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

Amino Acids, Emissions, and Reclaiming in the PZAS Pilot Campaign (NCCC)

DOE Contractors Meeting
DE-FE0031861

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

2024 Carbon Management Research Project Review Meeting
August 5 – 9, 2024

Outline

- Project objectives and approach
- 2023 NCCC campaign overview
- Amino acids
- Gas phase data and emissions
- Reclaiming
- Conclusions

Project objectives and approach

Understand and address the sources of amine oxidation.

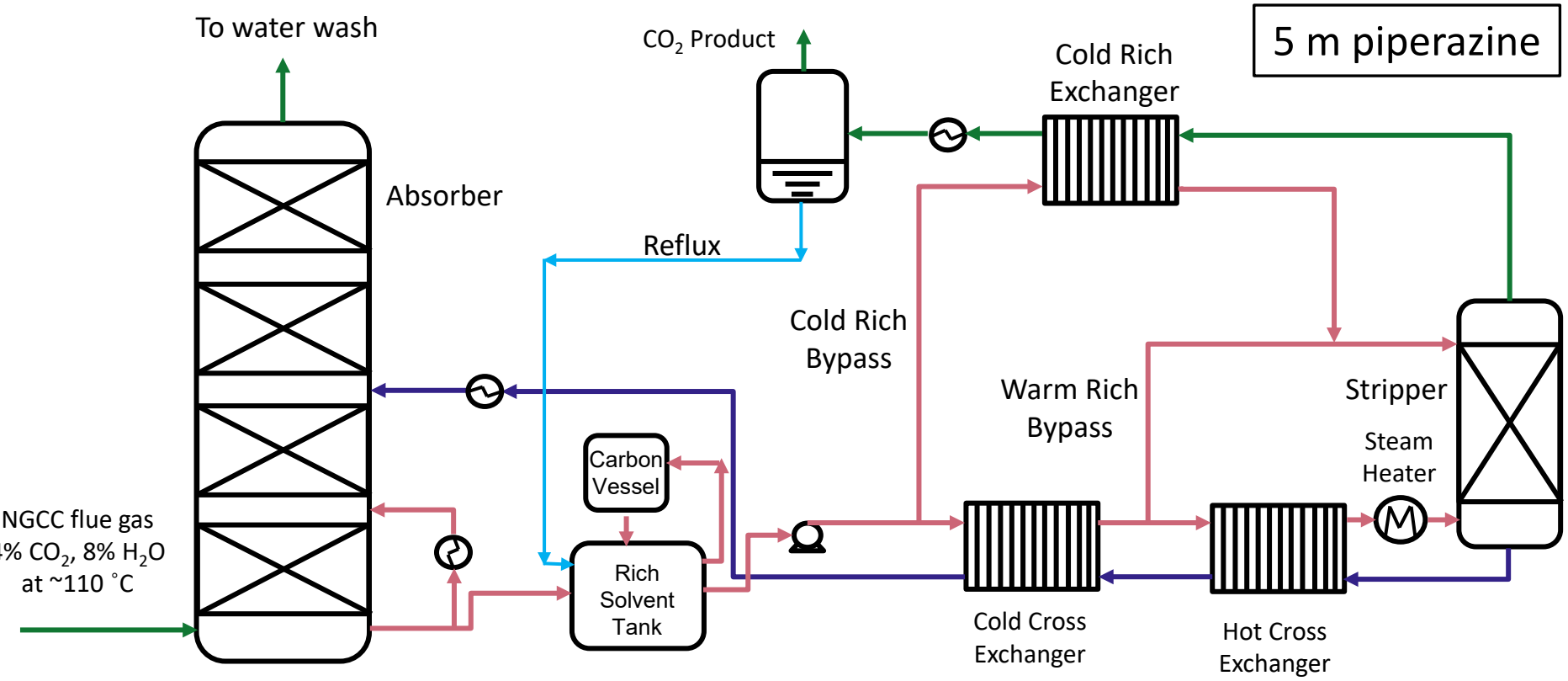
Pilot test oxidation mitigation technologies:

- 0.1- MW_e - UT SRP
- 1 MW_e - NCCC
- 10 MW_e - TCM

Oxidation sources of interest

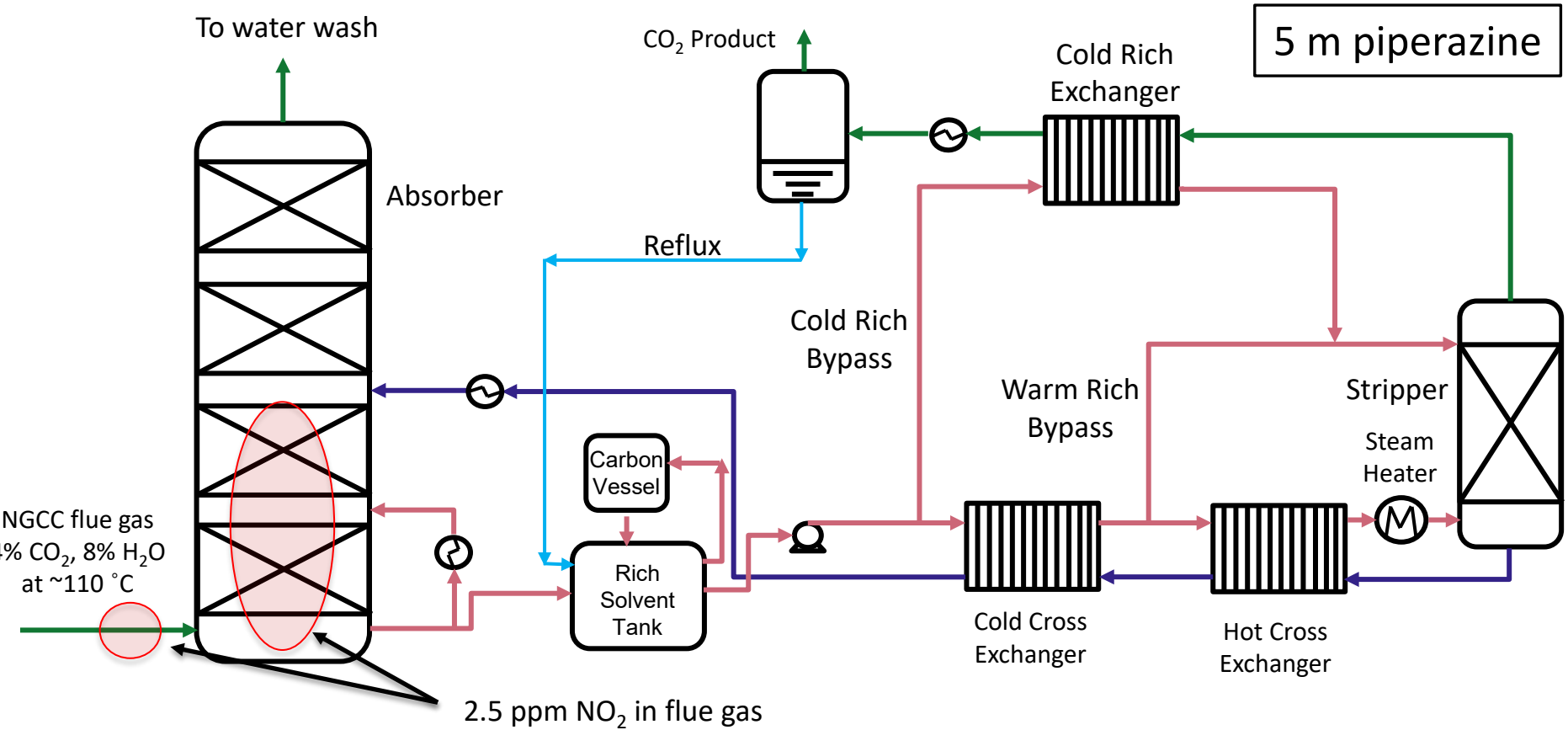
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

PZAS™ process flowsheet



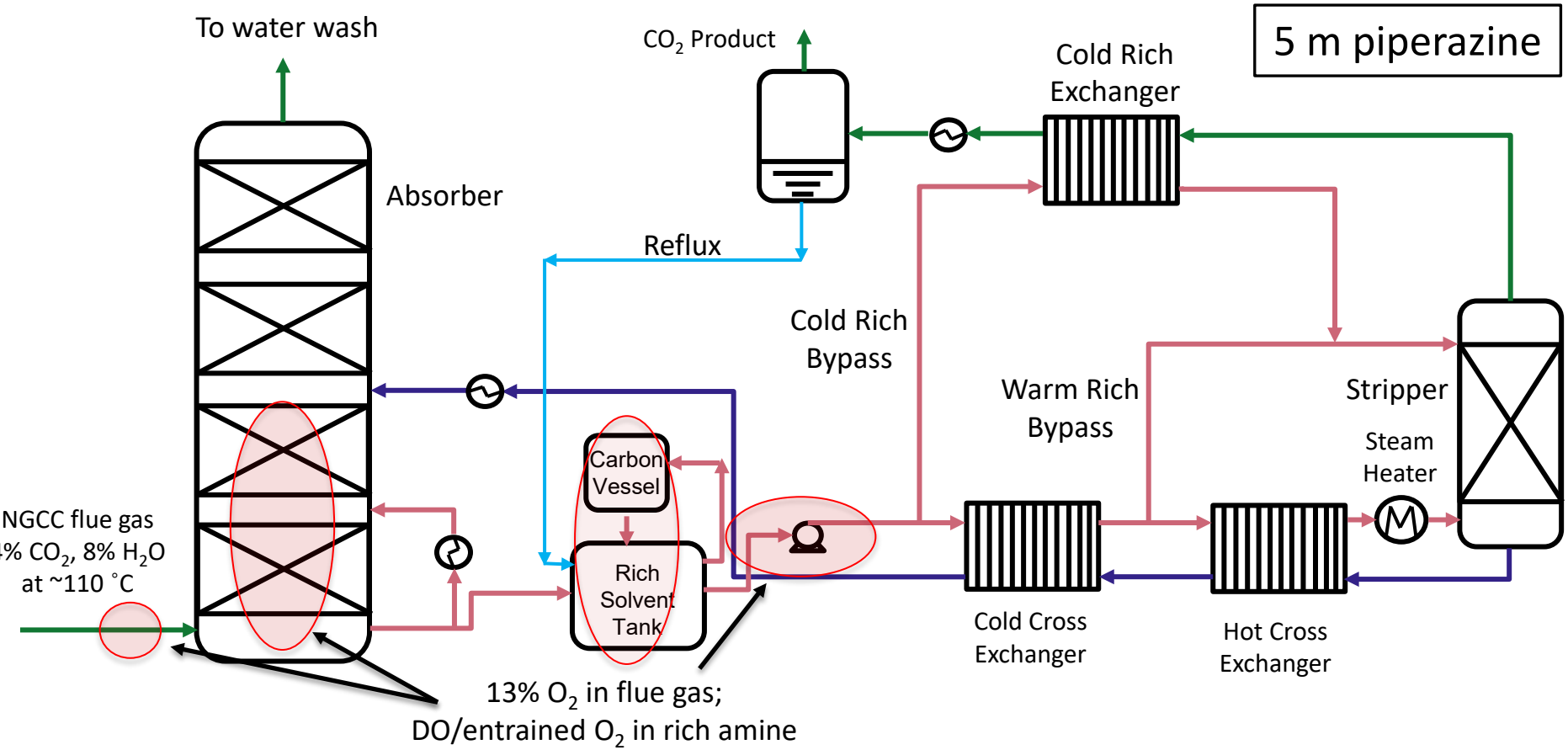
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

PZAS™ process flowsheet



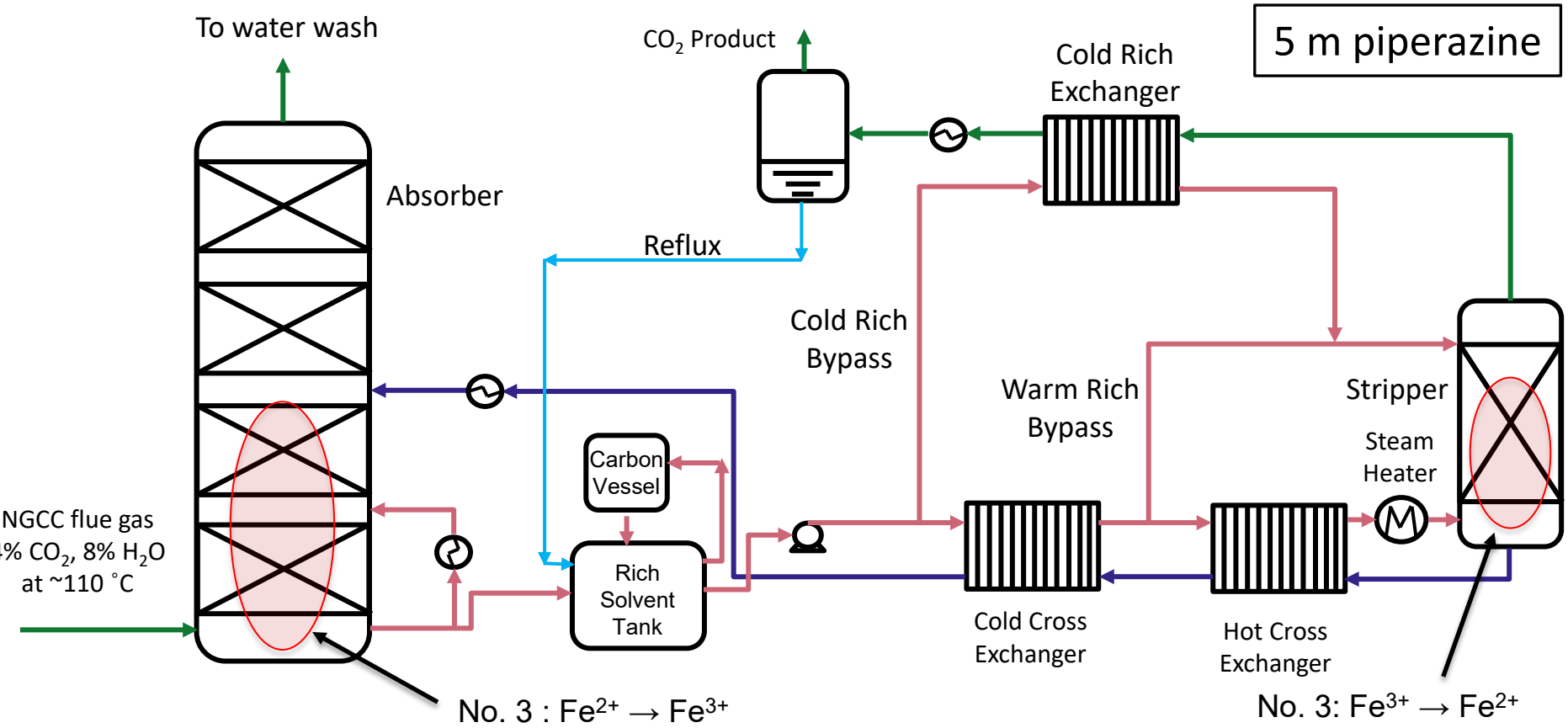
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

