The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

Safeguarding Amines from Oxidation by Enabling Technologies

DOE Contractors Meeting
DE-FE0031861

Fred Closmann, Ph.D., The University of Texas at Austin

U.S. Department of Energy

National Energy Technology Laboratory
Carbon Management Project Review Meeting
August 15 - 19, 2022

Outline

- Project objectives and structure
- Background on solvent oxidation and losses
- SRP pilot modifications
- SRP pilot data
- Dissolved oxygen stripping
- Plans for NCCC campaign (Q4 2022 – Q1 2023)

Project objectives

Develop technologies to safeguard scrubbing from solvent loss by oxidation. Project directly addresses safeguarding amine solvents against O_2 and NO_2.

Performance dates

Budget Period	Start Date	End Date
1	March 1, 2020	May 31, 2021
2	June 1, 2021	April 30, 2022
3	May 1, 2022	June 30, 2023

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Project budget

Description	BP1 ($)	BP2 ($)	BP3 ($)
Salaries (PI/staff/grad students/SRP)	342,316	416,116	278,123
Fringe	95,361	118,687	91,036
Travel	7,016	9,601	23,498
Equipment*	230,100	5,000	102,657*
Supplies	54,450	74,153	73,801
Tuition	38,658	39,435	40,260
Indirect/Overhead (56.5%)	282,015	349,766	263,549
Total by BP	1,049,915	1,012,759	872,924
Total cumulative	1,049,915	2,062,674	2,935,598
Total cost share	209,983	202,552	174,585

*Reflects redirection of Equipment budget for purchase of amino acid identification/quantification system.

Why is this project important?

Why this project is important

Solvent	Rate (kg/t CO_2)	Flue gas	CO_2 (%)	O_2 (%)	NO_x/NO_2	Facility	Author
CASTOR1, CASTOR 2	1.4	coal	12	NA	<65 ppm NO_x	Esbjergvaerket, Denmark	Knudsen, 2009
CESAR1	0.45	coal (lignite)	15.2	5	6-8 ppm NO_2, 100-160 ppm NO_x	Niederaussem	Moser, 2022
CDRMax	2	coal	14-16	NA	NA	CAER, UK	Frimpong, 2021
MEA	0.8-1.6	CHP (NGCC)	3.6-4	13-14	<5 ppmv NO_x	TCM	Morken, 2019
PZAS™	0.3/0.75	NGCC	4	12-14	<1 ppm	NCCC, Wilsonville, AL	Wu, 2021
PZAS™	0.6	synth NGCC	4	20	1 ppm	SRP, UT	Closmann, 2022
Aker ACC S26	0.15-0.2	cement kiln	17.8	7.5	180-250 mg/Nm³ NO_x	Norcem; Brevik, Norway	Knudsen, 2014

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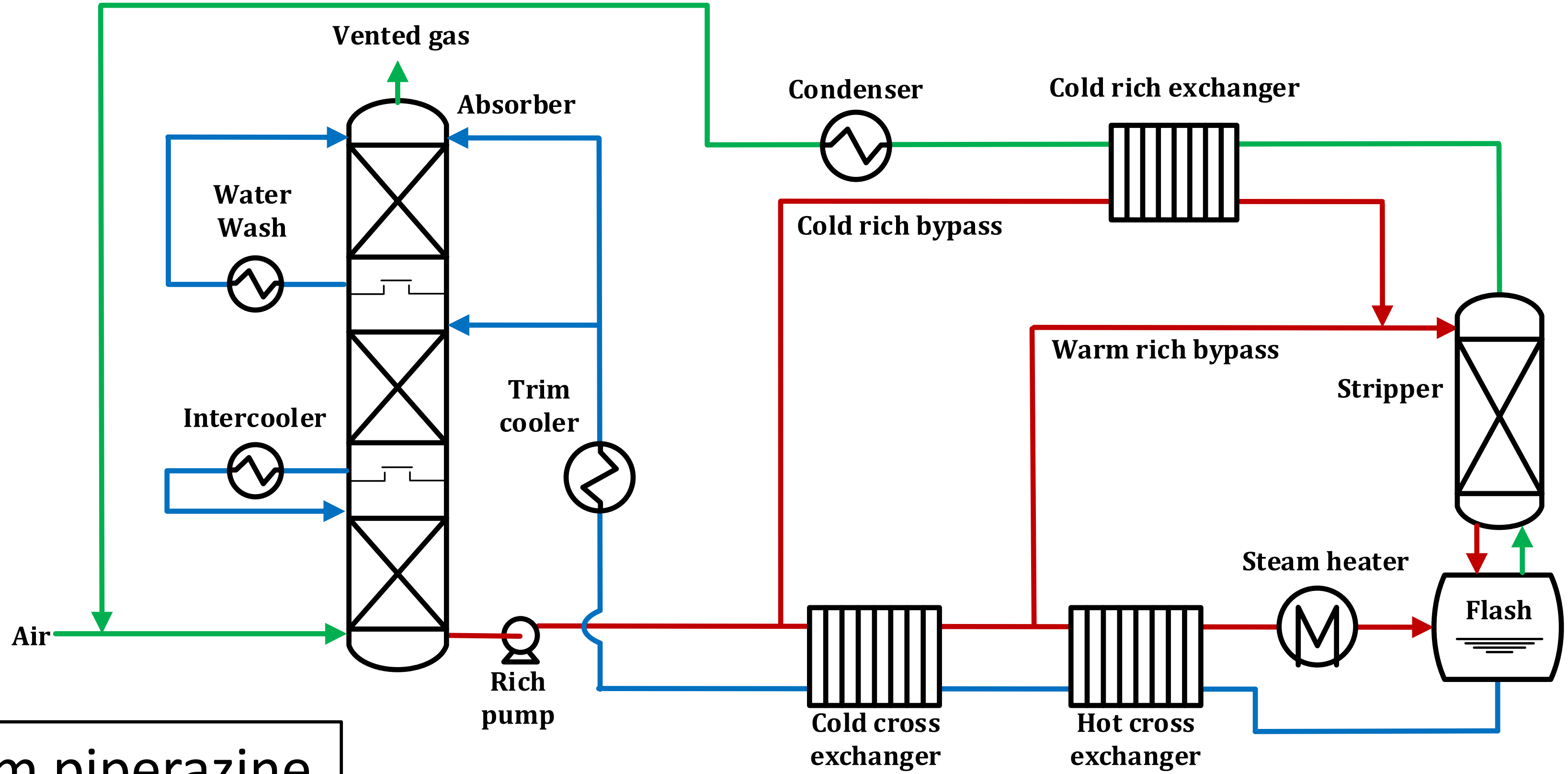
Investigate why lower oxidation observed in PZAS™ at SRP and NCCC

- Absence of NO_2 at SRP and NCCC – investigate role of NO_2 in oxidation
- PZAS™ flashes dissolved/entrained O_2 before stripper sump
- Stripper sump τ_{avg} at UT-SRP and NCCC <2 minutes, which may minimize oxidation of amine by Fe^{+3}

