Safeguarding Amines from Oxidation by Enabling Technologies (FE0031861)

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Point Source Capture — Lab, Bench, and Pilot-Scale Research
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Project Overview

- The project objective is to identify and test promising oxidation mitigation strategies for piperazine (PZ) and other solvents.
- Funding
  - Federal share $2,348,540
  - Cost share $587,058 (PI academic time + TxCMP funds)
- Overall Project Performance Dates
  - BP1: 3/1/2020 – 5/31/2021 (includes 3-month NCTE)
    - Bench-scale
  - BP2: 6/1/2021 – 2/28/2022
    - Bench-scale: HTOR, HGR, ASAP
    - SRP pilot (air/CO_2/0.2 MW)
  - BP3: 3/1/2022 – 2/28/2023
    - Bench-scale
    - NCCC pilot

Three important oxidation mechanisms

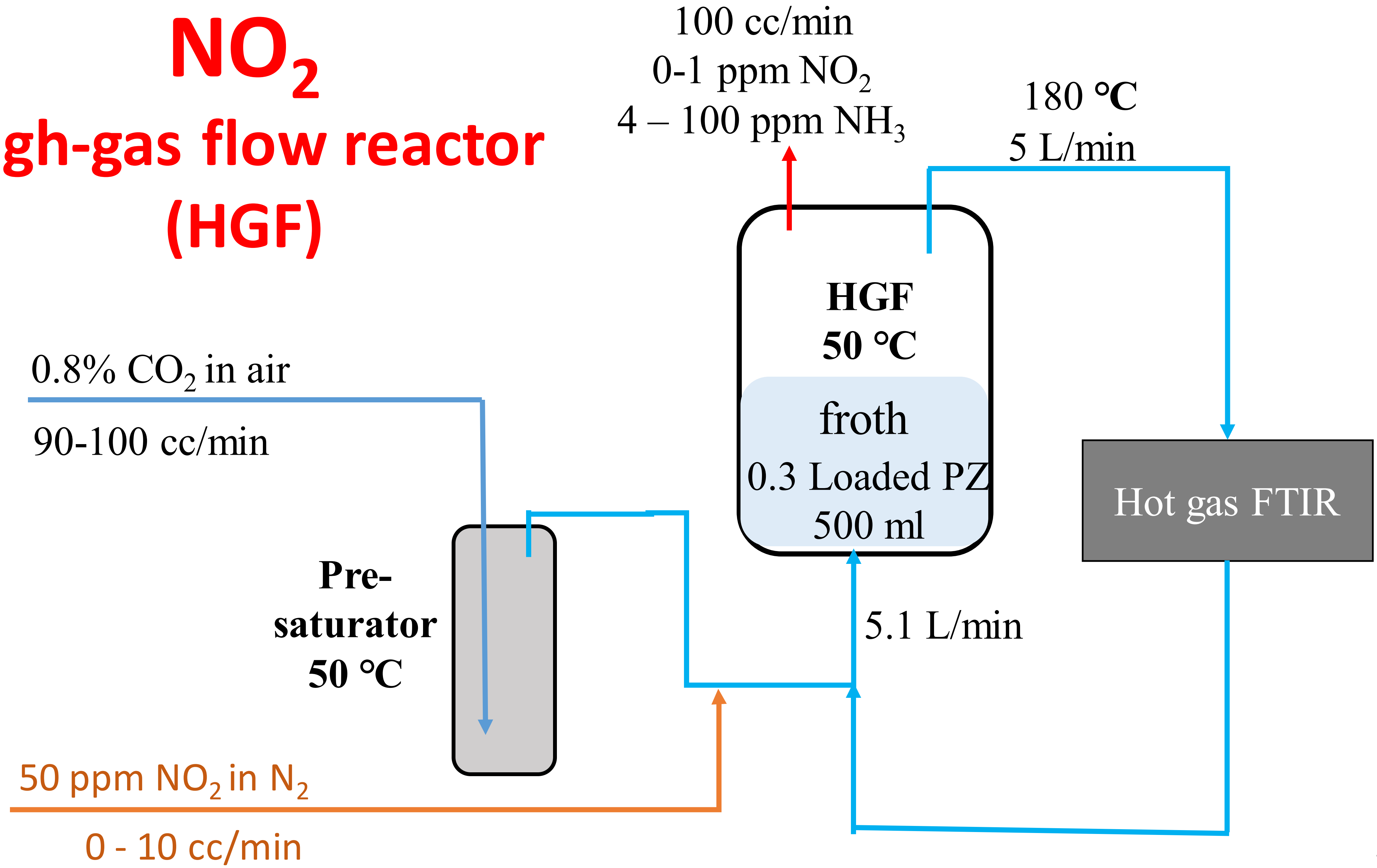
- 1. NO_2 oxidizes all amines at 0.2 to 5 ppm in the flue gas
- 2. Dissolved oxygen oxidizes amines at elevated T before the stripper
- 3. Fe^{+3} oxidizes amines at stripper T and is regenerated from Fe^{+2} in absorber

- Amine selection is an important task of the developers. It will be important as some amines are more resistant to these mechanisms than others.

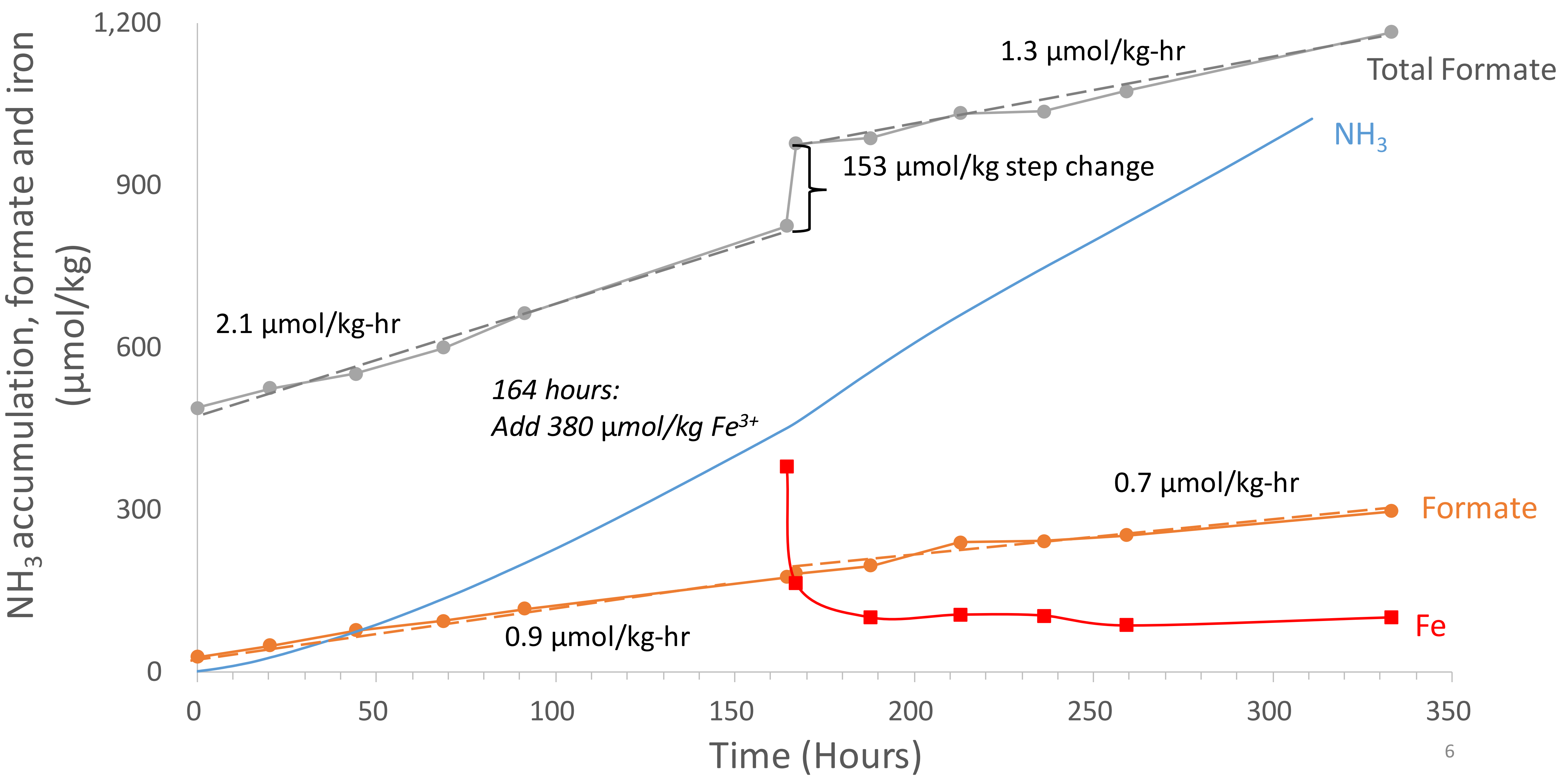
NO_2: Testing to quantify the effects of NO_2

