What we know and don't know about amine oxidation

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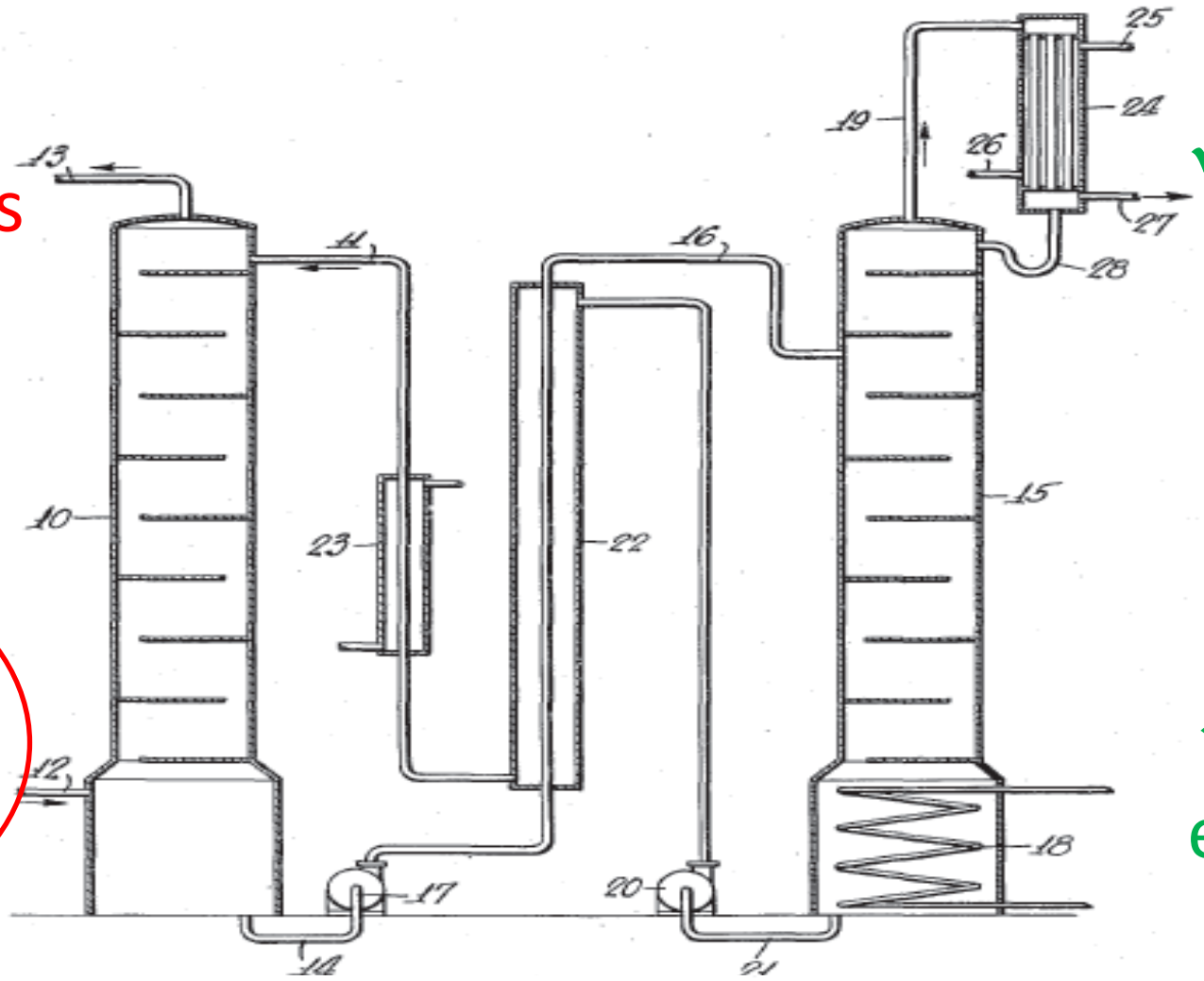
Adapting acid gas treating to CO_2 capture

✓ Much larger overall cost

X Health & safety impact of emissions To atmosphere

✓ Larger absorber at 1 bar

X Amine oxidation by O_2 and NO_2 Risk!! $$$



Dec. 2, 1930. R. R. BOTTOMS 1,783,901

PROCESS FOR SEPARATING ACIDIC GASES

Filed Oct. 7, 1930

✓ Compression to 50 bar

✓ Greater energy use

Extensive research on amine oxidation

>20 yrs >8 institutions > 40 investigators

Questions > Answers

UT Austin
2008 Goff
2011 Sexton
2011 Closmann
2013 Freeman
2015 Voice
2016 Nielsen
2020 Wu
2024 Chen
2025 Plantz
2025 Obute

NTNU/SINTEF
2013 Vevelstad
2021 Buvik
2016 Fytianos
2024 Francois
2024 Braakhuis
2025 Mullen

