

The main challenges in corrosion assessment and prevention fields for the next 10 years

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Content

1. Context

2. Replacement of Cr-VI

- Alternative to Cr-VI
- Laboratory experiments

3. Development of corrosion tests for Cr-free alternatives

- Salt spray versus field exposures
- Reliable atmospheric testing conditions

4. Predictive maintenance

- Monitoring techniques
- FEM modelling
- Perspectives of the use of AI

5. Conclusions

Context

- Aluminum alloys are not immune to corrosion (pitting, intergranular or exfoliation corrosion) → Protection with paint (surface treatment/ primer/topcoat)
 - Environmental legislations issued by REACH (in particular CrVI)
- ⇒ **Challenge 1: Need to develop new Al alloys and surface finishes**
- Several tests (ASTM B117, ISO 4623-2, ASTM 2803...) exist to assess the corrosion behavior of painted aluminum alloys
 - ☹ Not representative of service conditions
- ⇒ **Challenge 2: Need to qualify new materials and surface finishes for different applications in the aerospace sector.**
- There is a need to improve and lower the cost of the maintenance in the aerospace industry
- ⇒ **Challenge 3: Need to develop corrosion monitoring, modelling and the use of AI**

Alternatives to CrVI

	Name	Advantages	Drawbacks
Anodizing	Phosphoric acid anodizing	Good adhesion on substrate	Poor corrosion protection
	Phosphoric sulfuric acid anodizing		
	Sulfuric acid anodizing	Good corrosion protection	Poor adhesion on substrate
	Tartaric-sulfuric acid anodizing		
Conversion coatings	Self-assembled nanophase particle	Excellent adhesion and barrier properties	Limited corrosion resistance when the paint is damaged → solved by the addition of corrosion inhibitors
	Trivalent chromium process	Environmentally friendly effective barrier	Possible re-oxidation of Cr(III) to Cr(VI)
Inorganic corrosion inhibitors	Reducible hypervalent transition metals Mo, Vn, Mn Tc	Inhibiting effect	Mo and Mn too soluble
	Difficult to reduce transition metal oxides Zr, Hf, Ta, Ti, Y	Stability of the oxides	Soluble and mobile precursors of these oxides are unstable
	Boehmite, hydrotalcite coatings, rare-earth (Ce...)	Corrosion protection of aluminum	
	Metallic magnesium	Corrosion protection of the substrate	Coating density, incompatible with the lightening of structures (aeronautic)
Organic corrosion inhibitors	Nanocontainers or reservoir species	Self-healing properties	Limited according to the solubility of inhibitors
	Exchange ion pigments	Corrosion protection of aluminum	Can be activated by any metallic cations present in solution → non-expected release
Pigments	BTA, 2-MBT, Lithium salt ...	Effective corrosion protection	Non-permanent adsorption of BTA and 2-MBT
Sol-gel coatings		Green coating technologies Corrosion protection performance when loaded with corrosion inhibitors	Energy intensive heat treatment to densify the network → solved using photopolymerization

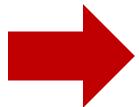
F. Peltier and D. Thierry: Coatings, 12(4),518, 2022.

Coatings performance: testing conditions

Several tests (ASTM B117, ISO 4623-2, ASTM 2803...) exist to assess the corrosion behavior of painted aluminum alloys

Yet, they are:

- Not developed specifically for the aerospace industry
- Not representative of service conditions



Need to develop robust & reliable accelerated corrosion tests for aerospace materials

Comparison of field exposures & NSST

- Painted Aluminium Alloys

System	Alloy	Pretreatment	Primer	Top coat
1	AA 2024 T3 clad	Chrome free organic sol-gel, treatment with sanding based on Zr without fluoride and silane	Chrome free high solid epoxy primer A (based on nanotechnology and adhesion promoter)	PU
2	AA 2024 T3 unclad	Zr-Cr ³⁺ conversion coating	Chrome free high solid epoxy primer A (based on nanotechnology and adhesion promoteur)	
3	AA2024 T3 unclad	Nitric and sulfuric-based chrome and fluoride free deoxidizer	Anodic epoxy chrome free electrocoat primer	
4	AA2024 T3 unclad	Zr-Cr ³⁺ conversion coating	Air-drying epoxy chrome free primer B	

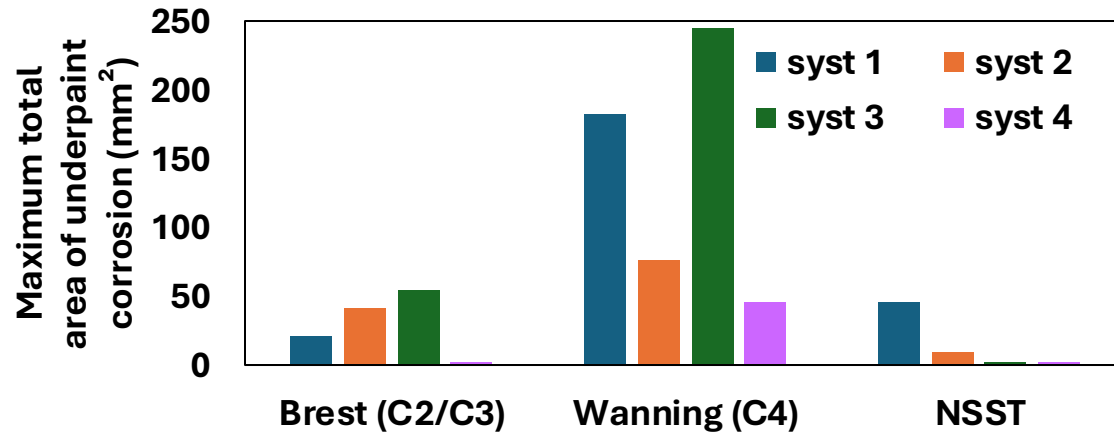
⇒ Standardised neutral salt spray test (NSST)

