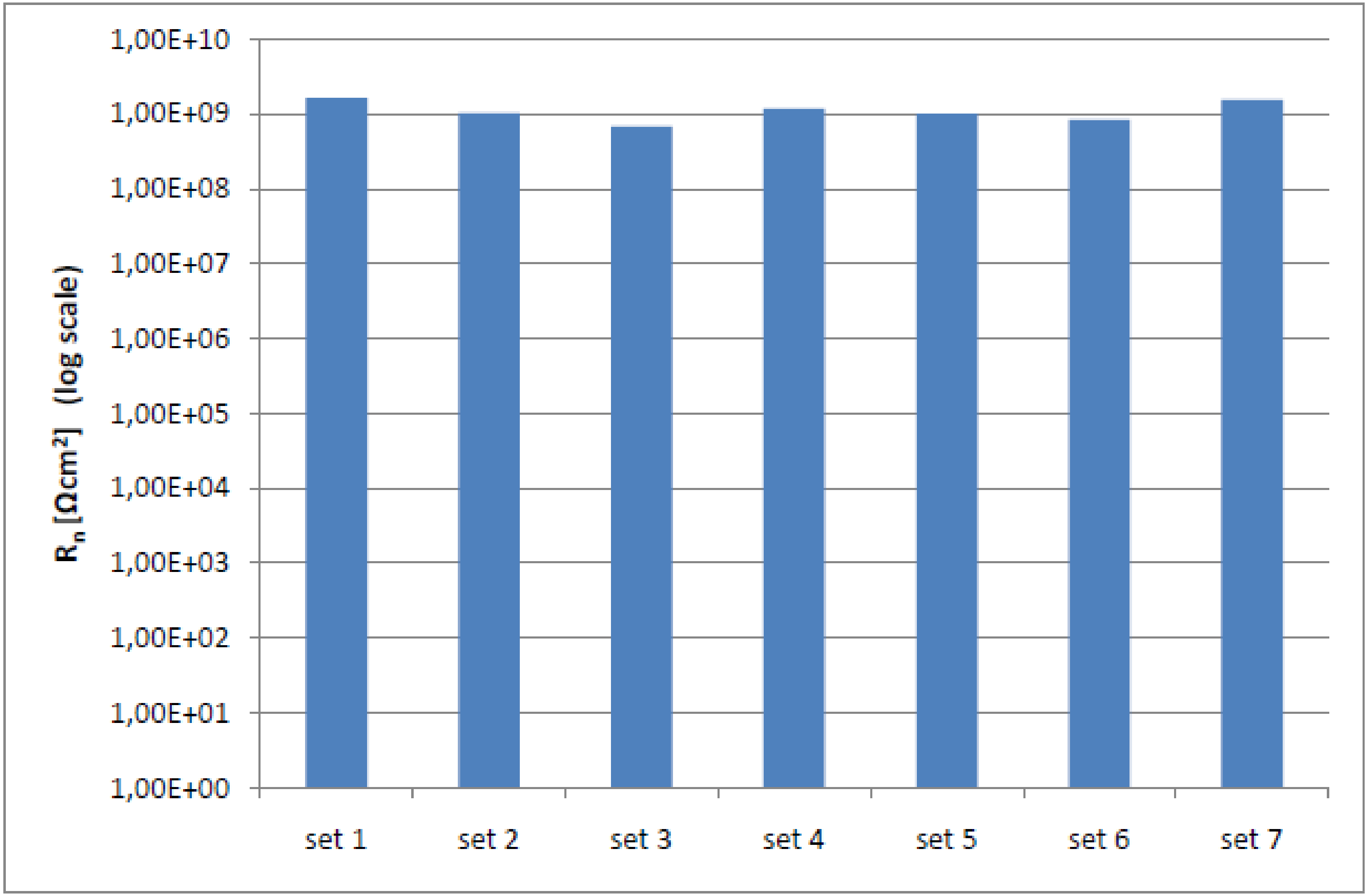
(Done with copper pad, electrodes with defined areas using silicone sealant)

