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Advanced once-through flow cell methodology for validation of a new ‘staged’ inhibition approach for matrix acidizing treatments

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ICorr Aberdeen
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INSTITUTE OF CORROSION

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Outline

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- Background
  - Matrix acidizing and acid corrosion inhibitors (ACIs)
  - Success of ACIs for inhibition of carbon steel
- ‘Staged’ inhibition approach
  - Background to the staged inhibition approach and motivation for study
  - Existing techniques
- Once-through flow cell for electrochemical evaluation of ACI approach
  - Concept and application in this study
- Staged approach results
  - Control (fixed ACI dosage) experiments vs staged experiments
  - Significance of pre-corrosion

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Authors

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Associate Professor

Introduction: Matrix Acidizing

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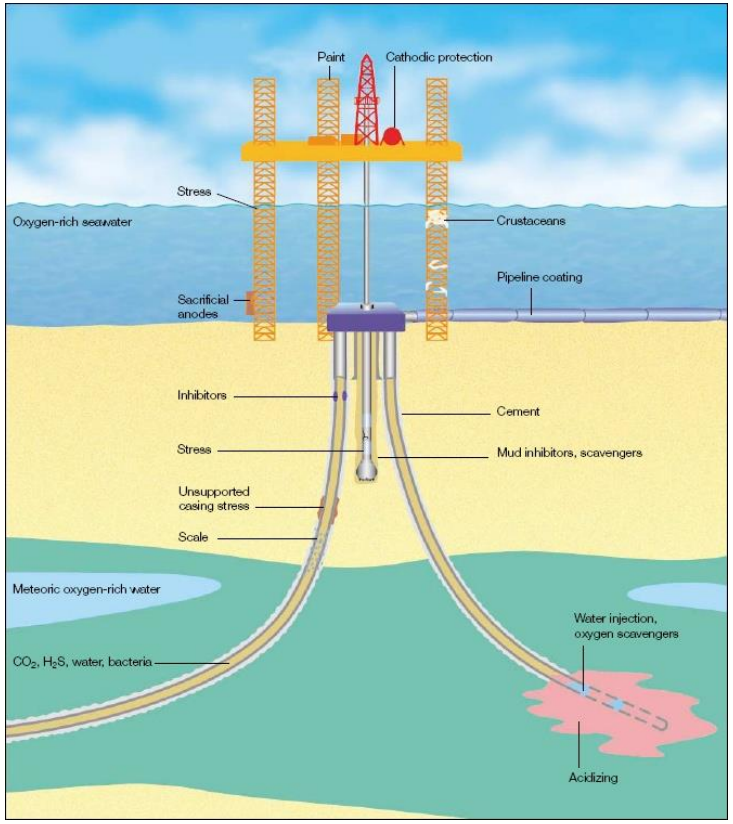


Frenier, W., et al. 1989, Oilfield Review, **15**

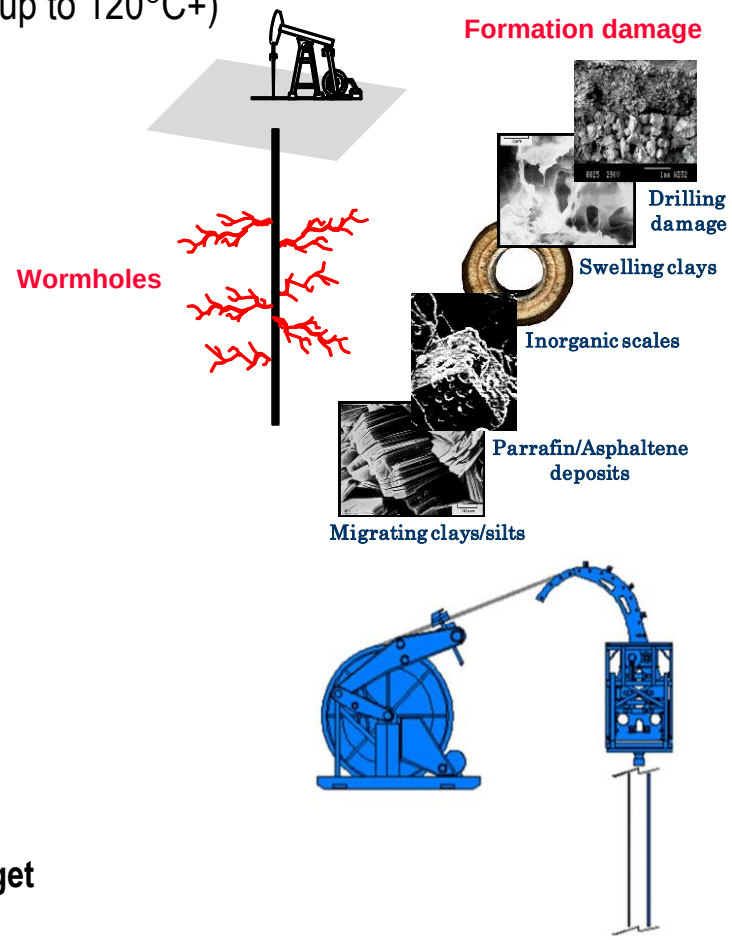
Highly corrosive fluids (10-28 wt.% HCl) & Temperature (up to 120°C+)

3-6 hrs (injection) + 1-2 days (flowback)

Contact with C-steels, low & high alloys

Essential to employ acid corrosion inhibitors (ACI)

Coiled tubing used to inject acidizing fluids directly into target formations to minimise exposure of wellbore casing and completions hardware.



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Corrosion Challenge

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Main corrosion challenges in matrix acidizing environments:

High strength acid: 15% to 28% HCl creates significant corrosion challenge for most metals

Corrosion rates: ~1000 mm/year on uninhibited carbon steel

Corrosion inhibition: acid corrosion inhibitors (ACIs) required in high concentrations to maintain acceptable corrosion rates in high strength HCl environment

Various materials/components effected: HCl delivered through carbon steel coiled tubing (CT), wellbore casing exposed

Flow back: after matrix acidizing procedure, unspent HCl can flow into the well when production restarts. This can impact on sensitive corrosion monitoring equipment

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Acid Corrosion Inhibitors

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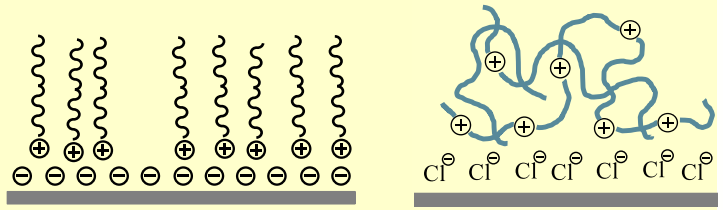
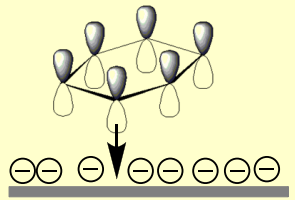
A: Physi-Sorbed



Electrostatic interaction of cationic surfactant with negatively charged surface

Inhibition Efficiency (I.E.) *decreases* with increasing T

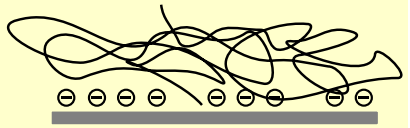
B: Chemi-Sorbed

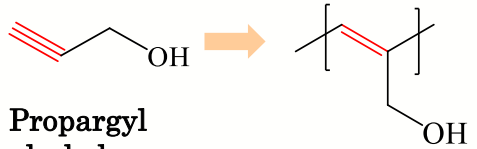


Electron transfer from inhibitor to vacant orbitals in metal: hetero-atoms (N, O, S), aromatic rings, multiple bonds

I.E. *increases* with increasing T

C: Polymerisable





Propargyl alcohol

Chemi-sorption & *polymerization* of inhibitor

Polymerizable inhibitors are enabling:

- in ACIs for high T acidizing;
- for *film persistence* → *Staged ACI concept*

ACI products are mixtures of the above classes in an appropriate liquifying solvent package

