Methodology of studying corrosion inhibitor efficiency and synergy for coated galvanized steel

Mats Meeusen

11.12.2018

M2i conference

materials innovation institute

Nederlandse Organisatie voor Wetenschappelijk Onderzoek

Defensie erkent aansprakelijkheid chroom-6-ziekten; verzweeg gezondheidsrisico's voor medewerkers

De Volkskrant
04-06-2018

Staatssecretaris Barbara Visser van Defensie gaat diep door het stof voor oud-medewerkers die ziek zijn geworden door het werken met chroom-6. Zij biedt excuses aan omdat Defensie decennialang heeft verzuimd aan personeel te vertellen dat zij zijn blootgesteld aan de schadelijke verfstof. Defensie erkent aansprakelijkheid voor diverse ziekteklachten en zal een schadevergoeding aan slachtoffers betalen.

AD
28-07-2018

'Defensie negeerde strafbare feiten werken met chroom-6'

Het ministerie van Defensie wist niet alleen al veel langer van de schadelijke effecten van het werken met kankerverwekkende verf door zijn medewerkers, maar het stak ook bewust de kop in het zand bij oproepen iets aan de problemen te doen. Zo negeerde het onder meer een proces-verbaal van de Arbeidsinspectie en een 'SPOED SPOED SPOED'-mail van medewerkers in de jaren negentig.

'Defensie maakt gebruik van dubbel zoveel giftige chroom-6-verf'

NRC
21-12-2018

Het gaat om nieuwe verf die gebruikt wordt bij het onderhoud van vliegtuigen en helikopters. Dat blijkt uit interne stukken ingezien door Nieuwsuur.

Chroom-6-verf zal nog even gebruikt blijven worden

Trouw
22-10-2018

Alternatieven voor een verf met daarin de kankerverwekkende stof chroom-6 zijn niet zomaar toepasbaar, zegt hoogleraar corrosietechnologie Arjan Mol. Volgens hem moet nog veel kennis worden opgedaan.

NRC
16-11-2018

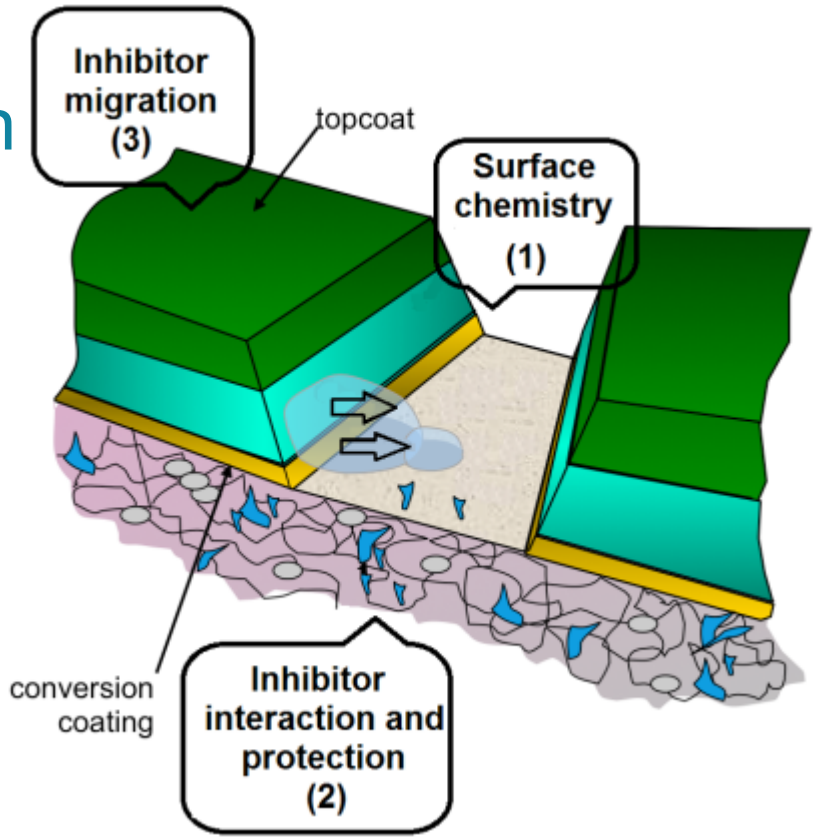
Chroom-6 is nog steeds de beste beschermer tegen roest

Materialen

Het kankerverwekkende chroom-6 beschermt vliegtuigen en voertuigen tegen corrosie. Maar er wordt hard gezocht naar een alternatief.

Towards chromate-free inhibitor technology

Inhibitor – coating interaction



Inhibitor – metal interaction

→ Understanding inhibitor performan

S.J. García, J.M.C. Mol, T.H. Muster, A.E. Hughes, J. Mardel, T. Miller, T. Markley, H. Terryn, J.H.W. de Wit, Chapter 9 in Self-Healing Properties of New Surface Treatments, EFC-Maney Publishing vol. 58, 2011, pp. 148–183, Ed. Lorenzo Fedrizzi; ISBN: 978 1 906540 36 4.

Approach

Corrosion inhibitor screening → Possible Synergism → In-depth analysis

1- Surface analysis
- High-throughput corrosion testing
- SEM-EDS
- GDOES

2- Basic electrochemistry
- Potentiodynamic polarization
- Combined OCP + LPR

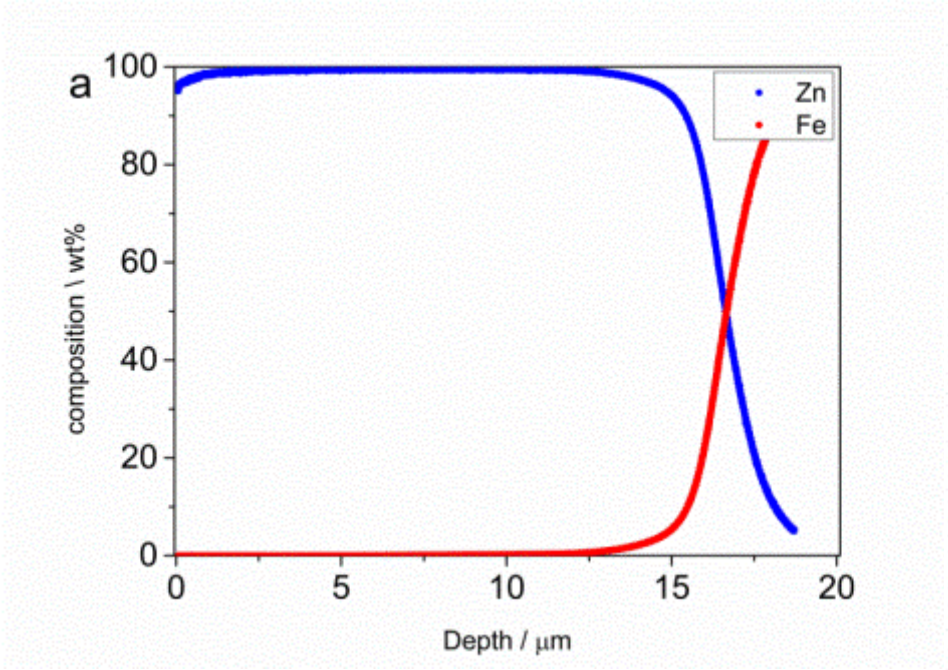
3- Advanced electrochemistry
- EIS
- ORP-EIS
- NM

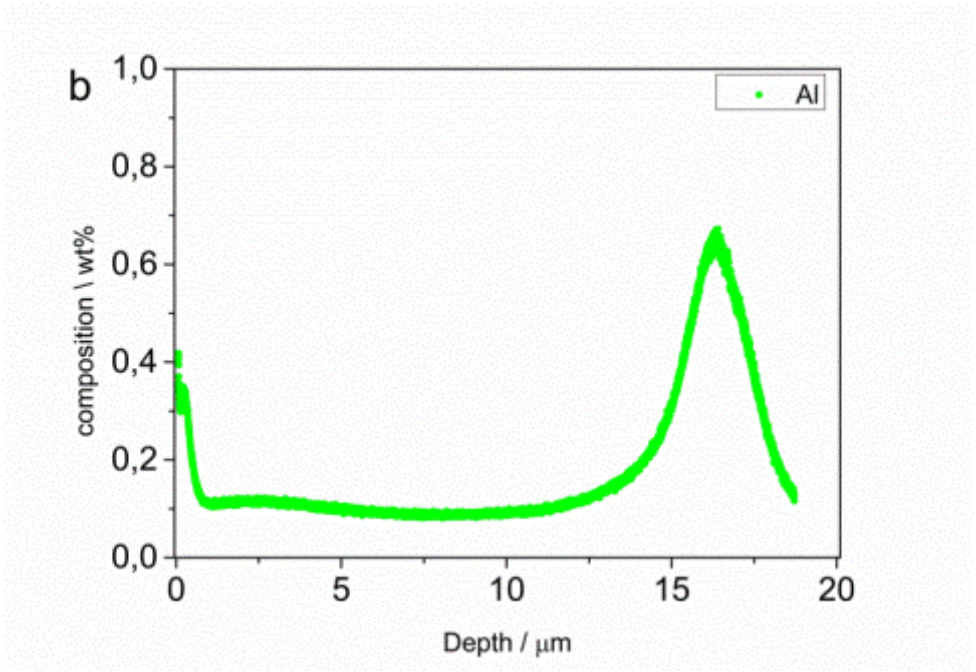
Fundamental knowledge
- working mechanism & dosage

Detailed knowledge
- corrosion protective properties
- Corrosion inhibitor mechanism

Corrosion inhibitor screening

- Glow discharge optical emission spectroscopy (GDOES)
  - HDG substrate characterization

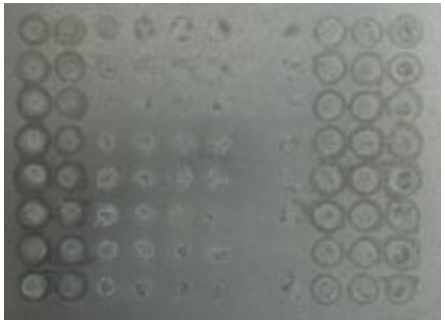


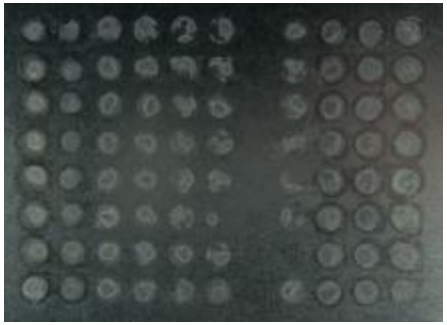


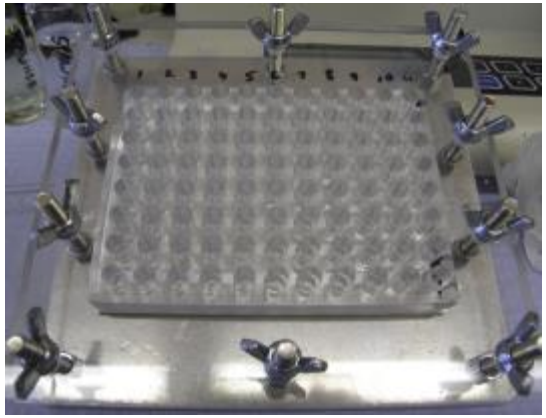
Corrosion inhibitor screening

1. Surface analysis

- High-throughput corrosion testing
  - Rapid screening of available inhibitors







	5 h	
Solution	Corrosion value	Std. dev.
0.5% NaCl	2	2.7
0.05% NaCl	5	2.3
0.005% NaCl	6	2.4
0.0005% NaCl	6	2.0
0.00005% NaCl	6	1.4
0.000005% NaCl	6	1.4
demineralized water	6	0.9
empty	5	0.1
inhibitor 2 (0.5 mM)	5	1.6
inhibitor 3 (0.5 mM)	5	1.6
inhibitor 6 (0.5 mM)	6	1.1