- Does NO_2 have a catalytic effect on amine oxidation?
- Will incremental oxidation be 1-2 mol/mol NO_2 or 5-10 mol/mol NO_2?
  - More likely to see an effect in absence of other mechanisms, but it probably interacts with other mechanism.
  - More likely to be catalytic at lower NO_2
- Measure oxidation with and without 1-5 ppm NO_2
  - Bench-Scale High gas flow reactor [Baseline experiment completed]
    - absorber conditions missing other mechanisms
  - ASAP (Amine screening apparatus) [Commissioning almost complete]
    - Bench-scale absorber /120^{o}C stripper
  - SRP pilot plant campaign, Fall 2021
  - NCCC pilot plant, summer 2022

NO_2
High-gas flow reactor (HGF)



cumulative results 5m PZ from Alfa Aesar (0.3 loading), 50 °C, 0.8% CO_2 in air



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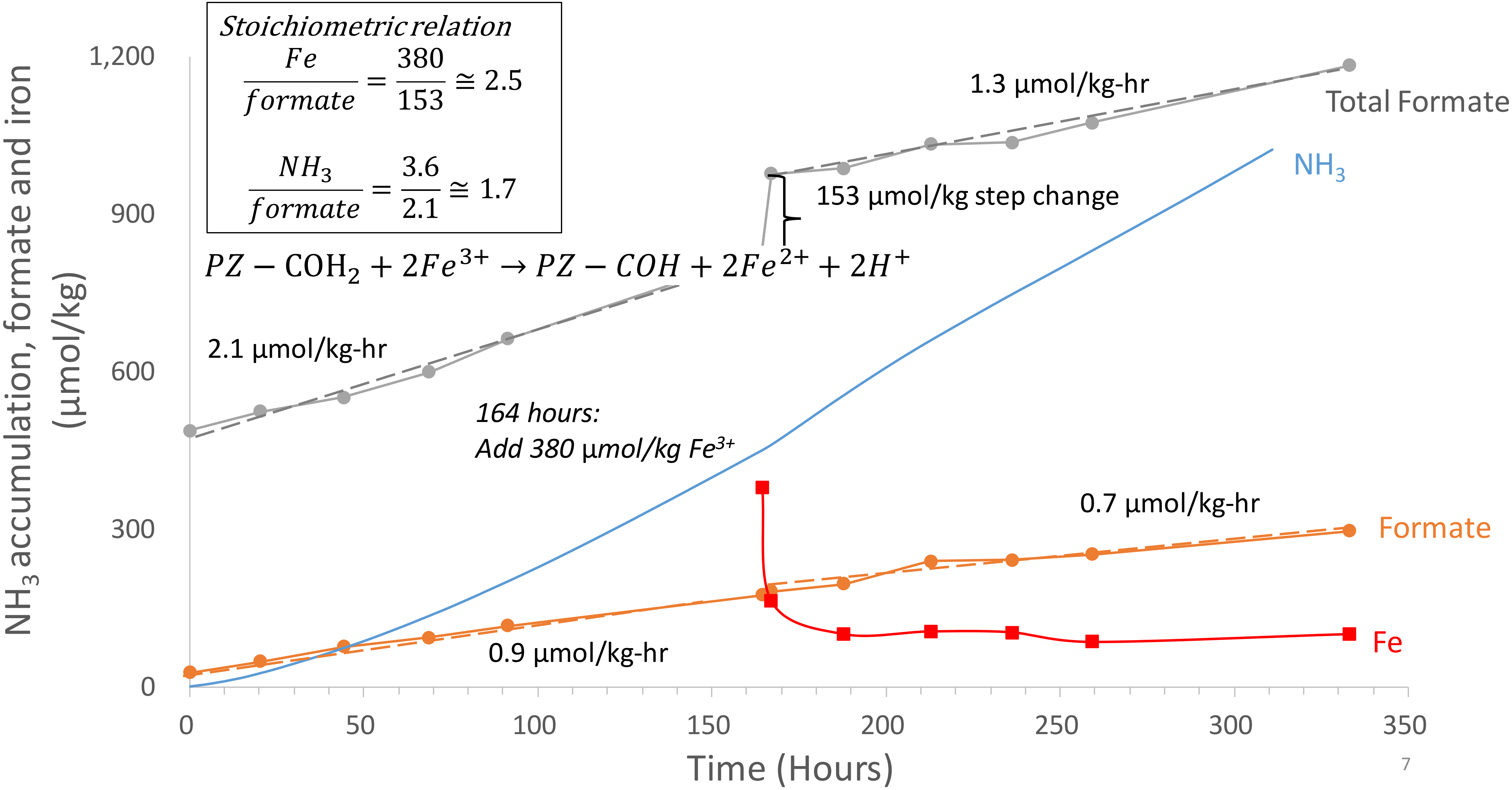
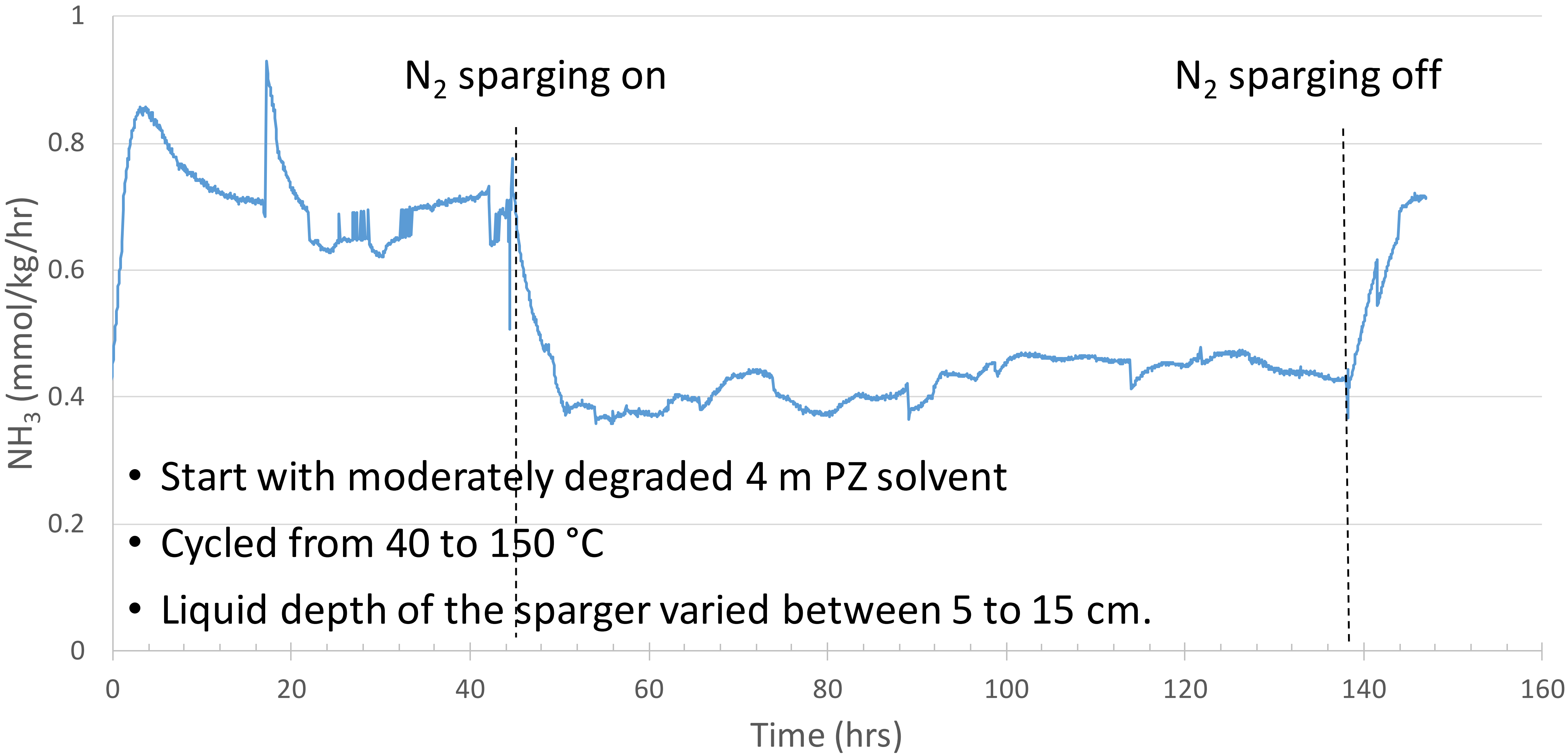


Dissolved Oxygen

- Vary residence time in high T rich line before stripper
  - SRP pilot plant will vary time from <1 s to 40 s [modifications completed]
  - Measure oxygen in product CO_2 at SRP (Fall 2021) and NCCC (Summer 2022)
- Remove DO from rich solvent by N_2 sparging
  - Measure DO in cold rich solvent
- Previous testing in HTOR (High Temperature Oxidation Reactor)
- SRP pilot with N_2 sparging in sump (Fall 2021) [modifications completed]
- NCCC pilot with sparging in sump or new column (Summer 2022
  - Design of sparging column – preliminary results

N_2 Sparging in HTOR Reduces NH_3 Production



- Start with moderately degraded 4 m PZ solvent
- Cycled from 40 to 150 °C
- Liquid depth of the sparger varied between 5 to 15 cm.