⇒ Two outdoor marine sites (5-years)

- Brest (France):** T-12°C / RH-82% / Rain-1000mm/y / Cl-490 mg/m²,d / no SO₂
C3-Al, C4-C5-Steel

- Wanning (China):** T-26°C / RH-83% / Rain-2000 mm/y / Cl-70 mg/m², d / SO₂-12µg/m³
C4-Al, CX-Steel

Comparison of field exposures & NSST



Syst.	NSST	Brest	Wanning
1	B	B	F+B
2	B	F+B	F+B
3	B	F+B	F+B
4	B	B	B

B: blistering, F: filiform



NSST



Brest



Wanning

NSST is not representative of field exposure

➔ Need to develop reliable & representable testing conditions for aerospace alloys

Painted Aluminium Alloys

Nr	Alloy	Pretreatment	Primer	Topcoat
1	2024 T3 sheet	TSA	Cr free primer 1 (Epoxy primer)	Top coat 1 (Polyurethane)
2		CrIII Conv. Coat.		
3	2024 clad	TSA	CrVI primer 1 (2 or 3 components amine cured epoxy primer)	
4	2024 T351 clad	Sol-gel	CrVI primer 2 (epoxy primer)	Top coat 2 (Polyurethane)
5	2324 T39	TSA	CrVI primer 3 (3 components amine cured epoxy primer)	
6	7055 T7751	TSA	CrVI primer 4 (epoxy primer)	
7	2024 T351 clad	Sol-gel	CrVI primer 5 (epoxy primer)	
8	2324 T39	TSA	CrVI primer 4 (epoxy primer)	

Artificial defects: 1 scribe of 1x100 mm + 1 scribe of 1.6x100 mm forming a cross (depth 300µm)

Outdoor Exposure

Marine field station of **Brest (France)** 5 years @ 45° facing South

Average temperature (°C)	Average relative humidity (%)*	TOW (%)	Total Rainfall (mm)	Mean Chloride deposition (mg/m ² ,d)	Corrosivity class (ISO 9223)	
					Al 1050	Carbon steel
13	82	59	5485	960	C2/C3	C4-C5

February 2018 to June 2023



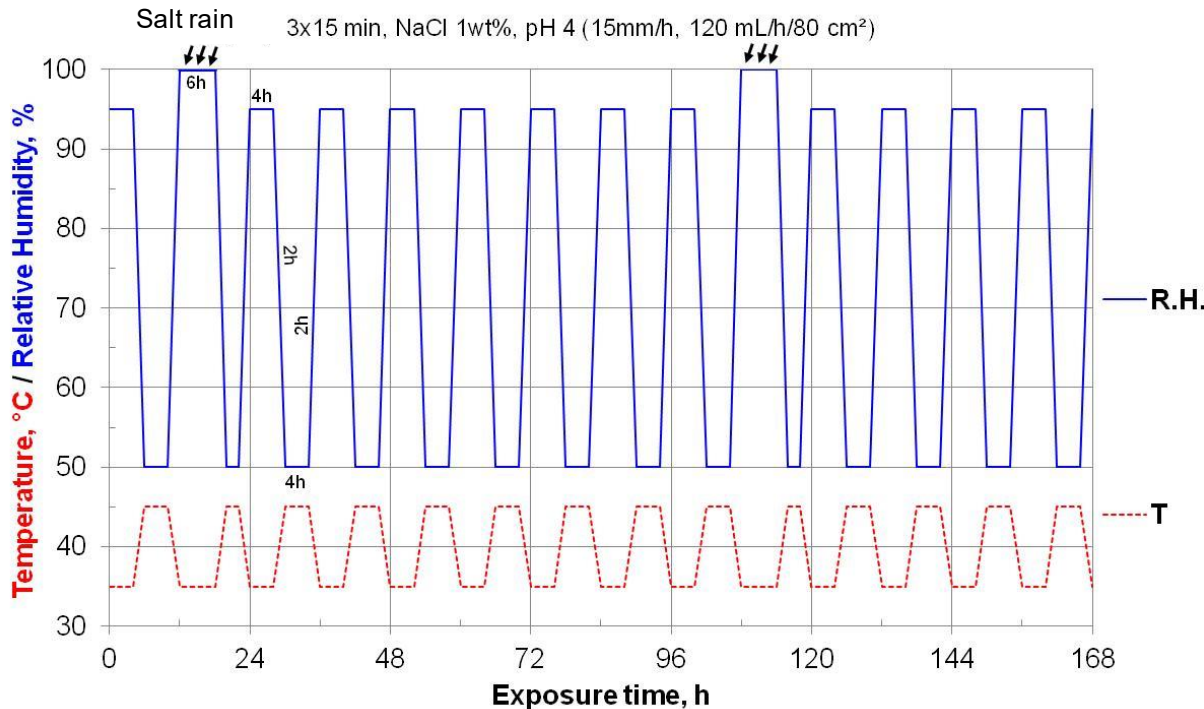
Accelerated Corrosion Tests

Standardized accelerated corrosion tests

- Neutral salt spray test (NSST-ASTMB117) - 3000 h
- Filiform Corrosion Test ISO 4623-2 - 1000 h
- Cyclic Corrosion Test Volvo STD 423-0014 - 2000h

