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Beyond the Performance of Traditional Corrosion Protective Pigments; A Comparative Study

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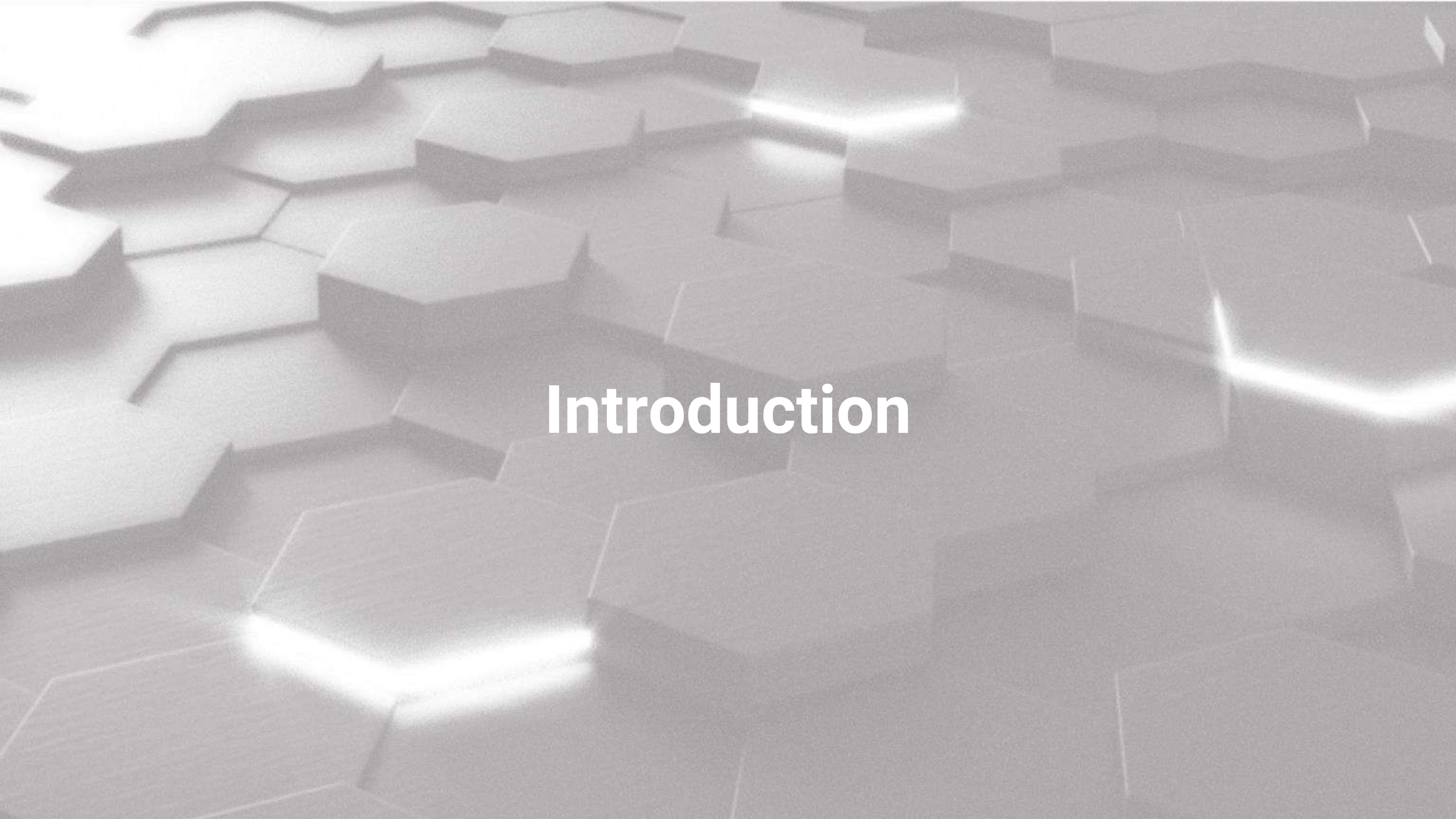

Introduction

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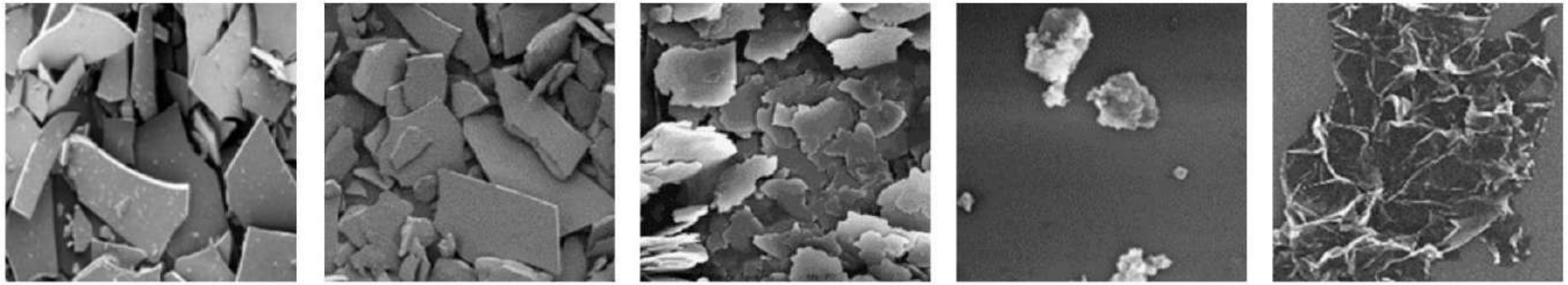
- Anticorrosive pigments act to reduce the development of corrosion through three main mechanisms:
  - **Galvanic protection**
  - **Active**
  - **Physical barrier**
- Graphene as a 2D nanomaterial has been extensively researched as a new additive to **improve barrier performance** and therefore **reduce corrosion**
- There are several materials commonly employed as physical barrier pigments
  - **Aluminium flake**
  - **Micaceous iron oxide**
  - **Glass flake**
- The common distinguishing lamella structure shared by all these products acts to increase the tortuosity of the system
- Increasing the diffusion path length for corrosive species to reach the substrate surface