EXPOSURE OF THE SAMPLES AND MEASUREMENTS*:*

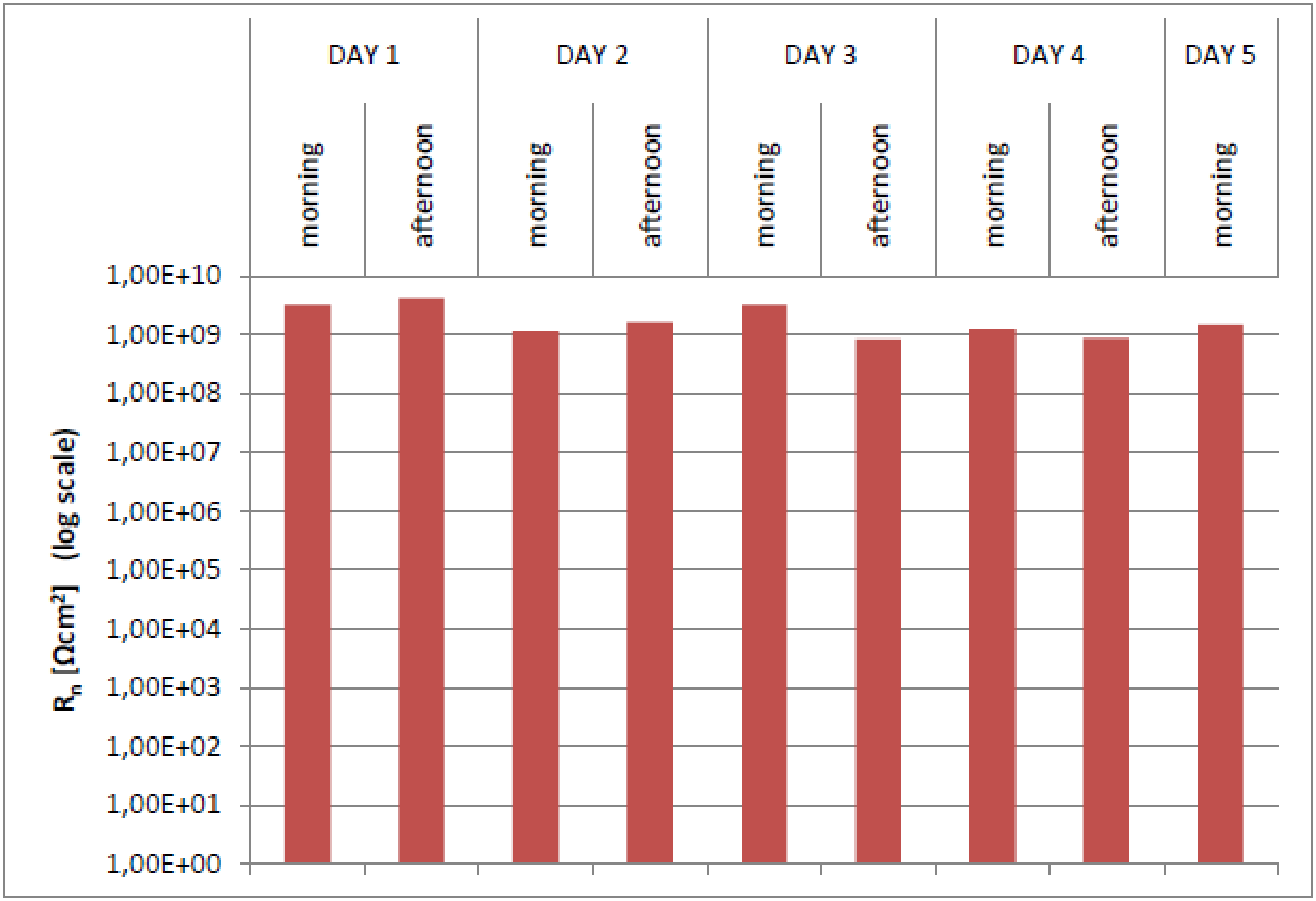
•Samples were immersed in 3% NaCl in a beaker.

•Before each measurement the samples were taken out from the solution, washed with deionised water and dried.

•Measurements were performed during 5 days, every morning, every afternoon. Each time the tests were repeated 7 times one after another.



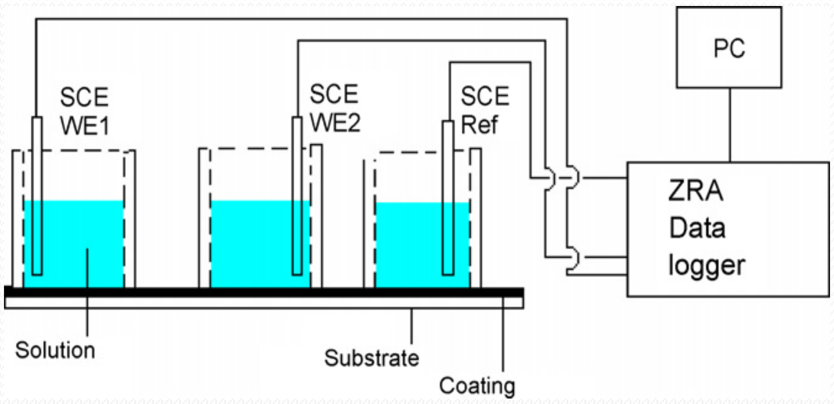
Rn values in log scale showing reproducibility of 7 data sets.



Rn values in log scale showing the reproducibility of results.

Results (3)

NOCS EXPERIMENTS



AIM : to investigate the situation when the R_n value of one area is different than for the other two – are we able to detect the odd one? If so can we measure its value ?

