Cyclic Oxidation of Piperazine

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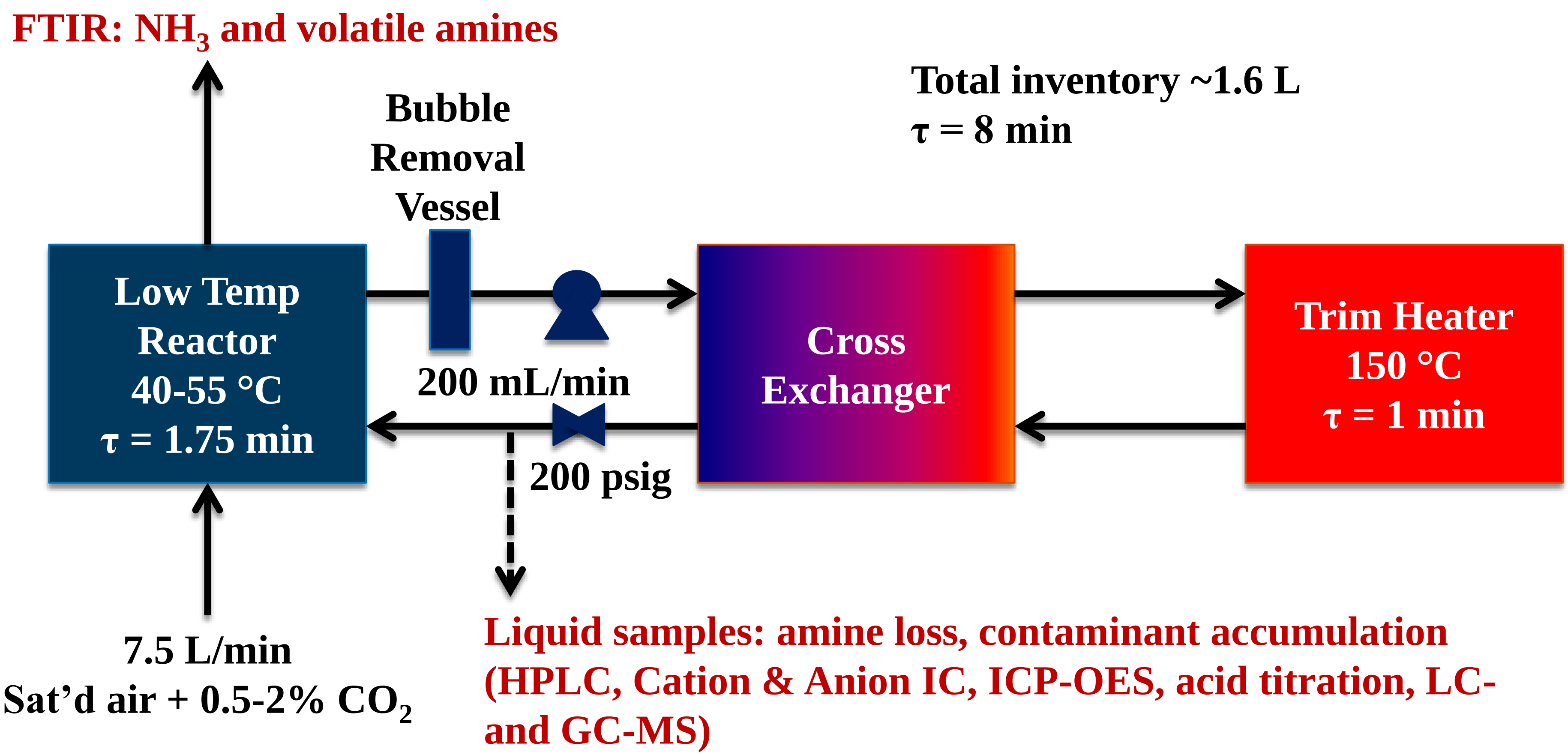
Amine Oxidation

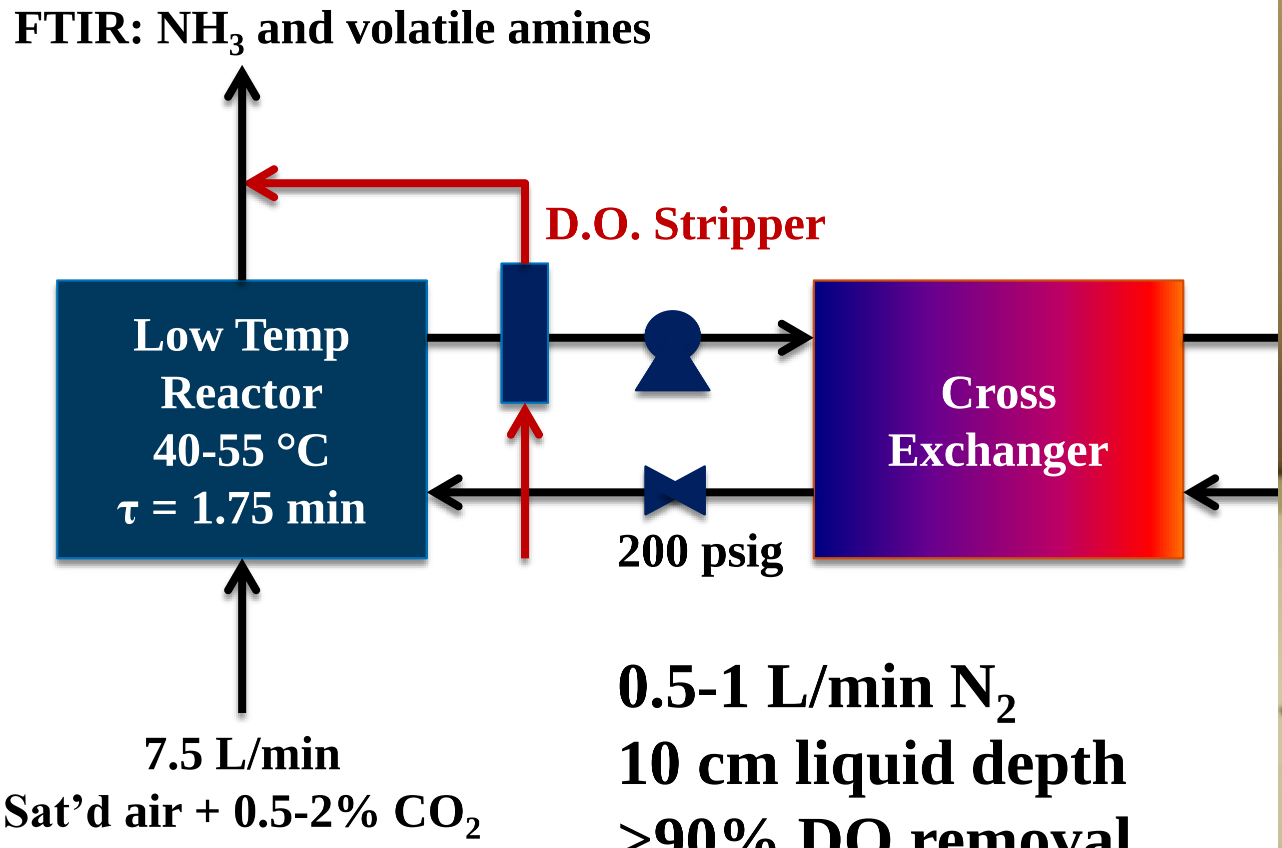
- Free radical reaction with O_2 catalyzed by dissolved metals [1]
  - PZ: stable at absorber conditions, oxidizes in cyclic systems [2]
- Most significant cause of amine solvent loss in pilot plants [3]
  - Increases solvent make-up cost (~$1-3/MT CO_2) [4]
  - Degradation product accumulation
    - Heat stable salt (HSS: formate, etc.) ↑ = viscosity ↑ = W_{EQ} ↑
    - Increased toxicity
    - Additional solvent loss due to reclaiming process
  - Volatile emissions (ammonia, aldehydes, amine fragments)
  - Nitrosamine accumulation
    - 1° and 3° amines form stable 2° amine degradation products from degradation [5]

High Temperature Oxidation Reactor (HTOR)



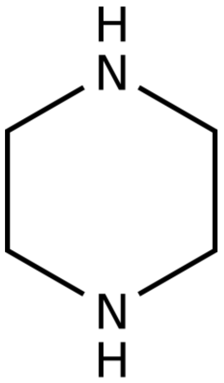
Contained in fume hood with spill containers