PZAS™ process flowsheet



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

PZAS™ process flowsheet



NCCC campaign (Dec. 2022 – Oct. 2023)

- NGCC flue gas (4% CO_2, 8% H_2O, 13% O_2) at 8,000 lb/hr from gas boiler; captured 6 tpd CO_2
- Prescrub NO_2 to $\leq$1 ppm with sulfite
- Sparge N_2 in absorber sump for DO removal
- Run slipstream over activated carbon bed
- Test acid wash for NH_3 control
- 5,900 hours of operations w/ oxidation mitigation methods + reclaiming

Amino acids in solvent samples

Chelation of metal ions and corrosion

Amino acids remove FeS passivating layer in gas plants through chelation of dissolved metal ions (Critchfield & Jenkins, 1999; Lawson, 2003; Thompsen, 2013).

↓

Do the amino acids we see in oxidized PZ remove a passivating layer?

↓

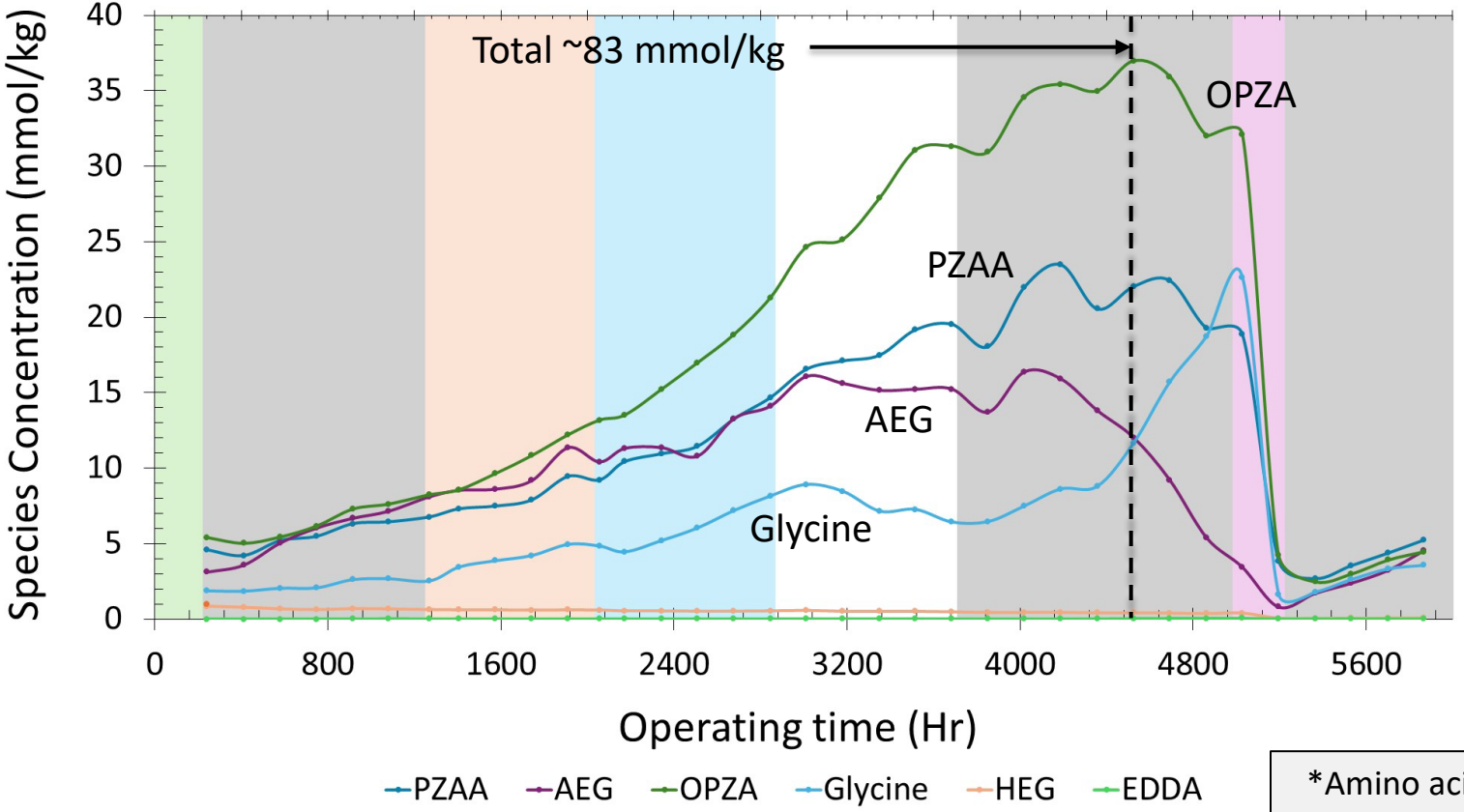
Liu reported removal of siderite layer ($FeCO_3$) in carbon steel systems (UT, 2022).

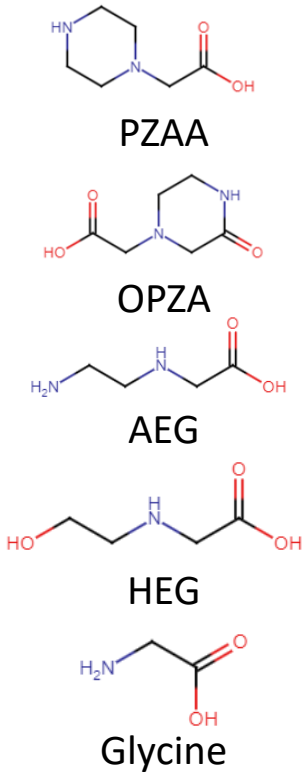
↓

Quantified amino acids and iron in degraded PZ from NCCC pilot (2023-2024).

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

*Amino acids in NCCC lean samples (2023)



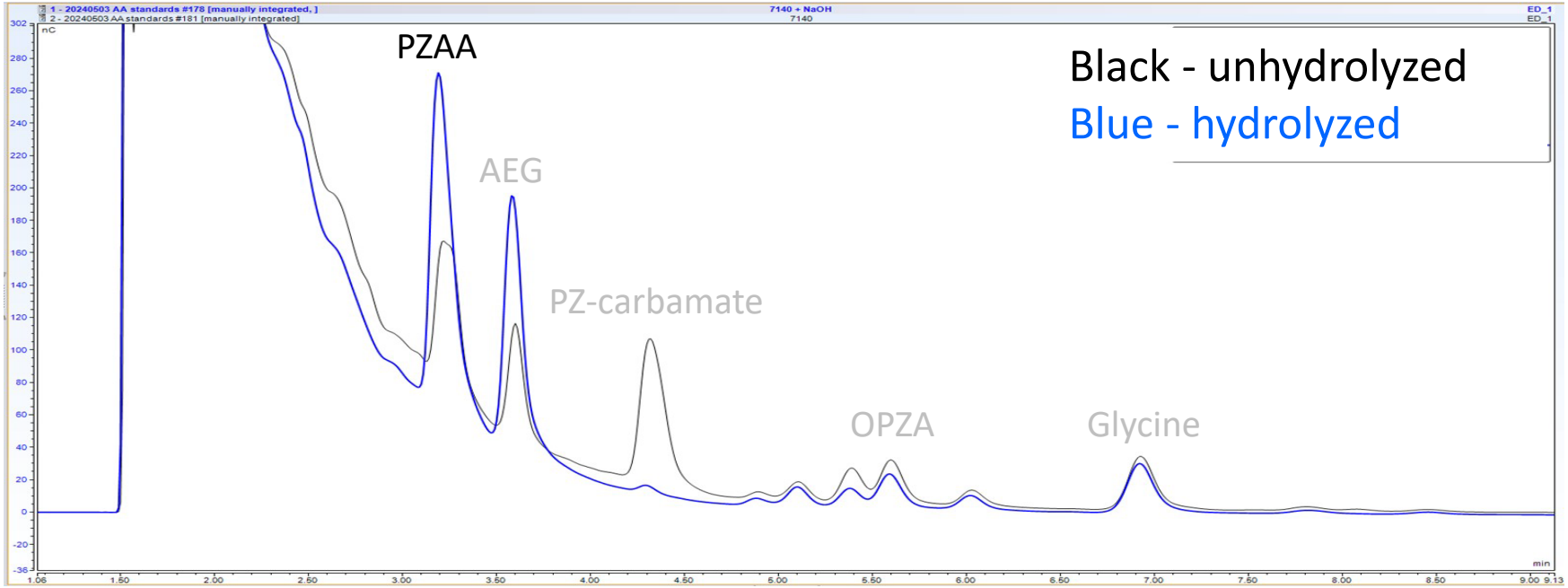


*Amino acids quantified with Dionex AAA-Direct method.

Amide measurement – samples hydrolyzed with NaOH

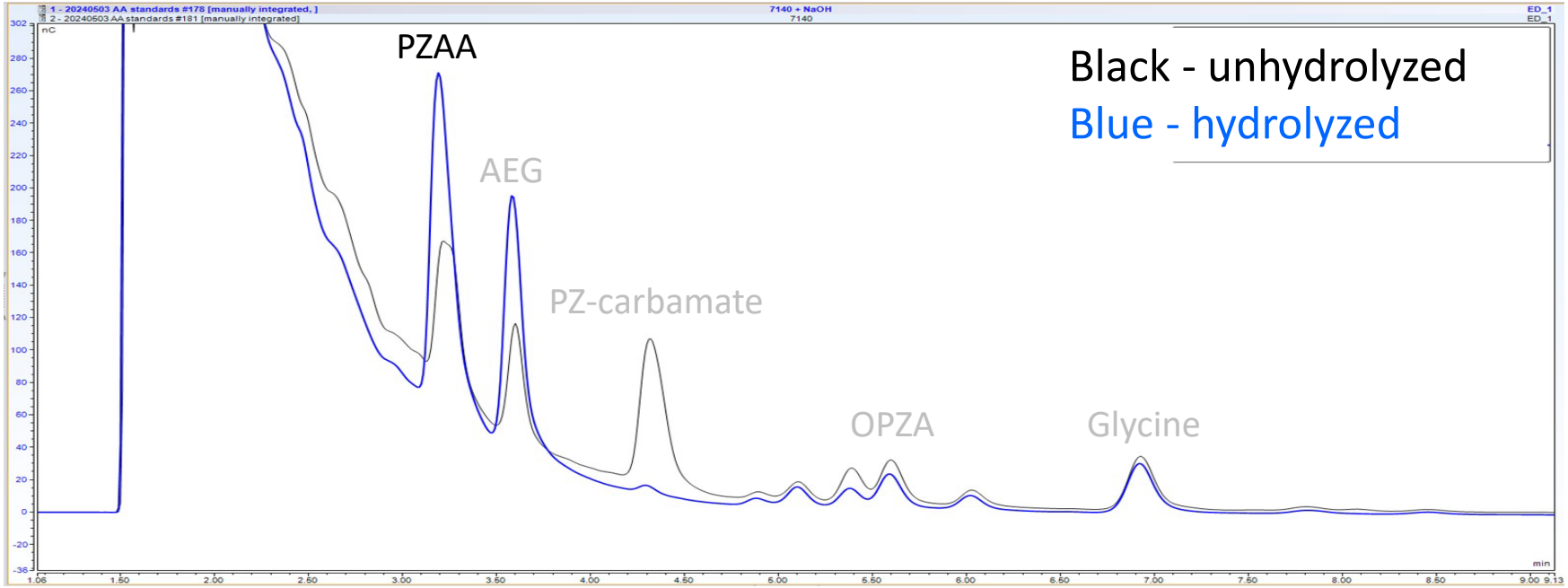
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

Sample hydrolysis in NCCC samples

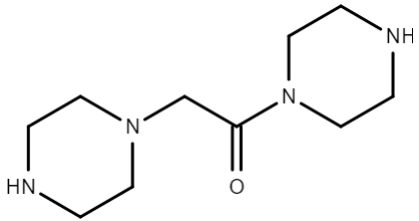


The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

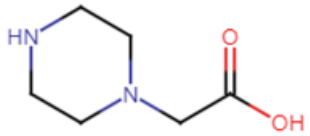
Sample hydrolysis in NCCC samples



Amides of PZAA including this one (Confirmed with QTOF).