From Automotive Industry

Volvo
STD 423-0014



Accelerated Corrosion Tests

Accelerated corrosion test - Design of experiment (DoE)

Based on Volvo STD 423-0014 test (2000h)

→ Study of the influence of 3 parameters at 2 levels → Reduced matrix of 8 tests

	Level -	Level +
Salt (NaCl) Concentration, %wt (SC)	0.5	2
Wet Time, h (WT)	4	8
Wet Relative humidity, % (WRH)	80	95

From the results of the 8 first tests → development of 4 other tests

- To study the effect of the temperature (single or cycle)
- To study the type of salt
- To mimic the behavior of the different systems according to the experience acquired on them

Accelerated Corrosion Tests

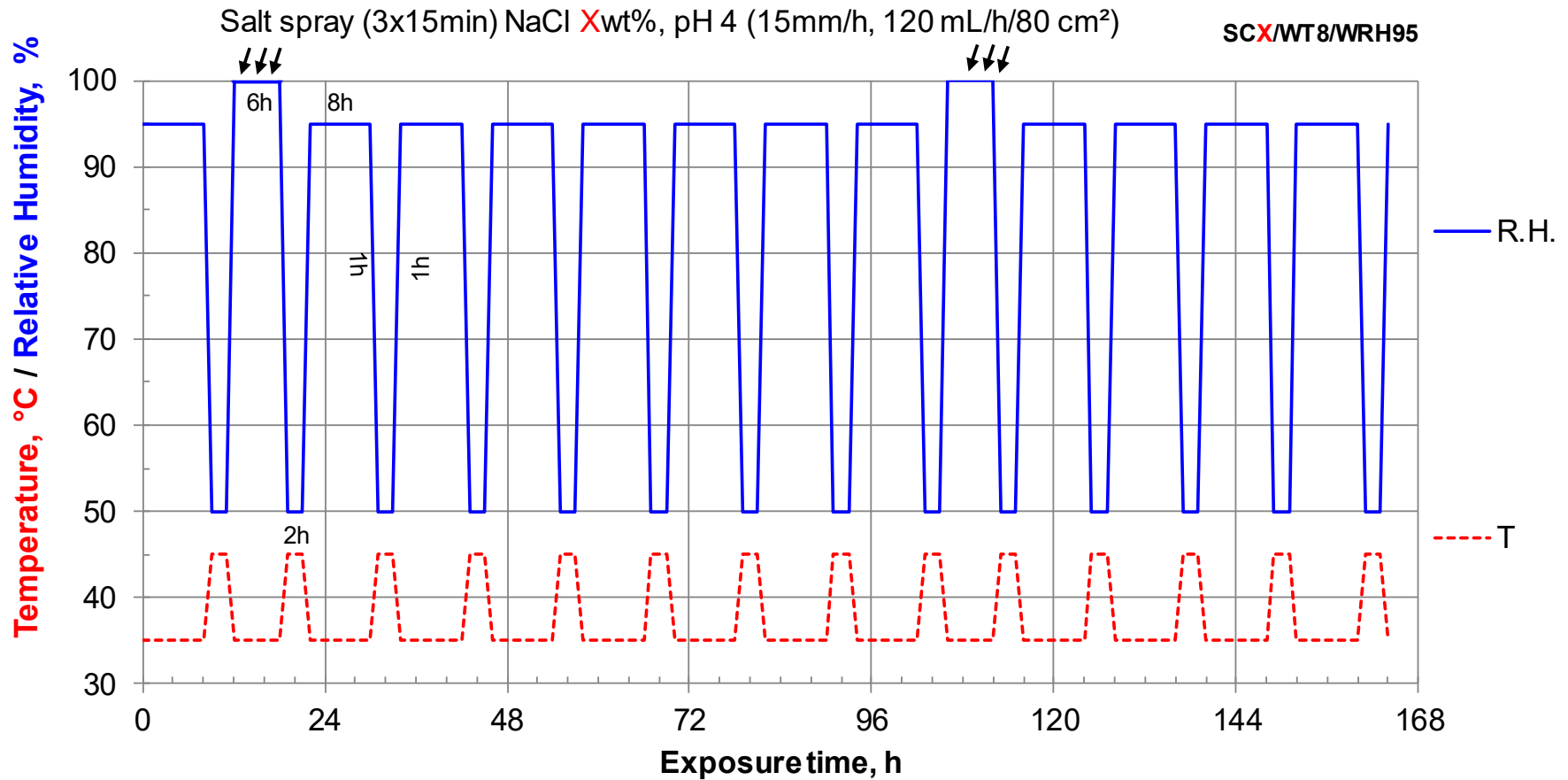
Accelerated corrosion test- Design of experiment (DoE) : tests