- Six areas were used: 3 with high resistances A,B,C and 3 with lower resistances X,Y,Z

Designation of cell	DC resistance value [Ω]
A	6,40E+09
B	6,35E+09
C	6,40E+09

Designation of cell	DC resistance value [Ω]
X	5,50E+07
Y	1,05E+07
Z	1,30E+07

- Measurements were performed in 4 configurations:

  A-B-C (high, high, high) X-Y-Z (low, low, low)

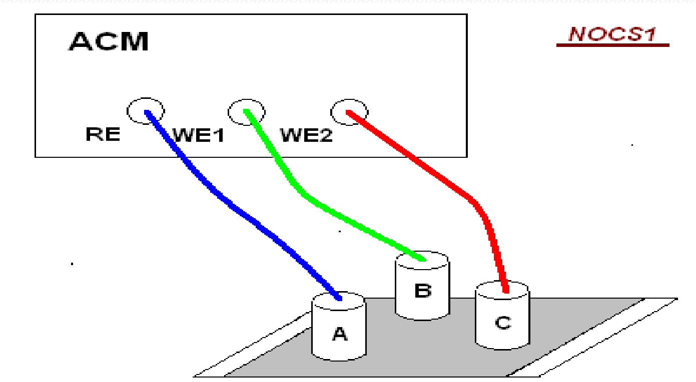
  Z-C-A (low, high, high) Z-Y-A (low, low, high)
- Each configuration – 6 combinations (varying the way the cells are connected to the ACM box).

- NOTE *with the ProCoMeter this switching is done automatically by the "BOX" using the MNCS (Multiple NOCS) configuration*

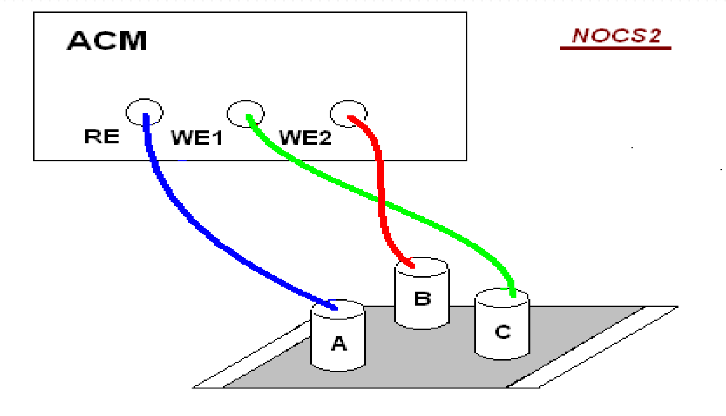
<u>Eg Combinations of NOCS arrangement</u> : 1) (top) and 2(below)

Similarly for NOCS 3 NOCS 4 NOCS 5 and NOCS 6

	RE	WE1	WE2
NOCS 1	A	B	C
NOCS 2	A	C	B
NOCS 3	B	A	C
NOCS 4	B	C	A
NOCS 5	C	A	B
NOCS 6	C	B	A



	RE	WE1	WE2
NOCS 1	A	B	C
NOCS 2	A	C	B
NOCS 3	B	A	C
NOCS 4	B	C	A
NOCS 5	C	A	B
NOCS 6	C	B	A



A-B-C				
	RE	WE1	WE2	R_n
NOCS 1	A	B	C	2,24E+09
NOCS 2	A	C	B	2,52E+09
NOCS 3	B	A	C	1,12E+09
NOCS 4	B	C	A	1,08E+09
NOCS 5	C	A	B	1,13E+09
NOCS 6	C	B	A	1,40E+09

ABOVE Sequence of measurements + Rn values for each single NOCS measurement in A(high)-B(high)-C(high) configuration.
BELOW Sequence of measurements + Rn values for each single NOCS measurement in Z(low)-C(high)-A(high) configuration

Z-C-A				
	RE	WE1	WE2	Rn
NOCS 1	Z	C	A	1,70E+09
NOCS 2	Z	A	C	1,25E+09
NOCS 3	C	**Z**	A	**1,63E+07**
NOCS 4	C	A	Z	1,06E+09
NOCS 5	A	**Z**	C	**1,82E+07**
NOCS 6	A	C	Z	1,30E+09

X-Y-Z				
	RE	WE1	WE2	R_n
NOCS 1	X	Y	Z	3,03E+07
NOCS 2	X	Z	Y	2,47E+07
NOCS 3	Y	X	Z	7,48E+07
NOCS 4	Y	Z	X	1,31E+07
NOCS 5	Z	X	Y	7,46E+07
NOCS 6	Z	Y	X	2,29E+07

ABOVE Sequence of measurements + Rn values for each single NOCS measurement in **X**(low)**-Y**(low)-**Z**(low) configuration.
BELOW Sequence of measurements + Rn values for each single NOCS measurement in **Z**(low)-**Y**(low)-**A**(high)configuration

Z-Y-A				
	RE	WE1	WE2	Rn
NOCS 1	Z	Y	A	1,91E+07
NOCS 2	Z	**A**	Y	**1,01E+09**
NOCS 3	Y	Z	A	1,87E+07
NOCS 4	Y	**A**	Z	**1,09E+09**
NOCS 5	A	Z	Y	3,88E+07
NOCS 6	A	Y	Z	1,48E+07

Conclusion from NOCS work

- In one single NOCS measurement, made with ACM equipment when one cell is different than the other two, we can, by making multiple measurements obtain the different value of Rn in the combination when the odd one is connected to WE1.