+ NaOH →

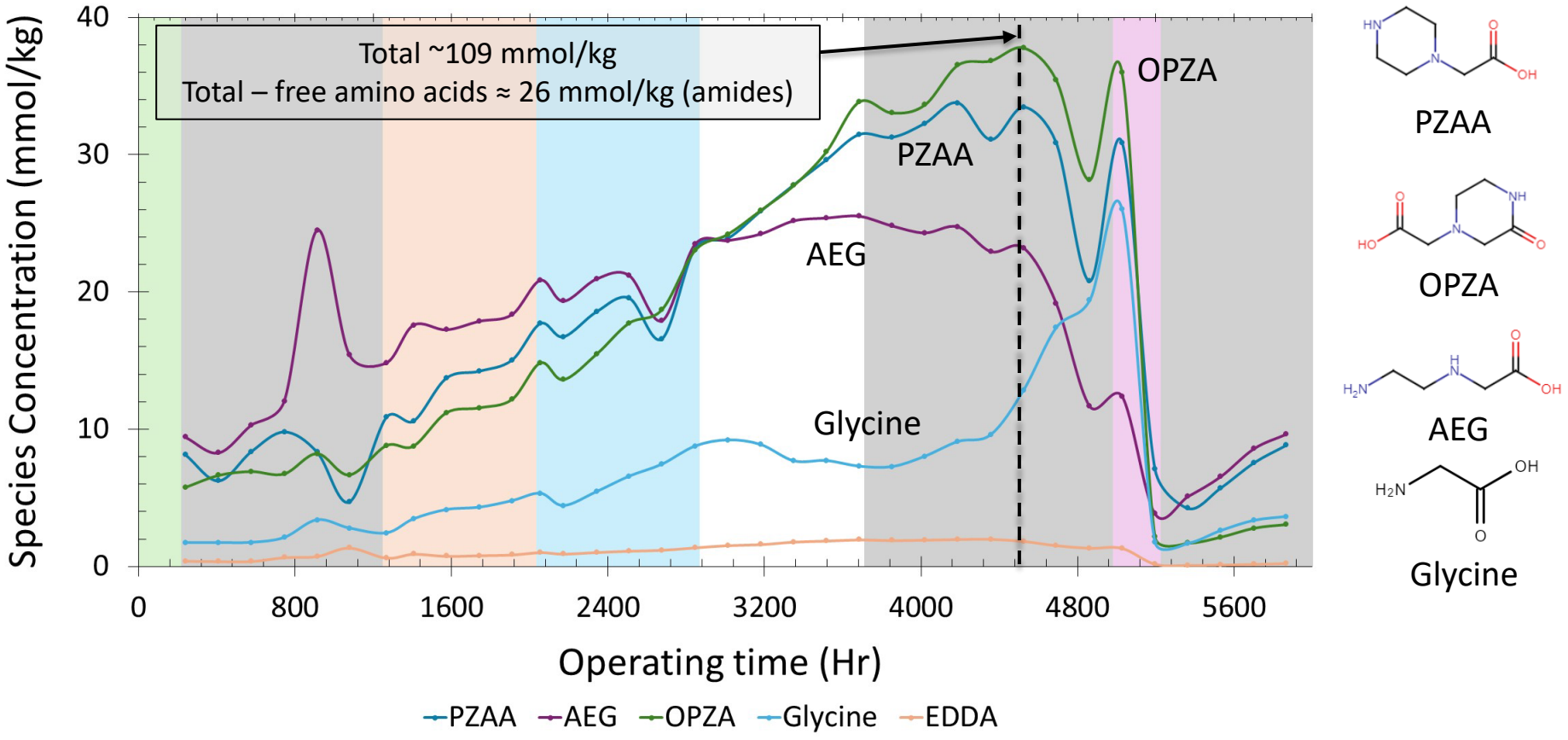


PZAA

PZAA peak increases when hydrolyzed.

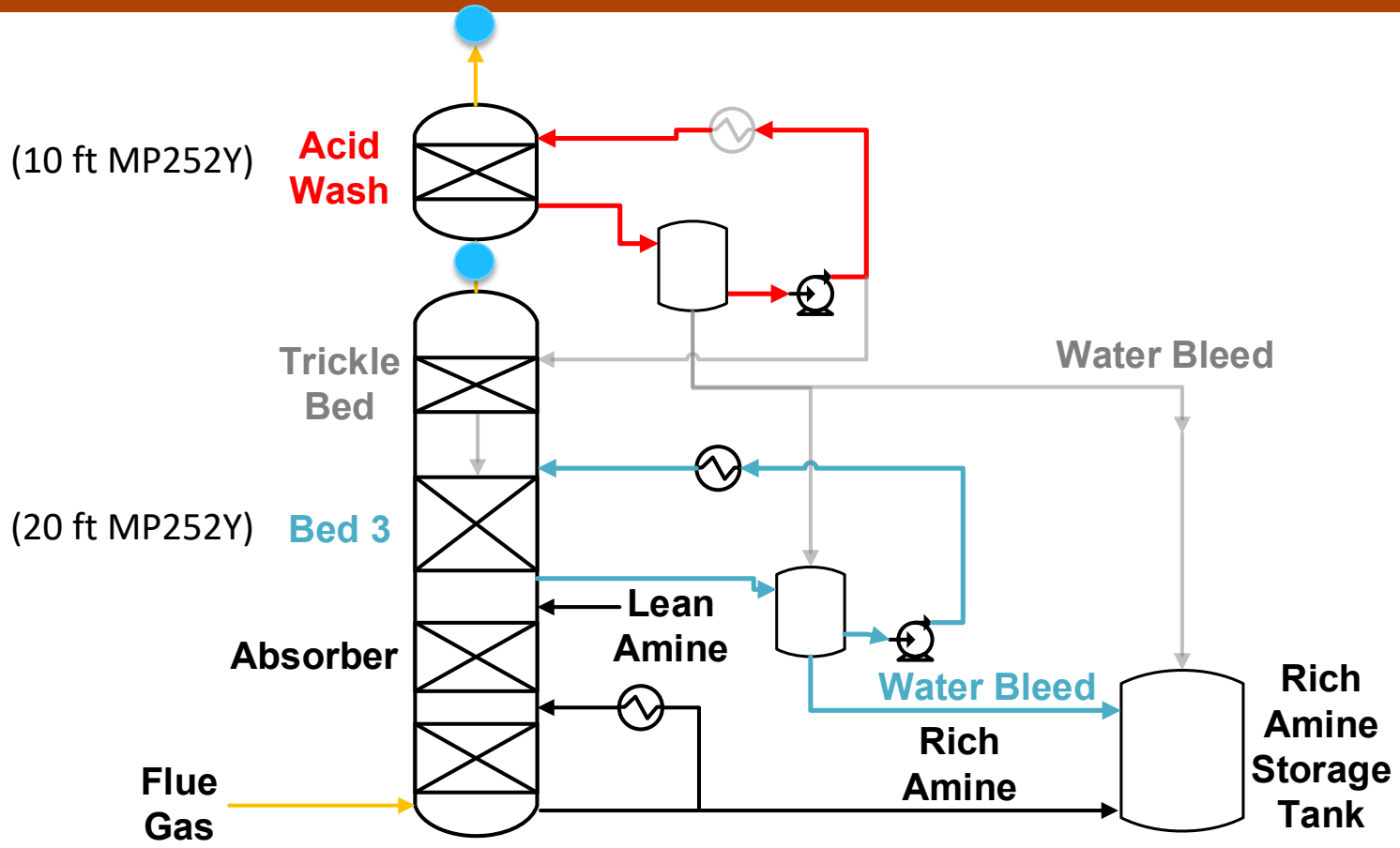
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

Amino acids in NCCC hydrolyzed lean samples (2023)



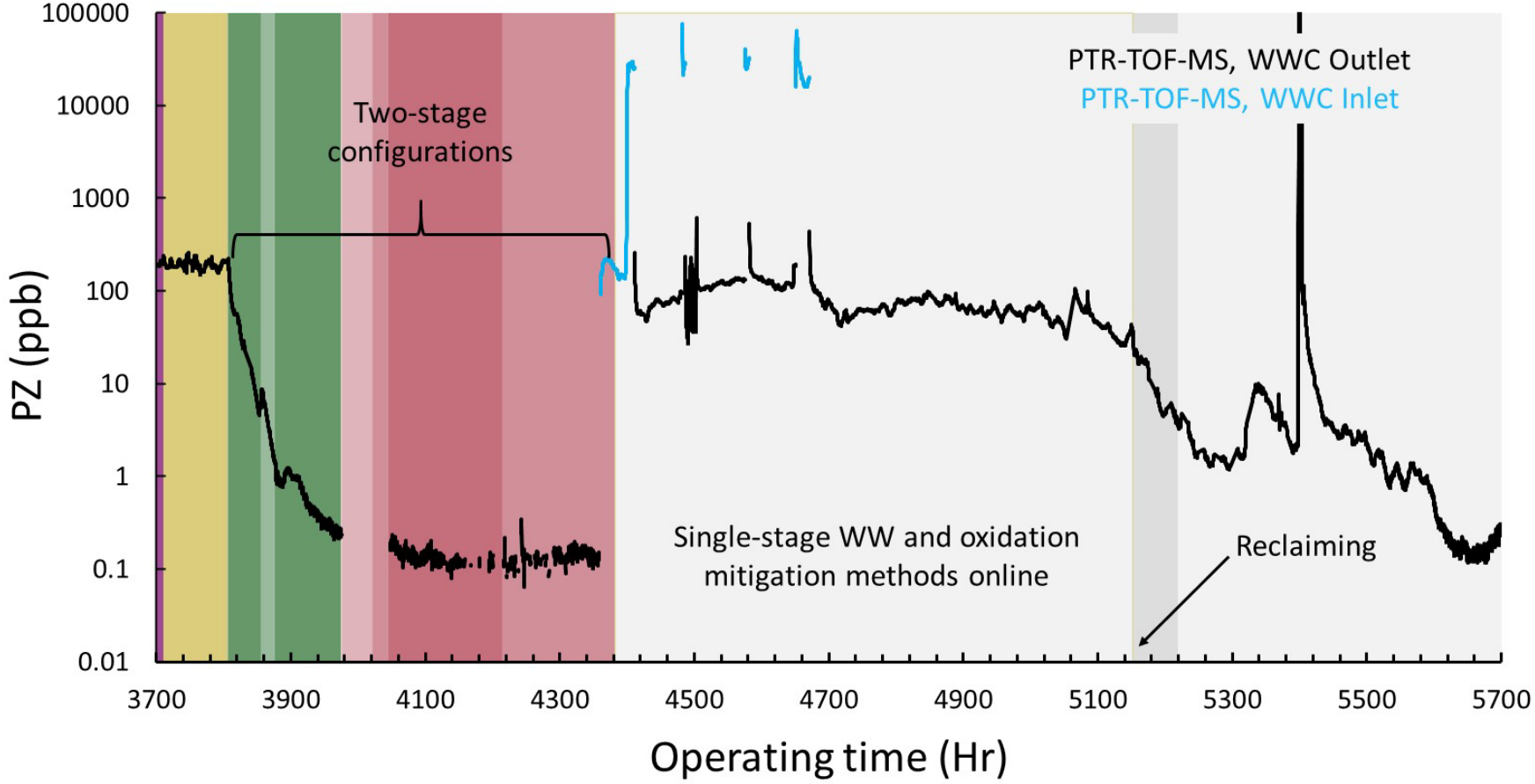
Gas phase data and water wash testing (2023)

Bed 3 + acid wash



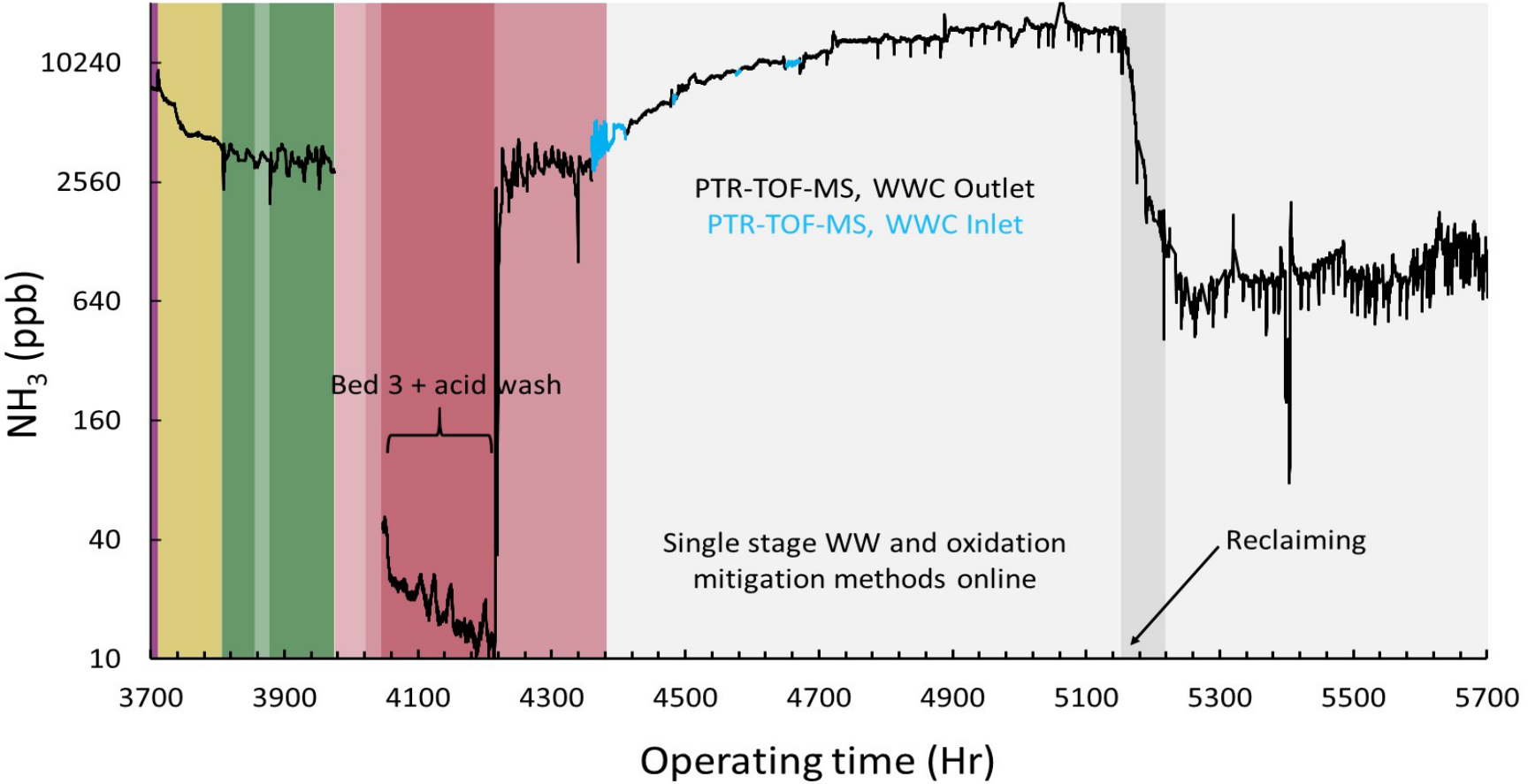
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