Test	Test label	Salt Conc. Wt%	Type of salt	Wet time, h	Wet RH, %	Temperature, °C
		SC		WT	WRH	T
1	SC0.5/WT4/WRH80	0,5	NaCl	4	80	35-45°C (cycle)
2	SC2/WT4/WRH80	2		4	80	
3	SC0.5/WT8/WRH80	0,5		8	80	
4	SC2/WT8/WRH80	2		8	80	
5	SC0.5/WT4/WRH95	0,5		4	95	
6	SC2/WT4/WRH95	2		4	95	
7	SC0.5/WT8/WRH95	0,5		8	95	
8	SC2/WT8/WRH95	2		8	95	
9	SC0.5/WT4/WRH80/T 45	0.5		4	80	45°C (Constant)
10	SC0.5mix/WT4/WRH8 0	0.5	NaCl+MgCl ₂ + CaCl ₂	4	80	35-45°C (cycle)
11	SC1/WT4/WRH80	1	NaCl	4	80	
12	SC0.75/WT4/WRH95	0.75		4	95	

Duration: 12 weeks (2000h)

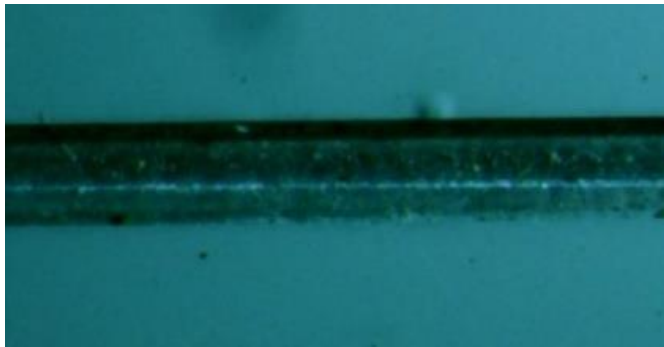
Accelerated Corrosion Tests

SCX/WT8/WRH95

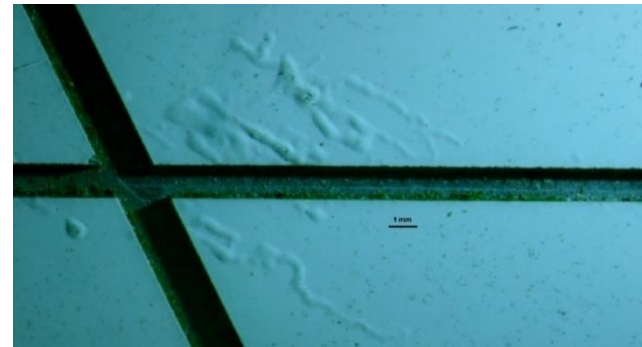


Evaluation Procedure

- **Aspect of underpaint corrosion from the scribes**
- **Extent of filiform corrosion (underpaint corrosion) from the scribes** using a microscope and image analysis software
 - Number of initiations
 - Max length of FFC perpendicular to the scribes
 - Total area of filiform corrosion
- **Measurements of the deepest attacks in the scribes** after removal of corrosion products in the scribes by chemical pickling (HNO_3) and



Blistering (B)



Filiform Corrosion (FFC)

Standardized Corrosion Tests

- Aspect of underpaint corrosion from the scribe

System Nr	NSST (3000 h)	Volvo STD 423-0014 (2000 h)	ISO 4623-2 (1000 h)	Field (5 years)
1	B	B	F	B
2	B	F+B	F	B
3	B	B	B	B
4	B	F	F	F
5	No corrosion	B	B	F+B
6	No corrosion	B	F	B
7	B	F	F	F
8	B	B	F	B

B: Blistering; F: Filiform

➔ NSST : Majority of blistering

➔ ISO 4623-2 : Majority of filiform

➔ Attacks morphologies in Volvo STD 423-0014 close to the field

Design of Experiments

Aspect of underpaint corrosion from the scribes

SC	0.5	0.5	0.5 (mix)	1	2	0.5	2	0.5	0.75	1	2	0.5	2	Field exp. 5 Y
WT	4	4	4	4	8	8	8	4	4	4	4	8	8	
WRH	80	45	80	80	80	80	80	95	95	95	95	95	95	
1	F	F+B	F+B	B	F	F+B	F+B	F+B	B	B	F+B	F+B	B	B
2	F	F+B	F+B	F+B	F+B	F+B	F+B	F+B	F+B	F+B	F+B	F+B	B	B
3	B	B	B	B	B	B	B	B	B	B	B	B	B	B
4	F	F	F	F	F	F	F	F	F	F	F	F	F	F
5	B	F+B	F+B	F+B	B	-	B	B	B	B	B	B	-	F+B
6	B	F	-	B	B	B	B	B	B	B	B	B	B	B
7	F	F	F	F	F	F	F	F	F	F	F	F	F	F
8	B	B	B	B	B	B	B	B	F+B	B	B	B	B	B

B: Blistering; F: Filiform

Good agreement between **Field** and **SC0.75/WT4/WRH95**
SC1/WT4/WRH95 (Volvo STD 423-0014)
SC0.5/WT8/WRH95

