



MIC: why is biology important and how to better understand and detect the underlying biological and electrochemical processes?

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TNO | Knowledge for business



Revised title:
Microbial corrosion: major gaps in understanding and the TNO approach, including results obtained so far

Lots to cover in 15 minutes...

1. TNO: who are we?
2. MIC: studied for decades but... major gaps in knowledge
3. TNO approach (starting with ENM)



MIC damage: heat exchanger pipe (Al) (van Pelt, 2006)



MIC damage: uncoated (left) and coated (right) ballast tanks (TNO survey, 2006)



The five core areas of TNO

Dutch contract research company, 5000 people
Bridging the gap between academic and industrial research



**TNO Quality of
Life**



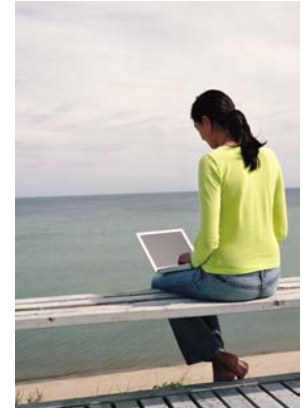
**TNO Defence,
Security and
Safety**



**TNO Science
and Industry**



**TNO Built
Environment
and
Geosciences**



**TNO Informa-
tion and
Communication
Technology**

TNO offices in the Netherlands



Den Helder (Corrosion and Fouling since 1960)

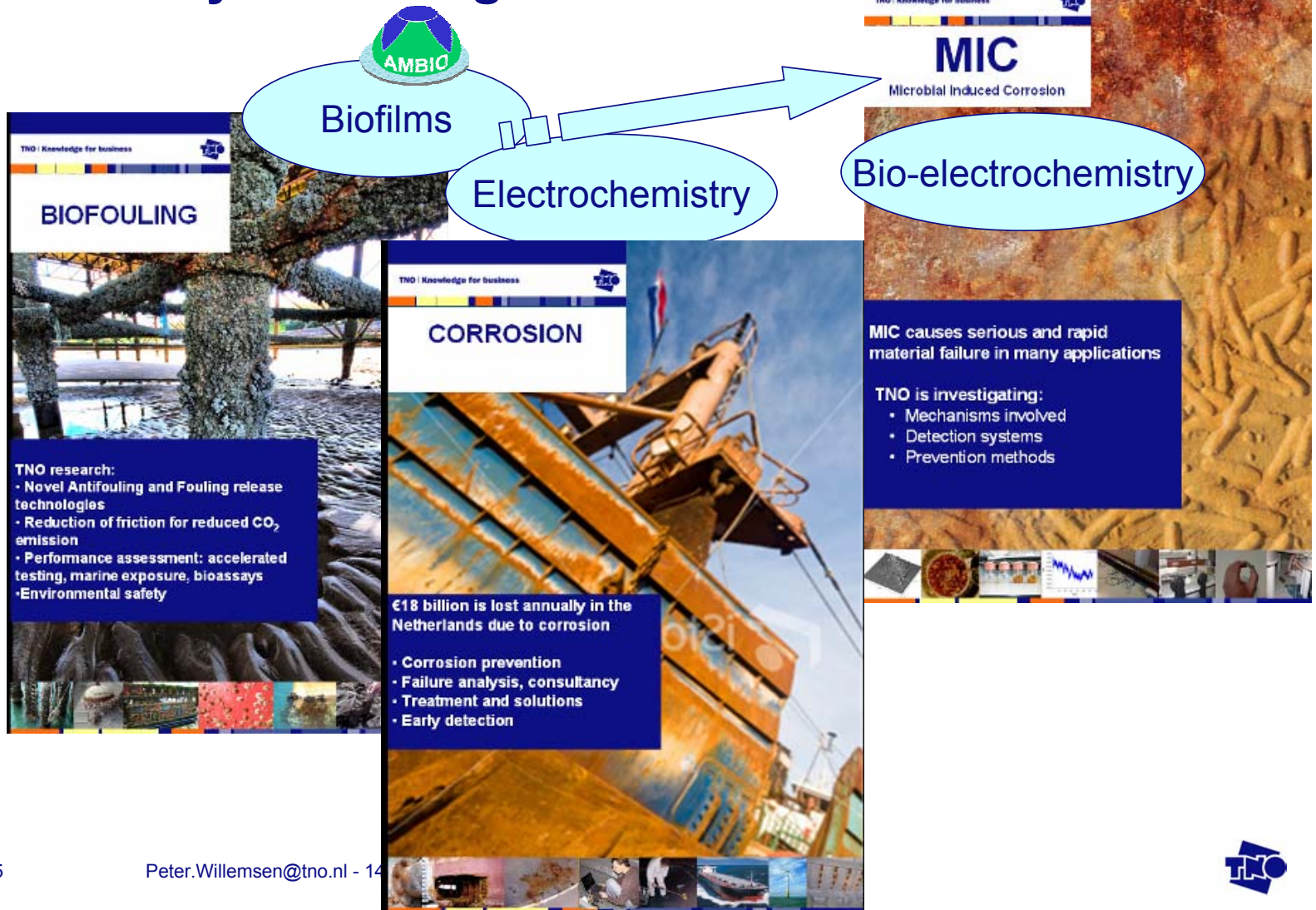


Delft
(head-
quarters)

Eindhoven
(Bus.Unit
Materials
Technology)



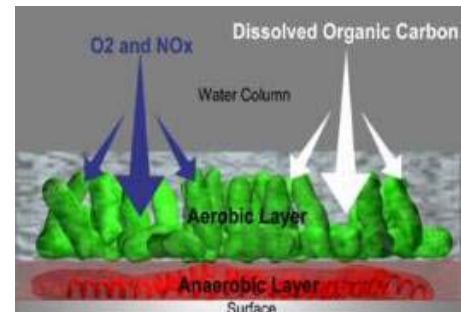
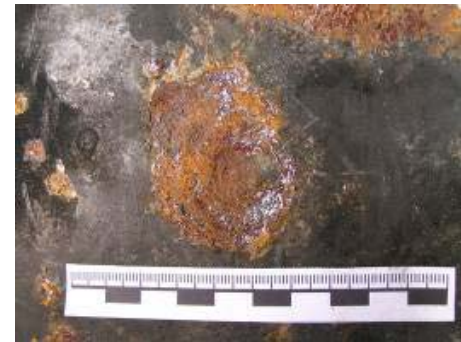
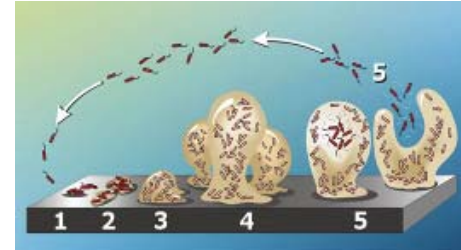
Our key technologies