Liege U
2013 Fredericksen
2014 Wang
2024 Lefèbvre

U Regina
2001 Supap
2005 Bello
2006 Lawal
2007 Uyanga
2012 Chanchey
2024 Muchan

U KY
2014 Thompson
2015 Chandan
2024 Jorgensen

IFP/EDF
2009 Lepaumier
2014 Gouedard
2018 Delgado

TNO
2025 Gomez-Rueda

Australia
2015 Reynolds
2016 Dickinson
2017 Dhingra

With results from MEA, PZ, and Cesar-1

We Know

1. $Fe^{2+/3+}$ catalyzes oxidation
2. Dissolved O_2 reacts w amine throughout
3. NO_2 catalyzes amine oxidation in the absorber
4. Common products incl NH_3, formate, et al.
5. Stable amines incl PZ, AMP et al.
6. When oxidized, amines can emit hazardous pollutants

1. We know

Amine oxidizes by a radical mechanism catalyzed by $Fe^{2+/3+}$

$[Fe^{2+/3+}]$ may be limited by corrosion or solubility

As solvents degrade, $Fe^{+2/+3}$ and oxidation rate increase

We do not know

If Mn^{+2}, $Cr^{+2/+3}$ Ni^{+2} et al. catalyze oxidation?

The detailed free radical mechanism?

If peroxide decomposition is the dominant initiation?

If there are useful inhibitors?