Design of Experiments

- **Acceleration factor & coefficient of variation**

	3 years		5 years	
	Acc. Factor	Coef. of variation	Acc. Factor	Coef. of variation
SC0.75/WT4/WRH95	373	0,4	581	0,4
Volvo test	387	1,4	588	1,3
SC0.5/WT8/WRH95	331	0,5	510	0,5

$$Acceleration = \frac{X(Acc.Test)}{X(Field)} \times Const$$

X = Underpaint corrosion from scribe (Area)
 $Const.$ = Exp. Duration in field (60 weeks) / Exp. Duration in Acc. Test (12 weeks)

$$Coefficient\ of\ variation = StDev / Acc.Factor$$

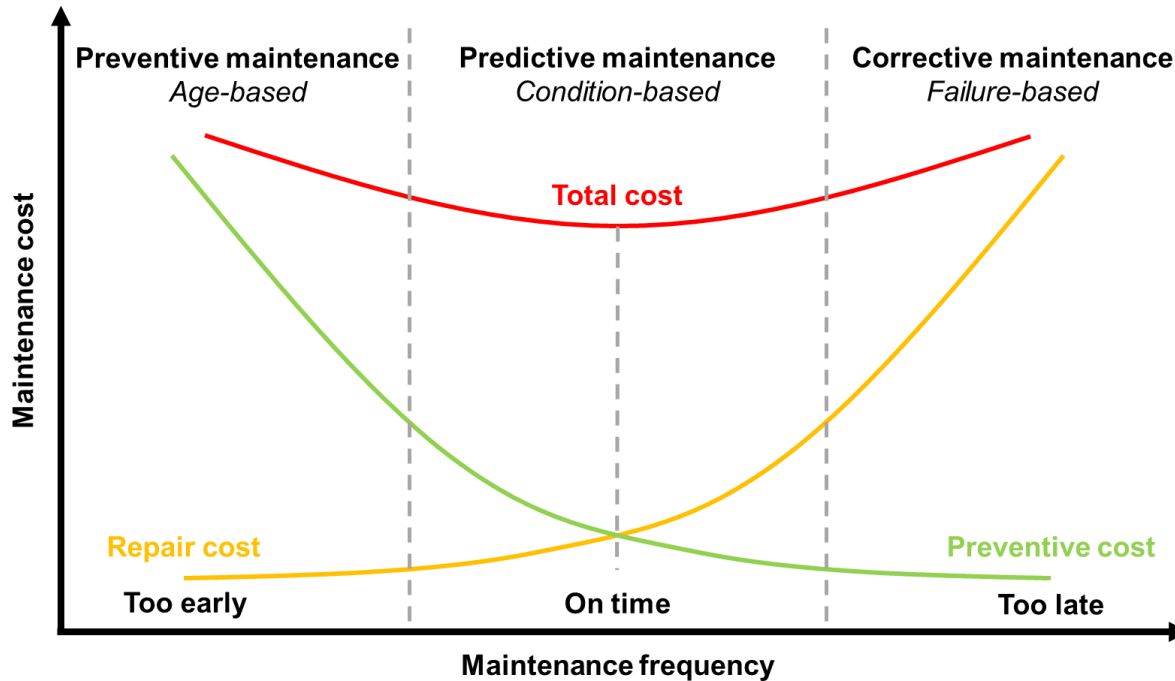
Conclusions - Test development

- Sol-gel and Cr-free systems showed the worst resistance to corrosion compared to Cr-VI systems.
- Tests **SC0.75/WT4/WRH95**, **SC0.5/WT8/WRH95** & **Volvo ACT1** generated the same type of corrosion from a defect as observed in outdoor exposure (marine atmosphere).
- Tests **SC0.75/WT4/WRH95** & **SC0.5/WT8/WRH95** are the best candidates to simulate the degradations observed outdoor from a defect = low coefficient of variation & sufficient acceleration (underpaint corrosion from a defect).

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Preventive, predictive & corrective maintenance



- Aircraft/helicopters maintenance is mainly based on fixed scheduled – costly + lack of efficiency
- **Need of predictive/condition-based maintenance to reduce cost and increase aircraft availability**
- **Monitoring techniques described in SAE AIR6970 - Environment Spectra and Corrosivity Monitoring Using Electrochemical and Electrical Resistance Sensors**

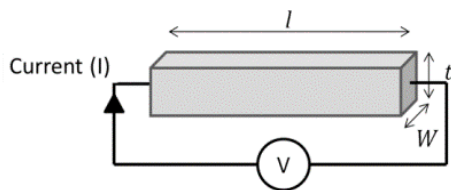
Corrosion monitoring solutions as maintenance tools

Main advantages and drawbacks

Method	Sensitivity	Immersion	Atmospheric	Advantages	Drawbacks
Quartz Crystal Microbalance	++++	Yes	Yes	Sensitivity	Very thin metallic film
Optical Fibre Corrosion Sensor (OFCS)	+	Yes	Yes	Sensitivity, small footprint	Very thin metallic film
Acoustic Emission	++	Yes	Yes	Event location identification	Data processing, no corrosion rate
Linear Polarization Resistance	+++	Yes	Complex	All materials and thicknesses	Data processing/integration
Galvanic Cell sensors (ACM)	+++	Yes	Yes	Reactivity under cyclic conditions	Representativity, robustness with sensor ageing
Electrochemical Impedance Spectroscopy	+++	Yes	Complex	Mechanism insight	Cost, time
Electrical Resistance (ER)	+++	Yes	Yes	Sensitivity	Model, thin materials
RFID (amplitude)	+	Complex	Yes	Low cost	Reading distance, precision
Passive and Wireless Inductance resistance	+	Complex	Yes	Low cost	Reading distance, precision
Inductance resistance	++++	Yes	Yes	Sensitivity	Very thin metallic film
Electrochemical noise	++	Yes	No	All materials and thicknesses	Data processing/integration