Traditional Barrier Pigments Vs Graphene Nanoplatelets



Product	Glass Flake	Micaceous Iron Oxide	Aluminium Flake	GNP Type-A	GNP Type-B
Thickness (Microns)	2.3 - 3.3	3	4	0.1	0.003
PSD (D50) (Microns)	27 - 32	85	50	50	25
Tapped Density (g/cm^3)	0.7	1.6	2.7	0.2	0.01

GNPs Type A - Exfoliation of natural graphite   **GNPs Type B** - Synthetic reaction process

Tortuosity in Barrier Coatings

The Nielsen Model:

- A greater diffusion path length can be achieved through the use of barrier pigments with **thinner** and **longer platelets** at **higher volume fractions**

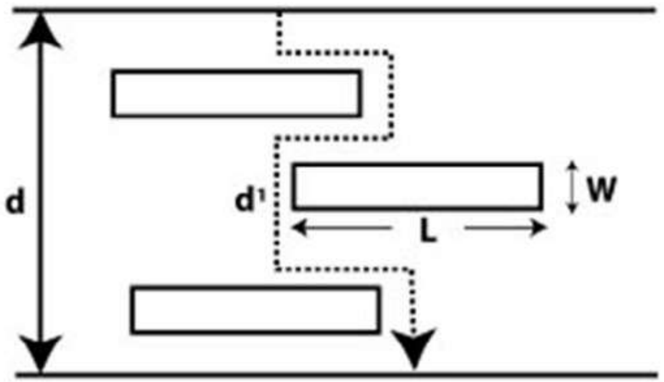
- There are some limitations of such models:
  - Orientation of the pigments not always accounted for
  - Possible agglomeration of the pigments
  - Interaction of pigments with other particles/fillers
  - Morphology of the pigments

The Nielsen Model

$$d^1 = \frac{d + d \times L \times V_f}{2W}$$

Where:

d^1 = diffusion length
d = coating thickness
L = platelet length
V_f = volume fraction of platelets
W = platelet thickness

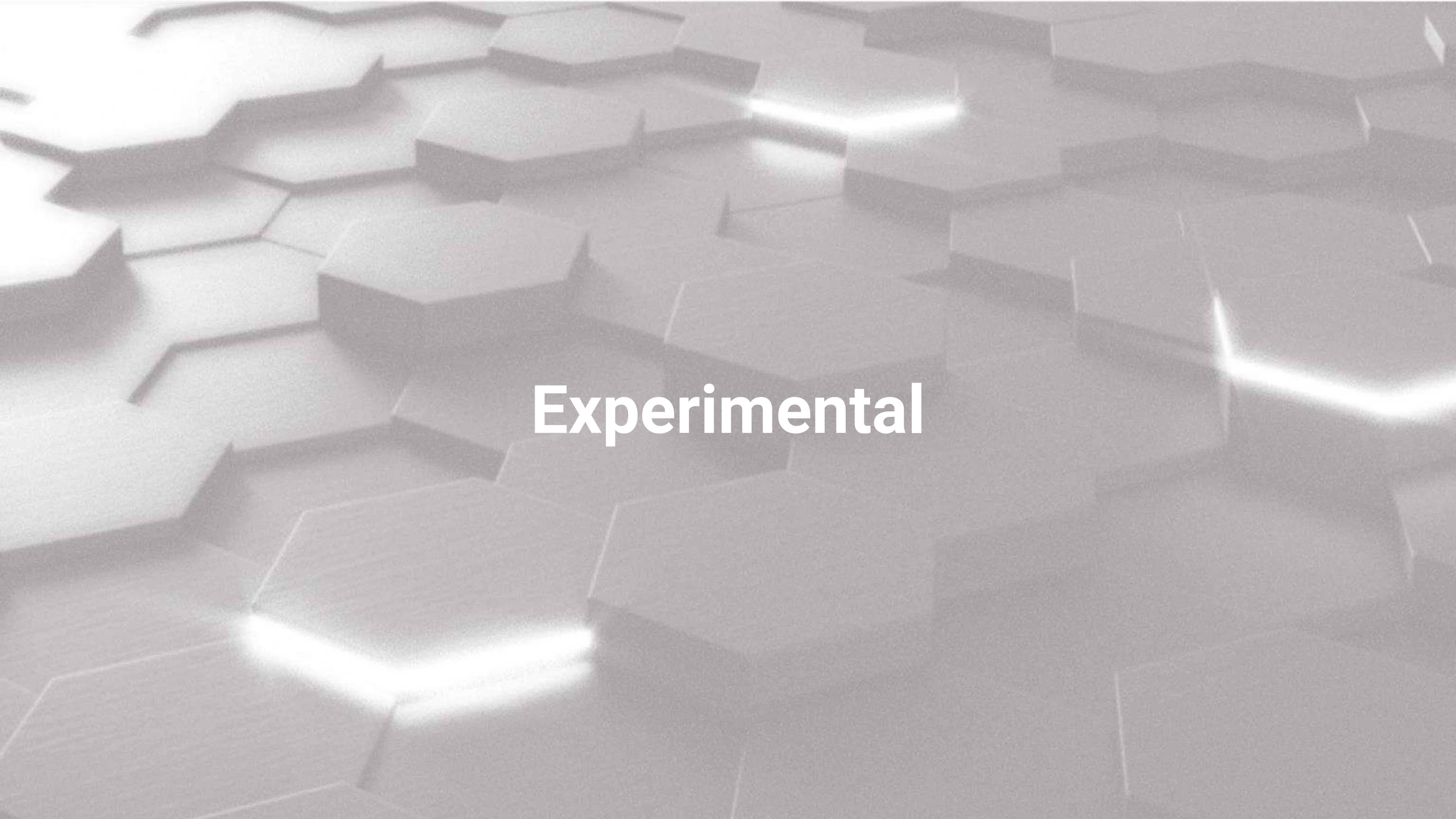


Objectives

Universal Matter GBR Ltd. has previously demonstrated the inclusion of graphene nanoplatelets in coatings improvements in barrier properties and anticorrosive performance

In extending this field of work, the authors aim to:

