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

2023 Carbon Management Research Project Review Meeting
August 28 – September 1, 2023

Outline

- Project objectives and approach
- Project budget, structure, and performance dates
- Solvent oxidation sources
- NCCC pilot oxidation data (2023); focus on mitigation methods
- Conclusions

Project objectives and approach

Develop technologies to mitigate oxidation of amines due to presence of O_2 and NO_2 in flue gas.

- Test solvent oxidation mitigation methods in lab
- Test promising oxidation mitigation technologies at UT Austin SRP (0.1 MW_e) - Completed April 2022
- Test oxidation mitigation technologies at larger scale at National Carbon Capture Center, Wilsonville, AL (1 MW_e) - Ongoing
- Perform economic analysis of oxidation mitigation strategies

Performance dates

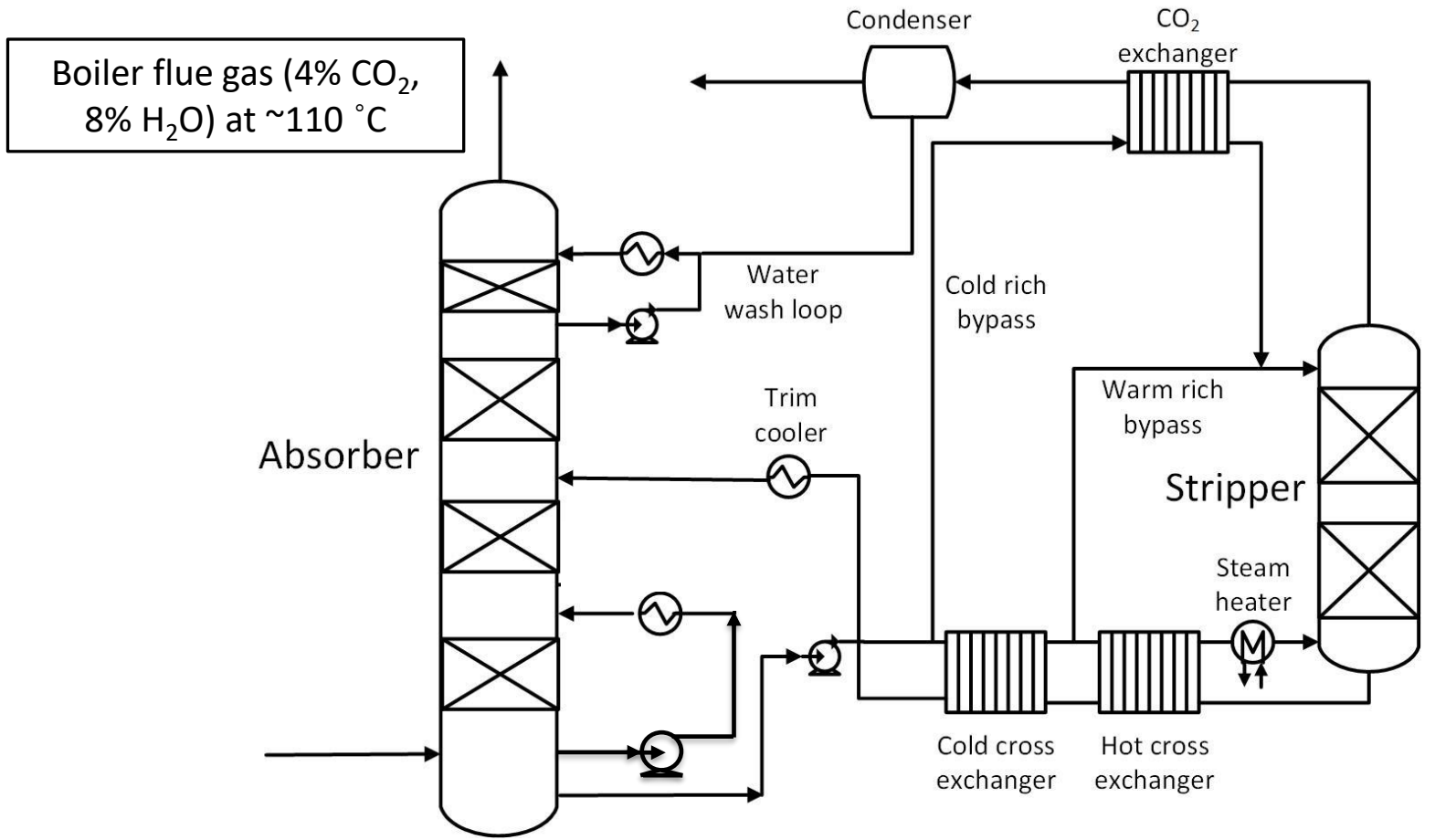
Budget Period	Start Date	End Date
1	March 1, 2020	May 31, 2021
2	June 1, 2021	April 30, 2022
3	May 1, 2022	March 31, 2024

Project budget (DE-FE0031861)

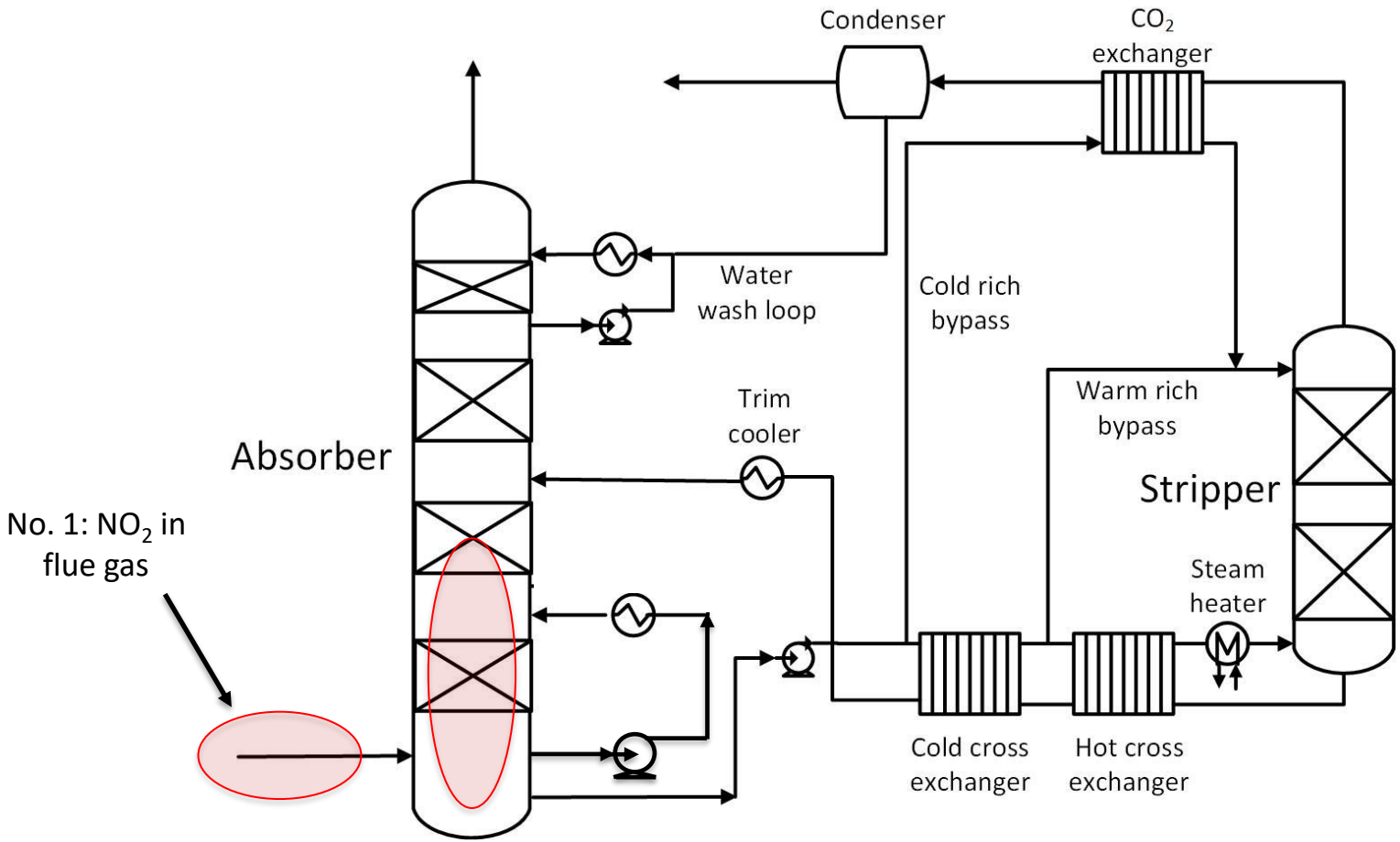
Description	BP1 ($)	BP2 ($)	BP3 ($)
Salaries (PI/staff/grad students/SRP)	342,316	416,116	278,123
Fringe	95,361	118,687	91,036
Travel	7,016	9,601	23,498
Equipment	230,100	5,000	102,657
Supplies	54,450	74,153	73,801
Tuition	38,658	39,435	40,260
Indirect/Overhead (56.5%)	282,015	349,766	263,549
Total by 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