The probable free radical mechanism

Initiation

$$PZOOH \rightarrow PZO^{\cdot} + OH^{\cdot}$$

Fe^{3+}

$$PZH + PZO^{\cdot} \rightarrow PZ^{\cdot} + PZOH$$

$$PZH + NO_2 \rightarrow PZ^{\cdot} + NO_2^{-} + H^{+}$$

Propagation

$$PZ^{\cdot} + O_2 \rightarrow PZOO^{\cdot}$$

$$PZH + PZOO^{\cdot} \rightarrow PZ^{\cdot} + PZOOH$$

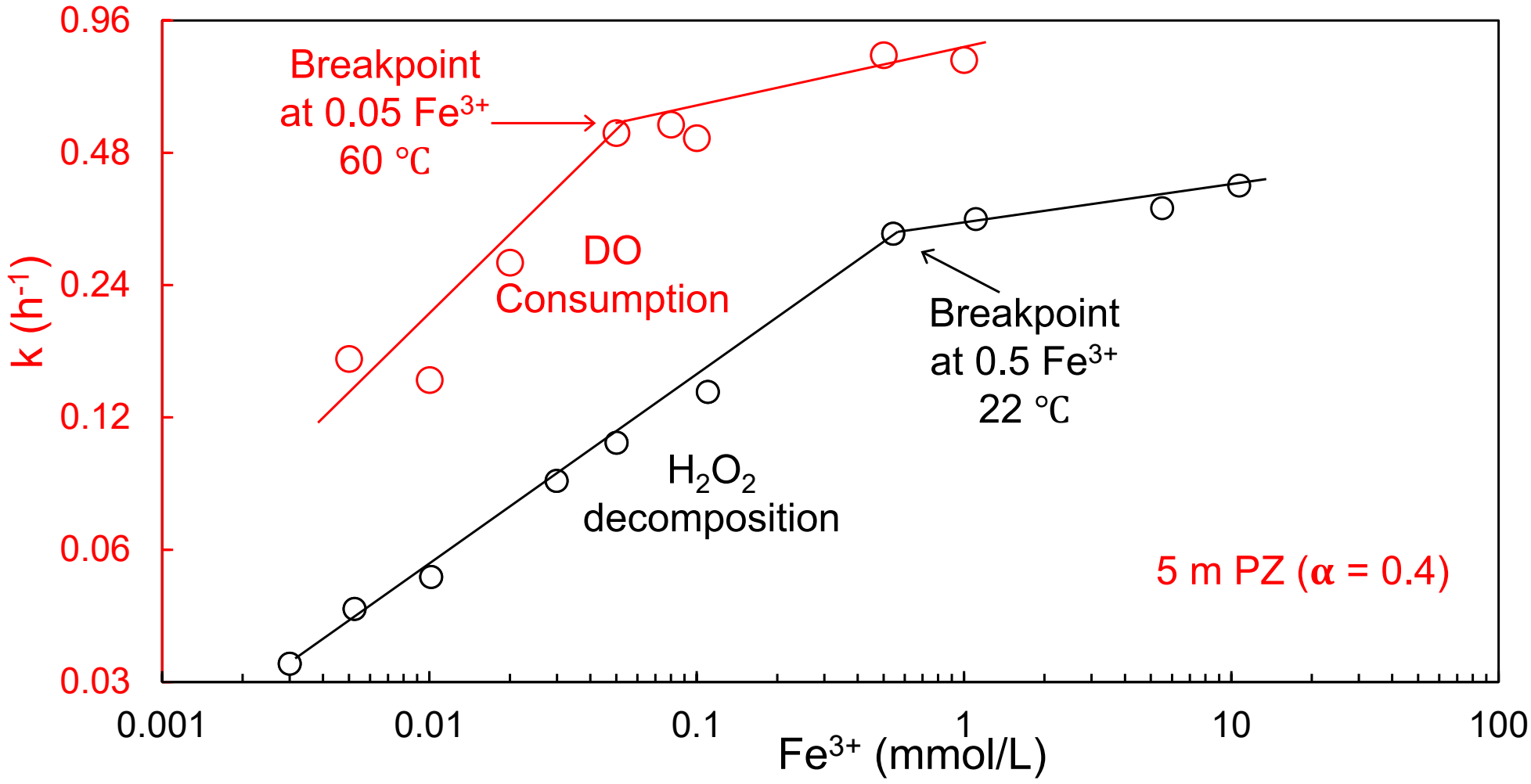
Termination

$$2\ PZ^{\cdot} + H_2O \rightarrow PZOH + PZH$$

We Know

- $Fe^{+2/+3}$ is provided by corrosion
  - Equipment design and operating conditions matter
  - Effective mitigation of oxidation may result in corrosion by dissolving the Cr_2O_3 on stainless steel at greater T
- $Fe^{+2/+3}$ solubility and activity may be increased by complexing with amine carbamate or amino acid degradation products