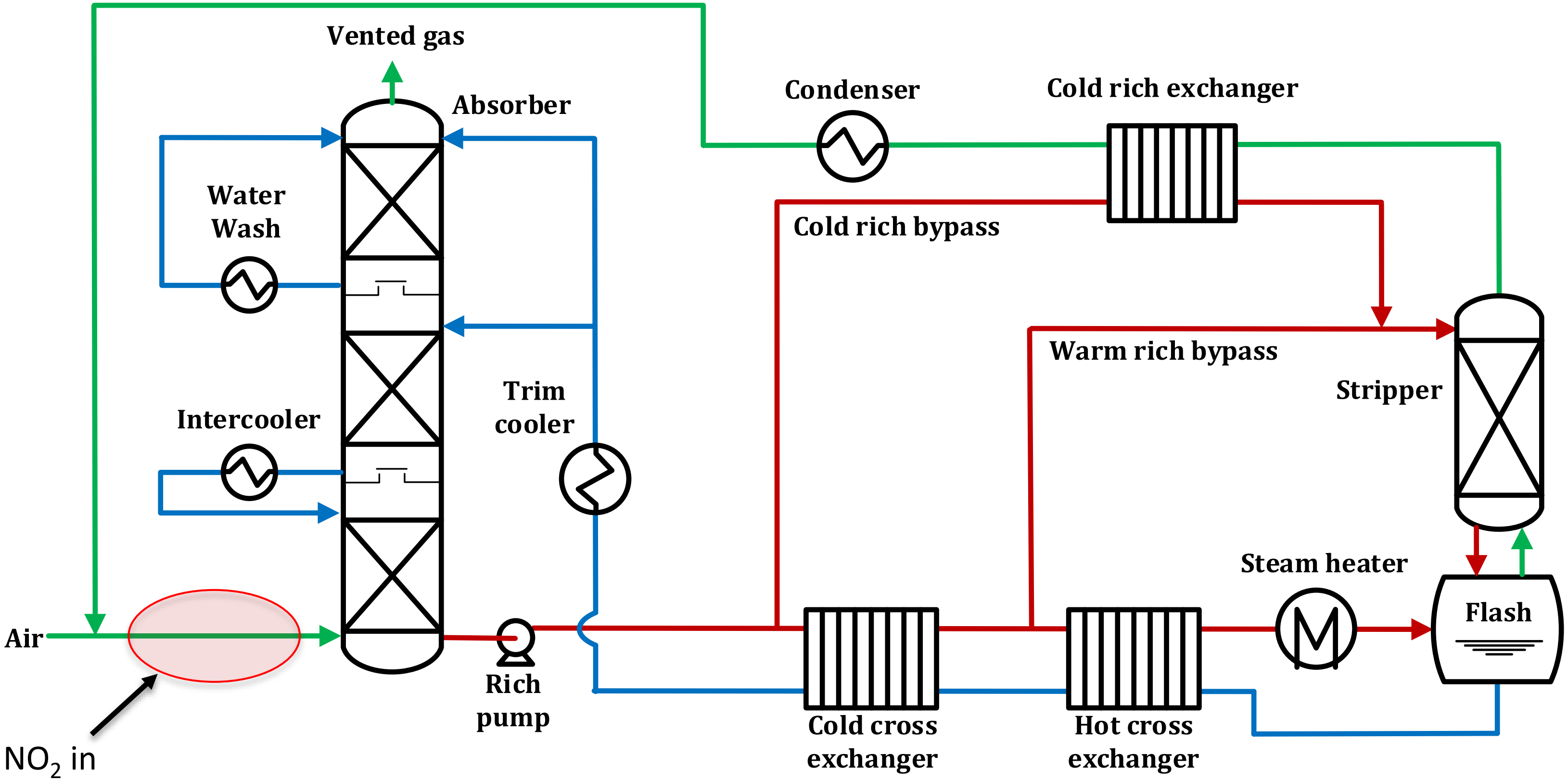
PZAS™ process flowsheet



5 m piperazine

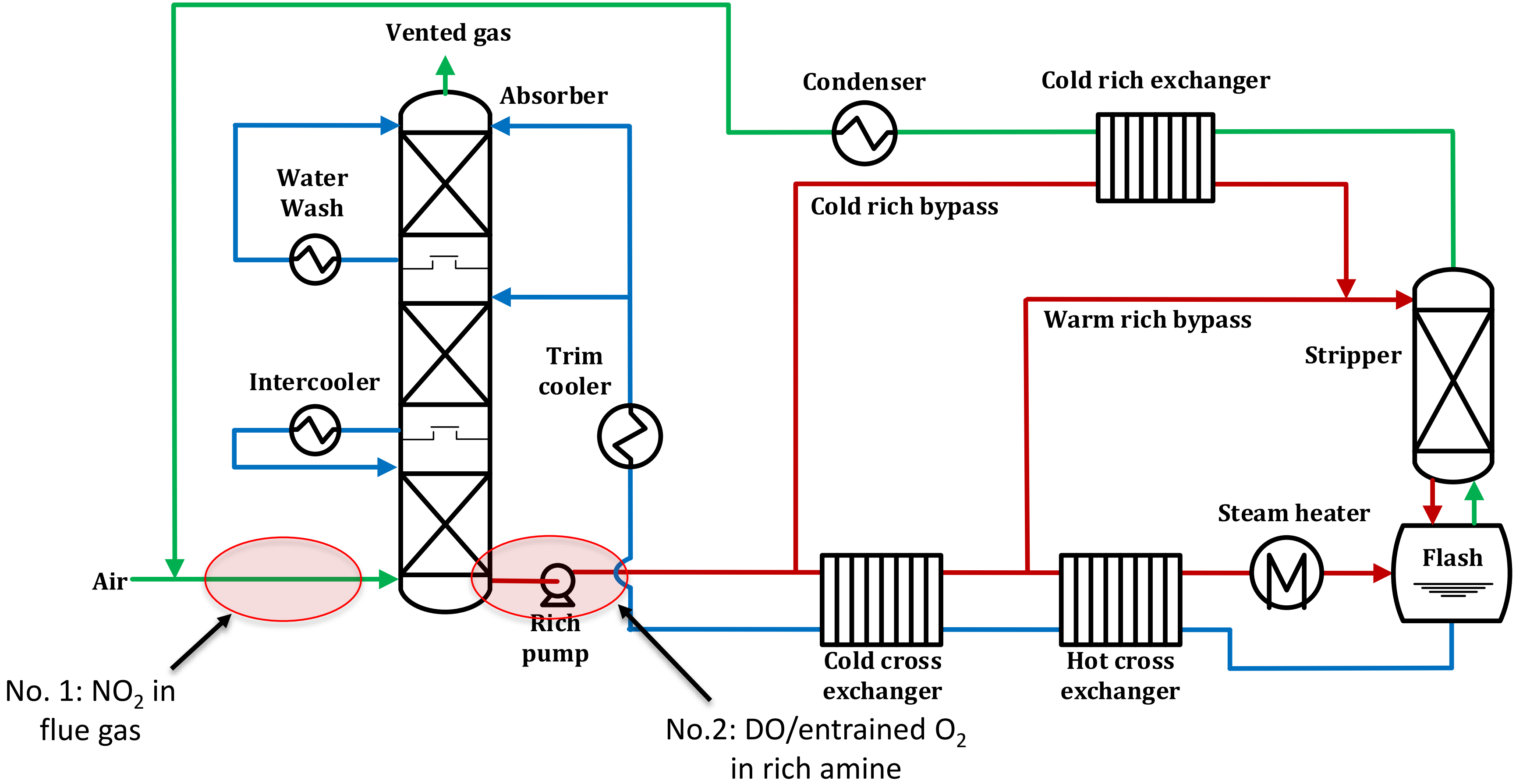
Three oxidation mechanisms of interest

Amine oxidation mechanisms

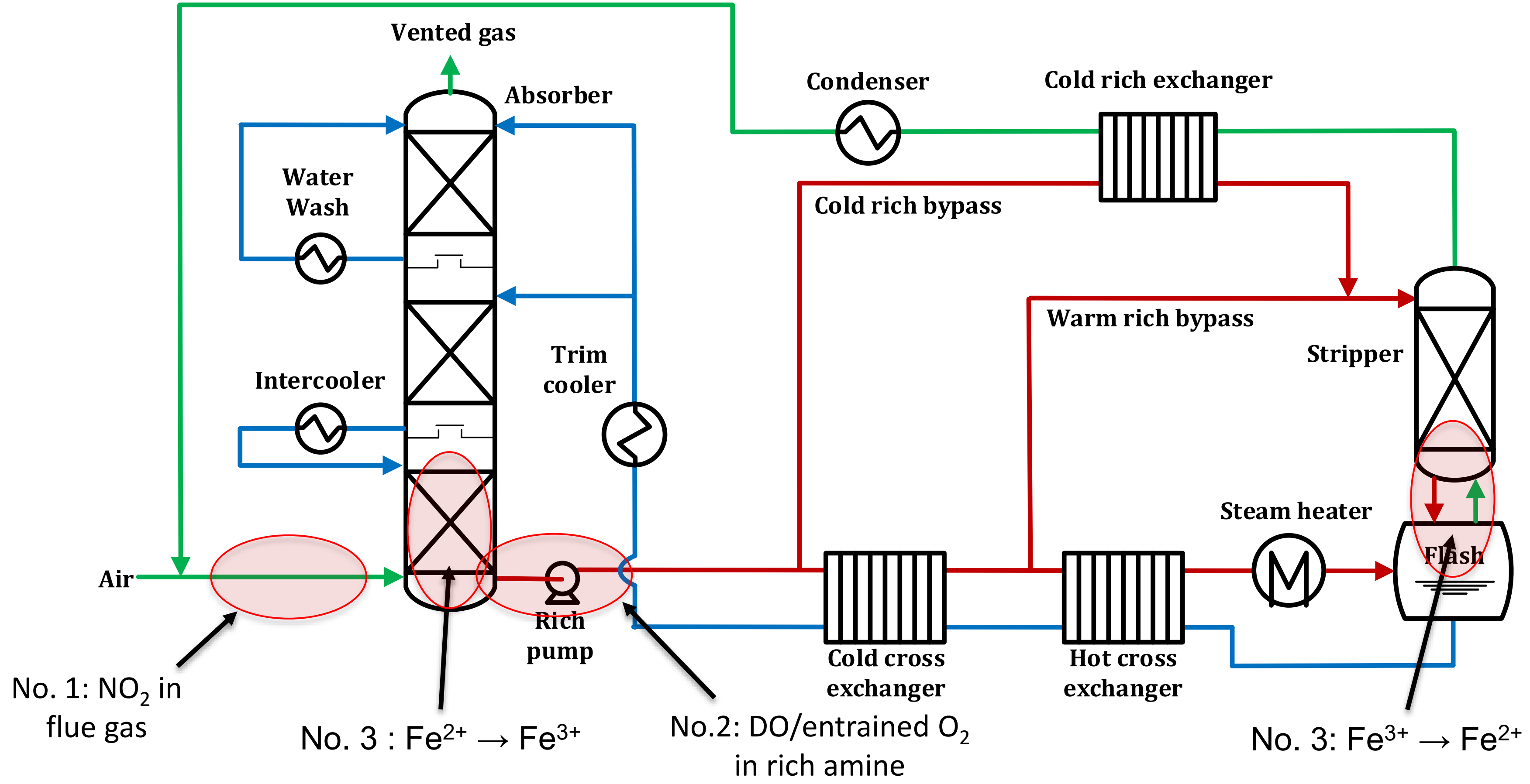


No. 1: NO_2 in flue gas

Amine oxidation mechanisms



Amine oxidation mechanisms



SRP pilot campaign modifications

Strategies tested at SRP

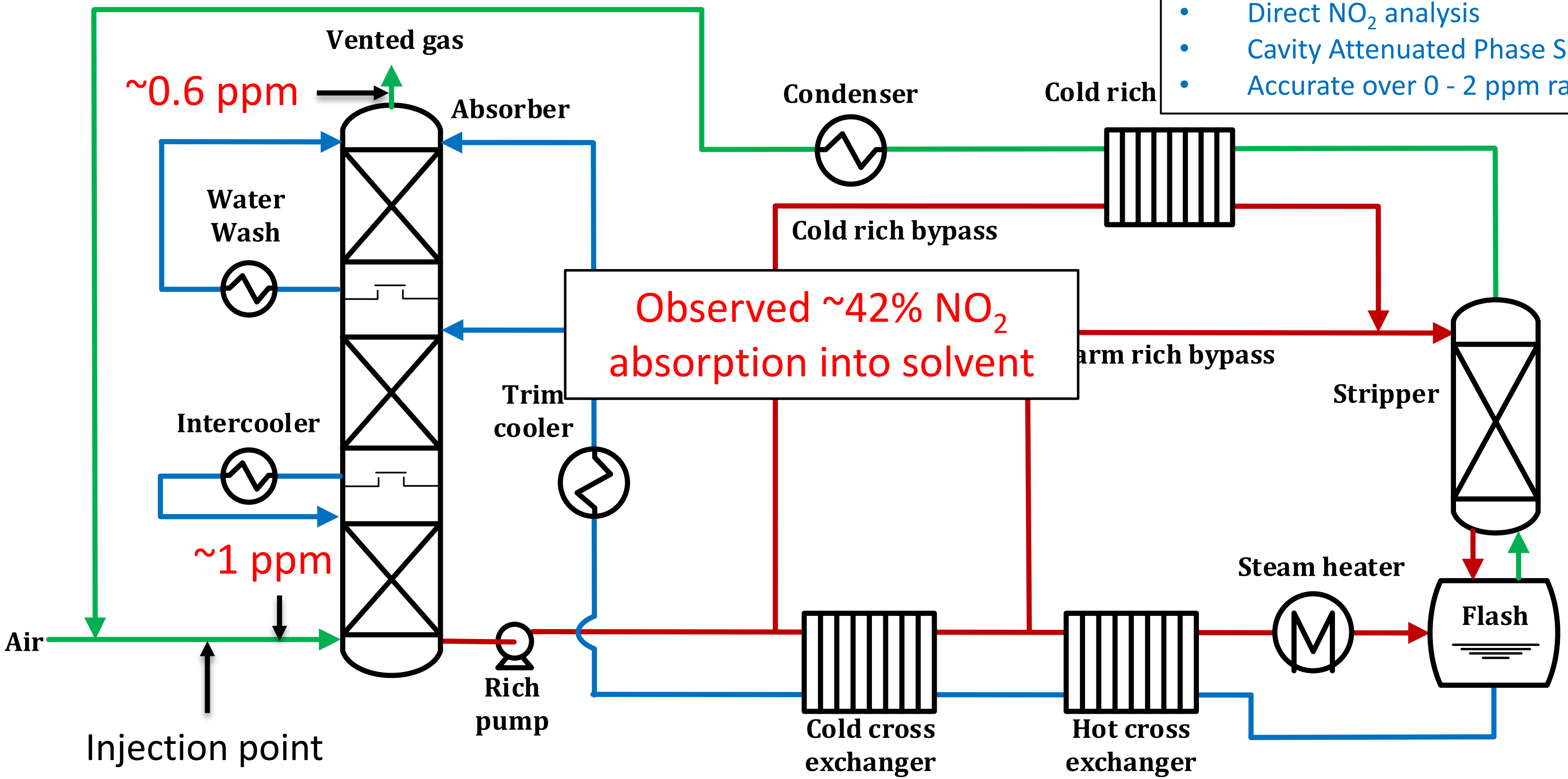
Modification	Purpose
Inject and measure NO_2 at 1 ppm	Create baseline oxidation similar to commercial flue gas
N_2 sparging and entrained bubble coalescence in the absorber sump	Test efficacy of DO stripping and entrained bubble/oxygen removal
Increase τ on warm rich bypass (WRB) from <0.5 to >1 min	Confirm high-T degradation in rich amine
Add carbon bed in rich amine line to remove iron	Test impact of removing oxidation catalysts

Pilot campaign results

NO_2 measurement in flue gas – initial test

American Ecotech S60 analyzer:

- Direct NO_2 analysis
- Cavity Attenuated Phase Shift
- Accurate over 0 - 2 ppm range