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Performance of ACIs

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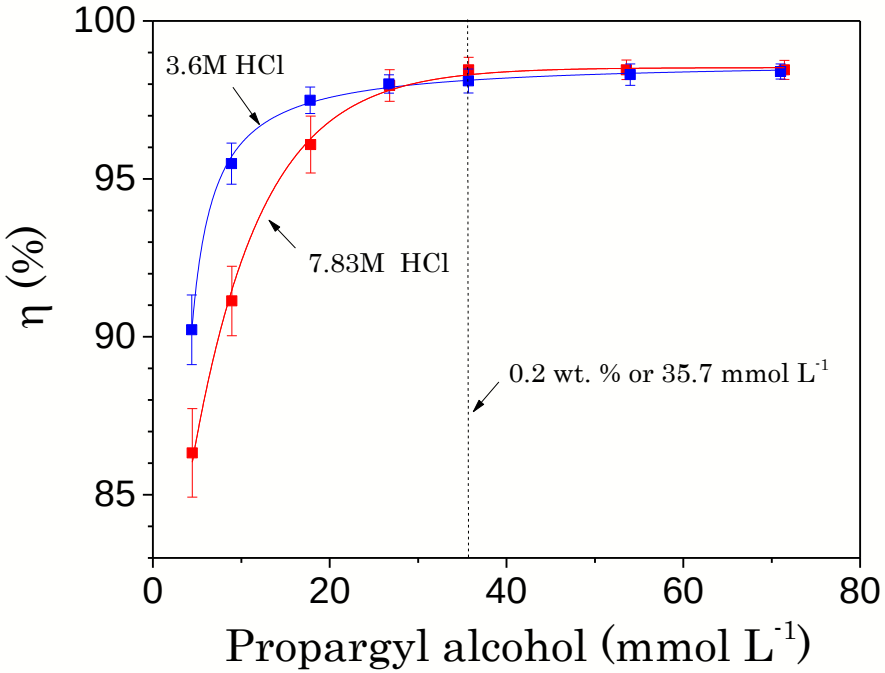
- Typical ACIs are acetylenic alcohol-based, e.g. propargyl alcohol
- Inhibitor efficiency (η) very high in sufficient concentrations
- Formation of film on surface and polymerisation of the film once established
- Previous research indicated **lower ACI concentrations** required for **polymerisation stage**

1 hr, static test, 80 °C, carbon steel



Barmatov, E. et al. (2021). Materials Chemistry and Physics, **272**. p: 125048

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Staged ACI Approach

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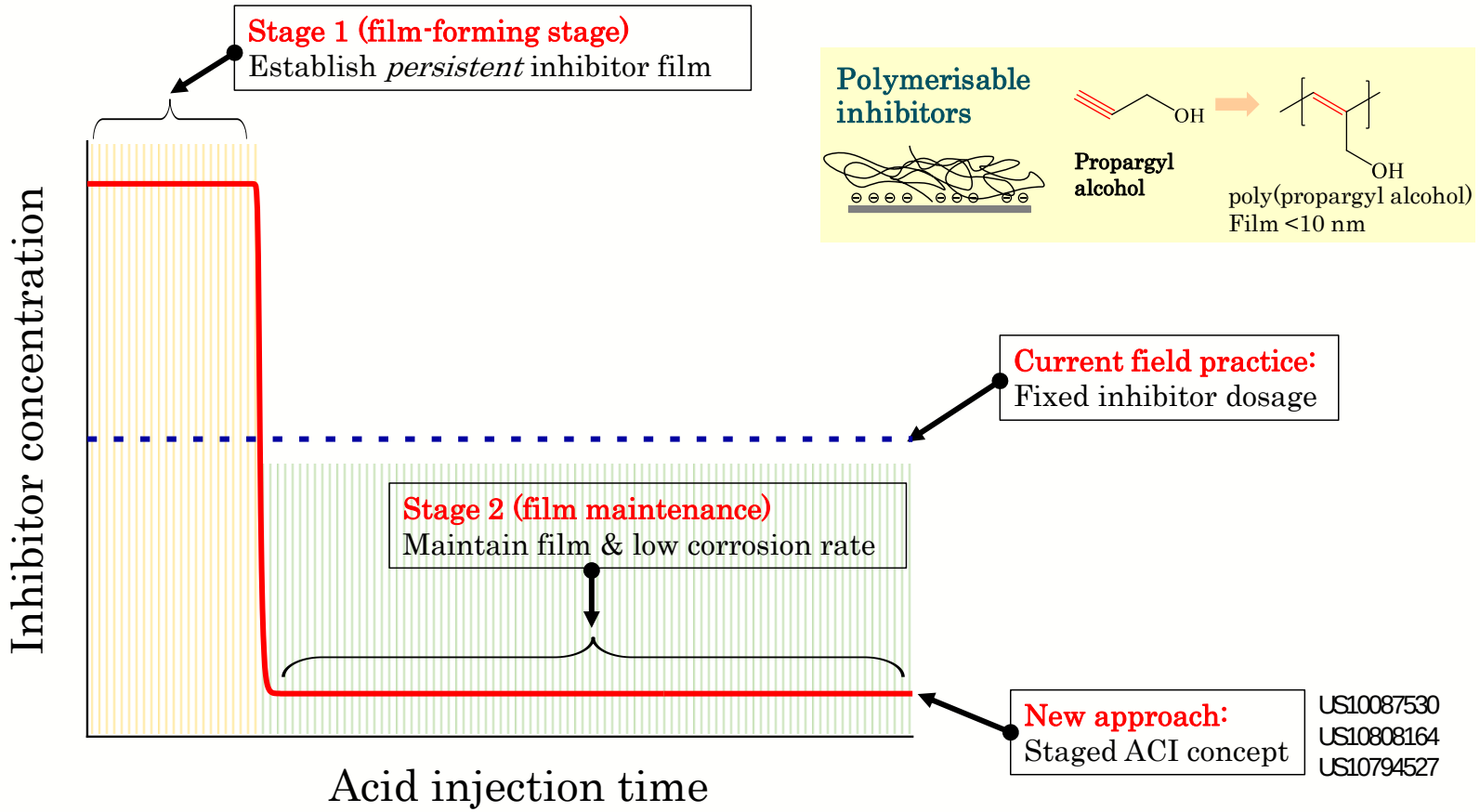

Aim: to maintain low corrosion rates despite significantly reducing inhibition concentration once a persistent inhibitor film established

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Preliminary Evaluation of Staged Approach

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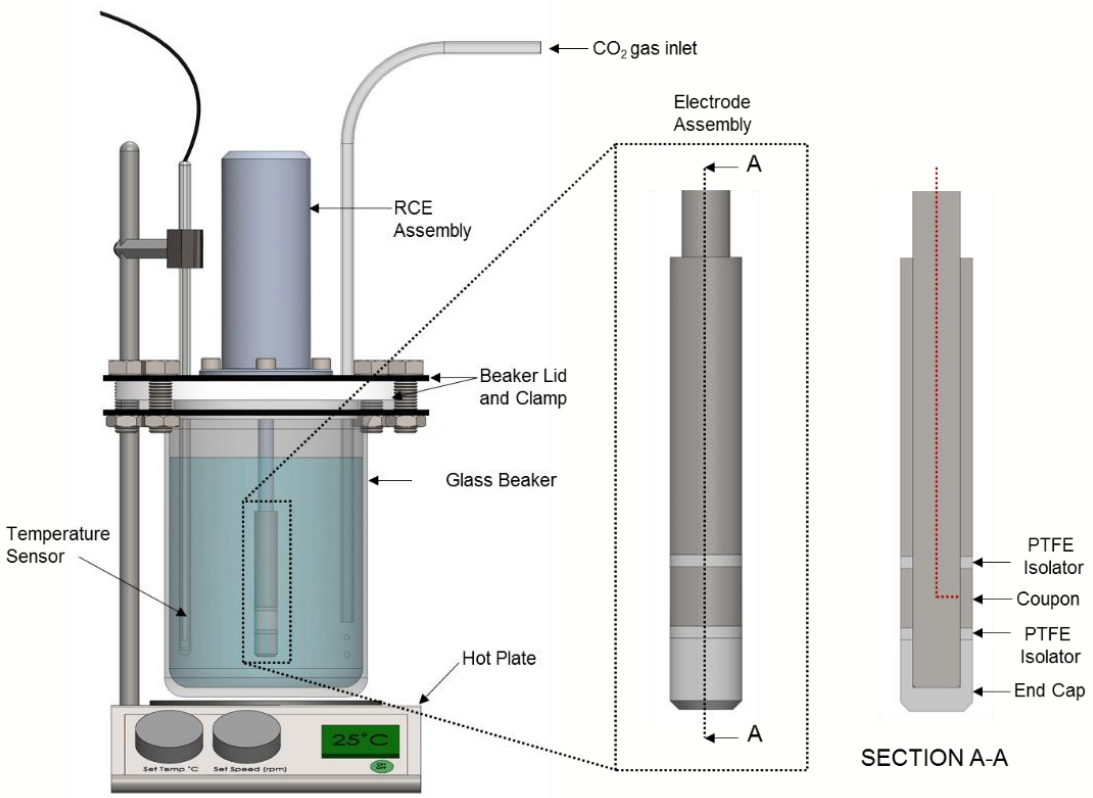

