Development of a Corrosion Inhibitor Micelle Detection Method: A review with case studies

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Institute of Corrosion Aberdeen, 25th February 2014

Presentation Outline

- LUX Assure background
- Technology development in oil and gas
- Development case study – micelle detection
- Field case studies
  1. Variable inhibitor dose on offshore platform (North Sea)
  2. Oil terminal reception (Europe)
  3. Audit of large onshore network (North America)
  4. Subsea Tieback Diagnosis (North Sea)
  5. Inter-platform Pipeline Diagnosis (North Sea)
  6. Accumulation in a MEG Recycling Facility (North Sea)
  7. Pigging operations (North America)
  8. Sea-water injection system (Middle East)
- Q&A

LUX Assure

LUX Assure

Company Profile

- **Novel chemical monitoring technologies**
- Product and service provider for the oil and gas industry
- Focus on:
  - Difficult to detect chemicals
  - Rapid results
  - On-site analysis
  - Interpretation – information rather than data
  - Independence from 3rd parties

LUX Assure

Products

oMic™

- Service to measure functional dosage of corrosion inhibitor
- LUX staff and instrument deploy – typically 1-3 days
- Diagnosis or optimisation

MMICA™

- Detection kits, for methanol or monoethylene glycol (MEG) detection
- Simple procedure for platform chemist/technician to run
- Rapid results

Technology Development in Oil and Gas

- New technology is needed
- Technology which can increase revenues or decrease costs is massively valuable

- An inherently high-risk process
  - New ideas
  - High failure rate
  - Untested
- In an inherently low-risk industry
  - Safety paramount – nothing unexpected
  - Short-term production critical
  - Budgetary pressures

Solutions

- Operators have pushed R&D to service companies
- Service companies later recover their costs from operators

- New ideas can be crystallised in SMEs
- Investor support
- Government support
- Operator & service company support
- Controlled testing facilities accessible

- Somebody takes a risk!
  - Technology validation needs field testing

Micelle Detection Concept

- A. Weisstuch and K. Lange *Mater. Performance.* 10 (1971) pp.23-32

Link between micelles and corrosion widely reported for more than 40 years

John, D., Blom, A., Bailey, S., Nelson, A., Schulz, J., De Marco, R. and Kinsella, B. *Physica B* **385-386** (2006) 924-326

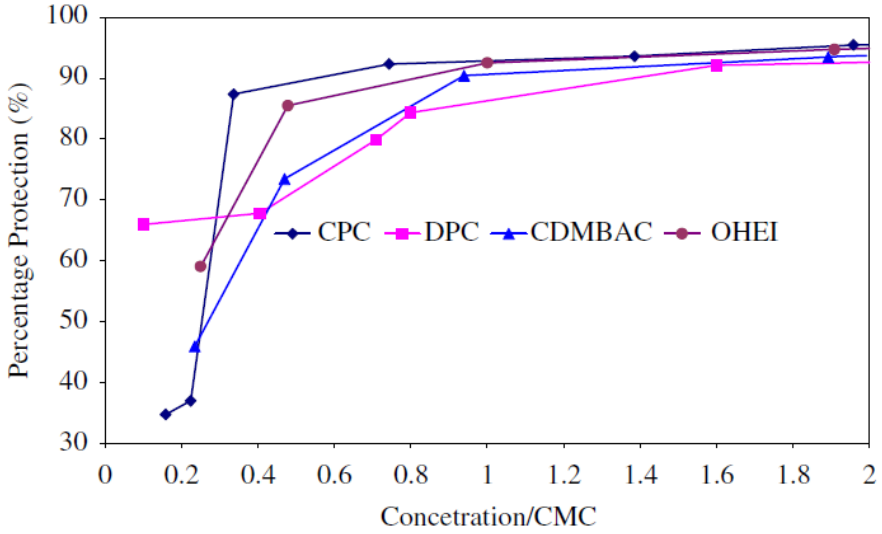
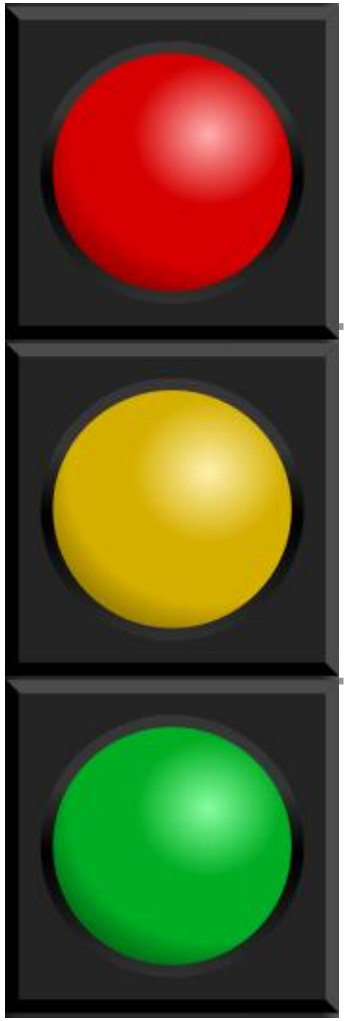


Fig. 3. The corrosion protection afforded by the generic surfactants DPC, CPC, OHEI and CDMBAC with respect to the CMC.

- V.Abbasov, H.El-Lateef, L.Aliyeva, E.Qasimov, I.Ismayilov, A.Tantawy, S.Mamedxanova, *Am. J. Mater. Sci. Eng.*, 1 (2013) pp.18-23

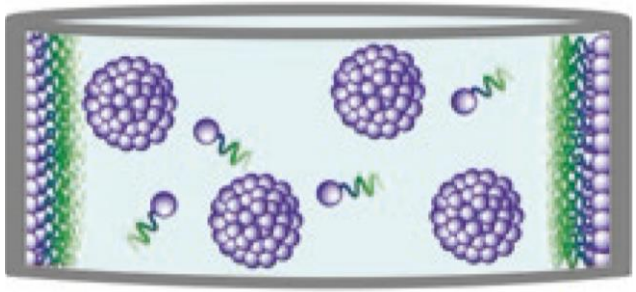
Micelle Detection Concept



Under-dose
< CMC

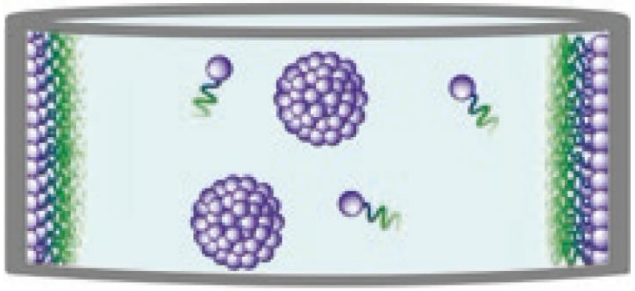
Increased risk of corrosion

Over-dose
> CMC



Increased separation issues and chemical cost

Optimum dose
= CMC



Balance between risk and cost

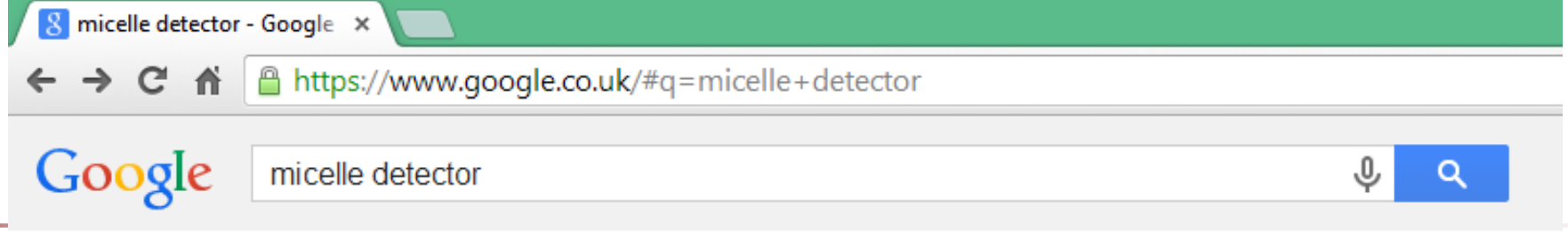
TD Case Study: Micelle Detection

- Conversation in a corridor 2008
  - Fact-checking
  - Technical evaluation
  - Commercial evaluation
  - IP evaluation
- Decision point
  - Funding
  - Rapid incremental experimentation (fall forward)
  - Access to relevant test samples
  - Access to expertise
  - Access to fields
- Commercialisation

Development Process – Micelle Detection

- Concept:
  - ✓ Corrosion inhibitors are surfactants
  - ✓ Surfactants form micelles at a certain concentration (CMC)
  - ✓ Literature has shown CMC=optimal inhibitor concentration
  - ✓ Micelle Detector = Dosage Optimiser

- All we need is a micelle detector!