PTR-TOF-MS data



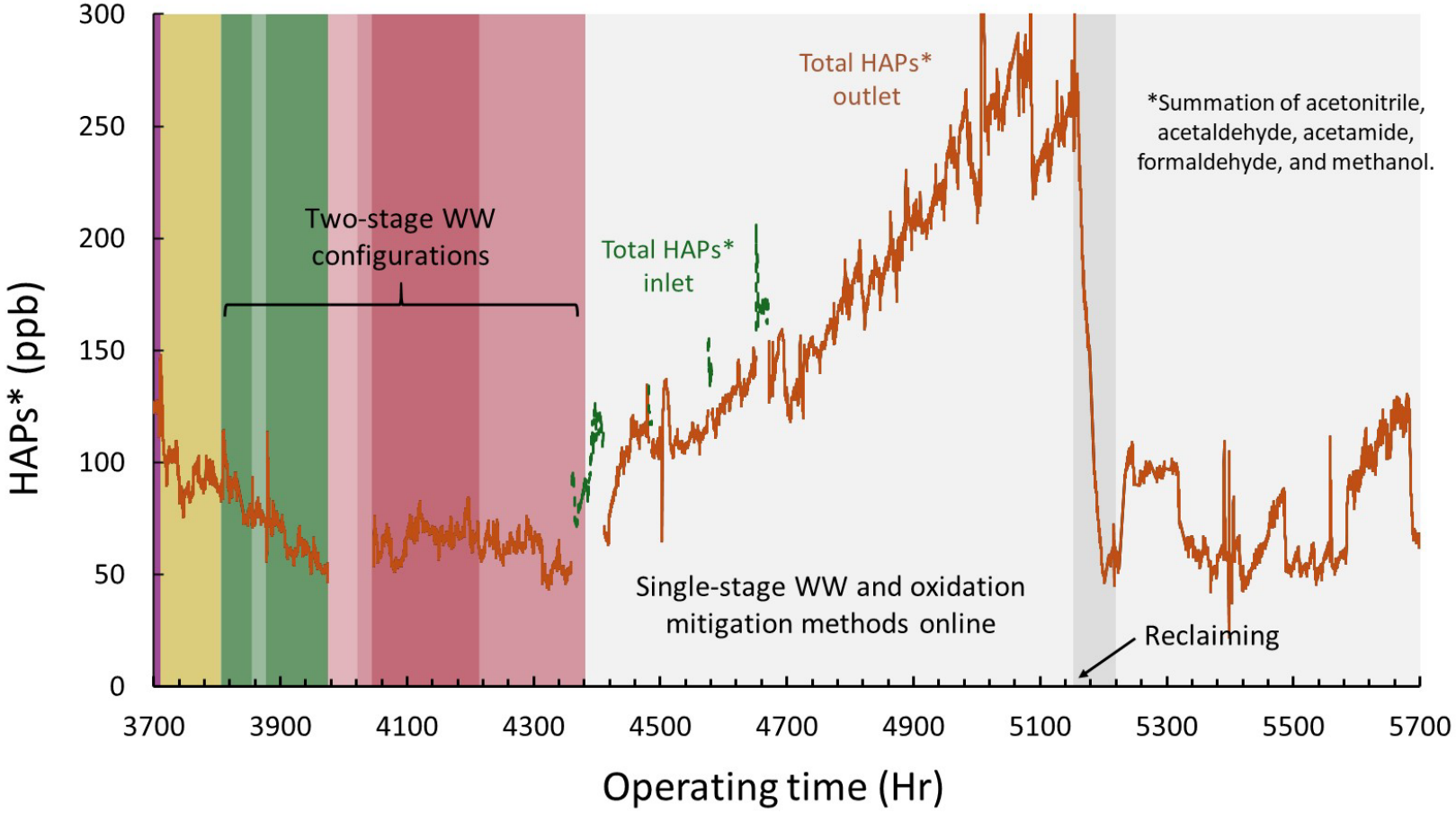
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

PTR-TOF-MS data



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

PTR-TOF-MS data

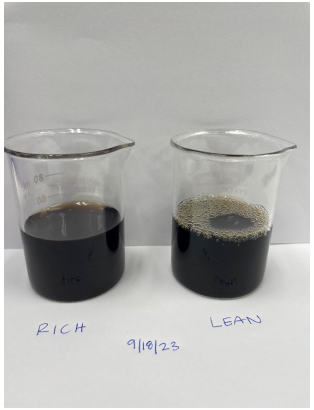


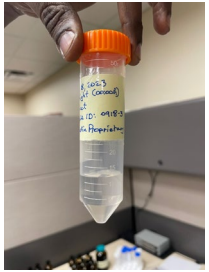
Solvent reclaiming

CCR solvent reclaiming (Sept. 18 – 21)

- Semi-batch thermal reclaiming
- Processed ~4,187 gallons of solvent (3X inventories)
- Processed lean amine (1.1 gpm); returned to rich amine tank

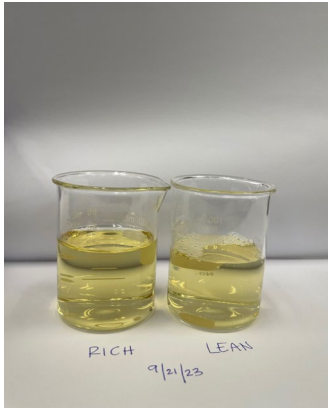
Before – 9/18



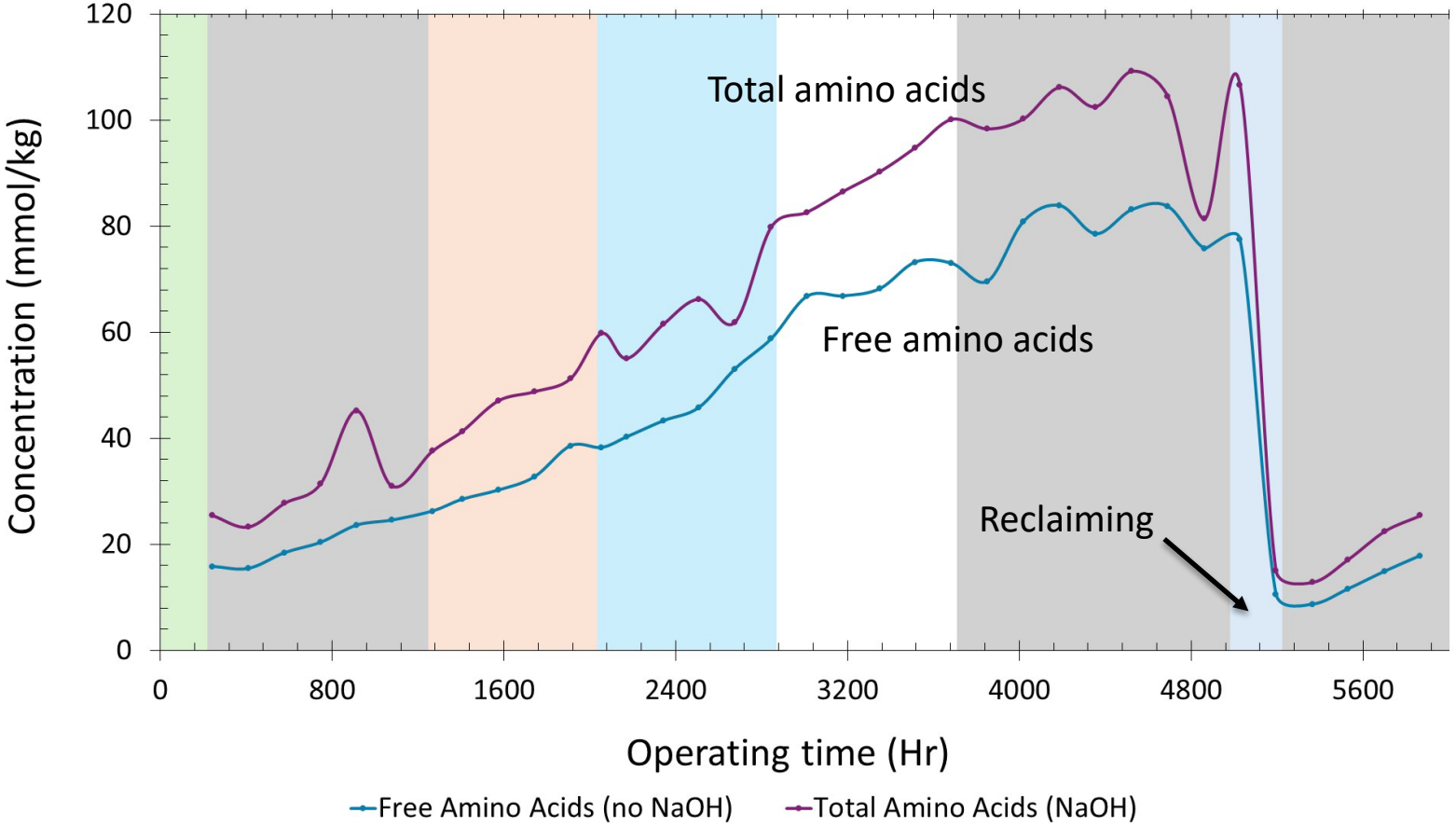


Product from CCR unit

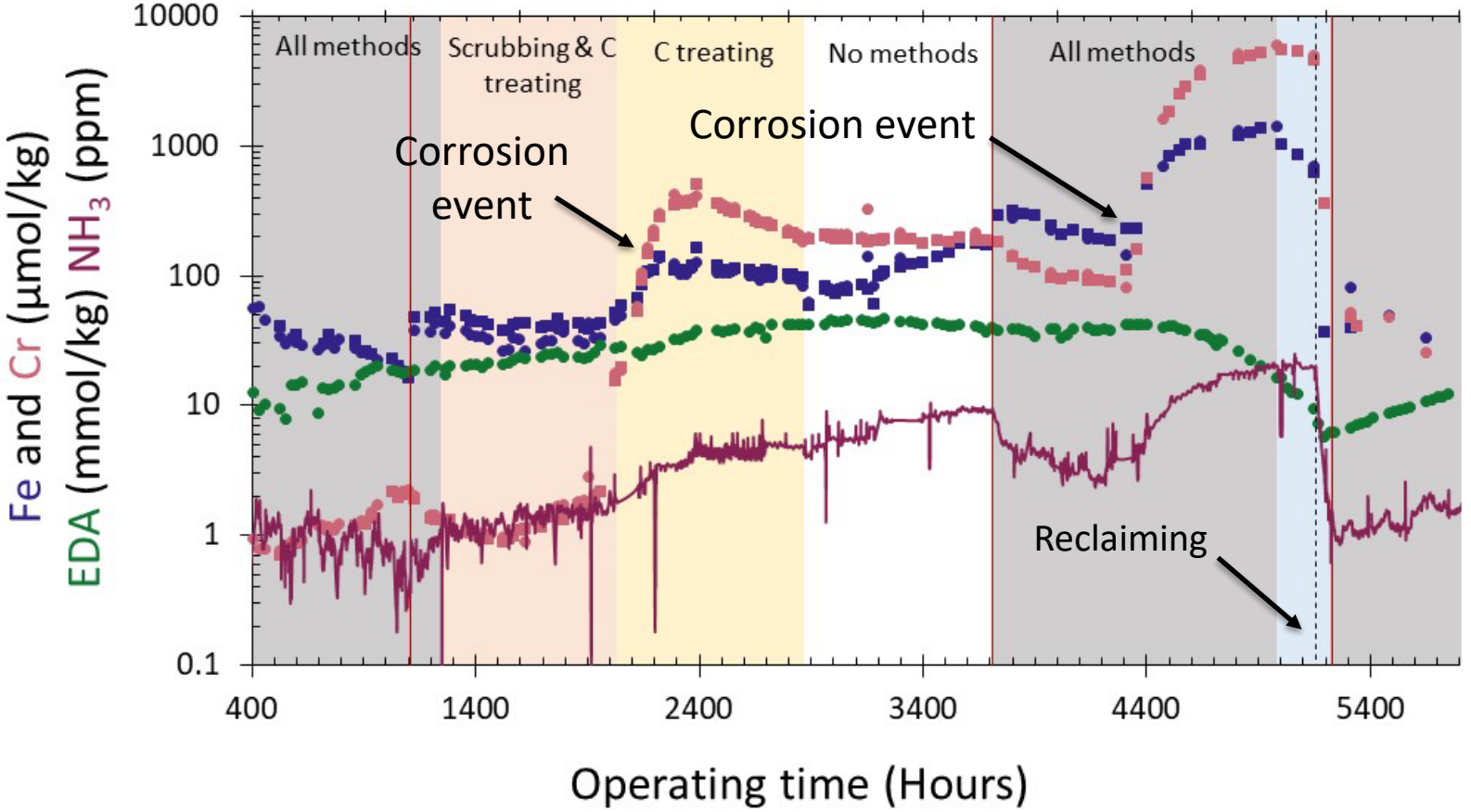
After – 9/21



Total amino acids at NCCC (2023)