N_2 Sparging Model

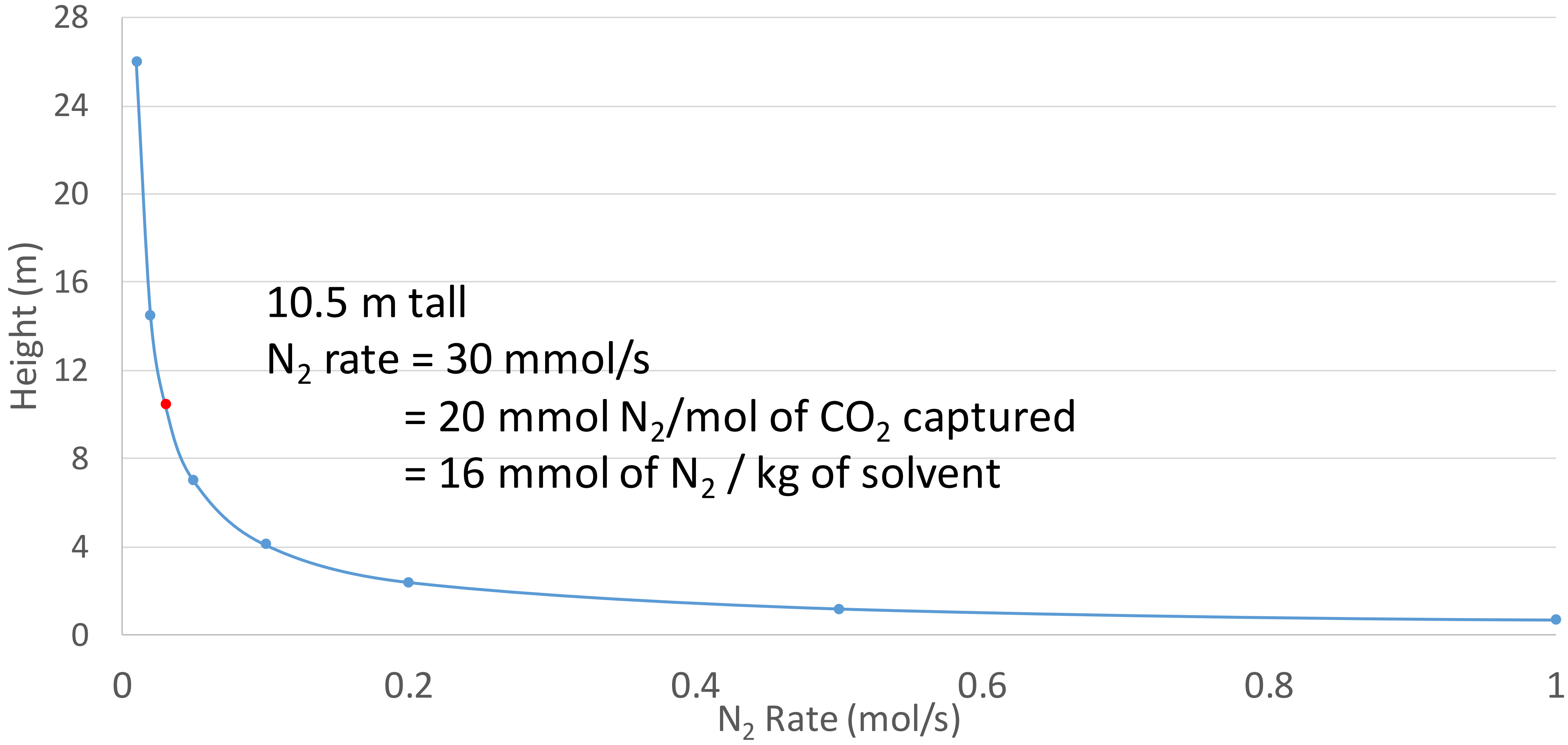
- Mass Transfer in Liquid Phase
- Z = NTU * HTU
- No Back-mixing
- Estimation of K_La were from experiments with batch liquid by Hikita

$$\frac{(k_L a) u_G}{g} = 14.9 \left(\frac{U_G \mu_L}{\sigma} \right)^{1.76} \left(\frac{\mu_L{}^4 g}{\rho_L \sigma^3} \right)^{-0.248} \left(\frac{\rho_G}{\rho_L} \right)^{0.243} \left(\frac{\mu_L}{\rho_L D_{G/L}} \right)^{-0.604}$$

H. Hikita, S. Asai, K. Tanigawa, K. Segawa, M. Kitao. The volumetric liquid-phase mass transfer coefficient in bubble columns. The Chemical Engineering Journal. 22(1).1981: 61-69. https://doi.org/10.1016/0300-9467(81)85006-X.

N_2 sparger design for NCCC

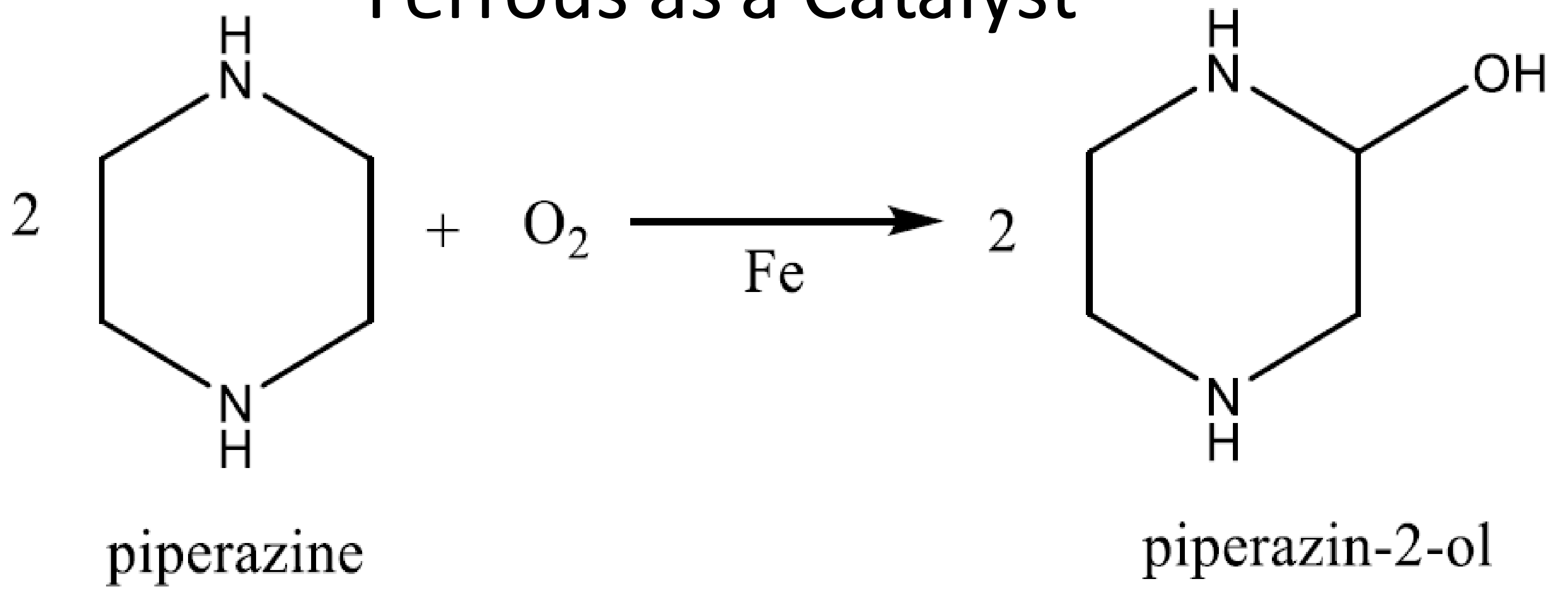
Liquid Rate: 1.89 kg/s (15000 lb/hr), 40 C, 90% DO Removal, CO_2 Capture Rate = 1.26 mol/s, D = 0.1 m so that liquid velocity is equal to bubble rise velocity



Fe^{+2}/Fe^{+3}

- Measure Fe^{+2} and Fe^{+3} solubility as function of degradation [in progress]
- Measure Fe^{+2} and Fe^{+3} in solvent
- Adsorb dissolved Fe on activated C
  - NCCC 2018-19
  - Niederaussem 2021
  - HTOR 2021-22
  - Bench-scale experiments 2021
  - SRP pilot 2021
  - NCCC pilot 2022
- Measure corrosion with PZ solutions: a source of soluble Fe