About 3,850,000 results (0.28 seconds)

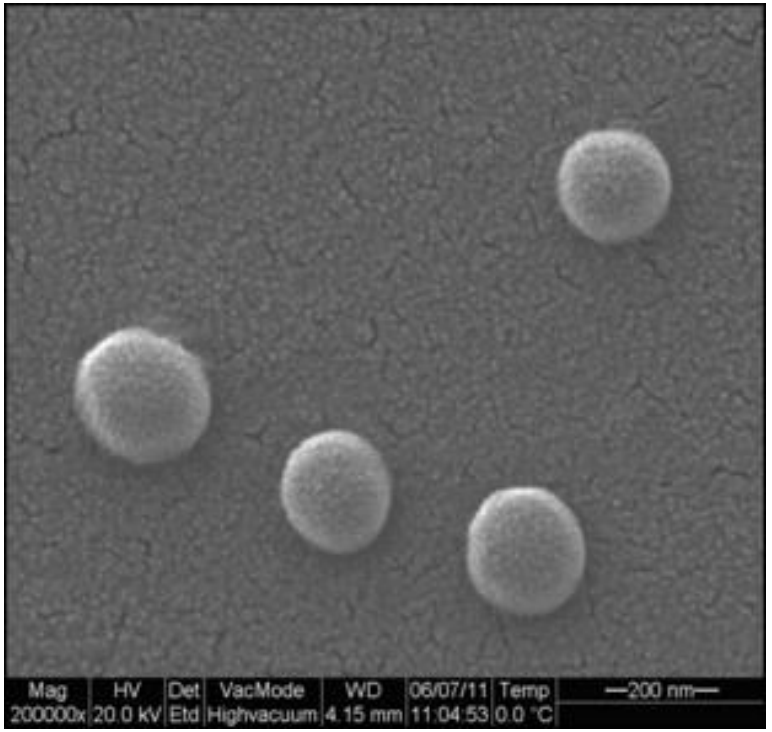
Detection of the critical **micelle** concentration of cationic and anionic ...
link.springer.com/article/10.1007%2Fs11426-009-0119-7
by L Tang - 2009 - Cited by 16 - Related articles
1 Jun 2009 - We report a fluorescence "turn-on" method to detect the critical **micelle** concentration (CMC) of surfactants. This method works well for both ...

Real time **micelle detection** in development - OE Digital
www.oedigital.com/.../3215-real-time-**micelle-detection**-in-development
1 Jun 2013 - An additional tool for corrosion management: the power of corrosion inhibitor **micelle detection**. Management of internal corrosion typically ...

DNA aptamer–**micelle** as an efficient **detection**/delivery vehicle ...
www.pnas.org/content/107/1/5
by Y Wu - 2010 - Cited by 91 - Related articles
5 Jan 2010 - Abstract. We report the design of a self-assembled aptamer–**micelle** nanostructure that achieves selective and strong binding of otherwise ...

[PDF] A surfactant type fluorescence probe for **detecting micellar** growth
www.chem.pku.edu.cn/.../2011%20A%20surfactant%20type%20fluores...
by L Gao - 2011 - Cited by 7 - Related articles
21 Oct 2010 - We report on the **detection** of **micellar** growth in anionic, cationic, and ... very sensitive for directly **detecting** the **micellar** growth in **micelles** ...

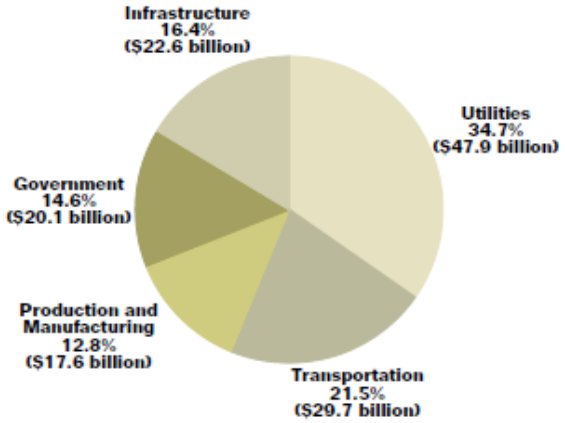
A “Micelle Detector”



Driving Forces in Development

- Operator with:
  - TD budget – long-term goals, risk assumed
  - Business need
  - Technical vision
  - Willingness to invest non-financially

FIGURE 1
COST OF CORROSION IN INDUSTRY CATEGORIES
($137.9 BILLION)



Percentage and dollar contribution to the total cost of corrosion for the five sector categories analyzed.

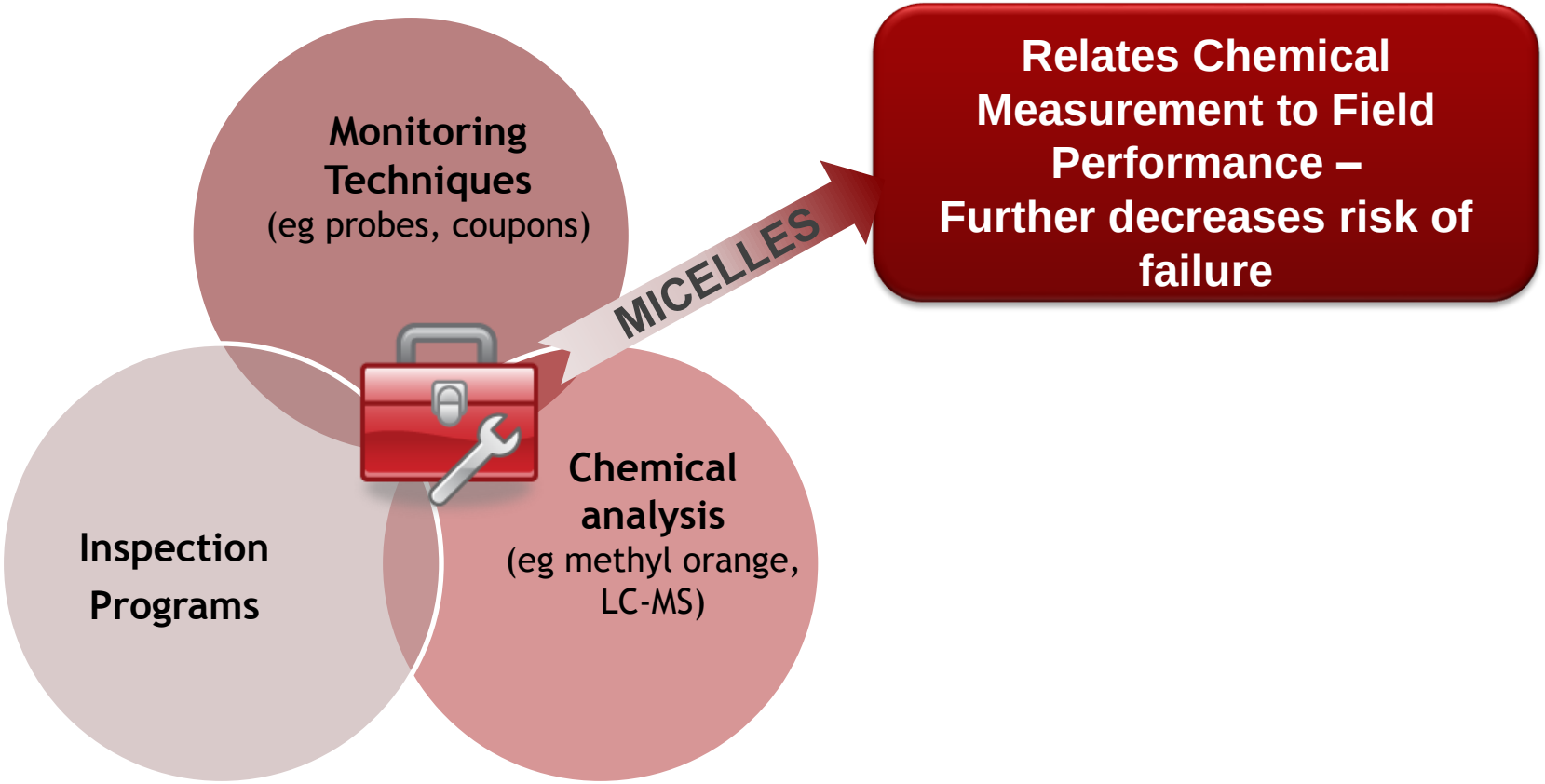
Technology Strategy Board
Driving Innovation