- Subsequent recent work using Silver/Silver Chloride electrodes and the ProCoMeter was not so successful On-going investigation as to why that might be. Possible reasons :

1) Too big a difference between the values in recent work (1E3 and 1E9) compared with earlier work (1E7 to 1E9) ?
2) Different wiring in ProCoMeter compared with ACM box ?

Overall conclusions

- Good reproducibility of the ENM method has been proven.
- The use of "copper pads" enable ENM to be applied in the field (a satisfactory way of connecting temporarily to the coated substrate).
- More recent work Copper pads have been replaced with Ag /AgCl electrodes in contact with 3% NaCl (typically) again in a pad format .
- NOCS –variable resistance of three areas The original work with ACM box indicated it was possible to determine the resistance value for individual examined areas - the result of a single measurement of NOCS could be dominated by cell which acts in this configuration as a working electrode 1 (WE1).
- The reason why this hasn’t worked so well with the ProCoMeter is being investigated

Making EC measurements on an aircraft carrier -underside of hull

Part 2: Inhibitors Outline of talk

- 1) Background
- 2) Experimental detail on ENM applied to assessing inhibitors (novel cell, stirring etc)
- 3) Results for Inhibitors in acid solution
- 4) Results for Inhibitors in CO_2 saturated 3% NaCl solution.
- 5) Comparison of R_n values with LPR (linear polarisation resistance) values.
- 6) Conclusions

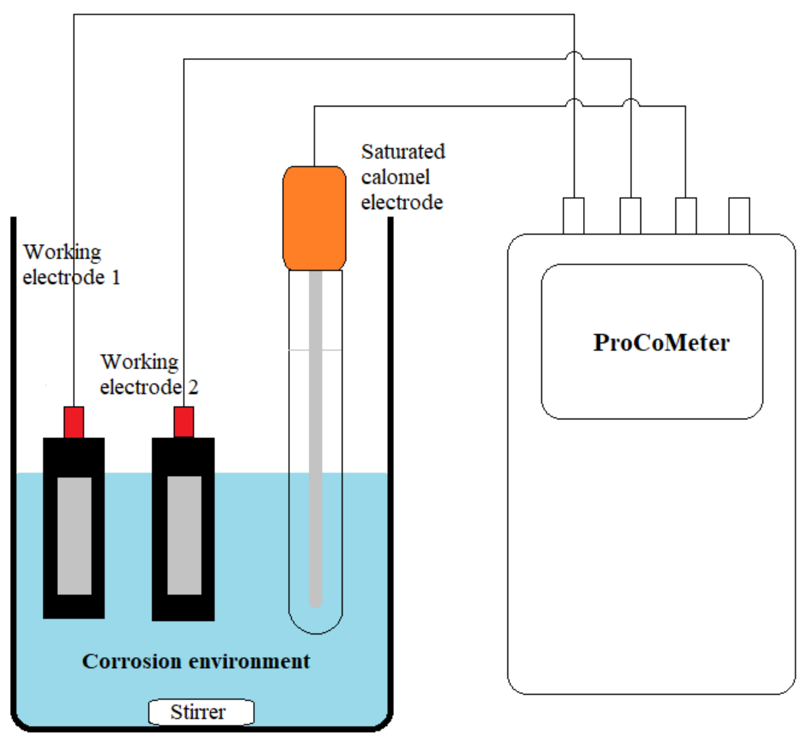
Part 2: Inhibitors Background

- First application goes back to mid 90s. Talk attended by DJM in London in around 1995. BP used ENM probes inserted in pipelines to detect when inhibitor dosing was required.

- Not much published work to our knowledge where EN was used for testing inhibitors (there is much work using weight loss or LPR/EIS (electrochemical impedance spectroscopy) as the assessment method). That is until University of Nottingham with their interest in developing "green" inhibitors started to use the method with myself (Tianyang) as the lead investigator. It is a summary of some of that work that I would like to present here.