MIC: studied for decades

- Metabolic activity of microorganisms accelerate corrosion reactions (directly or indirectly)
- Production corrosive metabolites or may directly precipitate the metal into solution
- Formation of aeration cells with anodic and cathodic sites as a result of uneven biofilm distribution
- [Good reviews in Brenda Little & Jason Lee (2007): Microbiologically Influenced Corrosion]

Paul Stoodley /Peg Dirckx
from www.erc.montana.edu/Res-Lib99-SW/Image_Library

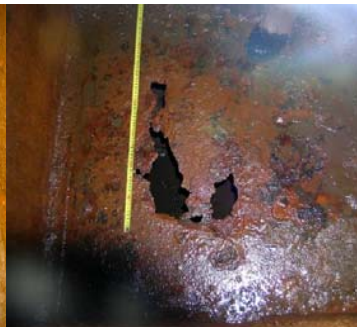


<http://www.zetacorp.com/bioco>
[rosion.shtml](http://www.zetacorp.com/bioco)

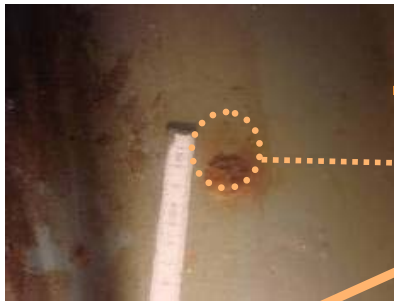


MIC: widely dispersed

- Rapid, unpredictable → fast local corrosion.
- E.g.
 - enclosed, inaccessible areas such as ballast tanks, settling tanks and cargo tanks;
 - fuel tanks, heat exchangers, sprinklers, etc...
- Caused by wide variety of micro-organisms, e.g.
 - SRB: Sulphur reducing bacteria (anaerobic)
 - IOB: Iron oxidising bacteria (aerobic)
 - APB: Acid producing bacteria (sulphuric acid)
 - Also fungi
(and mixed communities!)
- [Kobrin (2003): A practical manual on Microbiologically Influenced Corrosion]



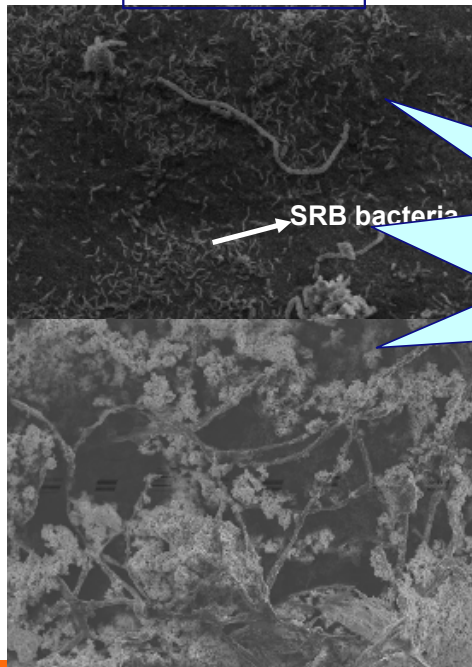
Clear role of MIC after second investigation: pump room onboard of naval vessel (TNO survey 2006, blistering)



Localised corrosion: pits, tubercle formation



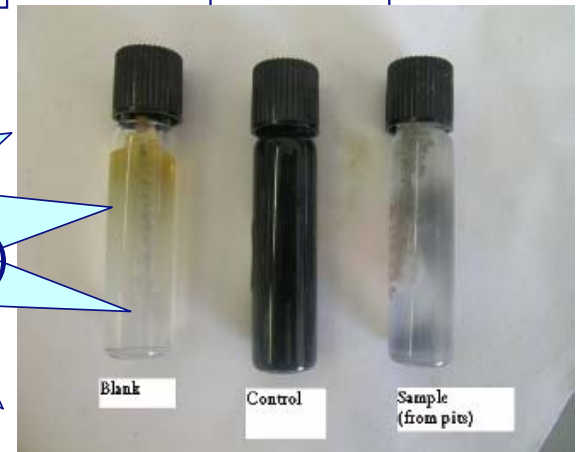
SEM images



Microscopy (DNA staining)



SRB test



MIC! (fungi and SRB)

4th ICMC

Monopile foundation: enclosed area (TNO survey)

- Offshore windfarm
- After 1 year: SO₂ gas formation
- Water samples: SRB's present
- Action: biocide injection



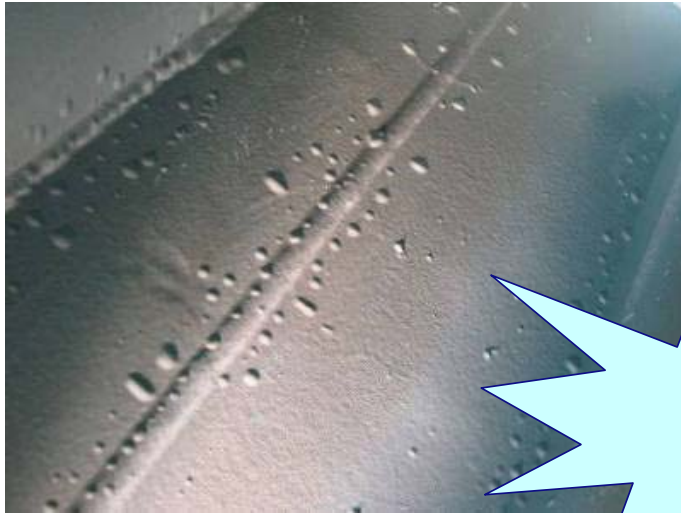
Blyth windfarm



Installation monopile

So how big is the problem really?

Coating survey air command frigates (TNO survey, 2006)



Hr.Ms. "Zeven Provinciën"
(LCF 1). Potable water tank 2:
Blistering along welds/welding
corners in stripe coated areas.

MIC?

Hr.Ms. "Tromp" (LCF 2). Potable
water tank 4:
Corroded spots along welds.



Hr.Ms. "De Ruyter"
(LCF 3). Sewage
storage tank:
Corrosion on tank
bottom

(and how about macrofouling?)