1. Compare theoretical tortuosity values for the coatings to the actual coating performance test results
2. Benchmark of the behaviour of graphene nanoplatelets against industry standard barrier pigments



Experimental

Paint Formulation and Panel Preparation

Samples
Control primer
20 wt.% Glass flake
20 wt.% Micaceous iron oxide
8 wt.% Aluminium flake
2 wt.% GNPs type A
0.1 wt.% GNPs type B

Paint Preparation

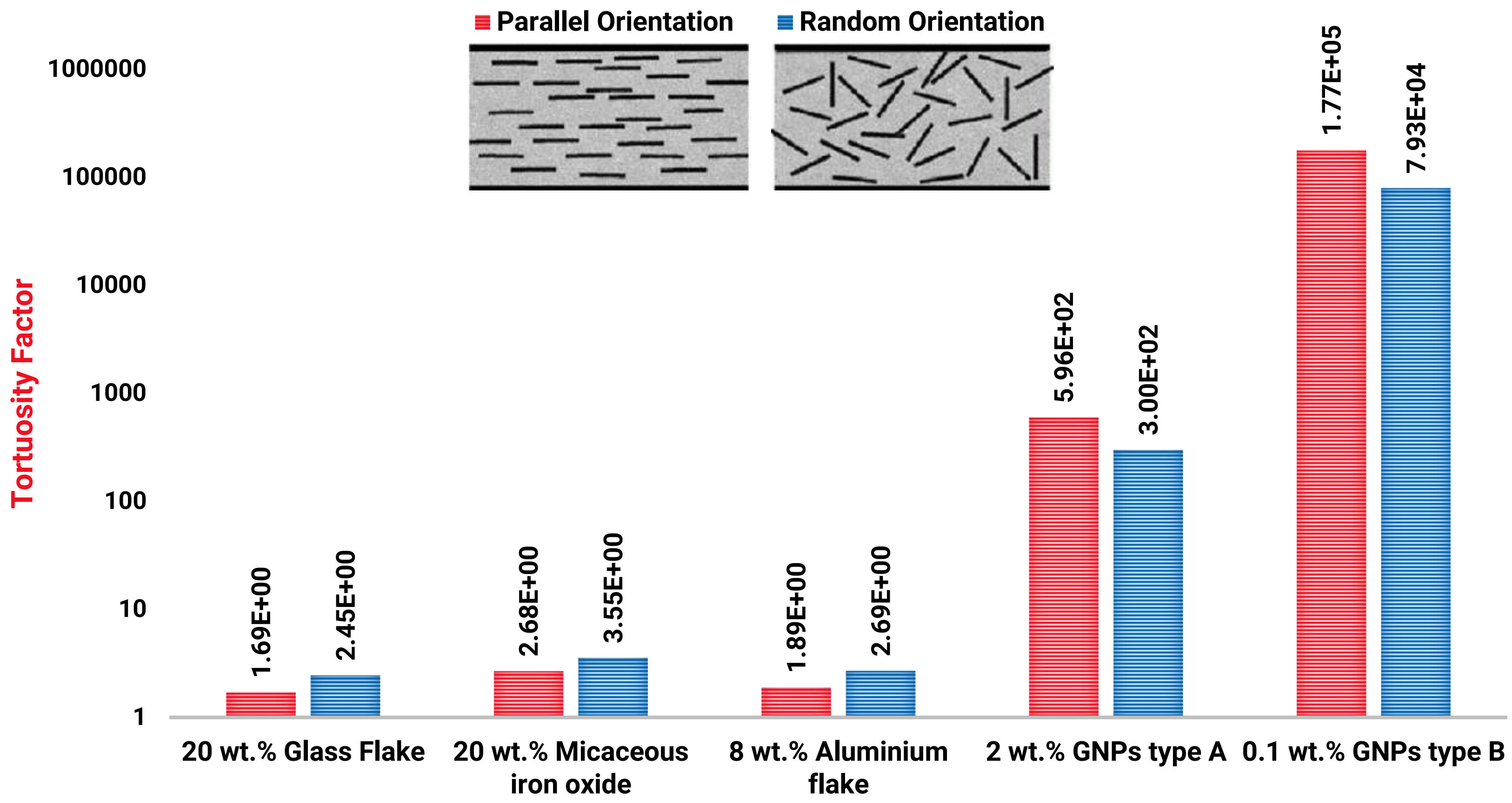
- Prototype base was formulated to be representative of a typical epoxy primer
- Five different paints were prepared, containing different barrier pigments
- Loadings used for each barrier pigment were based on recommended levels for each pigment
- The pigment volume concentration for each coating was kept constant at ~26% by adjusting the amount of barium sulphate, filler and epoxy resin
- All systems were formulated to a stoichiometry of 85%

Panel Preparation

- Coatings were applied using conventional spray application methods
- Cold rolled steel panel substrates blasted to SA 2.5
- All panels were cured for 7 days under ambient lab conditions
- The dry film thickness of the prepared coatings was in 120 ± 5 μm range

Tortuosity in Berrier Coatings

Cussler Model –Theoretical Values



- ➢ The Cussler model allows for both parallel and random platelet orientation
- ➢ Similar tortuosity values for the traditional barrier pigment samples
- ➢ Several orders of magnitude increase in tortuosity factor for the GNP samples

Tortuosity factor values based on barrier pigment volume fractions used in the paint formulations

Test Programme

Techniques of Corrosion Assessment

Neutral Salt Spray (NSS)

- Assessments carried out at 240, 480, 720 and 1440 hours.
- Panels visually inspected for the degree of blisters and corrosion creep as per ISO 12944-6

AC Impedance Spectroscopy (EIS)

- All EIS measurements were made using a Gamry 1000E potentiostat/FRA
- Each individual channel was connected to a Gamry PCT-1 paint test cell
- A conventional three-electrode setup was employed
- Tests run using 3.5 wt.% NaCl electrolyte, using an AC voltage of 20 mV over a frequency range of 1 MHz to 0.05 Hz