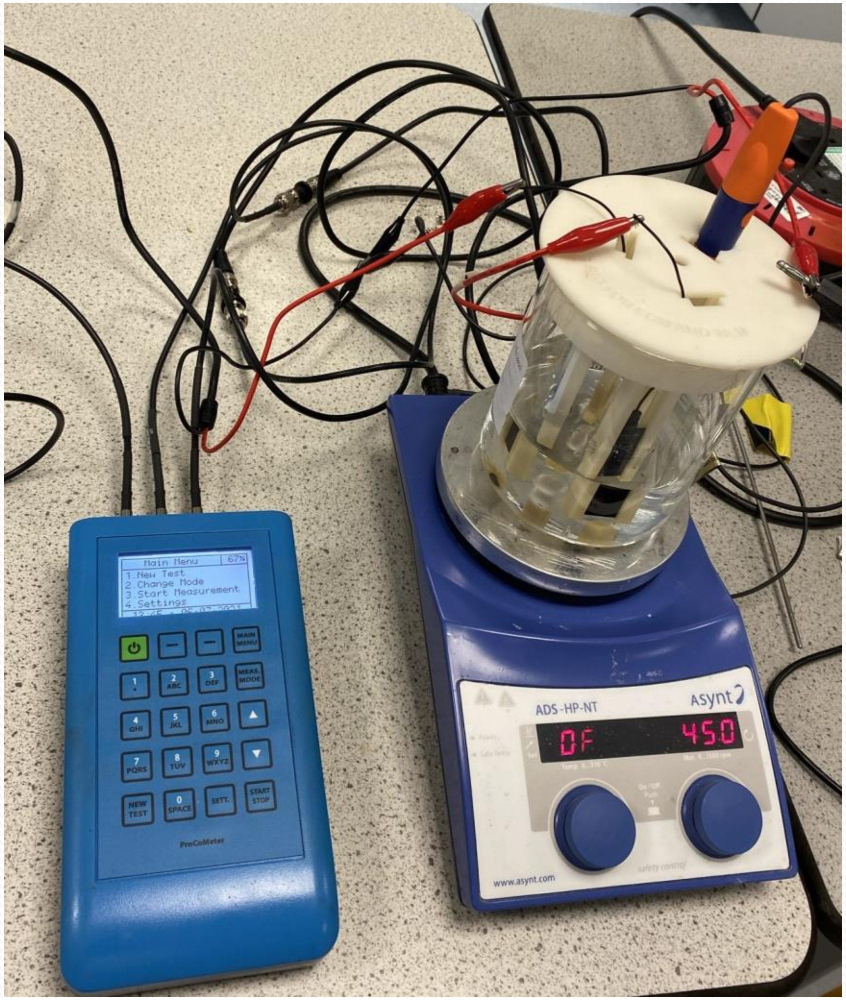
Experimental set-up

- Bridge arrangement (solution acts as bridge)
- The connection method is salt bridge with two working electrodes (5*2 cm^2 carbon steel) and a Sat'd Calomel Electrode as the Ref.
- The specimens had been blanked off using Zip E Coating supplied by the Corrocoat company. The exposed area was 4.5*1.5cm^2).
- The special specimen holder was ABS material made by 3D printing.
- The stirring speed is depending on the size of the stirrer (around 300RPM for 3cm stirrer).

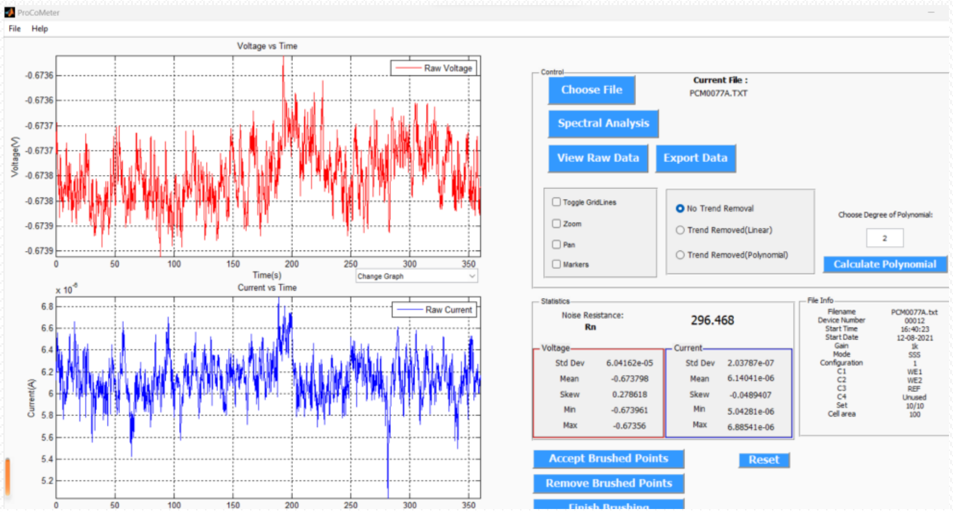


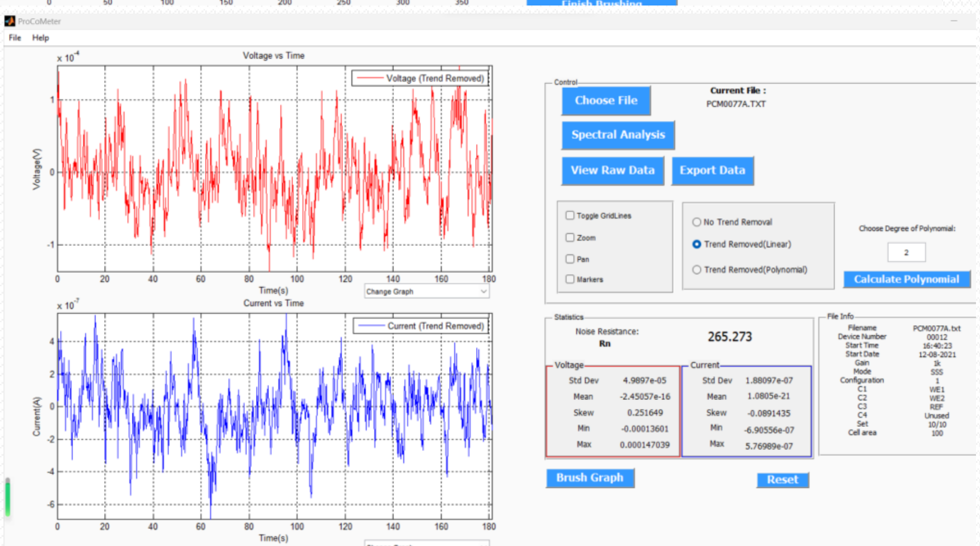
Experimental

- The environments used were:
- 1% Propargyl alcohol in HCl (0.37%, 2.6%, 5.5%)
- 0.25% Green inhibitor (Broccoli or sugar beet) in 3%NaCl +CO_2/ 2.6%HCl, including two commercial inhibitors.
- Comparison of EN and LPR with the same environment and set up
- NOTE Propargyl alcohol (C_3H_4O).. is commonly used as an effective inhibitor in HCl solutions in the oil and gas industry.