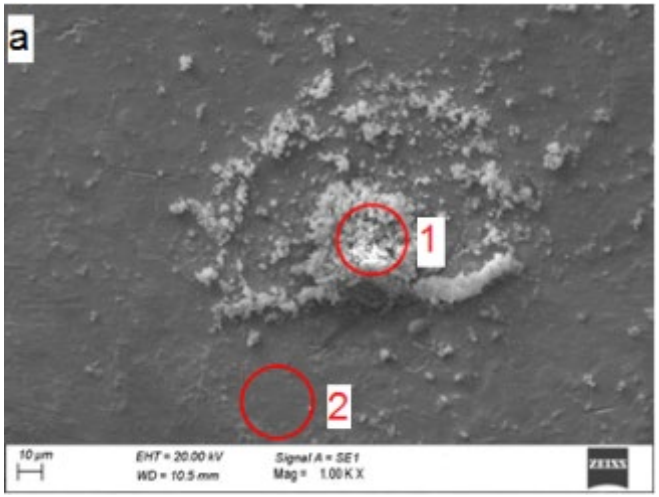
	24 h	
Solution	Corrosion value	Std dev.
0.1 M NaCl	4	0.8
0.05 M NaCl	4	0.1
demineralized water	9	1.5
empty	8	1.5
inhibitor 1 (0.5 mM)	6	1
inhibitor 2 (0.5 mM)	6	1.7
inhibitor 3 (0.5 mM)	7	1.6
inhibitor 4 (0.5 mM)	6	1.5
inhibitor 5 (0.1 mM)	4	0.9
inhibitor 6 (0.5 mM)	3	1.2
inhibitor 7 (0.02 mM)	3	0.2

Corrosion inhibitor screening

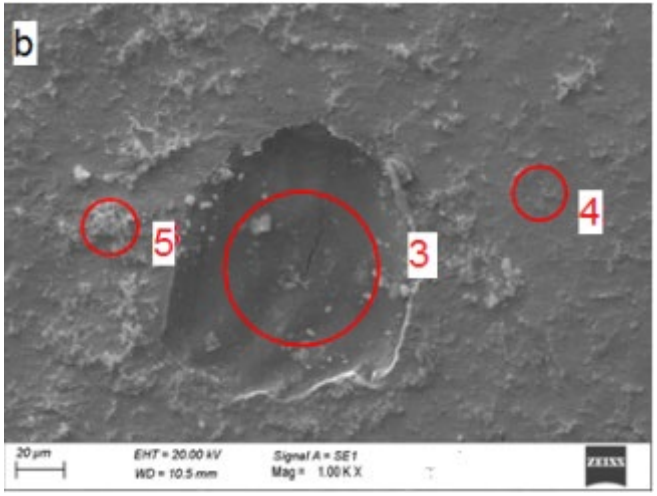
1. Surface analysis

SEM – EDS measurements

HDG 1.5h



HDG 1.5h



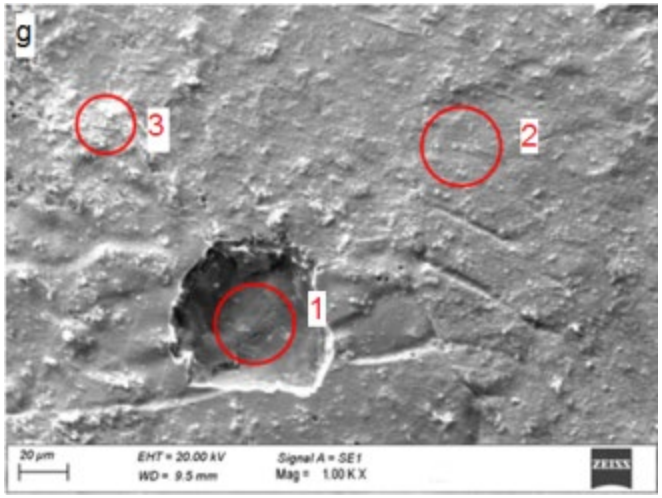
inhibitor	time	spot	Zn	Al	Fe	O	Cl
no	1.5 h	1	63.01			26.32	10.67
		2	93.20	1.26		5.54	
		3	63.89	5.16	1.66	23.99	5.30
		4	93.11	1.40	0.83	4.66	
		5	66.54	0.79		31.98	0.69

Corrosion inhibitor screening

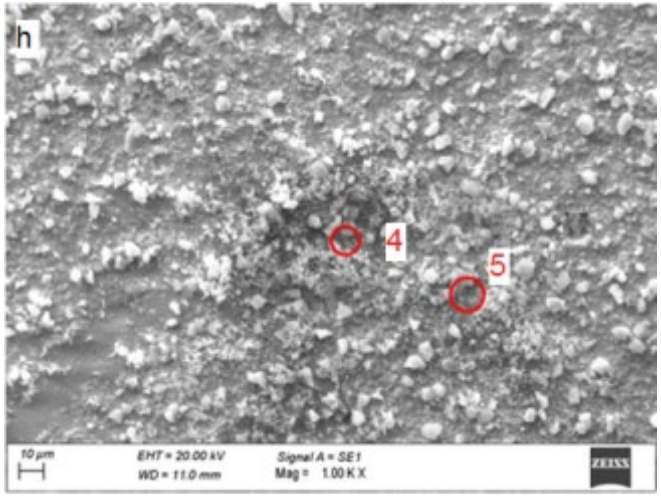
1. Surface analysis

SEM – EDS measurements

INH 3
1.5h



INH 3
24h



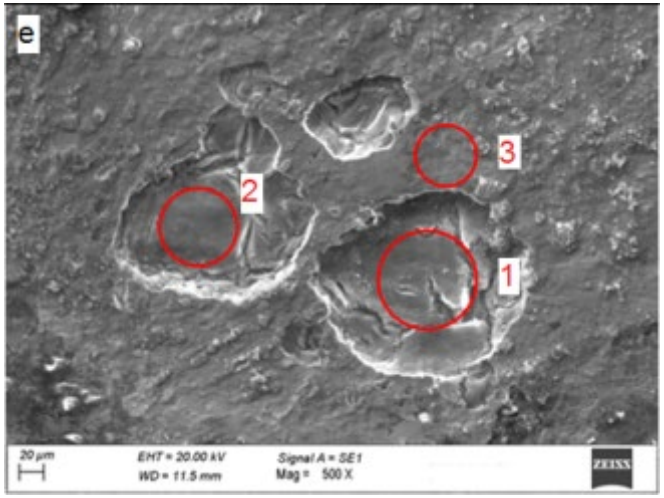
inhibitor	time	spot	Zn	Al	Fe	O	Cl	Si	C	Mg	Ca
3	1.5 h	1	70.06	4.94		21.31	2.67	1.02			
		2	92.63	1.71		5.17		0.49			
		3	86.49			11.99		1.52			
	24 h	4	22.19			56.12	0.68	21.01			
		5	20.49			52.48		26.56			0.47

Corrosion inhibitor screening

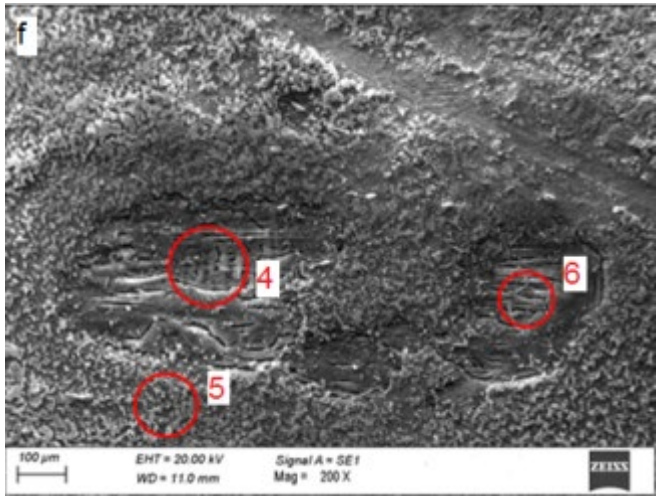
1. Surface analysis

SEM – EDS measurements

INH 6
1.5h



INH 6
24h



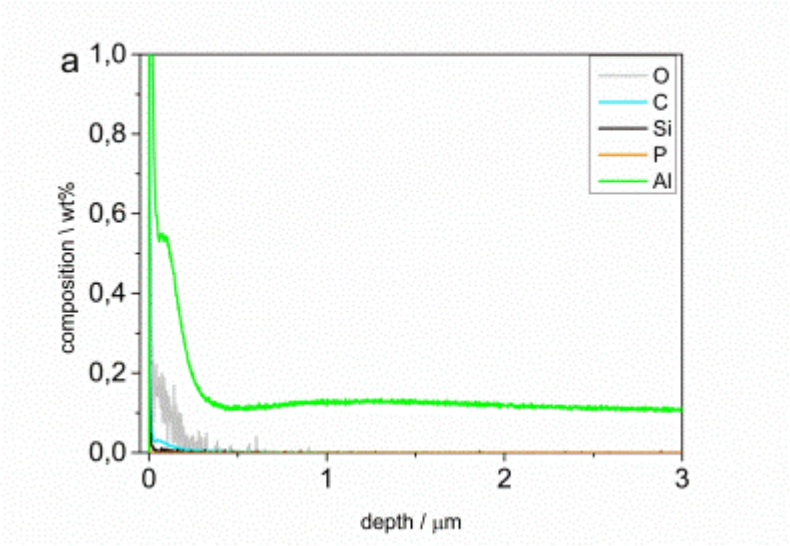
inhibitor	time	spot	Zn	Al	Fe	O	Cl	Si	C	Mg	Ca	P	S
6	1.5 h	1	38.24	7.29	37.57	10.76	5.17	0.97					
		2	64.59	4.03	1.97	23.6	5.04	0.77					
		3	77.57	0.67		18.83		2.93					
	24 h	4	44.12	4.30	10.86	32.32	6.59	0.98			0.80		
		5	65.88	0.39		30.24	0.59	1.22			0.90	0.78	
		6	50.10	3.55	5.41	30.66	8.18	1.03			0.37	0.69	