DO consumption and peroxide decomposition have similar dependence on Fe^{3+}



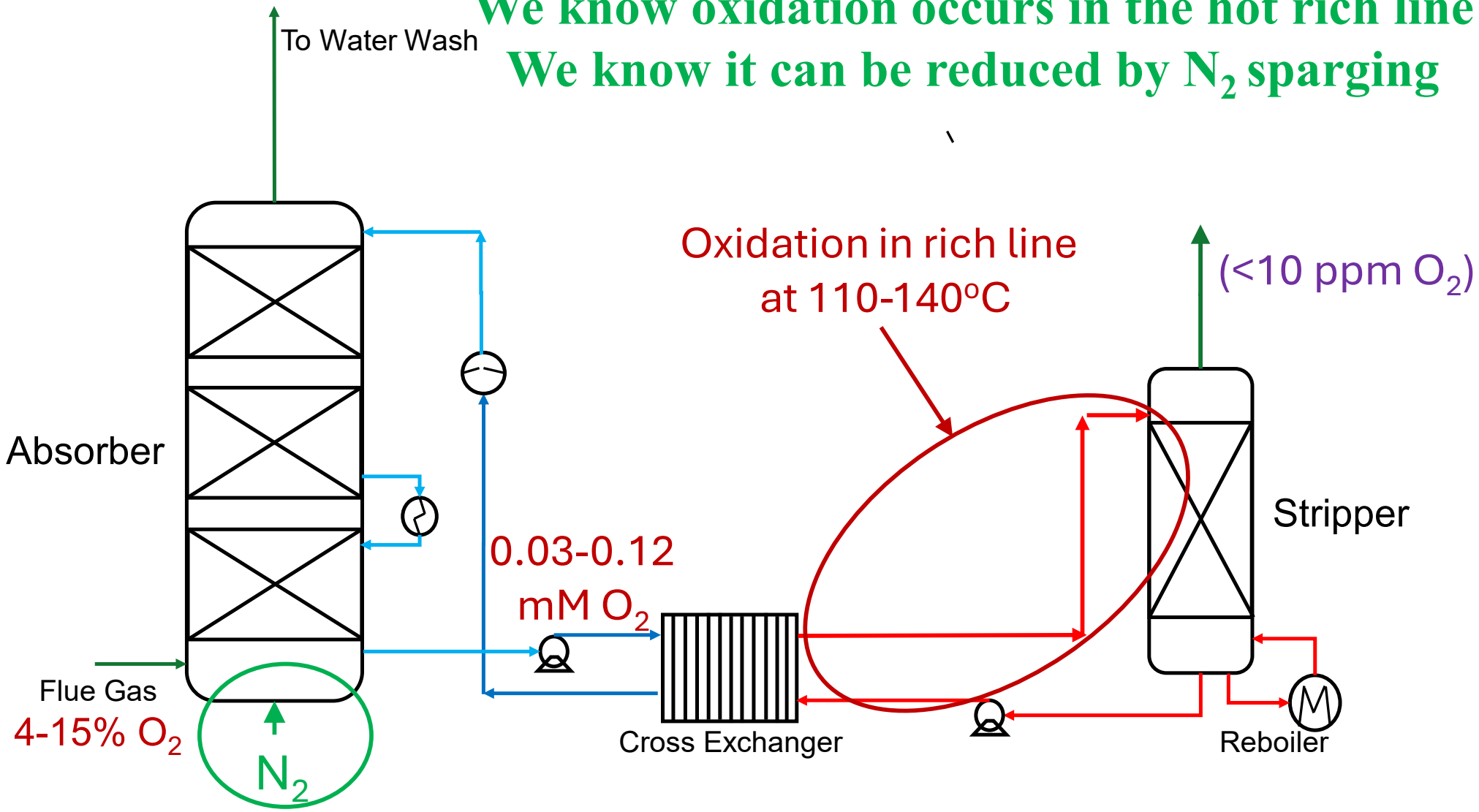
2. We know oxidation occurs

In the hot rich line at elevated T

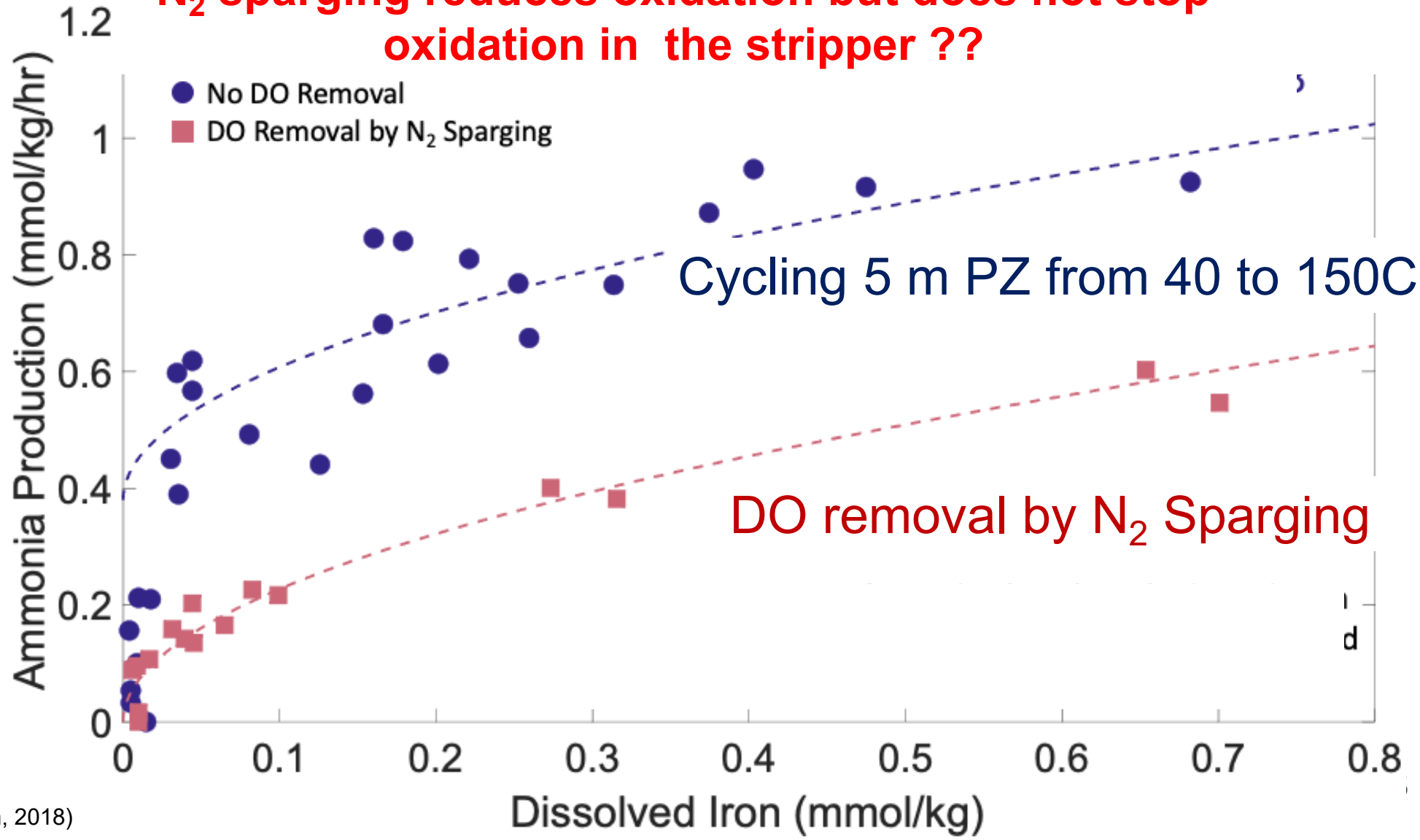
In the absorber & sump with degraded solvent

We suspect oxidation occurs in the stripper

We know oxidation occurs in the hot rich line
We know it can be reduced by N_2 sparging