Various species at NCCC (2023)

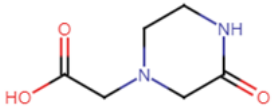


Reclaiming considerations

- Reached “tipping point” ~4,300 hours w/ all oxidation mitigation methods online
- Three conditions warranted consideration for reclaiming
  - NH_3 in abs outlet gas trending upward
  - Total HAPs in abs outlet gas trending upward
  - Step-change in dissolved metal ions – probable indicator of corrosion
- Operating concern for each
  - NH_3 emissions may eventually lead to aerosols in ambient environment
  - Total HAPs may eventually meet or exceed permitted limit
  - Corrosion rates in process equipment could exceed operating criteria
- CO_2 capture performance of solvent did not diminish during campaign

Conclusions

- Amino acids
  - Aggregate ~83 mmols/kg at 4,180 hours; OPZA at greatest concentration
  - When accounting for amides, increases to ~109 mmols/kg
  - Several other amino acids currently unidentified



- Gas phase emissions
  - Two-stage WW configurations all reduced PZ to <1 ppb
  - Acid wash + bed 3 WW reduced NH_3 to 10 ppb; two-stage did not reduce NH_3
  - 10 – 20 % of HAPs were removed by WW; HAPs trend matched NH_3
- Reclaiming
  - Three solvent inventories thermally reclaimed
  - Parameters including NH_3, amino acids, and dissolved metal ions all lowered
- Observed no increase in heat duty or change in capture performance as solvent degraded

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
ExxonMobil	Justin Federici	NCCC campaign funding
Honeywell	Carl Stevens Nathan Lozanoski Jeff Tyska	Technology development
University of Oslo	Armin Wisthaler Tomas Mikoviny	Gas phase measurements (TOF-MS)
NCCC	NCCC Team	Pilot implementation

Acknowledgments

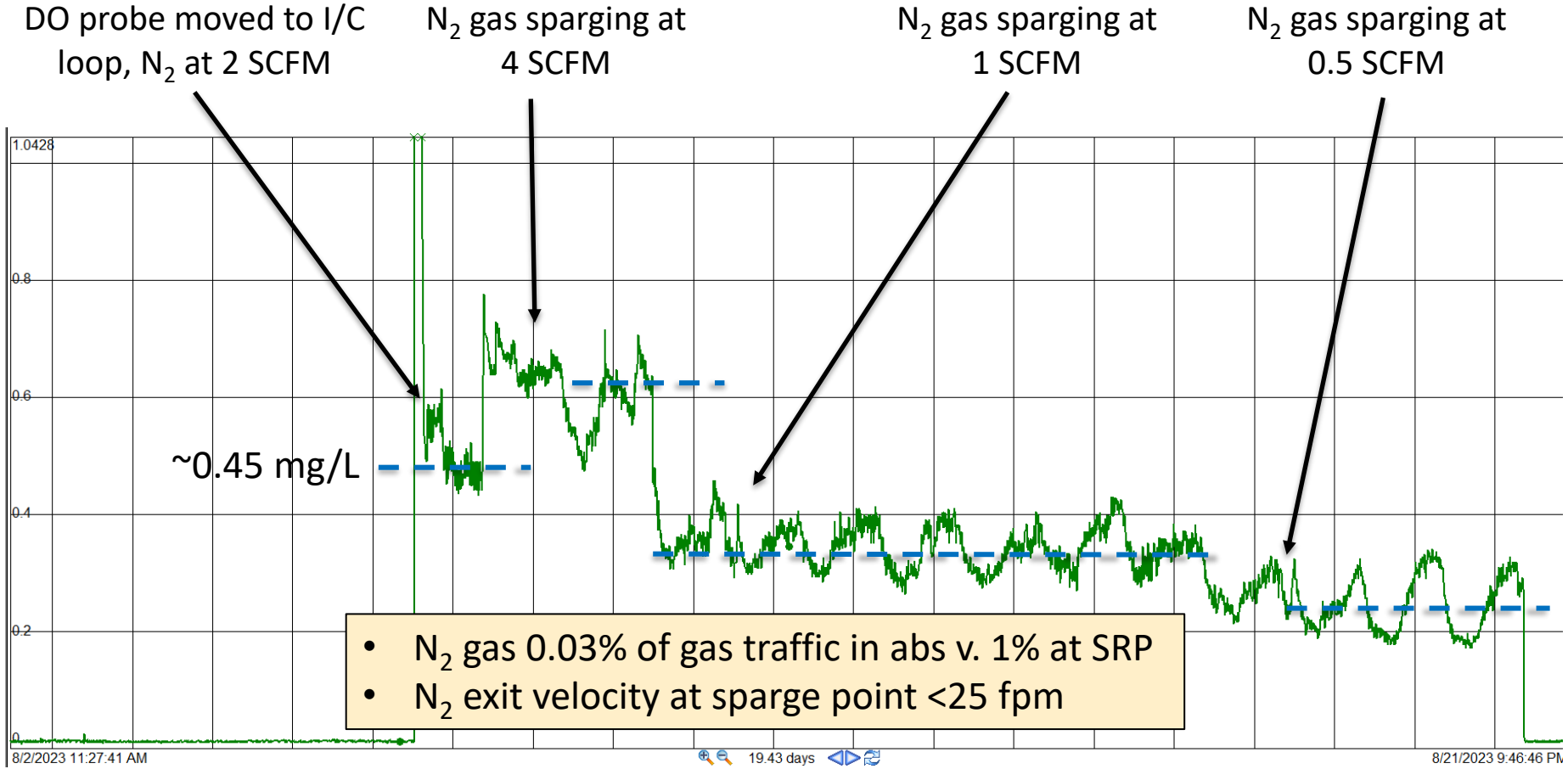
The pilot plant was supported by the U.S. DOE through the National Carbon Capture Center, FE0031861, and the LAUNCH project, with additional support from Honeywell UOP, ExxonMobil, and the Texas Carbon Management Program. The pilot plant was operated by personnel from Southern Services and the Southern Research Institute.

One author of this paper consults for a process supplier on the development of amine scrubbing technology. The terms of this arrangement have been reviewed and approved by The University of Texas at Austin in accordance with its policy on objectivity in research. One author also has financial interests in intellectual property owned by The University of Texas that includes ideas reported in this paper.

Questions?

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

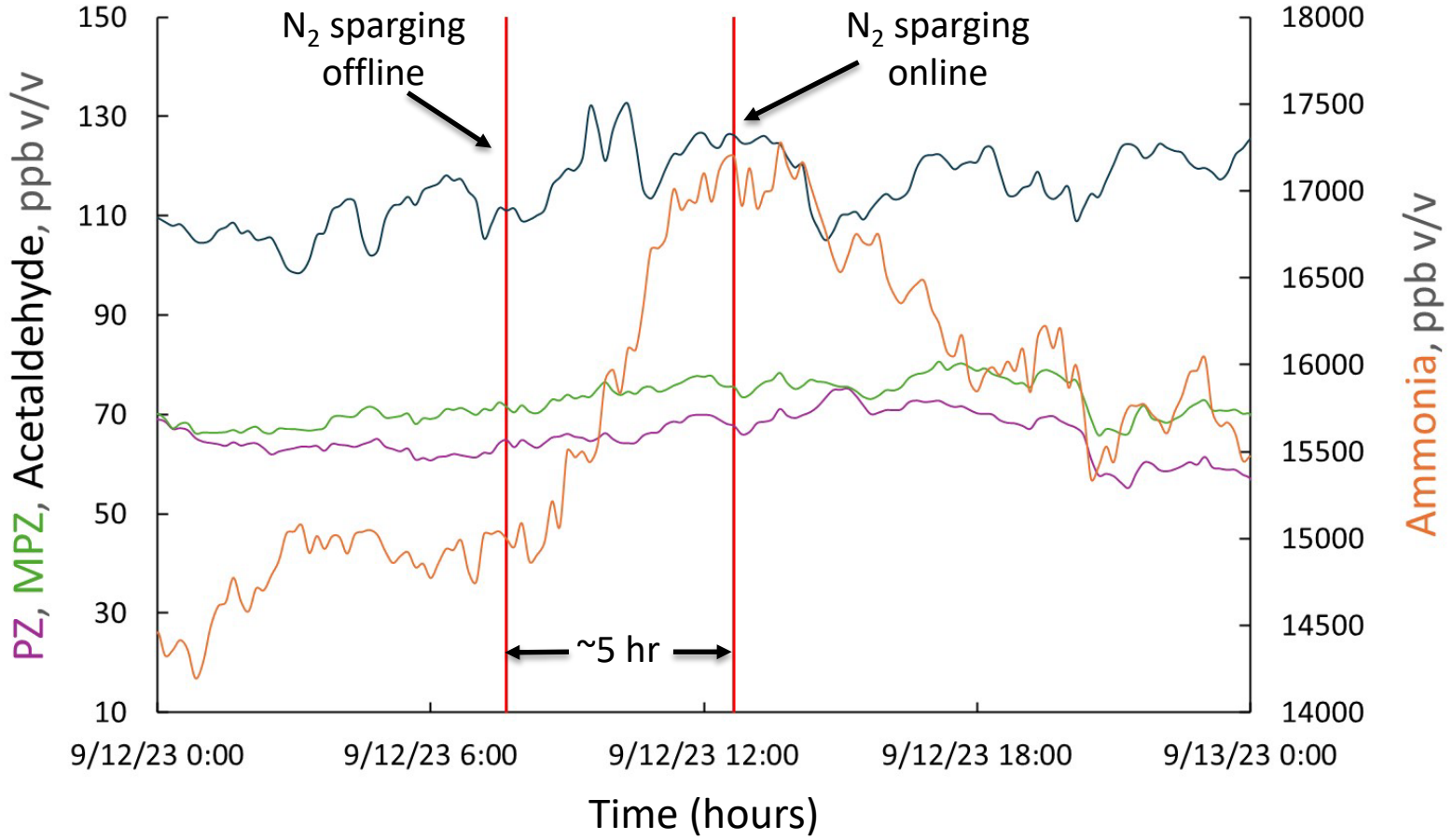
DO measurements over range of N_2 sparge rates



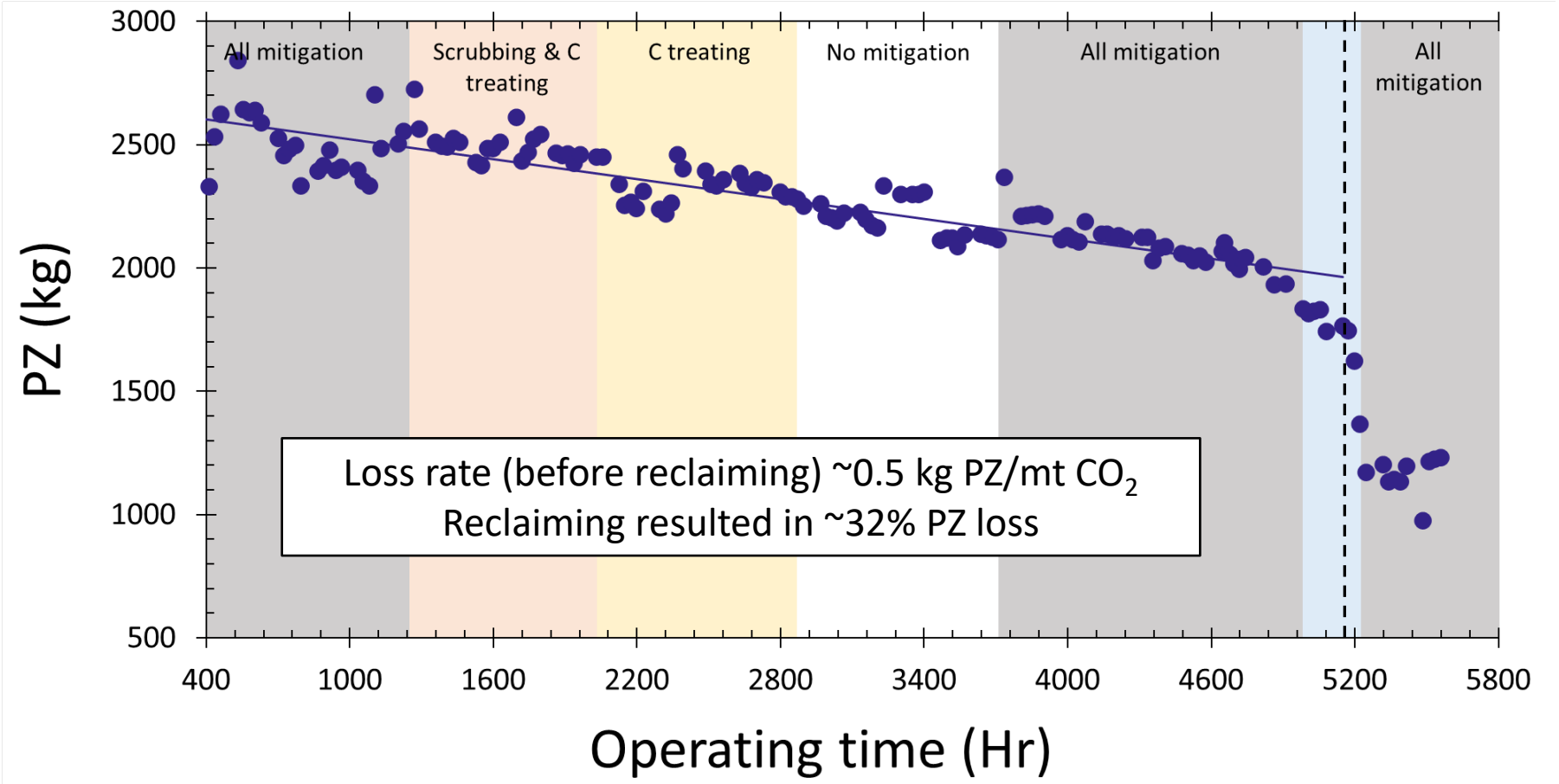
- N_2 gas 0.03% of gas traffic in abs v. 1% at SRP
- N_2 exit velocity at sparge point <25 fpm