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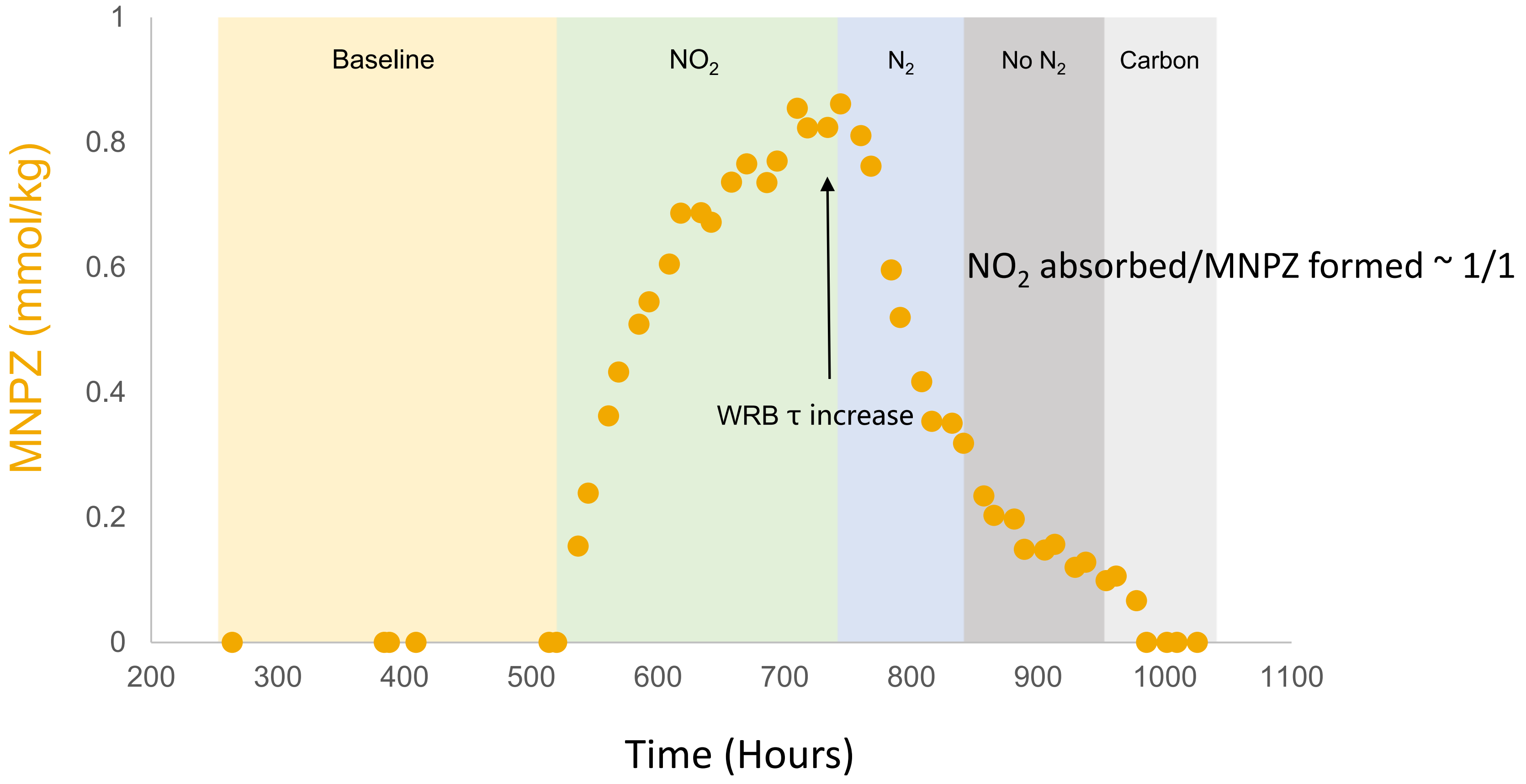
Mononitrosopiperazine (MNPZ) and NO_2 absorption at SRP



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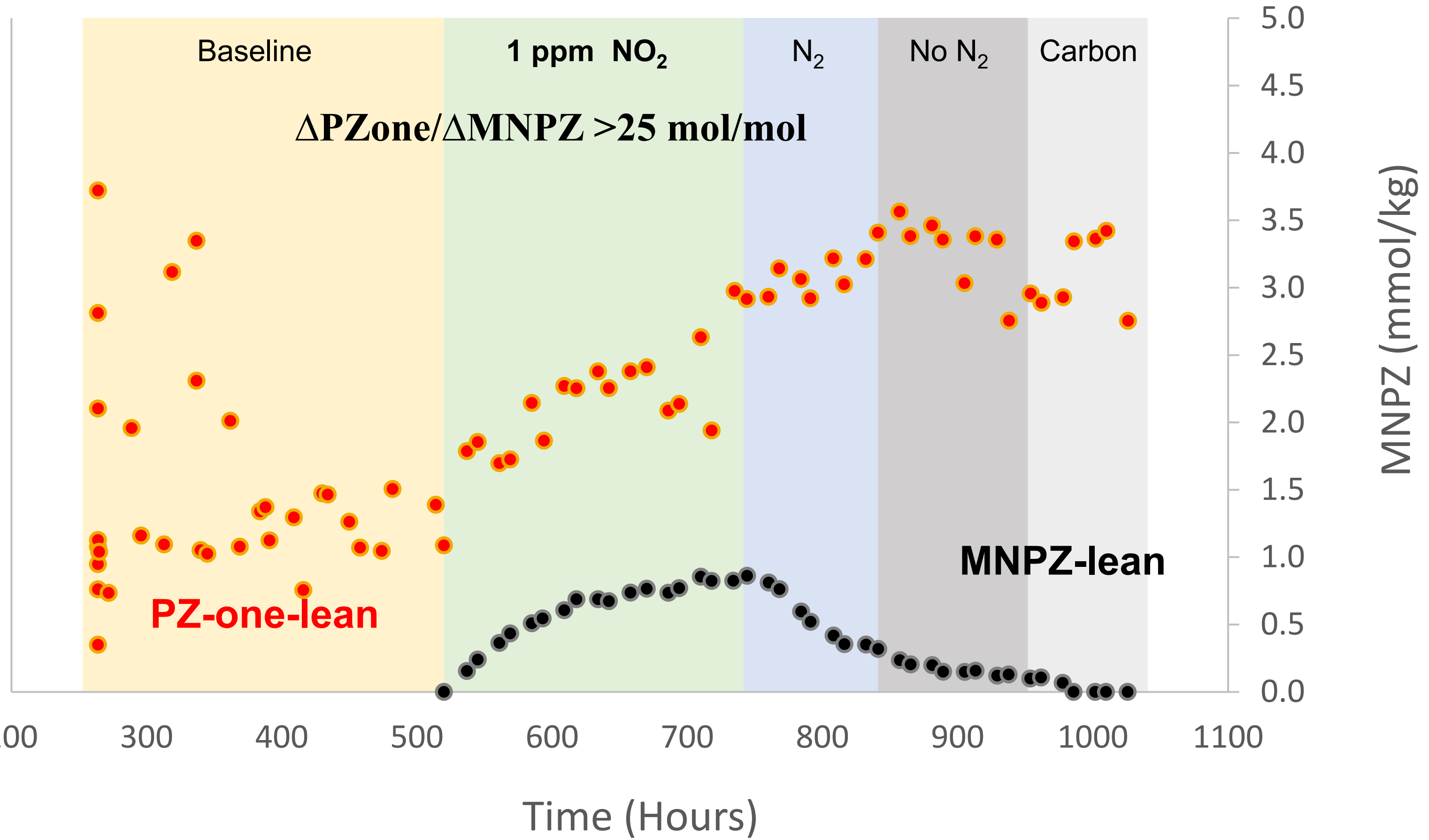
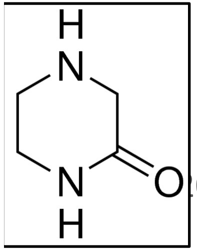
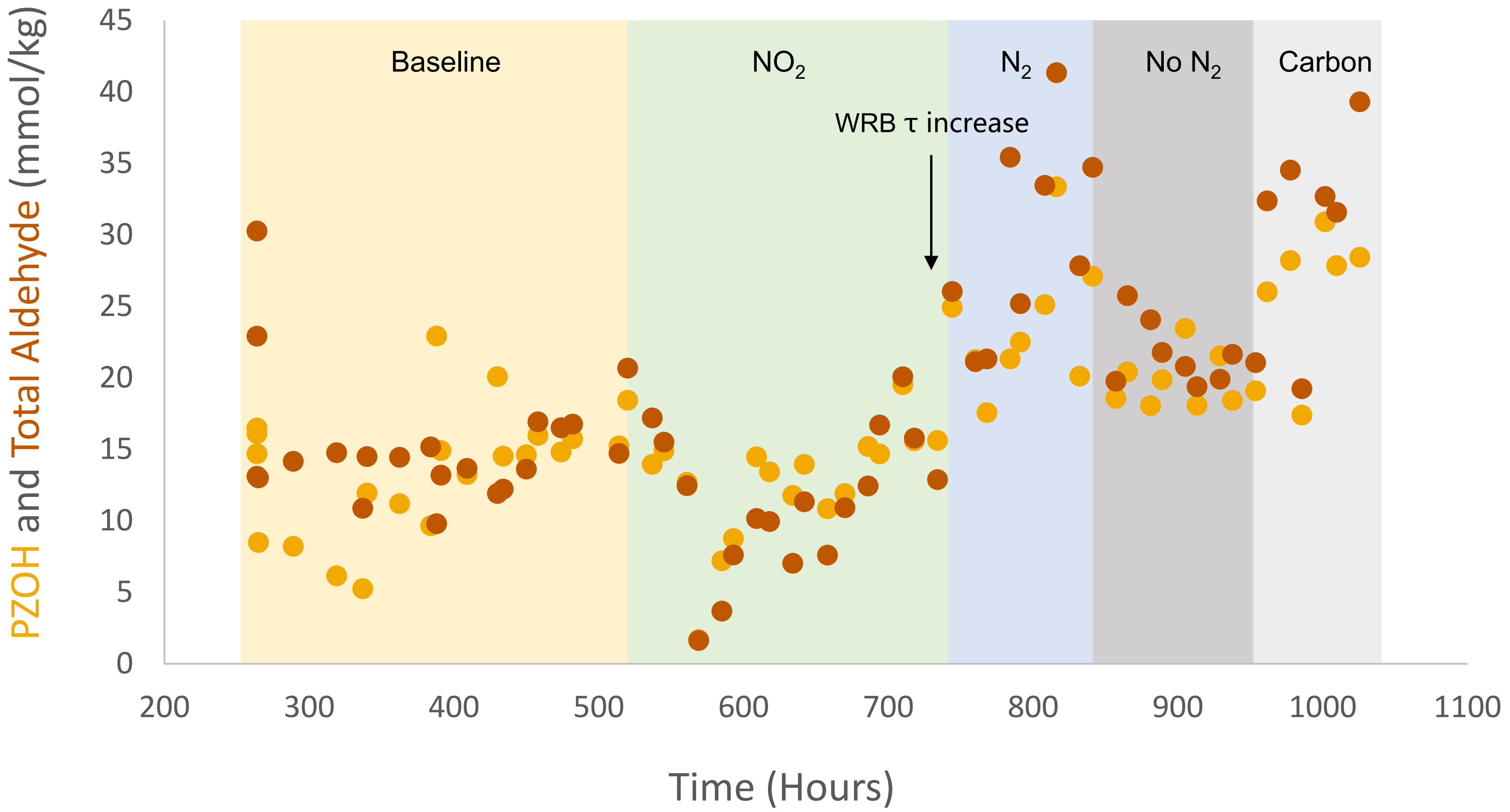
Piperazinone (PZone) & MNPZ at SRP