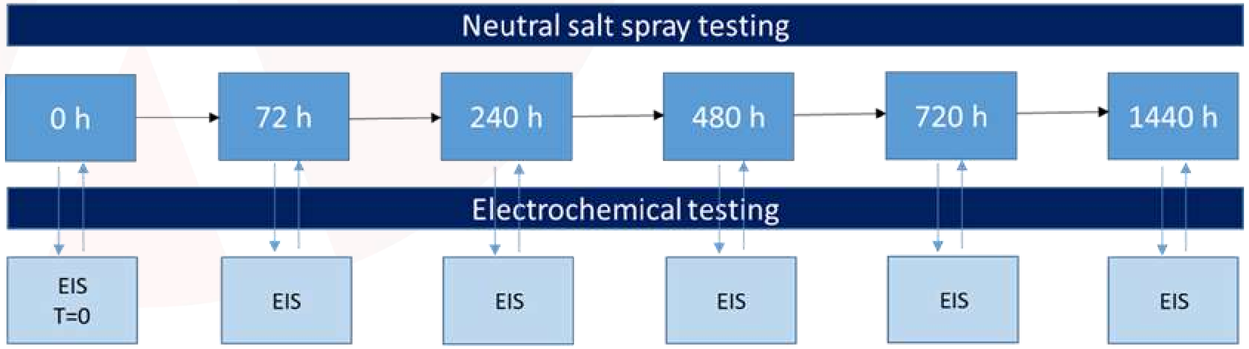
Test Programme

Standalone Constant Immersion EIS

- Allows for a higher resolution water uptake profile to be obtained
- Less accelerative than the combined EIS/NSS approach

Combined EIS/NSS

- Tests are complimentary to each other since EIS can determine relatively small changes within the coating prior to any visible coating changes noted from the examination of the test panels
- The combined test data from EIS and NSS may be used to gain insight and quantify coating performance



Neutral salt spray testing

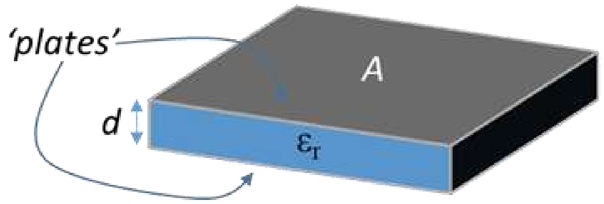
0 h → 72 h → 240 h → 480 h → 720 h → 1440 h

Electrochemical testing

EIS T=0
EIS
EIS
EIS
EIS
EIS

EIS of Organic Coatings

EIS Background - Determination of Water Uptake in Organic Coatings



$$C = \overbrace{\varepsilon_r}^{\text{Permittivity}} \varepsilon_0 \frac{A}{d} \qquad \varepsilon_r = \varepsilon_b^{f_b}\, x\, \varepsilon_w^{f_w}\, x\, \varepsilon_a^{f_a}\, x\, \varepsilon_f^{f_f}$$

C = capacitance

ε_0 = vacuum permittivity

ε_r = Relative permittivity of coating

A = plate surface area

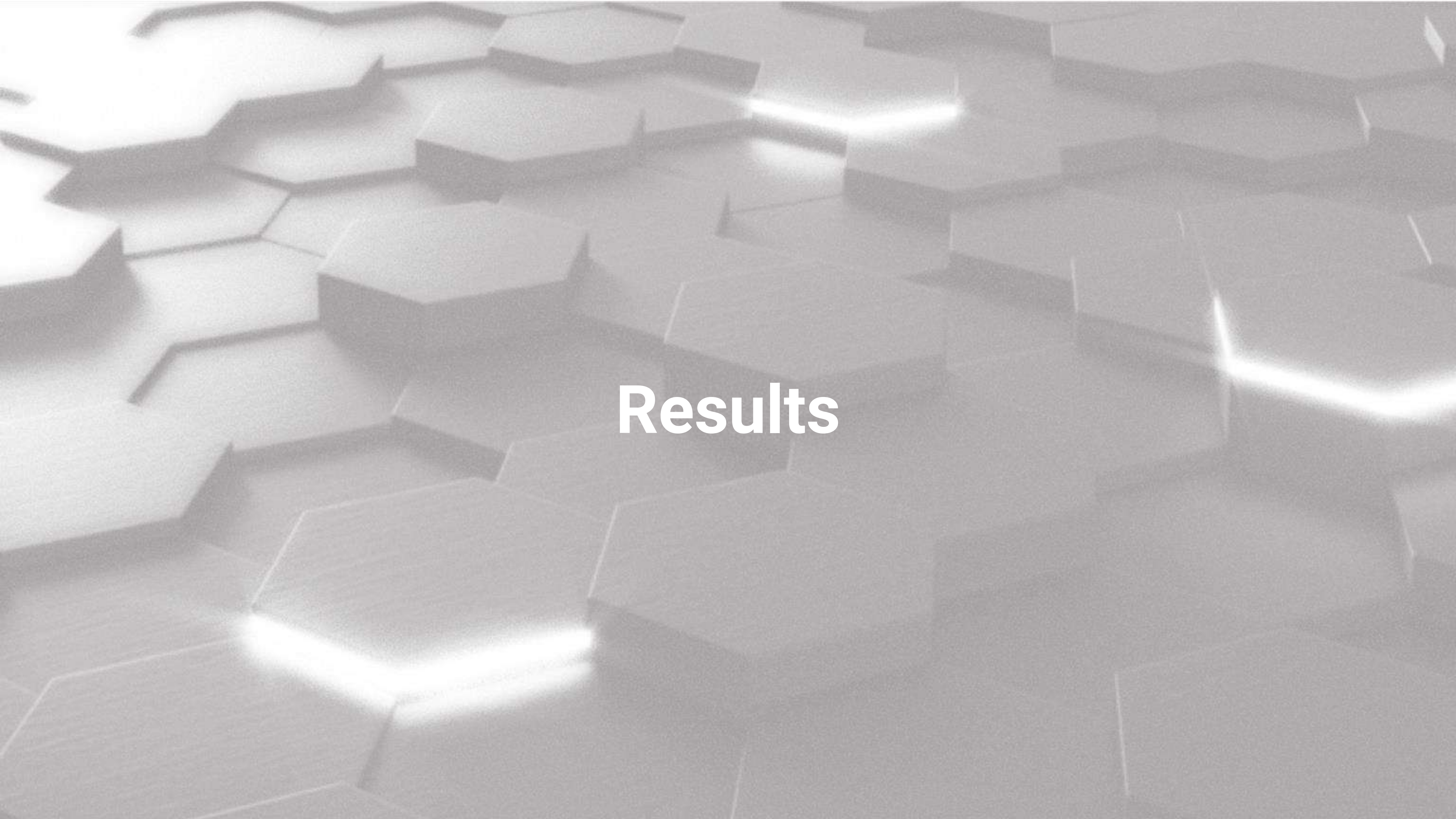
d = distance between plates (coating thickness)