Three oxidation mechanisms of interest

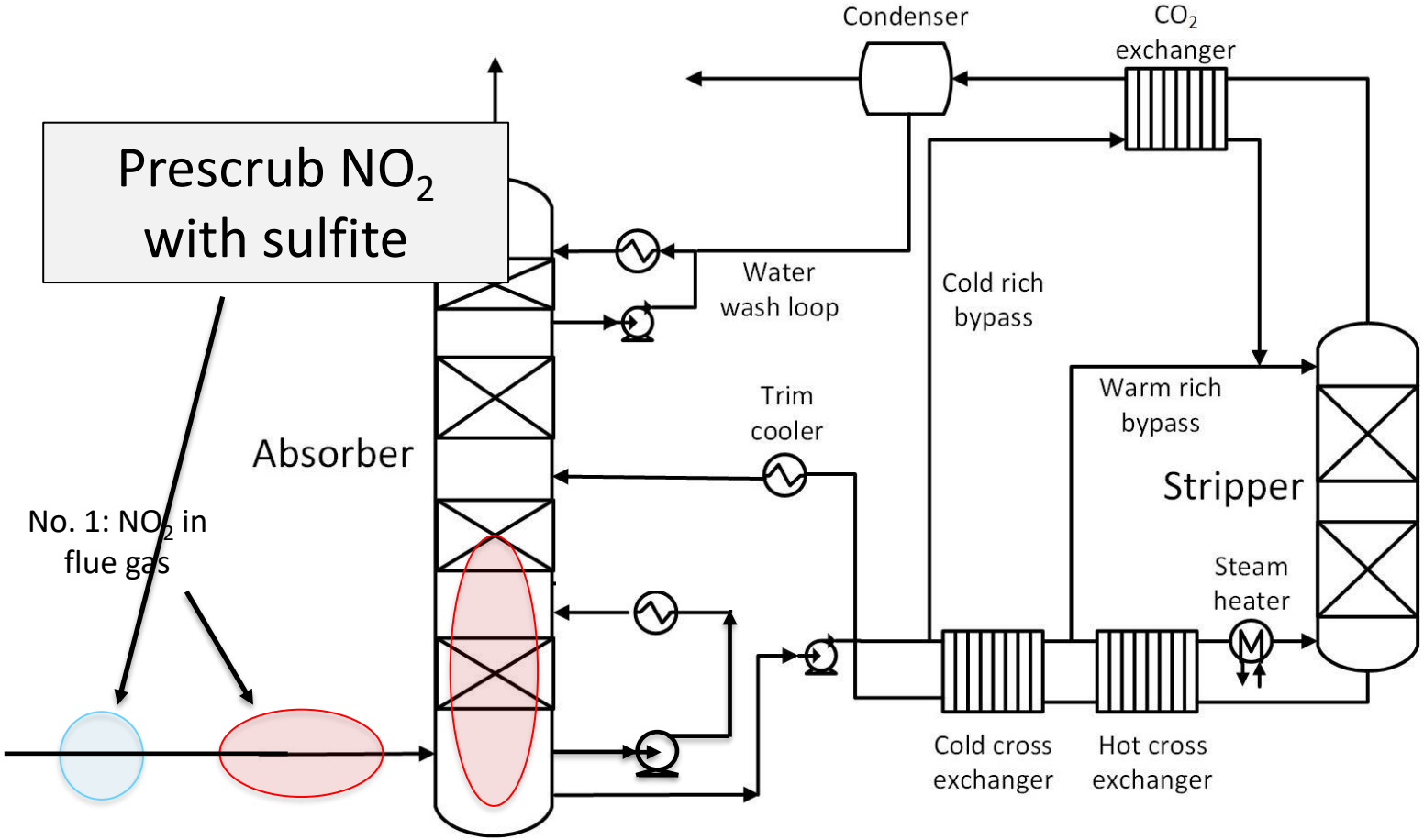
Amine oxidation sources



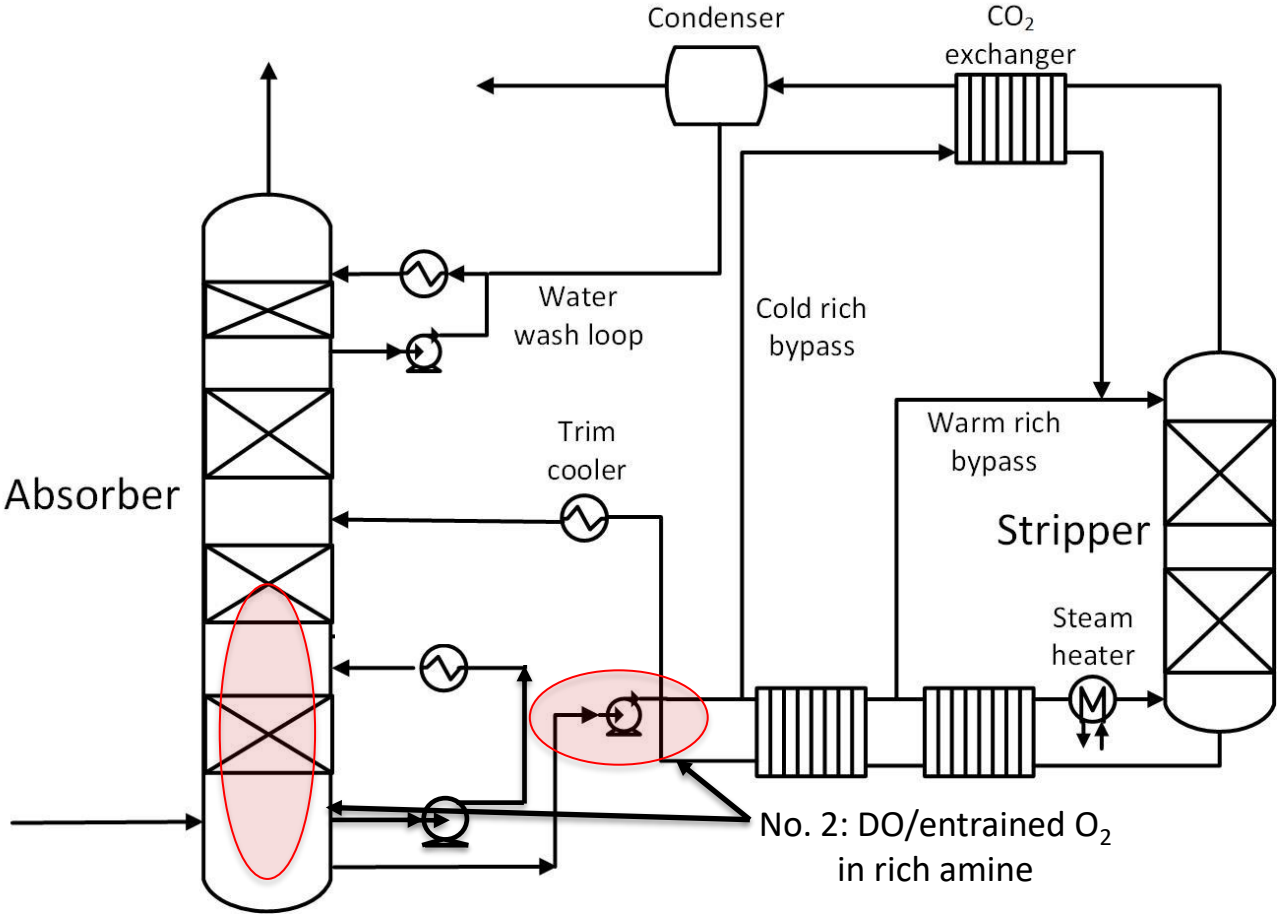
Amine oxidation sources



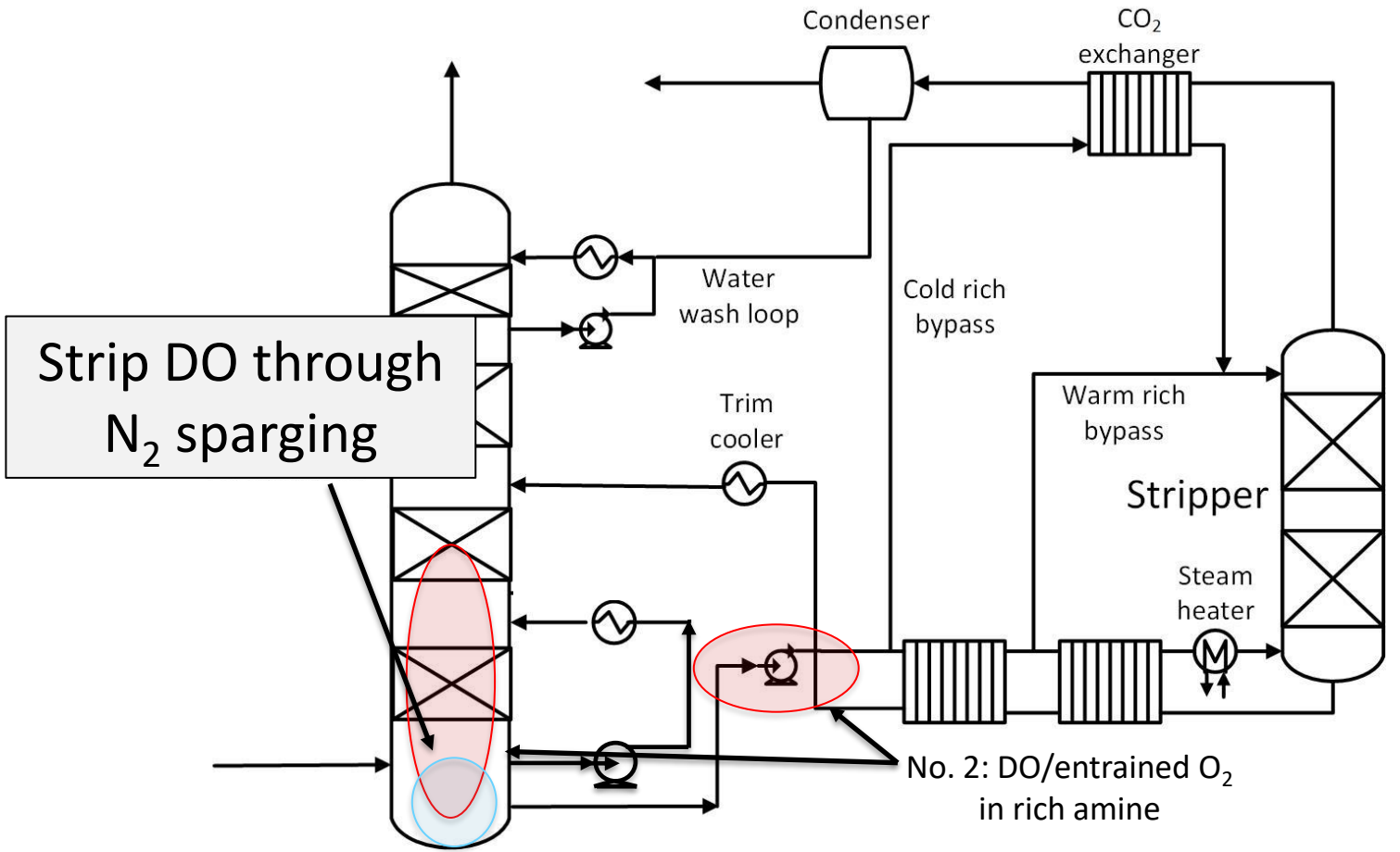
Amine oxidation sources



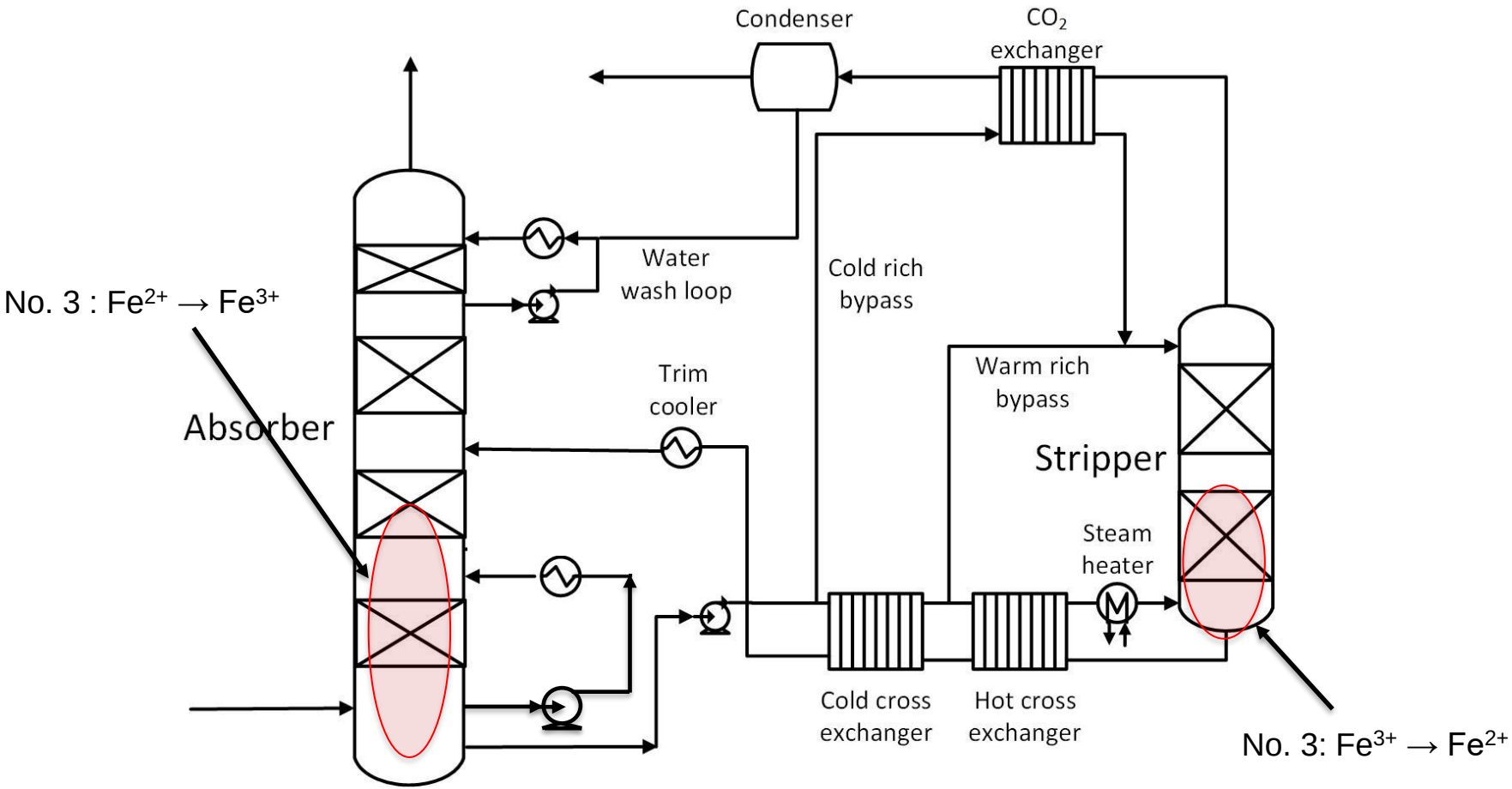
Amine oxidation sources



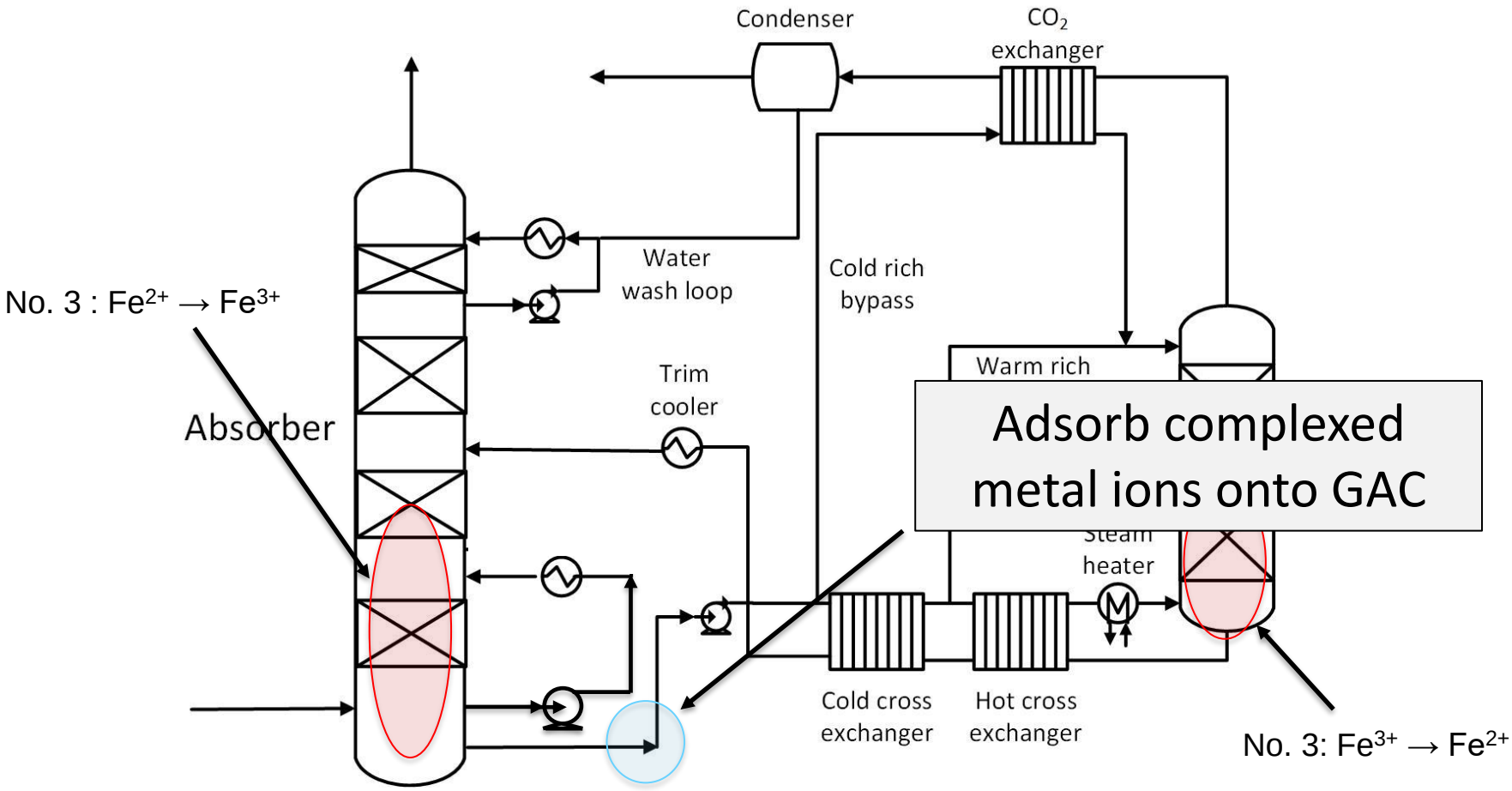
Amine oxidation sources



Amine oxidation sources