Electrical resistance (ER) sensor – Measurement principle

Electrical conductor

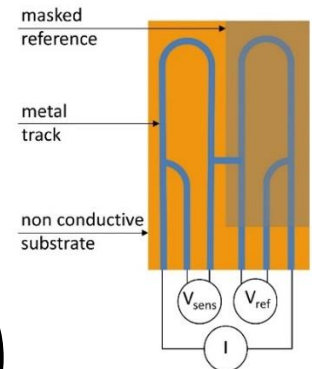
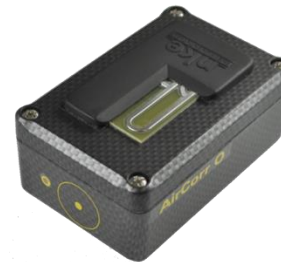


$$R = \rho \frac{l}{w * t}$$

ρ : electrical resistivity
 l : conductor length

w : conductor width
 t : conductor thickness

AirCorr O sensor



$$CD = t_i \left(\frac{R_{ref,i}}{R_{sens,i}} - \frac{R_{ref}}{R_{sens}} \right)$$

t_i : Initial reference track thickness

R_{sens} : Resistance of the sensor track

R_{ref} : Resistance of the reference track

$R_{sens,init}$, $R_{ref,init}$: Initial resistance

Assess the materials and environment interaction in real time...



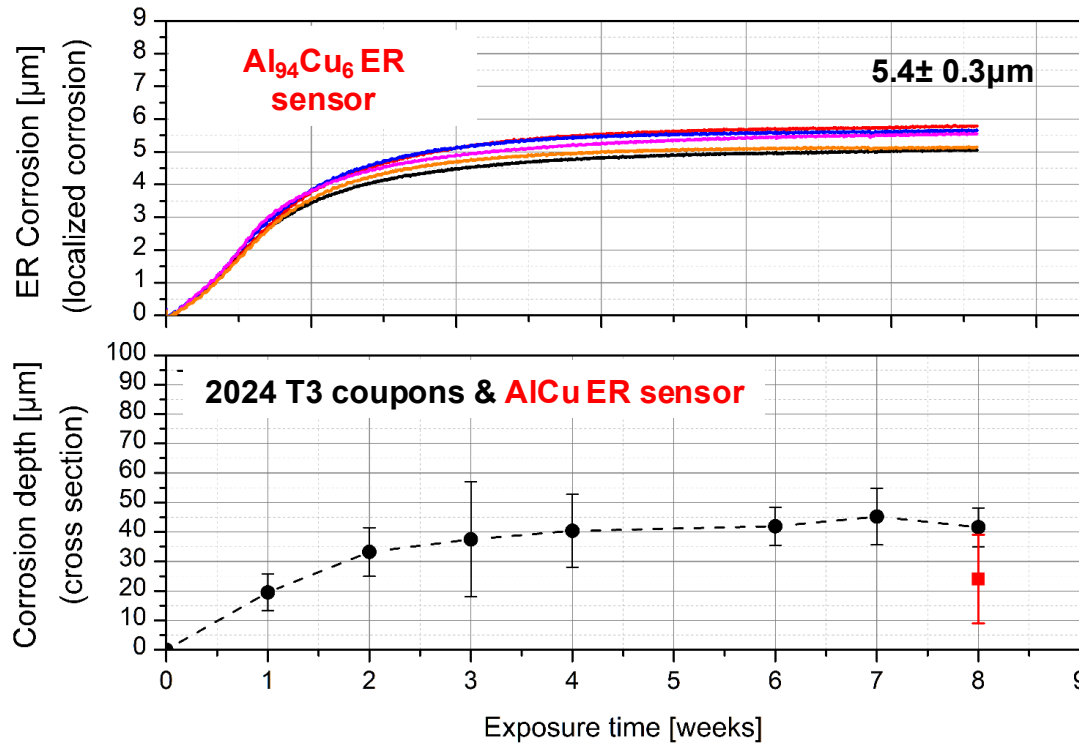
Simple principle and easy interpretation
Robust (mechanically non vulnerable)
Unaffected by humidity and dust



Theoretically limited to uniform corrosion
Uniform and localized attack cannot be distinguished
Method usually limited to "model" materials