Corrosion inhibitor screening

1. Surface analysis

GDOES measurements

HDG
1.5h

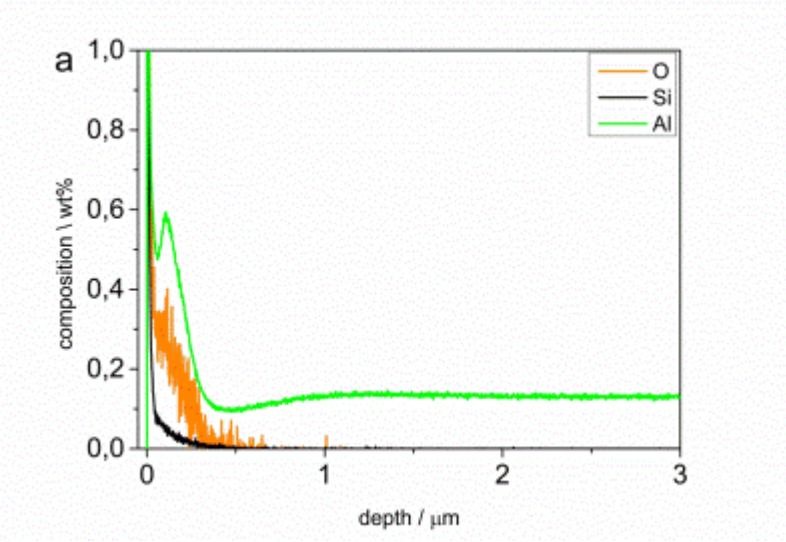


Corrosion inhibitor screening

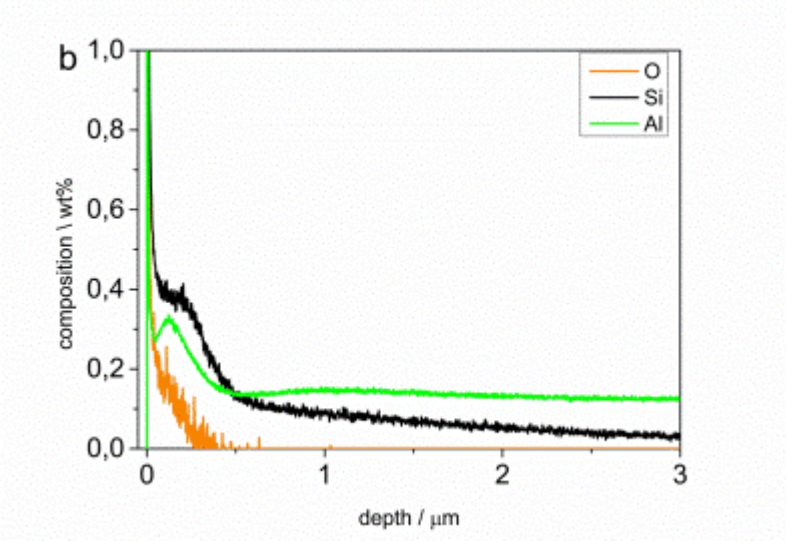
1. Surface analysis

GDOES measurements

INH 3
1.5h



INH 3
24h

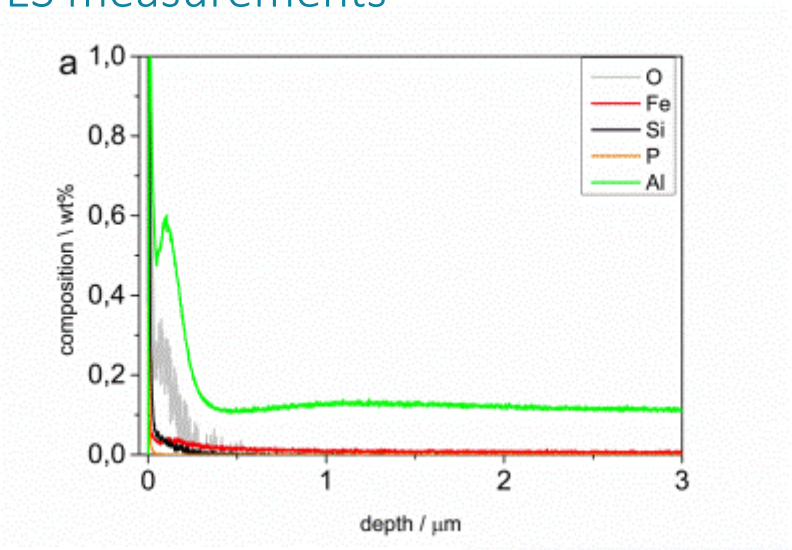


Corrosion inhibitor screening

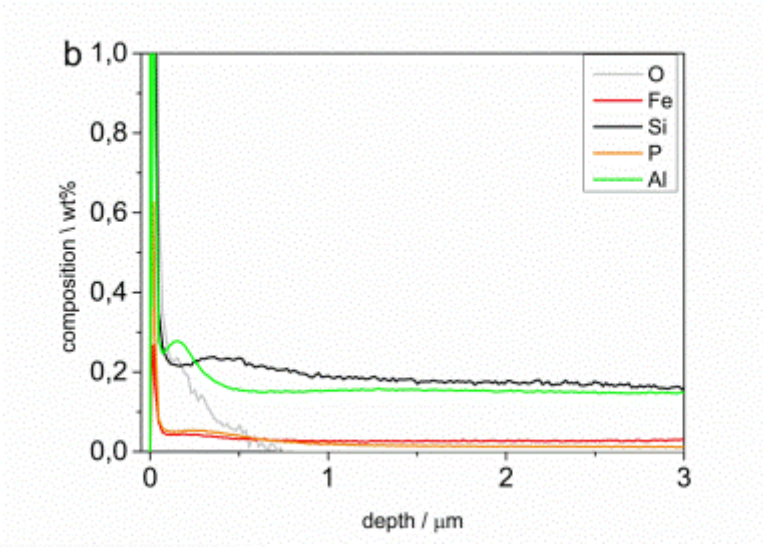
1. Surface analysis

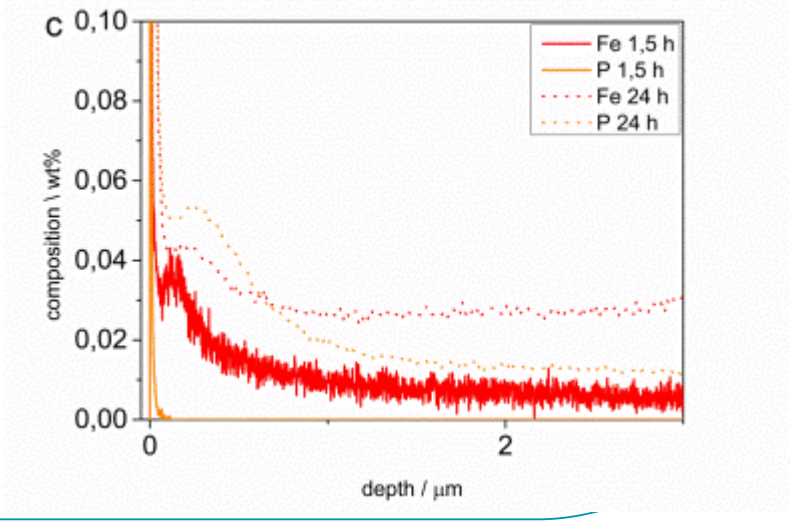
GDOES measurements

INH 6
1.5h



INH 6
24h

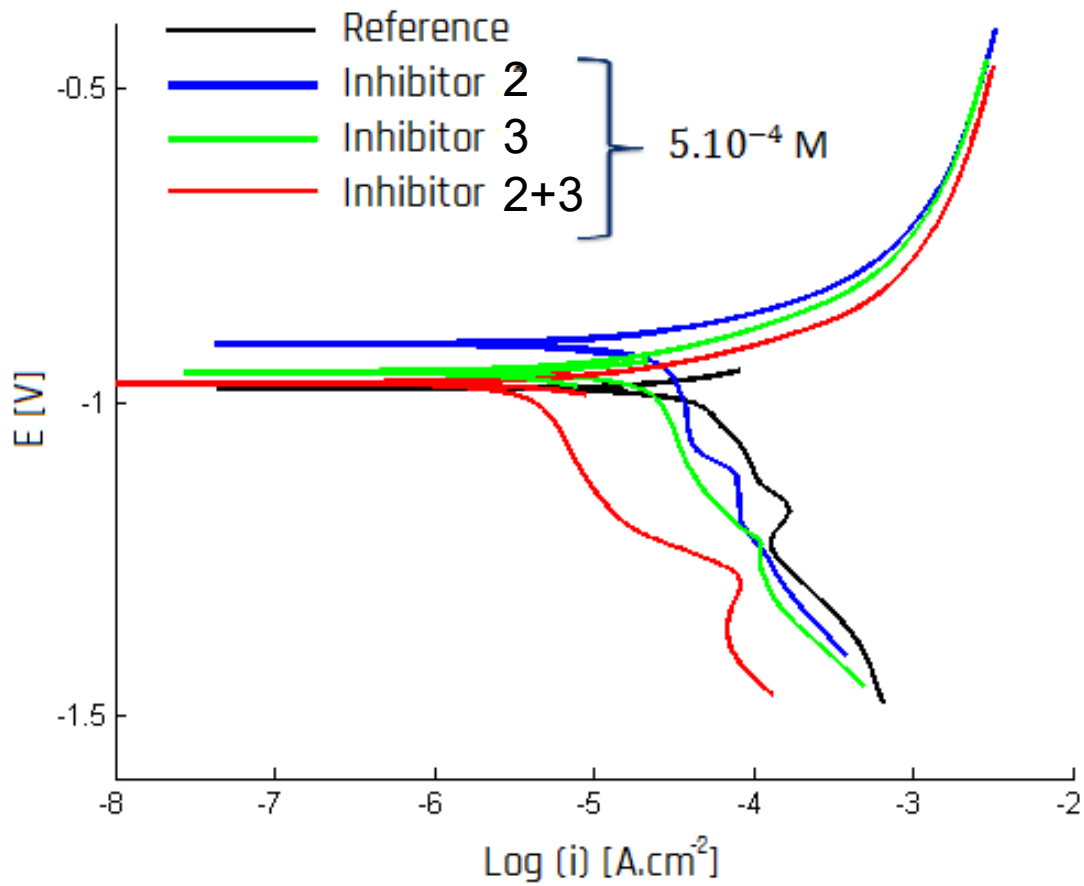




Corrosion inhibitor screening

2. Basic electrochemistry

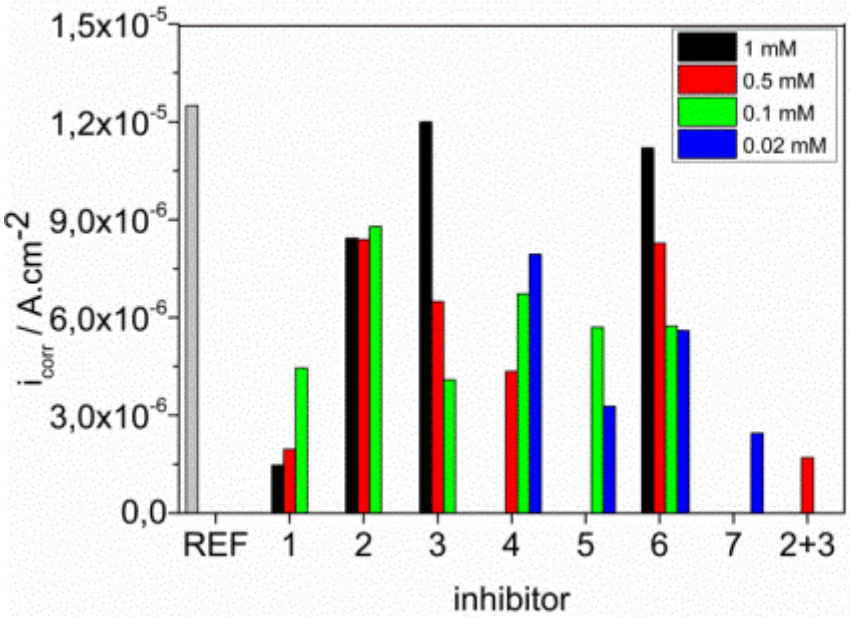
- Potentiodynamic polarization
  - Working principle (Anodic/Cathodic/Mixed)
  - Inhibitor dosage