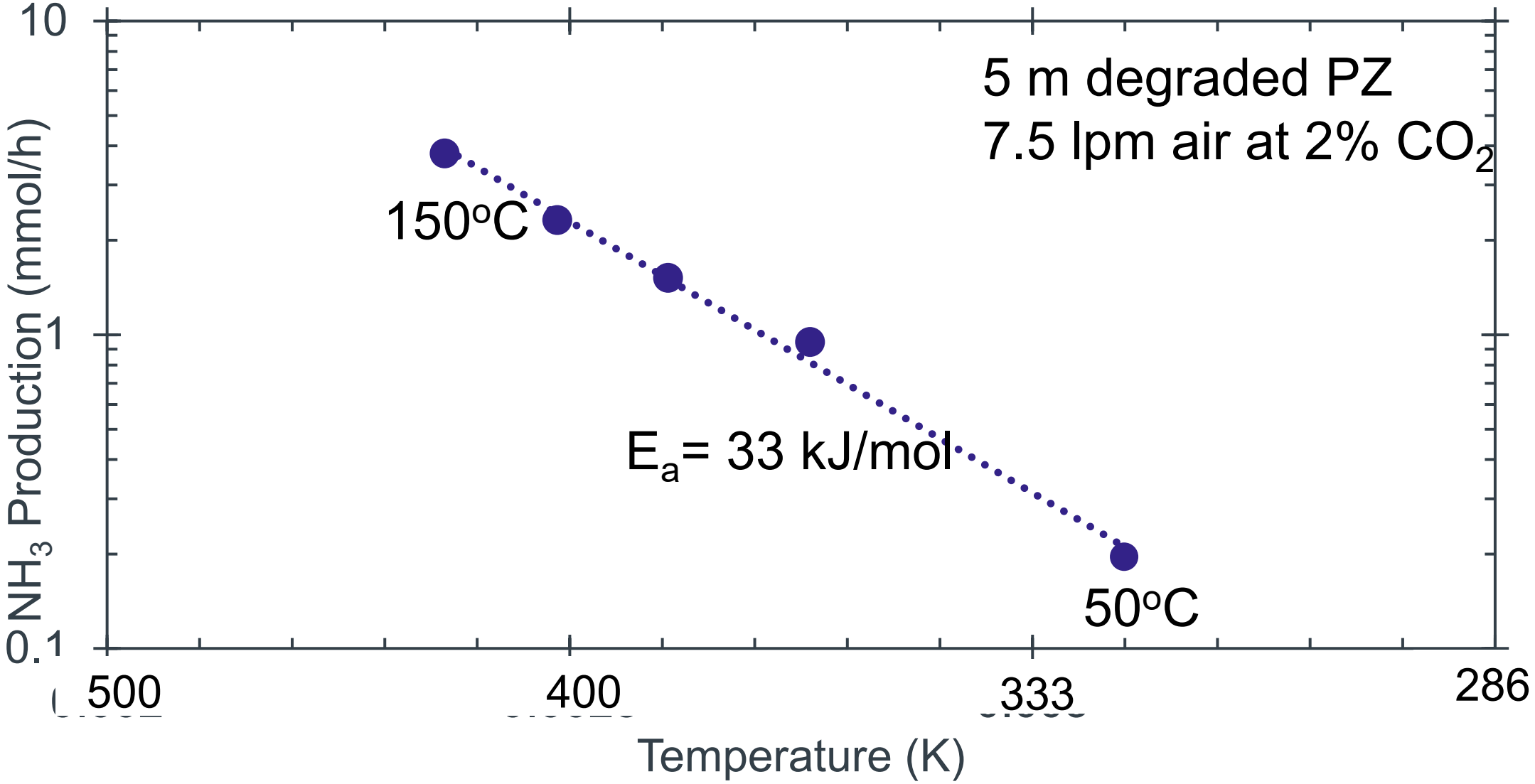
N_2 sparging reduces oxidation but does not stop oxidation in the stripper ??



(Nielsen, 2018)

(Nielsen, 2018)

PZ oxidizes at stripper T when cycled



3. We know NO_2 catalyzes oxidation in the absorber

With all amines, not just secondary amines

We should remove NO_x by SCR

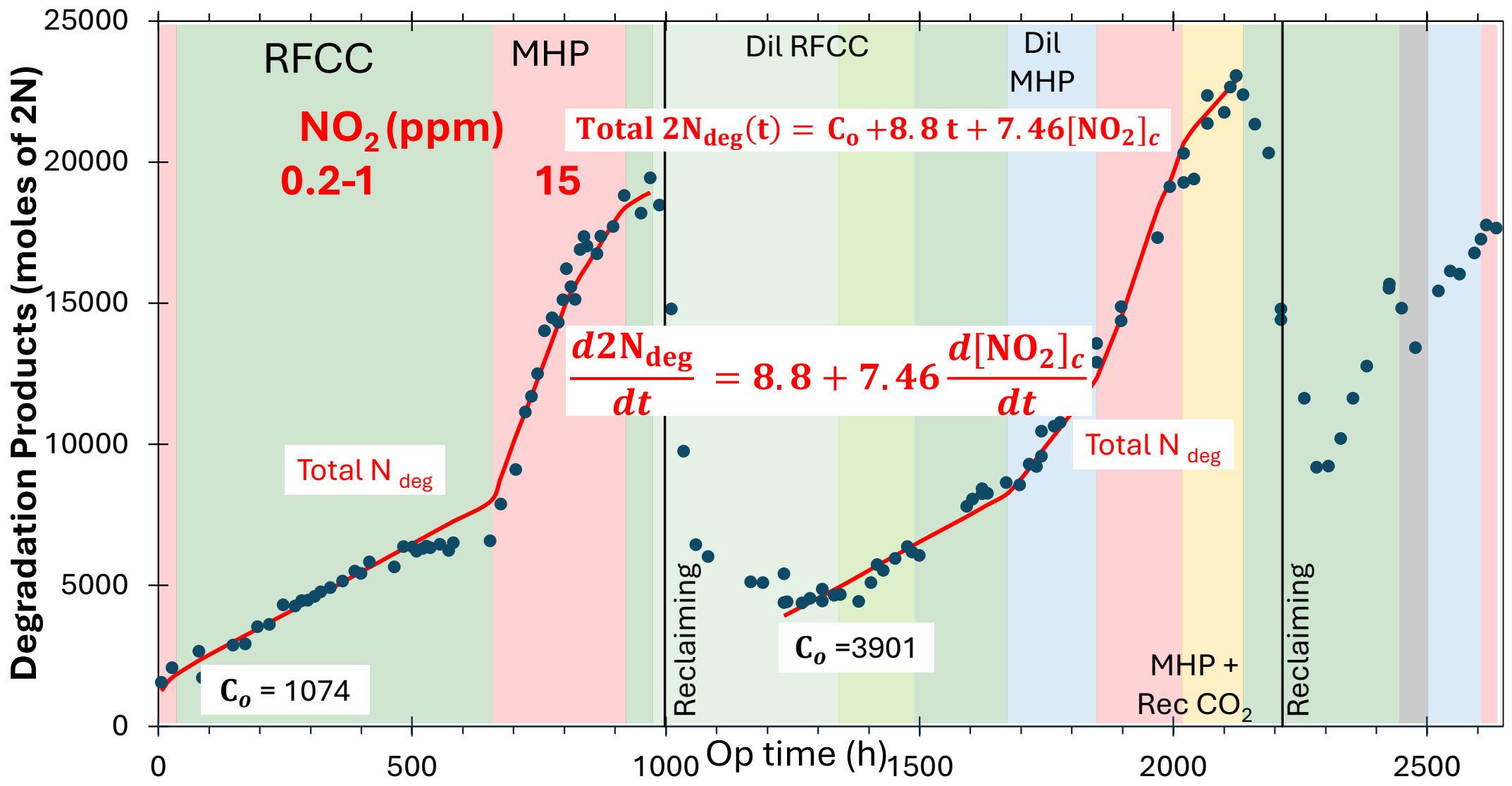
We can remove NO_2 with sulfite/thiosulfate