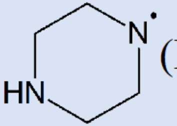


Piperazinol (PZOH) and total aldehydes at SRP



Amine oxidation in PZ – NO_2 pathway

Absorber

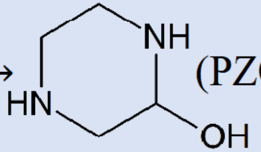
$NO_2 \cdot + PZ \rightarrow$  $(PZ \cdot) + \boxed{NO_2^-} + H^+$

Free radical propagation:

$PZ \cdot + O_2 \rightarrow PZOO \cdot$

$PZOO \cdot + PZ \rightarrow PZ \cdot + PZOOH$

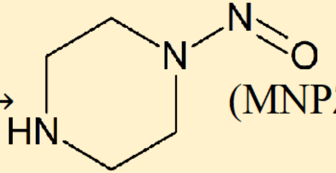
Termination:

$2PZ \cdot + H_2O \rightarrow$  $(PZOH) + PZ$

$PZOOH + PZ \rightarrow 2PZOH$

$PZOOH \rightarrow PZO \cdot + \cdot OH$

Stripper (High T)

$NO_2^- + H^+ + PZ \rightarrow$  (MNPZ)

$$MNPZ + 0.5\ H_2O \xrightarrow{\Delta,\ base} PZOH + 0.5\ N_2O$$

Dissolved oxygen stripping through N_2 sparging

DO and entrained oxygen removal

Wire mesh mist eliminator

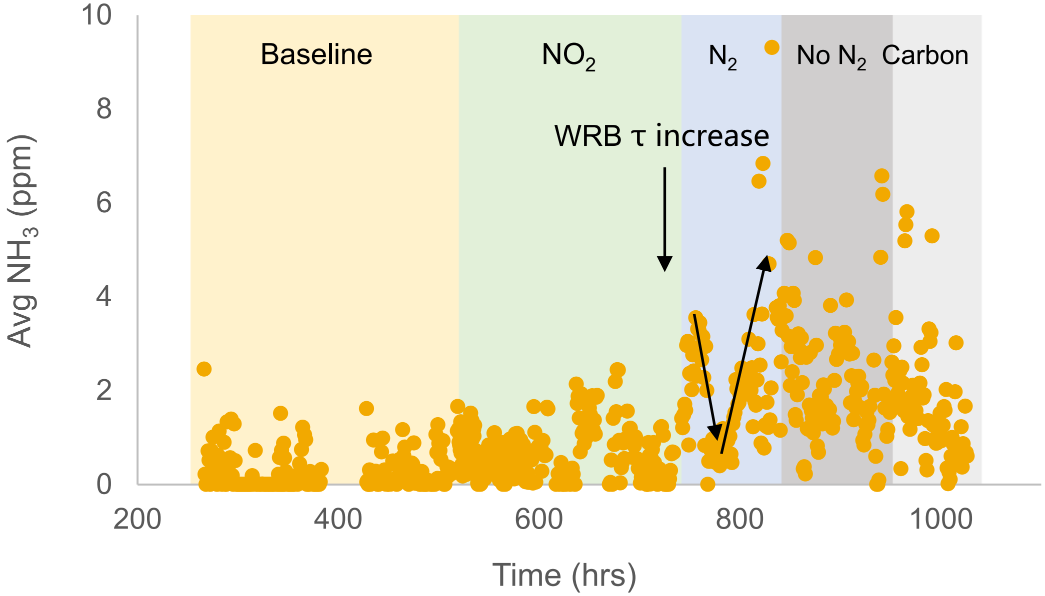
Mist eliminator and sparge pipe installed in absorber

DO and entrained oxygen removal

- Three tests conducted in absorber sump at N_2 sparging rates of 6, 10, and 20 SCFM
- Test at 6 SCFM N_2
  - Flue gas rate of 600 SCFM; N_2 ~1% of total gas traffic in abs column
  - Solvent rate of 4 gpm → τ_{abs} ~ 15 minutes
  - Rich amine DO decreased from 7.4 ppm to 1.0 ppm
  - ~2.3 NTUs; abs sump level ~29 inches, so HTU ~ 12 inches
  - Sump level then increased from 29 to 35 inches -> increased NTU & lowered DO
- Foaming in absorber sump
  - As foam developed mass transfer improved & DO decreased
  - Operational issues managing abs sump liquid level - added anti-foam
  - Foam disappeared → DO increased, but N_2 sparging still effective

Did N_2 sparging reduce solvent oxidation?

- Best evidence in NH_3 data
- NH_3 experienced a drop during the 6 SCFM N_2 sparging test, followed by increase
- 6 SCFM N_2 sparge test coincided with WRB res time increase being brought online
- Possible test outcome: N_2 stripped NH_3 from solvent (apparent at abs knock-out)



SRP campaign conclusions

- PZone detected at greatest conc. (~85 mmol/kg) among products and likely evidence of catalytic reactions
- Observed 42% NO_2 absorption rate with each pass of flue gas through absorber
- MNPZ formed at 1:1 ratio w/ NO_2 absorbed (not catalytic)
- ΔPZone/ΔMNPZ ~40
- N_2 sparging in abs sump at 1% of column gas traffic reduced DO by >85%; unclear how much oxidation reduction occurred

NCCC campaign overview

NCCC pilot campaign overview

- Currently scheduled for Q4 2022 -> Q1 2023
- NGCC flue gas (4% CO_2, 8% H_20) at ~110 ˚C from gas boiler
- Reduce NO_2 concentration to ≤1 ppm with thiosulfate/sulfite
- Test N_2 sparging in absorber sump for DO removal
- Test carbon bed at slipstream rates of 1 – 5 gpm
- Use acid wash loop for NH_3 control
- Bottom packed section pump-around intercooling
- Multiple corrosion coupon locations

SRP and NCCC pilot plants

Parameter	SRP (UT Austin)	NCCC (Southern Co.)
Size equivalent (MW_{eq})	0.1	0.6
Solvent inventory (gal)	~350(a)	1300(b)
Abs diameter (inches)	16.8	25.3
Abs packing height (feet)	20	40
Abs sump residence time (min)	15(c)	8(d)
Flue gas source	Synthetic	Commercial - natural gas boiler or coal
Flue gas rate (lb/hr)	3,000	8,000
Flue gas (NO_2) ppm	0 (blended to 1 ppm)	1 – 2

(a) Lean amine tank bypassed; (b) includes carbon bed loop; (c) at L = 4 gpm; (d) calc at L ~ 12 gpm (~3.5 gpm/ft^2) & 3.5 ft liquid height.

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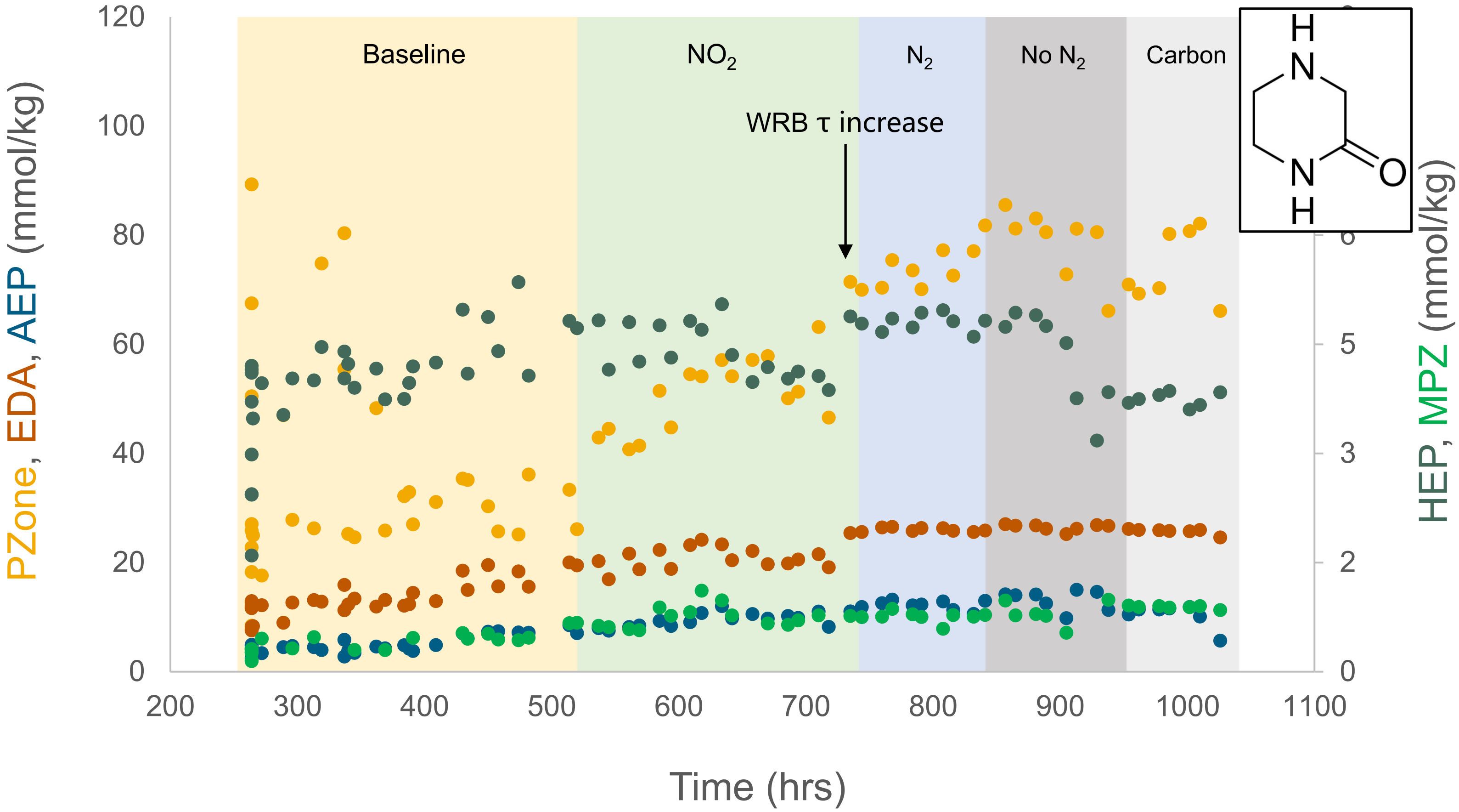
Project participants

Party	Person	Role
NETL	Krista Hill	Project Manager
UT-Austin	Dr. Gary Rochelle Dr. Fred Closmann	Principal Investigator Deputy PM
GRAs	Yuying Wu Ching-Ting Liu Chih-I Chen Ariel Plantz Miguel Abreu Athreya Suresh	HTOR, FTIR - pilot support Corrosion, Titrations – pilot support HGF - NO_2 studies Iron studies Pilot support Pilot support
SRP Staff	Dr. Frank Seibert JR Campos Yee Lee Chen	Director SRP Operations technician Night shift operator, pilot data analysis

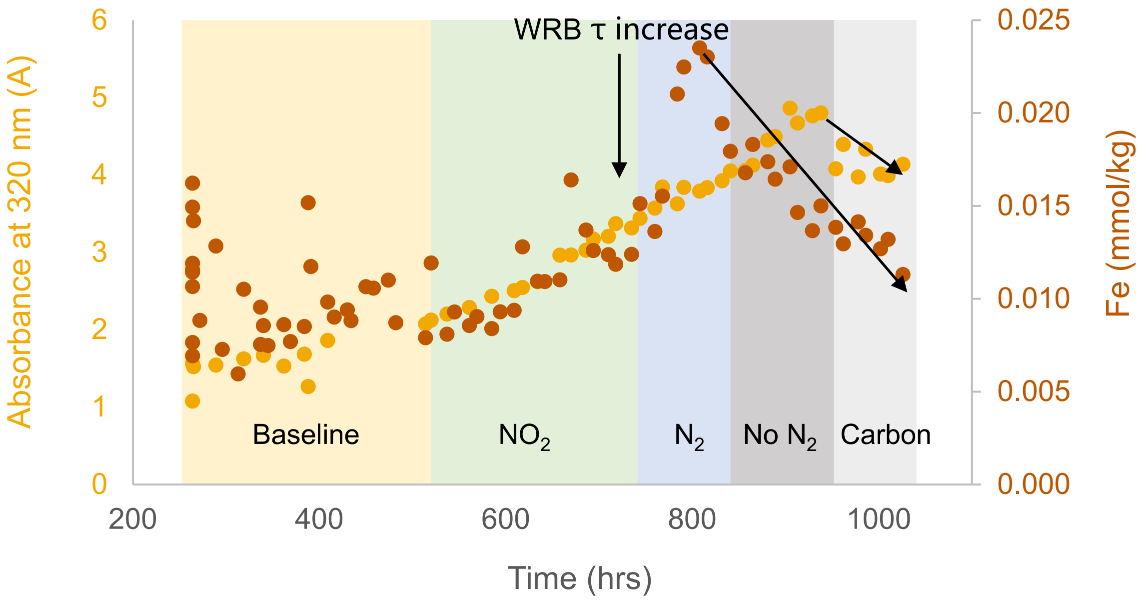
Questions?