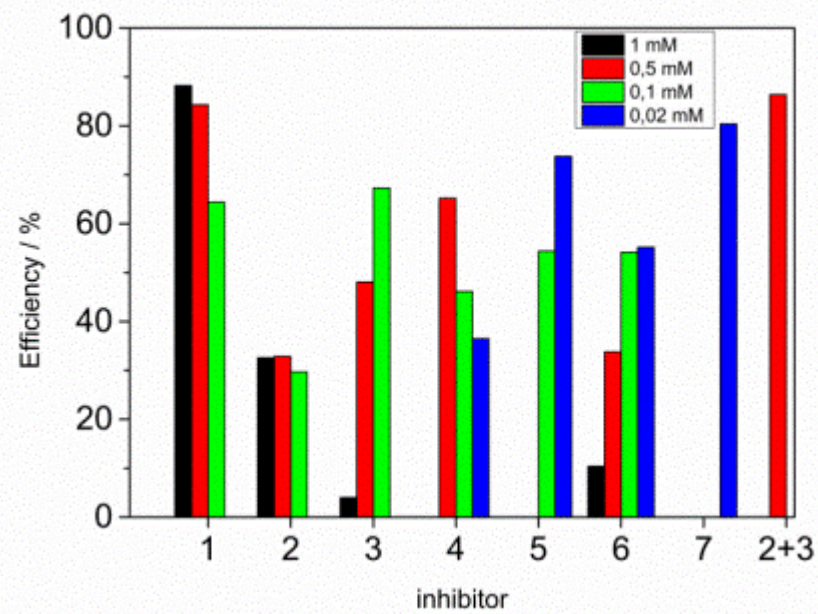


Corrosion inhibitor screening

2. Basic electrochemistry

- Potentiodynamic polarization

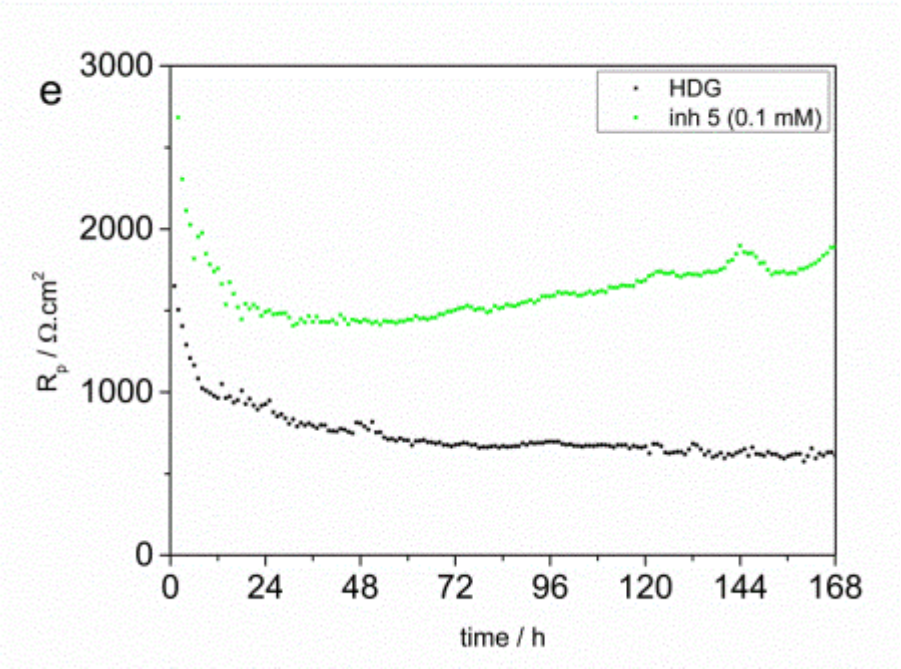


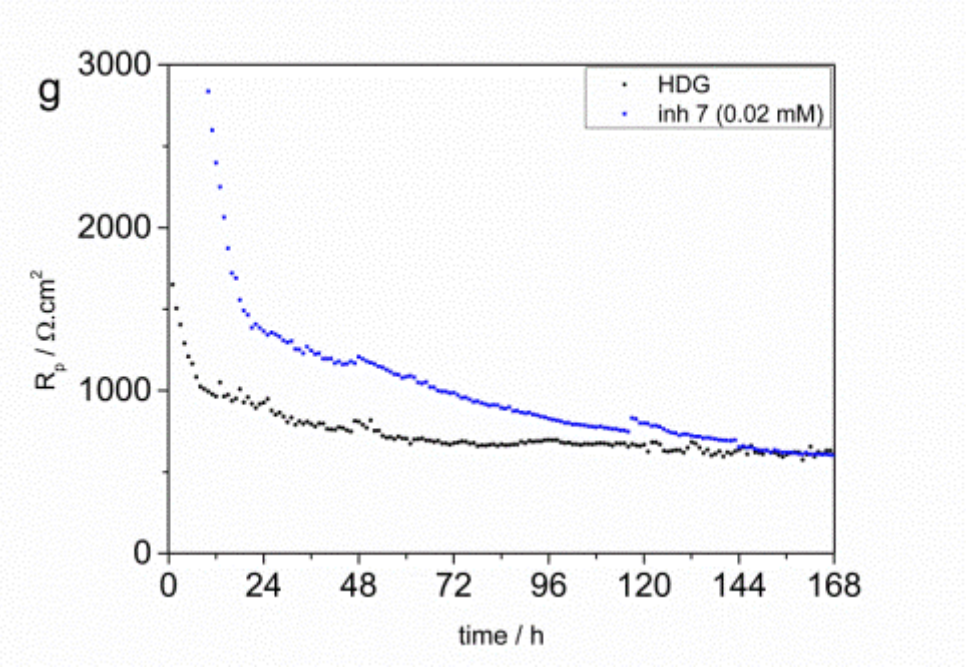


$$\eta\,(\%) = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}}\ x\ 100$$

Corrosion inhibitor screening
2. Basic electrochemistry

- Linear Polarization Resistance Measurements (LPR)
  - Continuous OCP measurment (1 week)
  - Superimposed LPR measurment (every hour, ± 5 mV vs OCP)
  - Calculation of polarization resistance Rp $Rp = \frac{\Delta E}{\Delta I}$



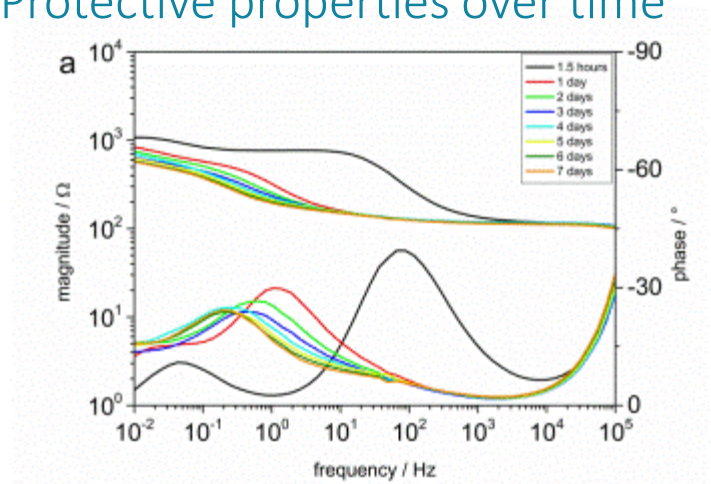


Corrosion inhibitor screening

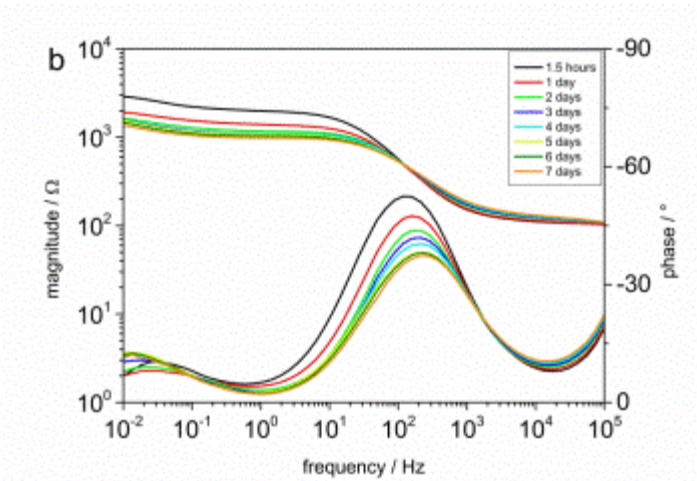
3. Advanced electrochemistry

- Electrochemical impedance spectroscopy (EIS)
  - Protective properties over time