Amine oxidation sources



NCCC campaign overview

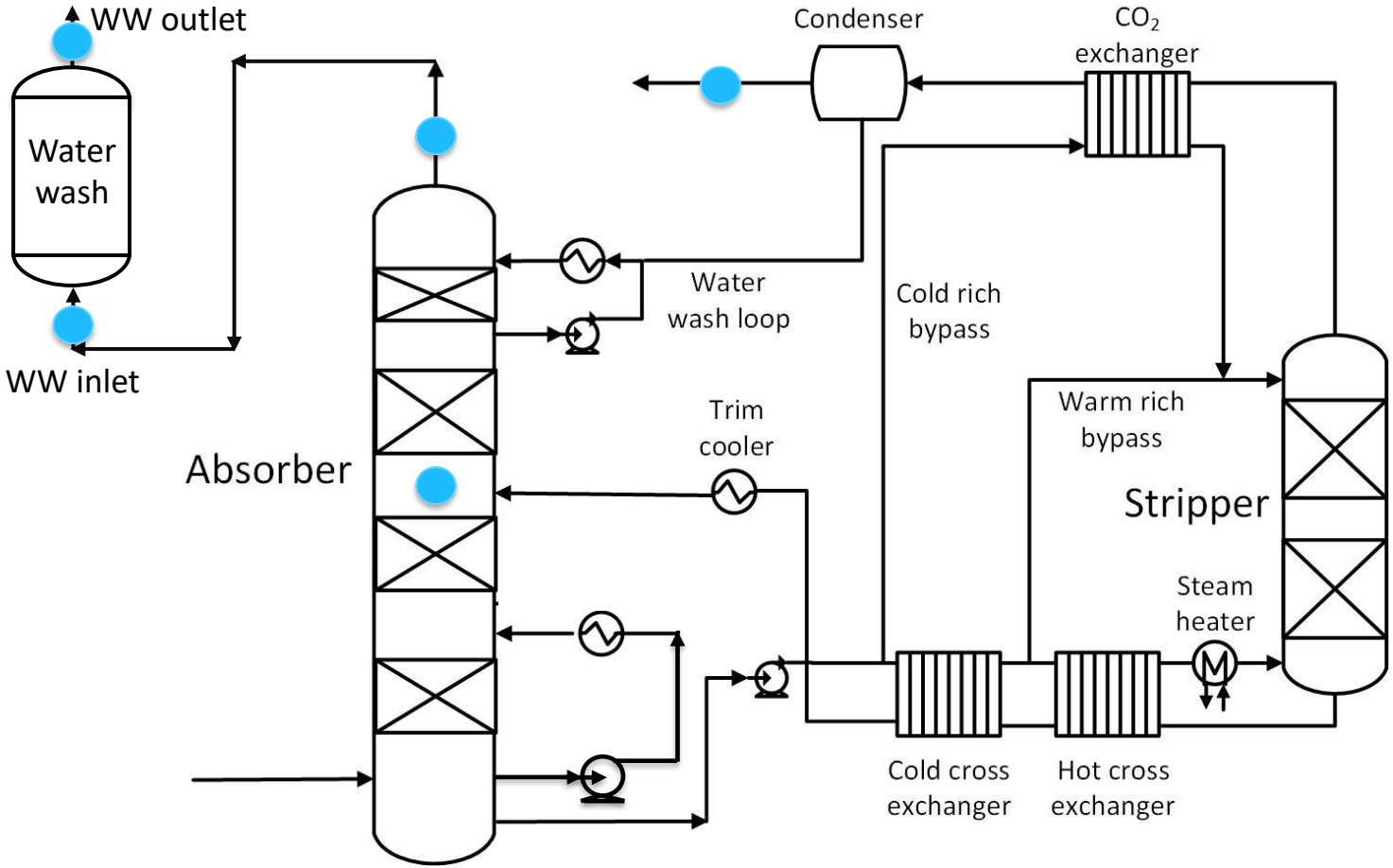
SRP and NCCC pilot plants

Parameter	SRP (UT Austin)	NCCC (Southern Co.)
Size equivalent (MW_{eq})	0.1	1.0
Solvent inventory (gal)	~350(a)	1500(b)
Abs diameter (inches)	16.8	25.3
Abs packing height (feet)	20	40
Abs sump τ (min)	15(c)	6(d)
Flue gas source	Synthetic	Commercial - nat gas boiler or coal
Flue gas rate (lb/hr)	3,000	8,000