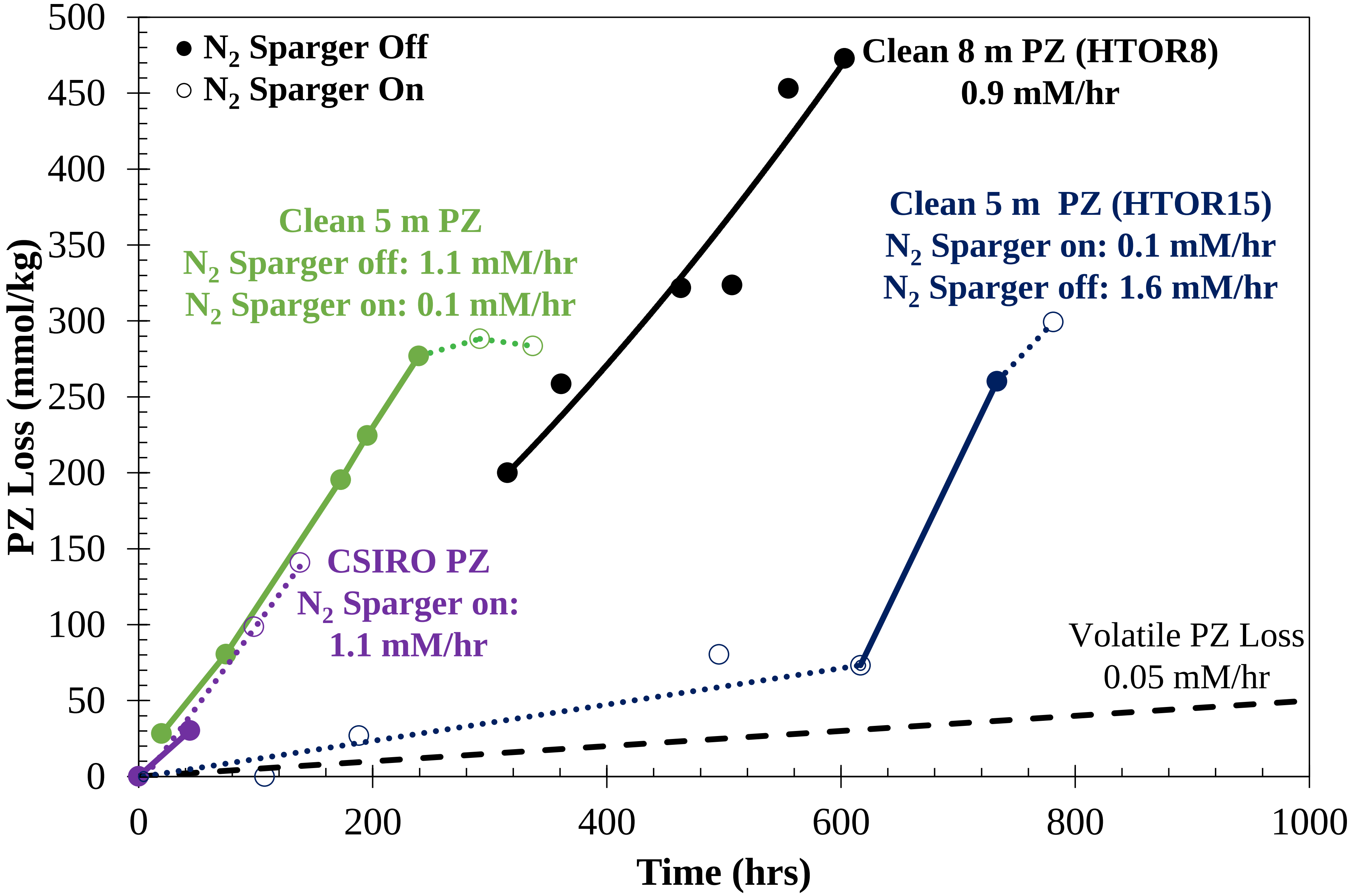
Dissolved Oxygen Stripping



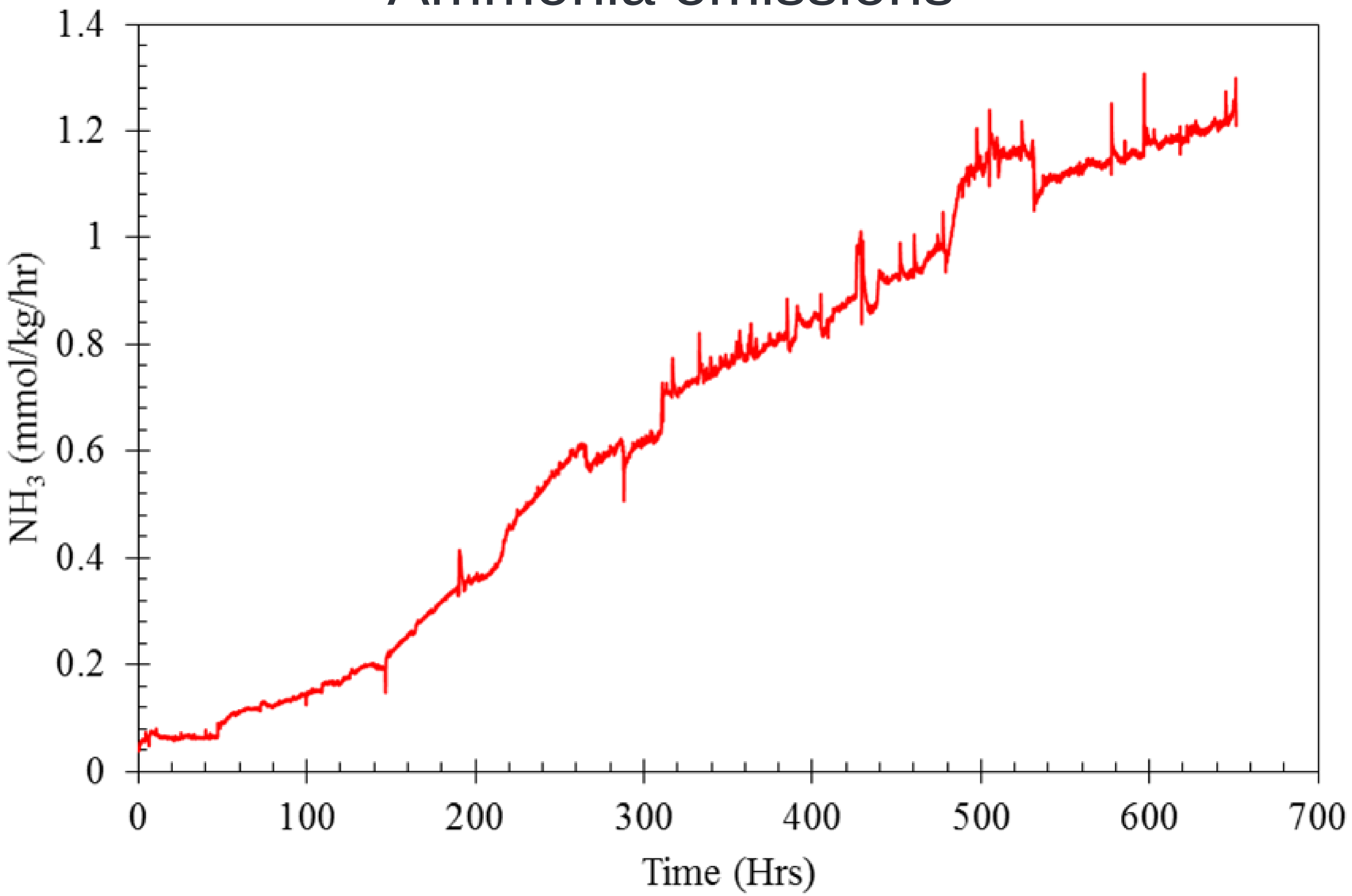
0.5-1 L/min N_2
10 cm liquid depth
>90% DO removal

PZ loss in the HTOR

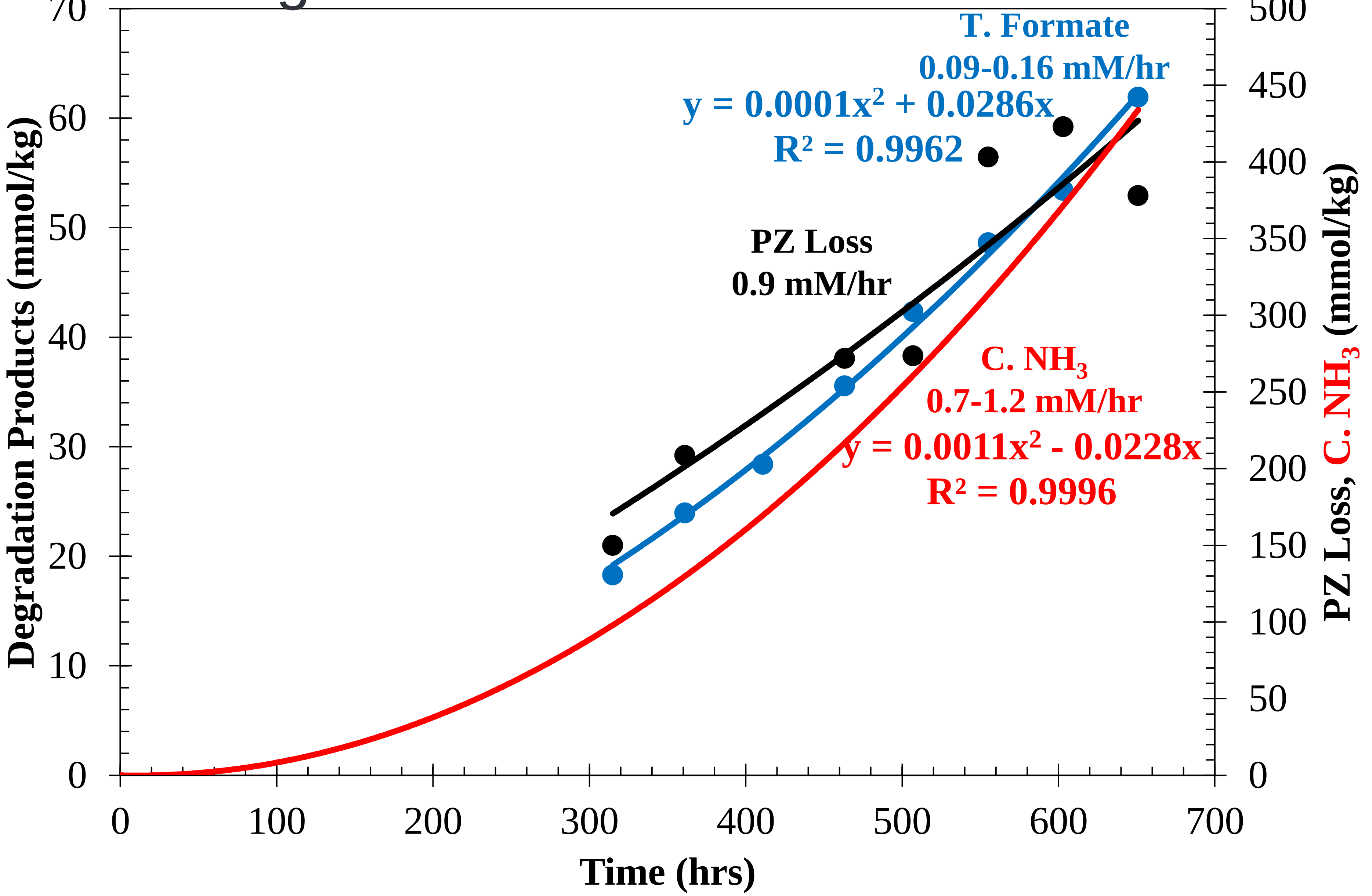




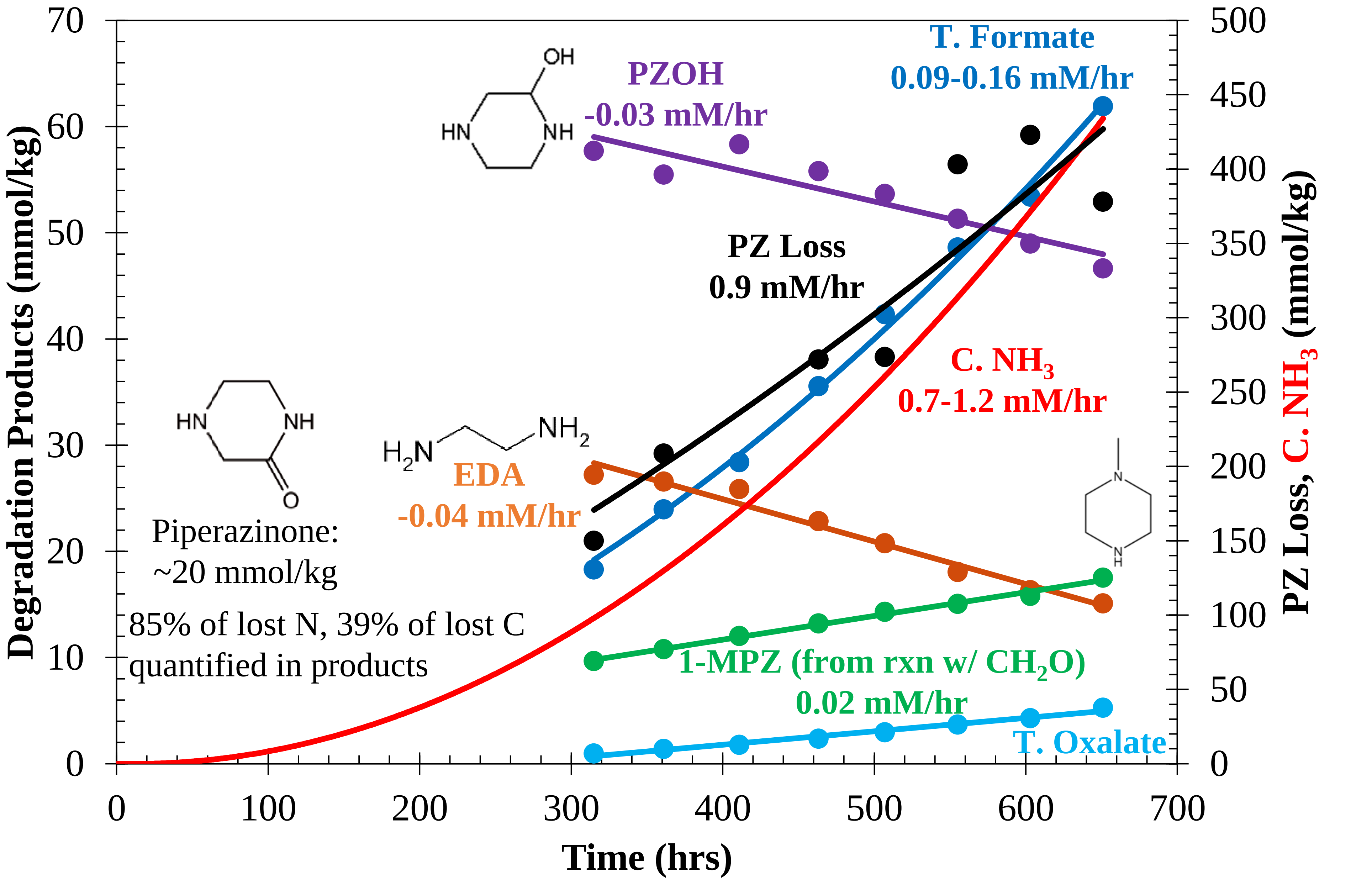
Steady state oxidation of clean 8 m PZ (no N_2 sparging)
Ammonia emissions



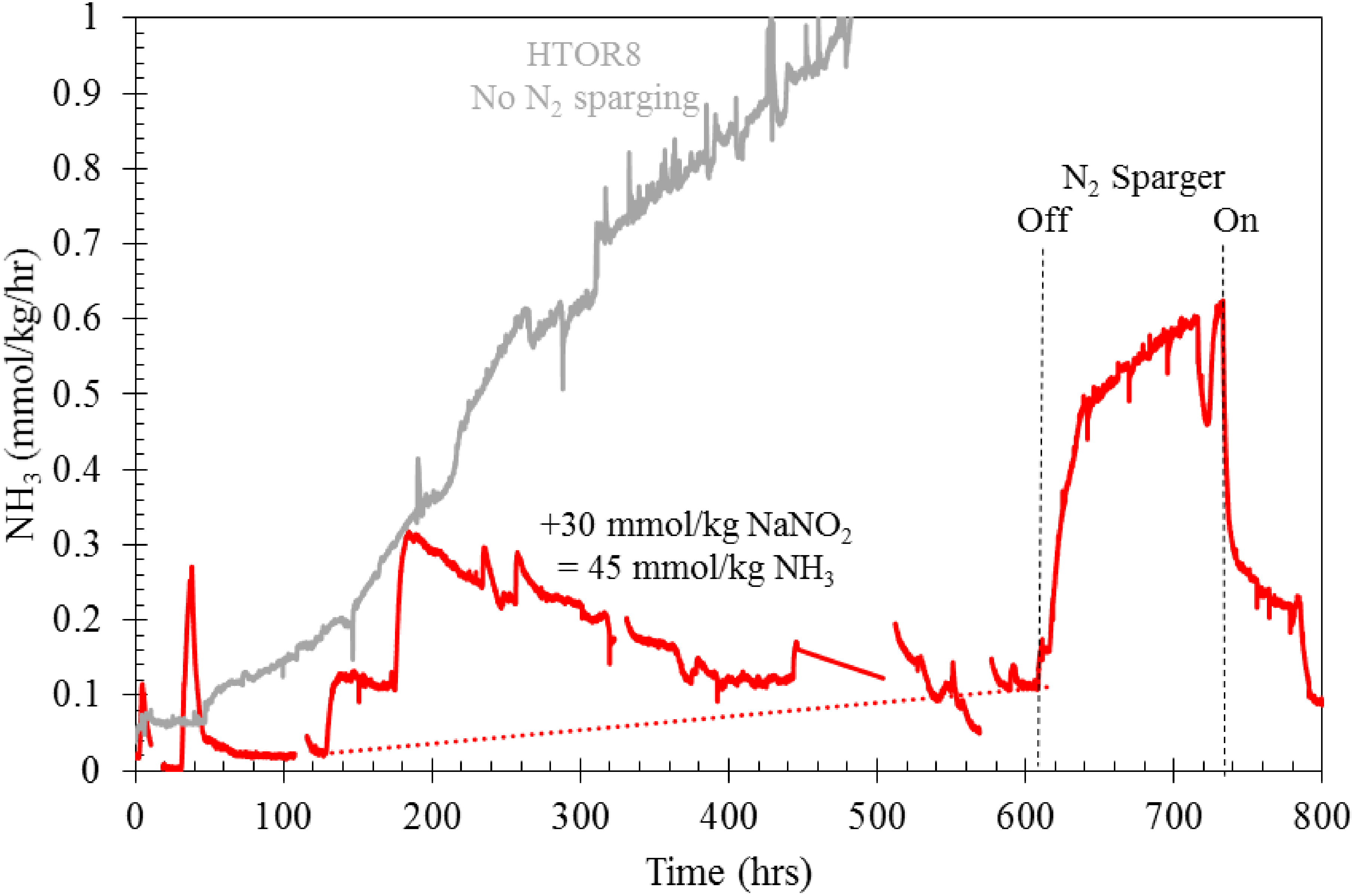
Steady state oxidation of clean 8 m PZ (no N_2 sparging) Degradation Product Accumulation