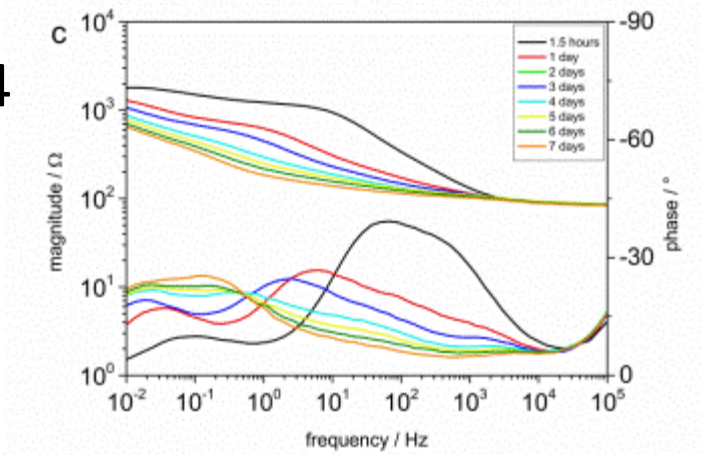
HDG



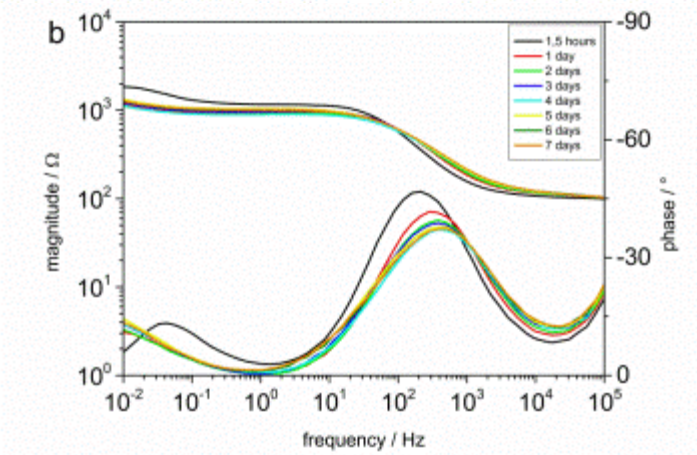
INH 1



INH 4



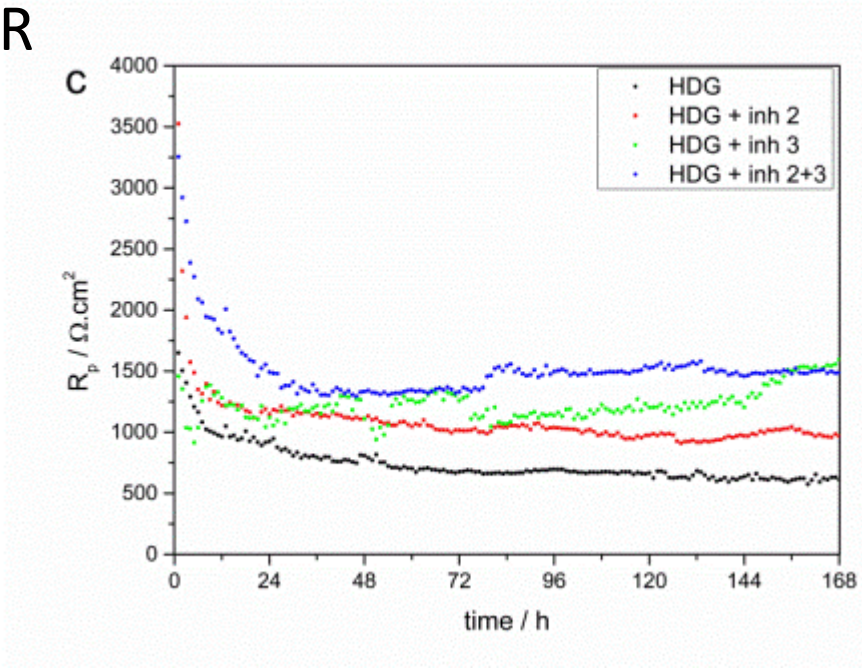
INH 2



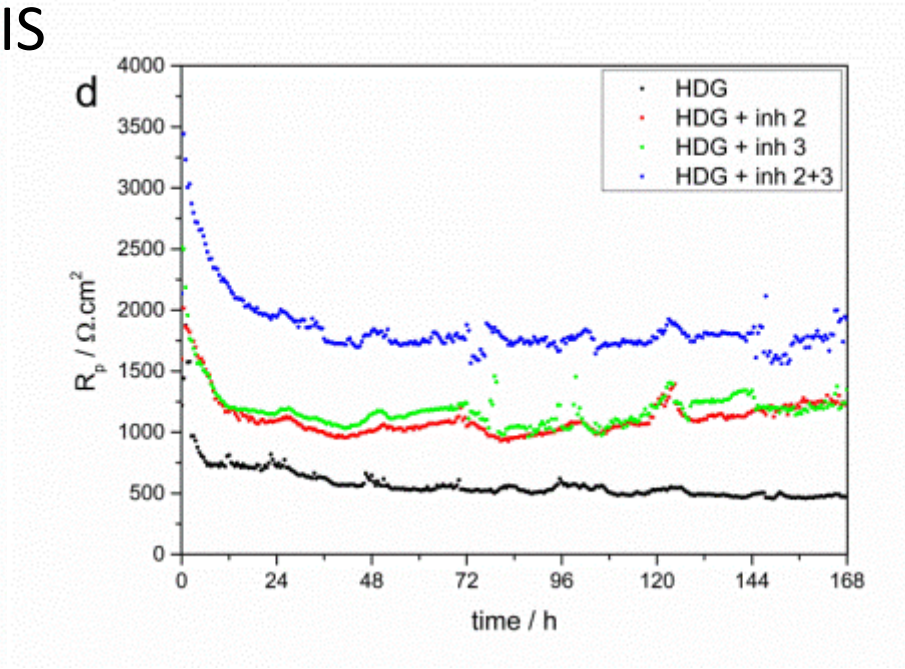
Corrosion inhibitor screening
3. Advanced electrochemistry

- Comparison Polarization Resistance (R_p) from LPR & EIS

LPR



EIS



Corrosion inhibitor screening
3. Advanced electrochemistry

- **Application of ORP-EIS vs EIS**

- Necessities for a reliable EIS measurement:
  - ❖ Causality
  - ❖ Linearity
  - ❖ Stationarity

- Solution: apply a small perturbation Va in the stationary regime of the process

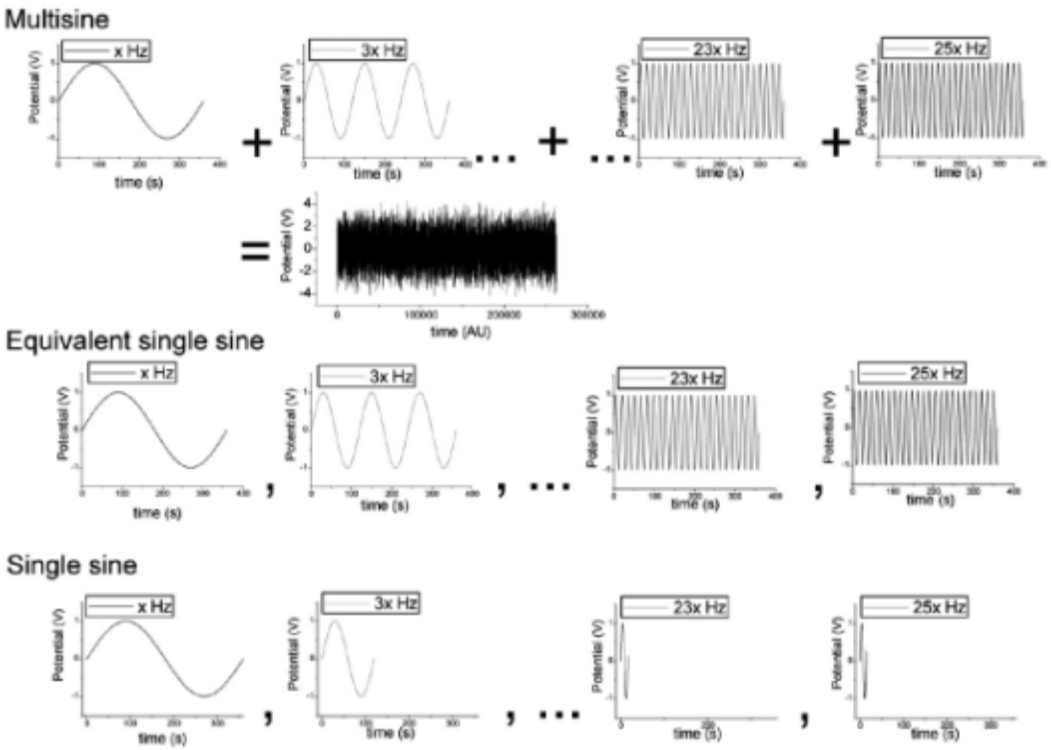
- Problems:
  - ❖ poor S/N ratio
  - ❖ initial, rapidly evolving stages of processes are not described

→ Odd-Random-Phase EIS

Van Ingelgem, Y., Tourwé, E., Blajiev, O., Pintelon, R., & Hubin, A. *Electroanalysis 21* (2009) 730.
Breugelmans, T, Van Ingelgem, Y, A. Hubbin. Electrochemistry communications 12 (2010) 5.

Corrosion inhibitor screening

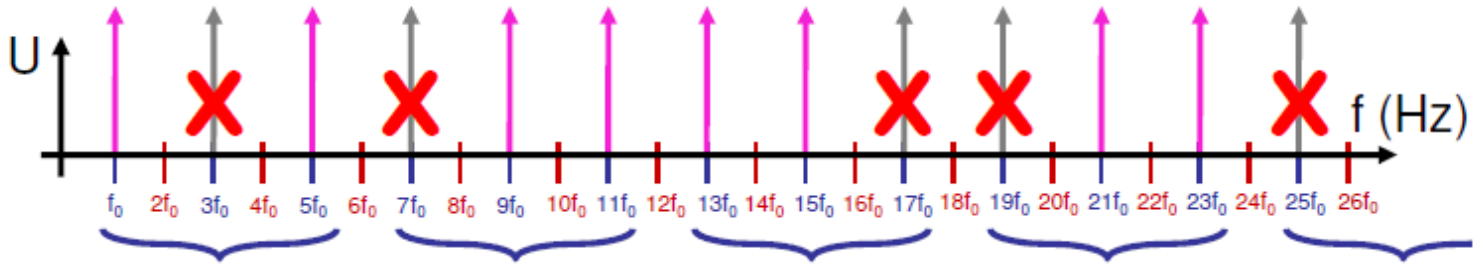
3. Advanced electrochemistry



- Advantages:
  - High frequencies are excited many times more
  - Measurement time decreases

Van Ingelgem, Y., Tourwé, E., Blajiev, O., Pintelon, R., & Hubin, A. *Electroanalysis 21* (2009) 730.
Breugelmans, T, Van Ingelgem, Y, A. Hubbin. Electrochemistry communications 12 (2010) 5.

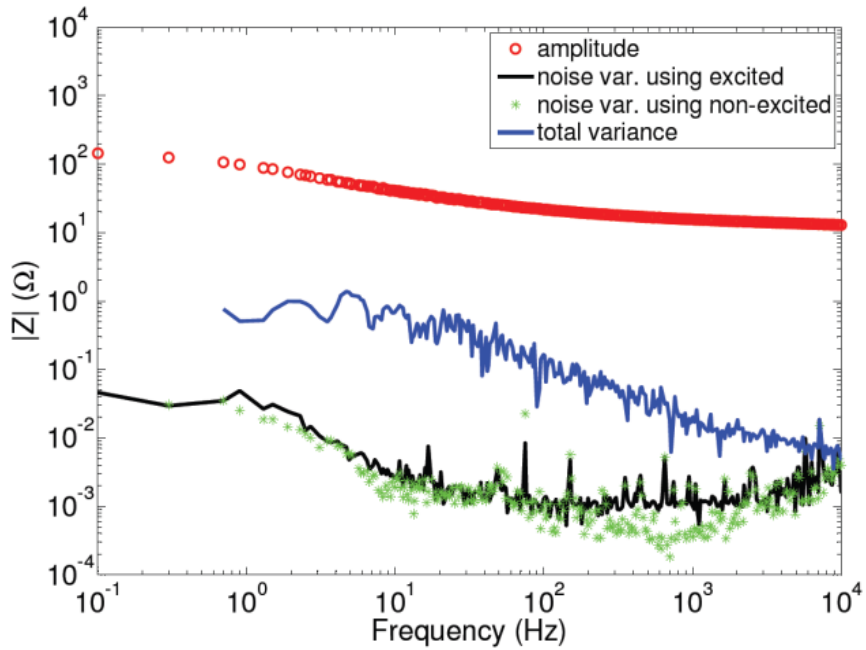
Corrosion inhibitor screening
3. Advanced electrochemistry



- Advantages:
  - Data analysis:
    - ❖ 5 periods measured
    - ❖ Last 4 used to calculate the standard deviation at the excited and non-excited frequencies
  - Extra information
    - ❖ Noise
    - ❖ Non-linearities
    - ❖ Non-stationarities

Van Ingelgem, Y., Tourwé, E., Blajiev, O., Pintelon, R., & Hubin, A. *Electroanalysis 21* (2009) 730.
Breugelmans, T, Van Ingelgem, Y, A. Hubbin. Electrochemistry communications 12 (2010) 5.