ε_b, ε_w, ε_a, and ε_f are the relative permittivity's of the coating binder, water, air and coating fillers, respectively

- The dielectric constant of the coating dictates the capacitance value
- Capacitance calculated from EIS at high frequency (10 kHz)
- The relative permittivity of the coating is typically between 2-7
- The relative permittivity of water is ~80
- Influx of water into the coating leads to an increase in the volume fraction of water and so an increase in overall permittivity
- The increase in coating capacitance is related to water uptake

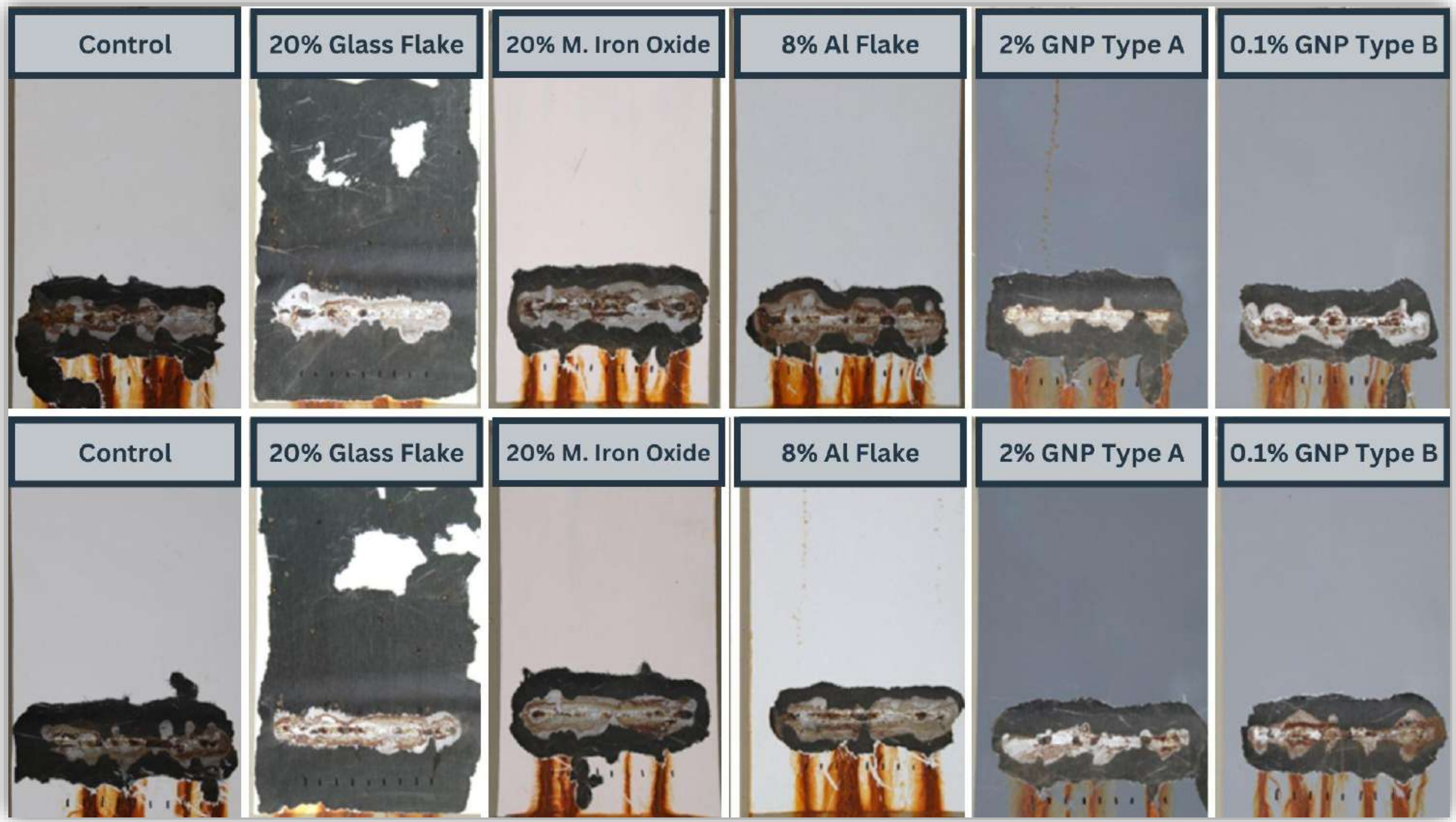
Brasher and Kingsbury equation