Ferrous as a Catalyst

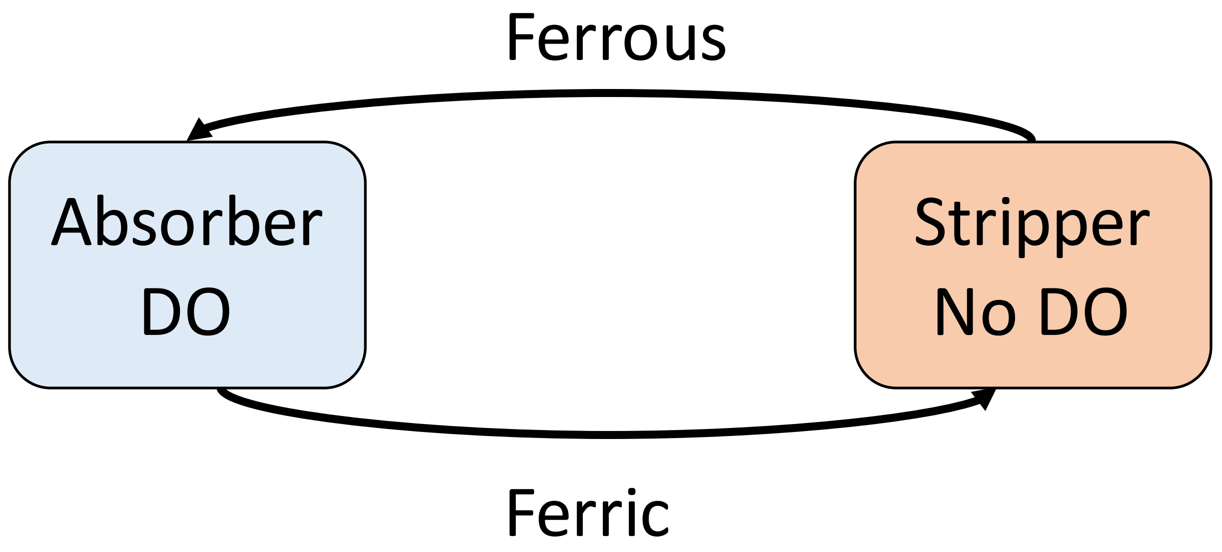


- Fe increases the rate of oxidation of many amine solvents
- Work on MEA focused on oxidation in the absorber
- Ferrous can catalyze a free radical reaction between MEA and O_2
- Possible reaction pathway for PZ also
- In the absence of O_2, Fe still speeds up oxidation. How?

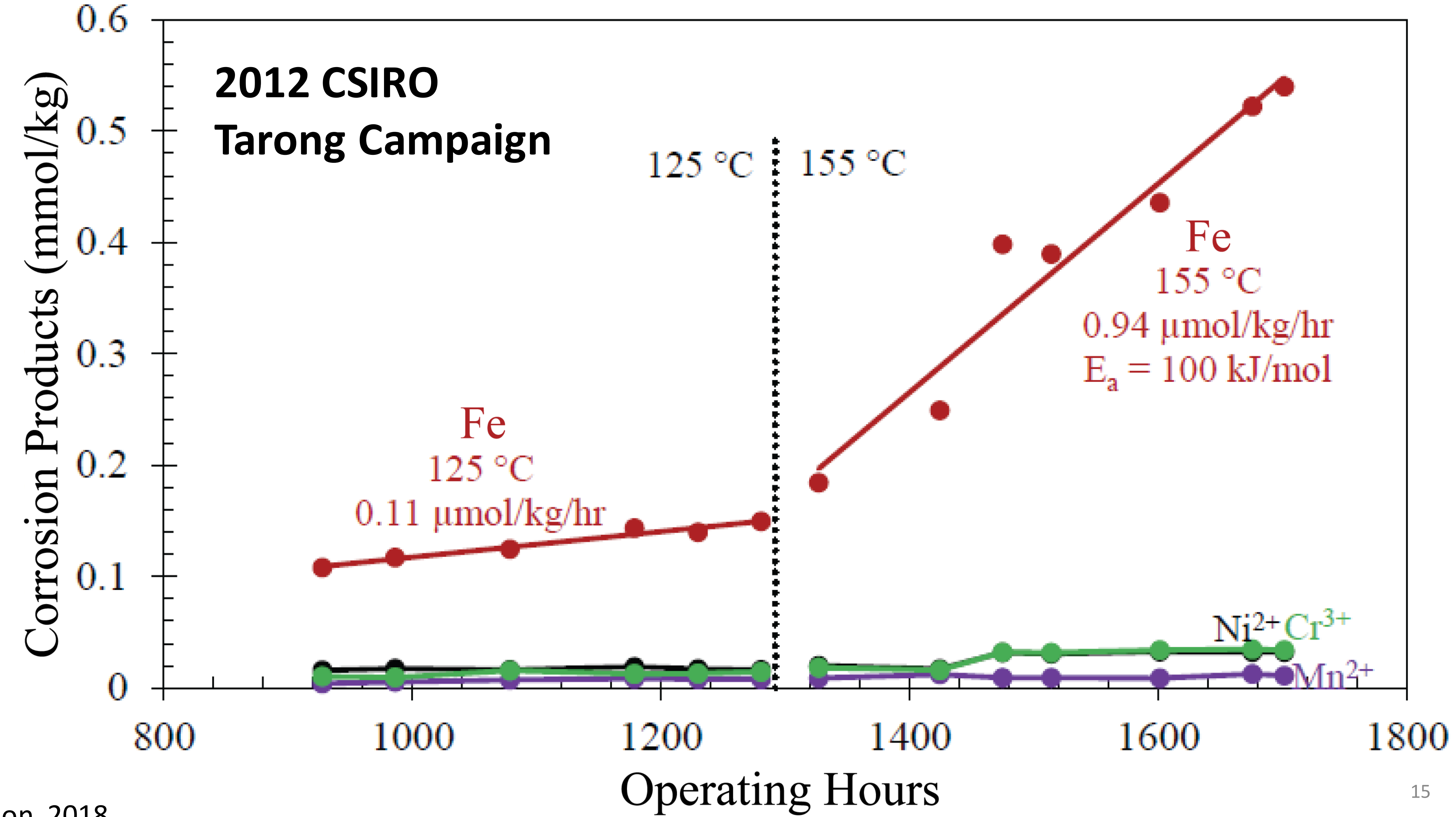
Fe^{+2}/Fe^{+3} : Iron as an Oxidation Carrier to Degrade PZ in the Stripper

- PZ oxidation occurs at high T in stripper
- Ferrous should oxidize readily in the presence of DO