Corrosion inhibitor screening
3. Advanced electrochemistry



- impedance value
- noise level
- non-stationary behaviour
- non-linear behaviour (total variance)

Linear : σ_{tot} overlaps $\sigma_Z(\omega_{ne})$

Stationary : $\sigma_Z(\omega_e)$ overlaps $\sigma_Z(\omega_{ne})$

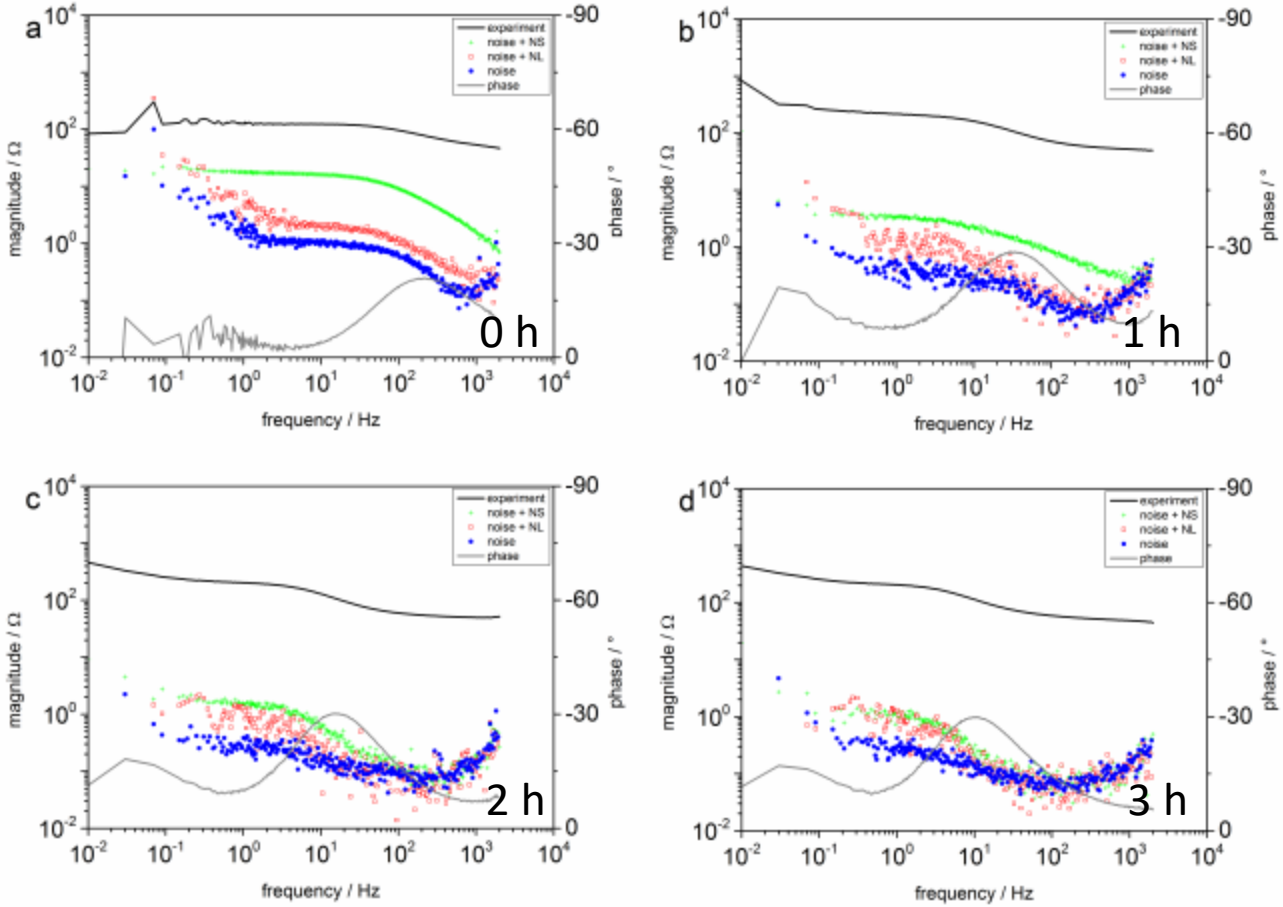
- Advantages:
  - Fitting ORP-EIS data to EEC:
    - ❖ Weight with std noise/non-linearities/non-stationarities
    - ❖ Evaluation residual vs noise curve

Corrosion inhibitor screening

3. Advanced electrochemistry

Data-quality (qualitatively)

HDG

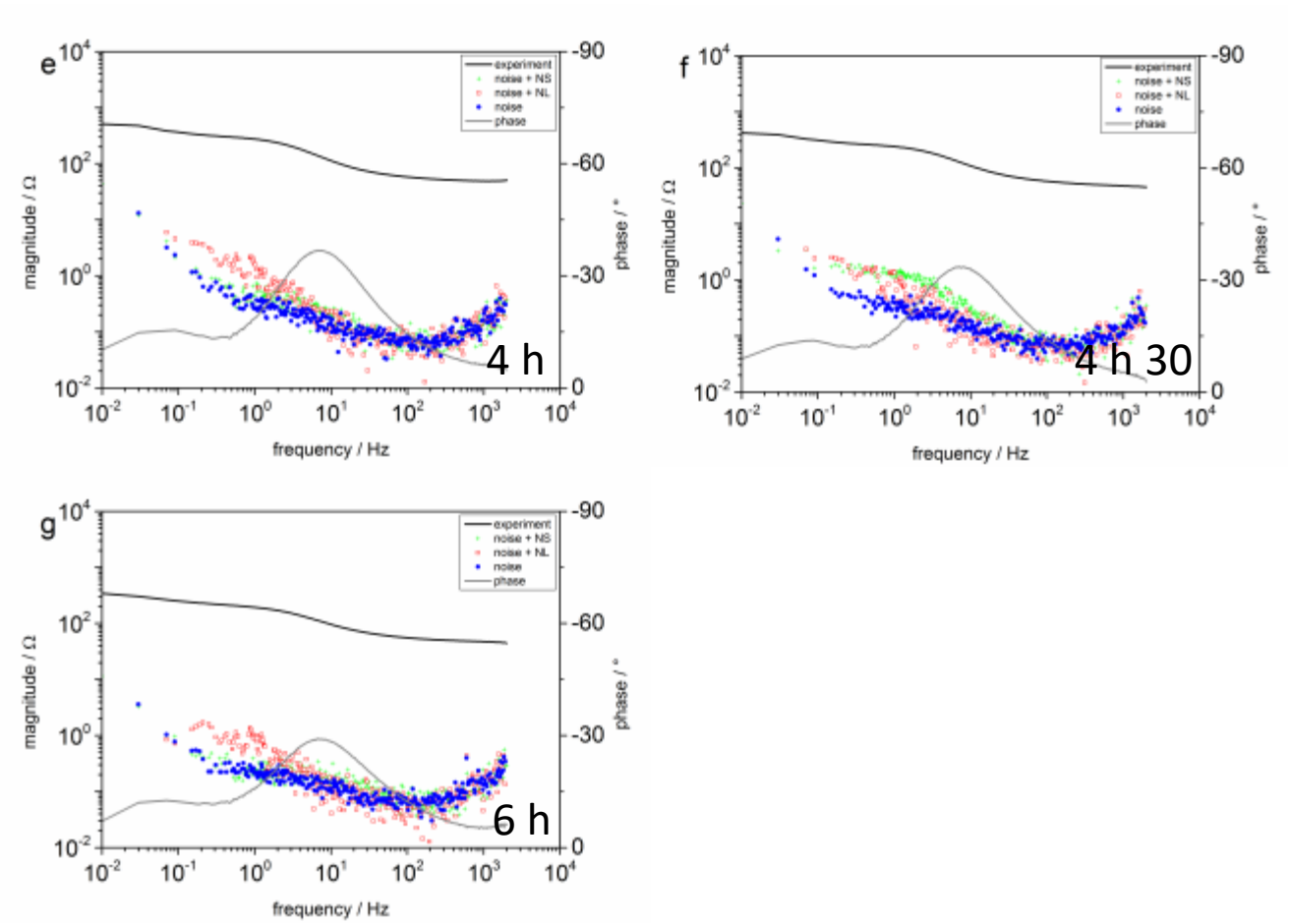


Corrosion inhibitor screening

3. Advanced electrochemistry

Data-quality (qualitatively)

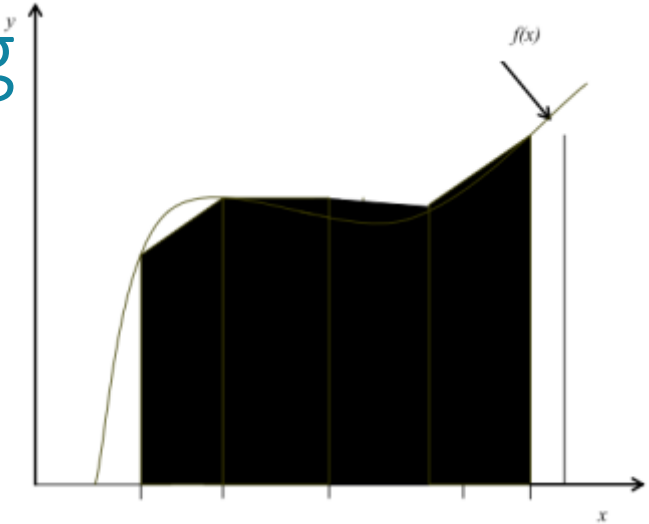
HDG



Corrosion inhibitor screening

3. Advanced electrochemistry

Data-quality (quantitatively)



Approach: numerical integration through interpolation

≡ Calculate individual contributions (per decade)

N, NL and NS

≡ Correct for |Z|

≡ Plot abs(N/Z),

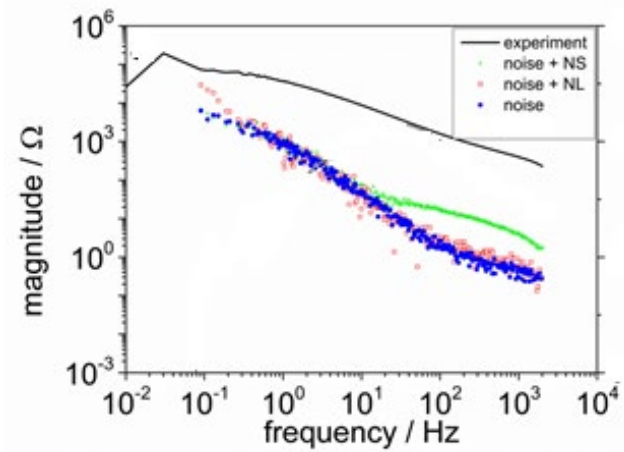
abs(NL/Z),

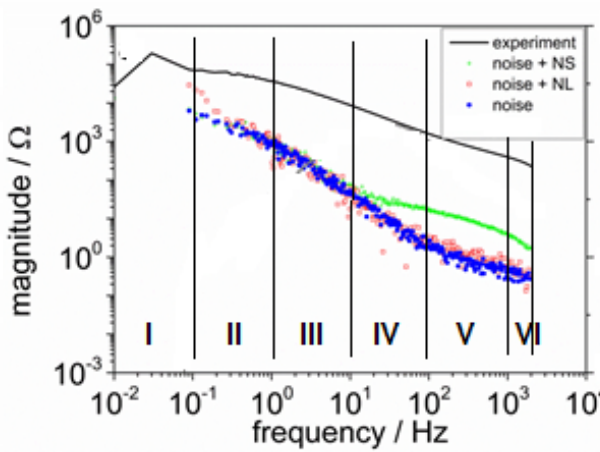
abs(NS/Z)