Detection, diagnostics



- Environmental conditions (pH, redox...).
- Corrosion: products, electrochemical. Other products: H_2S , H_2 ...
- Microbial (organisms, metabolites, molecular)



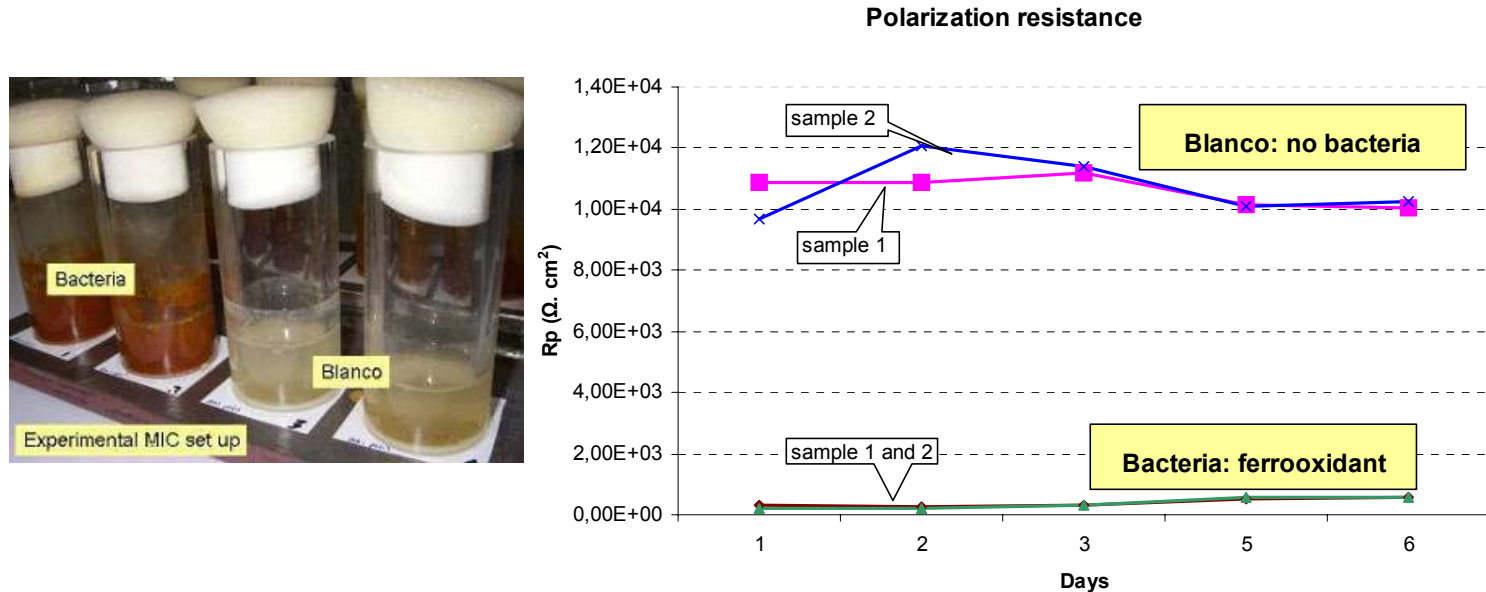
Test kits: overview of commercial products

Aerobic test kits	Methods	Numbers detected ml ⁻¹
<u>Dip slide Test kits</u>		
<ul style="list-style-type: none"> o Easicult Combi o ECHA Dip-slide o Oxoid o Difco Hycheck o Microbial-systems Int o Microcheck o Sanicheck AB o Sanicheck YM 	Dip slide into sample, drain off surplus and incubate 1-5 days. Compare result to calibration chart. Aerobic bacteria Yeast and Molds	<u>All tests</u> Range 10 ² – 10 ⁷ bacteria. Range 10 ² – 10 ⁶ yeasts Range light-heavy moulds
<u>Gel-medium based kits</u>	<div> <p>But:</p> <ul style="list-style-type: none"> •Time consuming •Not real-time •Not specific •Not sensitive(?) •Detection <i>after</i> problem occurs </div>	
Panatest		Approx. 10 ² and above (bacteria)
SMARTGEL		Range 10 ² – 10 ⁵ quantitative. Above 10 ⁵ semi-quantitative. (Bacteria, Yeasts and Moulds)
HUM-Bug Detector kit	Add sample to medium flask with colour indicator. Red or pink colour indicates positive.	Detection of hydrocarbon utilizing bacteria. Qualitative test.
Anaerobic test kits		
EasicultS	Stab capillary full of sample into gel. Incubate for up to 5 days.	Range slight to heavy (Bacteria)
Sig Sulphite	Pour 2ml of sample onto gel. Incubate for up to 5 days.	Range 10 ¹ – 10 ⁵ (Bacteria)
Sanicheck SRB	Immerse pipe-cleaner into sample and stab into gel. Add CO ₂ generating tablet. Incubate for up to 5 days	Range 10 – 10 ⁶ (Bacteria)

Electrochemical measurements

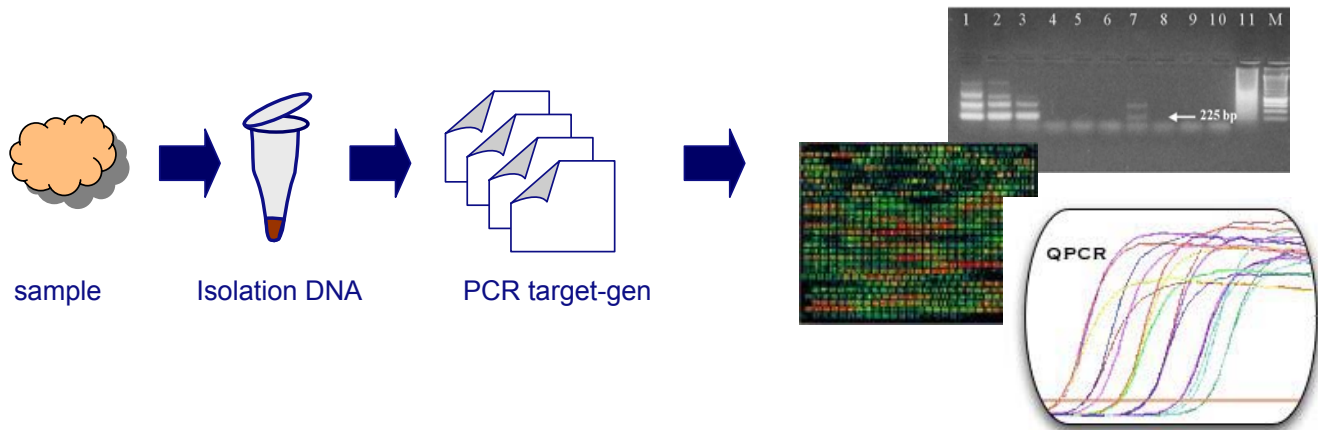
- Corrosion products, other products, e.g. H_2S , H_2 ...
- Electrochemical tools (corrosion research) → EIS, ENM, LPR/PC, OCP, ECP...