Example of EN results obtained using the ProCoMeter





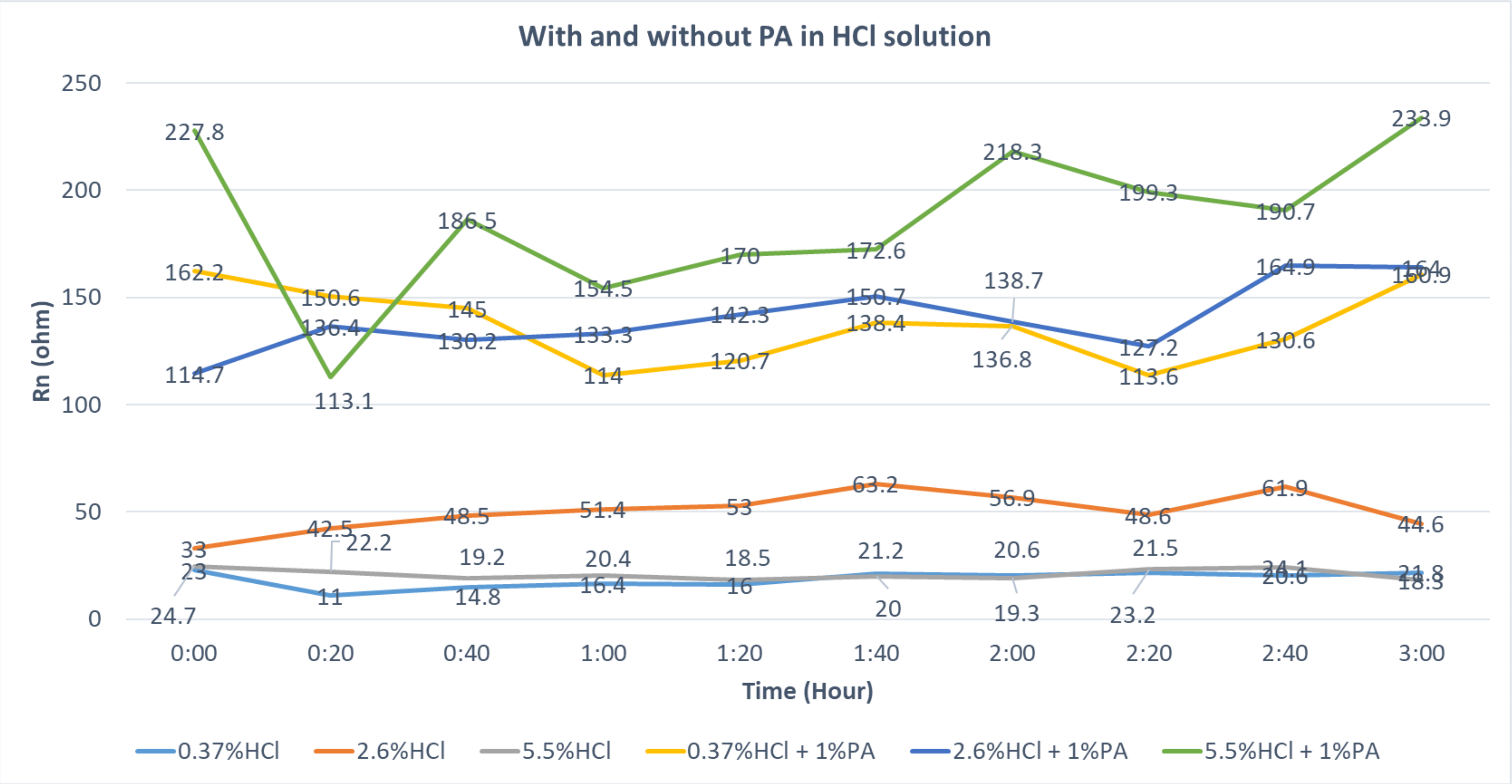
Example of the EN results from sugar beet inhibitor by ProCoMeter. (top graphs :original voltage and current).