- Initial studies evaluated staged approach using a rotating cylinder electrode (RCE)[1]
- Two beakers containing different concentrations of ACI
- Short (1 hr) **high ACI concentration** film forming stage (**FFS**) followed by longer (3+ hr), **low ACI concentration** film maintenance (**FM**) stage
- RCE shaft with carbon steel coupon transferred between beakers from FFS to FM stage

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[1] Barmatov, E. et al. (2021). SPE-205032, SPE International Oilfield Corrosion Conference and Exhibition

Preliminary Evaluation of Staged Approach

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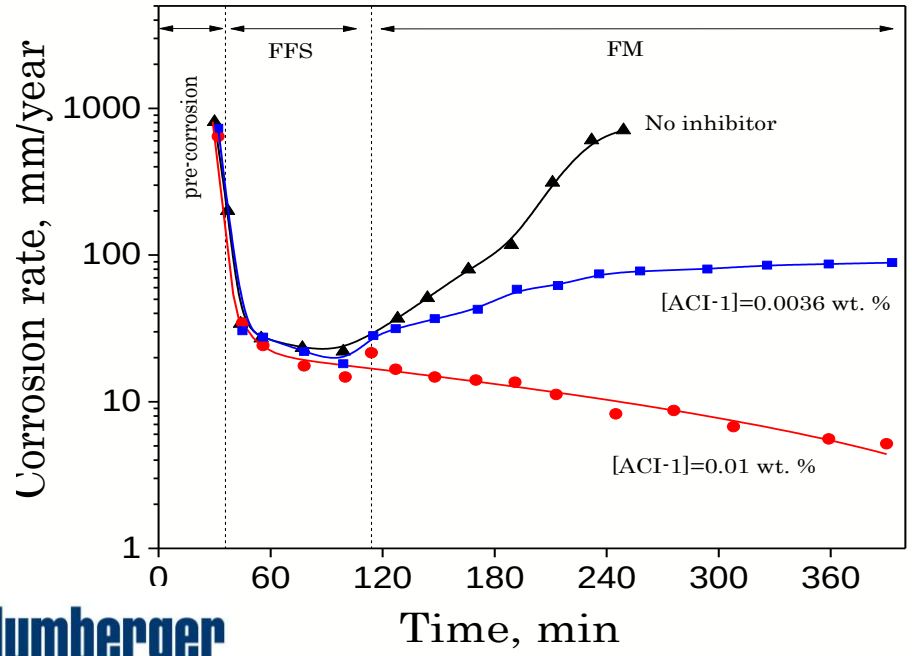
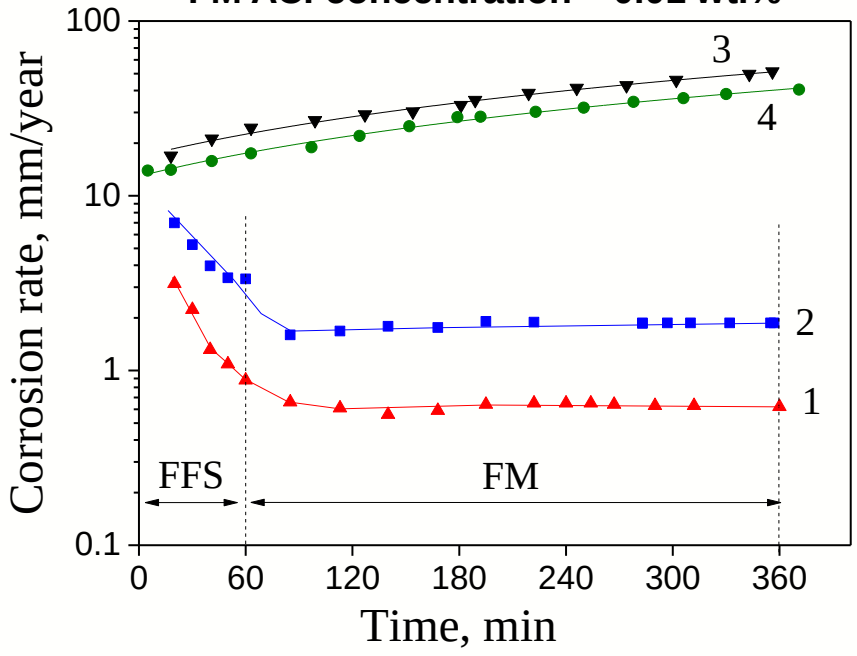
- Evaluation of staged approach in static and hydrodynamic conditions showed success
- FFS ACI concentration = 0.2 wt.% followed by lower ACI concentration FM stage
- ACI concentration in second stage, flow and pre-corrosion have critical influence on staged approach success

Static test, 4 M HCl, 80 °C, HS80 carbon steel



Dynamic RCE test, 4 M HCl, 80 °C, HS80 carbon steel, FM ACI concentration = 0.01 wt.%



1 – staged, 5 rpm
2 – staged, 6000 rpm
3 – control (fixed dose), 5 rpm
4 – control, 6000 rpm

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Preliminary Evaluation of Staged Approach

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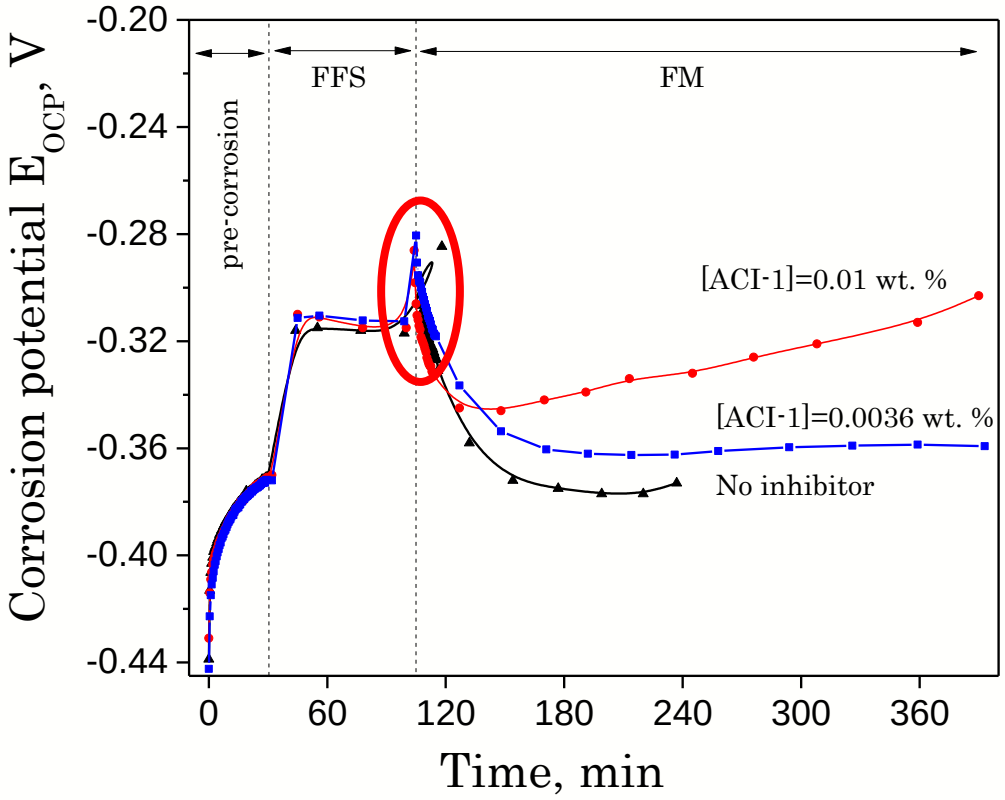
- Coupons (and **ACI film**) were **exposed to air during transfer**
- **OCP increase** observed during the transfer
- **H^+ ions** and **ACI consumed** in the 'closed' system and not replenished (i.e. not representative of application)

In view of above it was decided to evaluate a flow through approach which does not involve transfer from FFS to FM solution.