❖ measured every 15'

❖ f(time) for the first 12 hours

❖ expressed as difference in order of magnitude to |Z|





N

NL

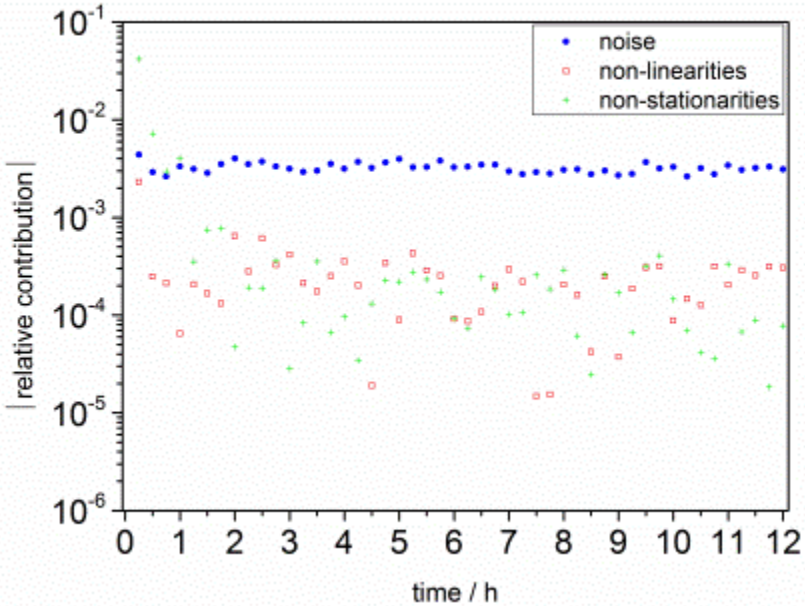
NS

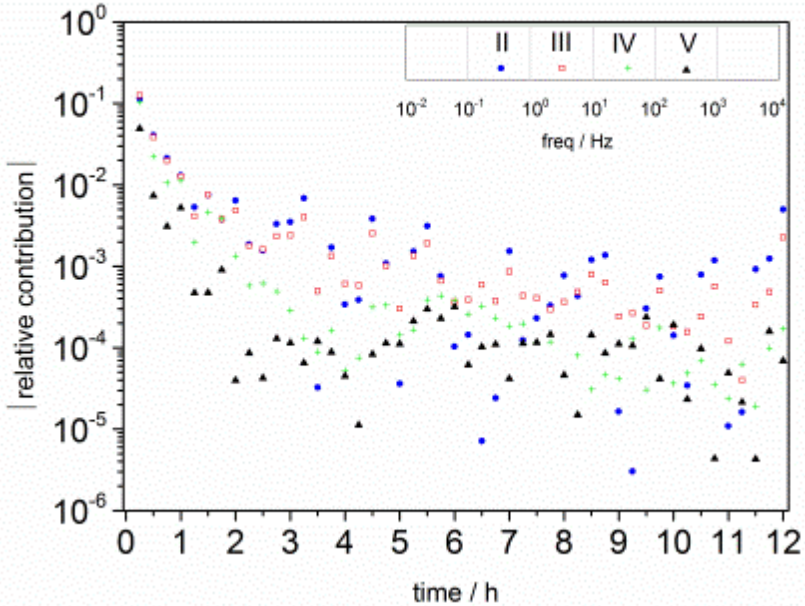
NS

Corrosion inhibitor screening
3. Advanced electrochemistry

Data-quality (qualitatively)

HDG





2 important observations

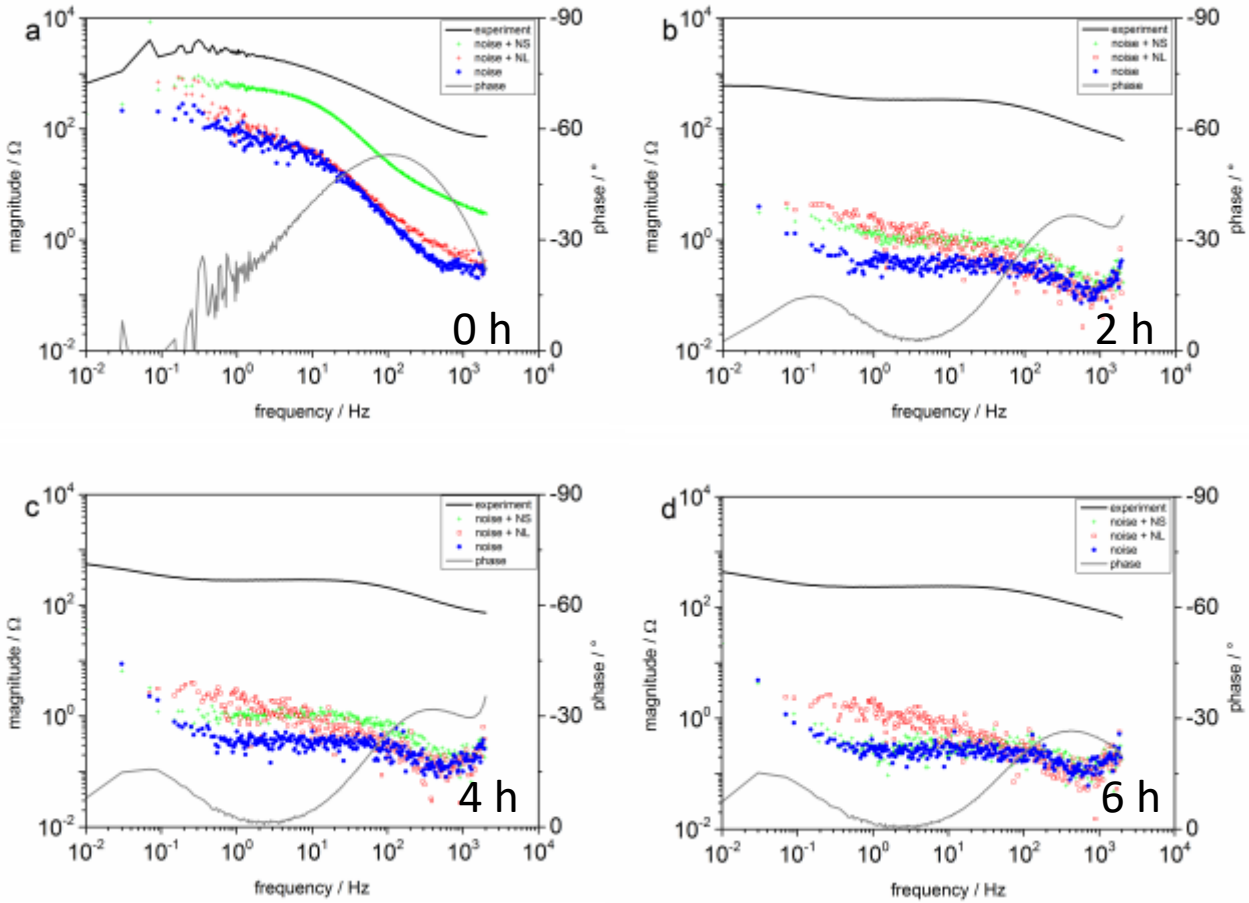
- Time when contribution becomes stable
- Magnitude of the respective contributions

Corrosion inhibitor screening

3. Advanced electrochemistry

Data-quality (qualitatively)

INH 3

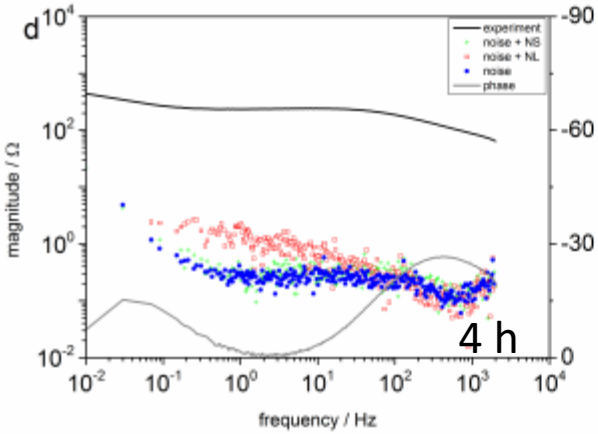


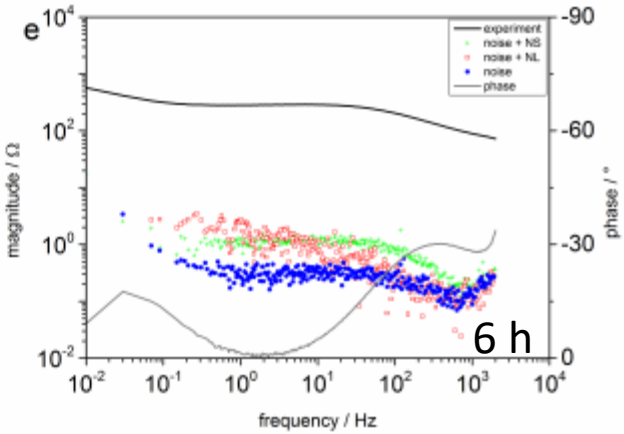
Corrosion inhibitor screening

3. Advanced electrochemistry

Data-quality (qualitatively)