Development Timeline

- Conversation in a corridor 2008 — **2008**
  - Fact-checking
  - Technical evaluation
  - Commercial evaluation
  - IP evaluation
- Decision point — **2009**
  - Funding
  - Rapid incremental experimentation
  - Access to relevant test samples — **2011**
  - Access to expertise
  - Access to fields — **2012**
- Commercialisation — **2013**

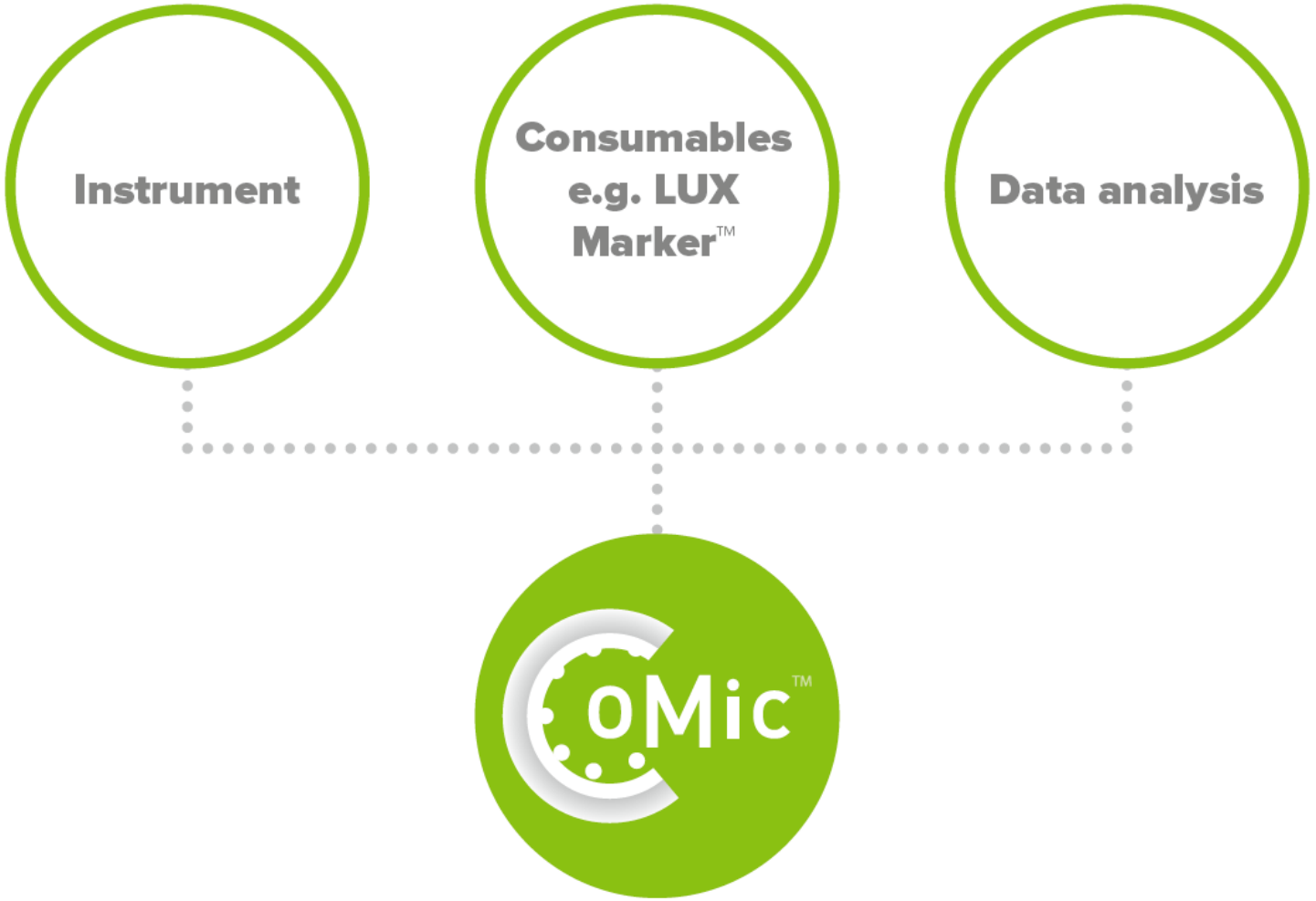
CoMic™ - a Corrosion Management Tool

What does it do?



CoMic™

What does it consist of?



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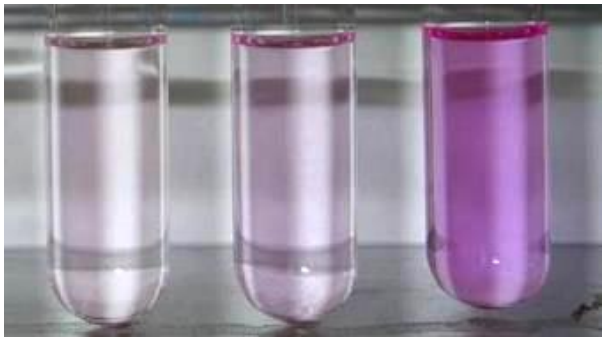
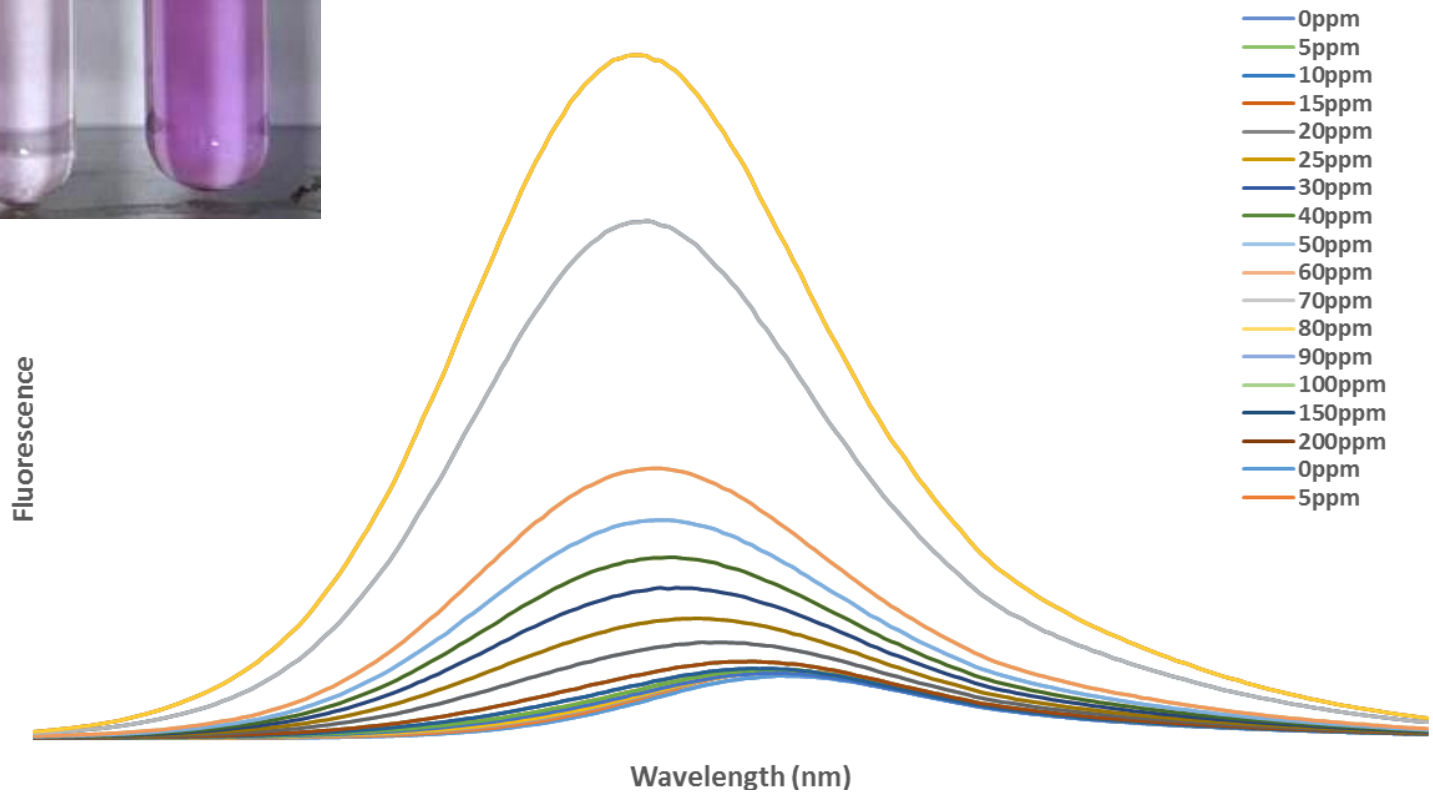
How does it work?