Piperazinone (PZone) and other degradation products at SRP

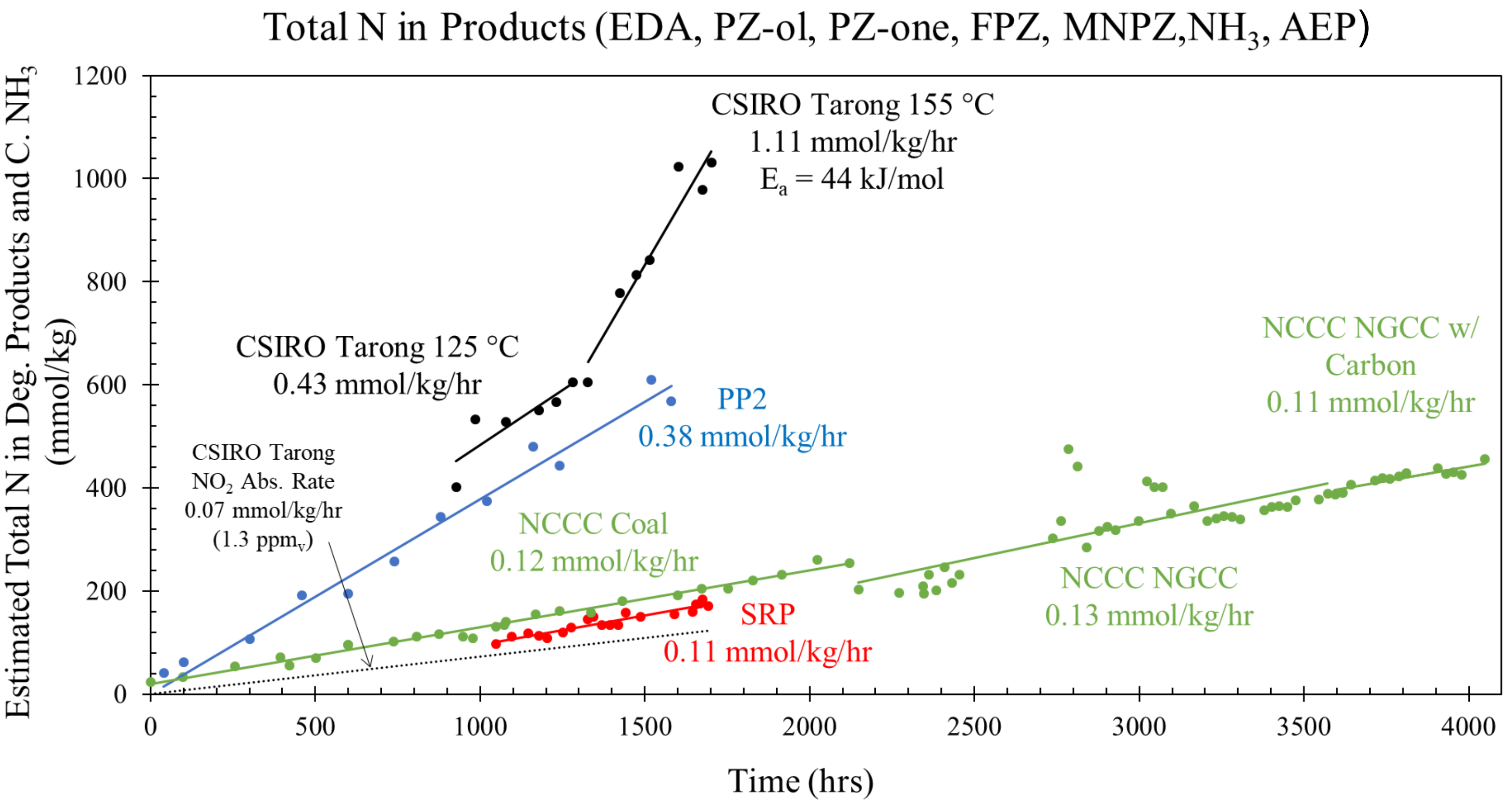


Did carbon bed reduce solvent oxidation?

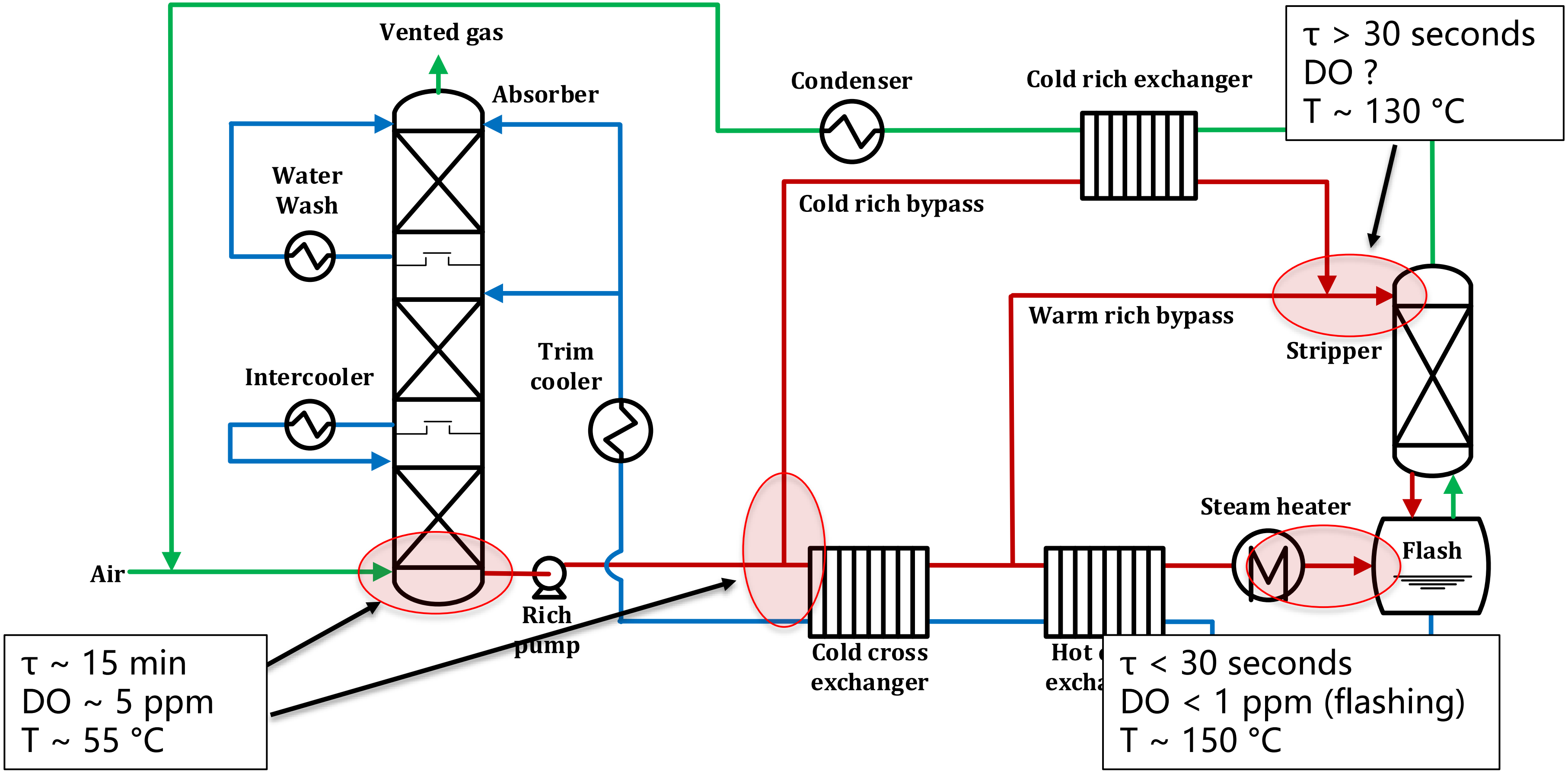
- Best evidence in UV-Vis absorbance data
- Absorbance (A) dropped when carbon bed brought online
- Iron continued a decreasing trend; chelated metal ion species were being removed
- Possible test outcome: Iron solubility limit was changing with step changes