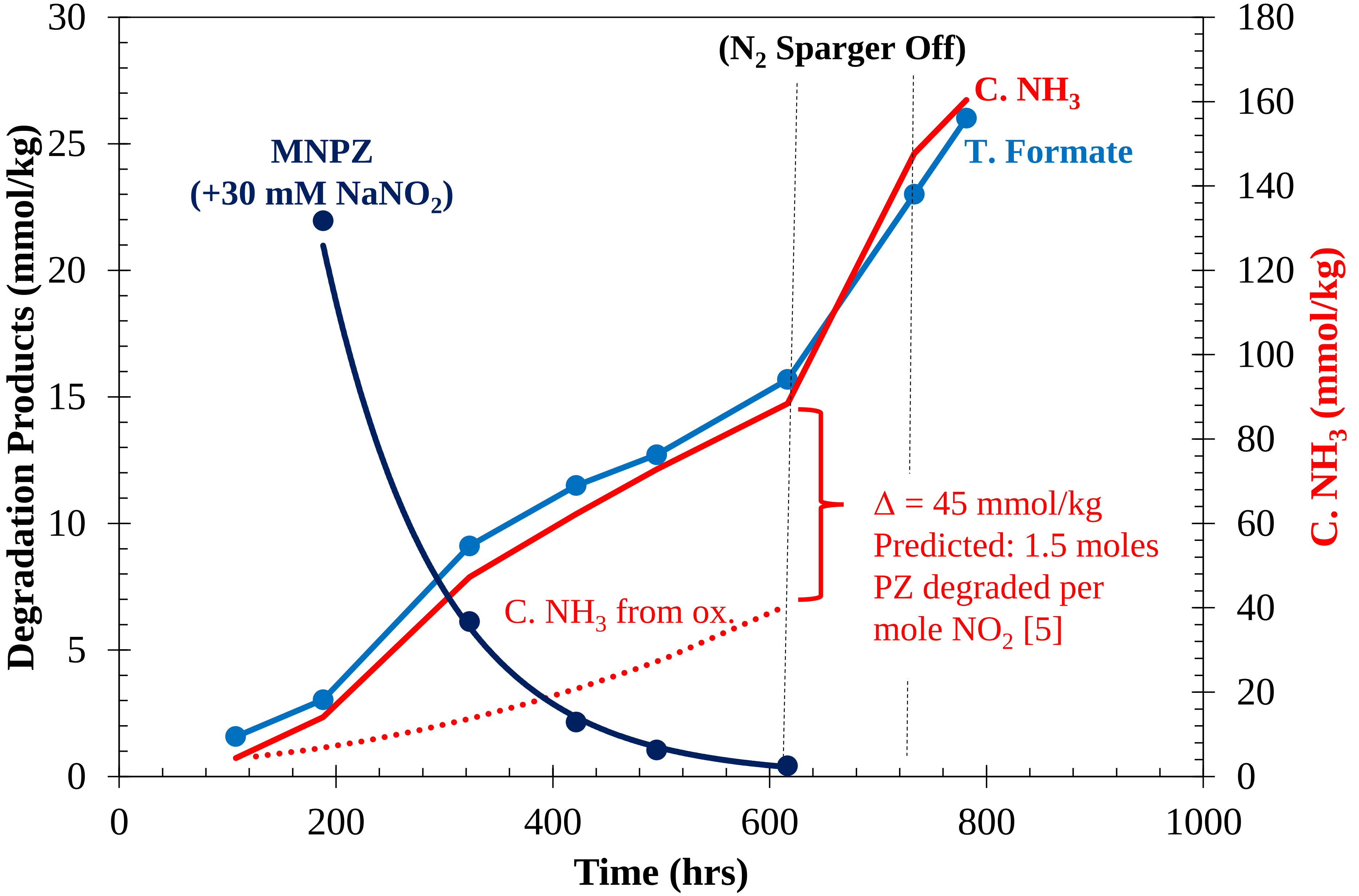
PZ → Intermediary products → Formate + NH_3



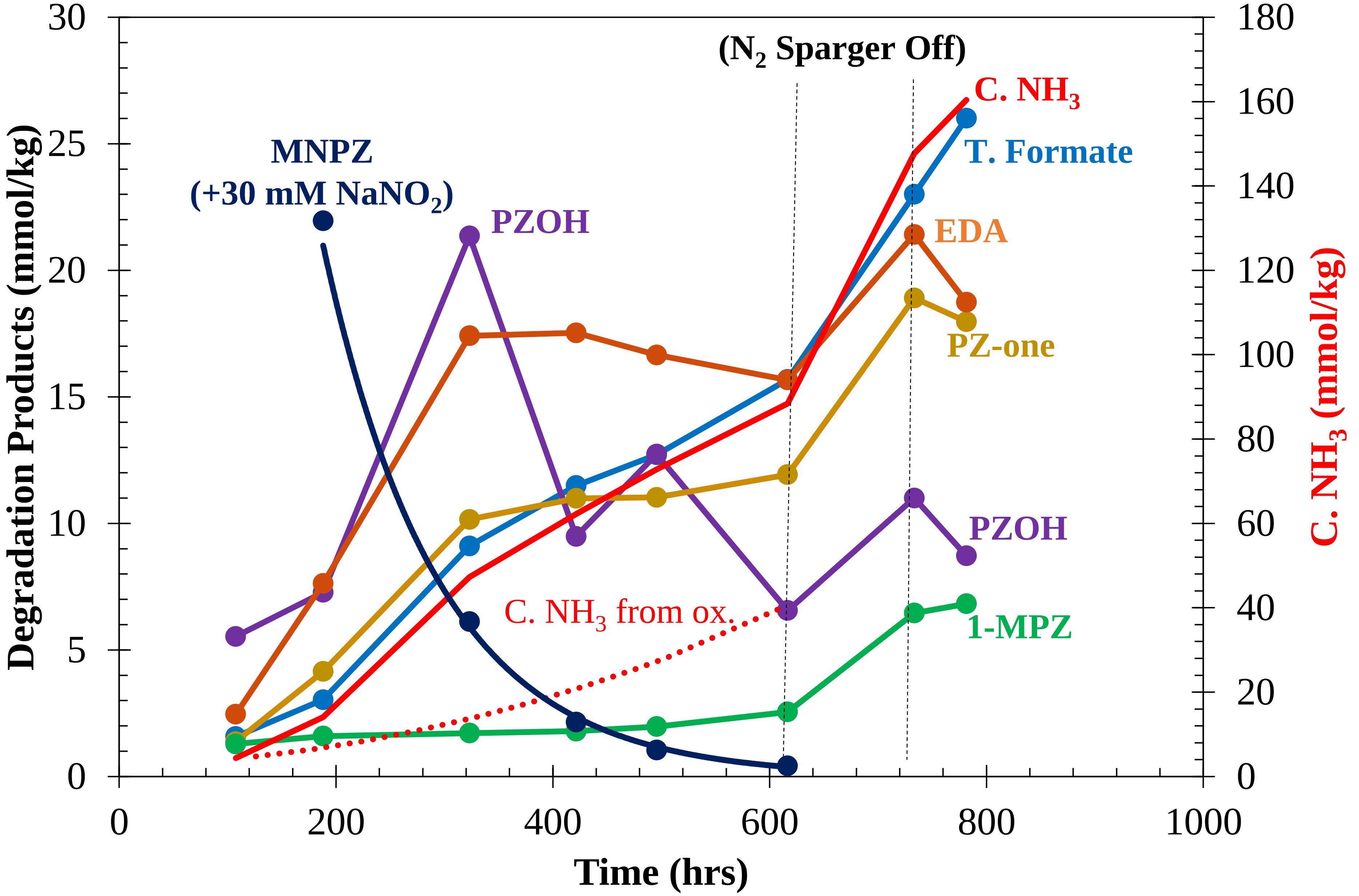
PZ oxidation in HTOR with continuous N_2 sparging (HTOR15) Ammonia emissions