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Alternative Approach: Once-Through Electrochemical Flow Cell

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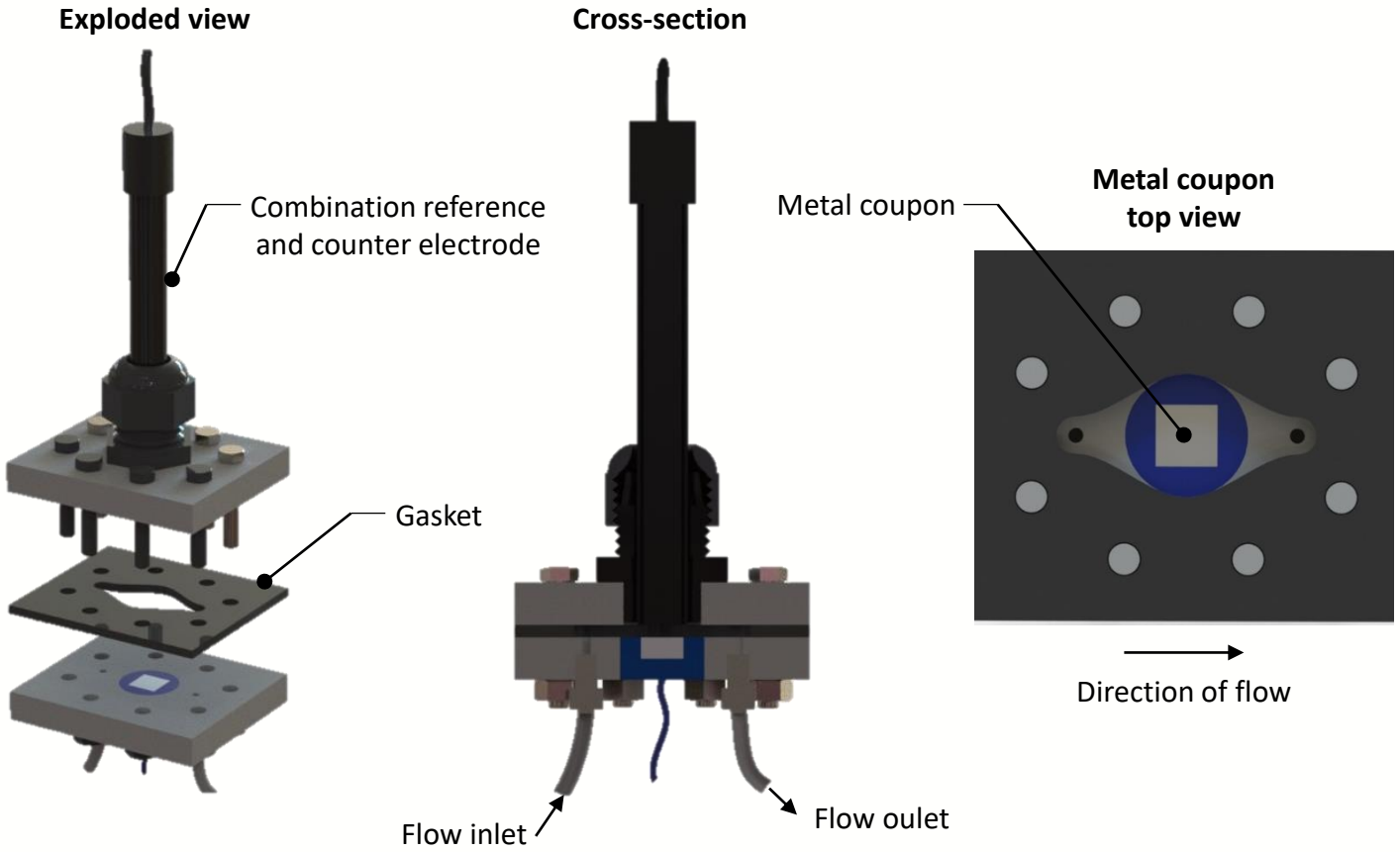

- Once-through flow cell designed by University of Leeds for corrosion studies
- 10 x 10 mm, 5 mm thick metal coupon mounted in cell
- Fluid flows across the coupon and is consistently replenished
- Capable of *in situ* electrochemical measurements

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Alternative Approach: Once-Through Electrochemical Flow Cell

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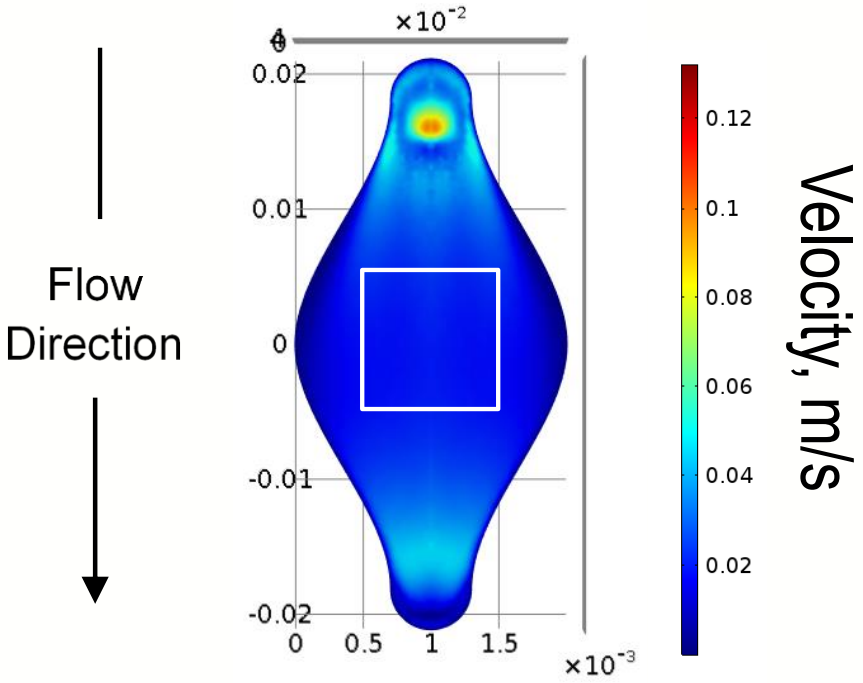
Advantages of the flow cell for application in ACI studies:

- **Well-defined hydrodynamics:** Consistent and predictable flow across metal surface
- **Once-through nature:** Fresh HCl and ACI are continuously replenished and flow into waste, maintaining consistency in experimental conditions throughout
- **In situ electrochemical measurements:** Measurements of corrosion rate in real time
- **Seamless condition changes:** Composition of fluid can be easily changed prior to inflow during an experiment (no exposure of coupon to air)



Barker, R., et al., 2018. *Corrosion Science*, **138**, pp.116-129.