$$Fe^{3+} + PZ \rightarrow Products + Fe^{2+}$$

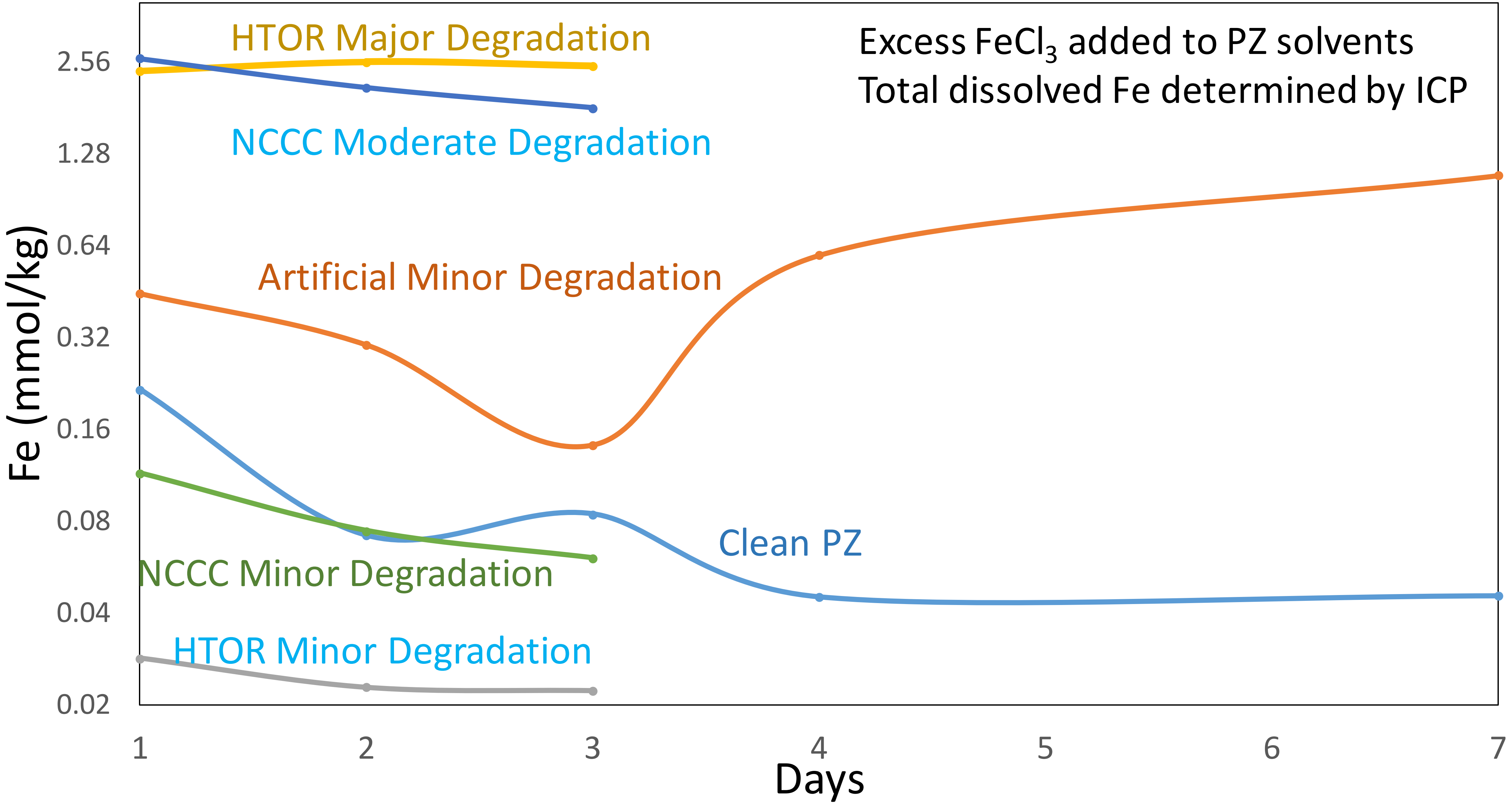


Iron Becomes More Soluble as Degradation Products Accumulate



Nielson, 2018

Solubility of $FeCl_3$ in 5 m PZ at 55°C



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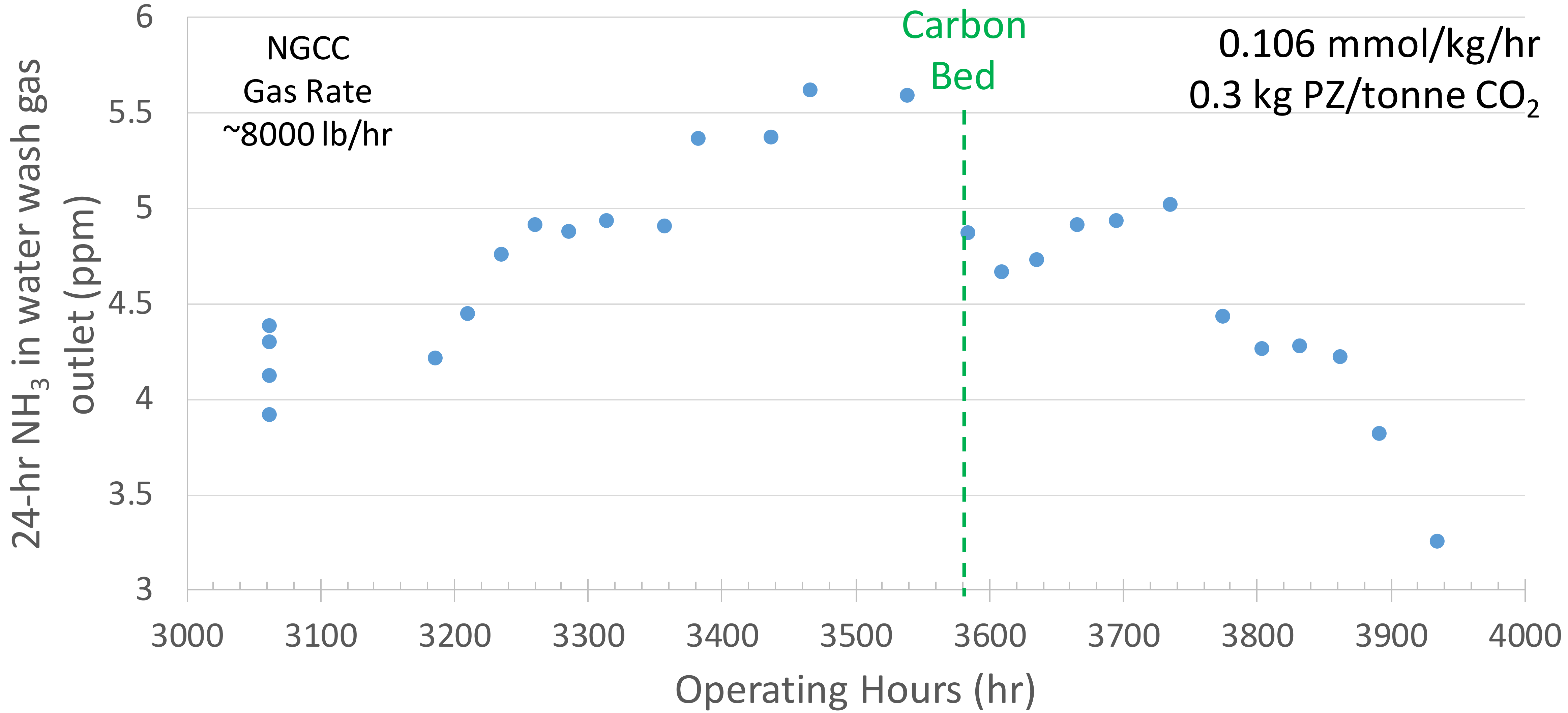
Fe^{+2}/Fe^{+3}: C Treating Reduces NH_3 with PZAS at NCCC 2019



* NO concentration relatively stable at 50 ppm

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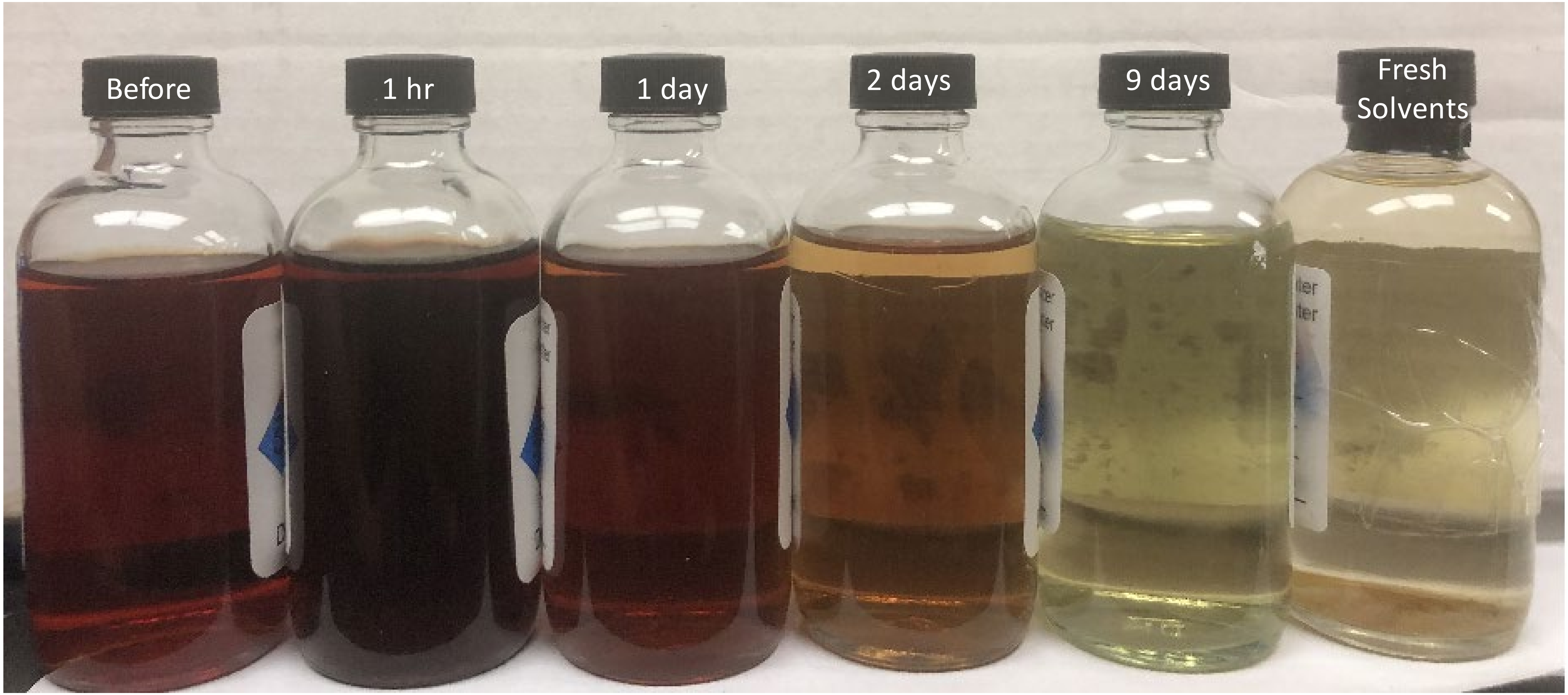
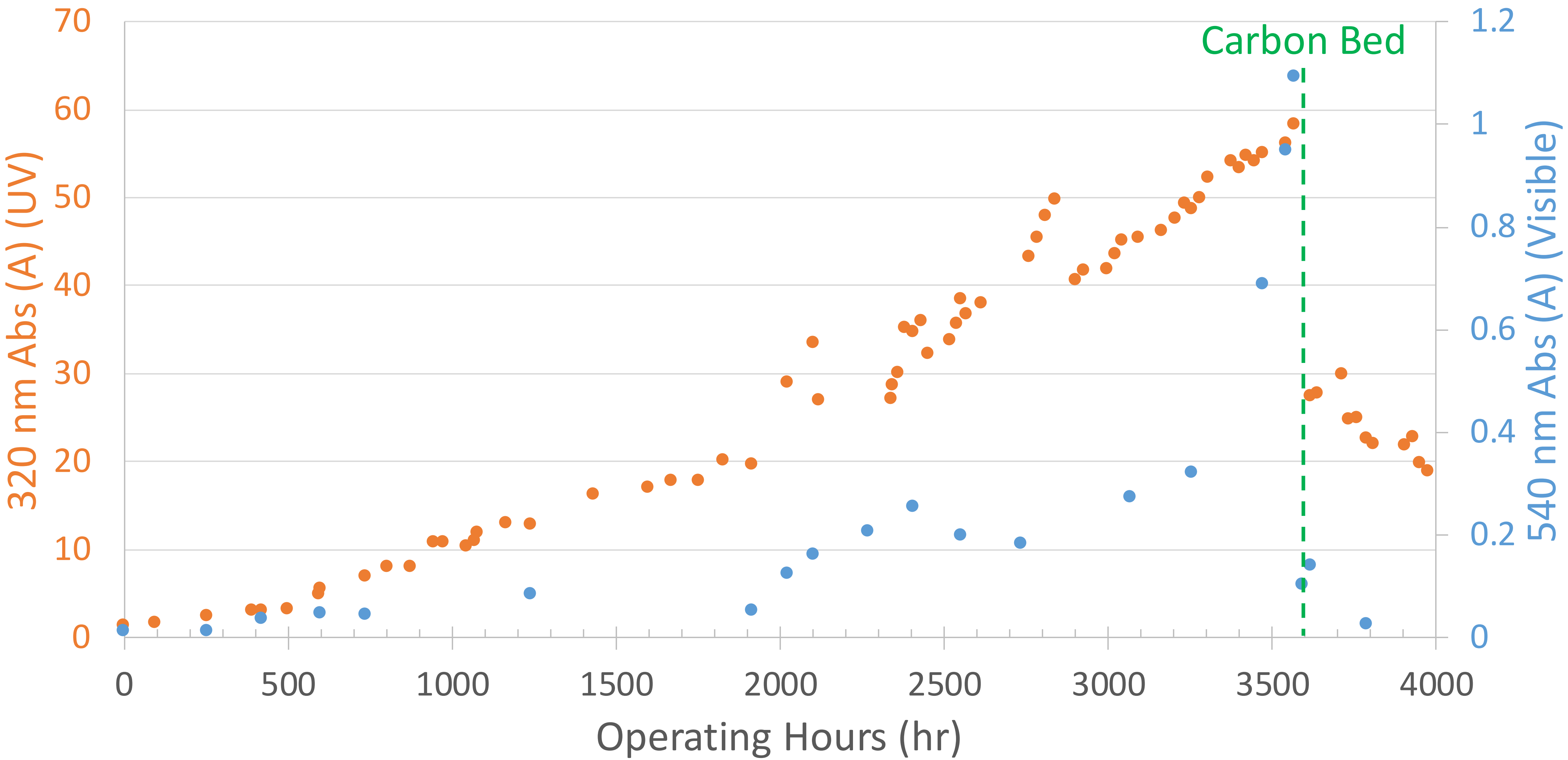
Visual Effect of Solvents by Carbon Bed