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

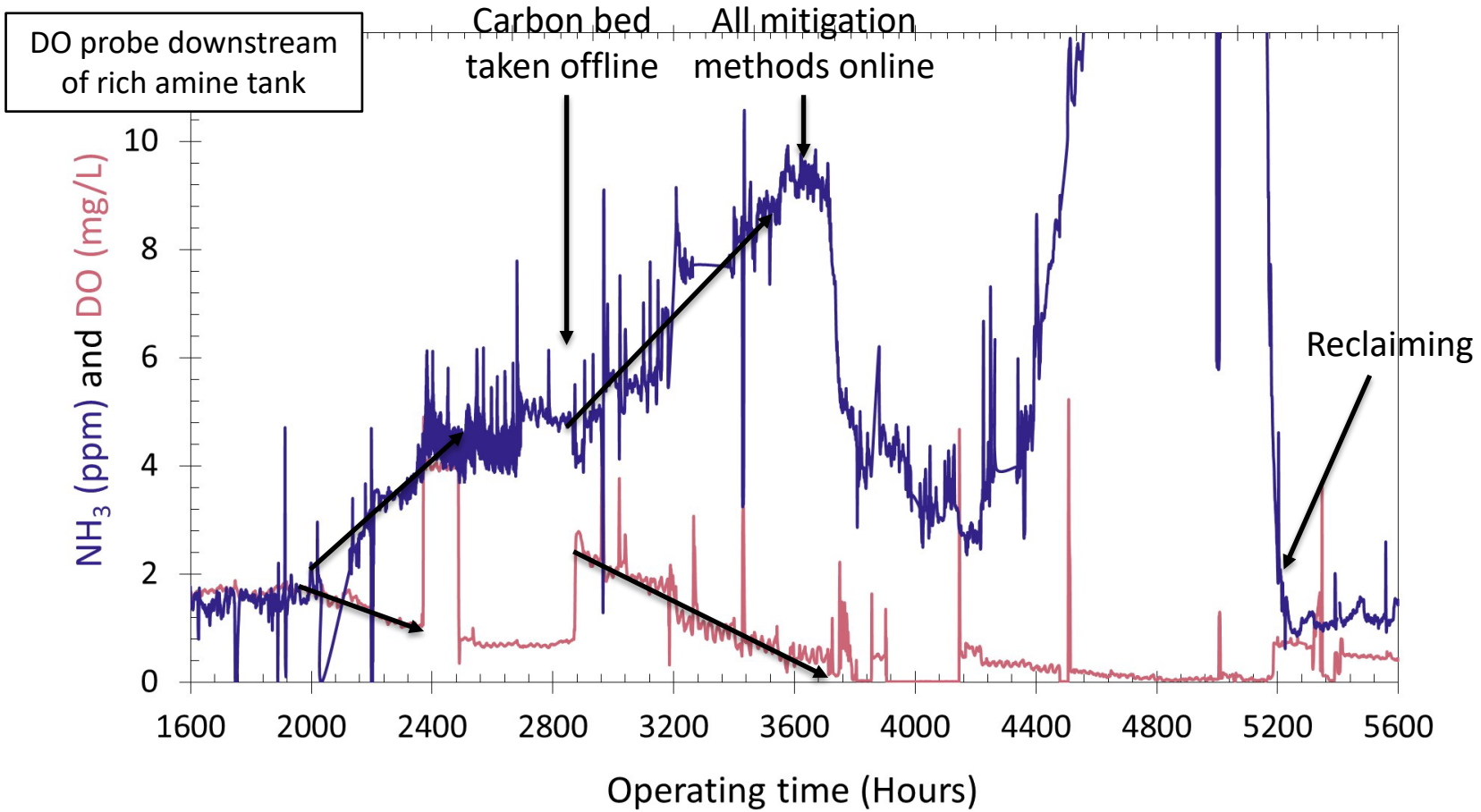
Short-term N_2 sparge test – PTR-TOF



Solvent inventory

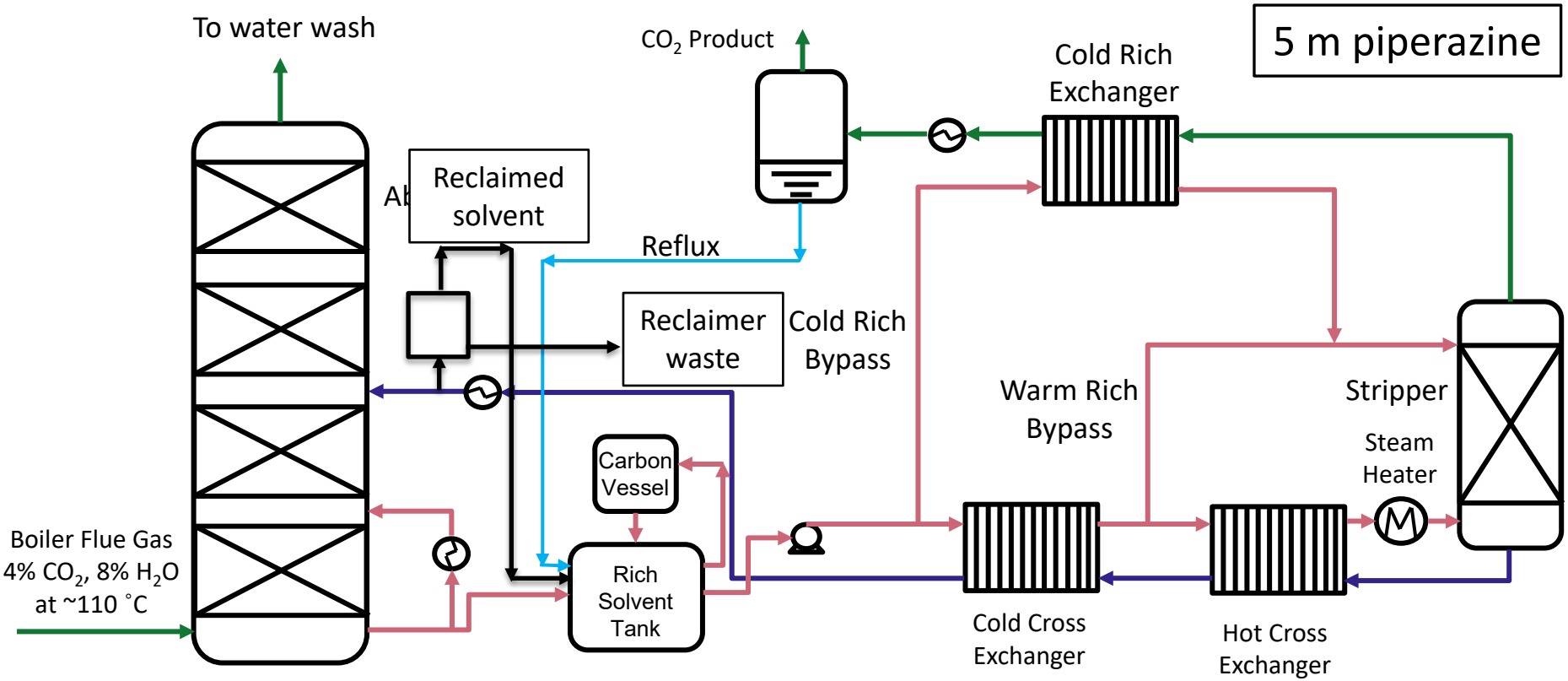


DO and NH_3 measurements



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

Reclaiming with PZAS™



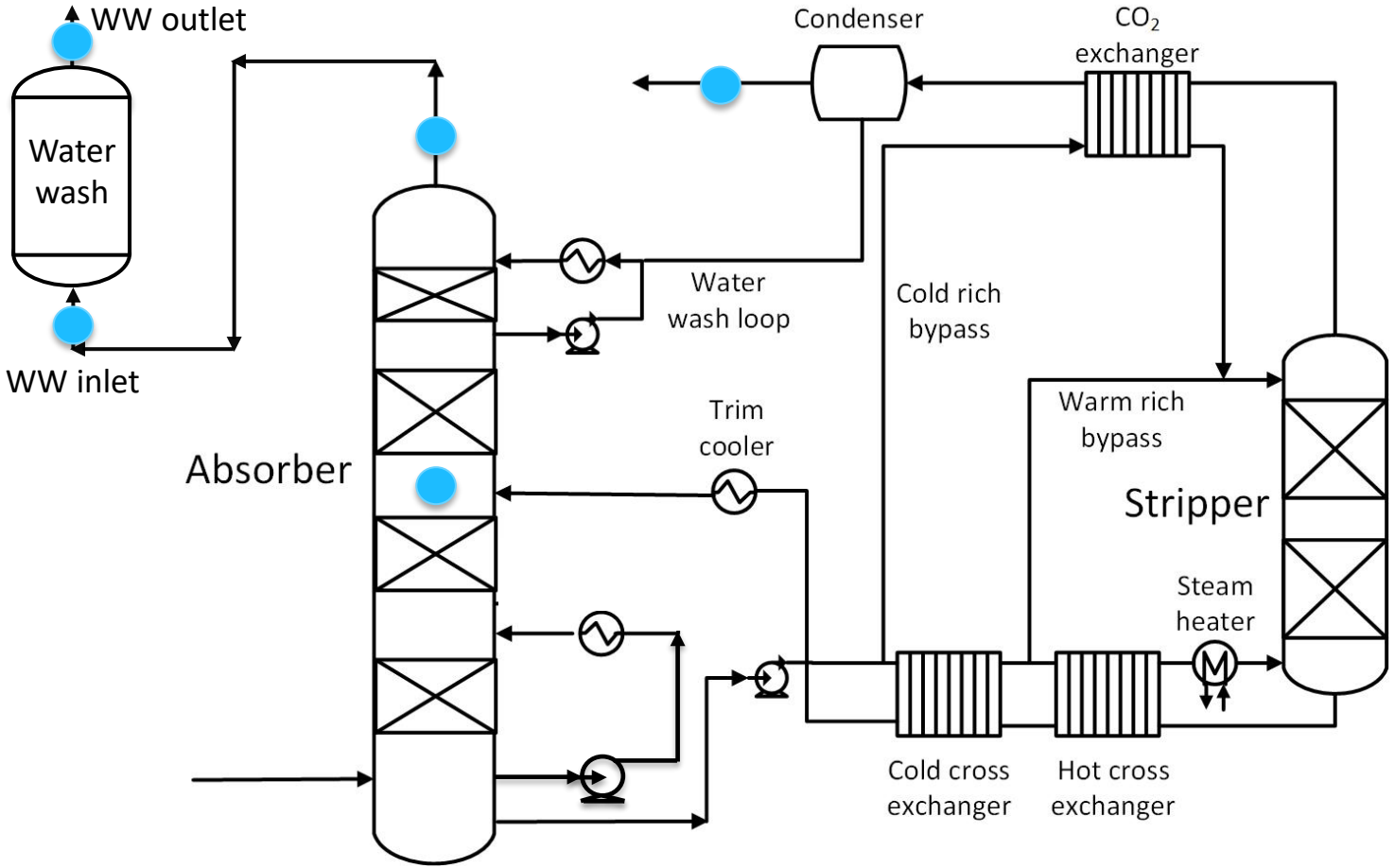
Performance dates

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

Gas phase monitoring points



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

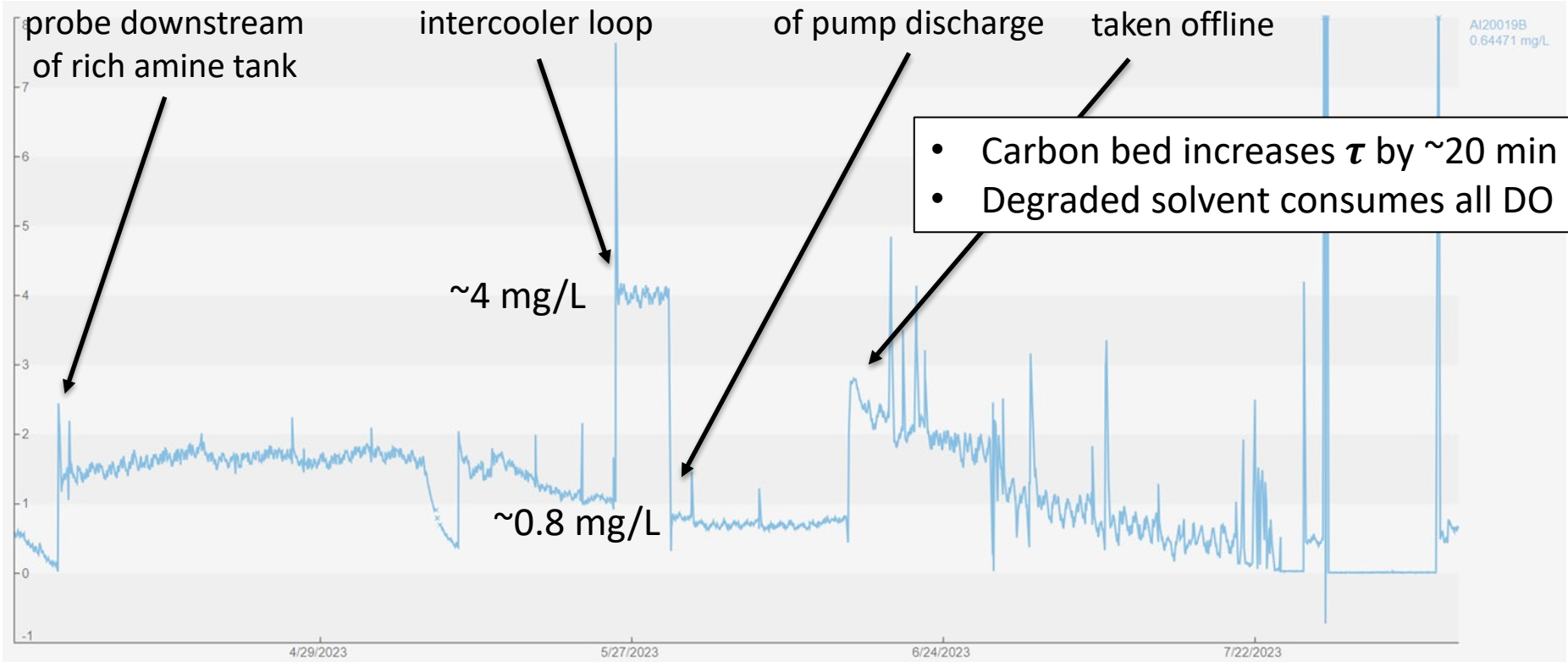
DO probe readings with N_2 sparging off

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