The sampling rate: 4 readings/s
Total data points: 1440
Time for one measurement: 360s

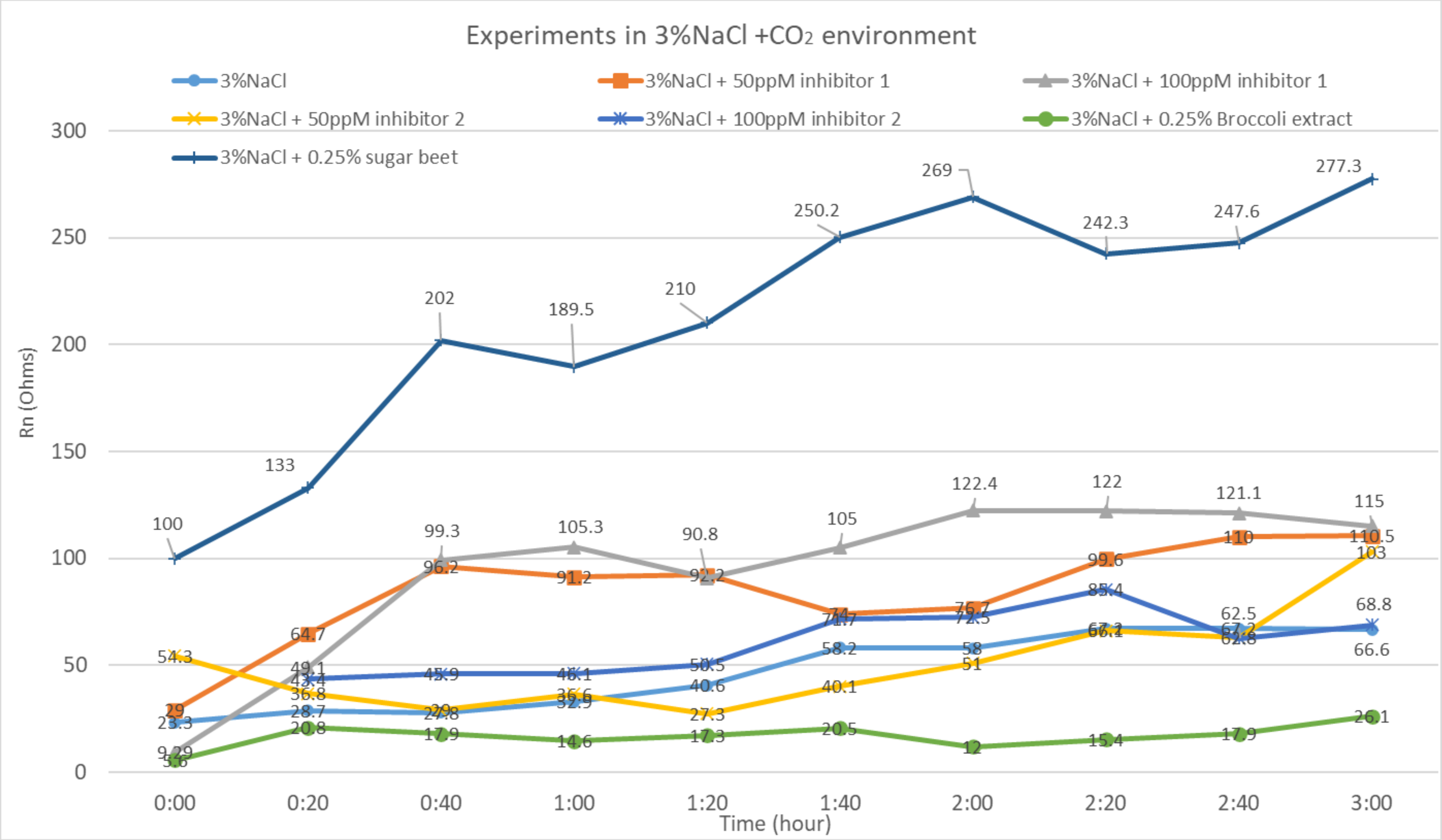
(lower graphs: after brushing and detrending). "Brushing": select or highlight the section. Then decide keep it or remove it for the analysis.

"Trend removal" is also a useful tool to make the R_n value accurate

Results using 1% PA with varying acid concentrations
(Higher the value of Rn the more effective the inhibitor)



Results (2): Various inhibitors in 3%NaCl + CO_2



Discussion of results 1 and 2

- 1) In Acid
- Propargyl alcohol provided significant corrosion protection (higher R_n), especially for in the high concentration of HCl (5.5% environment.
- The R_n value of 2.6% HCl without inhibitor was unexpectedly high. The average R_n value was higher than in 0.37% and 5.5%HCl solution

- 2) In 3% NaCl with CO_2 bubbling
- The R_n values were increasing over time apart from when the Brocolli was added. (it actually increased corrosion compared with the control)
- 100ppm did better than 50ppm for both commercial inhibitors.
- Sugar beet showed the highest R_n value and also the biggest increase over time.