1. A fluorescent marker
   - Fluorescence emission varies with polarity of environment

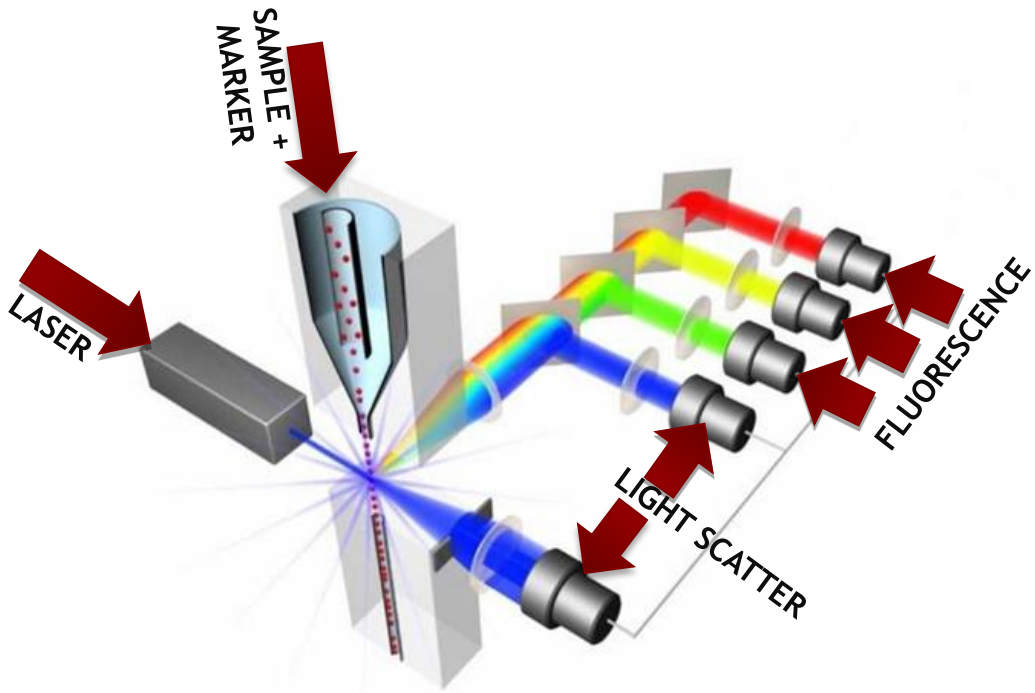




CoMic™

How does it work?

2. An optical flow analyser for detection
   - Per-particle detection in compact design (35 x 27 x 13 cm, 7 kg)



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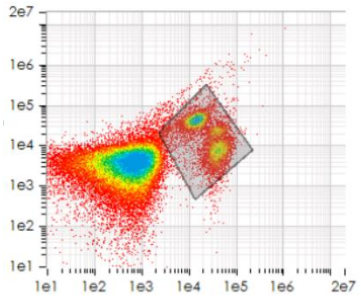
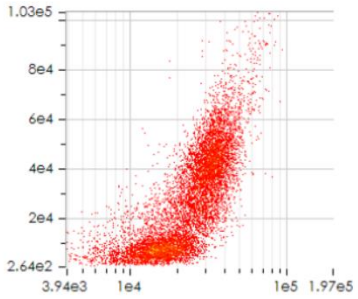
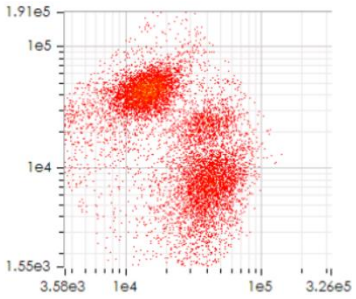
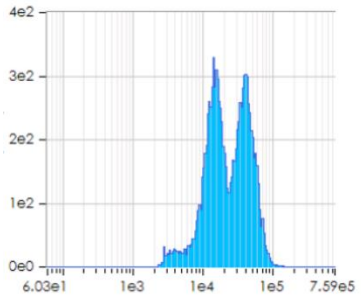
How does it work?

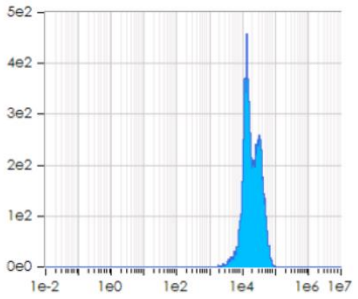
3. Analysis and interpretation → Micelle levels
   - In context of experience and field observations

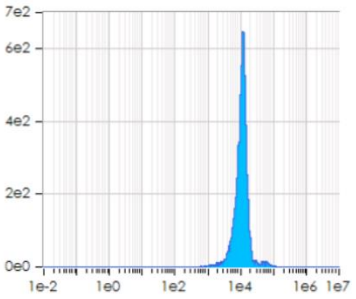


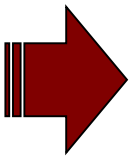


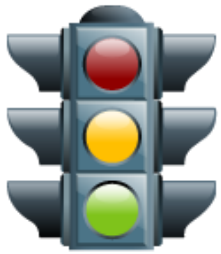






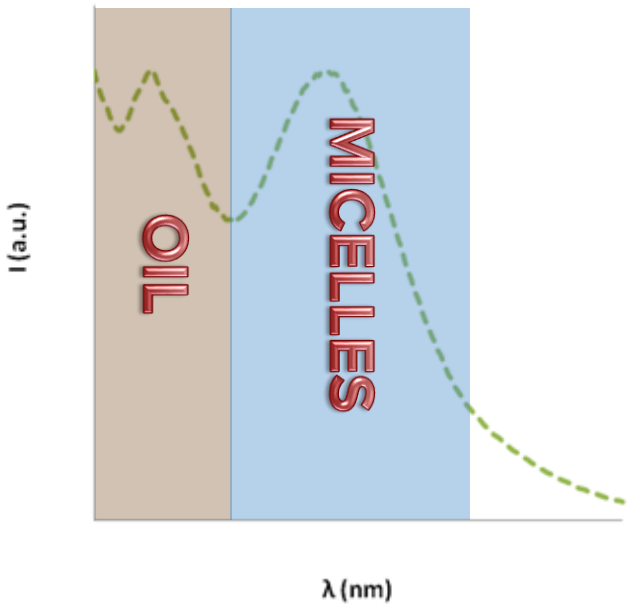




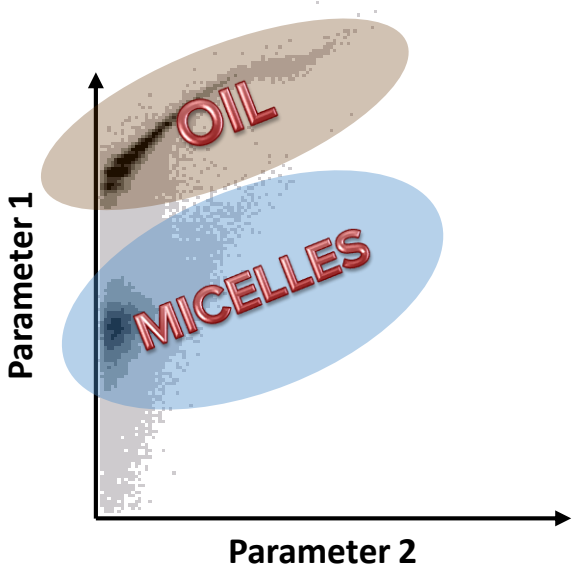


Bulk vs Per-Particle Measurement

- Fluorescence and ‘per particle’ approach removes interference



Bulk
“Average Reading”



Per-Particle
“Independent Reading”