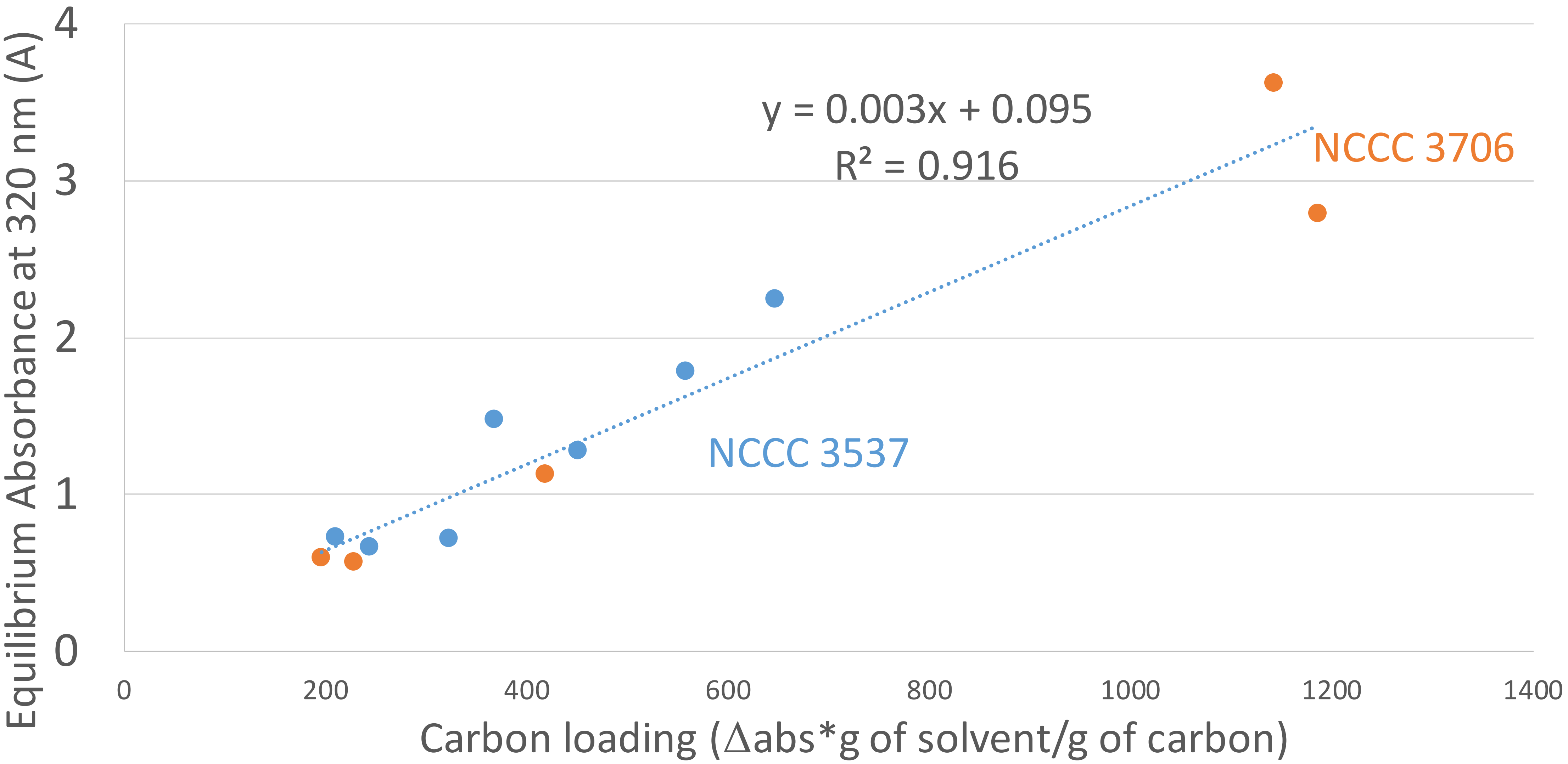
Carbon Bed turned on at 5/14/2019 8:59 (3600 hrs)