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Leeds/Schlumberger Collaboration

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- EPSRC Impact Acceleration Account funded project

- Aim: to translate research ideas into industrial application

Collaboration between Schlumberger and Leeds to **evaluate staged inhibitor approach using the once-through flow cell**, providing further performance evaluation, prior to industrial application

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Once-Through Flow Cell Methodology

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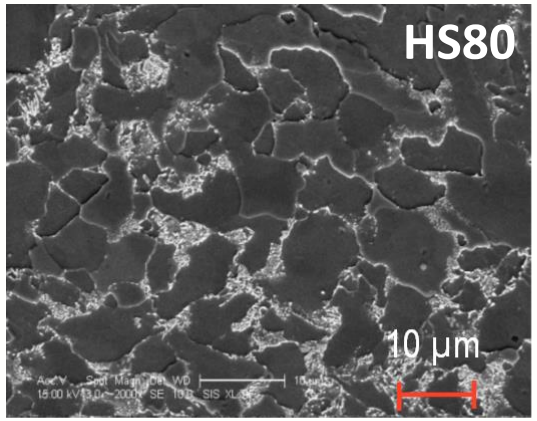
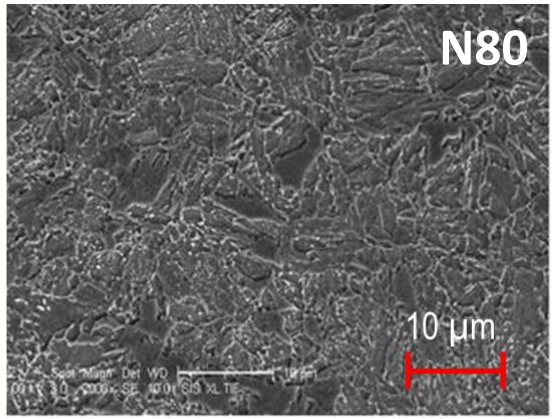
- HS80 (CT) and N80 (casing) carbon steels evaluated
- 80 °C, 4 M HCl, 5 mL/min flow rate (laminar)
- Carbon steel working electrode, Ag/AgCl reference electrode, Pt counter electrode
- LPR measurements (-5 mV vs OCP to + 5 mV OCP, 0.25 mV/s) every 15 min
- Acetylenic alcohol type ACI



(a)



(b)

Steel composition

Steel	C	Mn	P	S	Si	Cr	Cu	Ni	Mo	Fe
HS80	0.10	0.60	< 0.03	< 0.005	0.30	0.45	< 0.40	< 0.25	-	≥ 97.0
N80	0.24	1.19	0.011	0.013	0.22	0.036	-	-	0.018	98.3

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Methodology: Control Experiments

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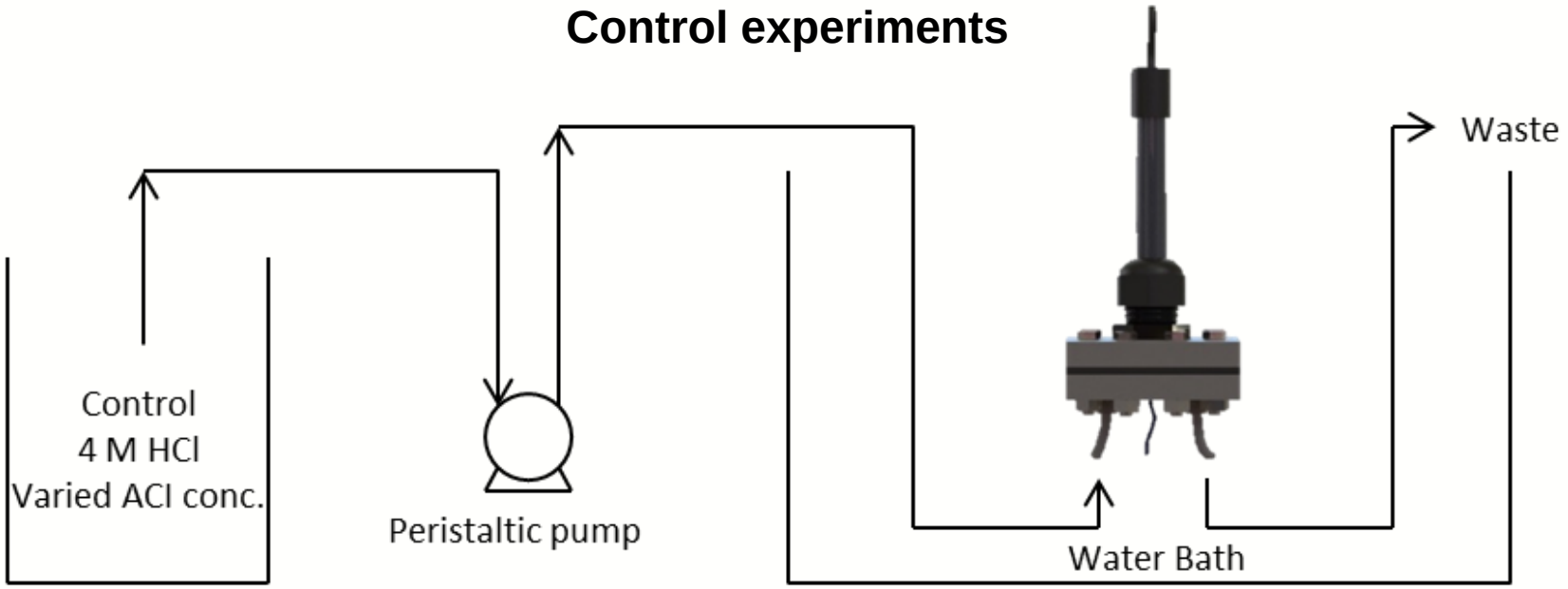
- **Control** experiments using a **fixed ACl concentration** for 4 h (0.2, 0.02, 0.01 and 0.005 wt.%)
- Coupon mounted in flow cell, sealed and immersed in water bath (set to 85 °C)
- Peristaltic pump controls flow rate of HCl and ACI through acid resistant tubing

Control experiments



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Methodology: Staged Experiments

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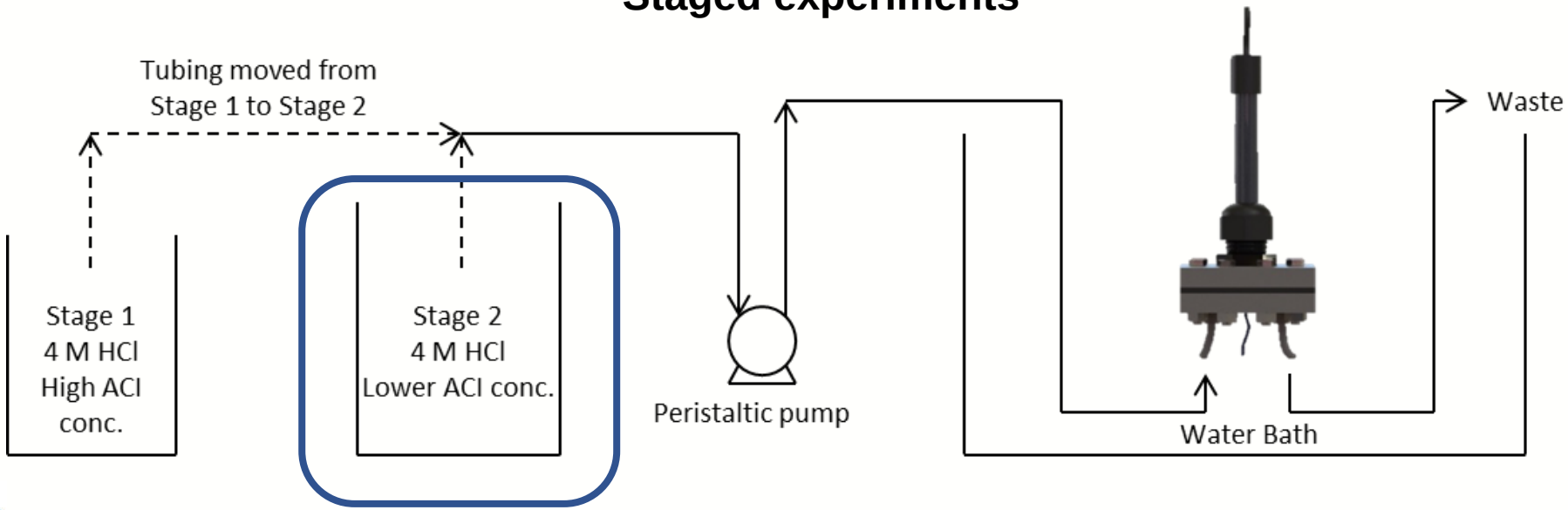
- **Staged** experiments establish a film during **FFS** with ACI concentration of **0.2 wt.% for 1 h**, followed by **FM stage for 3 h** with a **lower ACI concentration** (0.02, 0.01 and 0.005 wt.%)
- After 1 h, pump switched off, tubing removed and cleaned then placed into low ACI concentration solution and pump restarted

Staged experiments



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Results: Control Experiments