Field vs Lab Measurements

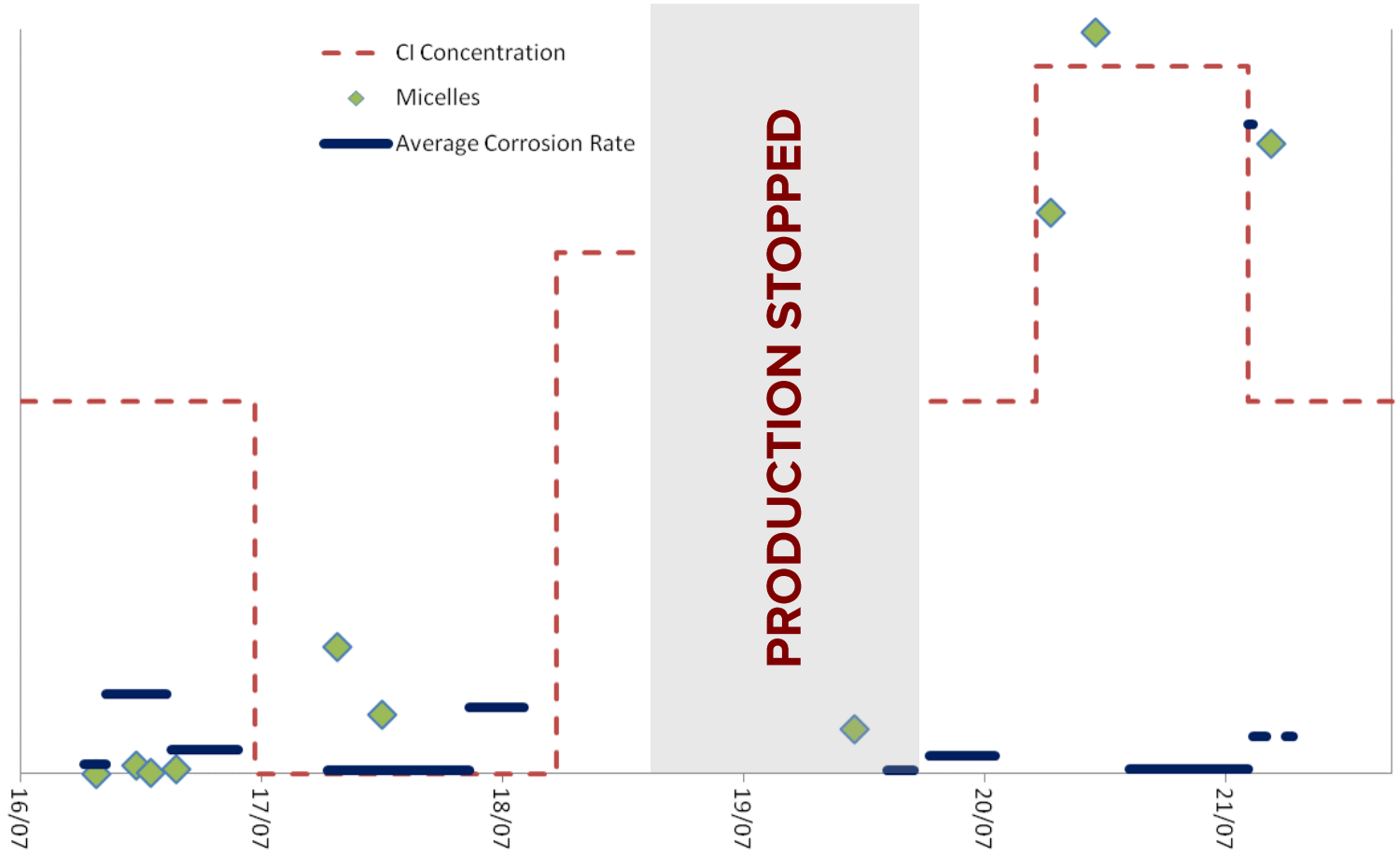
- After a sample is taken the following can occur:
  - Corrosion inhibitor sticks to bottle
  - Bacteria grow and excrete fatty acids
  - Fatty acids interact with micelles
  - Inorganic precipitate can form
  - Corrosion inhibitor sticks to precipitate
  - The pH changes
  - Chemical degradation of the corrosion inhibitor
  - The fluid becomes oxygenated
  - The effective water cut is different
  - The oil chemistry changes
  - Micelle structure changes
- The amount and rate at which of these happen is variable and unpredictable

➢ Analyse field sample

1. Variable Inhibitor Dose Study

- Asset in UK North Sea, oil production
- Subsea pipeline to well ~10 miles (~12 hours)
- Water cut increased 20% → corrosion issues
- Dose rate varied via pump on platform
  - Water taken from test separator
  - E-chemical probe in-line (3rd party)
  - Fluorometer on water samples on site
  - Flow analysis on samples sent to shore

Results – Transit Time Adjusted



2. Pipeline Reception at Oil Terminal

- Pipeline water tested:
  - Receiving spheres common drain
  - Scraper pig water
  - Intelligent pig water