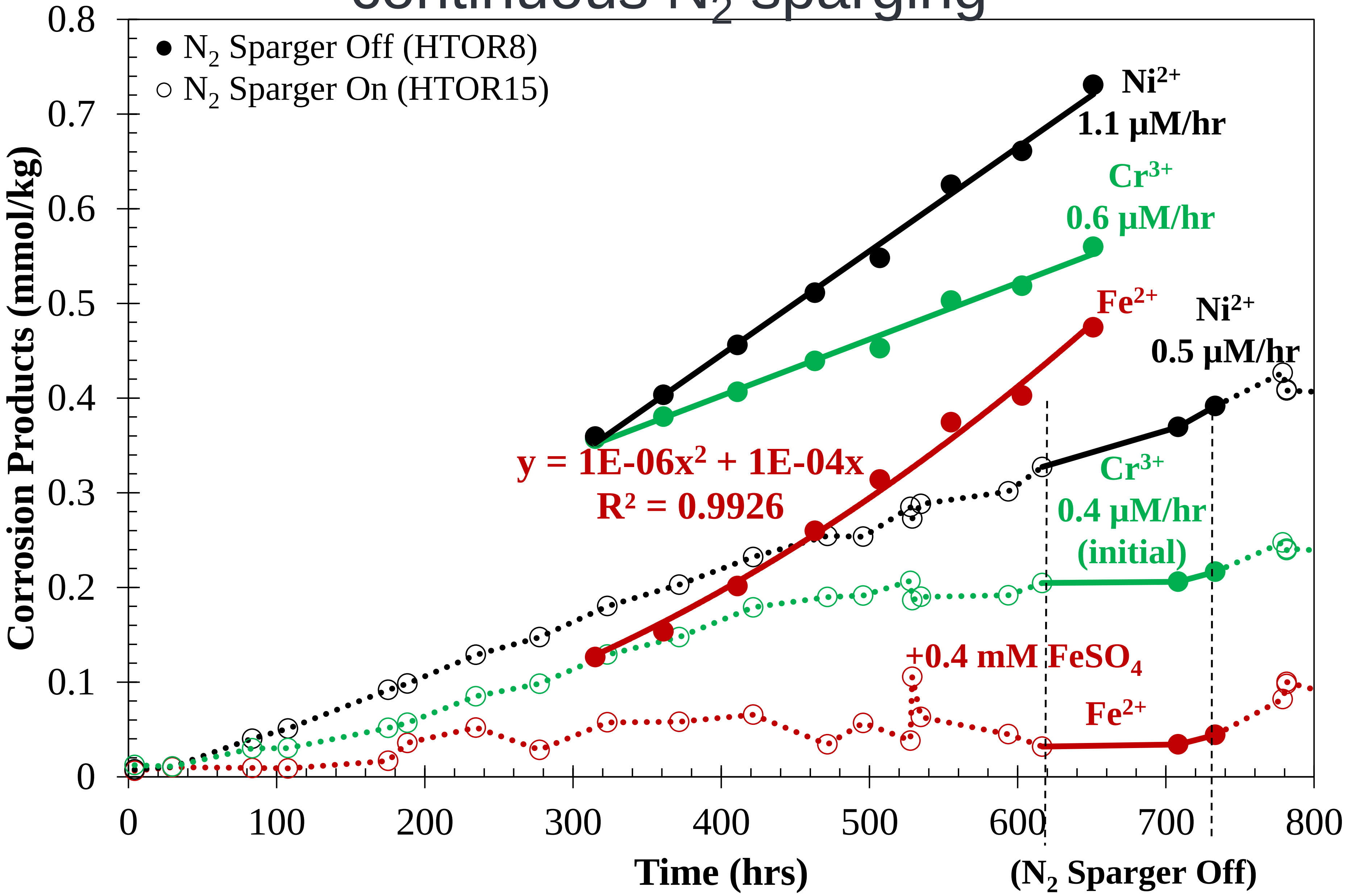
MNPZ decomposition → oxidation products



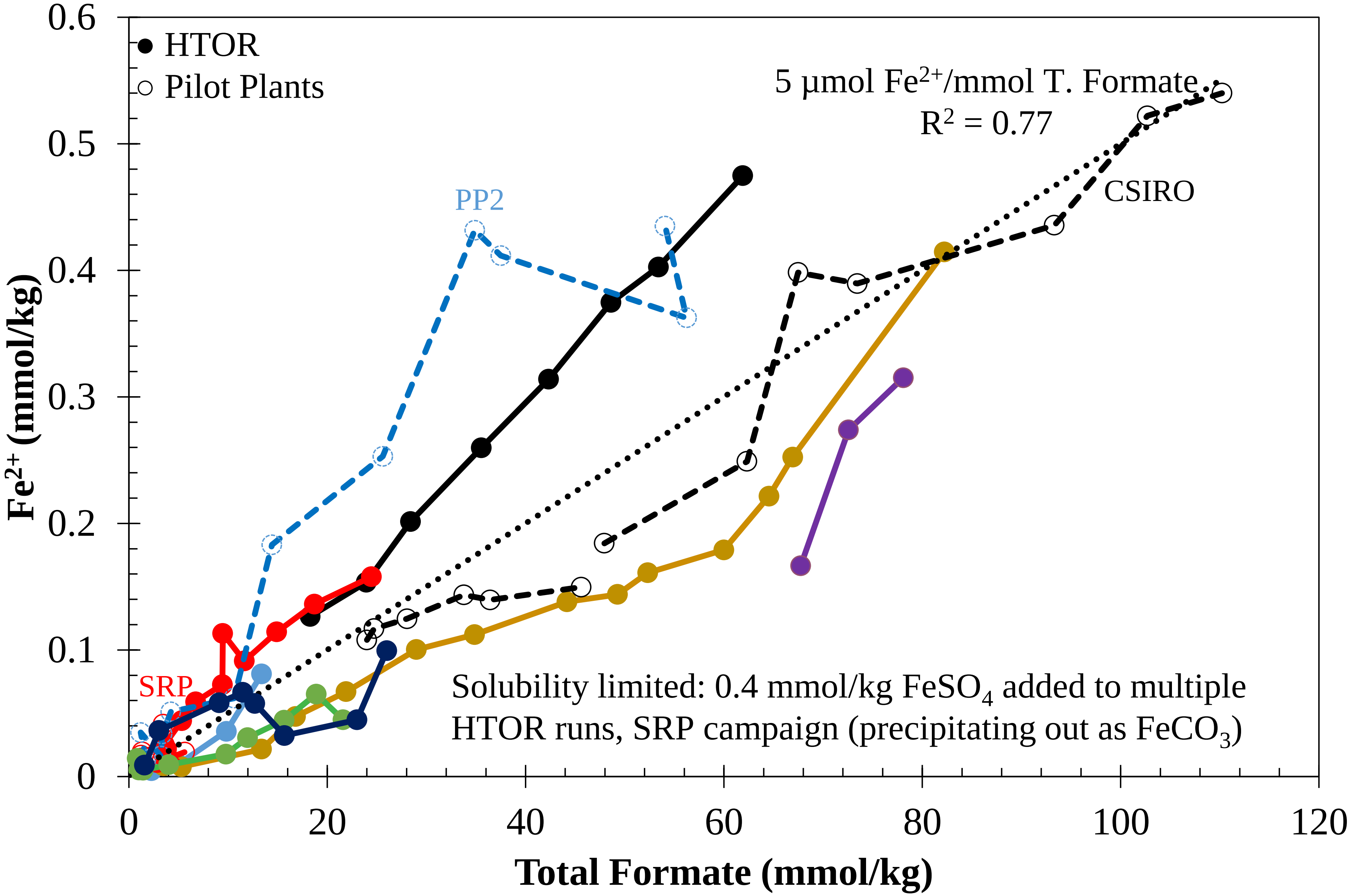
MNPZ decomposition → oxidation products



Iron solubility significantly reduced in clean solvent with continuous N_2 sparging



Iron solubility correlated to solvent degradation



Conclusions

- Oxidation of clean PZ in the HTOR reduced by 90% by N_2 sparging to remove dissolved oxygen
  - Degraded PZ continued to oxidize with N_2 sparging due to accumulation of nonvolatile oxidation carriers (Fe^{2+}, aldehydes, amides, etc.)
    - Solvent reclaiming to minimize accumulation recommended
- Ammonia production increases linearly over time as clean solvent accumulates intermediary degradation products and iron
- Nitrosamine degradation will result in oxidation product accumulation
  - 1.5 moles of ammonia produced per mole of NO_2 absorbed
  - NO_2 prescrubbing potentially critical to minimize degradation product accumulation
- Iron solubility in PZ correlated to cumulative solvent contamination
- Nickel, chromium, and manganese accumulation do not catalyze PZ oxidation

References

[1] Chi S, Rochelle GT. “Oxidative Degradation of Monoethanolamine.” *Ind Eng Chem Res*. 2002, 41(17), pp 4178-4186

[2] Voice AK. *Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing*. The University of Texas at Austin. Ph.D. Dissertation. 2013

[3] Strazisar BR, Anderson RR, White CM. “Degradation Pathways for Monoethanolamine in a CO_2 Capture Facility.” *Energy Fuels*. 2003;17(4):1034–1039

[4] Sexton A, Dombrowski K, Nielsen PT, Rochelle GT, Fisher K, Youngerman J, Chen E, Singh P, Davison J. “Evaluation of Reclaimer Sludge Disposal from Post-Combustion CO_2 Capture.” *Energy Procedia*. 2014, 63:926-939.

[5] Fine NA. *Nitrosamine Management in Aqueous Amines for Post-Combustion Carbon Capture*. The University of Texas at Austin. Ph.D. Dissertation. 2015.

[6] Nielsen PT, Le L, Rochelle GT. “Piperazine degradation in pilot plants.” *Energy Proc*. 2013;37:1912–1923

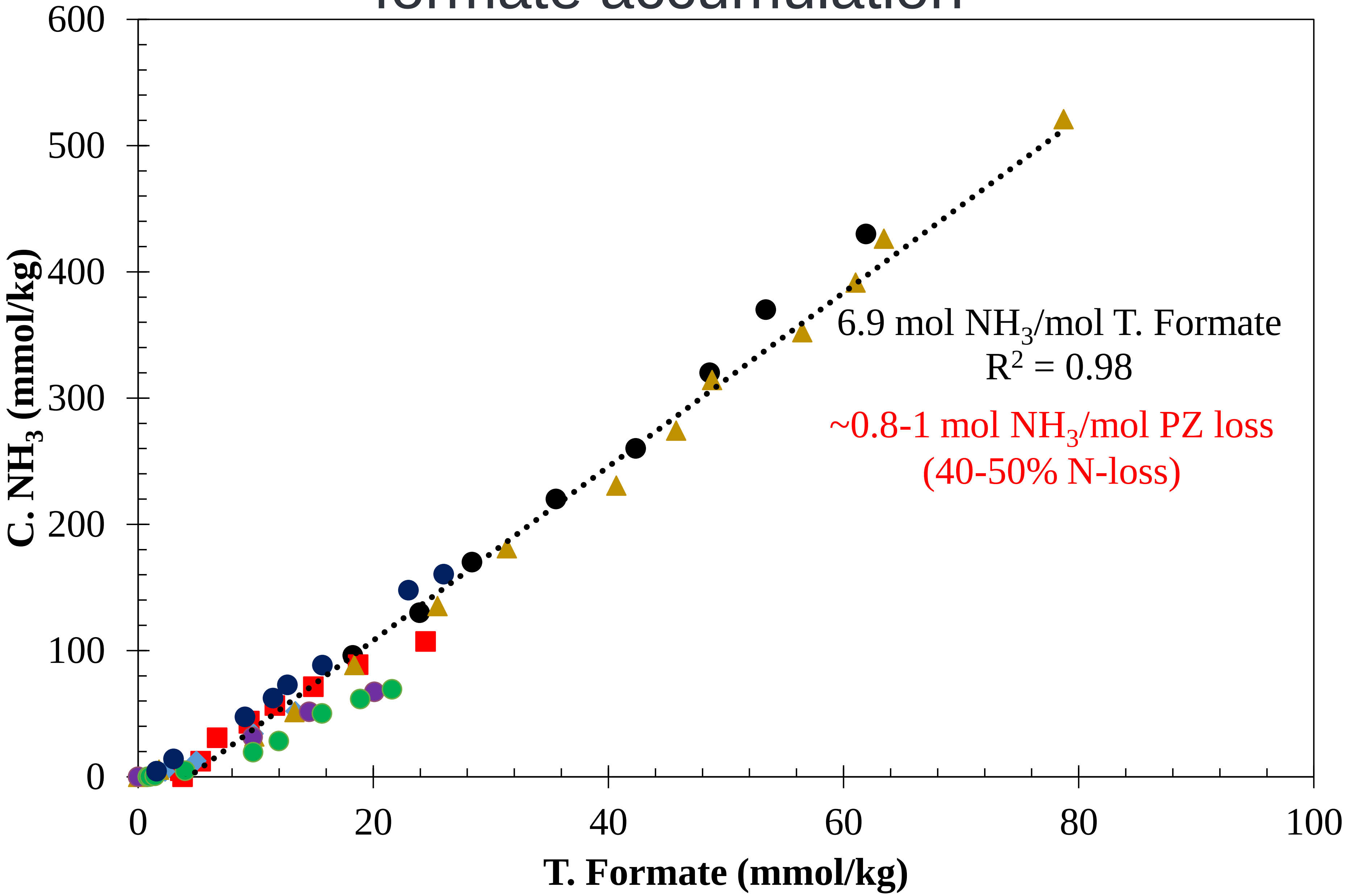
[7] Cousins A, Nielsen PT, Huang S, Cottrell A, Chen E, Rochelle GT, Feron PHM. “Pilot-scale evaluation of concentrated piperazine for CO_2 capture at an Australian coal-fired power station: duration experiments.” *Greenhouse Gas Sci Technol*. 2015;5:363-373.

[8] Zheng L, Landon J, Zou W, Liu K. “Corrosion Benefits of Piperazine As an Alternative CO2 Capture Solvent.” *Ind Eng Chem Res*. 2014, 53(29):11740-11746

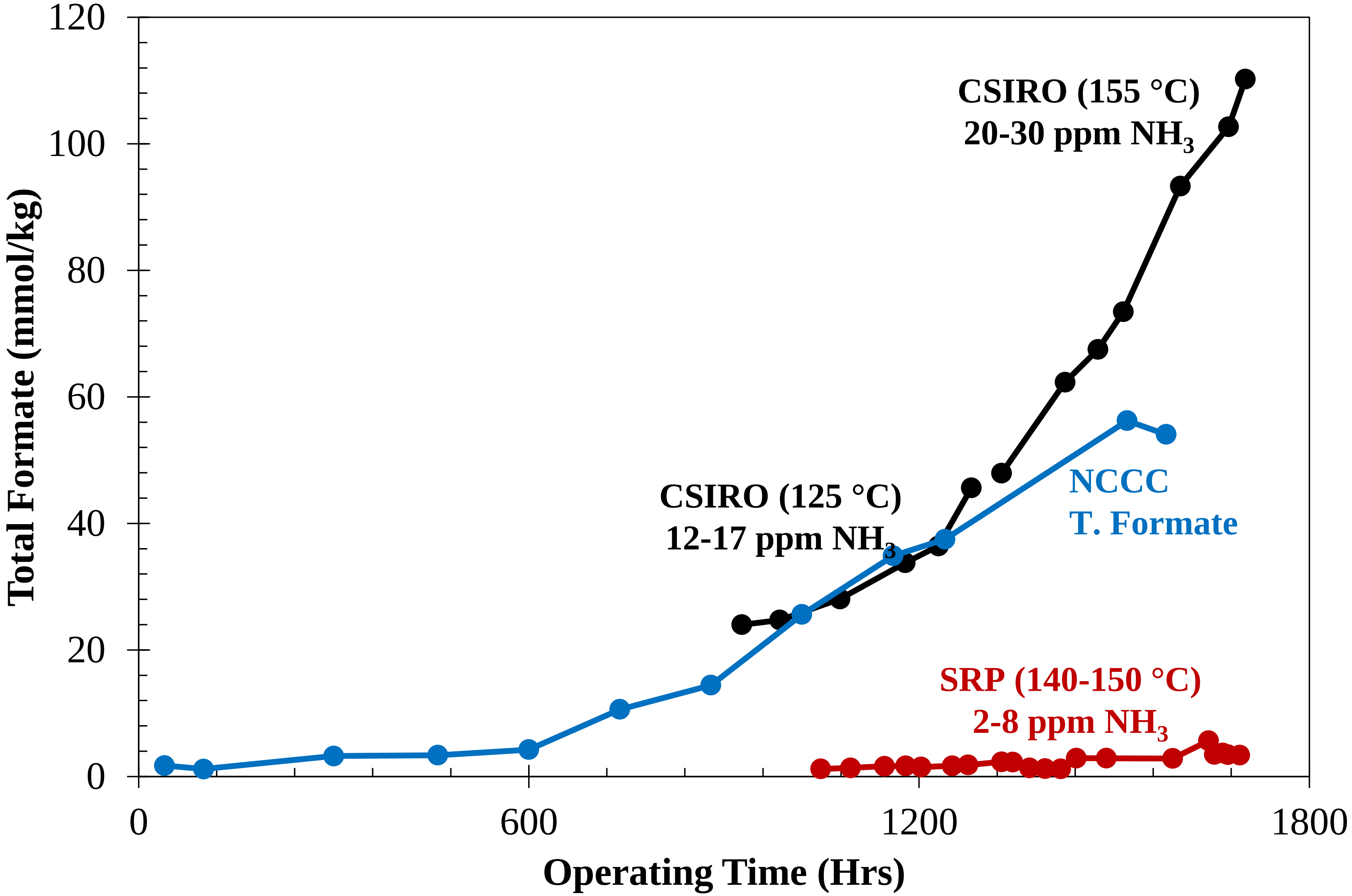
Questions?