CO_2 capture rate (MT/d)	1.5	6
Flue gas (NO_2) ppm	0 (added 1 ppm)	2.5 (nat gas boiler)

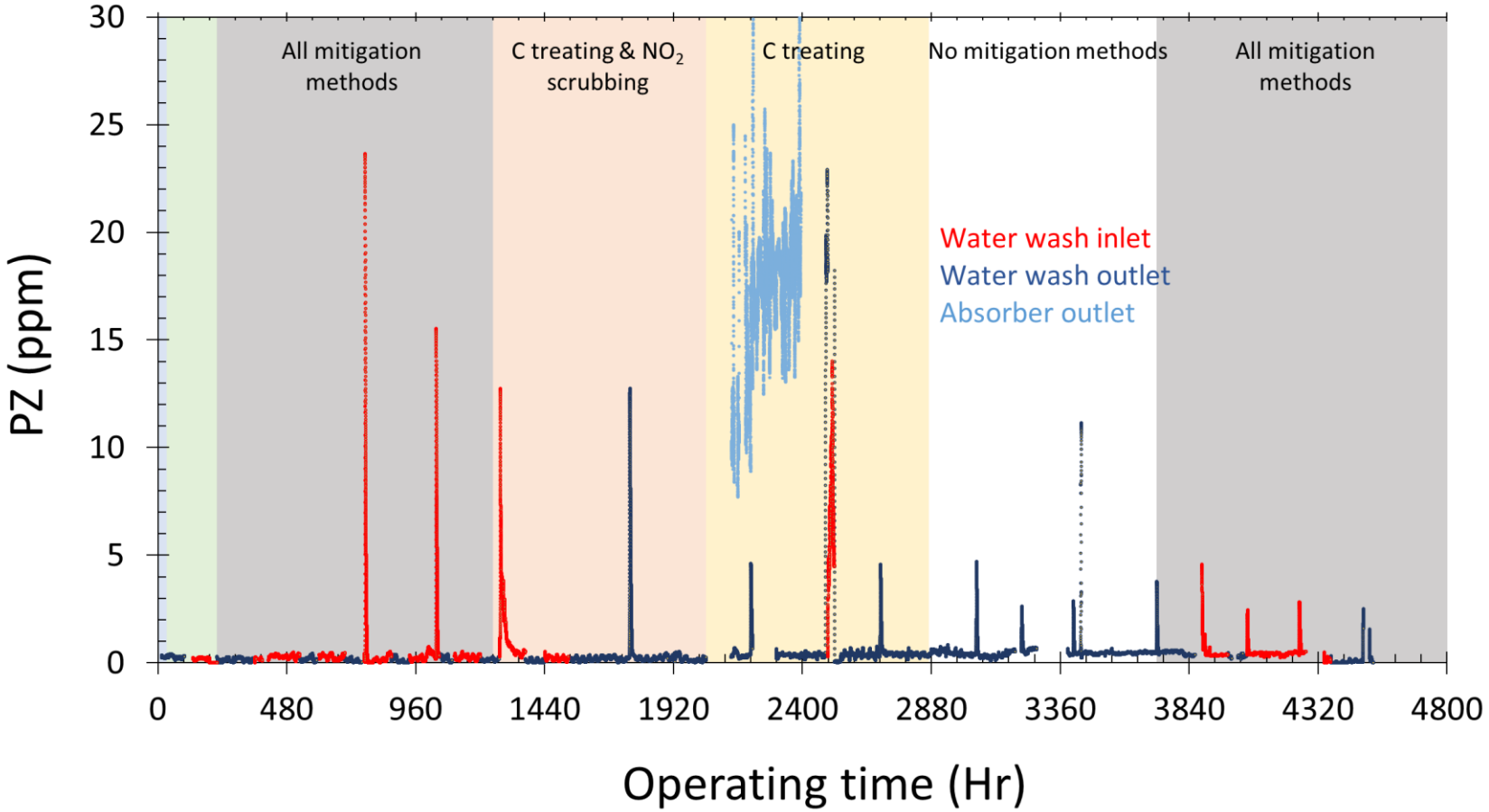
(a) Lean amine tank bypassed; (b) includes carbon bed loop; (c) at L = 4 gpm; (d) calc at L ~ 16 gpm (~3.5 gpm/ft^2) & 3.5 ft liquid height.

Gas phase monitoring data (2023)

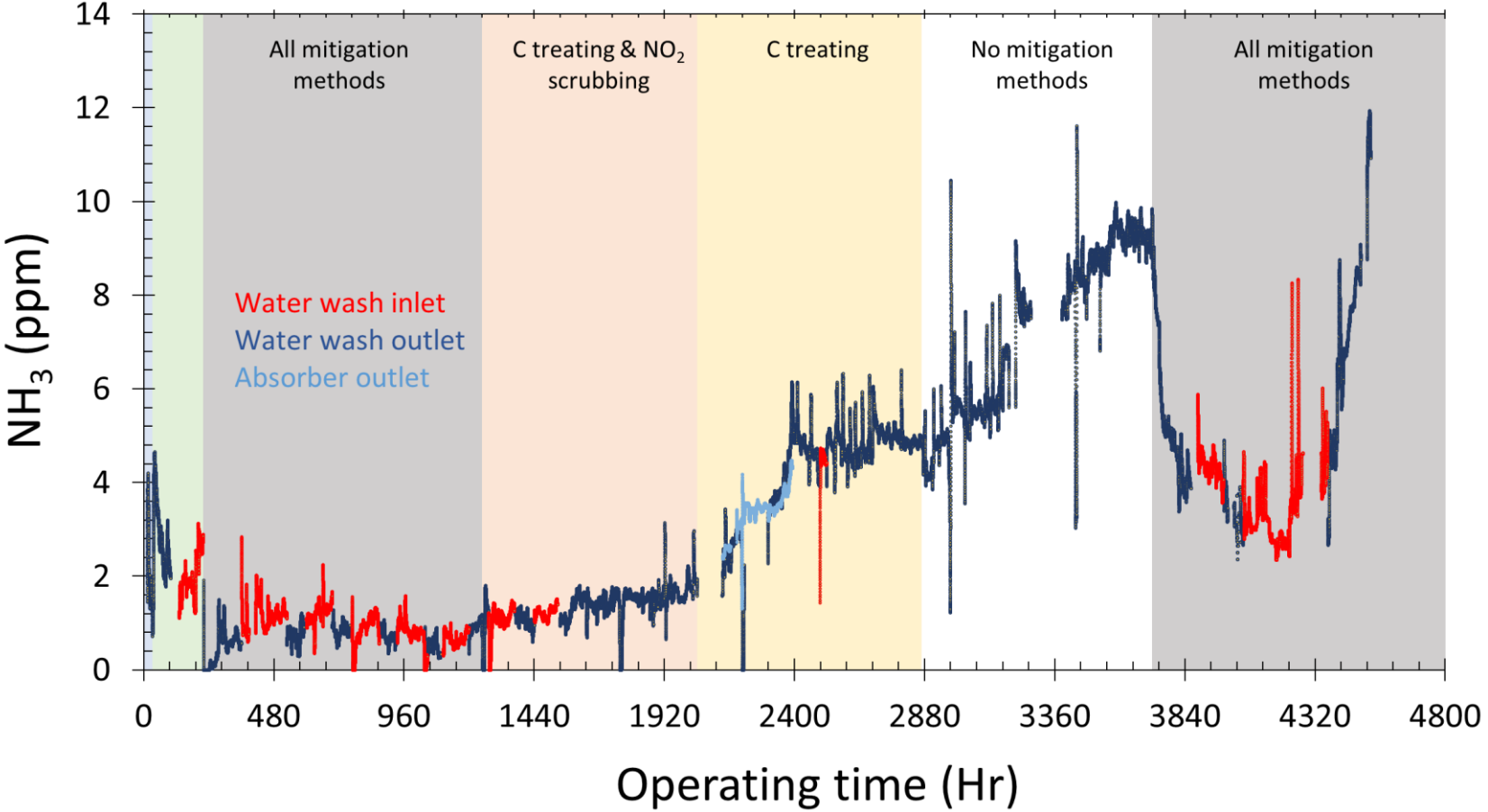
Gas phase monitoring points



Flue gas monitoring data (FTIR)