- Bespoke micelle model used to interpret functional inhibitor levels

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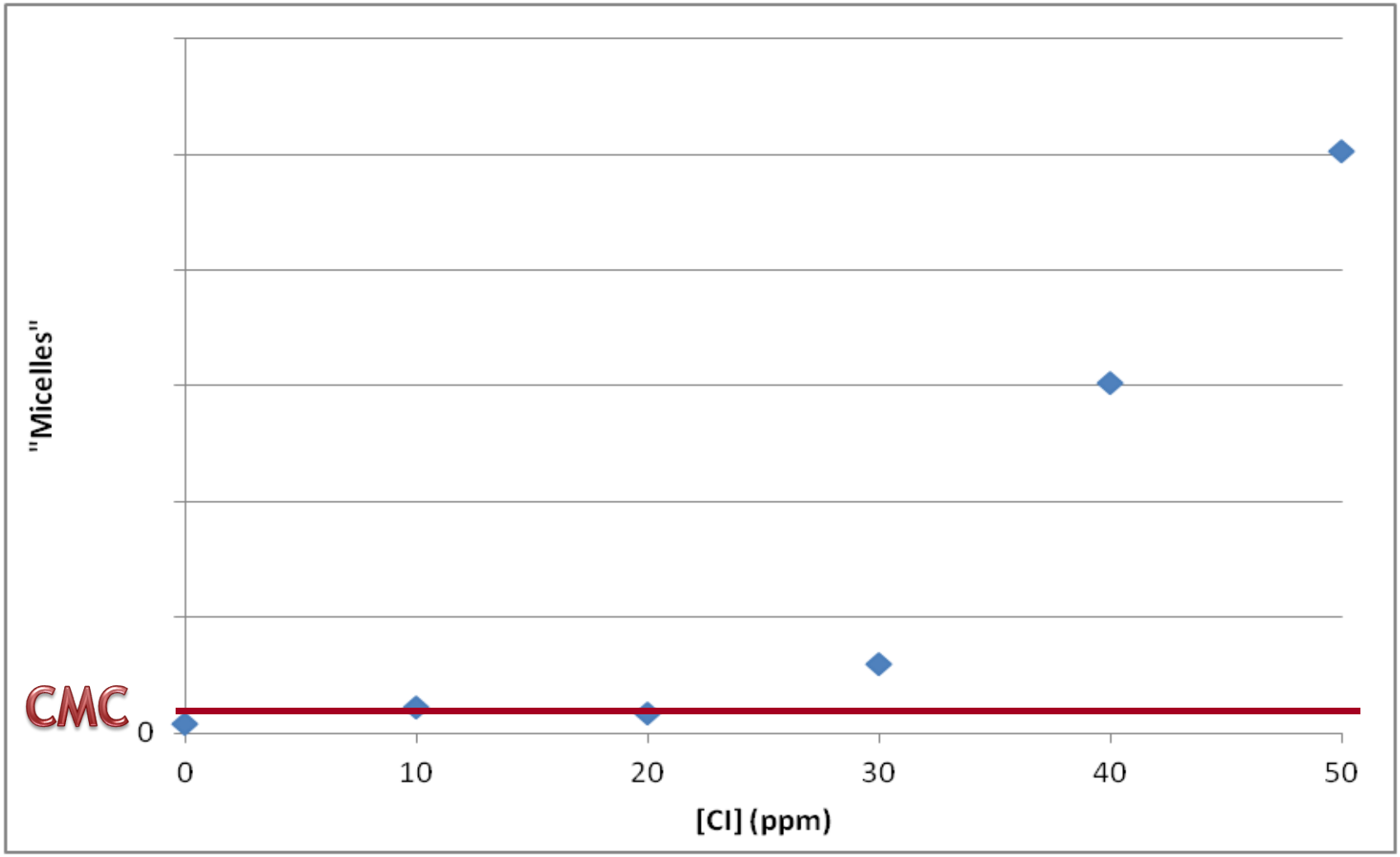
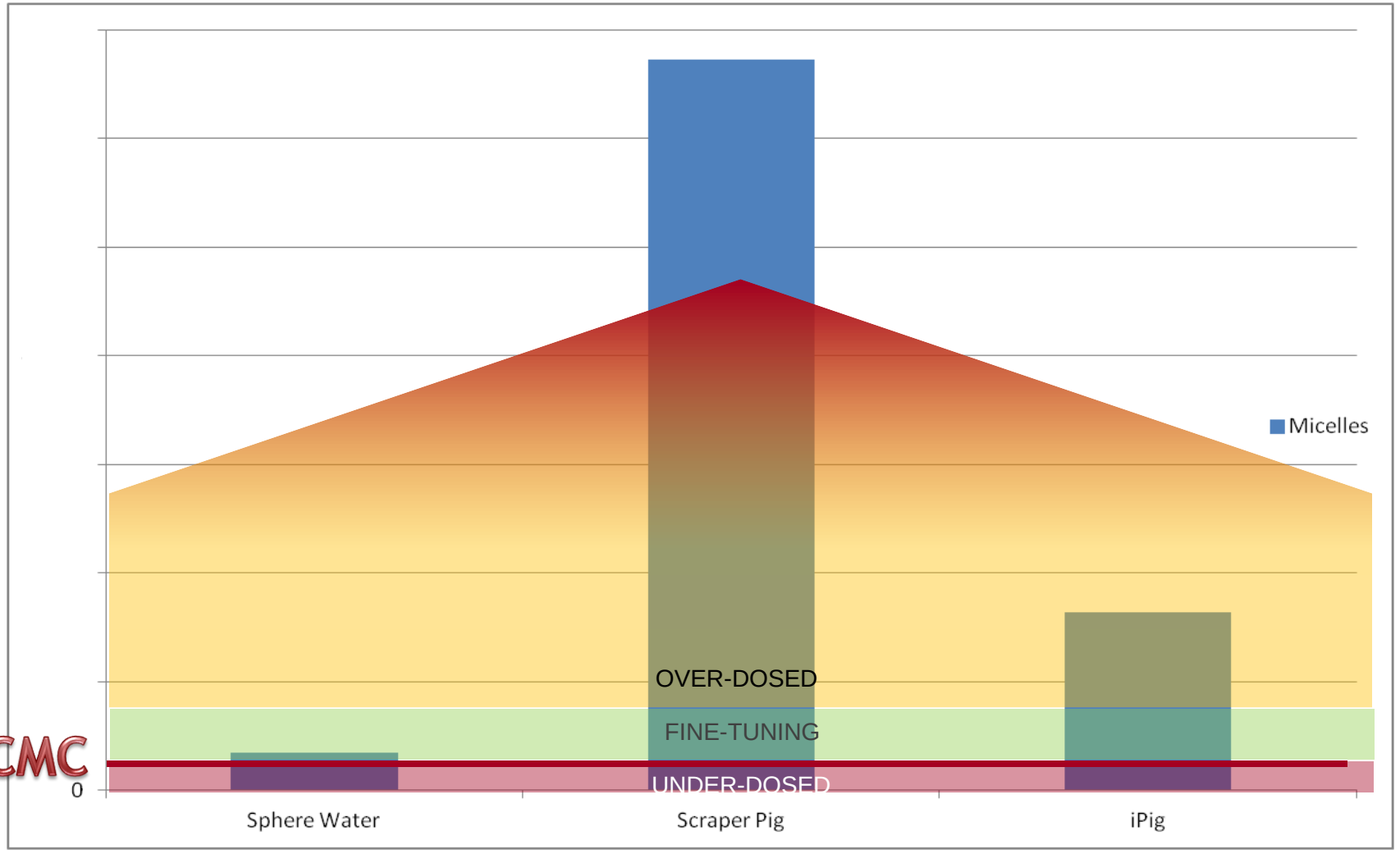
Oil Terminal Results

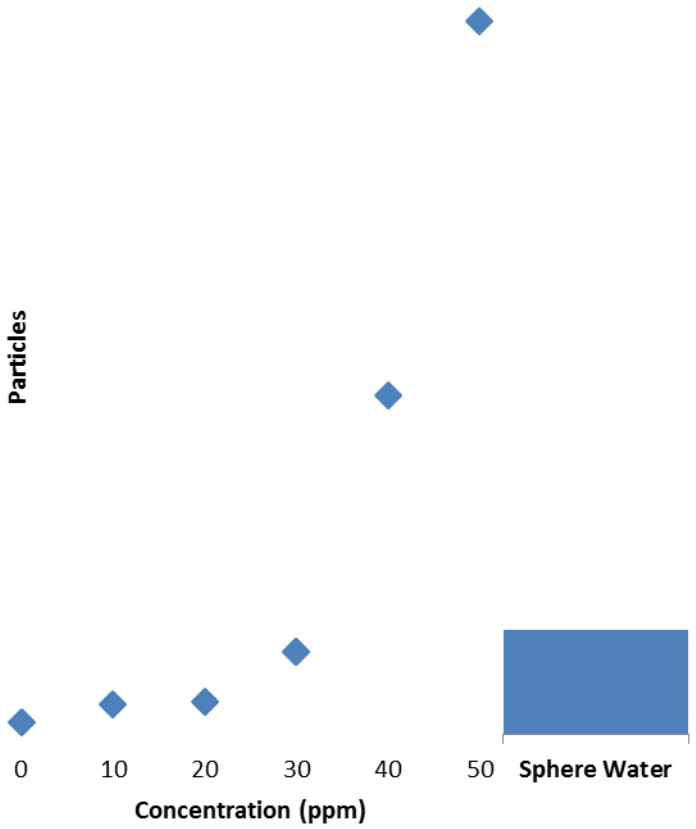


Oil Terminal Results

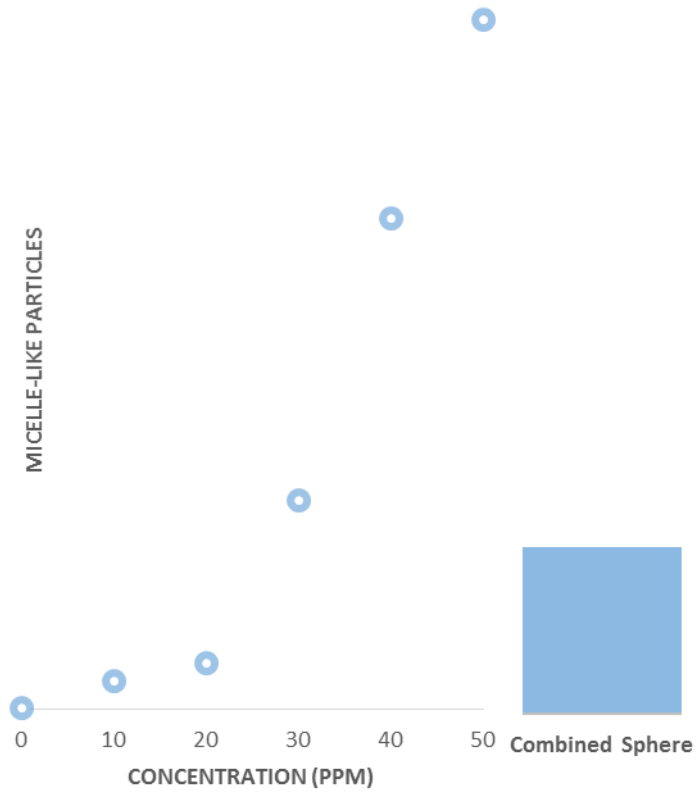


Follow-up (+ 2 years)