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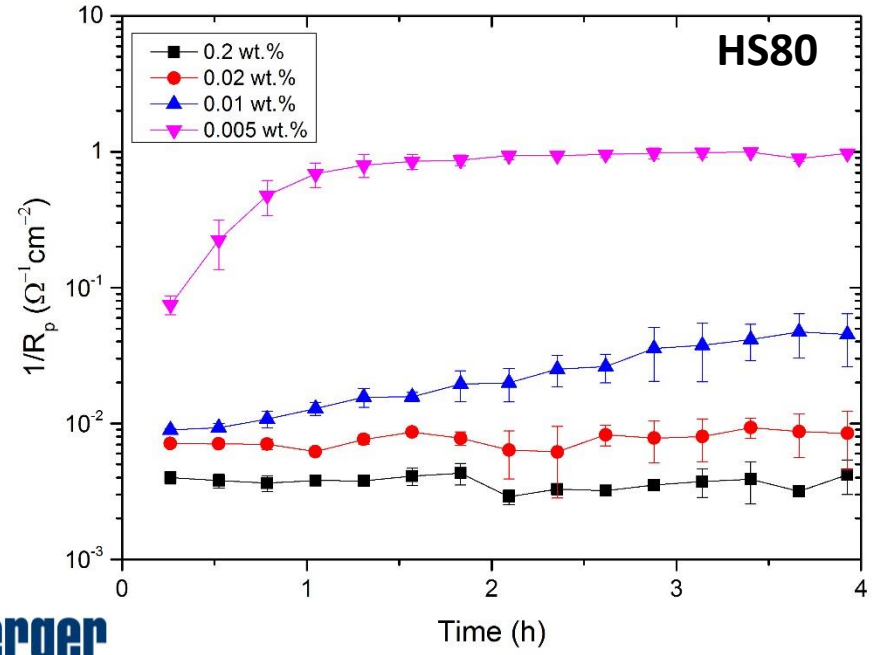
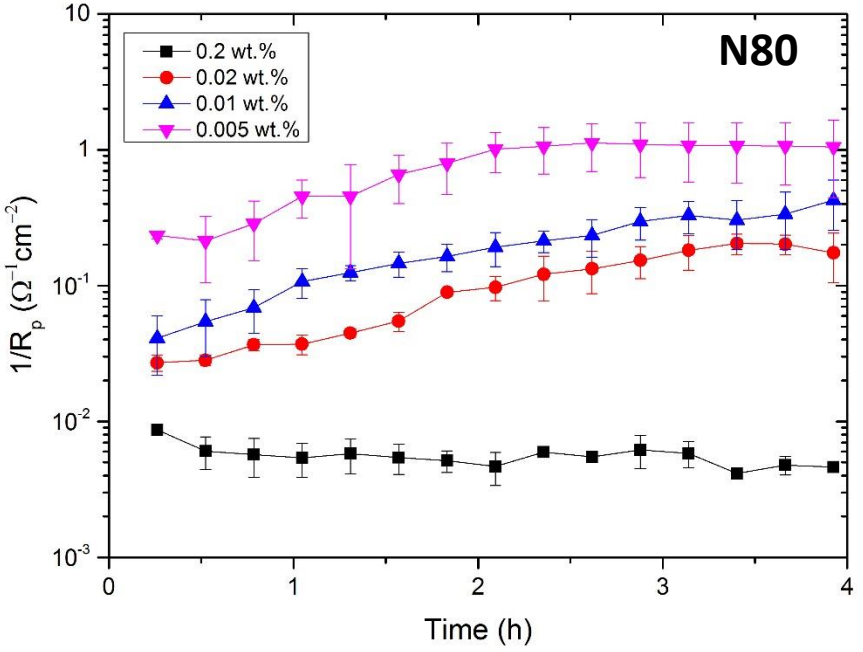
- Plotted as $1/R_p$ (polarisation resistance) vs time – directly proportional to corrosion rate
- Significant decreases in corrosion rate at high ACI concentrations, poor protection at 0.005 wt.%
- Generally higher corrosion rates observed on N80 carbon steel





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Results: Staged Experiments

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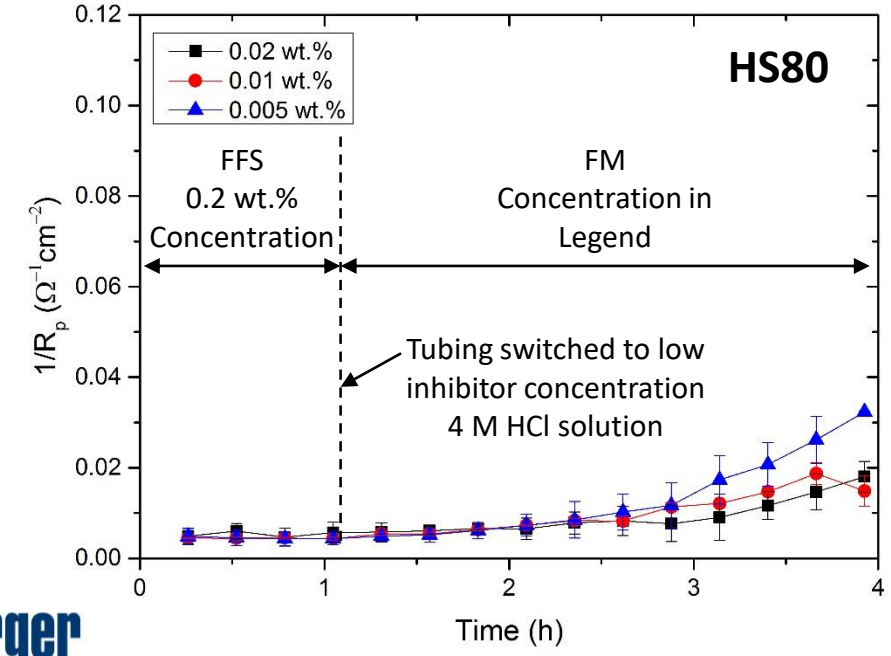
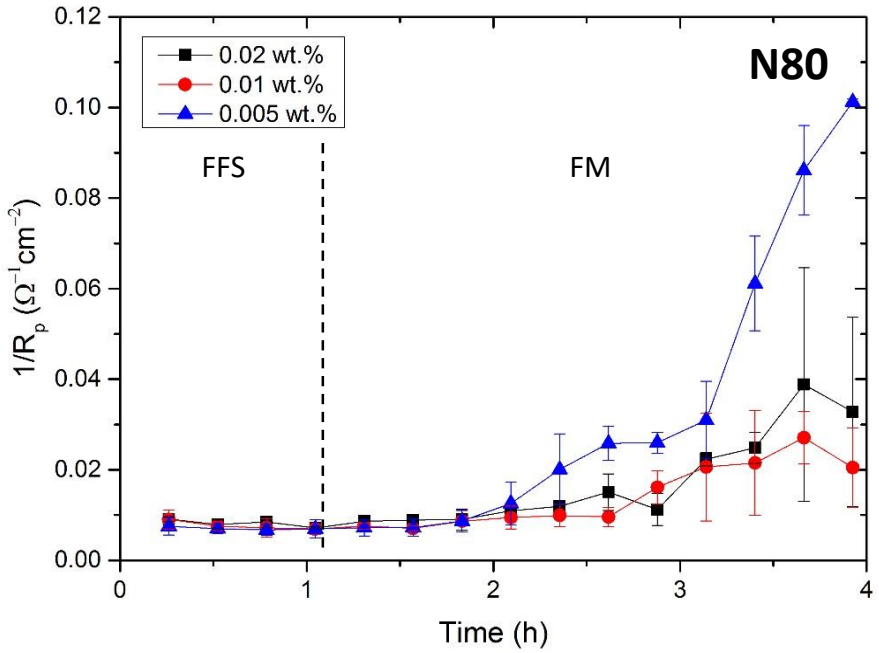
- **All ACI concentrations** in the FM stage **maintained a persistent film** on **HS80**
- For **N80**, **0.005 wt.% of ACI was inadequate** for protection
- Demonstrated success of staged approach in maintaining carbon steel protection at reduce ACI concentration