Corrosion rate under aerobic MIC (*Acidithiobacillus ferrooxidans*):



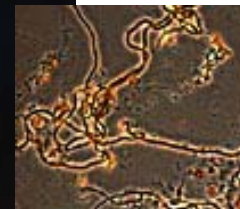
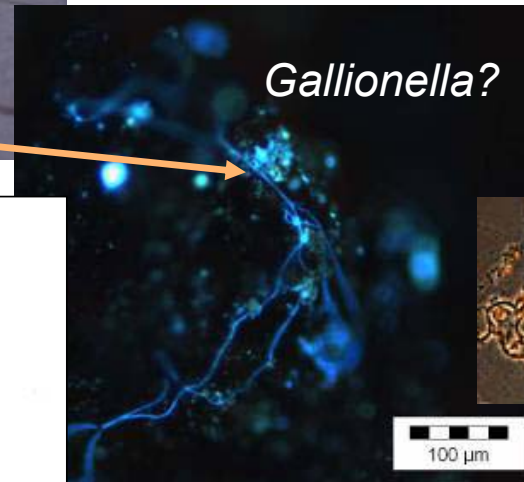
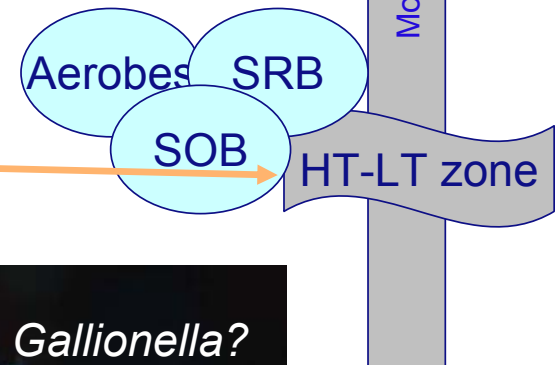
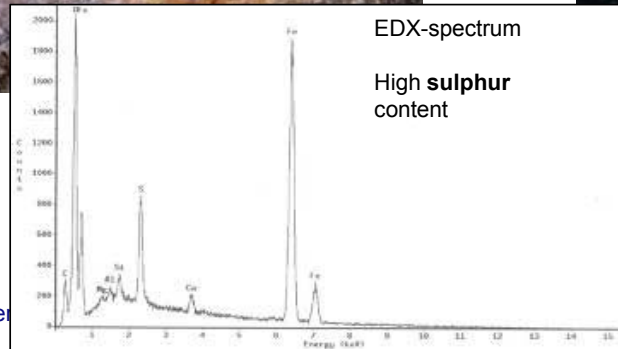
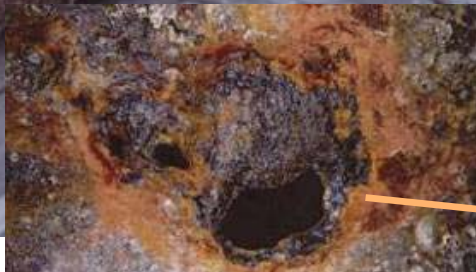
Molecular tools

- More advanced tools exist or in development, e.g. molecular based. E.g. PCR (Krooneman/Bioclear, 2006):



- But..... what we really need are real-time, on-line monitoring tools measuring the bio and electrochemical aspects of MIC and these are non-existent.

MIC mechanism example (TNO study): Mooring posts (damaged in 5 years)



MIC mechanism example: Ballast tank (TNO study)

Zone 1: Continuous cycle influenced by ballast water exchange

Anaerobic / aerobic changes in the water column

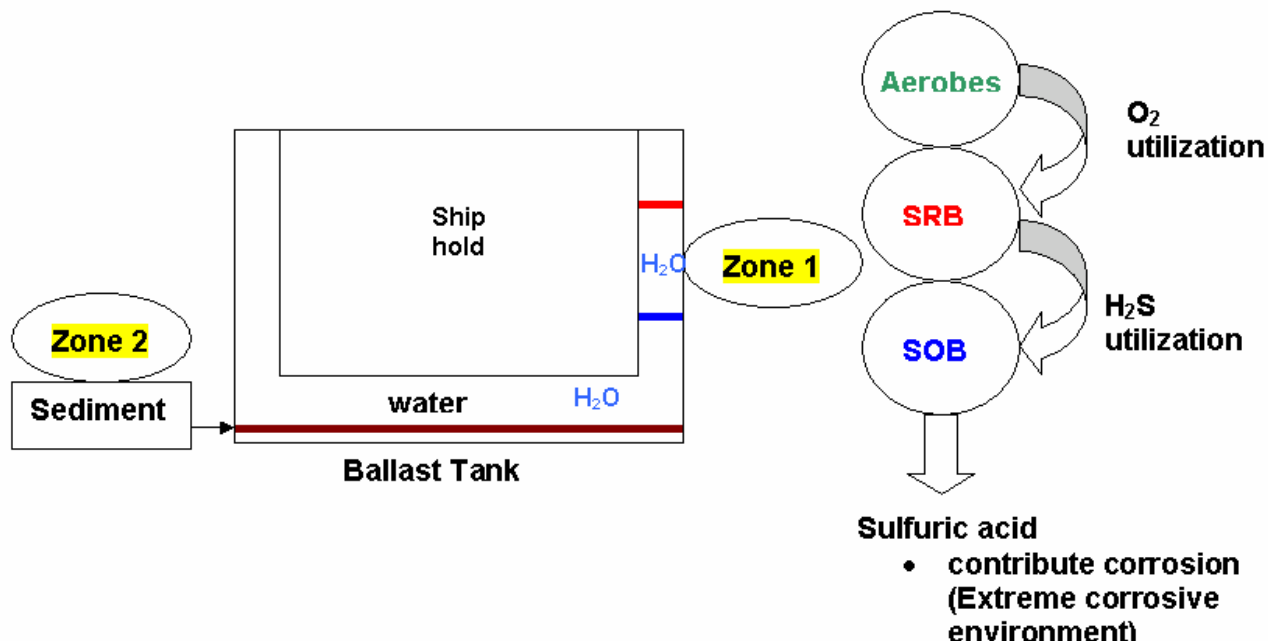
Aerobes consume O_2 , enables growth of SRB