- 2011
- 30ppm @ offshore production



- 2014
- 50ppm @ offshore production



4. Offshore Platform - Diagnosis

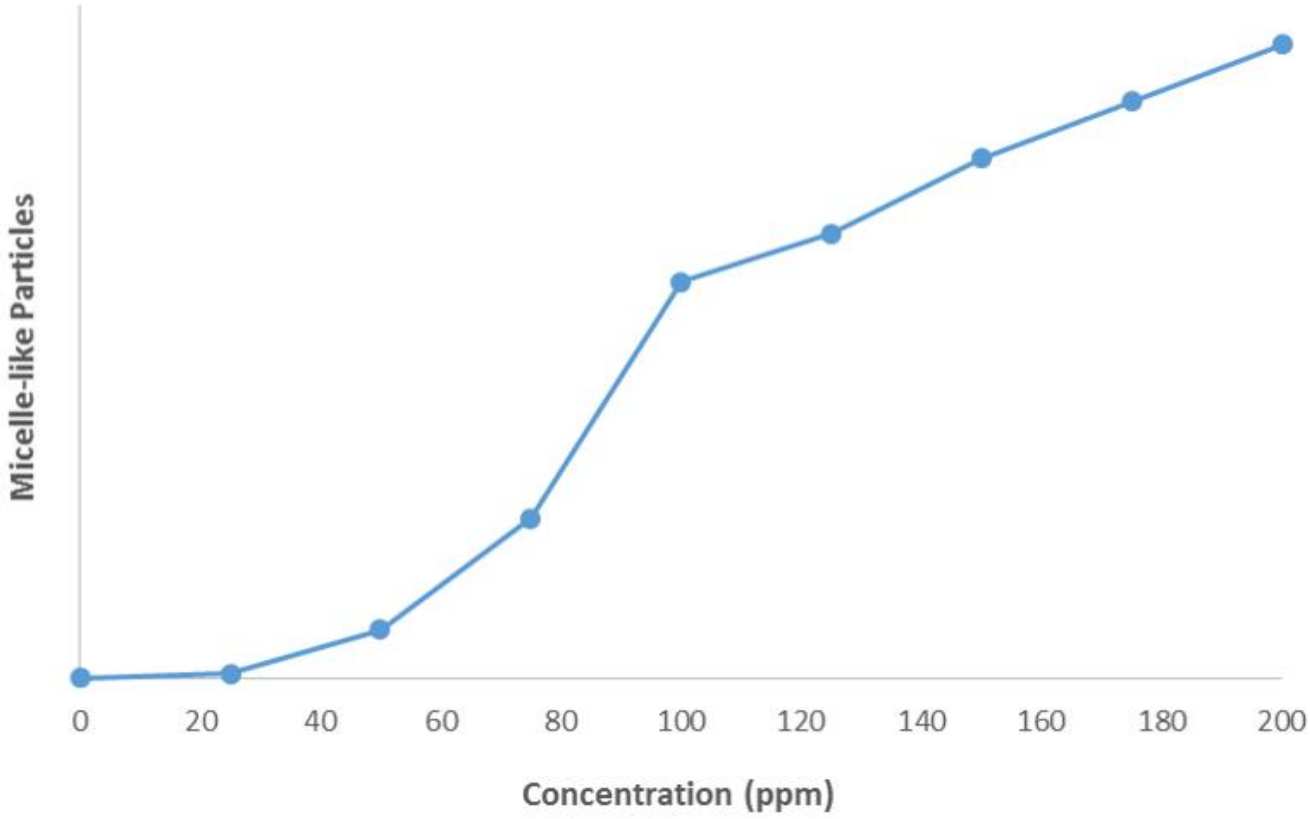
- Subsea tie-back (~25 km), central North Sea
- Lab simulation carried out in advance

- Instrument and personnel sited In platform lab
- Samples taken from separator, hydrocyclone and overboard over 4 days

- Operations confused over inhibitor dosage rate
  - Partitioning assumed

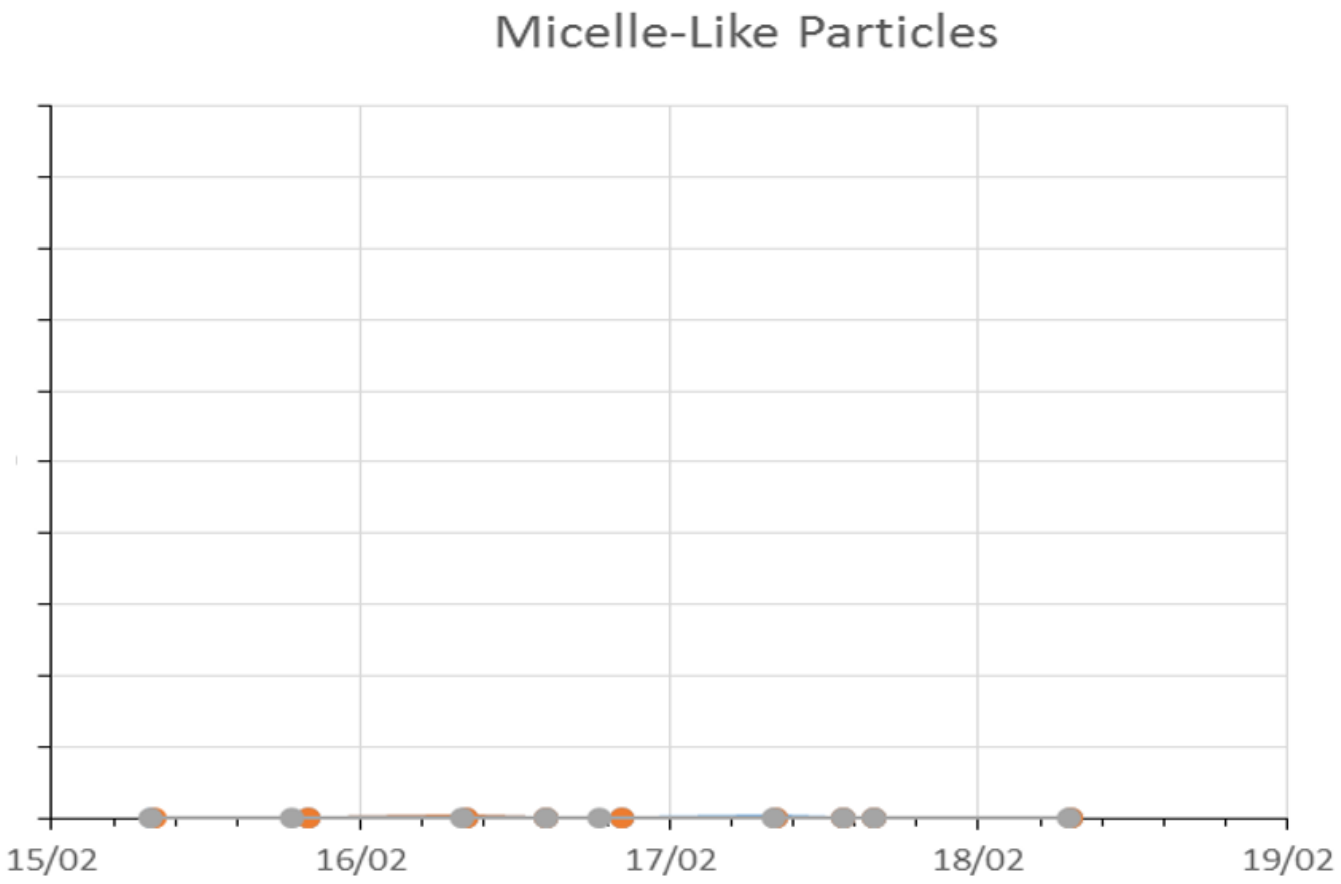
Offshore Platform Results

- Lab simulation showed typical micelle response curve



Offshore Platform Results

- Field samples showed absence of micelles (sub-optimal dosage)