Flue gas monitoring data (FTIR)



Flue gas monitoring data (PTR-TOF-MS)

Outlet to water wash (all data ppbv)

Date	Water wash Operation	NH_3	PZ	Acetaldehyde
7/21	Conventional	8,300 (6,600)	100 (180)	30 (2,670)
7/31	Trickle bed + WWC	4,200	0.2	22
8/7	Bed 3 + acid wash	165	0.1	45

Data in () measured with FTIR.

Flue gas monitoring data (PTR-TOF-MS)

Outlet to water wash (all data ppbv)

Date	Water wash Operation	NH_3	PZ	Acetaldehyde
7/21	Conventional	8,300 (6,600)	100 (180)	30 (2,670)
7/31	Trickle bed + WWC	4,200	0.2	22
8/7	Bed 3 + acid wash	165	0.1	45

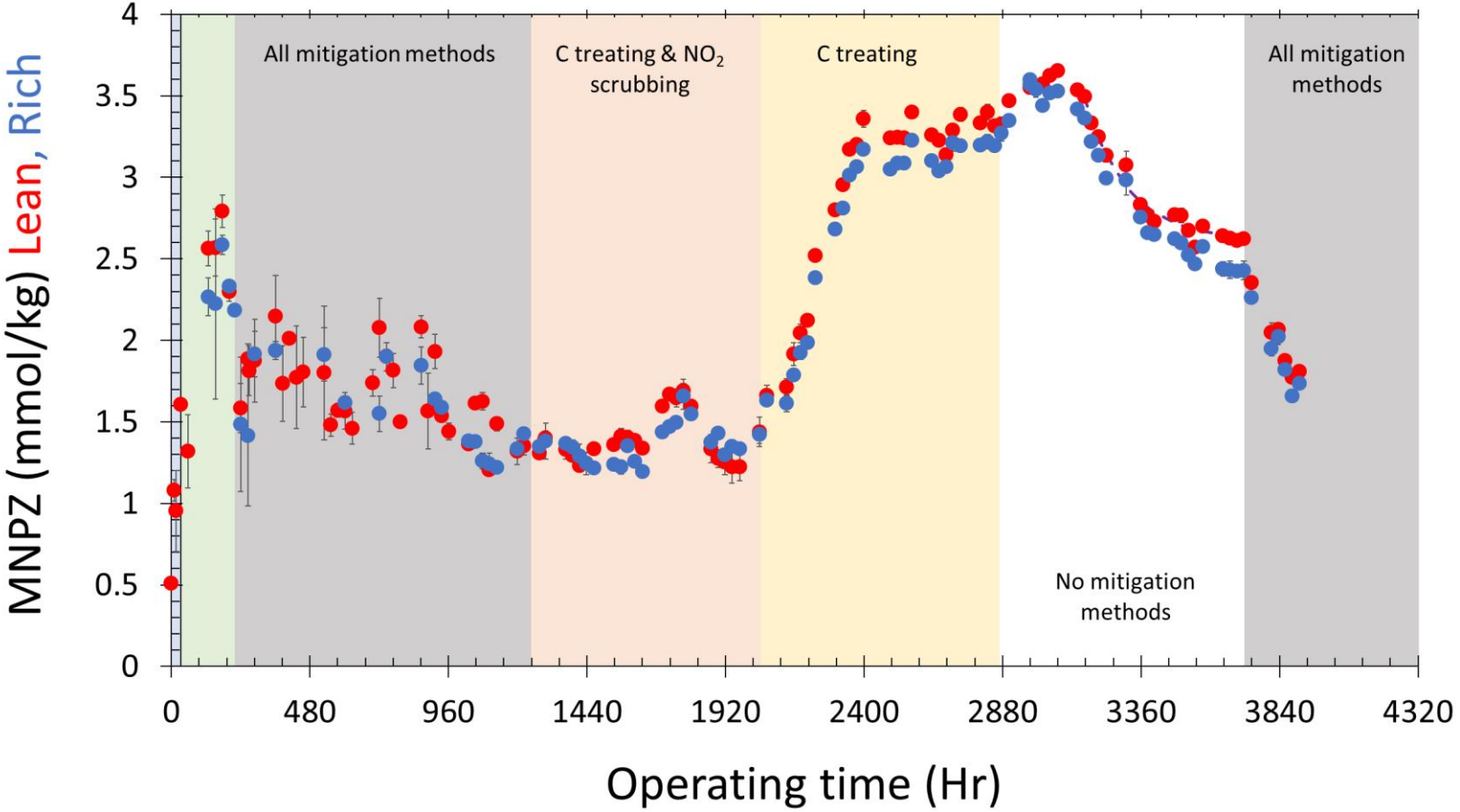
Data in () measured with FTIR.

- FTIR measuring NH_3 similar to TOF
- Other compounds interfere w/ FTIR measurement of acetaldehyde
- Acid wash reduced NH_3 by 95%

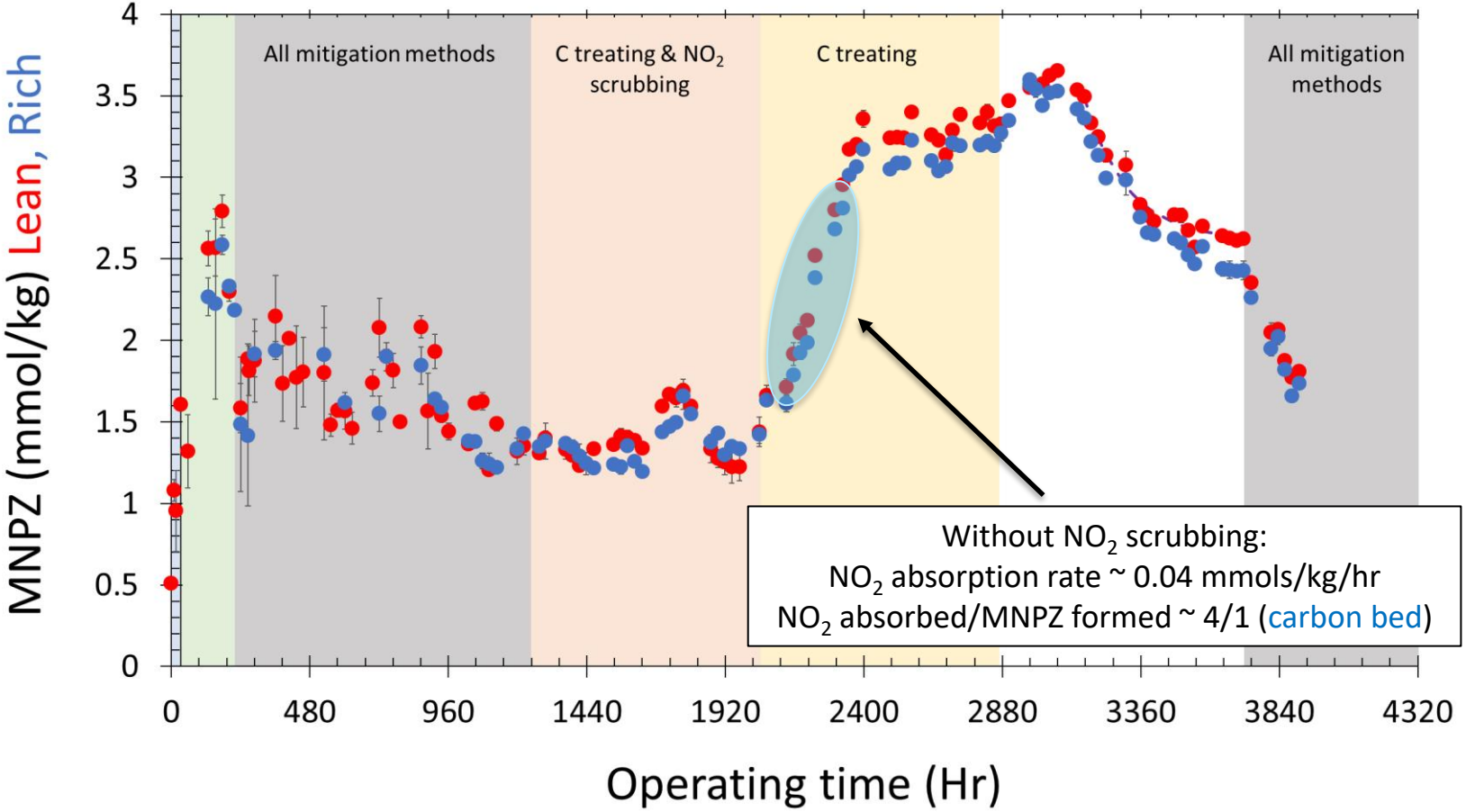
Degradation data (2023)