Corrosion monitoring solutions as maintenance tools

Electrical resistance (ER) sensor – AirCorr O light alloys sensors



Pre-contamination test of
Al₉₄Cu₆ – 125 μm

Cl⁻ concentration → 0.5 g/m²

Wet/dry cycles of 4h → 50% - 90 %RH

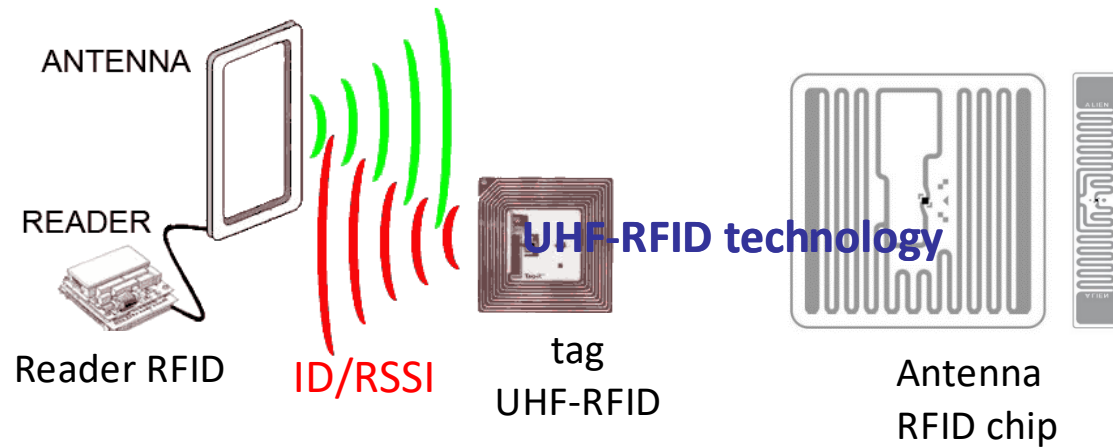
Constant temperature → 35±1 °C

- Good reproducibility of the ER sensors / similar evolution of the corrosion propagation between sensors and coupons
- Significant effect of Cl⁻ for both ER sensors and coupons during the three first weeks
- Mean corrosion depth > ER corrosion thickness → **localized corrosion**

E. Diler et al., Materials and Corrosion, 72 (8), 1377–1387

UHF-RFID technology

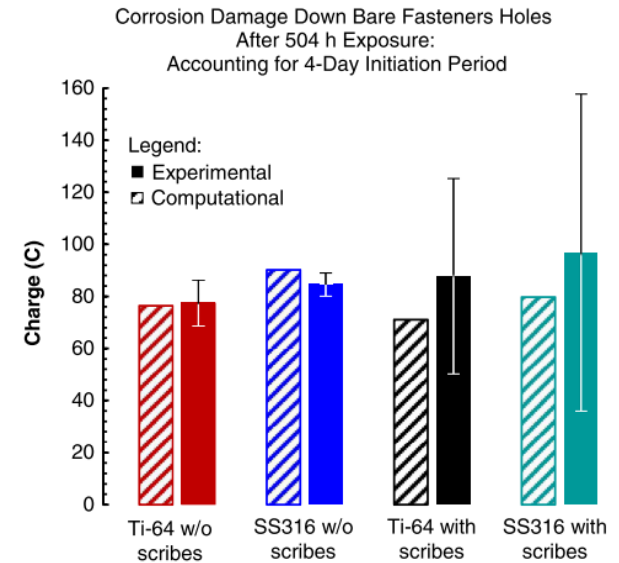
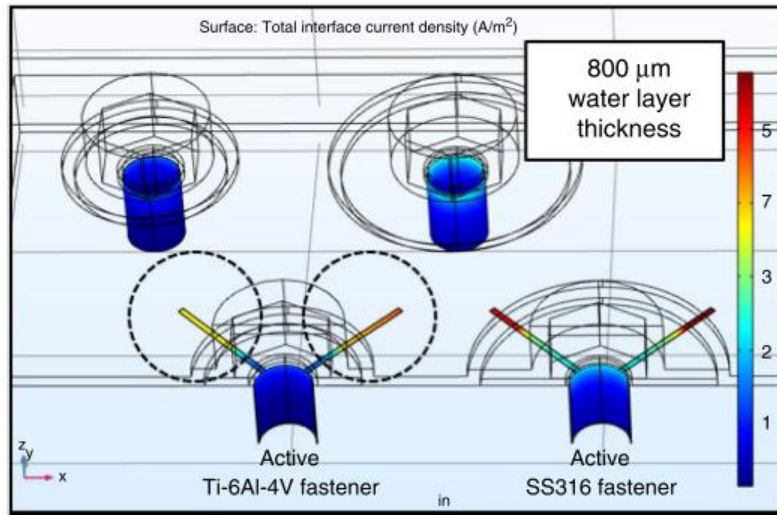
UHF-RFID Technology



applications UHF-RFID (< 1€)

Corrosion modeling and prediction

Galvanic corrosion between coated Al alloy plate and SS fasteners – Finite element modelling



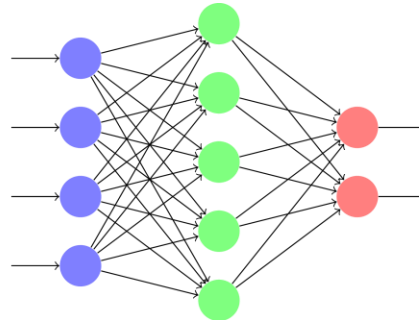
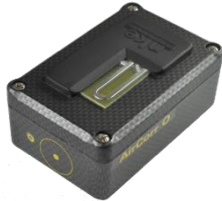
- **Modelisation of the current density** from a galvanic coupling between **AA7075-T6 / SS316** and **Ti-6Al-4V**
- Good approximation of the experimental results by finite element modelling

Marshall R. S. et al., *Corrosion*, 75(12), 1461–1473.