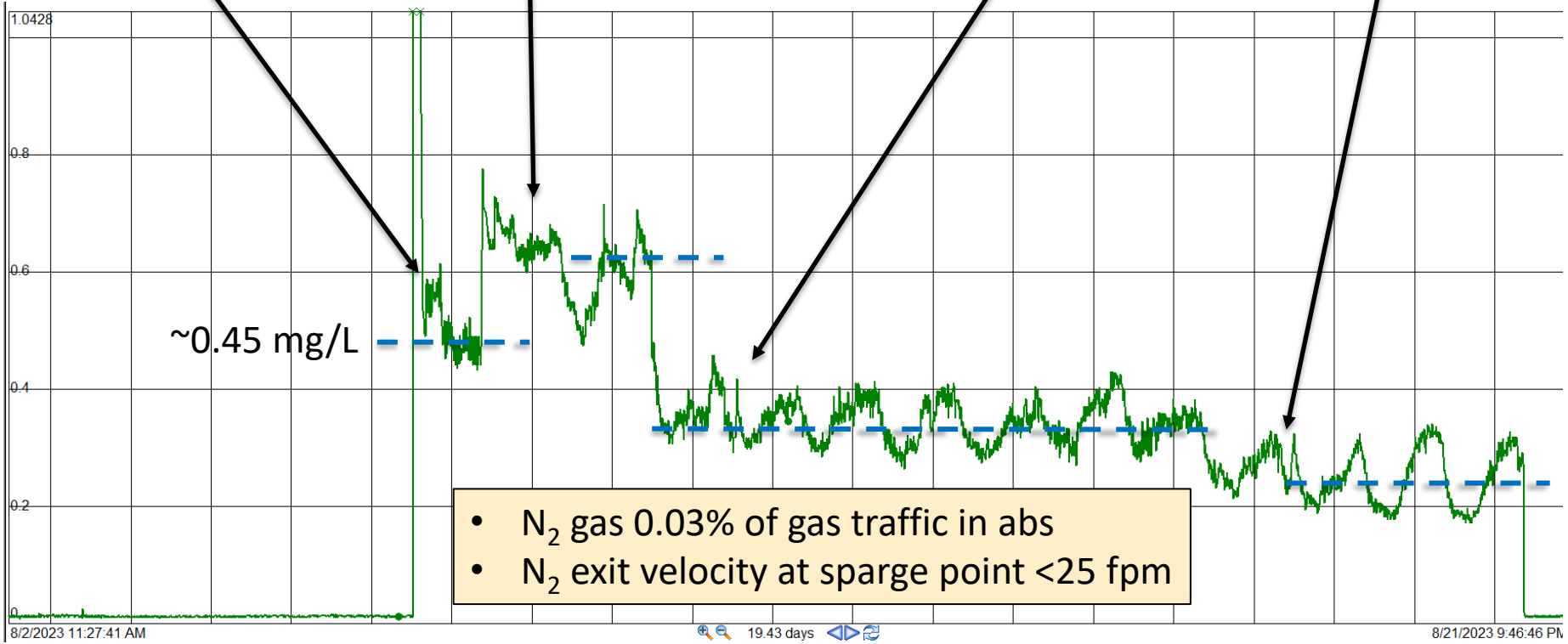
DO probe readings with N_2 sparging on

DO probe moved to I/C loop, N_2 at 2 SCFM

N_2 gas sparging at 4 SCFM

N_2 gas sparging at 1 SCFM

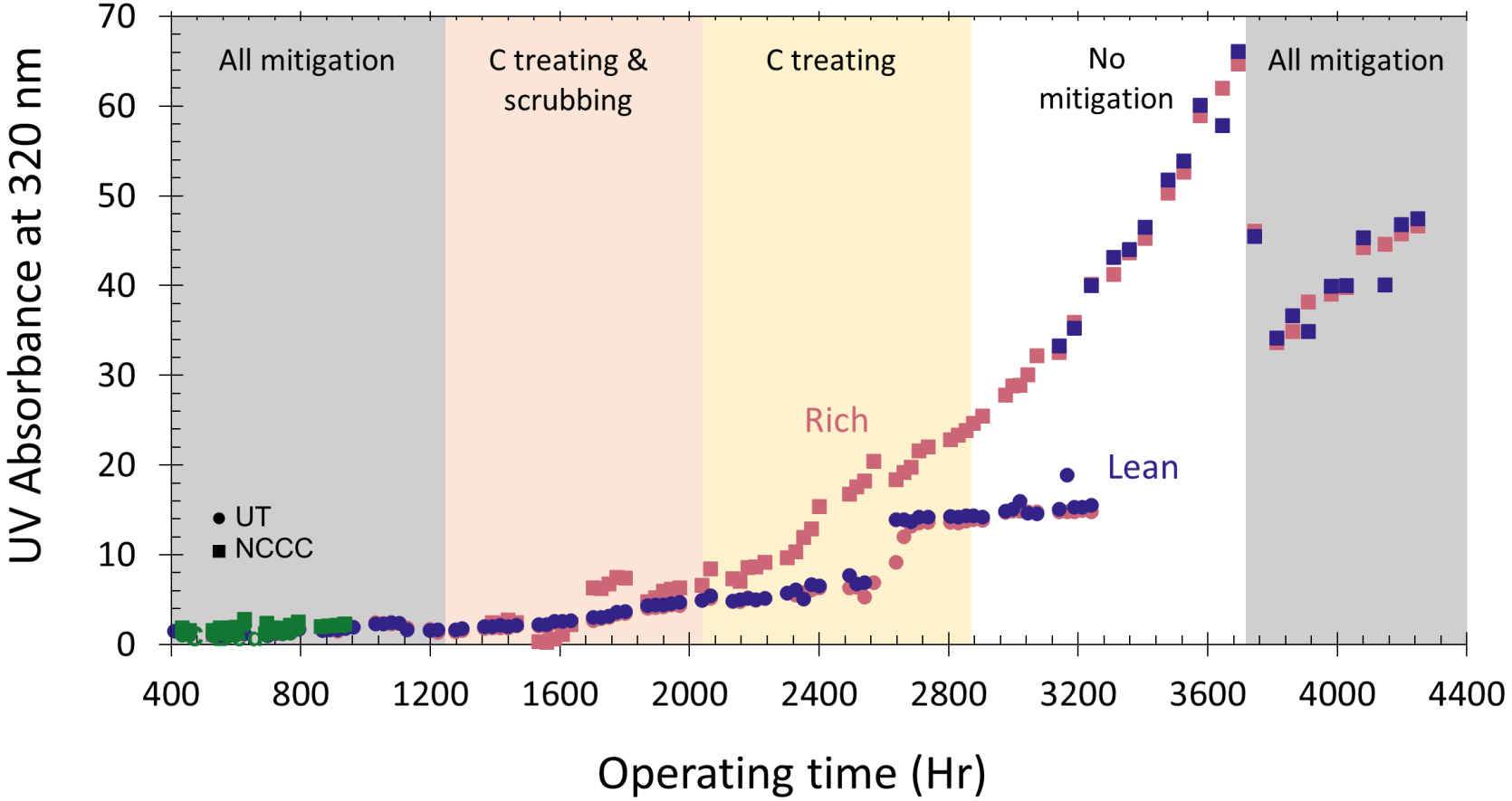
N_2 gas sparging at 0.5 SCFM



- N_2 gas 0.03% of gas traffic in abs
- N_2 exit velocity at sparge point <25 fpm

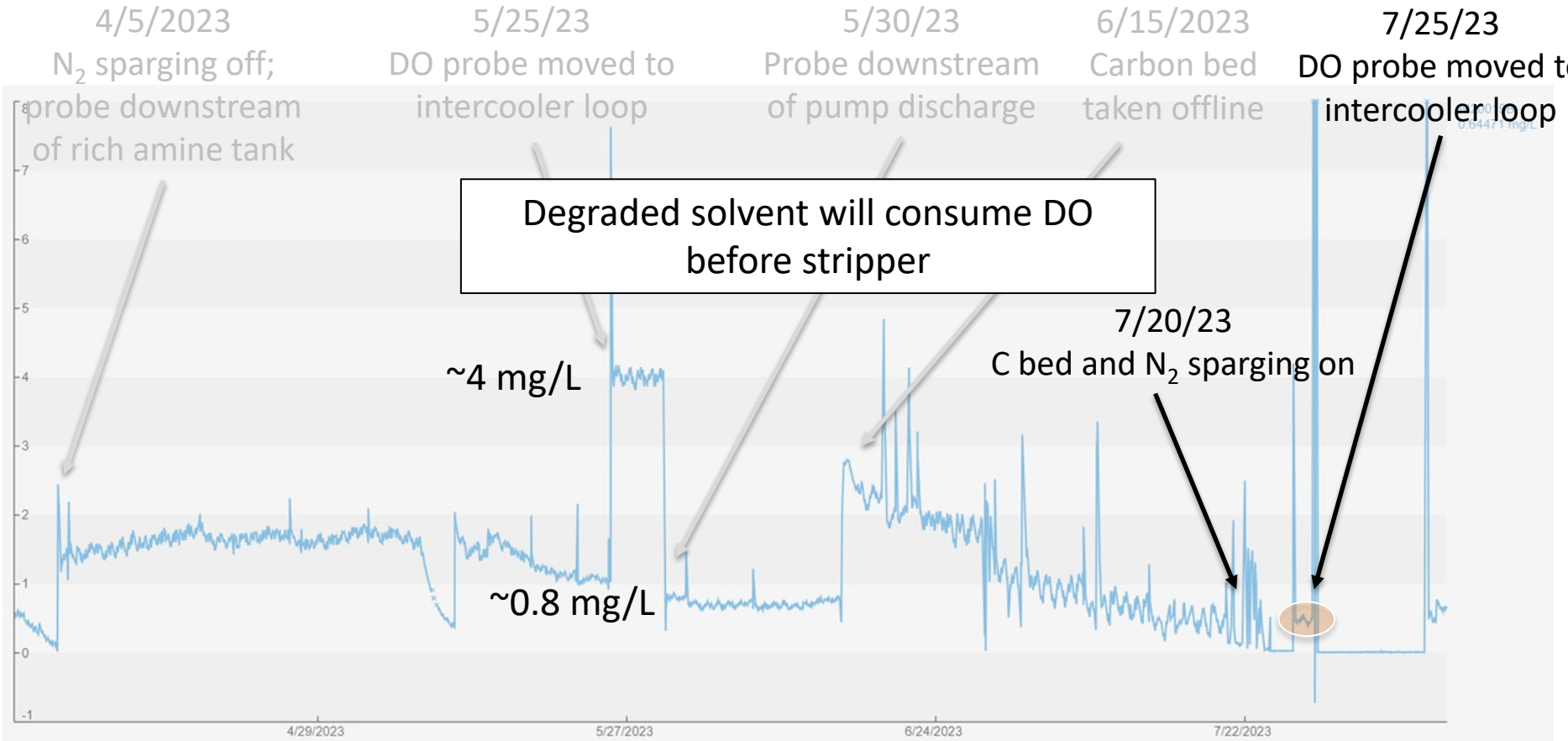
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

UV-Vis absorbance at NCCC (2023)

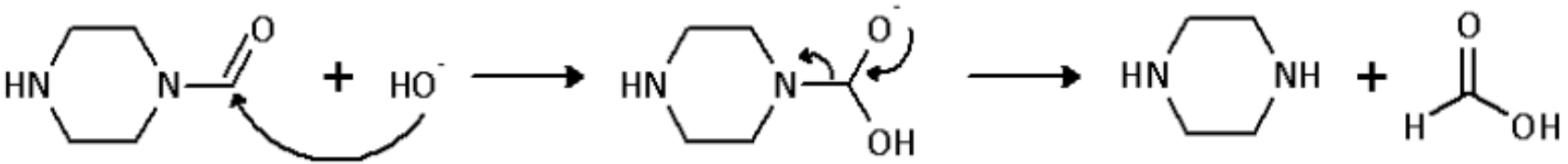


The University of Texas at Austin
McKetta Department of Chemical Engineering
Cockrell School of Engineering