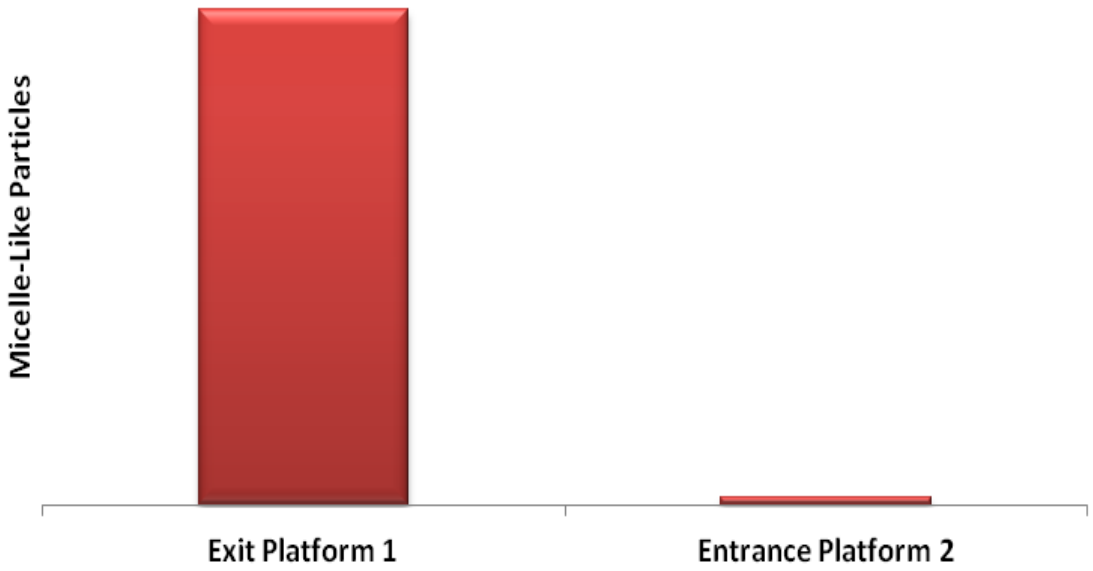
5. Inter-Platform Pipeline Diagnosis

- Short subsea pipeline transferring wet oil from one platform to a neighbouring platform (North Sea)
- Inhibitor added before transport
- Coupons and probe data conflicting

- Micelle analysis performed on fluids entering and exiting the pipeline
  - Data acquisition and analysis performed on-site, near real time

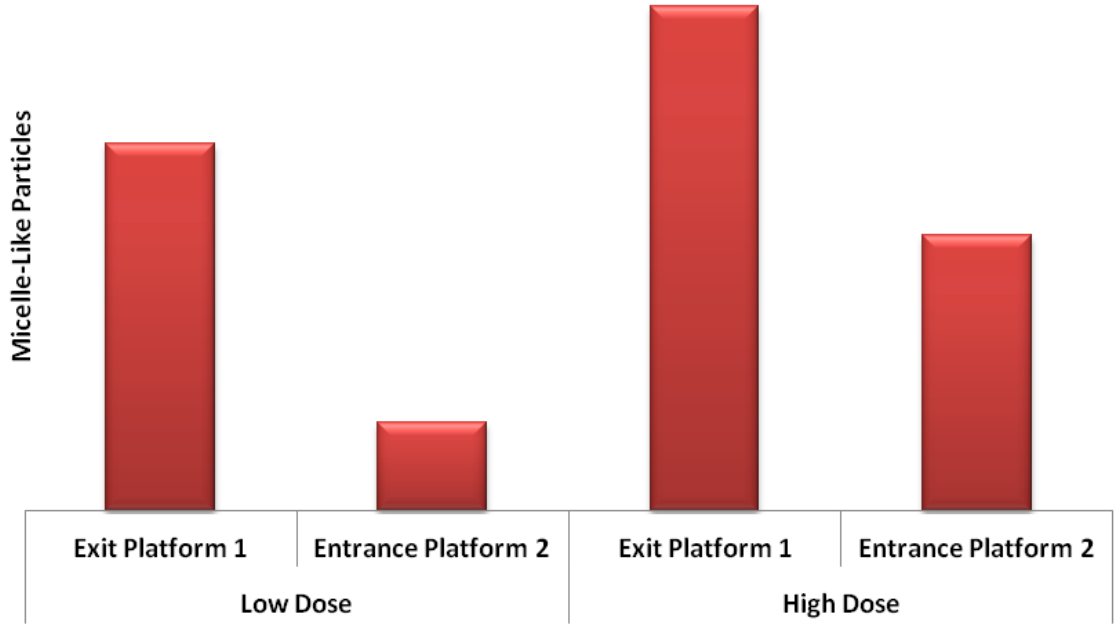
Inter-Platform Pipeline Diagnosis: CI1

- Could observe loss of inhibitor during transit
- Below CMC (sub-optimal) on exit



Inter-Platform Pipeline Diagnosis: CI2

- Follow-up study looking at dosage on new chemical

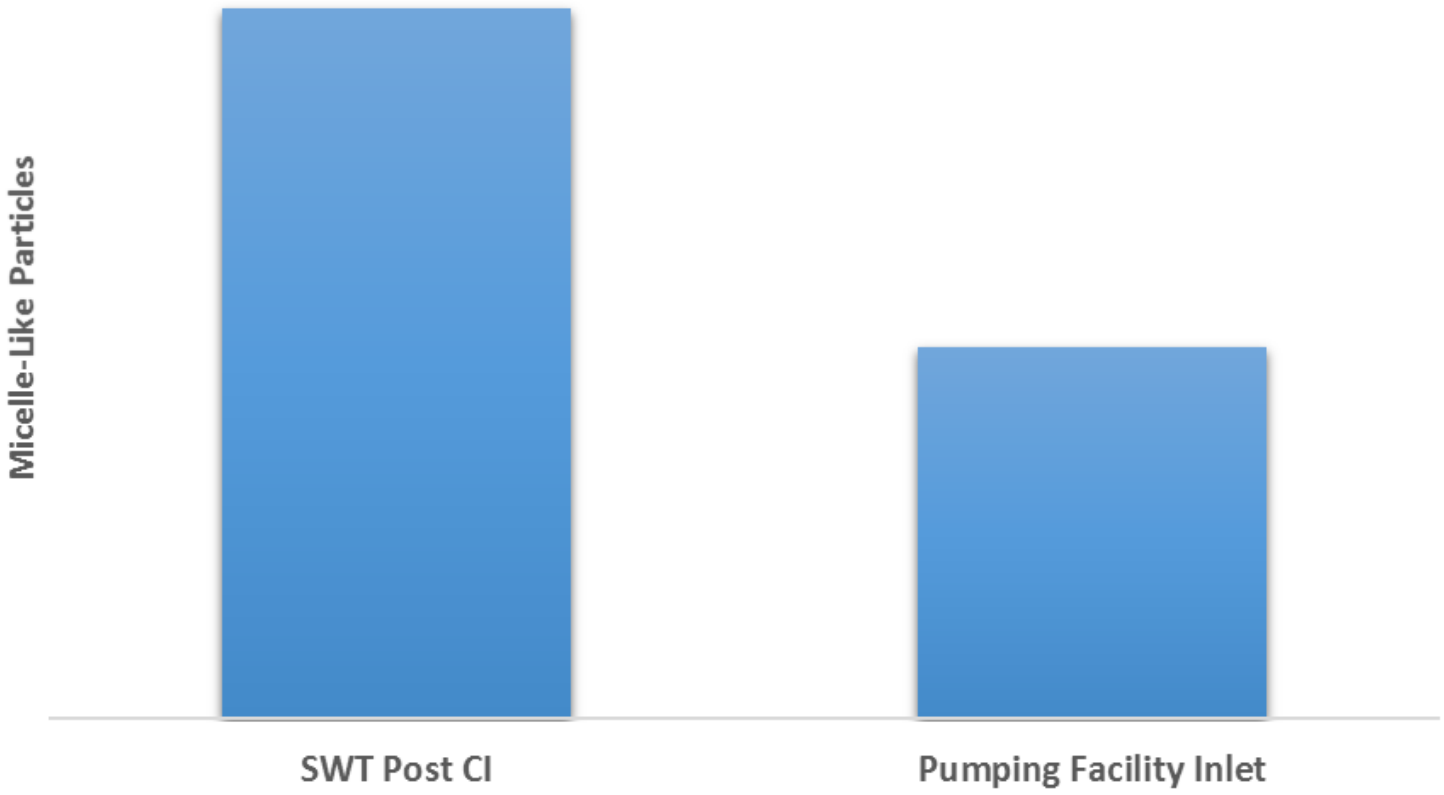


8. Seawater Pipeline

- Middle East onshore oilfield
- Seawater transportation:
  - From seawater treatment facility near shore (CI injected)
  - To water injection facility in oilfield
- CoMic analysis at each end to determine
  - Relative functional dosage
  - Any/extent of CI losses
- Added extra – chemical potency seen to degrade over time when stored under lab conditions

Field Analysis: SW Pipeline

- Good Cl levels at each end
- Potential for reduction



CoMic™ Summary

- CoMic™ is a novel technology for analysing the *in situ* dosage of corrosion inhibitor relative to performance potential
- It is non-invasive, fast, versatile and complementary
- It can provide new and valuable insights from large pipeline networks to simple single point trending

LUX Assure

Q&A

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