TxCMP

Cumulative NH_3 emissions strongly correlated with total formate accumulation

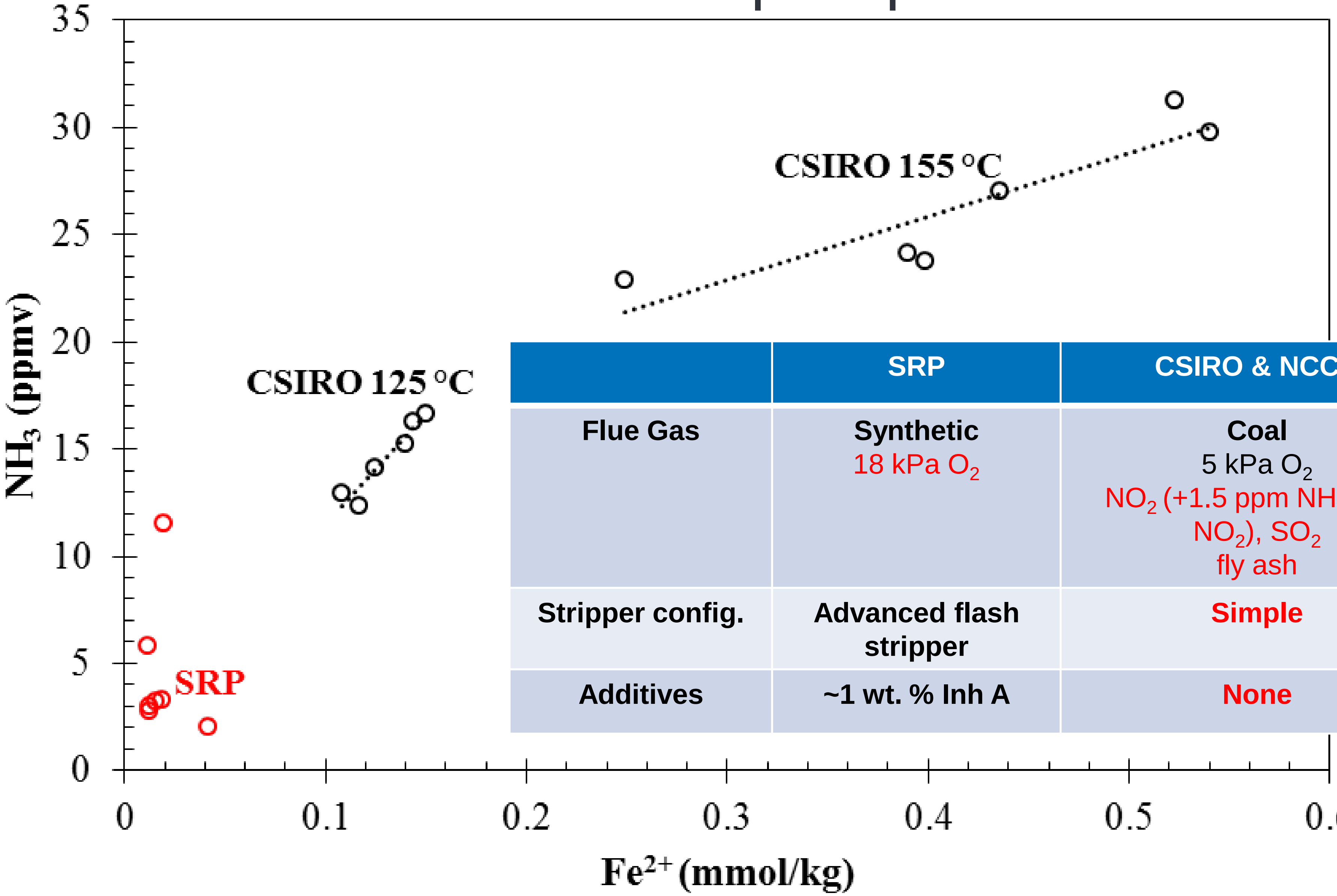


Pilot Plant Campaigns with PZ



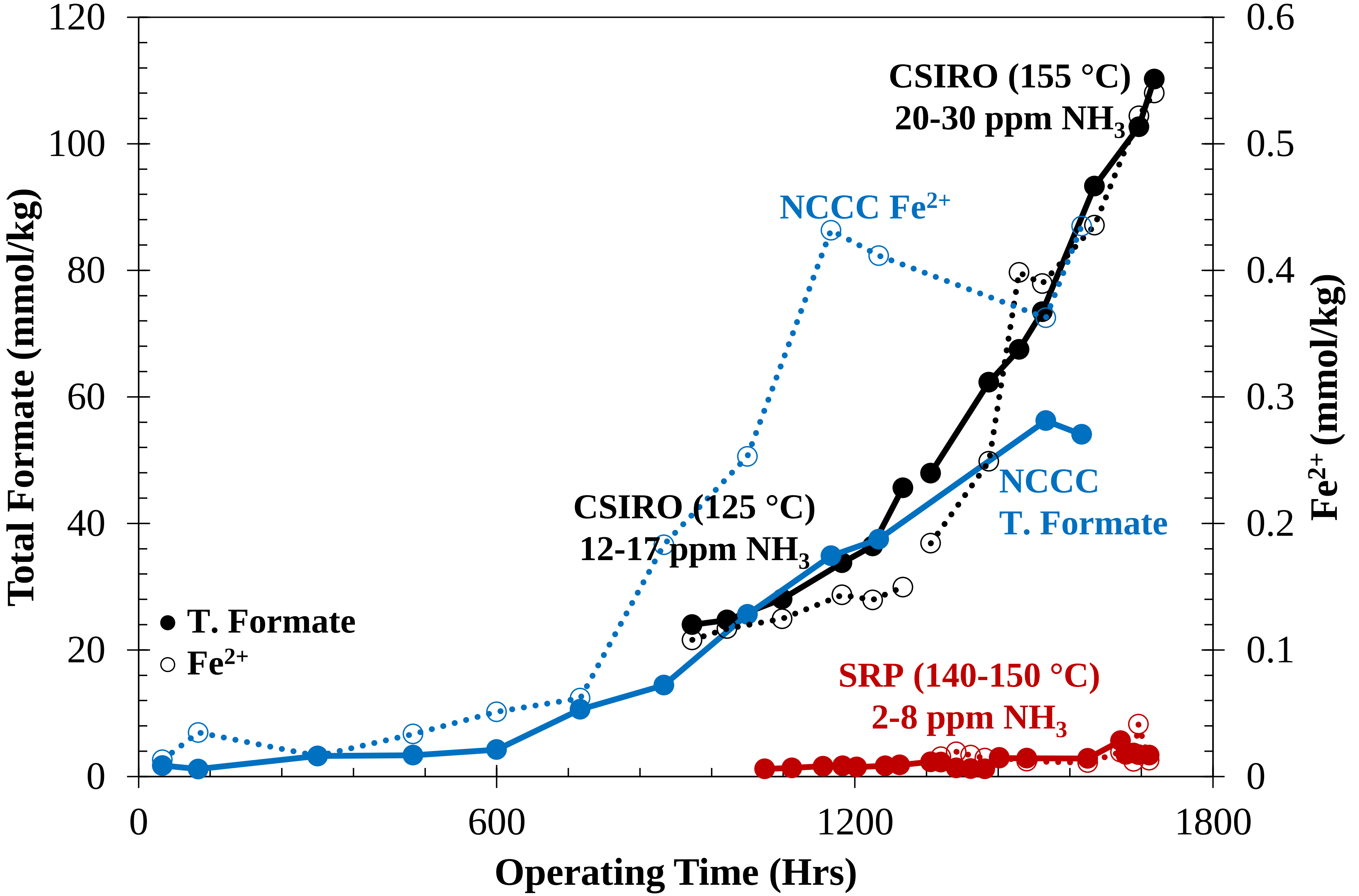
[6; 7]

Ammonia rate is correlated with dissolved iron accumulation in pilot plants



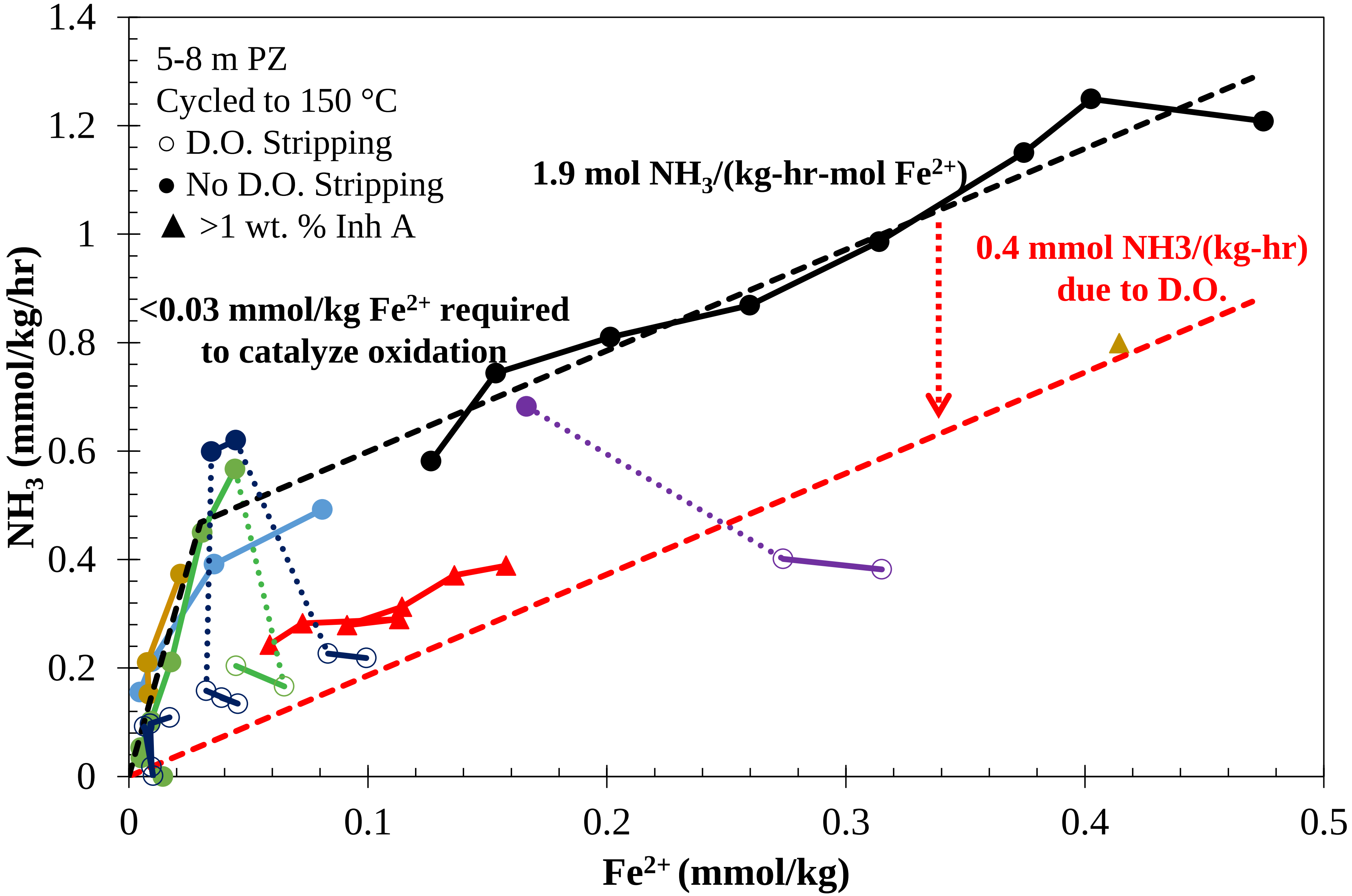
	SRP	CSIRO & NCCC
Flue Gas	**Synthetic** 18 kPa O_2	**Coal** 5 kPa O_2 NO_2 (+1.5 ppm NH_3/ppm NO_2), SO_2 fly ash
Stripper config.	**Advanced flash stripper**	**Simple**
Additives	**~1 wt. % Inh A**	**None**