We do not know

NO_2 Rate with other specific amines

If NO is readily converted to NO_2

If we can remove NO_2 with C or by other methods


N products in 5 m PZ + cumulative NH3 at TCM
Degradation Products (moles of 2N)
Op time (h)
RFCC
MHP
Dil RFCC
Dil MHP
NO2 (ppm)
0.2-1
15
Total 2Ndeg(t) = Co +8.8 t + 7.46[NO2]c
d2Ndeg/dt = 8.8 + 7.46 d[NO2]c/dt
Total N deg
Total N deg
Co = 1074
Co =3901
Reclaiming
Reclaiming
MHP +
Rec CO2
25000
20000
15000
10000
5000
0
0
500
1000
1500
2000
2500

We know NO_2 absorption will be high for all solvents

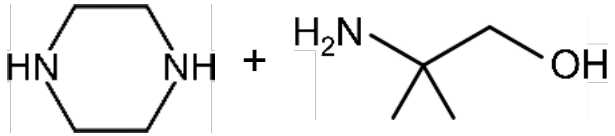
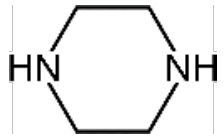
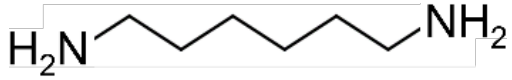
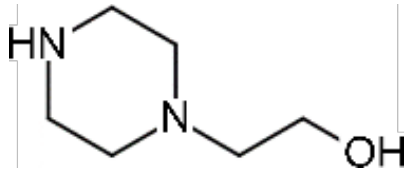
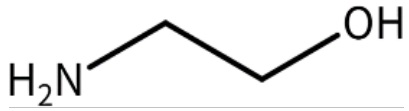
Fine (2015) measured NO_2 absorption kinetics & calculated NO_2 Uptake

Solvent	K_g (mol/m^2 s Pa)	NO_2 Uptake (%)
9 m MEA	3 e-7	73
8 m PZ	10 e-7	92
7 m MDEA/2 m PZ	= k_g (>>50 e-7)	>99

Fine, 2015

4. We know relative oxidation rates in simple experiments

Relative to MEA (w 1 mM Fe^{+3}) (Onomura et al., 2025)

Amine	Structure	k_{DO} ODBR	$K_{50, NH3}$ HGF
CESAR1		11	7
PZ		17	1
MPA		18	16
HMDA		24	100
HEP		62	13
MEA		100	100

We do not fully understand for other amines

- More complicated structures – such a 2-methyl- PZ
- $Fe^{2+/3+}$ solubility in other amines
- Relative reaction rate with peroxide
- Relative reaction rate with NO_2