High water level (O_2 limited) – SRB growth on steel surface

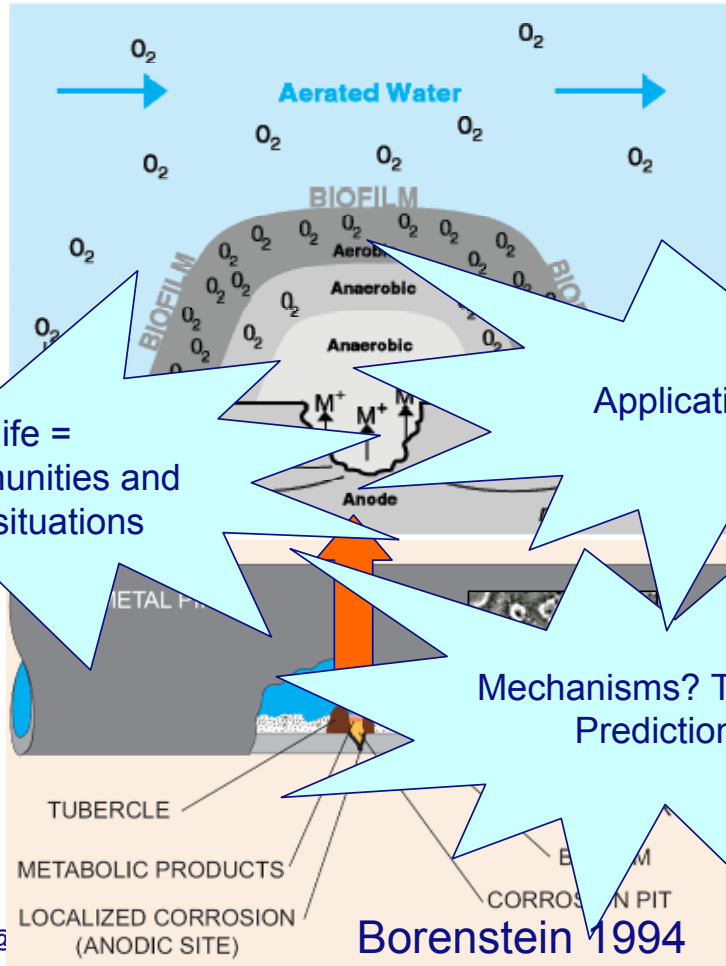
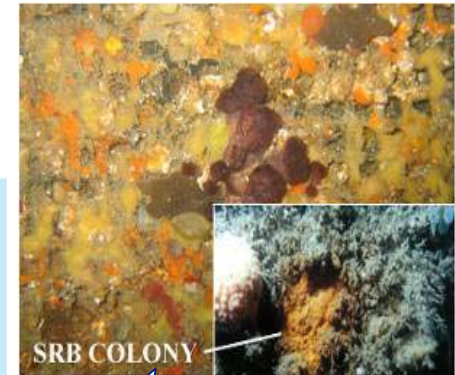
Low water level (O_2 not limited) – SOB utilize SRB products

Zone 2: Steady state process

SRB enriched in sediment which accumulates during shipping voyages



MIC: complicated!



Real life =
Mixed communities and
dynamic situations

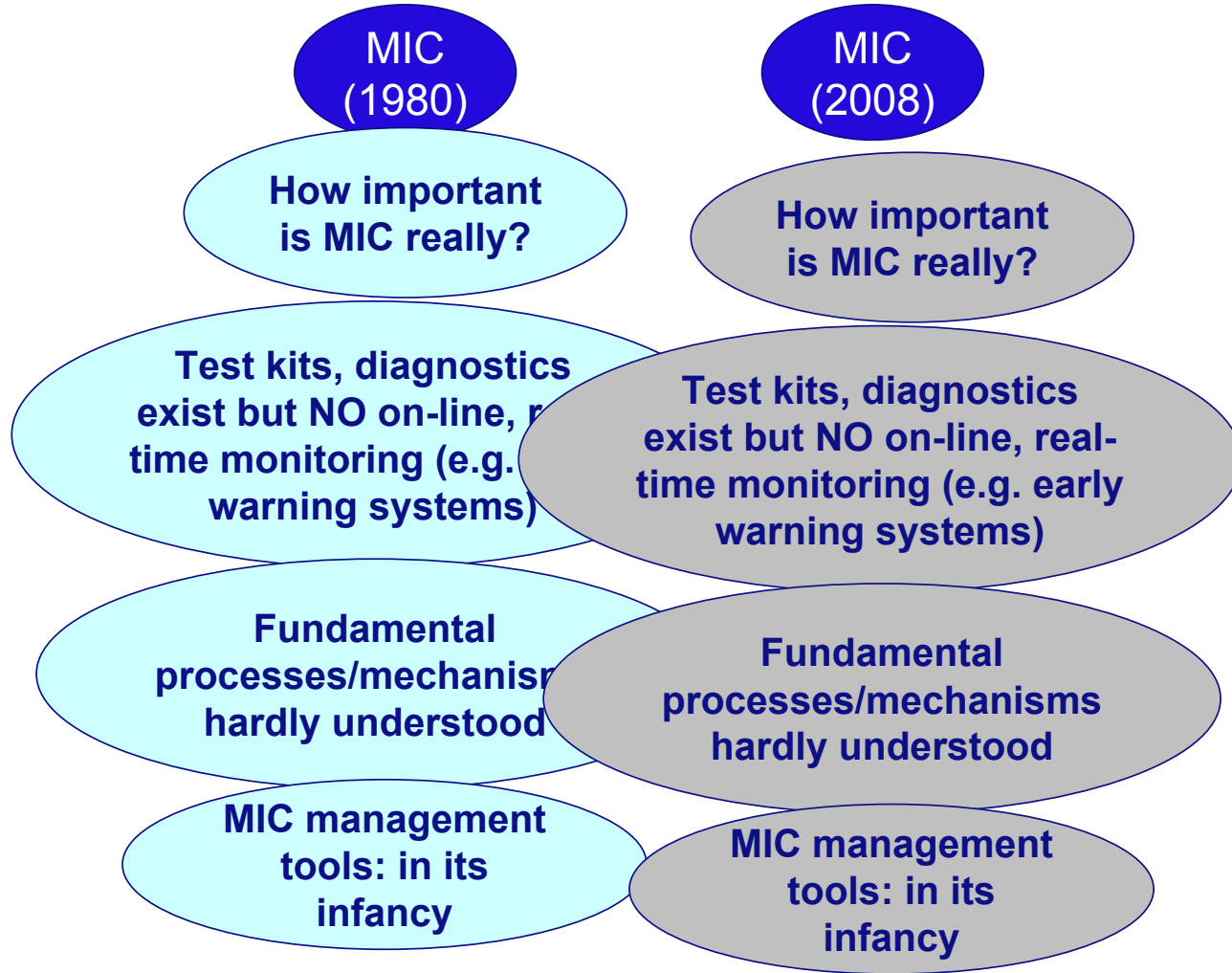
Application specific

Mechanisms? Triggers?
Prediction?