$$\chi_v = \frac{100.\, log C_m(t)/C_m(t=0)}{log \varepsilon_w}$$

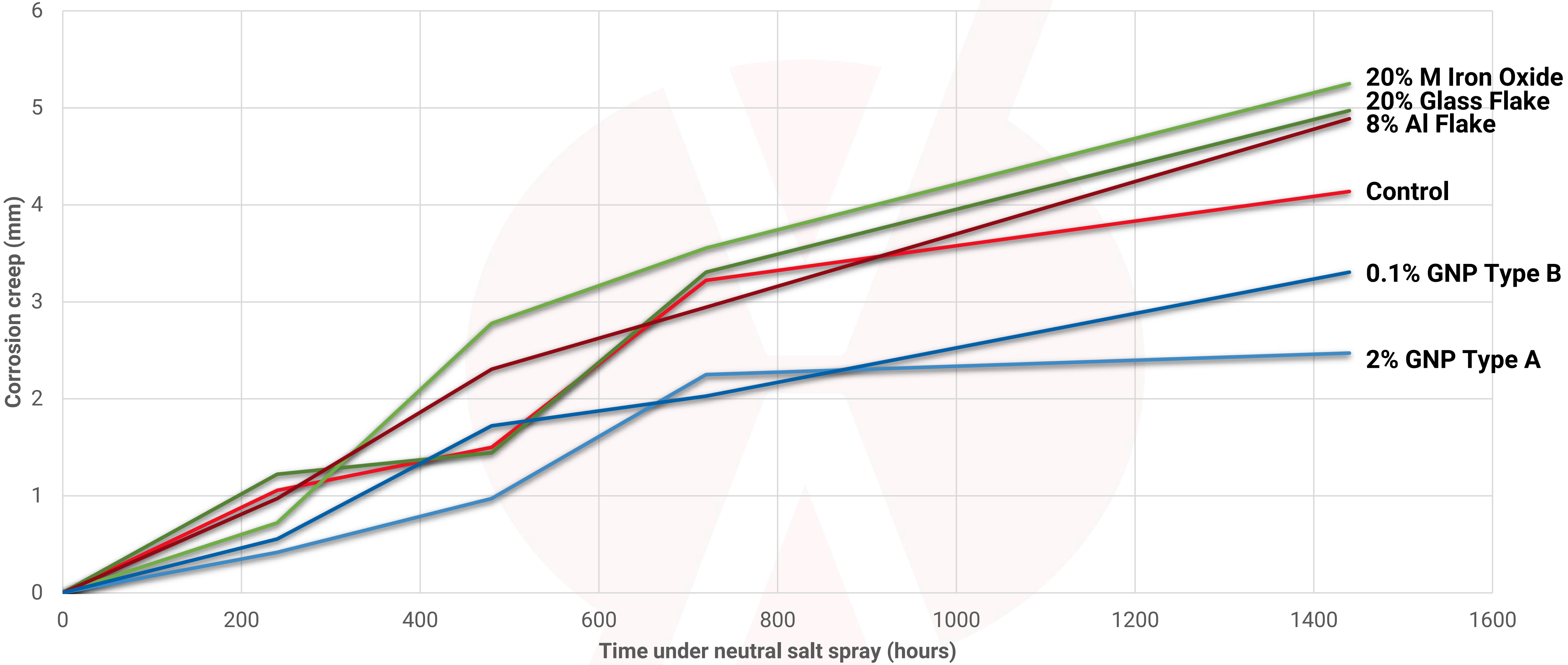


Results

Panel Images - 1440 Hours NSS and Creep Assessments

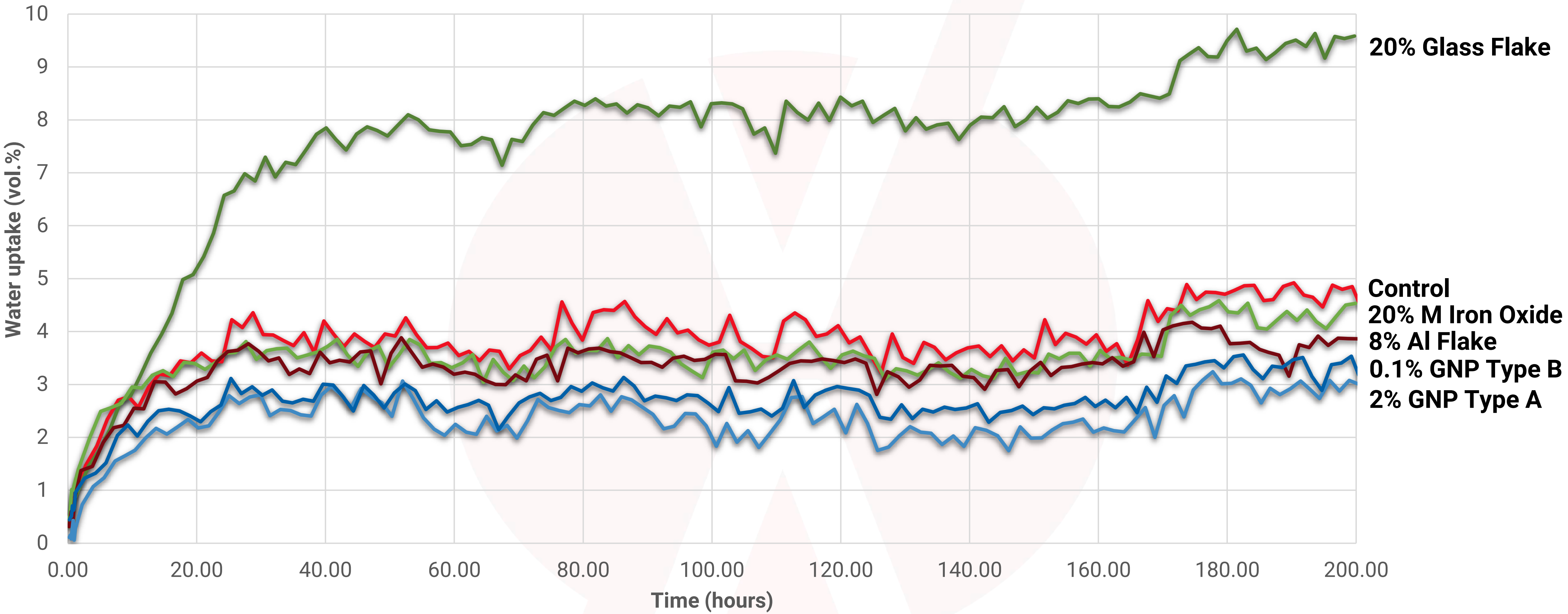


Corrosion Creep Following NSS Testing



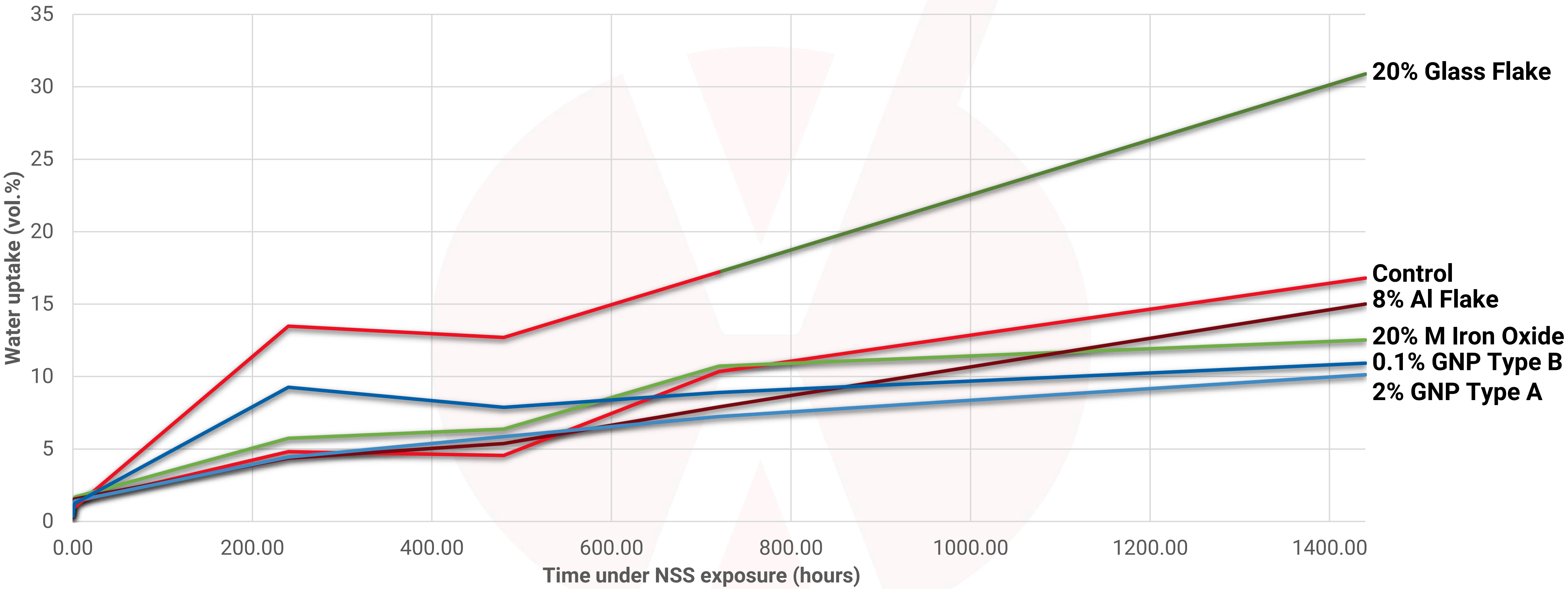
- **Both coatings containing GNP pigments offer the lowest levels of corrosion creep up to 1440 hours**
- Highest corrosion creep was for the micaceous iron oxide, glass flake and aluminium flake samples

Water Uptake Profiles - Constant Immersion EIS



- Water uptake value at saturation highest for the glass flake sample