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Results: Staged Experiments

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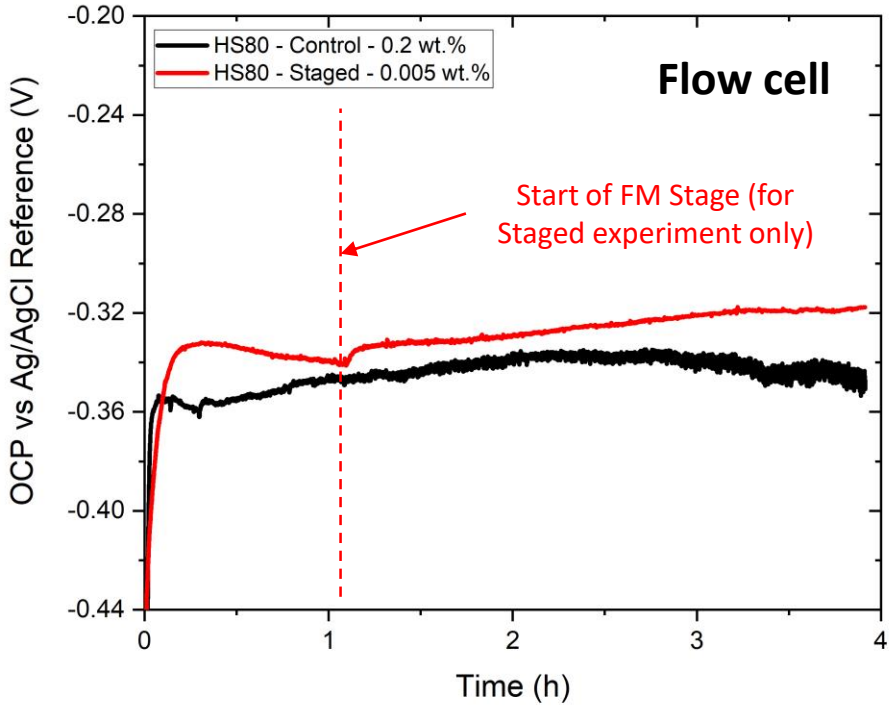
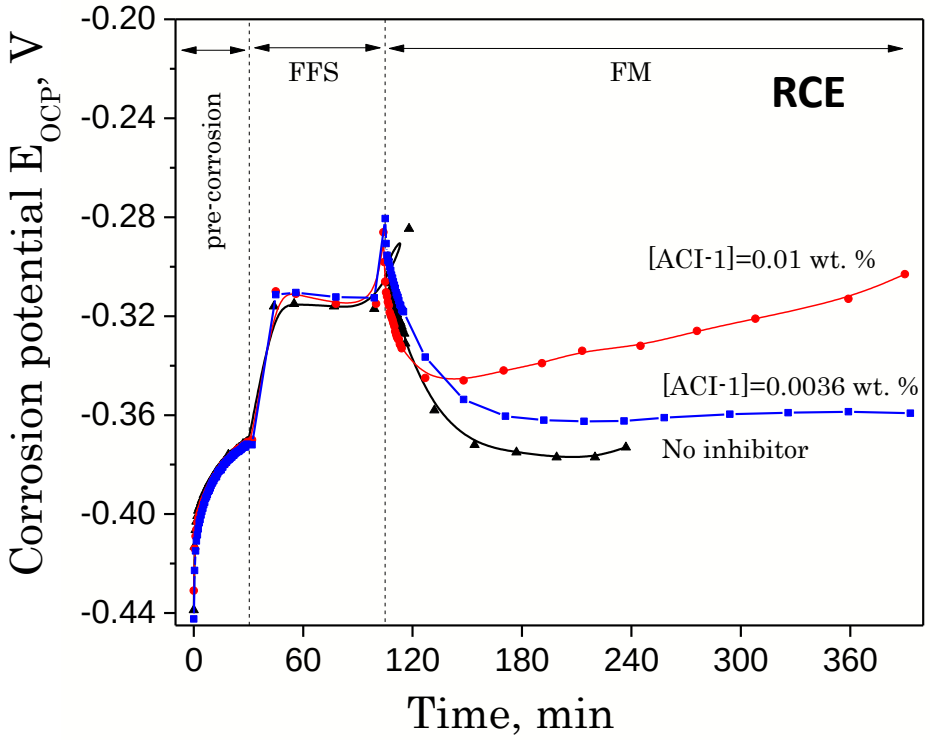
- Change in OCP after switching to the FM stage not significant (compared to RCE)
- Minor change in OCP likely due to lower ACI concentration





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Results: Staged Experiments

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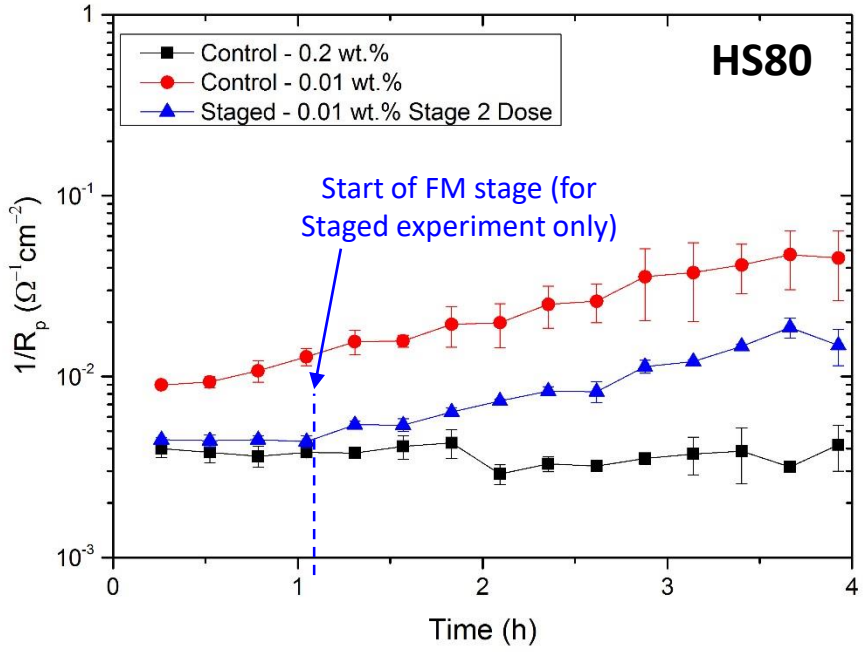
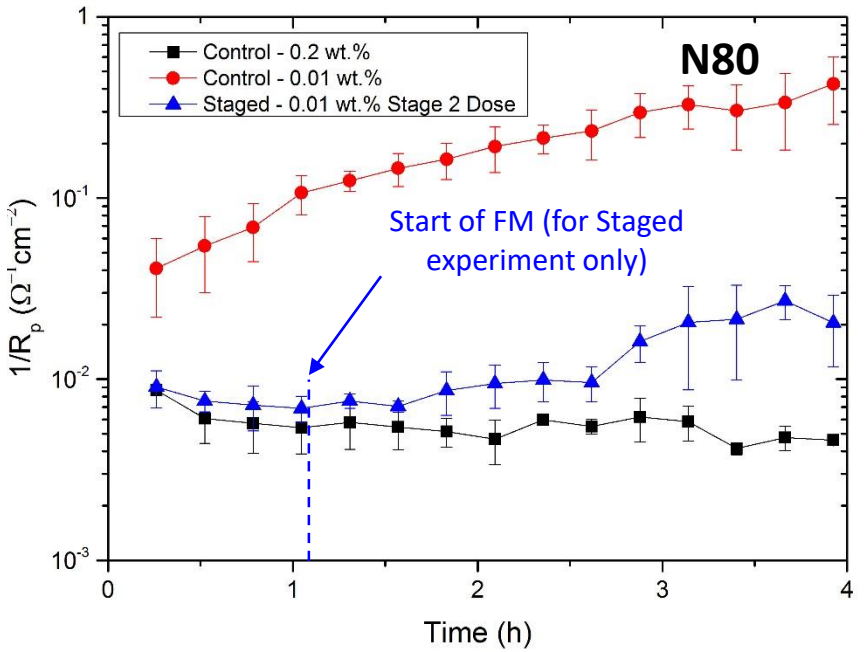
- FM stage ACI concentration of 0.01 wt.% chosen for further analysis (limited by N80 performance)
- Significant reduction in corrosion rate in staged experiments compared to control
- Acceptable staged test corrosion rates compared to 0.2 wt.% control