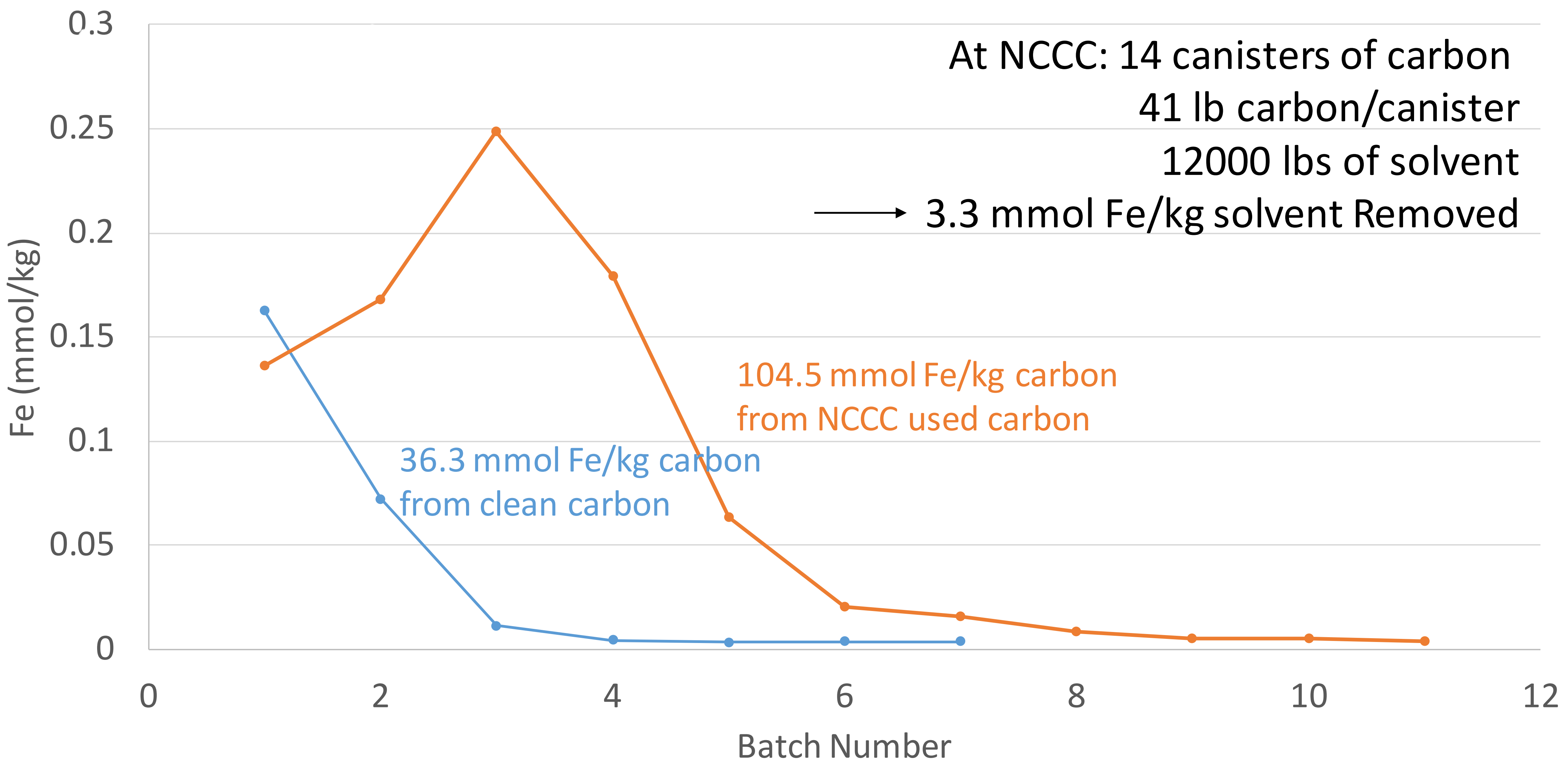
Absorbance Change during the Campaign



Equilibrium absorbance is linearly related to the carbon loading

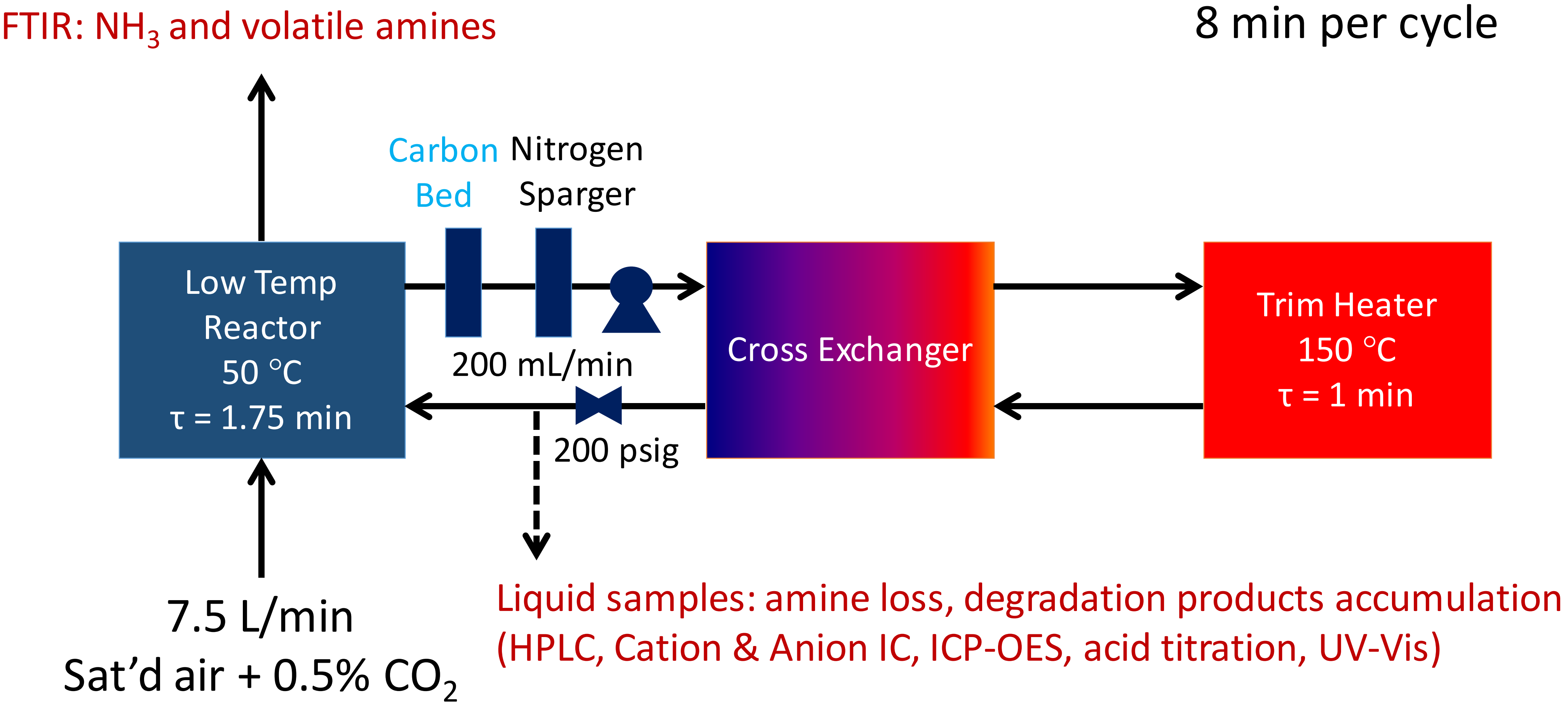


Fe removed from NCCC Used Carbon = 3.3 mmol/kg NCCC solvent

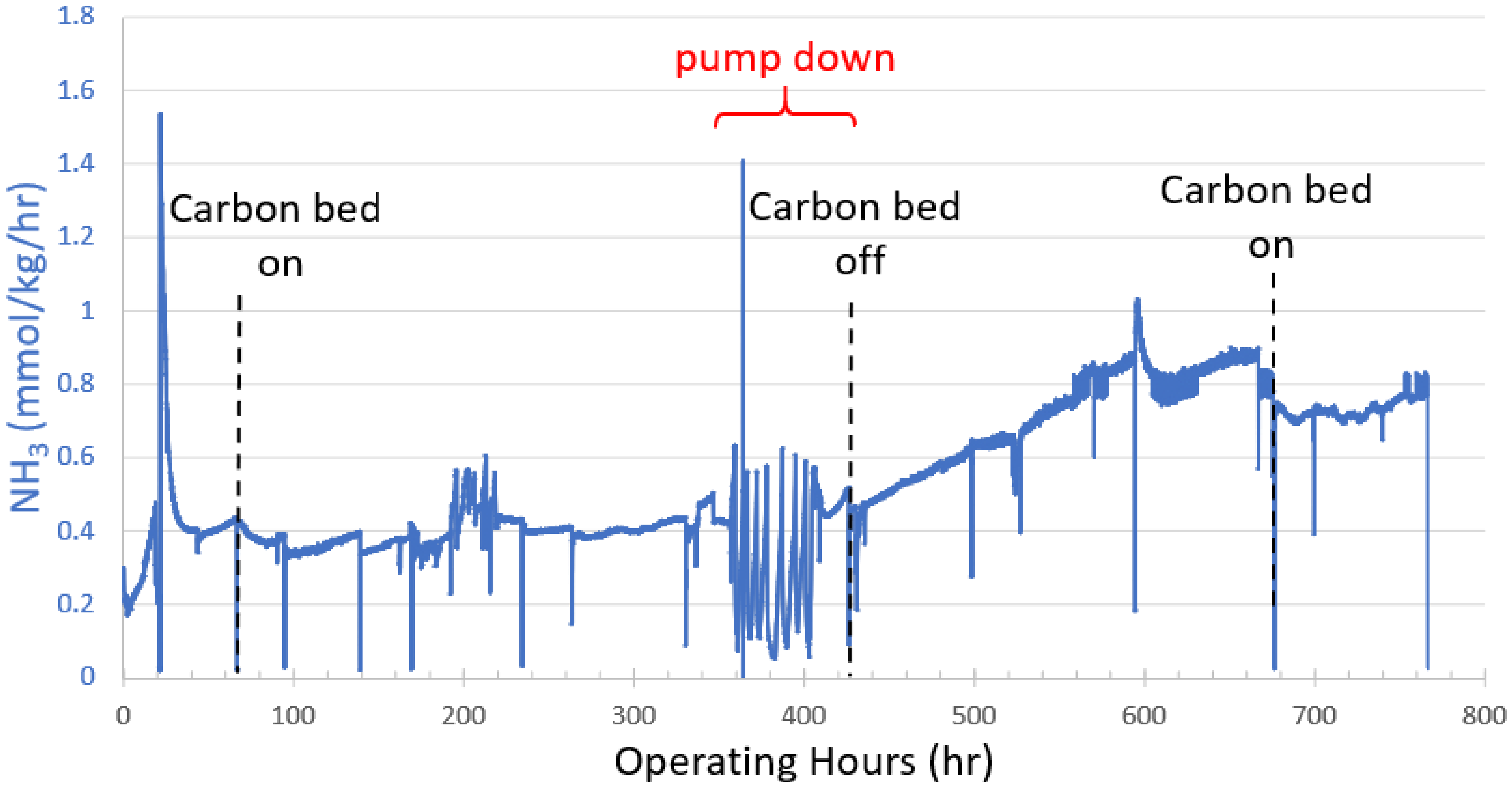


High Temperature Oxidation Reactor (HTOR)