- Saturation points of the micaceous iron oxide and aluminium flake samples below the control sample
- **GNP samples showing the lower saturation points**

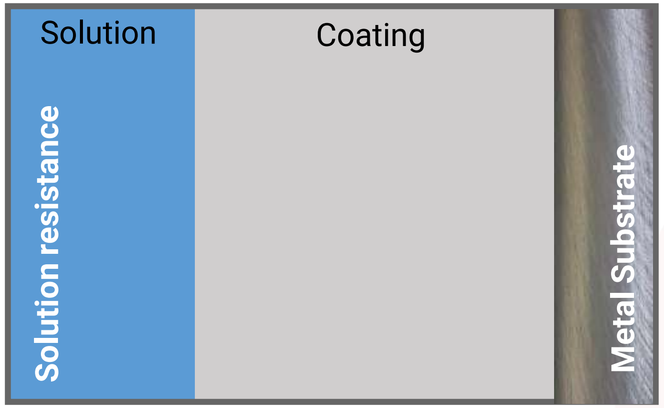
Corrosion Creep Following NSS Testing



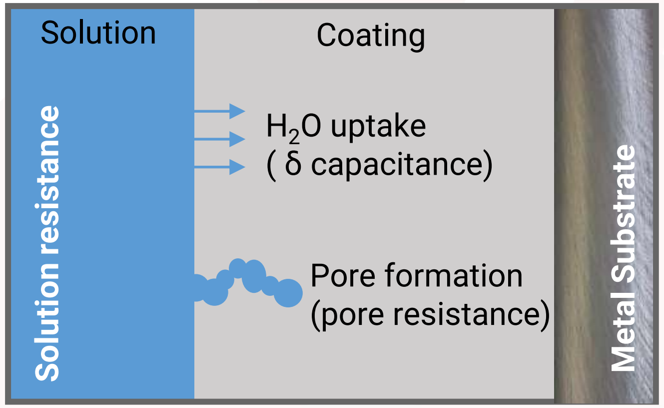
- Water uptake values highest for the glass flake sample
- Other pigmented samples show a lower water uptake at 1440 hours NSS
- **GNP samples showing the lowest levels of water uptake**

EIS of Organic Coatings - Equivalent Circuit Modelling

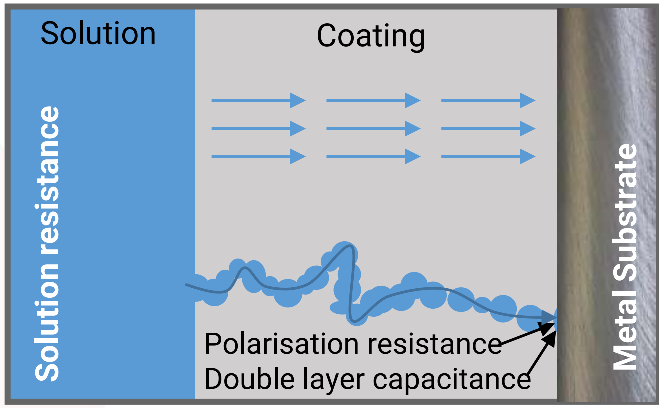
Initial Immersion, T = 0
(high impedance coating)