Pilot Plant Campaigns with PZ

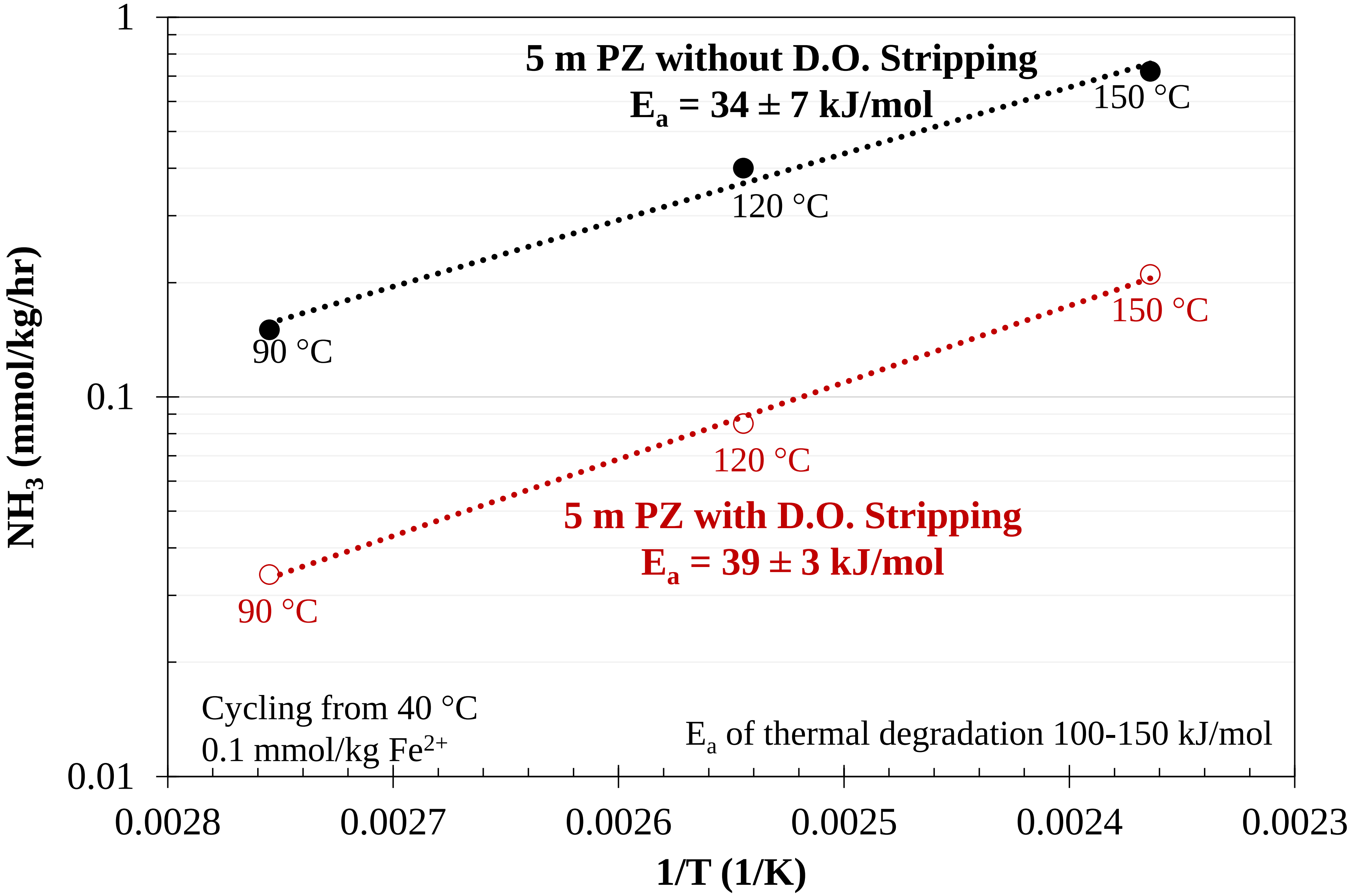


[6; 7]