5. We Know Oxidation Products in MEA & PZ

Analytical Methods

IC, LC/MS (QTOF), HPAE-PAD, GC/MS, PTR-ToF-MS

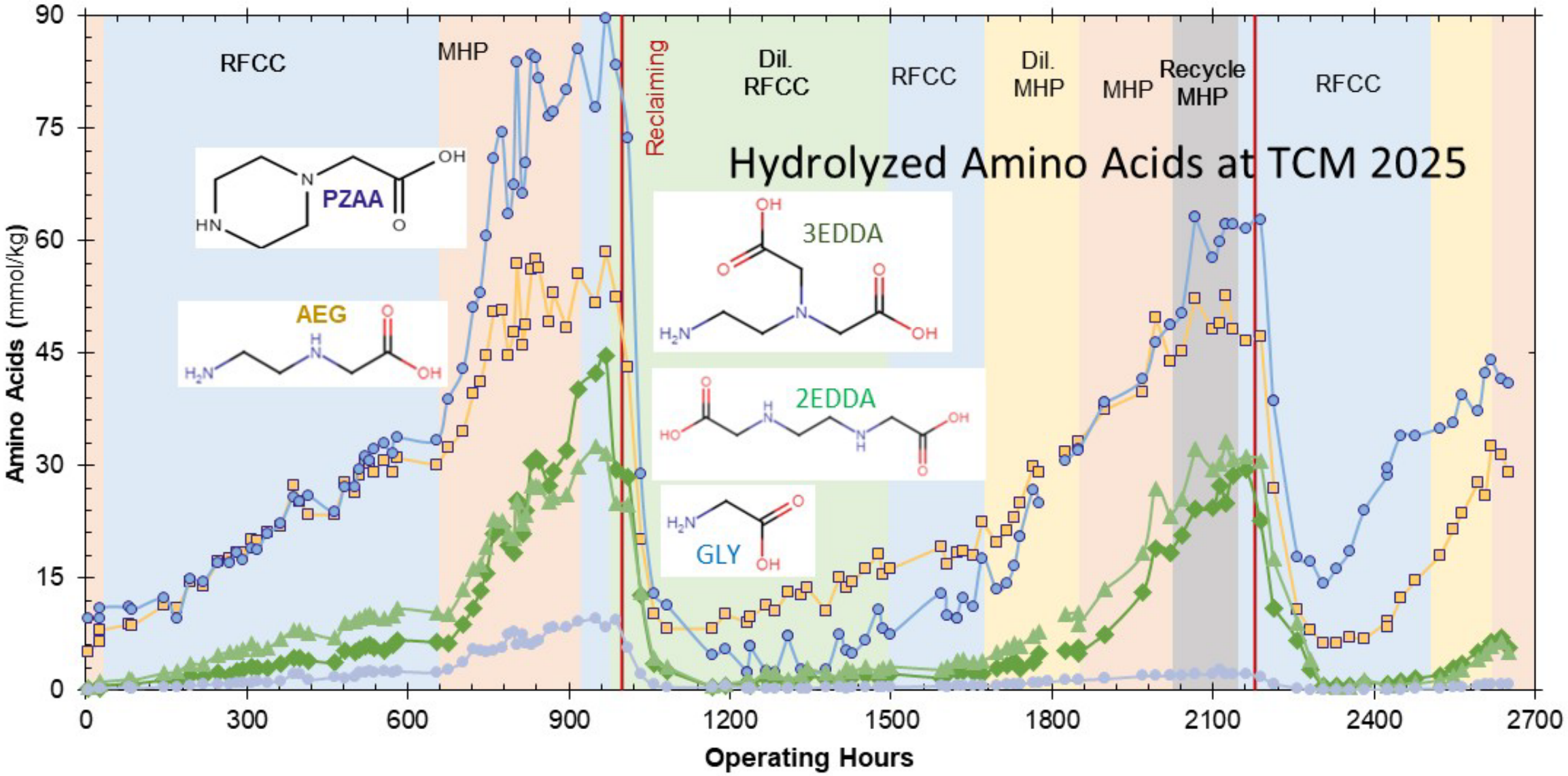
Small fragments

NH_3, volatile amines, organic acids/amides

Large fragments & oligomers

Imidazoles, amino acids/amides, diamines

Amino acids in oxidized PZ may solubilize metals



We do not yet fully understand

Smaller amines, aldehydes, nitriles, 2C fragments

Larger aldehydes, carbinolamines, & aminals

Efficient, useful analytical methods

for all amines

for all products

We risk not knowing

Alcohols, hydrocarbons

Unique products in proprietary amines

Other hazardous cats and dogs

6. We know and understand

When oxidized, amines can emit hazardous pollutants

- **We must <u>minimize oxidation!!!</u>**
- Manage ammonia to address PM2.5 by acid wash et al.
- Manage volatile amines by acid wash
- Manage nitrosamine by SCR, high T stripping, or using primary amine