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

MNPZ by HPLC at NCCC (2023)

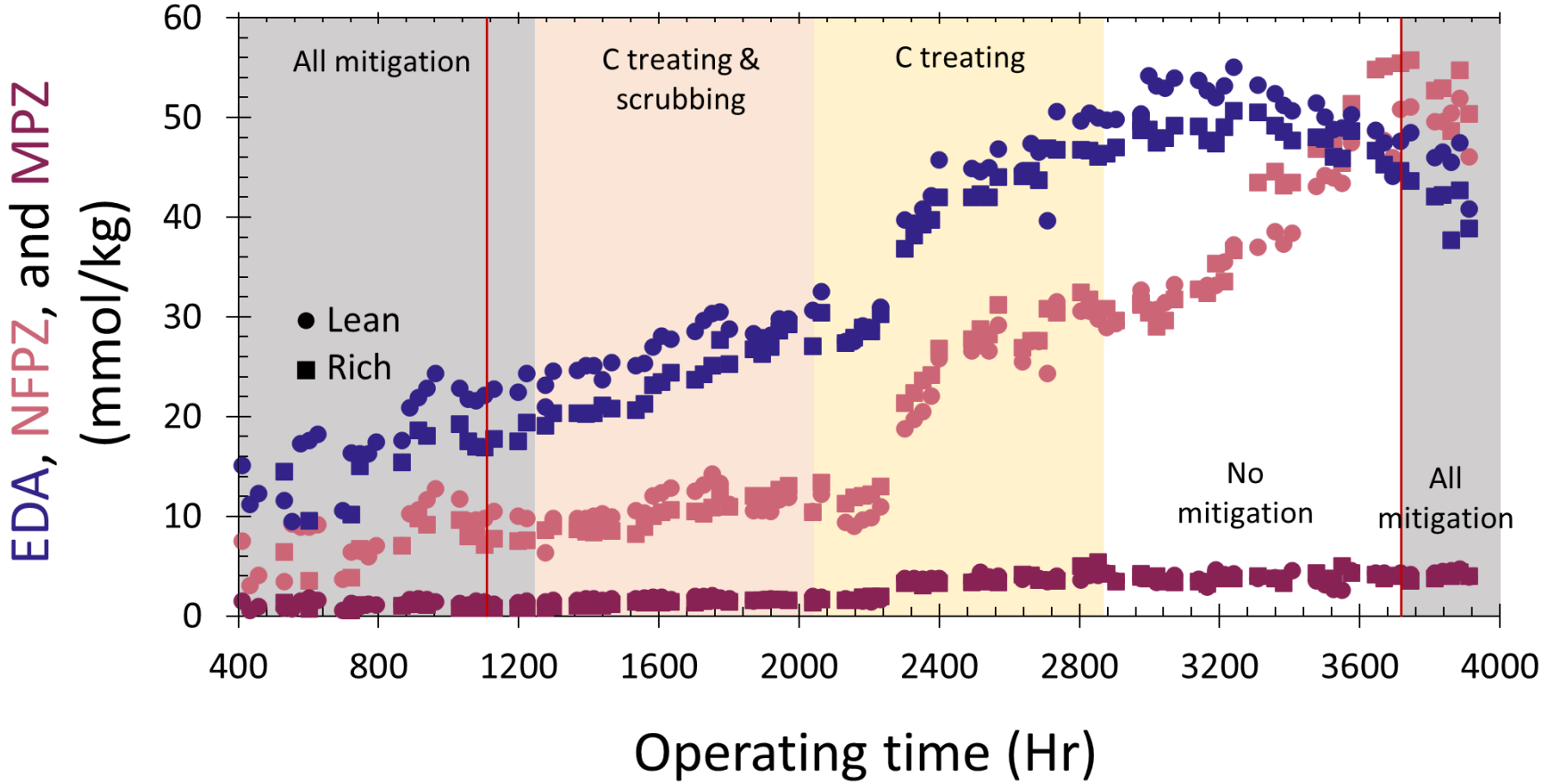


MNPZ by HPLC at NCCC (2023)



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

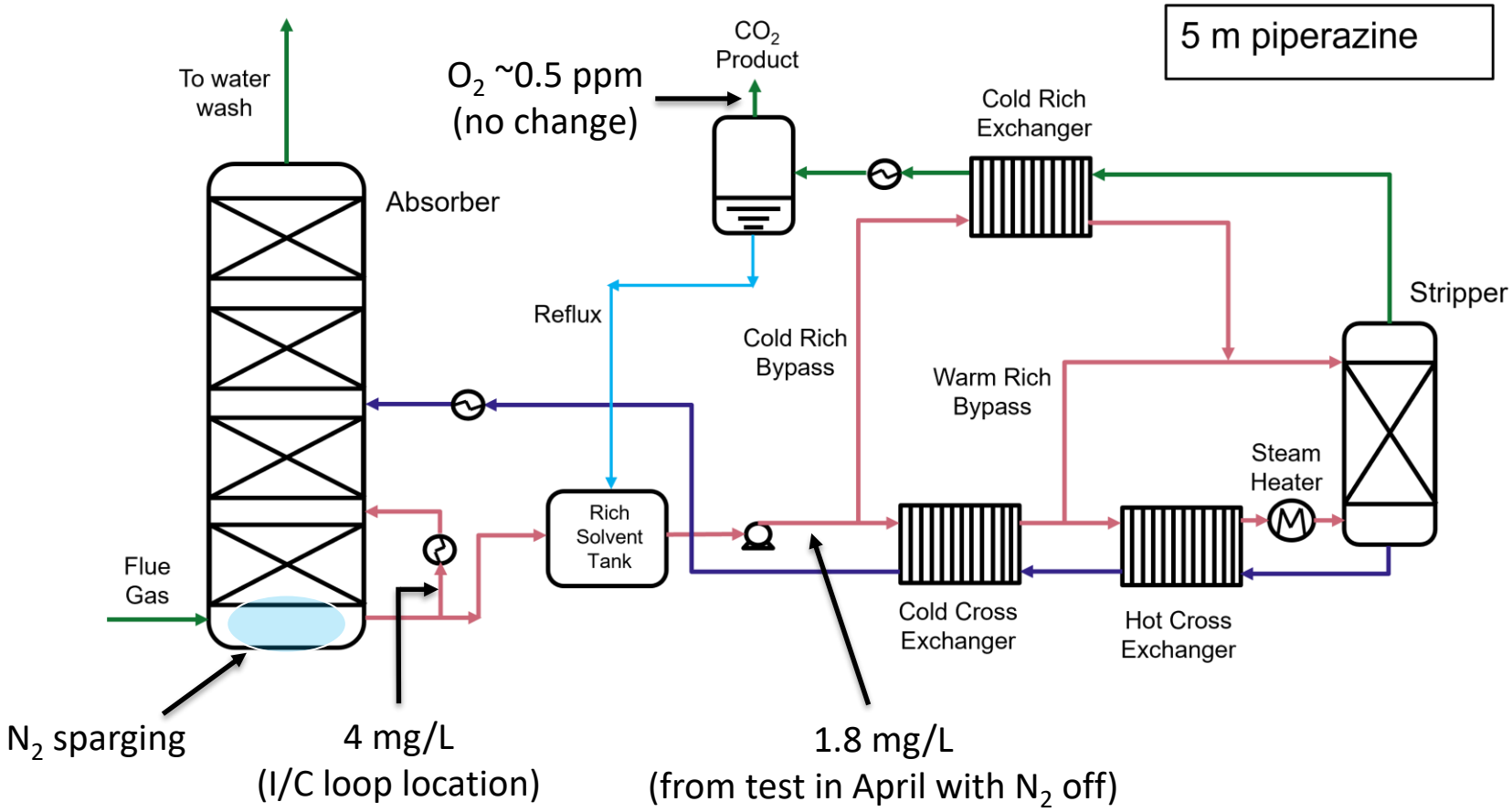
Degradation products by cation IC at NCCC (2023)