Corrosion modeling and prediction

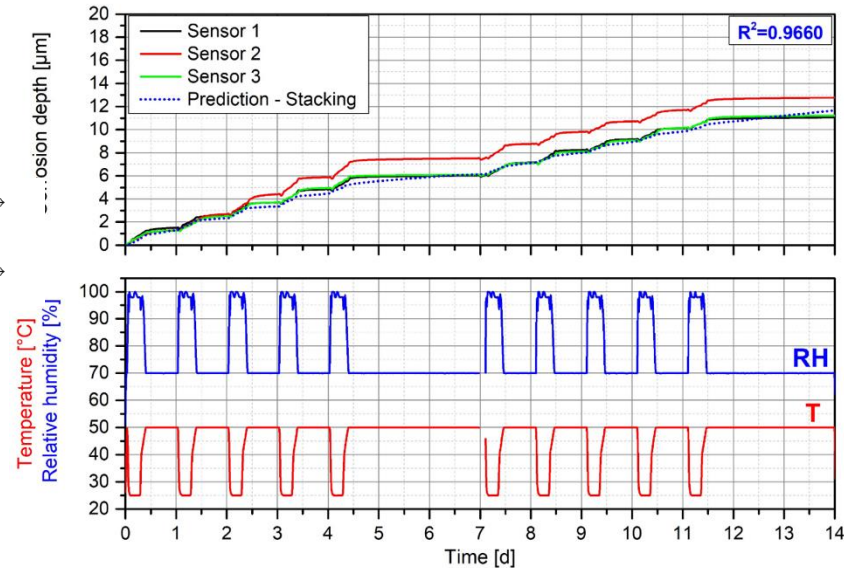
Prediction of Zn, Fe corrosion in accelerated corrosion test using ER sensors – Machine learning

- **15 training** corrosion tests (various NaCl wt%, RH, T ...)
- **1 validation** corrosion test **Not included in the training**
- About **100 sensors** used



Machine Learning (ML)

Zinc sensors and predictions

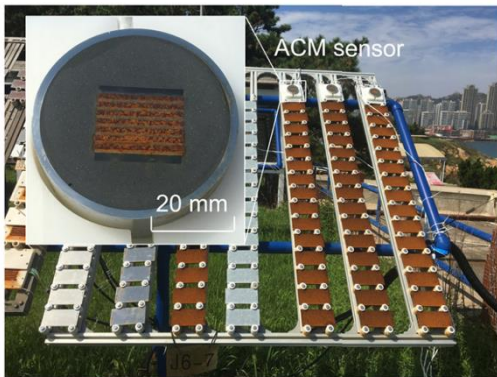


- Development of an **AI model for corrosion predictions based on accelerated corrosion tests using ER corrosion sensors**
- **Corrosion predictions** for steel and zinc are **in agreement with real sensor behaviors**
- Possible tool for the development of new accelerated corrosion tests

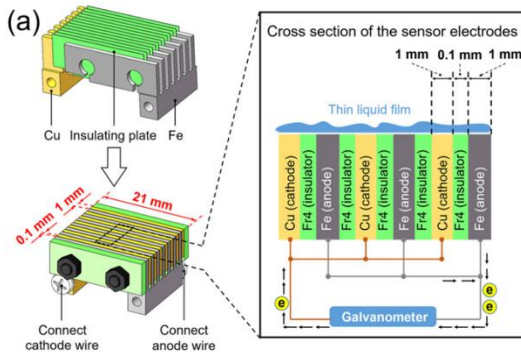
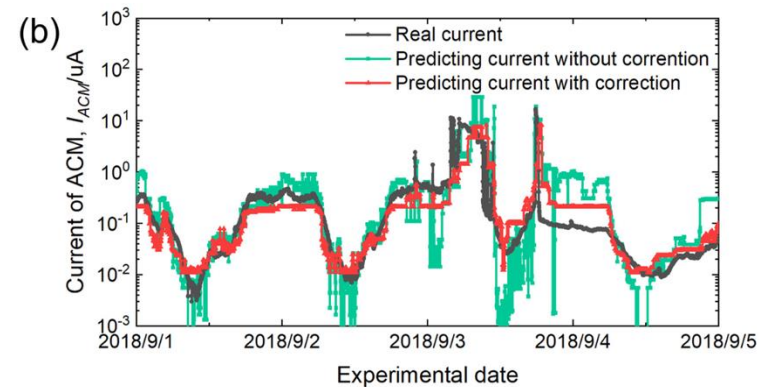
J. Becker et al., EUROCORR 2023, Brussels.

Corrosion modeling and prediction

Prediction of atmospheric galvanic corrosion using an Fe/Cu ACM sensors – Machine learning



Machine Learning (ML)



- Prediction of the atmospheric galvanic corrosion using an Fe/Cu ACM
- Short-term corrosion predictions using a Random Forest approach
- Ineffective during dry phases

Z. Pei et al., Corrosion Science. 170 (2020) 108697

Conclusions - Predictive maintenance

- New monitoring systems are currently developed or in development phase. ➔ This will allow to monitor the corrosion of aluminium alloys in service conditions
- Models based for instance on machine learning and FEM calculations will enhance our knowledge in corrosion mechanisms and allow long term prediction.

Acknowledgements

AIRBUS



LIEBHERR