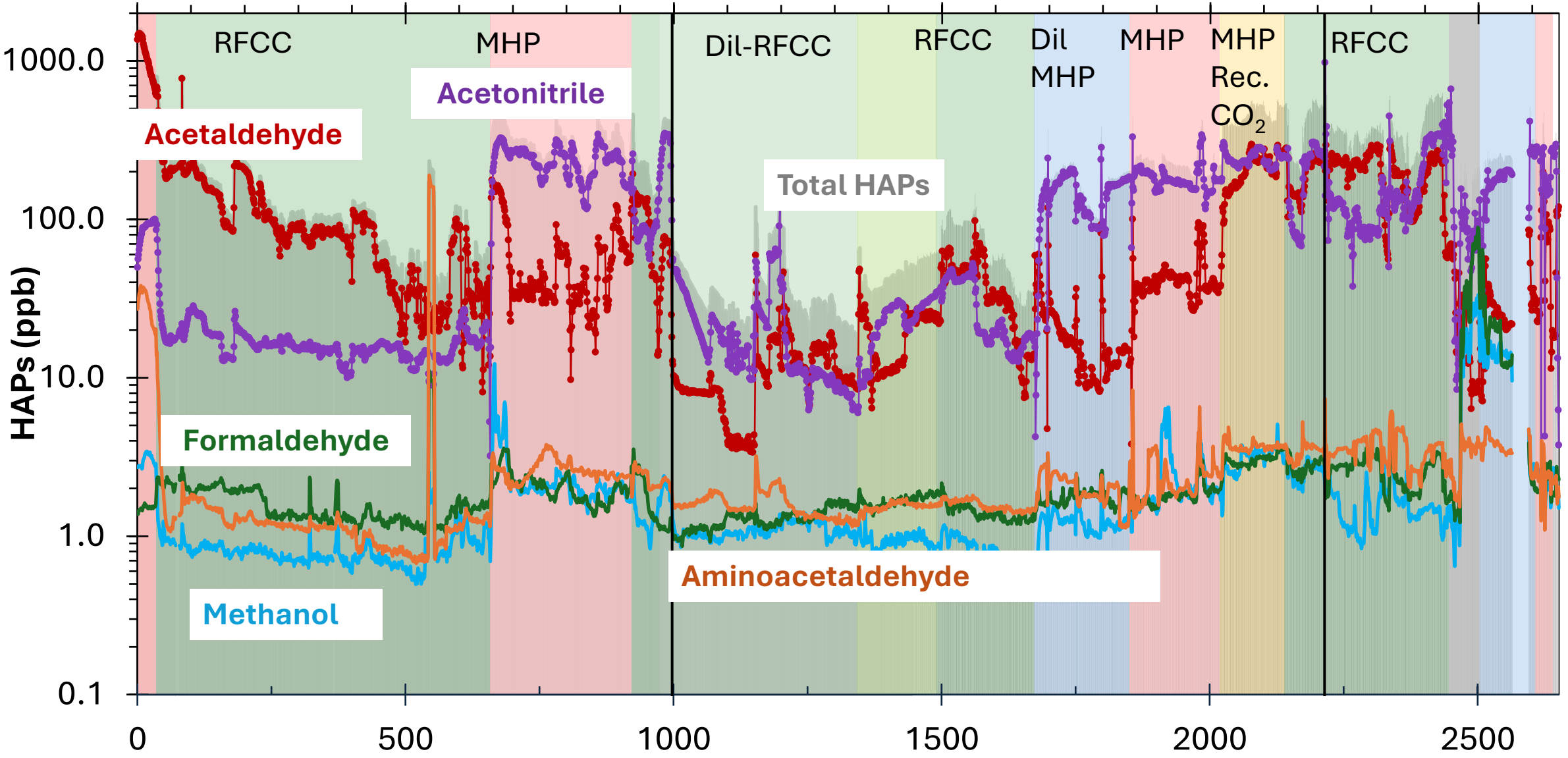
We do not yet understand

Mechanisms for formation and management of other HAPs

Emission levels of aldehydes, acetonitrile, et al.

- With a given solvent?
- With specific operating conditions?

Acetaldehyde & Acetonitrile dominate listed HAPs with PZ



We have made good progress in understanding and managing amine oxidation

- $Fe^{2+/3+}$ catalyzes oxidation by decomposing peroxides to free radicals
  - Reclaim and avoid corrosion
  - Amino acids and other degradation products solubilize and activate $Fe^{2+/3+}$
  - What other metals and impurities catalyze oxidation?
  - Are there any useful inhibitors?
- NO_2 catalyzes amine oxidation in the absorber
  - Remove NO_x by SCR or scrub NO_2 with sulfite/thiosulfate
  - Does NO also catalyze oxidation by conversion to NO_2 et al?
- Dissolved oxygen reacts with amine in the hot rich line
  - Remove O_2 by N_2 sparging or other methods
  - Does the stripper T further increase oxidation?
  - Does n2 sparging result in corrosion?

- Common oxidation products include
  - NH_3, organic acids, smaller amines, aldehydes, amino acids and amides, imidazoles
  - Analytical methods are needed for comprehensive analyses with new amines
- Stable Amines such as AMP have no alpha hydrogen
  - Why are PZ et al. resistant to oxidation? ,
  - Why do MEA et al. readily oxidize?
- When oxidized, amines emit ammonia, 2C HAPs, nitrosamines, volatile amines
  - Mitigate oxidation and/or enhance wash systems to manage emissions
  - How do HAPs & volatile amines vary w solvent?
  - How can HAPs & volatile amines be specifically minimized?

Take Heart

We will solve this problem in my lifetime!