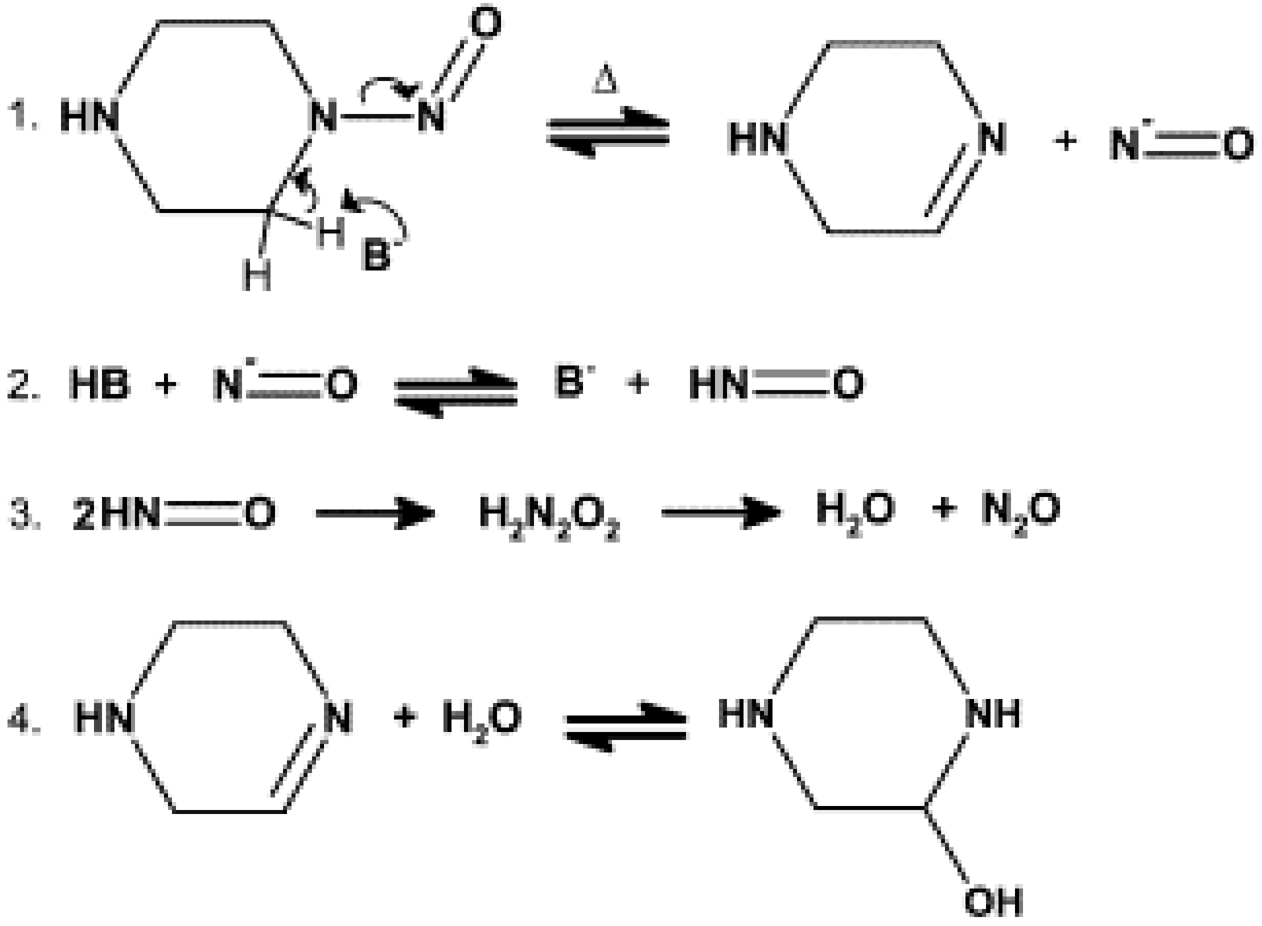
NH_3 vs Fe^{2+} in HTOR



Effect of stripper temperature

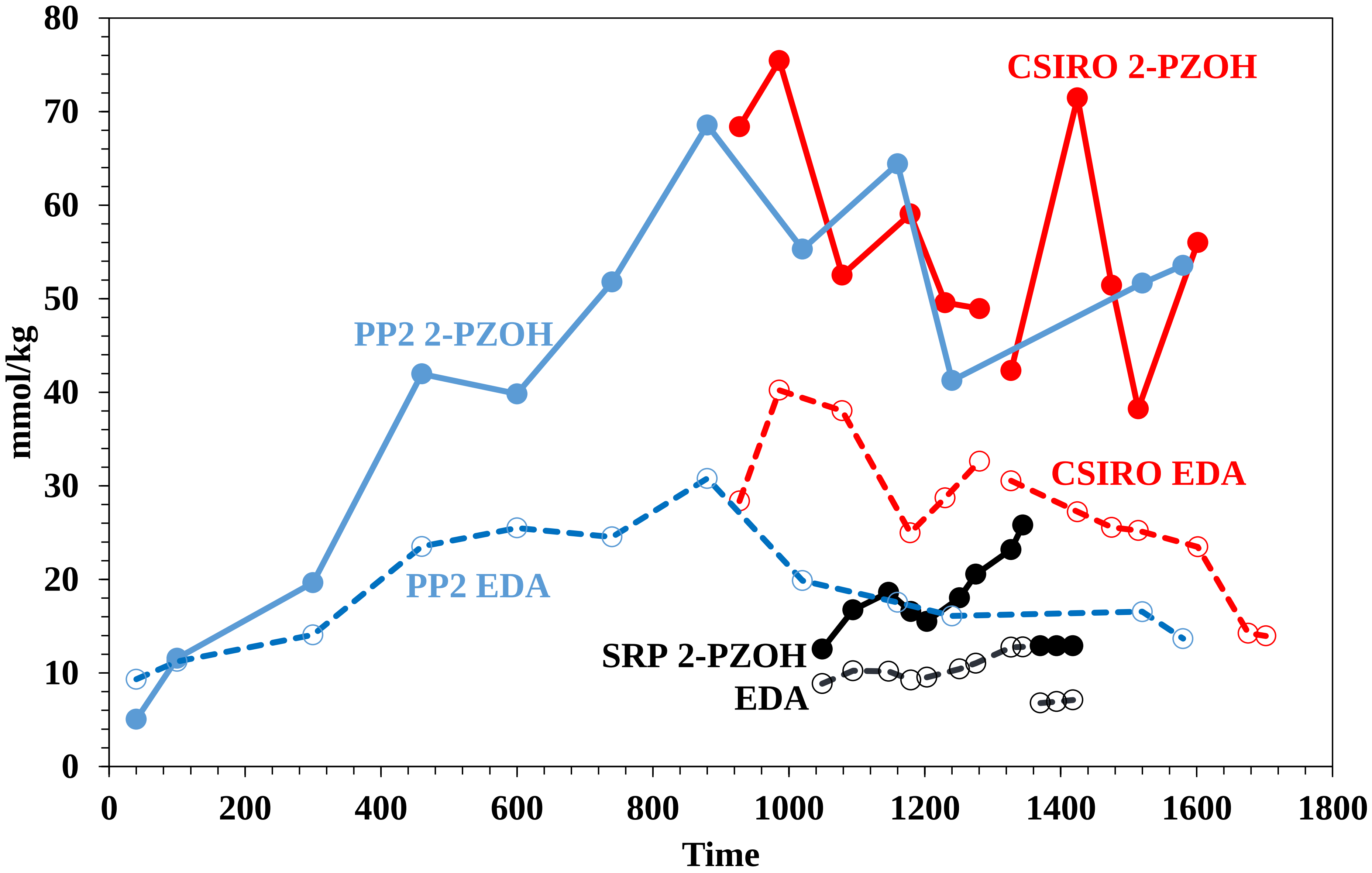


MNPZ Degradation

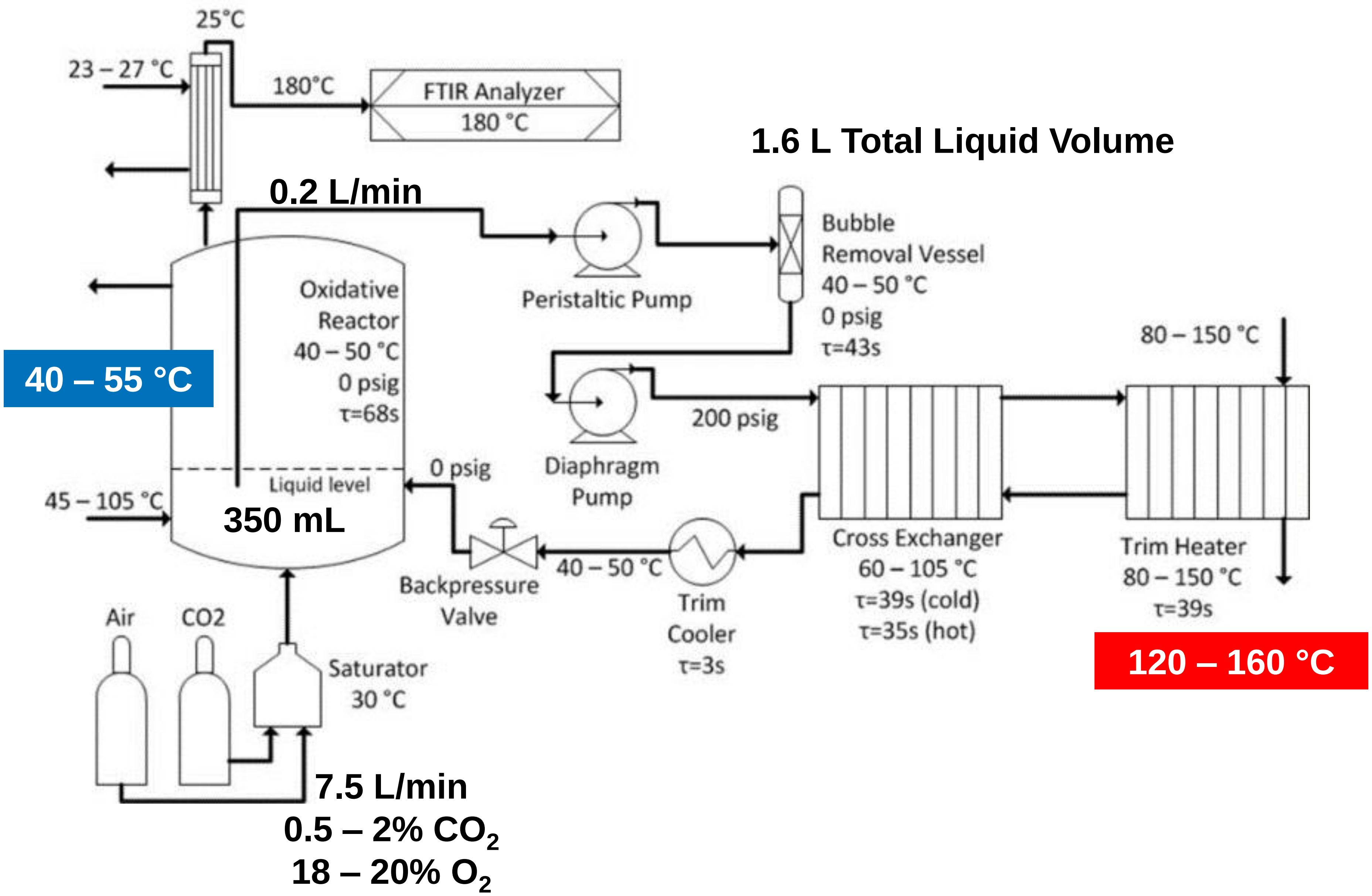


Fine, 2014

2-PZOH and EDA in pilot plants



HTOR Apparatus



Inhibitors in HTOR (MEA oxidation)

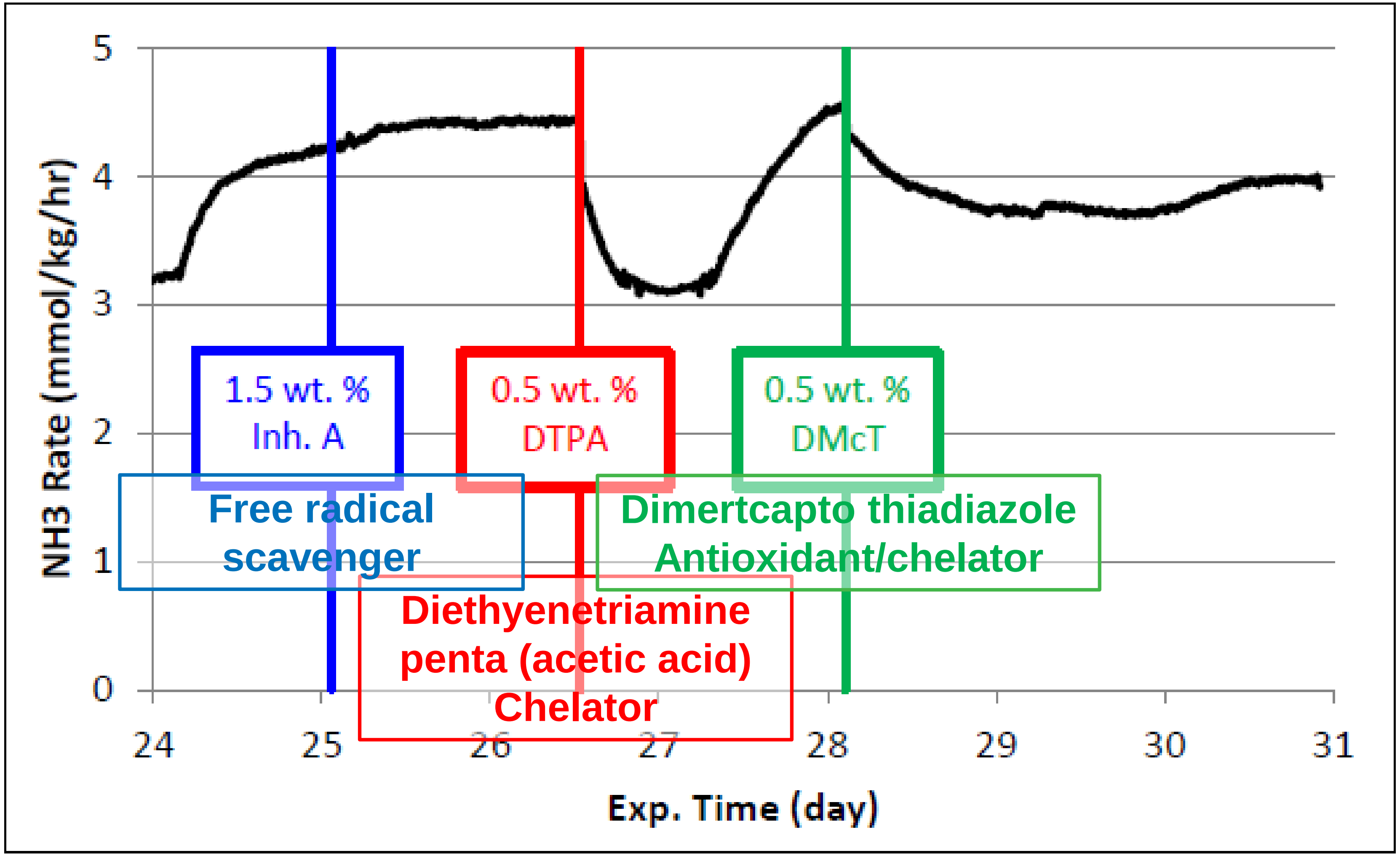
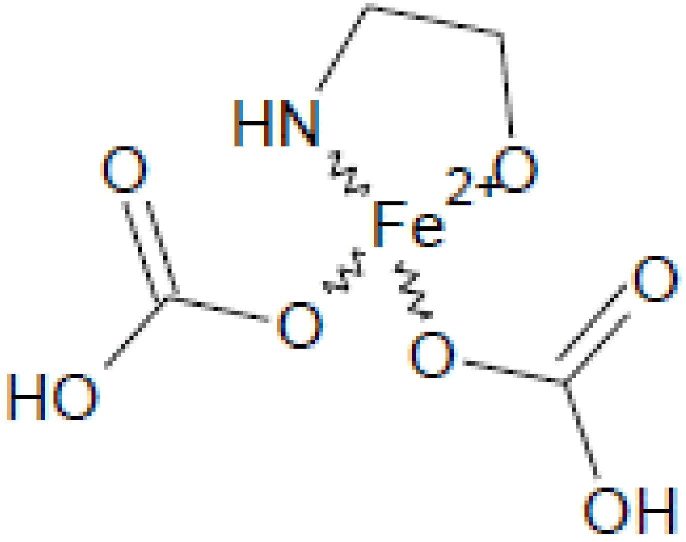


Figure 8.13: Effect of inhibitors of ammonia production from 7 m MEA oxidation in the HTCS with 2% CO_2 in air cycling from 55 to 120 °C. Metals added (mM): 0.4 Fe^{2+}, 0.1 Mn^{2+}, 0.1 Ni^{2+}, 0.05 Cr^{3+}

Voice, 2014

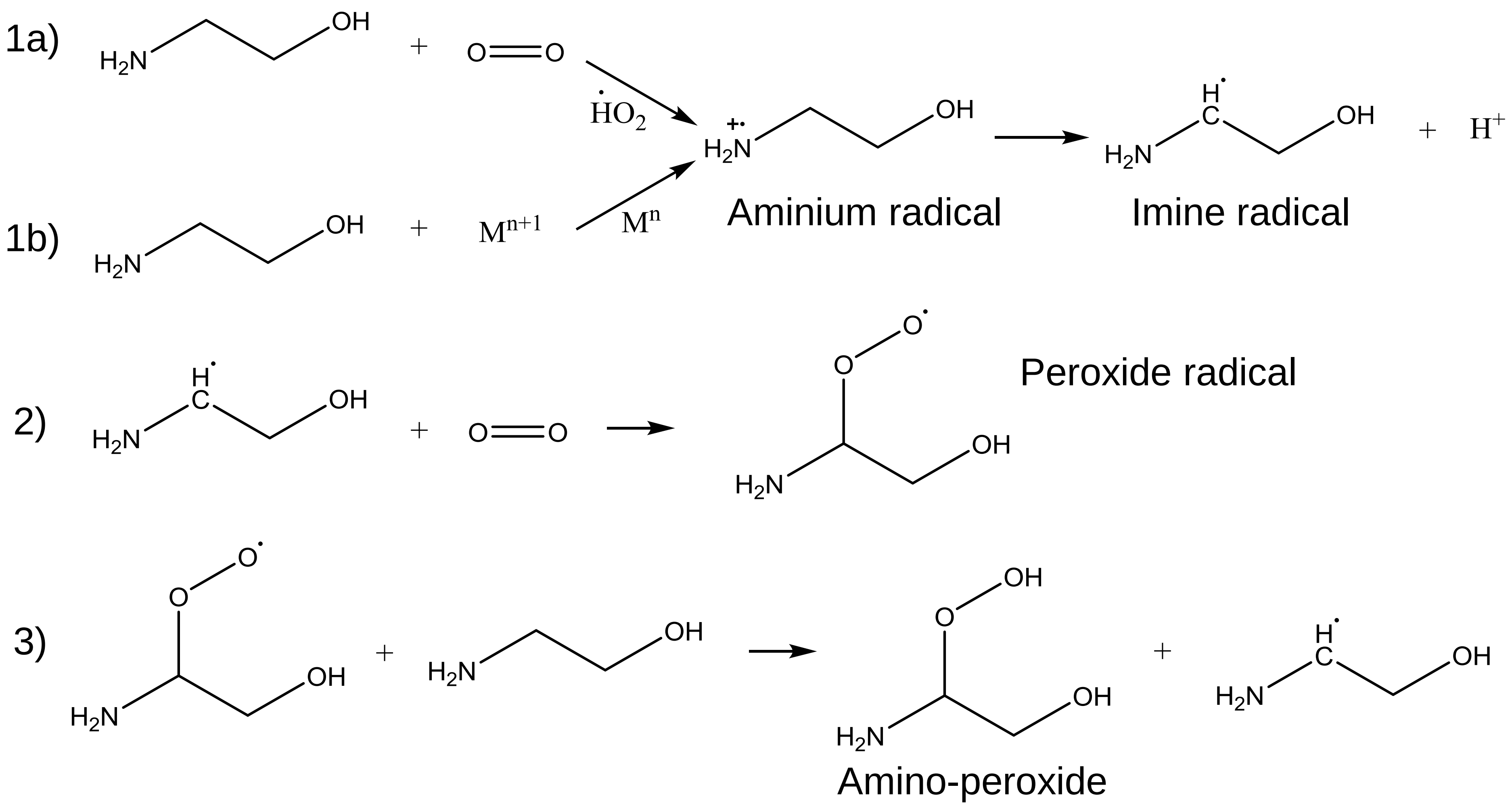
Iron-MEA Complex



PZ does not form complex?