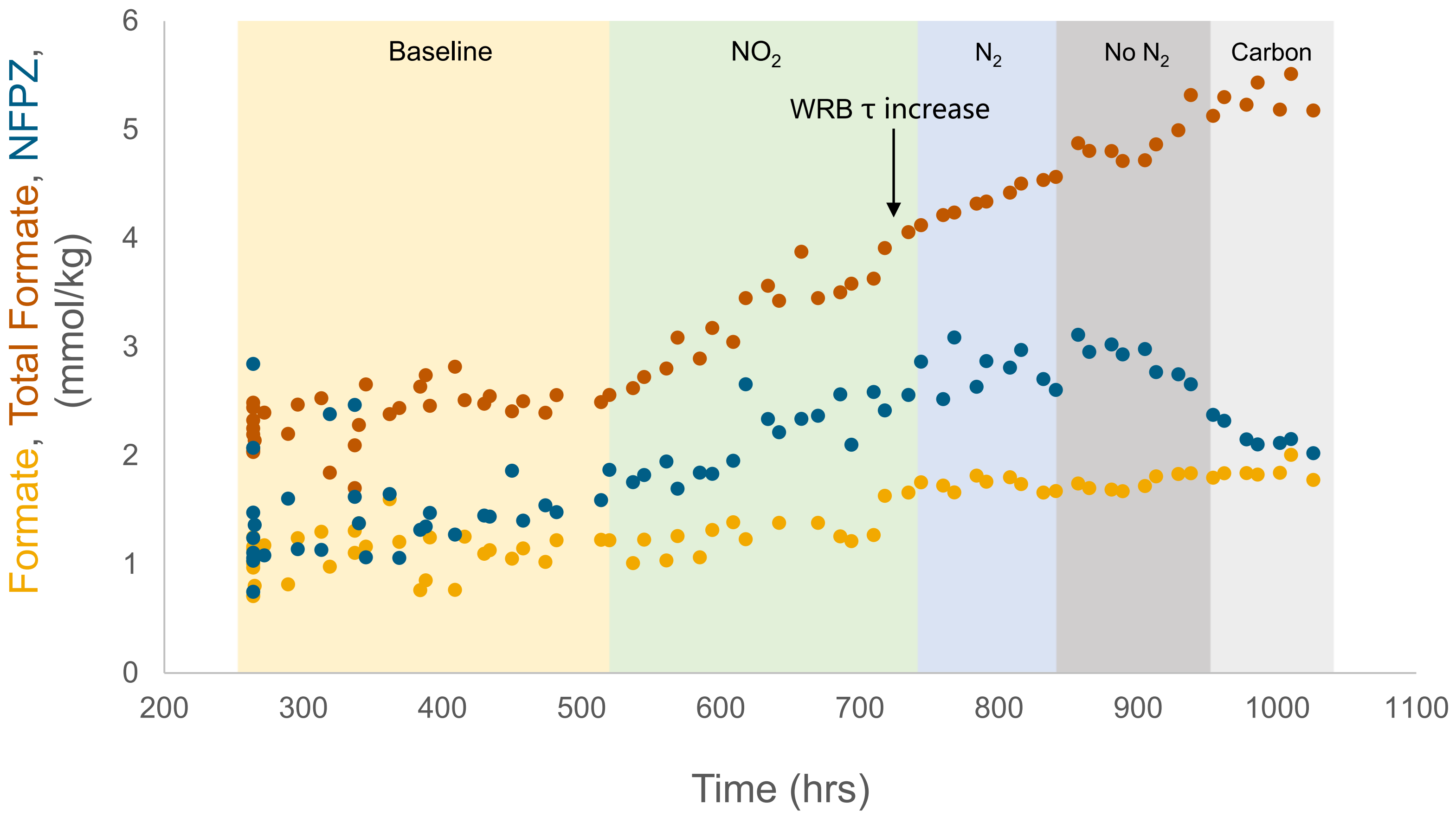
Amine (PZ) oxidation – role of NO_2



Where do we expect oxidation to occur?



Formate and formyl-amides at SRP



Amino acids in degraded amine solutions

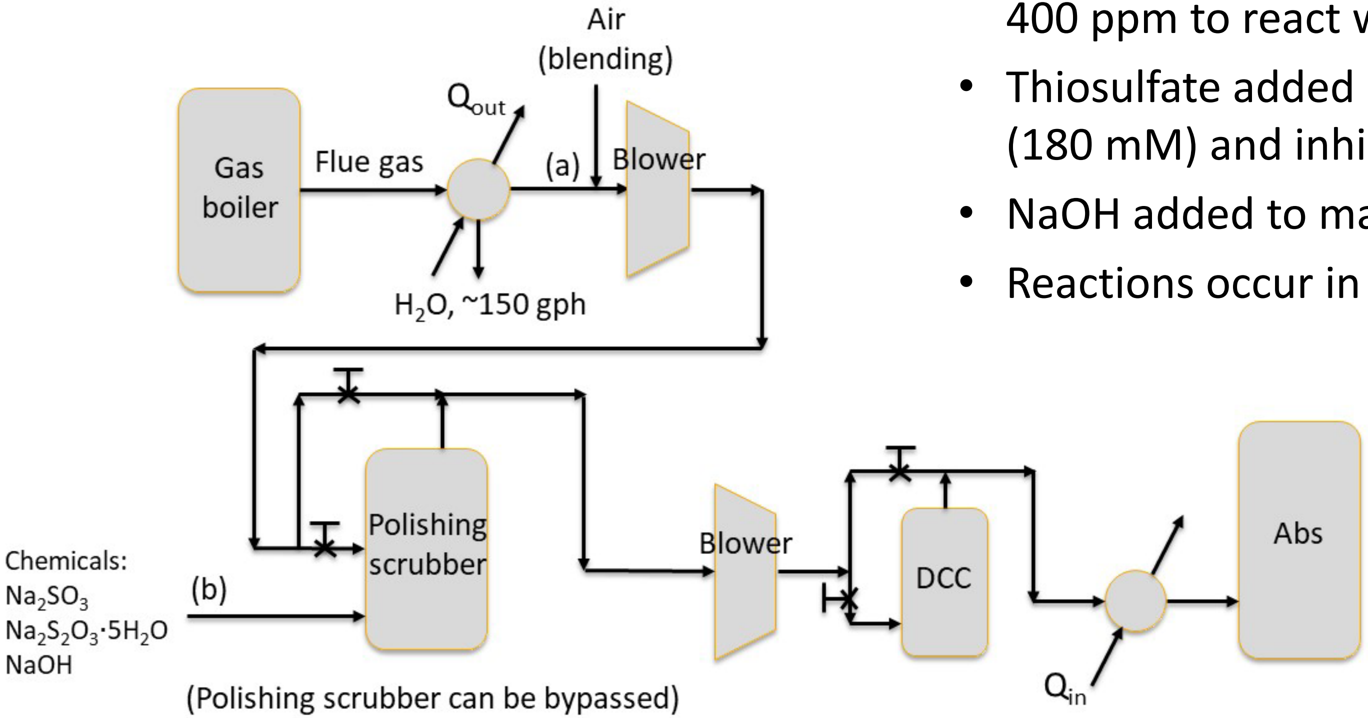
- Why investigate amino acids?
  - Ability of bicine to chelate metal ions (Lawson, 2003)
  - 2% mole N as amino acids in MDEA/PZ blends in gas conditioning plants (Thompsen, 2013)
  - Correlation to corrosion
- Ternary ligand complex formation stable at pH>7 (Mohamed, 2005)
- Amino acid analytical method history at UT (Closmann, 2011)
  - Dionex ICS-3000 with AminoPac PA10 column (Dionex AAA™-Direct)
  - Gold-oxide catalyzed oxidation of amino acids
  - Pulsed electrochemical detector
  - Bicine, glycine, HEG and HES all identified in degraded MDEA/PZ
  - Glycine detected at 5 mmol/L in temperature cycled (125 °C) 8 m PZ

Modifications at NCCC

NCCC pilot campaign – planned strategies

Modification	Purpose
Reduce NO_2 to < 1 ppm and measure	Use sulfite/thiosulfate in pre-scrubber to remove NO_2
N_2 sparging in the absorber sump	Test efficacy of DO stripping in the absorber sump
Remove iron (as chelates) with carbon bed	Test impact of removing oxidation catalysts over slipstream range 1 – 5 gpm
Test water wash configured as acid wash loop	Ammonia control
Perform pump-around intercooling of bottom packed section	Remove heat for process performance and lower emissions in stack
Adding corrosion coupons	Monitor corrosion simultaneous with oxidation

NO_2 reduction in flue gas prescrubber



- Chemistry in prescrubber (Selinger, 2018)
  - Sulfite (SO_3^{2-}) added as Na_2SO_3 to achieve 400 ppm to react with NO_2
  - Thiosulfate added as $Na_2S_2O_3$ to achieve (180 mM) and inhibit sulfite oxidation
  - NaOH added to maintain pH > 8
  - Reactions occur in liquid boundary layer

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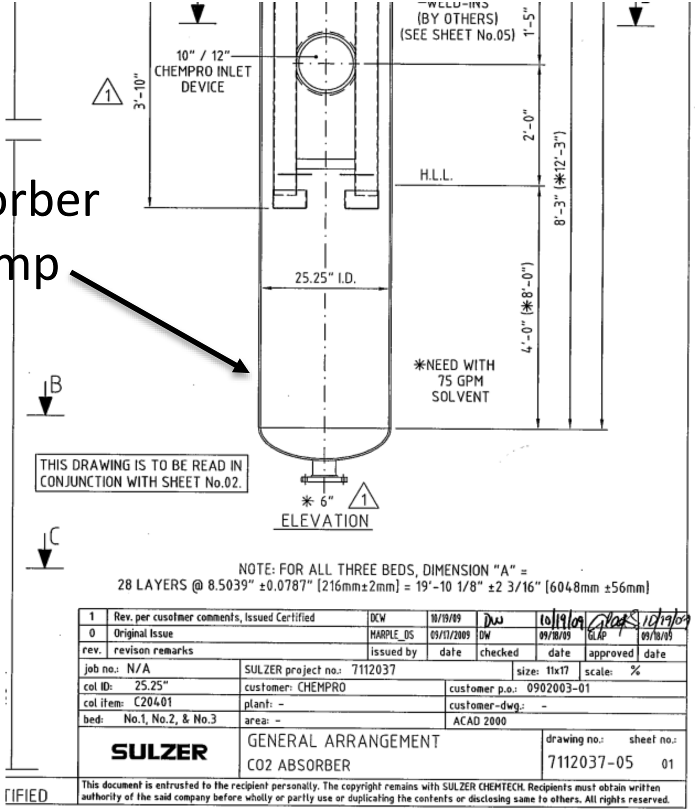
Dissolved oxygen stripping with N_2

- Will use new Mott sparge pipe with more A_{XS} than used in past to lower D_{bub}
- Abs pump-around intercooling will increase L by 4X in abs sump; will this affect sparge effectiveness?
- At ~2,400 SCFM, N_2 rates of 24 and 50 SCFM will be tested (start at 1% of abs gas traffic)
- N_2 sparge rate will be adjusted to maintain 5 - 25 fpm at nozzle/sparge pipe and $^*D_{bub}$ < 1 mm
- Will measure DO downstream and estimate NTU and HTU; expect ~2.5 NTU from SRP results

Absorber sump



*Design Guide & Part Selection, Mott Corporation (www.mottcorp.com); recommendations for water service.

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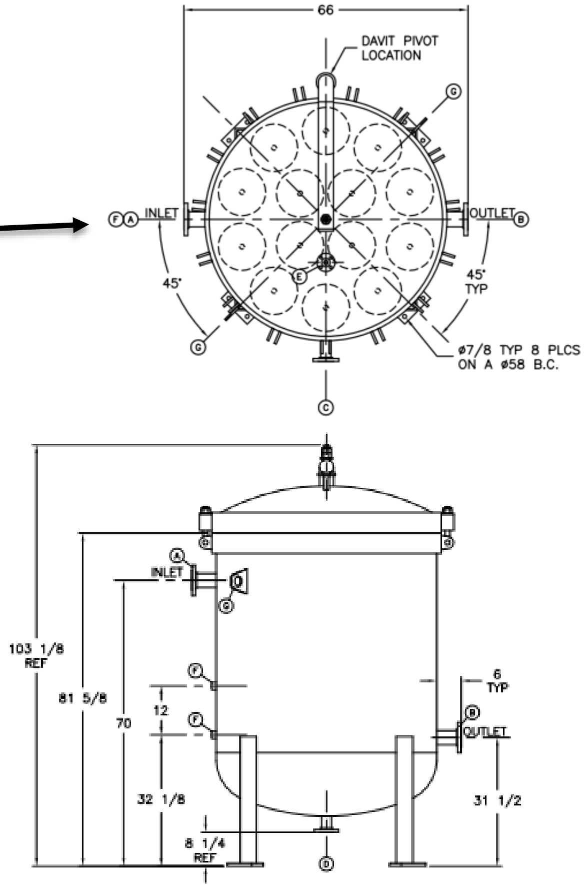
Remove degradation products & iron with carbon bed

- Will use existing equipment that has been used in past campaign(s)
- Fourteen sets of two cannisters (28 total); offers flexibility - will run 6 cannisters
- Desired flow range (1 – 5 gpm) at nominal L of 12 gpm (8 to 40%)
- Adds ~300 gallons of solvent inventory
- Will run minimum four weeks; capture breakthrough as color change (UV-Vis)