INH 3





NL (lower f)
No NS

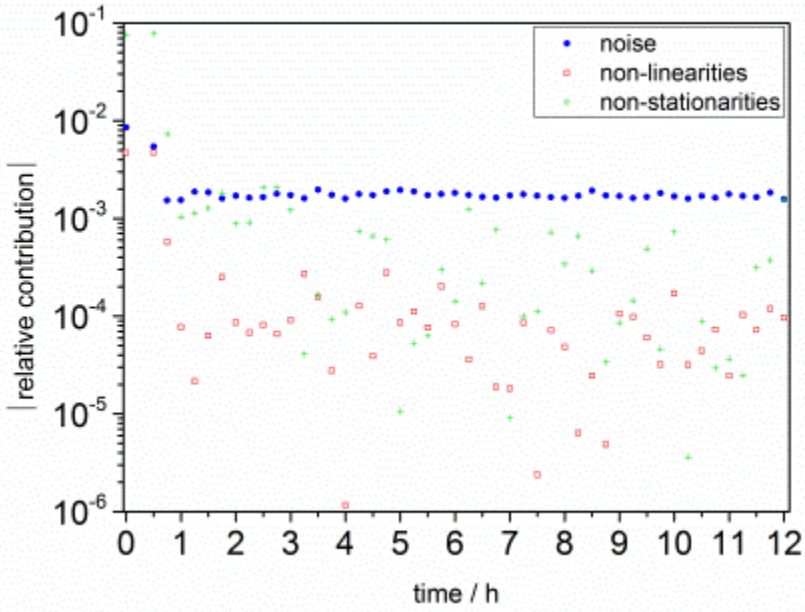
NL (lower f)
NS whole f-range

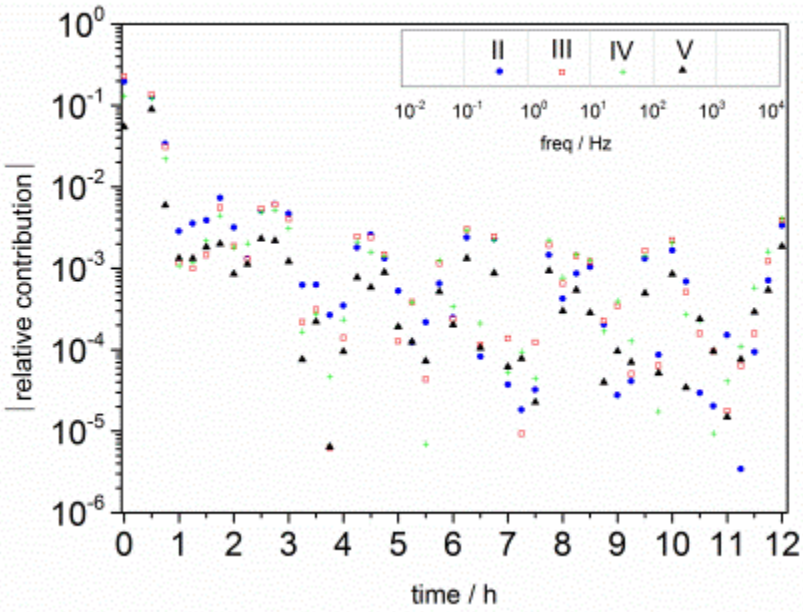
Corrosion inhibitor screening

3. Advanced electrochemistry

Data-quality (qualitatively)

INH 3

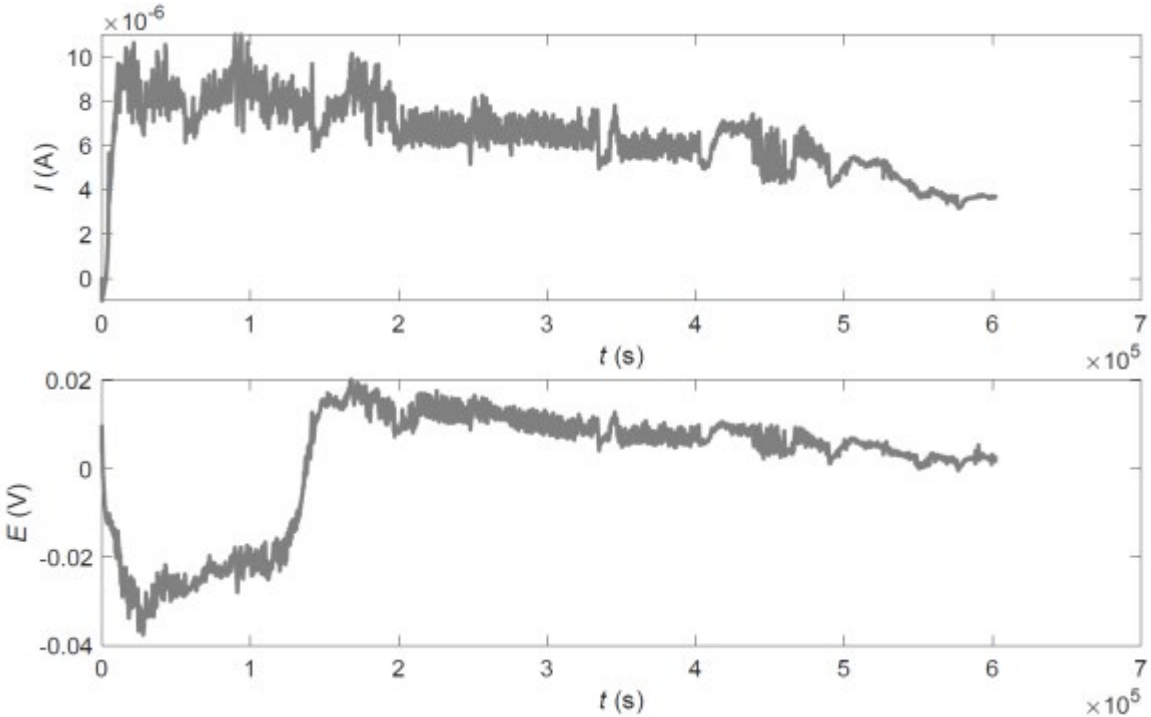


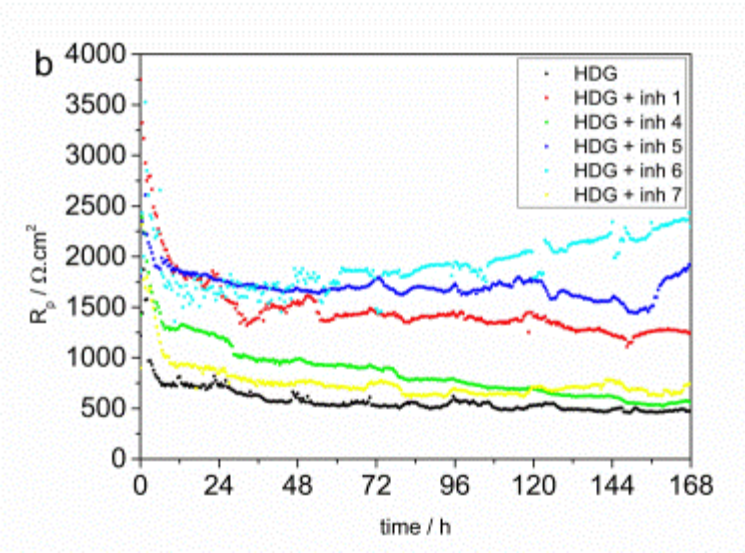


Corrosion inhibitor screening

3. Advanced electrochemistry

- NM on inhibitors





Link with earlier EC observations (EIS)

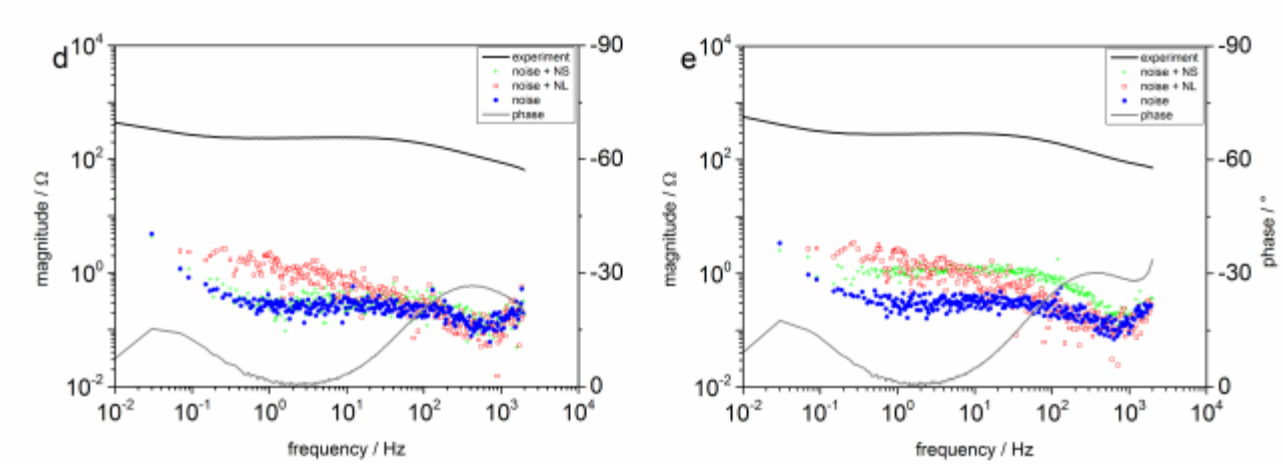
Conclusions

- Corrosion inhibitor screening
  - High-throughput corrosion testing
  - Polarization measurements: mechanistical information
  - LPR measurements: inhibitor and stability of inhibitor-metal interaction over time (non invasive technique)
  - EIS: protective performance over time + working mechanism

- Corrosion inhibitor in-depth analysis
  - ORP-EIS qualitatively: info NL and NS present (data quality)
  - ORP-EIS quantitatively: quantitative NL and NS
    - Starting point weighting for fitting

Ongoing & Future work

- NL study



Effect of varying excitation signal amplitude

Thank you

materials
innovation
institute

Nederlandse Organisatie
voor Wetenschappelijk Onderzoek

Commercial inhibitors

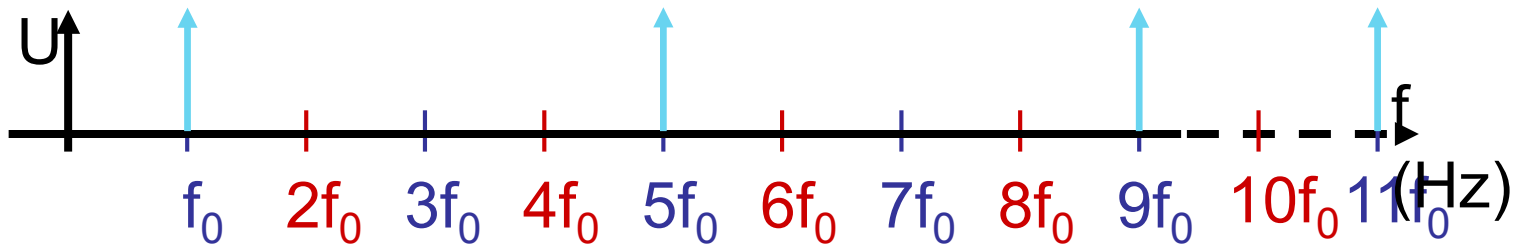
N	Name	Composition
1	Hybricor 206	SiO_2 – CaO – organinc content
2	Novinox ACE 110	SiO_2 amorph
3	Novinox XCA02	SiO_2 - Ca
4	Novinox PAS	Sr/Al polyphosphate
5	Halox SW-111	Sr phosphosillicate
6	Heucophos capp	SiO_2 – CaO – P_2O_5 – Al_2O_3
7	Heubach	$Zn_3(PO_4)_2$

SILICATES

PHOSPHATES

SILICATES + PHOSPHATES

Application of ORP-EIS vs EIS



1. Noise level: standard deviation on <u>non-excited</u> frequencies
2. Non-stationarities: standard deviation on <u>excited</u> frequencies
   difference std excited freq ↔ std non-excited frequencies
3. Non-linearities:
   - even non-linearities: standard deviation on <u>non-excited</u> even harmonics
   - odd non-linearities: by <u>omitting</u> 1 of 3 odd frequencies

Equivalent capacitance

- $C = R^{\frac{1-n}{n}} C^{\frac{1}{n}}$ Hirschorn
- Normal time constant distributions