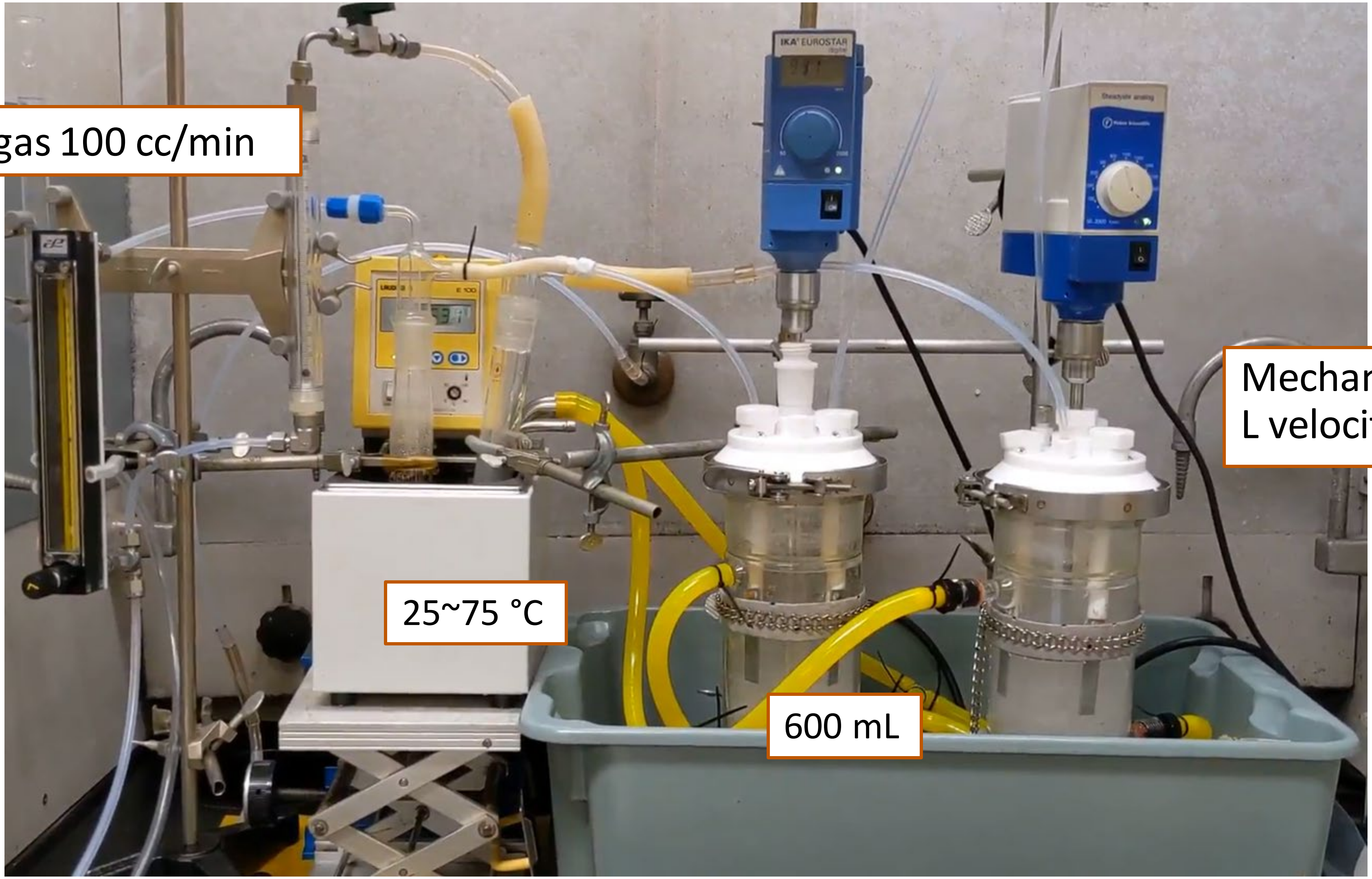
Total inventory ~1.6 L
8 min per cycle



NH_3 rate from FTIR



Corrosion Method: Low-gas flow reactor



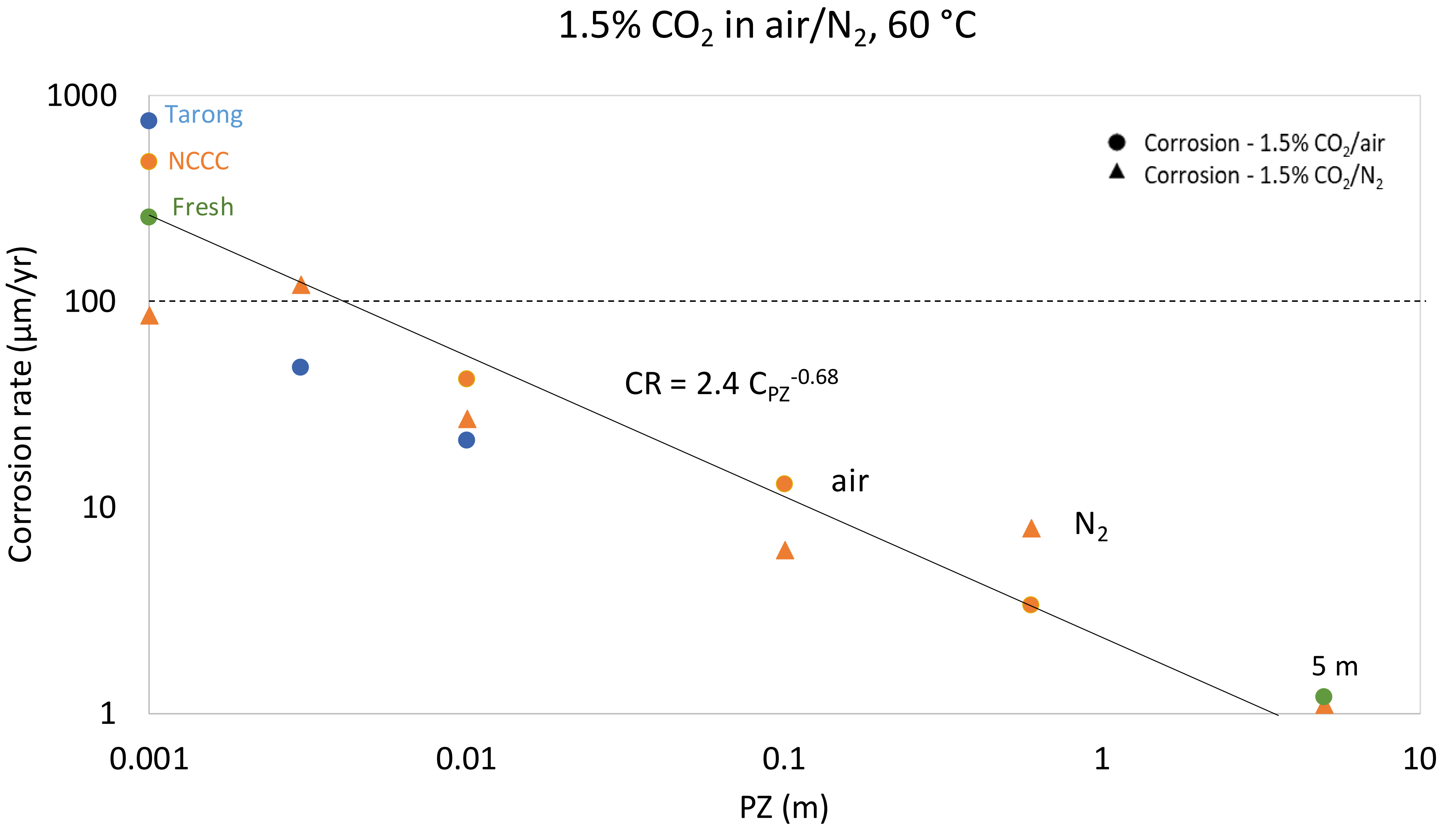
Inlet gas 100 cc/min

Mechanical agitation
L velocity around 0.5~1 m/s

25~75 °C

600 mL

C1010 corrosion & PZ concentration



SRP pilot campaign (Fall 2021) – test oxidation strategies

Modification	Purpose
Inject and measure NO_2 at 2 ppm	Create baseline oxidation similar to commercial
N_2 sparging in the absorber sump	Test efficacy of DO stripping
Increase τ on warm rich bypass from ~1 s to ~40 s	Confirm high-T degradation in rich amine
Bypass lean amine storage tank	Minimize amine inventory
Add carbon bed in rich amine line to remove iron	Test impact of removing oxidation catalysts
Adding O_2 analyzers on recovered CO_2 gas and rich amine	Monitor oxygen presence when perturbing system
Adding corrosion coupons	Monitor corrosion simultaneous with oxidation

Conclusions on Fe^{+2}/Fe^{+3}

1. Fe^{+3} solubility in PZ varies solvent degradation from 0.02 to 2 mM

2. C treating reduced ammonia production at NCCC and in HTOR. C treating removed 3 mM of "soluble" iron from NCCC solvent system. All of the "soluble" Fe must be removed to reduce oxidation.

3. C treating removes PZ degradation products that adsorb at 320 & 540 nm

4. >0.01 m PZ protects carbon steel from corrosion at absorber T

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