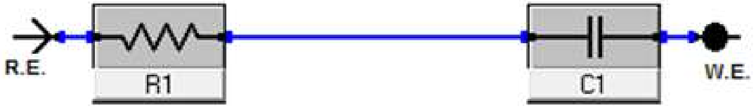
Short term

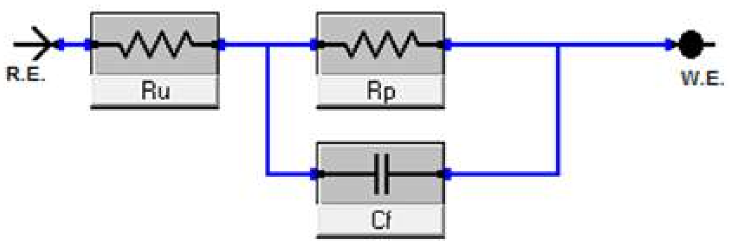


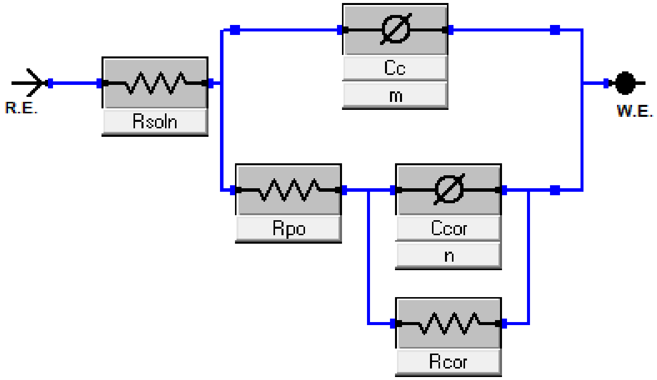
Longer term or scribed coating



Coating Degradation

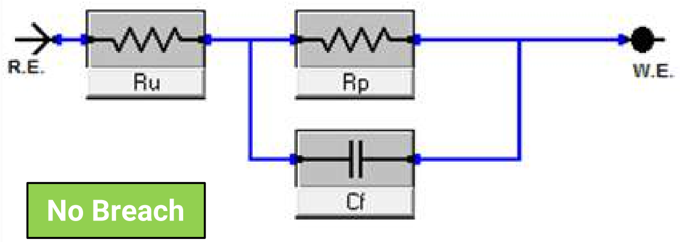




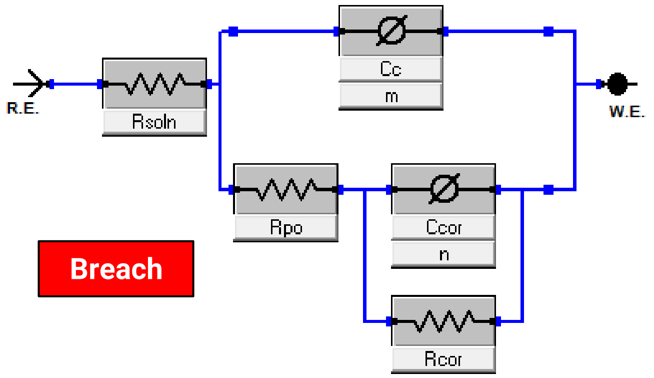


EIS Equivalent Circuit Modelling (ECM) (Combined NSS/EIS)

	Time under NSS exposure (hours)				
	0	240	480	720	1440
Control-Sample 1	No breach	Breach	Breach	Breach	Breach
Control-Sample 2	No breach	Breach	Breach	Breach	Breach
20 wt.% Glass flake-Sample 1	No breach	Breach	Breach	Breach	Breach
20 wt.% Glass flake-Sample 2	No breach	Breach	Breach	Breach	Breach
20 wt.% Micaceous iron oxide-Sample 1	No breach	Breach	Breach	Breach	Breach
20 wt.% Micaceous iron oxide-Sample 2	No breach	Breach	Breach	Breach	Breach
8 wt.% Aluminum flake-Sample 1	No breach	Breach	Breach	Breach	Breach
8 wt.% Aluminum flake-Sample 2	No breach	No breach	No breach	Breach	Breach
2 wt.% Graphene nanoplatelets type A-Sample 1	No breach	No breach	No breach	No breach	Breach
2 wt.% Graphene nanoplatelets type A-Sample 2	No breach	No breach	No breach	No breach	No breach
0.1 wt.% Graphene nanoplatelets type B-Sample 1	No breach	Breach	Breach	Breach	Breach
0.1 wt.% Graphene nanoplatelets type B-Sample 2	No breach	No breach	Breach	Breach	Breach



No Breach



Breach

- Two different equivalent circuit models could be used to model the impedance data
- For the control samples, ECM suggests interfacial electrolyte between 0 and 240 hours NSS
- ECM suggests interfacial electrolyte between 0 and 240 hours NSS for most of the traditional filler samples
- No coating breach noted for a 2 wt.% GNPs type A sample post 1440 hours NSS

Summary & Conclusion

Summary

- Glass flake, micaceous Iron oxide and aluminium flake showed significantly higher levels of corrosion creep compared to the GNP-containing coatings

- Glass flake showed the lowest level of performance in terms of water uptake

- Coatings containing either GNP pigments showed:
  - The **lowest levels of corrosion creep** up to 1440 hours
  - **Lower level of water uptake** compared to the coatings traditional barrier pigments
  - **Longest time to coating failure** noted for GNPs

Ongoing and Future Work

- Work to understand how the orientation of GNPs impacts the performance of a coating
- Work to understand the impact of additional fillers and pigments on GNP orientation and performance
- A study of the interaction of solvent/electrolyte with pigments, fillers and GNPs

Conclusions

- The Cussler and Nielsen theatrical models for the tortuosity determination of coatings predict a high tortuosity for the GNP coatings
    - Highest tortuosity values for GNP type B
    - Highest level of coating performance came from GNP type A
    - Some additional non-correlation between the traditional pigment test data and predicted tortuosity factors
- **Graphene materials**, incorporated into a standard epoxy primer, offer a **significantly improved coating performance** over traditional anticorrosive barrier pigments

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