EN VS LPR

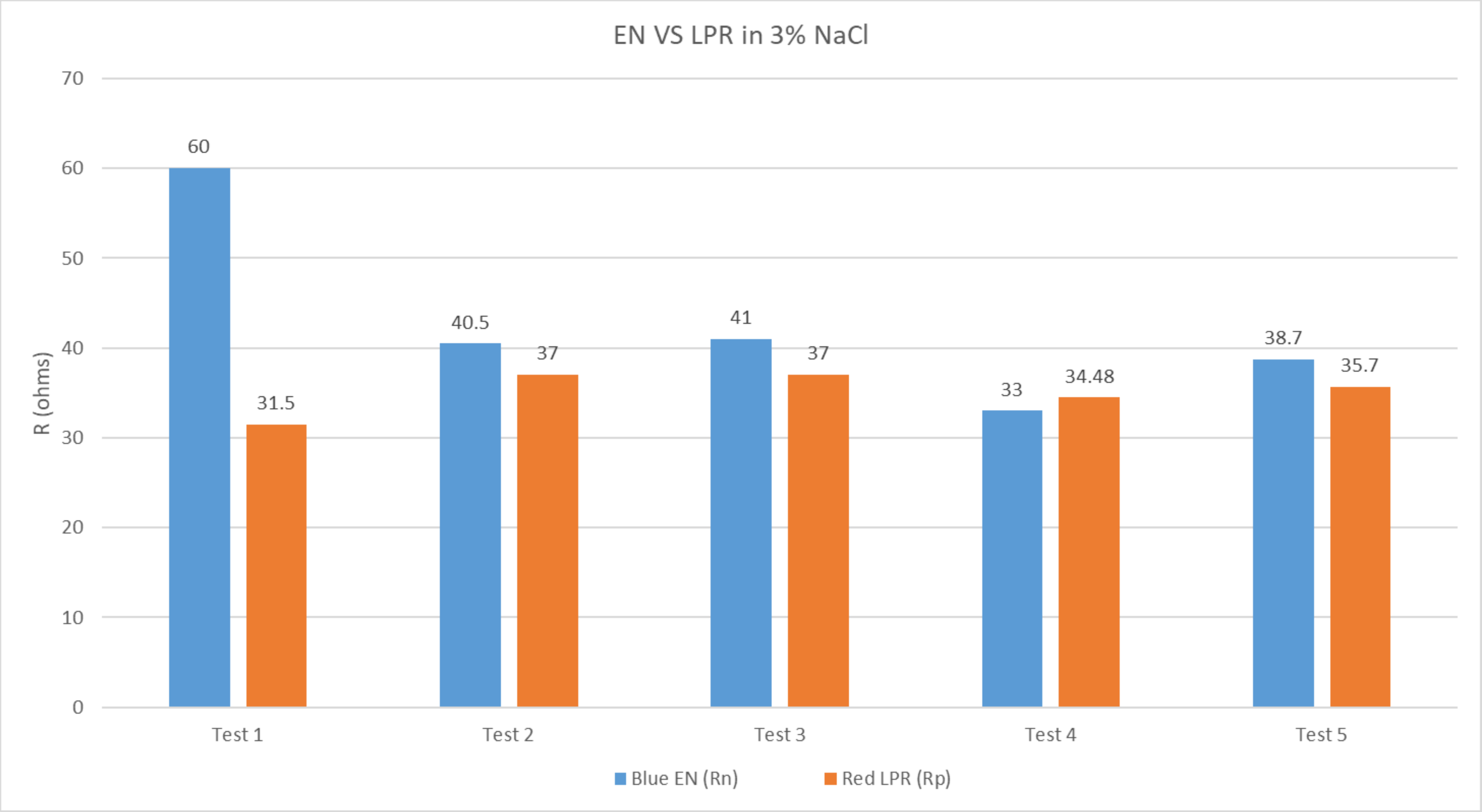
- Same iron specimens and solution.
- Connection difference:

EN requires two separate iron specimens as working electrodes and one reference electrode.

LPR measurement requires one working electrode, one reference electrode, and an additional counter electrode. It imposes an external current (±30mV) of the open circuit potential on the specimen.

- In this LPR experiment, a $1cm^2$ Platinum piece was used as the counter electrode, and the working electrode comprised the two iron specimens joined together.
- By switching around the connection after each set of measurements. Therefore, Any change of the condition eg any oxide film being formed, was minimised.
- Each EN measurement took 10 minutes to perform. LPR was similar Total time of the experiment was just under 2 hours.

Results (3):EN VS LPR in 3%NaCl



Conclusion: part 2

- It has been demonstrated that ENM, as the technique was used here (special cell, stirring etc), is a reliable and quick method to assess the corrosion process and the protection effects from inhibitors.
- In terms of their ability to perform effectively as green inhibitors, sugar beet has more potential in a 3% NaCl & CO_2 environment than broccoli.
- EN gave results that are closely comparable with LPR.

(The first result for EN was higher because the system had not yet reached equilibrium)

Acknowledgements

PART 1

- Thanks are due to the University of Northampton for providing laboratory facilities and allowing the experiments to be carried out.
- Thanks are due to the Sherwin Williams paint company for a grant which enabled the continuing work building and testing the hand held, ProCoMeter, dedicated to assessing paints on metal.
- Thanks are due to the DCVG company for the loan of this instrument and the provision of the Ag/AgCl electrodes.

Part 2

- Thanks to the Department of Chemical and Environmental Engineering at University of Nottingham (Professor Eleanor Binner) for providing the environment and support required to allow the research to be conducted.

Thank you for Attending our Meeting.

Questions?