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Results: Pre-corrosion

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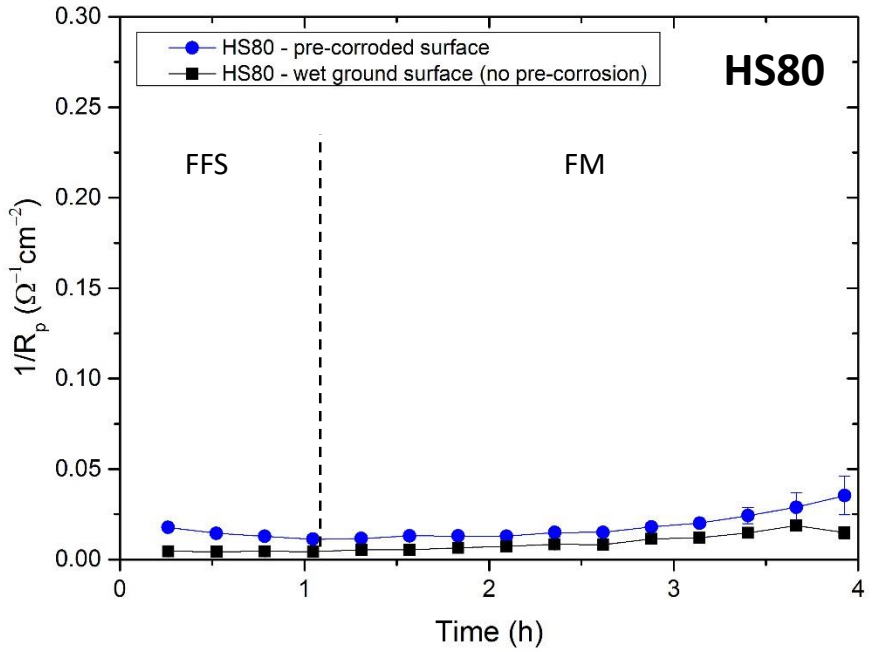
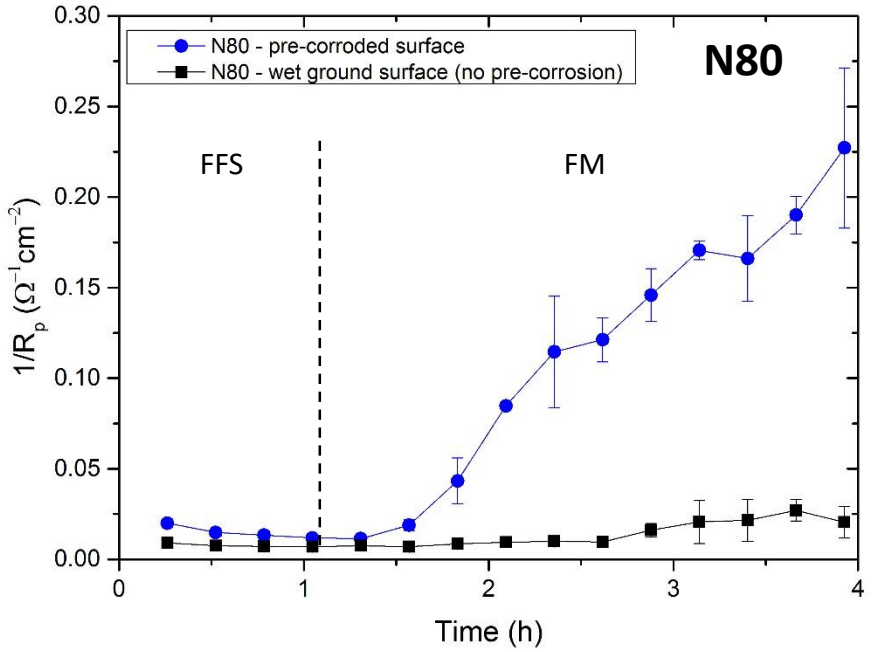
- 10 min of pre-corrosion in uninhibited 4 M HCl before start of FFS
- Significant influence on N80 corrosion rate, but not for HS80





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Results: Pre-corrosion

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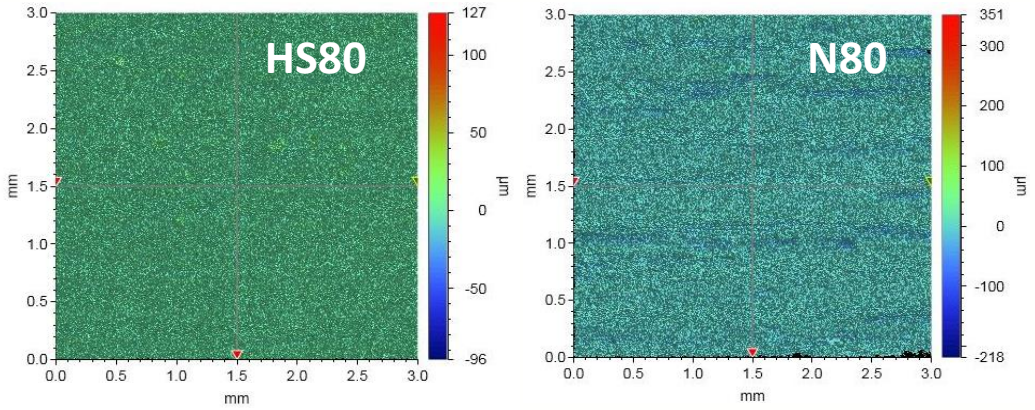
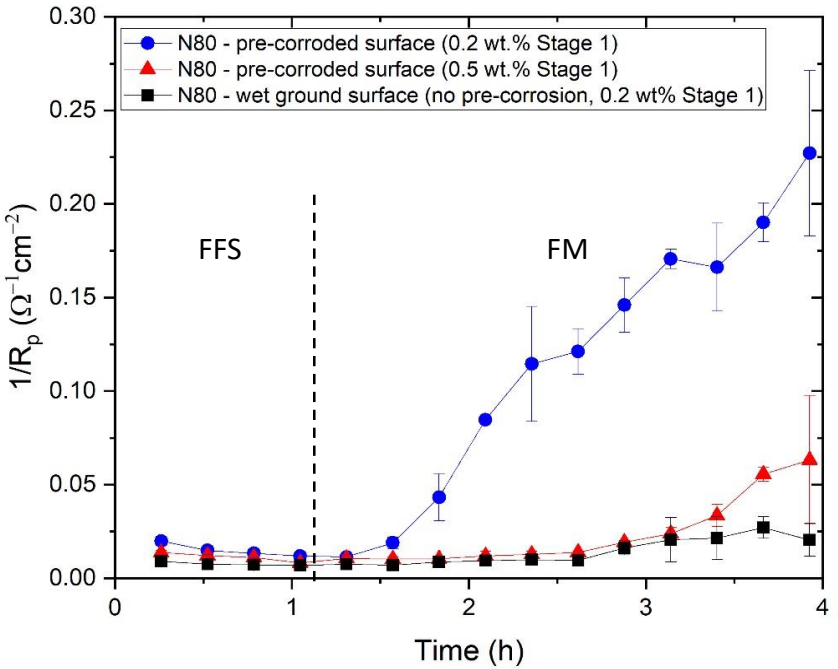
- 10 min pre-corrosion creates larger increase in roughness of N80 compare to HS80
- Increase in FFS ACI concentration for pre-corroded N80 restores good staged performance

Surface roughness, S_a (µm)		
Steel	0 min	10 min
HS80	0.11 ± 0.01	1.23 ± 0.22
N80	0.11 ± 0.01	3.04 ± 0.67





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Conclusions of Staged Approach Evaluation

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- Electrochemical once-through flow cell successful for evaluating staged approach
  - Seamless transition from stage 1 (FFS) to stage 2 (FM) without experimental uncertainty
  - Replenished HCl and ACI maintained experimental control
  - Design enabled LPR measurements *in situ* to evaluate ACI performance
  - Flexibility to evaluate different concentrations of ACI
- Protective film was maintained in staged approach
  - 20x reduction in ACI concentration in FM compared to FFS
- The effects of pre-corrosion are metal dependent.
  - Any adverse effects can be suppressed by proper optimization of the FFS dosage.

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Proposed Future of Staged Approach

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- Optimisation of ACI concentration and comparison of alternative ACIs possible using the flow cell for matrix acidizing applications
- Field trials to be completed to evaluate staged approach success and validate lab results
- Other corrosion inhibitors and ACIs in different applications can be evaluated to establish mechanistic understanding of film persistency using the flow cell
- Development of flow cells ongoing at Leeds to extend enable analysis in turbulent flow conditions (currently limited to laminar)

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Acknowledgments

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Thanks for listening

Funding

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EPSRC
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