Dissolved oxygen stripping

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

DO measurements



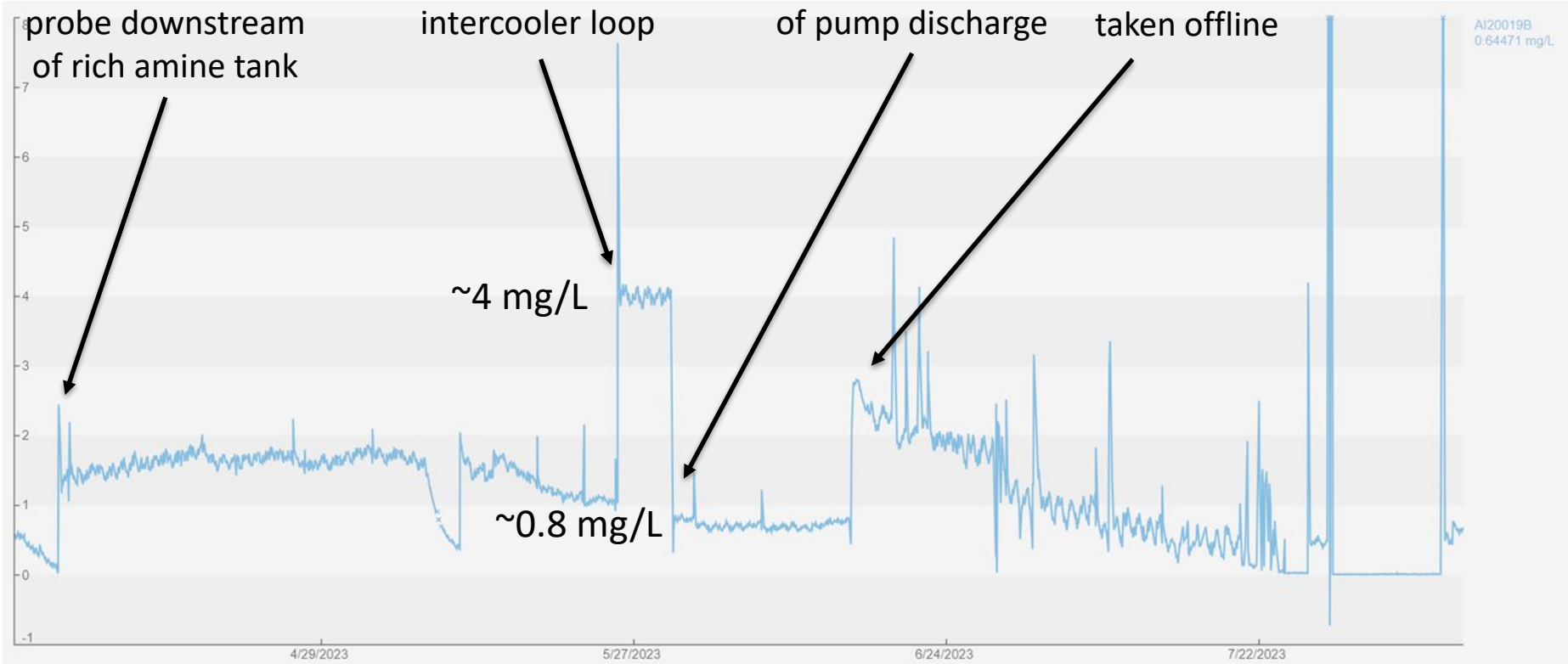
DO probe readings with N_2 sparging off

4/5/2023
N_2 sparging off; probe downstream of rich amine tank

5/25/23
DO probe moved to intercooler loop

5/30/23
Probe downstream of pump discharge

6/15/2023
Carbon bed taken offline



~4 mg/L

~0.8 mg/L

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

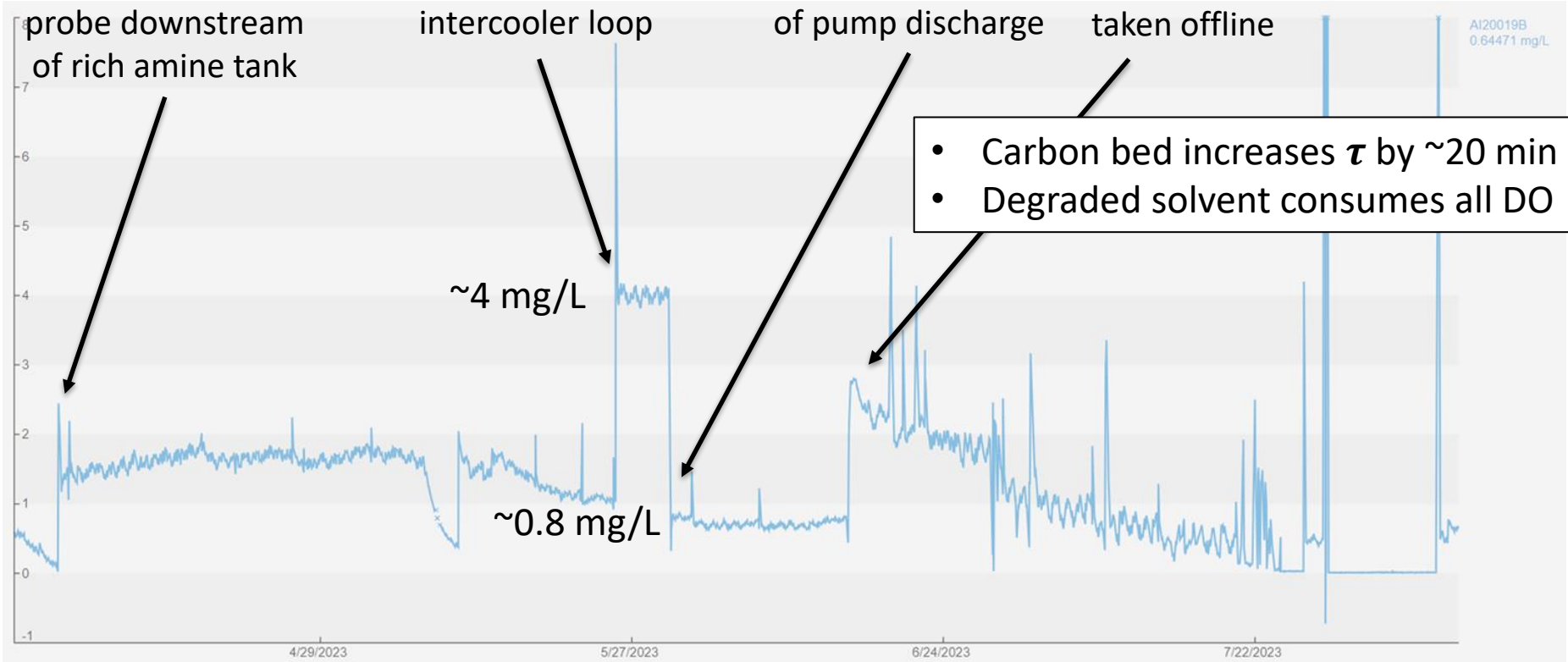
DO probe readings with N_2 sparging off

4/5/2023
N_2 sparging off; probe downstream of rich amine tank

5/25/23
DO probe moved to intercooler loop

5/30/23
Probe downstream of pump discharge

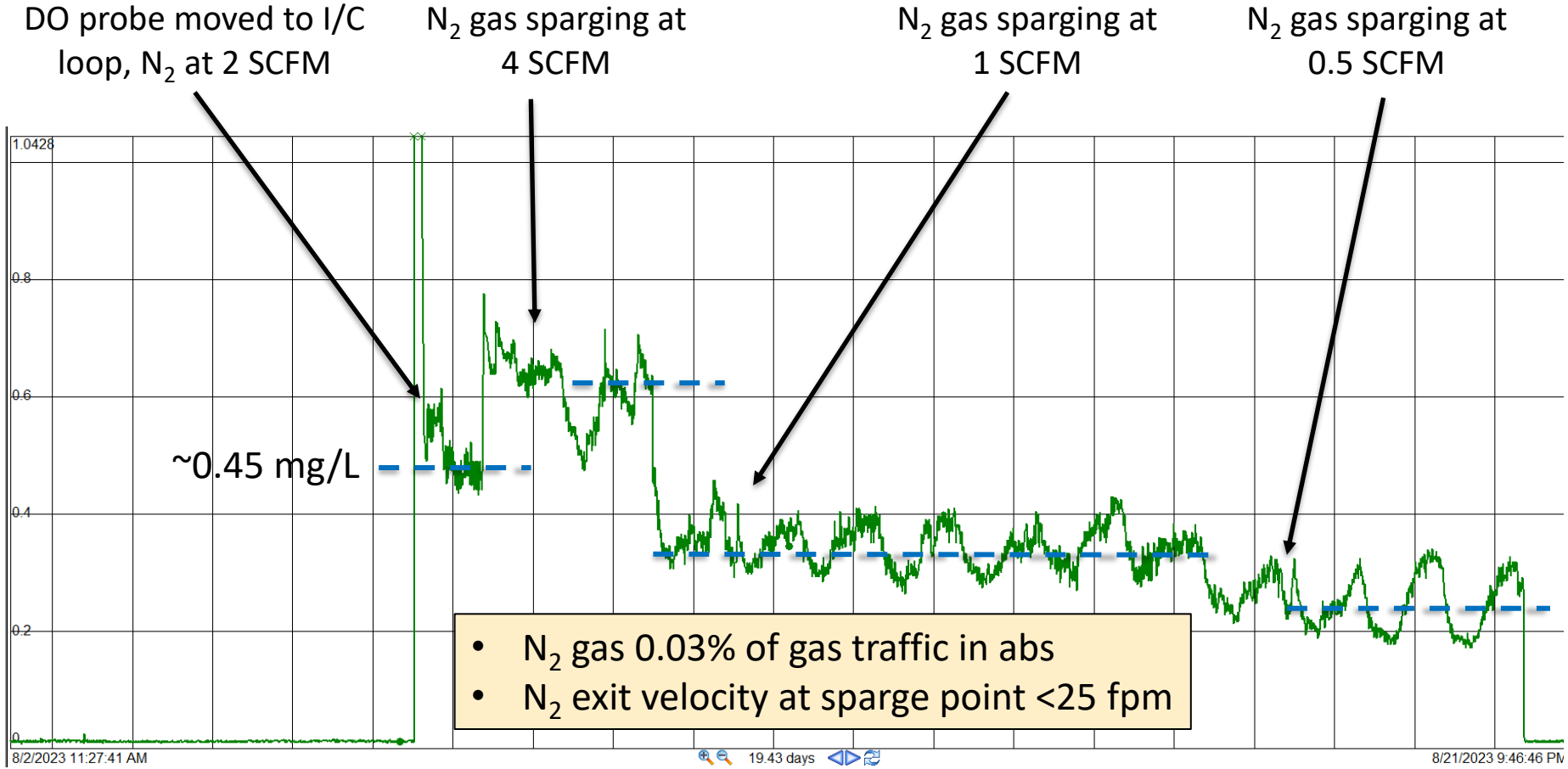
6/15/2023
Carbon bed taken offline



- Carbon bed increases τ by ~20 min
- Degraded solvent consumes all DO

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

DO probe readings with N_2 sparging on



Conclusions

- EDA is degradation product at greatest concentration (50 mmol/kg); decreasing with no mitigation (EDA oxidizes 5-10X faster than PZ; 2010)
- NO_2 prescrubbing
  - effective at reducing MNPZ accumulation
  - observed increase in all degradation products with prescrubbing offline
  - NO_2 absorbed/MNPZ formed ~ 4/1; observed 1/1 at SRP; carbon bed online at NCCC
- DO measurements
  - >95% DO consumption in abs + rich amine late in campaign – degradation products oxidized
  - carbon bed added ~20 minutes to rich amine τ – DO near complete consumption before reaching heat exchangers/stripper (<0.03 mg/L)
  - N_2 sparging at 0.5 SCFM reduced DO better than 1 - 4 SCFM → **design to reduce N_2 gas velocity to <25 fpm**
- Gas phase measurements
  - single stage water wash effective at controlling PZ (0.2 ppb) but not NH_3
  - bed 3 + acid wash decreased NH_3 by 95% (>8,000 ppb to <200 ppb)
- Overall PZ make-up rate ~0.48 kg/MT CO_2

Project participants

Party	Person	Role
NETL	Krista Hill	Project Manager
UT-Austin	Dr. Gary Rochelle Dr. Fred Closmann	Principal Investigator Project Manager
GRAs	Chih-I Chen Ariel Plantz Miguel Abreu Athreya Suresh Ben Drewry	HGF - NO_2 studies Iron studies Pilot support Pilot support Flue gas stream measurements
SRP Staff	Dr. Frank Seibert JR Campos	Director SRP Operations technician
Honeywell	Carl Stevens Nathan Lozanoski Jeff Tyska	Technology development
NCCC	NCCC Team	Pilot implementation

Additional funding for NCCC pilot campaign: ExxonMobil, LAUNCH, Honeywell, and the Texas Carbon Management Program (UT).