Borenstein 1994

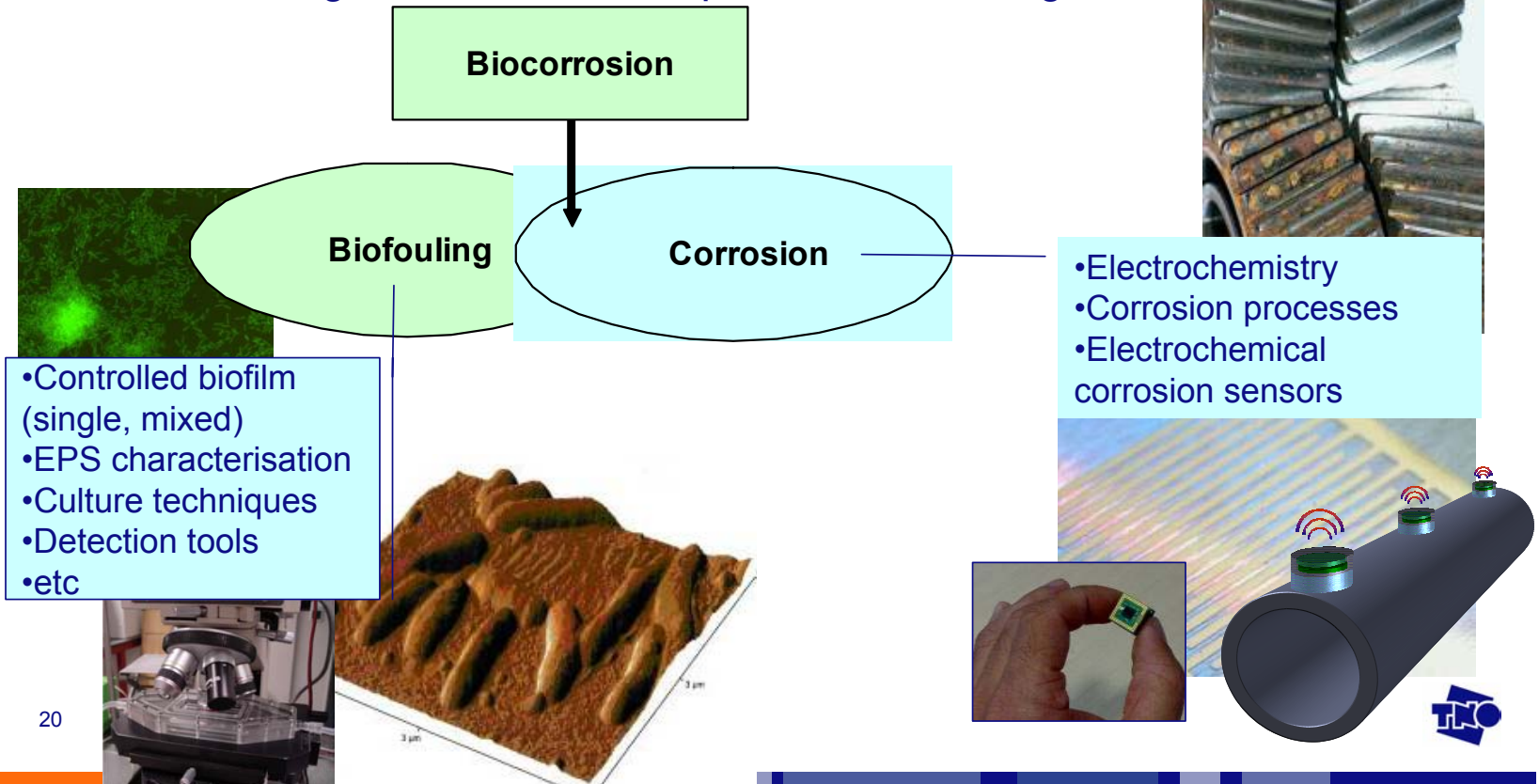


MIC studied for decades but...



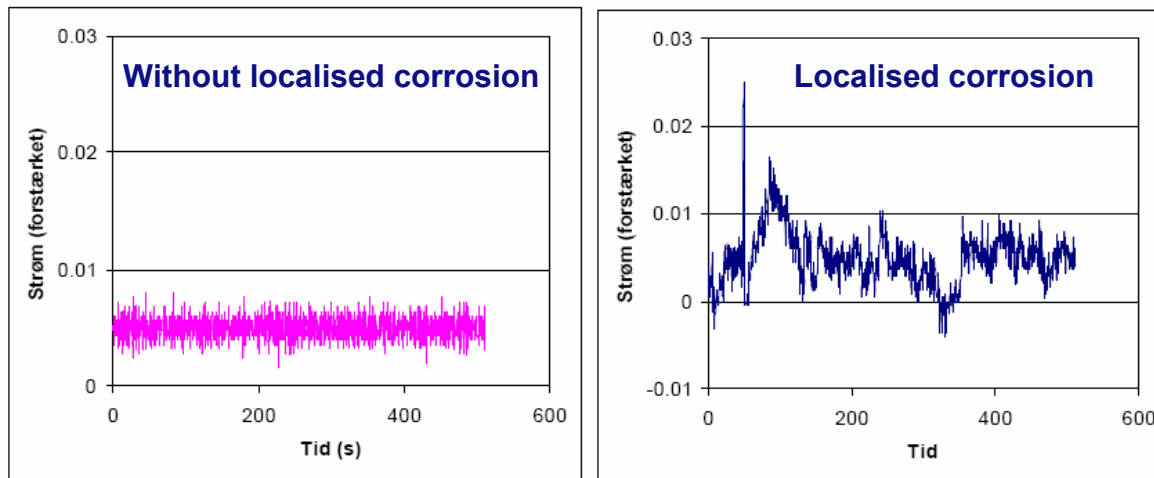
TNO bio-corrosion research

- Understanding of interactions between biological and electrochemical processes at material/water/oil interfaces
- Identification of critical steps in MIC process
- Monitoring/detection tools; improved MIC management



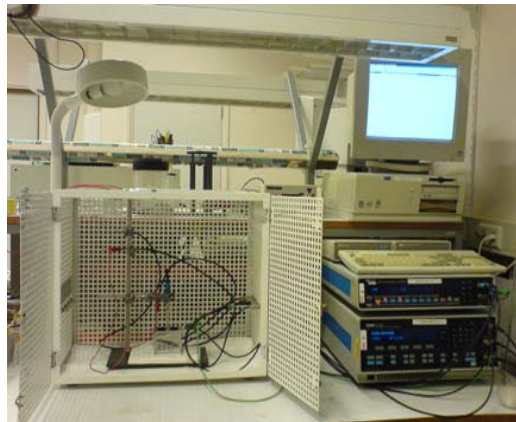
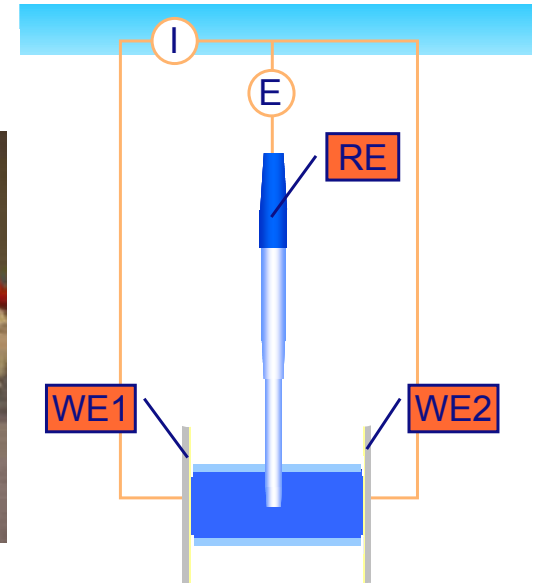
Initial work: ENM (Electrochemical Noise Measurements)