DO probe readings with N_2 sparging off



Hydrolysis of amides

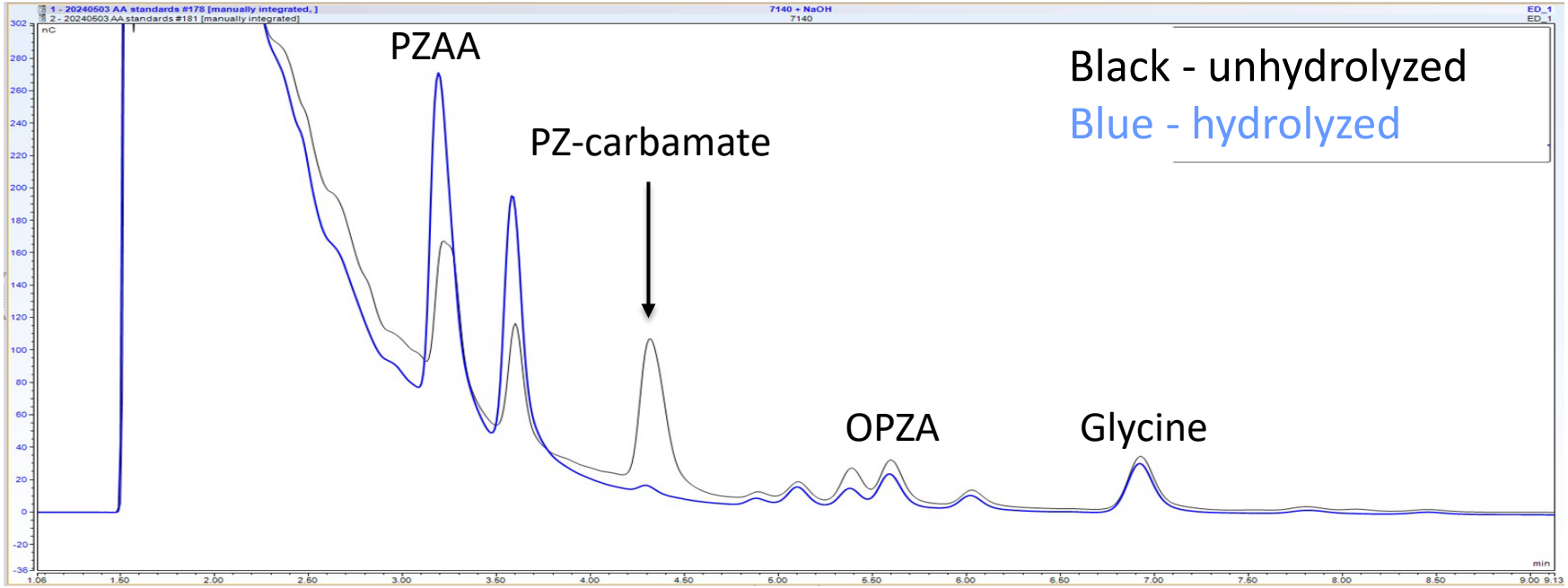


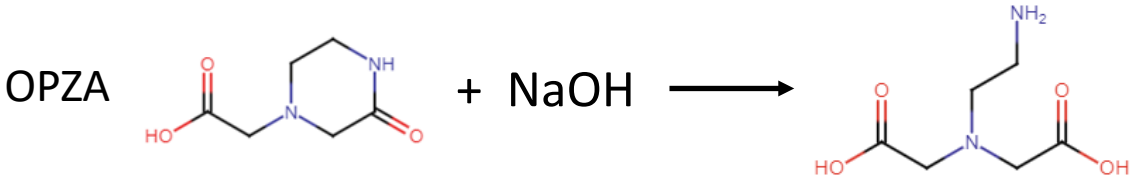
- Under alkaline conditions, hydrolysis involves attack by the strongly nucleophilic hydroxide ion on the amide (Morrison and Boyd, 1973)
- Lab procedures involves 1:1 treatment with 10 N NaOH for 24 hours
- Remeasure with ion chromatography or amino acid method to observe changes in chromatogram (i.e., PZ, NFPZ, OPZA)
- Results reported as “total” compound; difference between unhydrolyzed and hydrolyzed samples is considered amide

Figure taken from Freeman (2011).

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

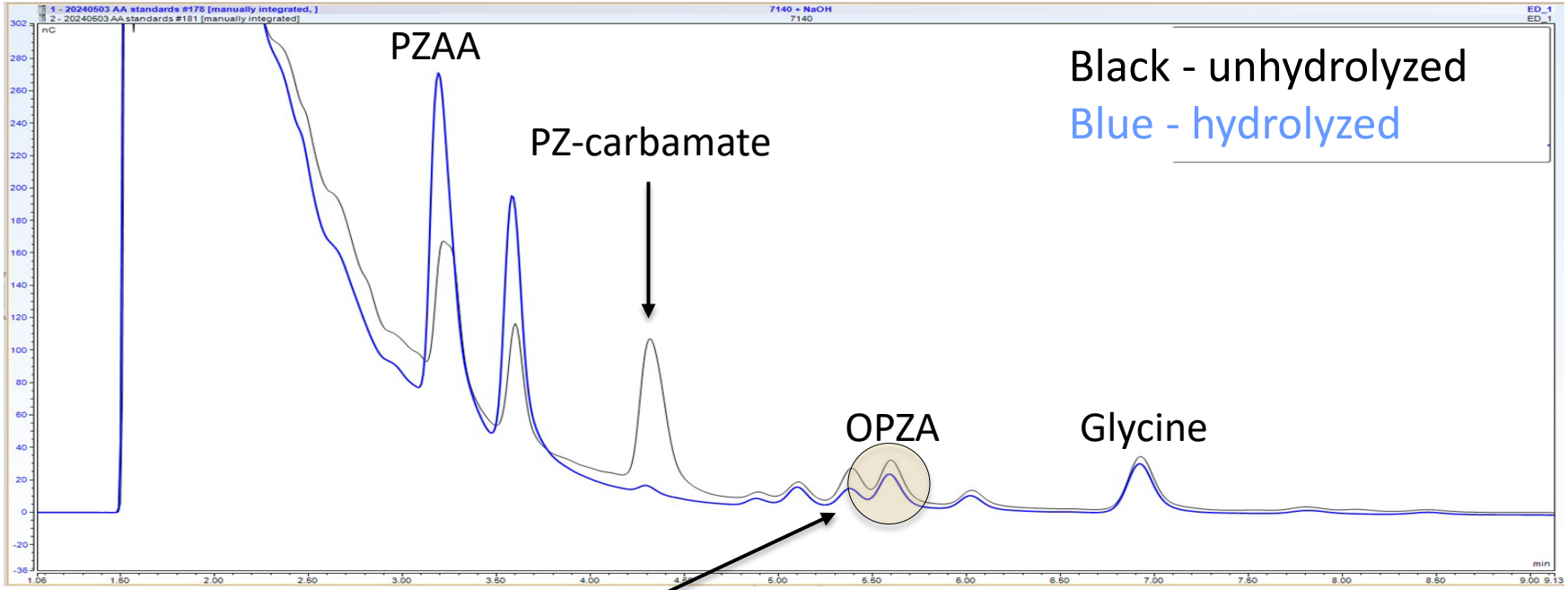
Sample hydrolysis in NCCC samples





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

Sample hydrolysis in NCCC samples



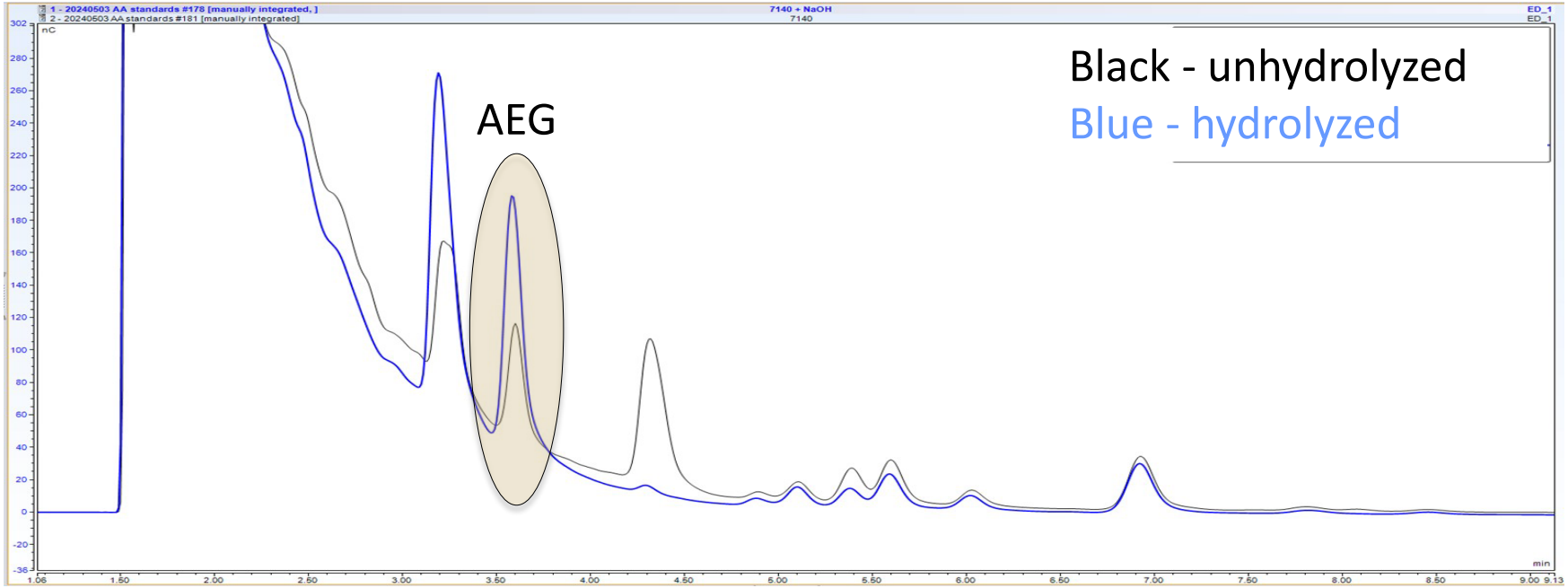
OPZA + NaOH →

OPZA largely not hydrolyzed.

Have yet to ID a peak and quantify this one.

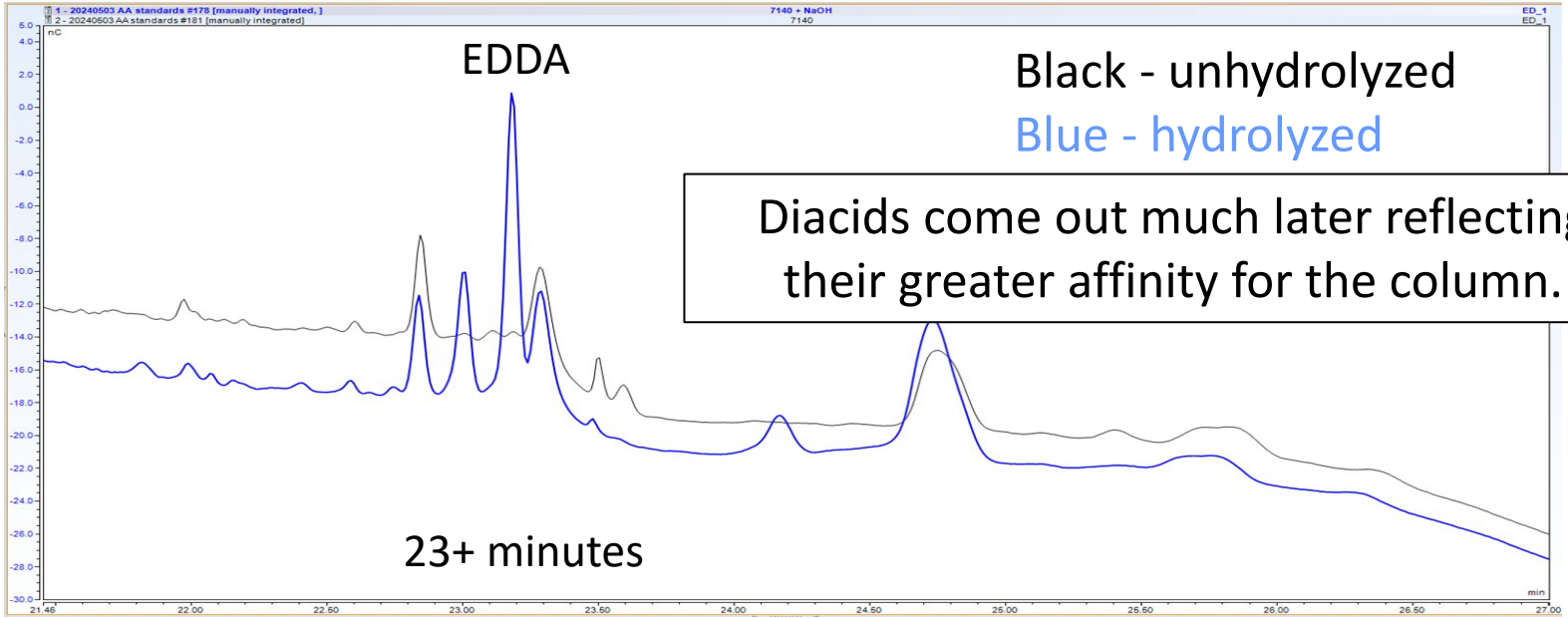
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

Sample hydrolysis in NCCC samples

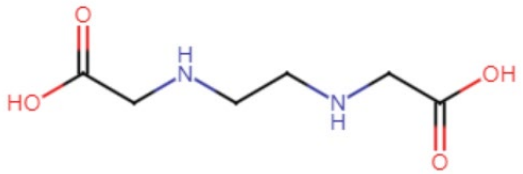


OPZ + NaOH → AEG

Sample hydrolysis in NCCC samples



Something is being hydrolyzed to form ethylenediamine diacetic acid (EDDA).



PTR-TOF-MS data – WW outlet

Unaffected but low

Op. time (Hr)	Water wash Operation	NH_3 (ppb)	PZ (ppb)	Acetaldehyde (ppb)
3,690	Conventional	7405 (8,795)	219	34 (1,034)
3,880	Trickle bed	3432	1.1	51
4,210	Bed 3 + acid wash	10	0.1	33
4,340	Bed 3 + WWC	2407	0.1	25
5,700	Conventional, post reclaiming	1111	0.3	39

Data in () measured with FTIR.

Flue gas monitoring with FTIR (NCCC)