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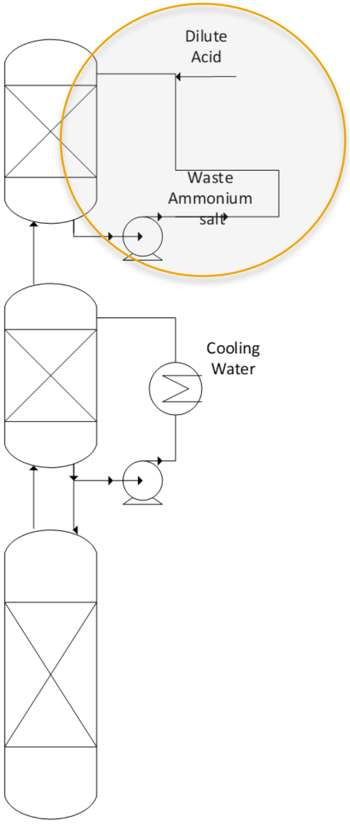
Test acid wash loop for ammonia control

- Water wash loop required for water balance
- Water wash does not remove ammonia if wash water is returned to the process; accumulates until emissions equal to rate of production
- Bleed of wash water or stripper condensate with high NH_3 can reduce emissions
- Acid wash (H_2SO_4) with bleed will be tested to remove NH_3
- Challenge will be to operate long enough to obtain steady state ammonia concentrations with and without acid wash



Water Wash +
Acid wash

NCCC pilot campaign – planned strategies

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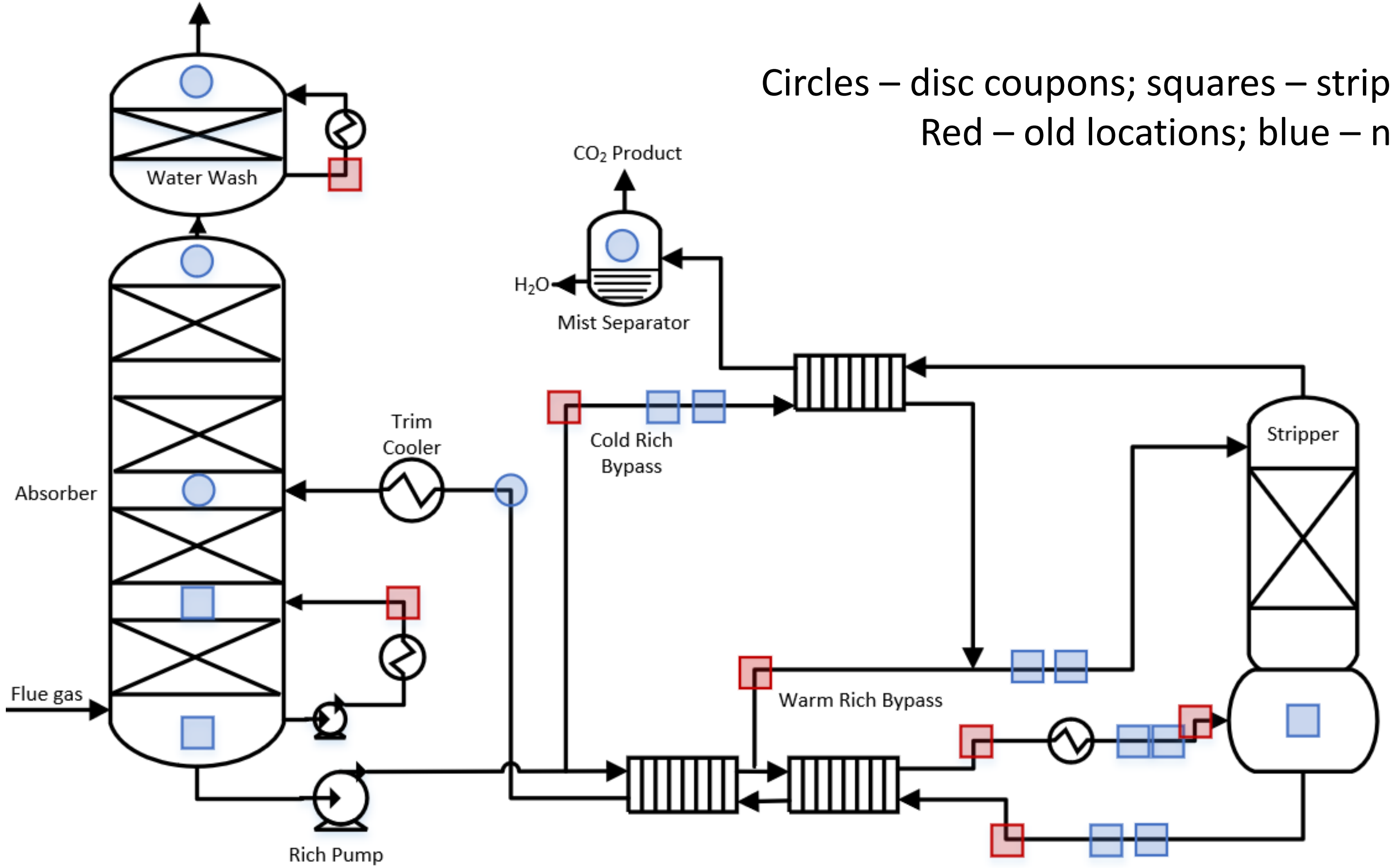
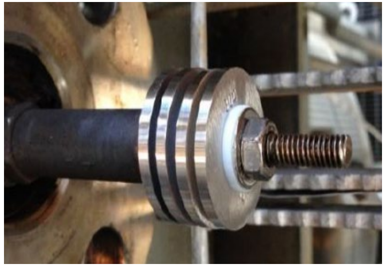
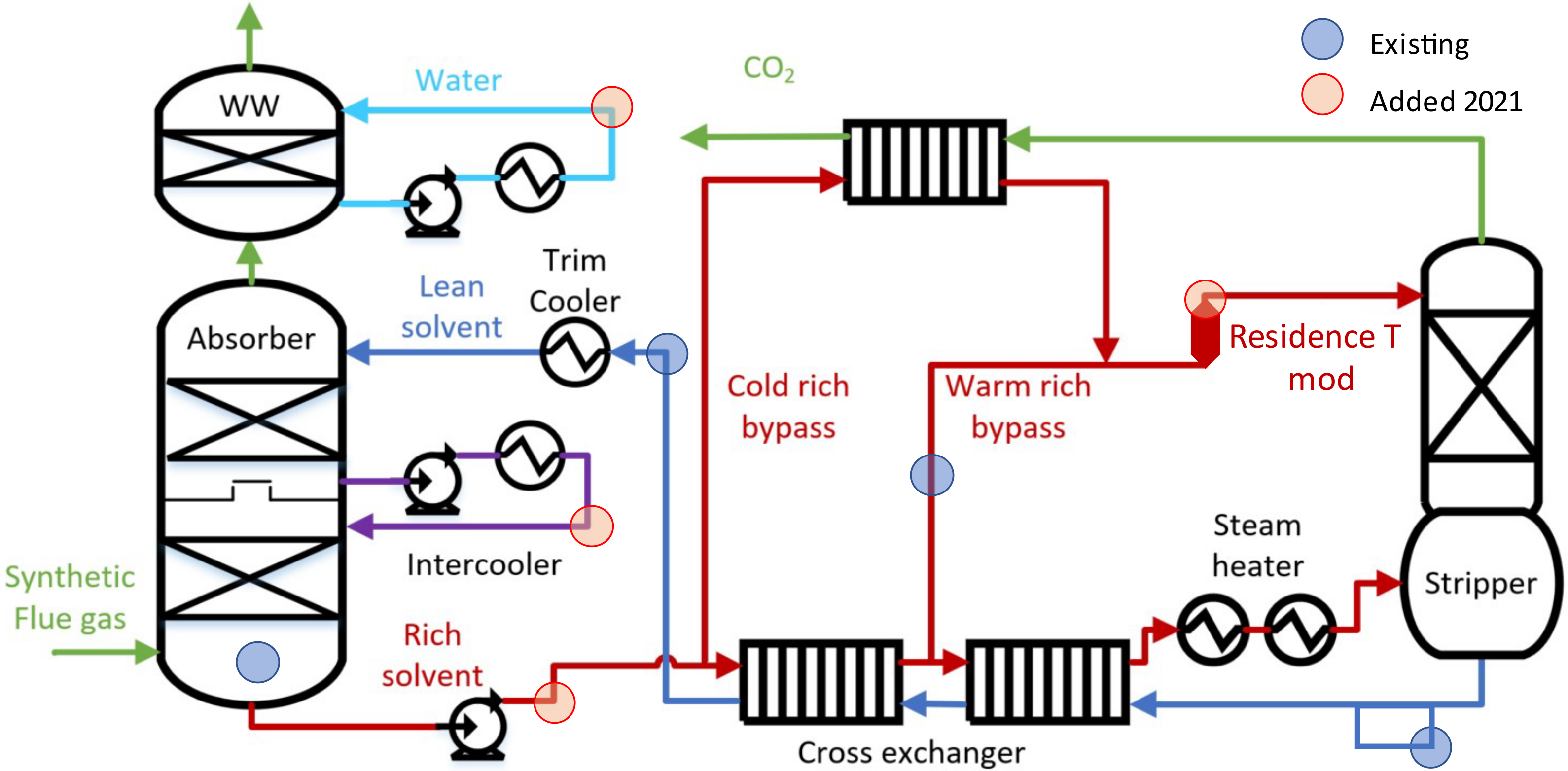
Proposed corrosion coupon locations

Circles – disc coupons; squares – strip coupons (see photos)
Red – old locations; blue – new locations



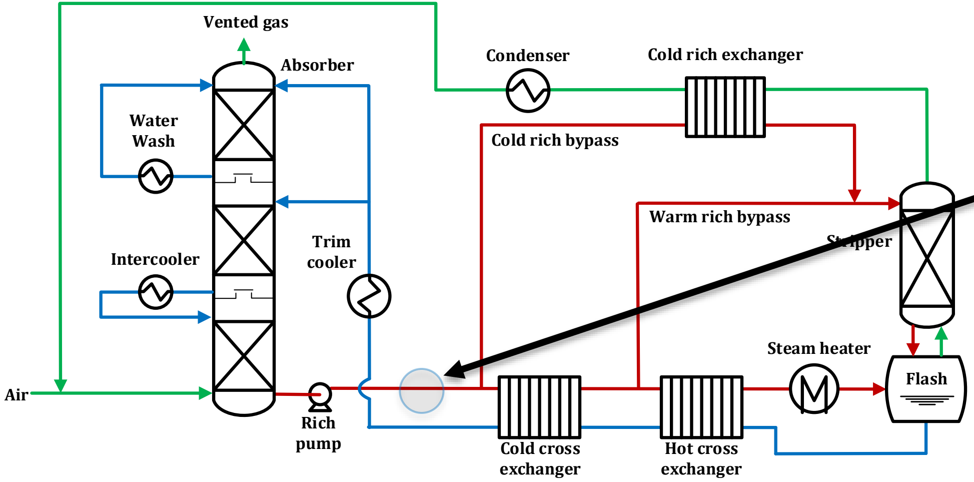


SRP corrosion coupon locations



SRP pilot campaign – add carbon bed in rich amine line

- Pass 5-10 % liquid rate slip-stream through carbon bed
- Single-pass removal sock design
- Size will limit time on stream due to break-through
- Using pressure of rich amine line downstream of pump to push liquid through carbon bed; return to absorber
- Same fresh carbon used at NCCC