- Generic term given to spontaneous fluctuations of current and potential in natural corrosion processes
- Relating outcomes to characteristics of specific corrosion mechanisms.
- Often used to study corrosion mechanisms:

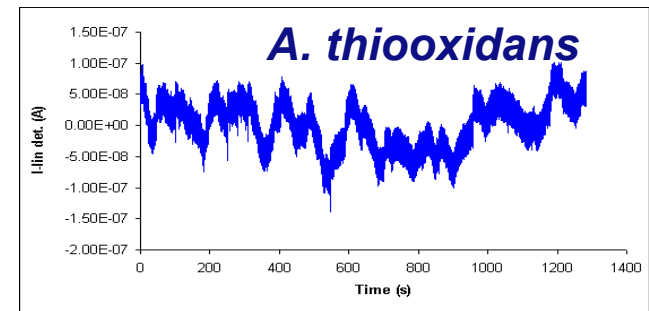
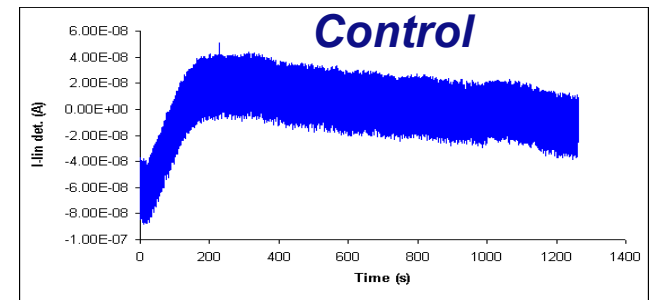
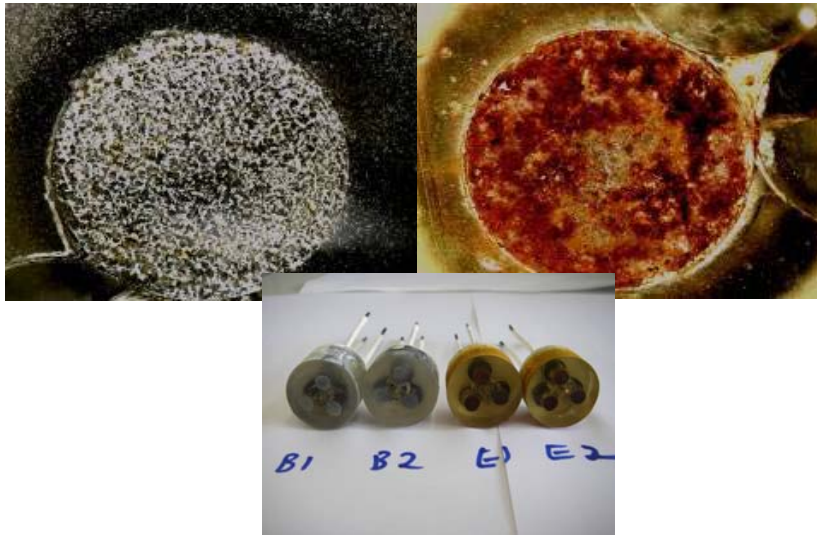


ENM: corrosion in power plant boilers (Cappeln 2002)

Initial ENM set up



Example measurement of MIC using ENM

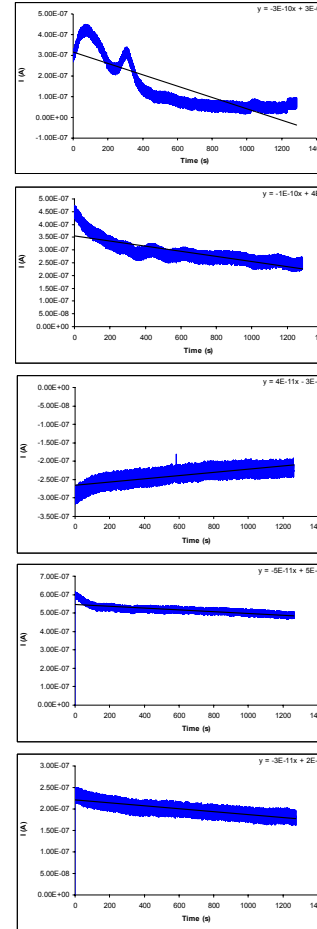


- Reproducible differences in ENM pattern
- Higher corrosion rate

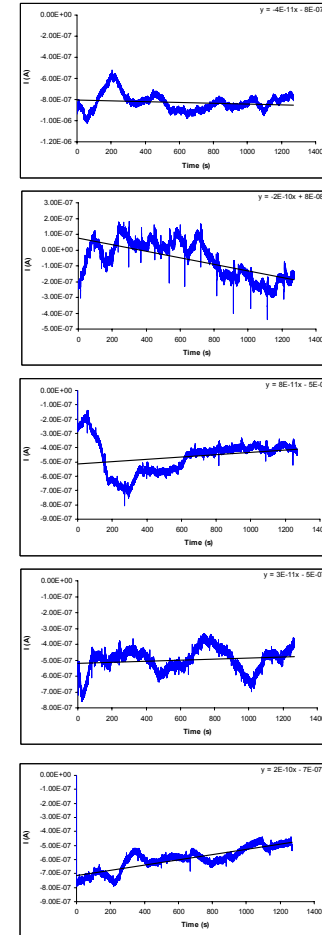
Similar results with *Acidothiobacillus ferrooxidans*