Questions?

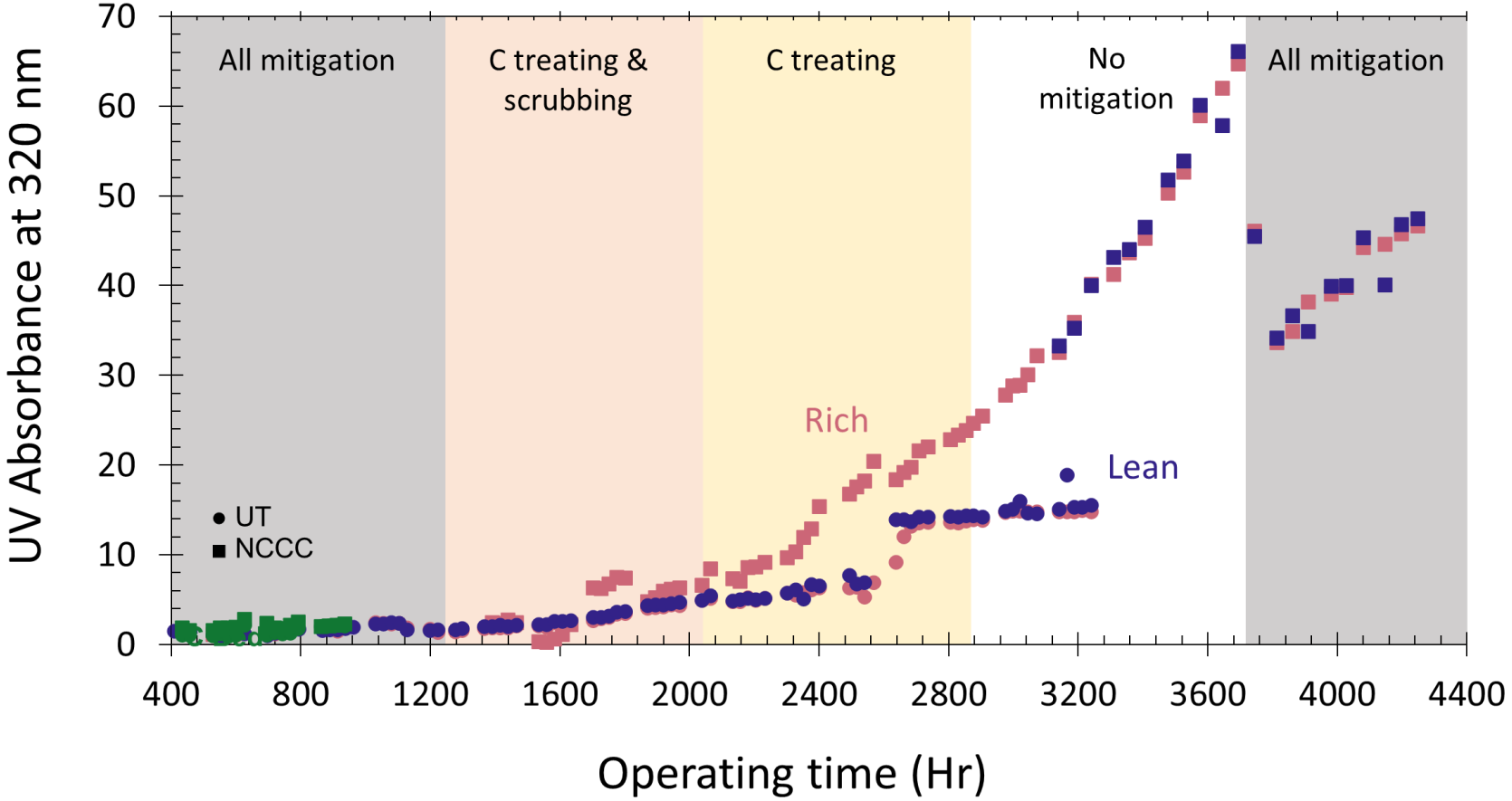
Solvent make-up rates

Solvent	Rate (kg/MT 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	0.15-0.2	CHP	3.7	14.9	11.3 NO_x	TCM, Norway	Hall, personal comm. , 2023
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
*PZAS™	**0.48**	NGCC	4	8	2.5 ppm	NCCC, Wilsonville, AL	UT, 2023

*Based on PZ reduction in inventory over entire campaign.

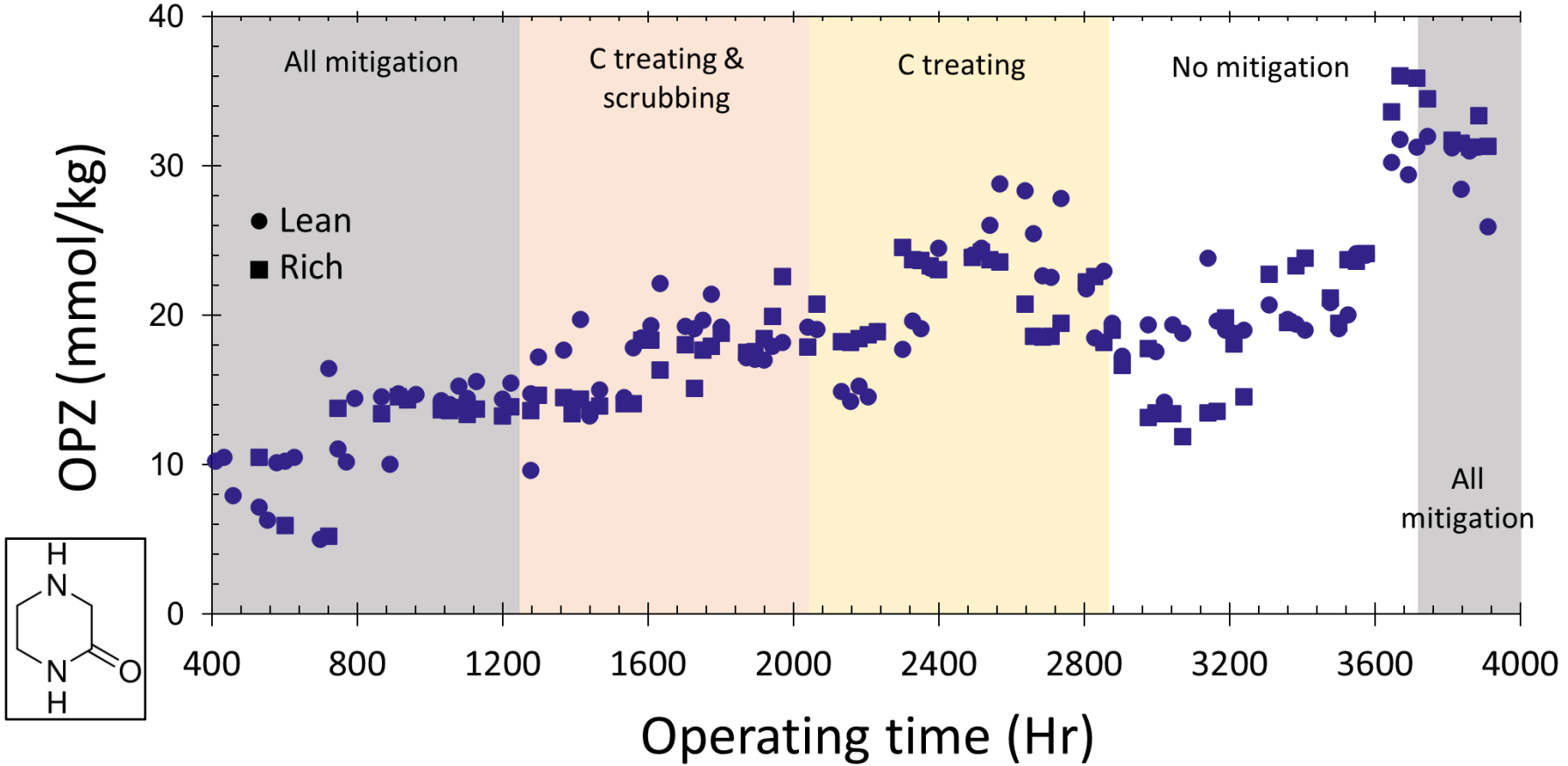
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

UV-Vis absorbance at NCCC (2023)



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

Degradation products by cation IC at NCCC (2023)



NCCC campaign (Dec. 2022 – Oct. 2023)

- NGCC flue gas (4% CO_2, 8% H_2O) at ~110 ˚C from gas boiler
- Prescrub NO_2 to $\leq$1 ppm with thiosulfate/sulfite
- Test N_2 sparging in absorber sump for DO removal
- Test carbon bed at slipstream rate of ~30 gpm
- Test acid wash for NH_3 control
- Bottom packed section pump-around intercooling

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

DO probe readings with N_2 sparging off