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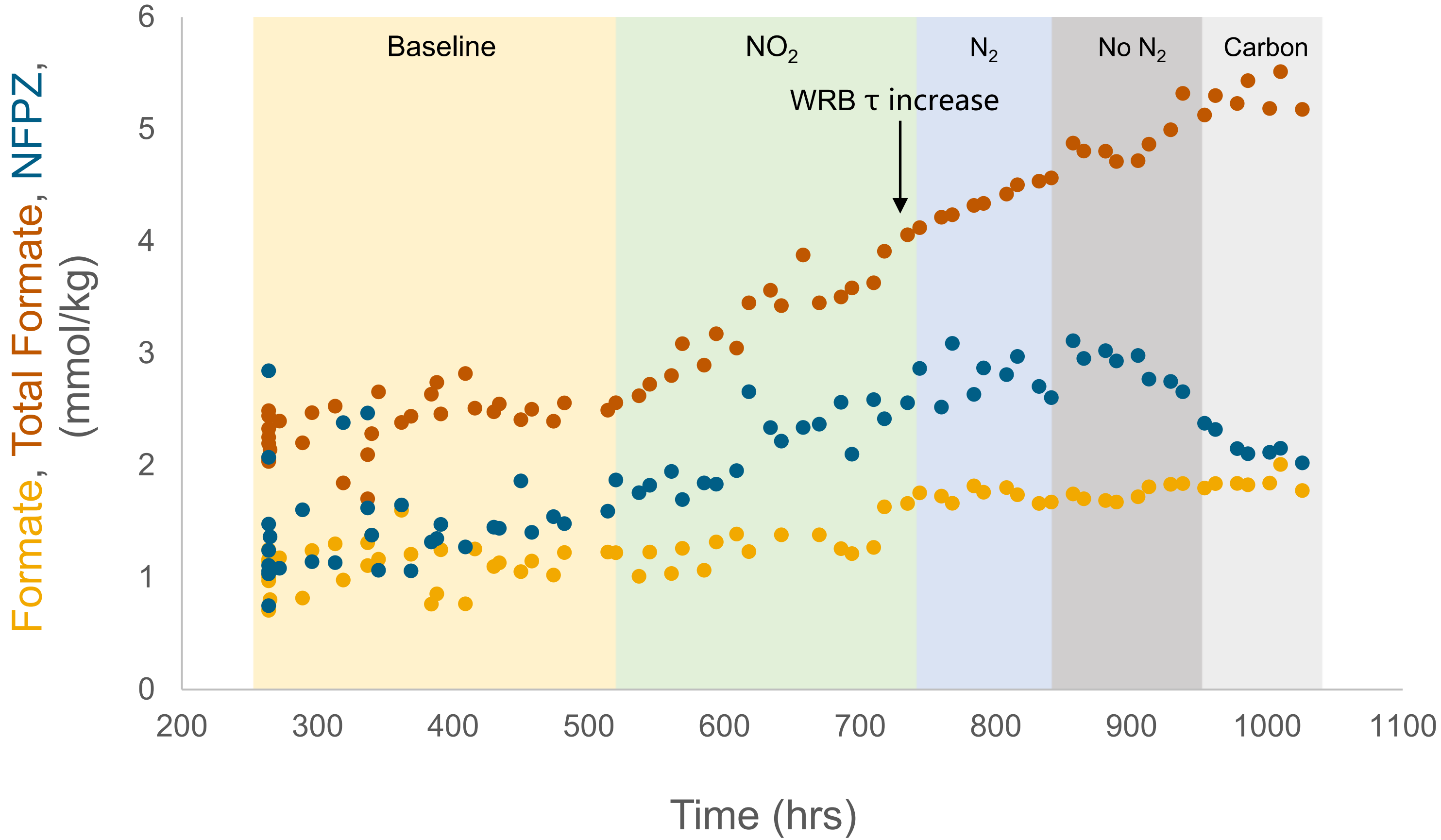
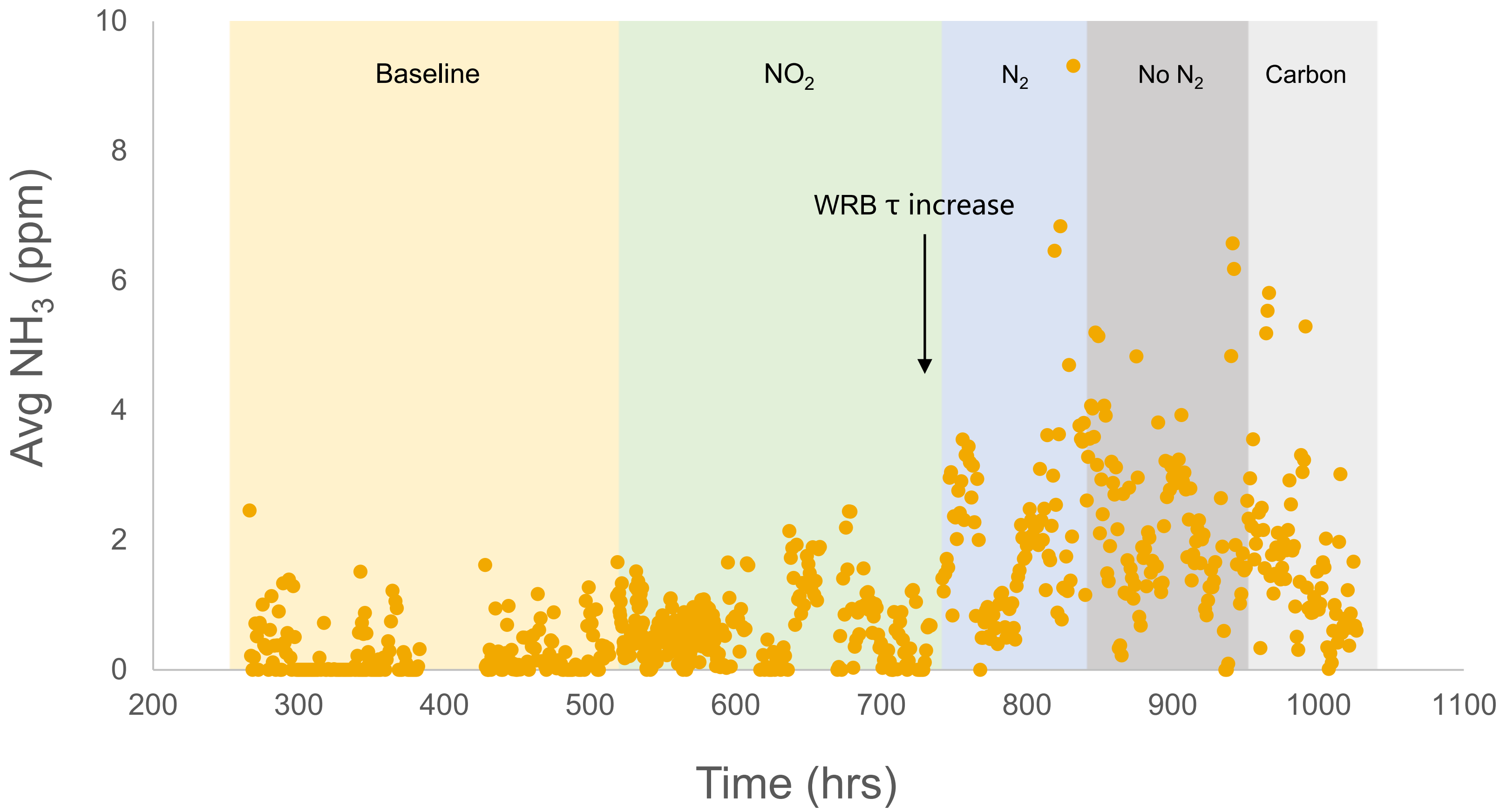
SRP pilot campaign – formate and N-formyl amides



SRP pilot campaign – NH_3 in absorber knock-out drum (FTIR)



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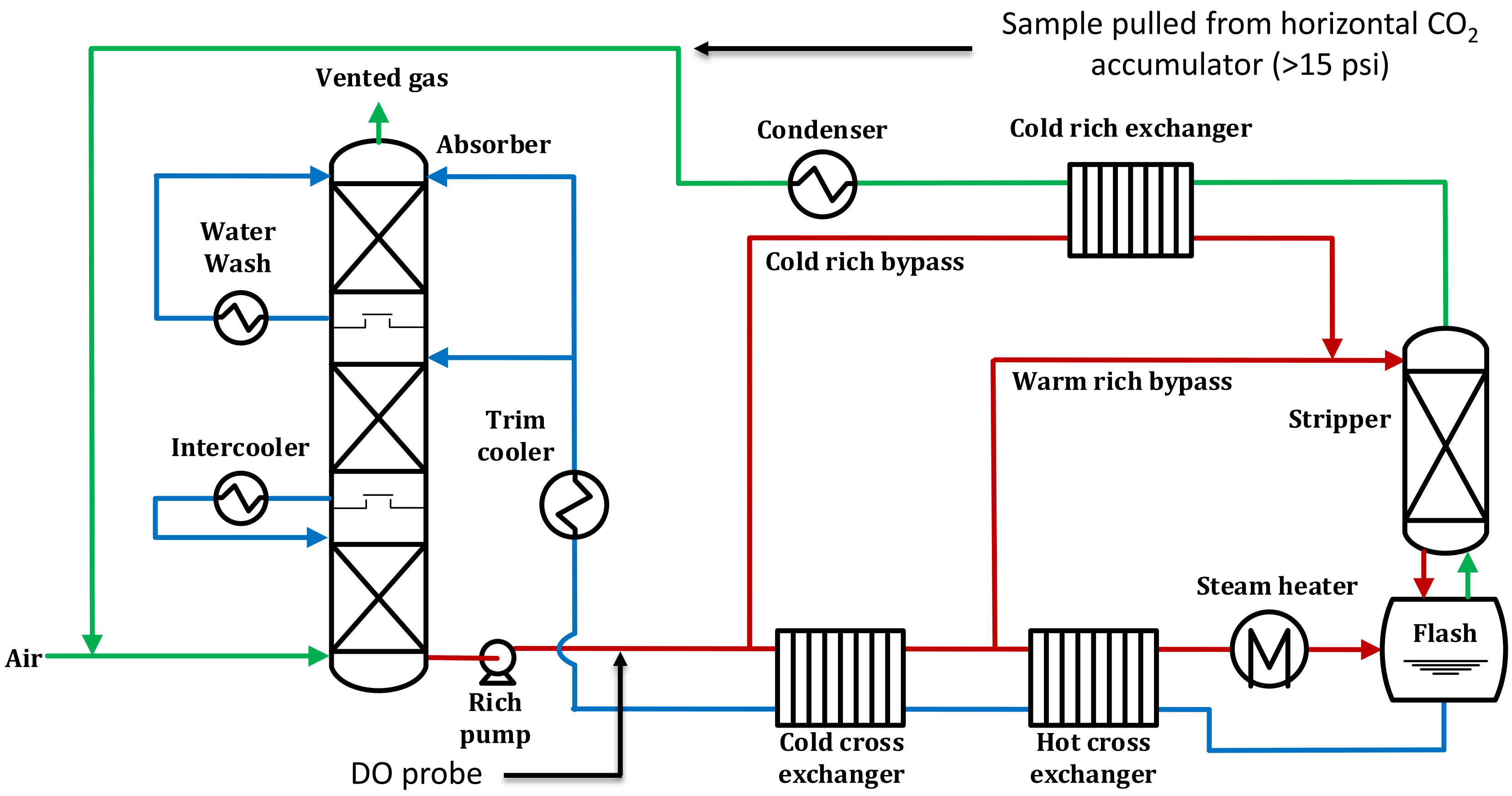
Oxygen measurement in CO_2 gas



DO and entrained oxygen removal