Control

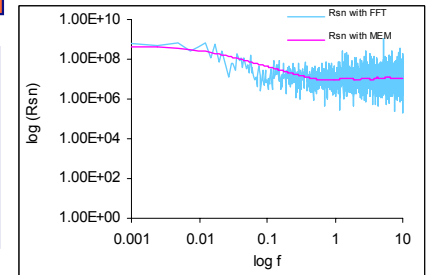
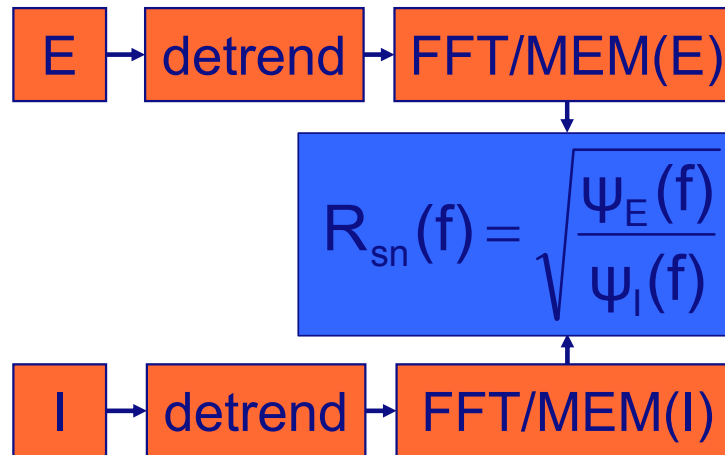
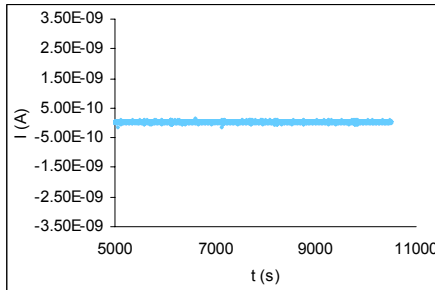
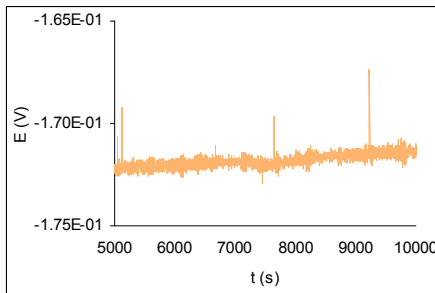


A. ferrooxidans



ENM data analysis: challenging

- Transform noise data from time series (time domain) into frequency domain. Methods: Fast Fourier Transformation (FFT) and the Maximum Entropy Method (MEM).



ENM: powerful tool

- Initial laboratory experiments: substantial differences between microbial and normal corrosion.
- Further work:
 - Discriminate between aerobic and anaerobic MIC.
 - More advanced noise analysis.
 - Correlate (bio)corrosion mechanisms with noise patterns.

ENM: useful tool

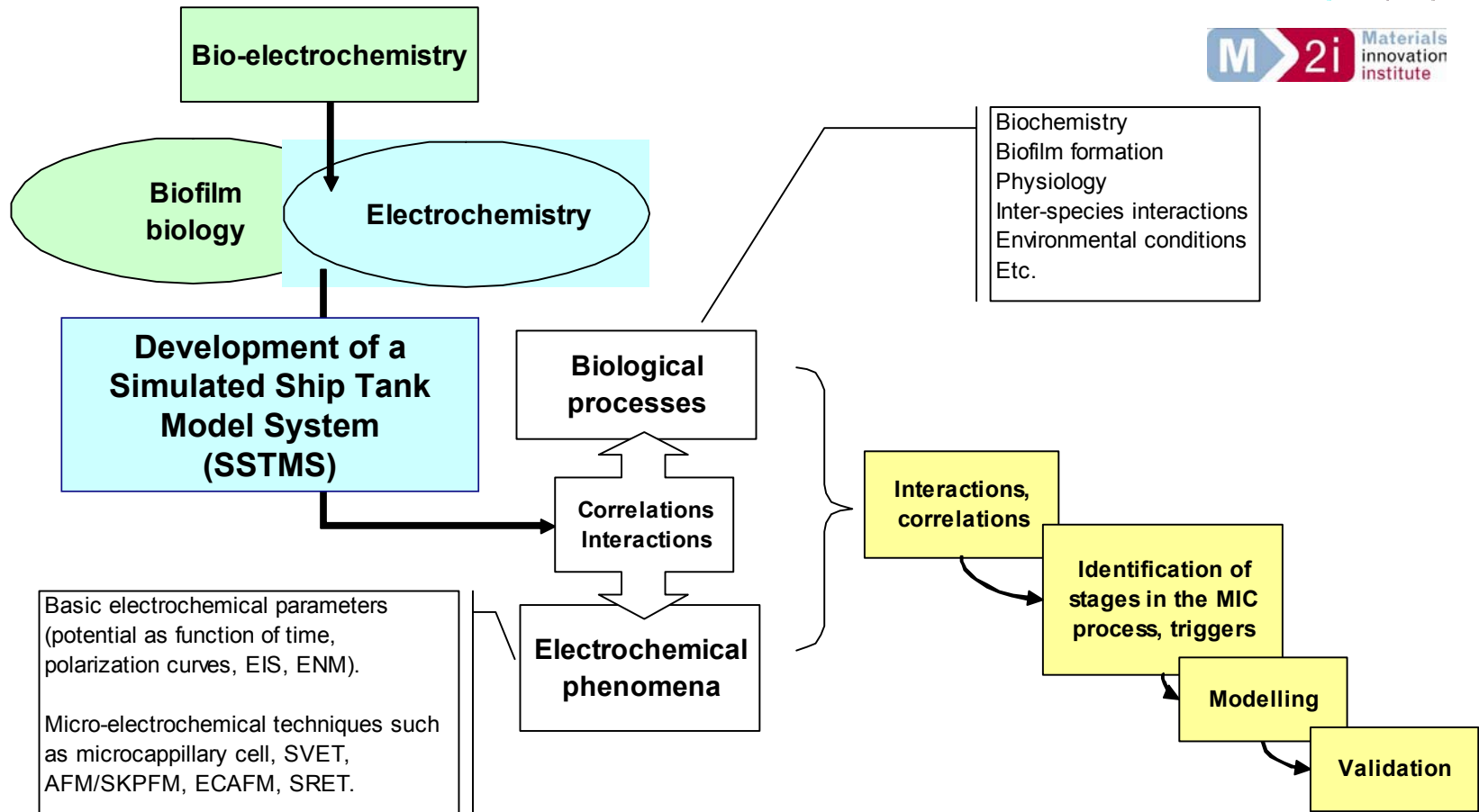
...but only a part of the puzzle

So: back to the fundamentals

→ Key questions TNO MIC research

1. Phases in maritime related MIC processes?
2. Triggers for subsequent phases in MIC process (biological, biochemical, electrochemical, environmental condition, substrate properties/defects)?
3. Relationships between aerobic and anaerobic processes?
4. Possible to predict maritime MIC based on detailed understanding of bio-electrochemical processes?

Microbiologically Induced Corrosion in Ship Tank Environments (with Techn. Univ. of Delft) (PhD started July 2008)





Thanks for your attention

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