Voice, 2014

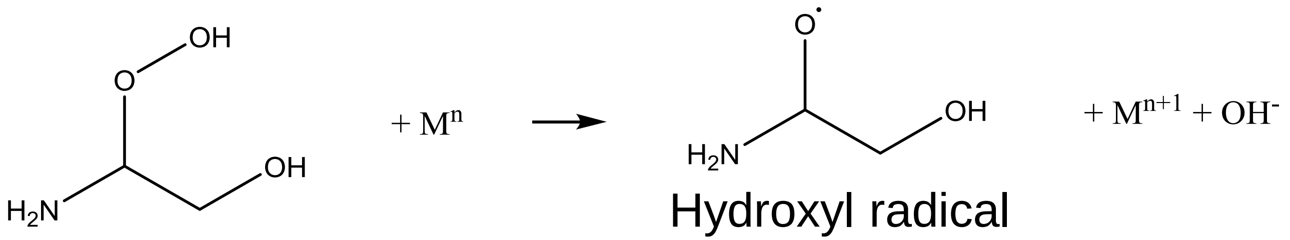
Oxidation: Electron abstraction



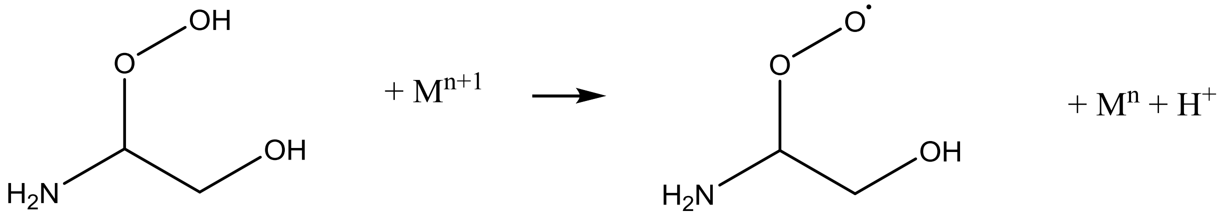
Chi and Rochelle, 2002

Oxidation: Electron abstraction

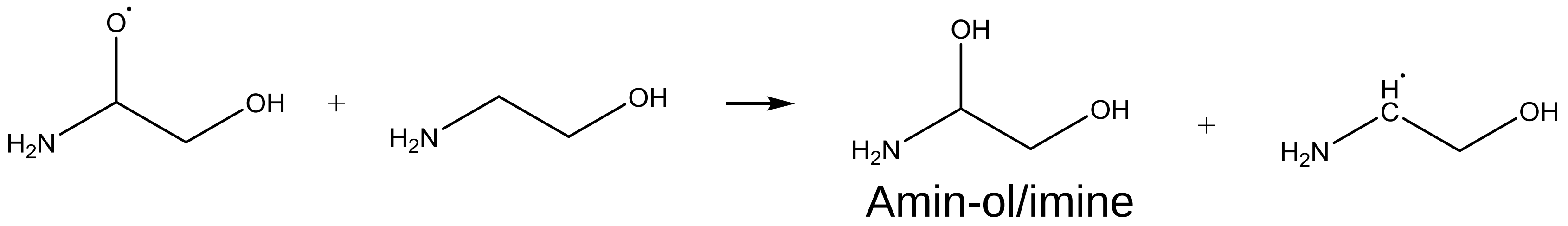
4a)



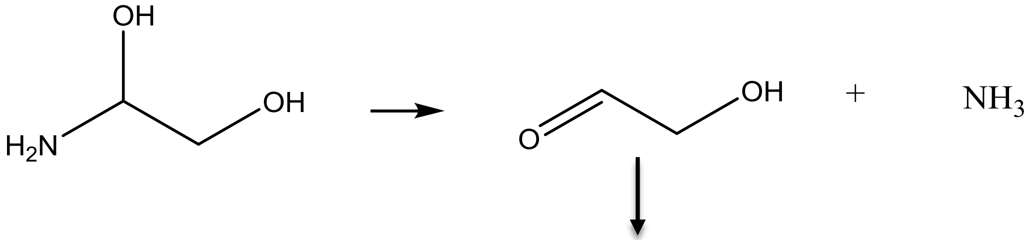
4b)



5)



6)

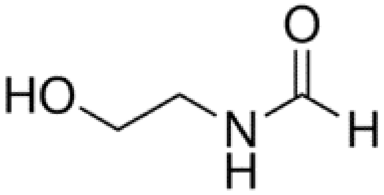


Best markers for oxidation: NH_3, formate

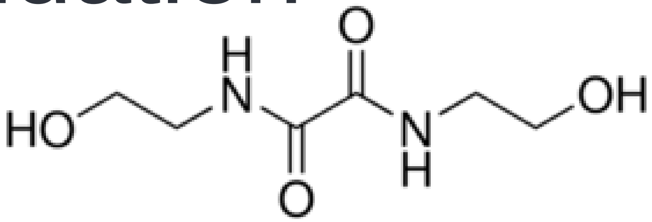
Aldehydes, Heat stable salts (formate, oxalate, acetate, etc.), CO_2

Chi and Rochelle, 2002

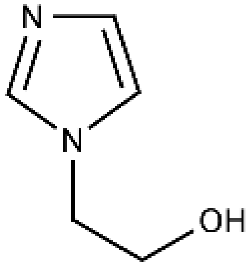
Secondary products of MEA Oxidation



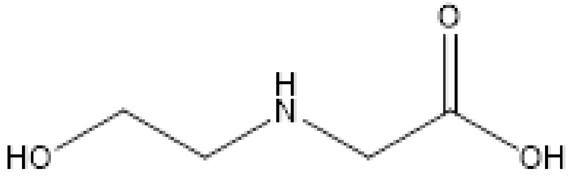
HEF



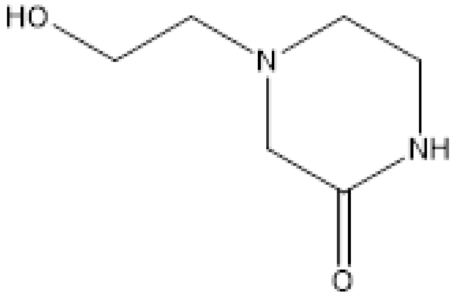
BHEOX



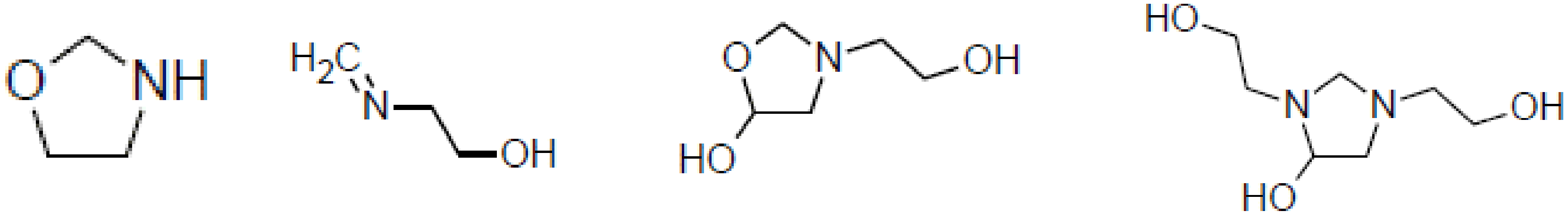
HEI



HEGly
(will form stable NNO)



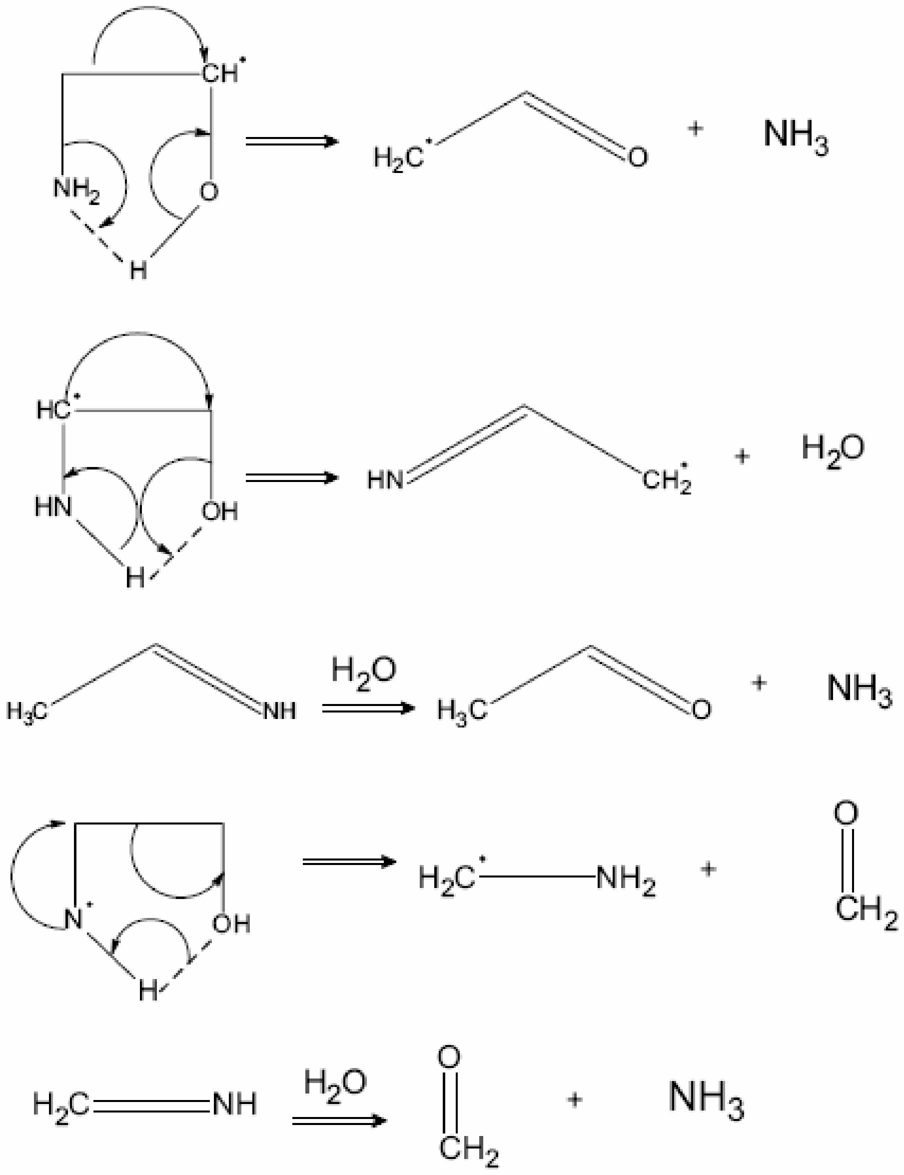
HEPO



Cyclic aldehydes and imines

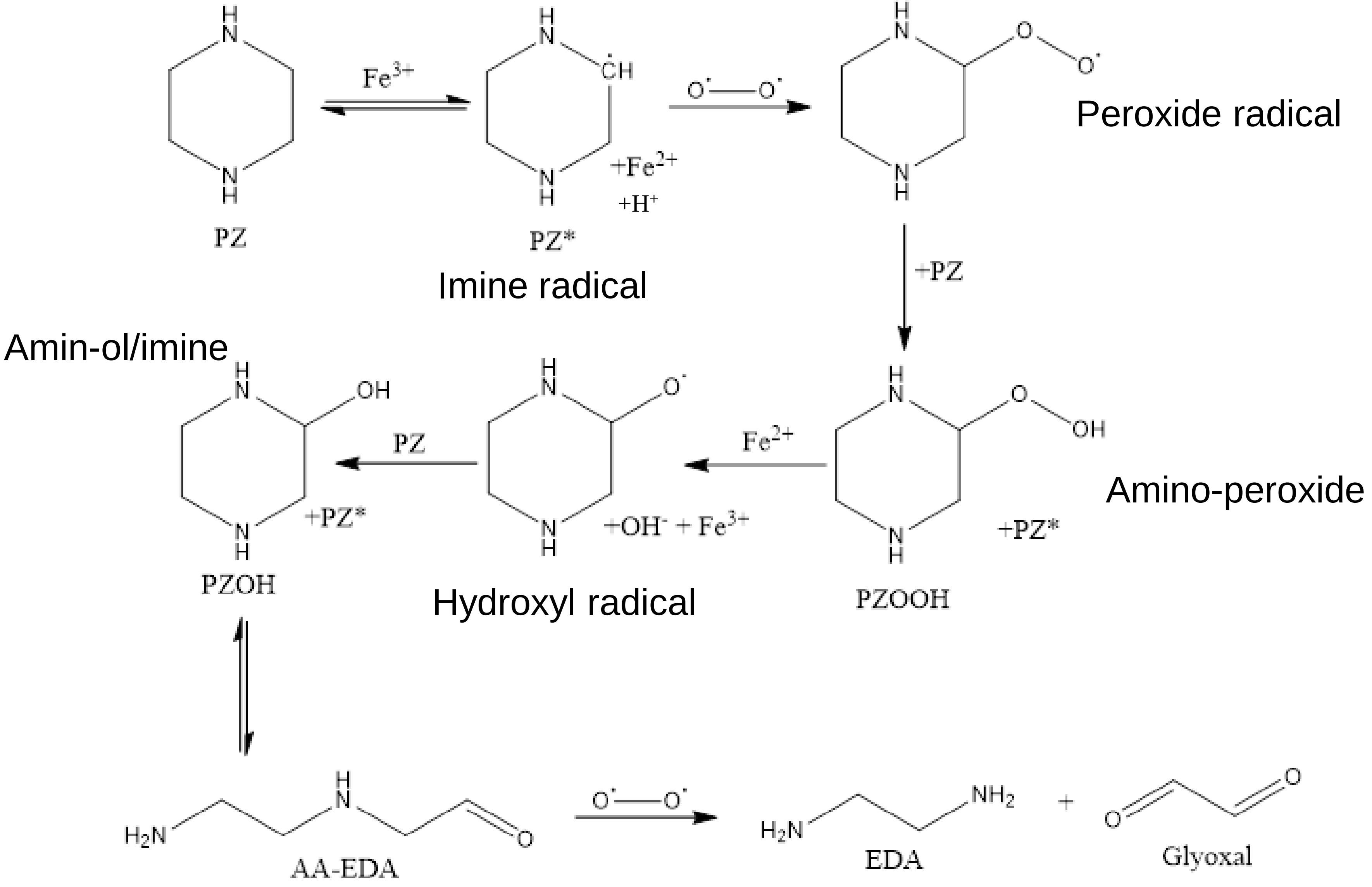
Voice, 2014; LePaumier 2009; da Silva, 2012

Oxidation: Hydrogen abstraction

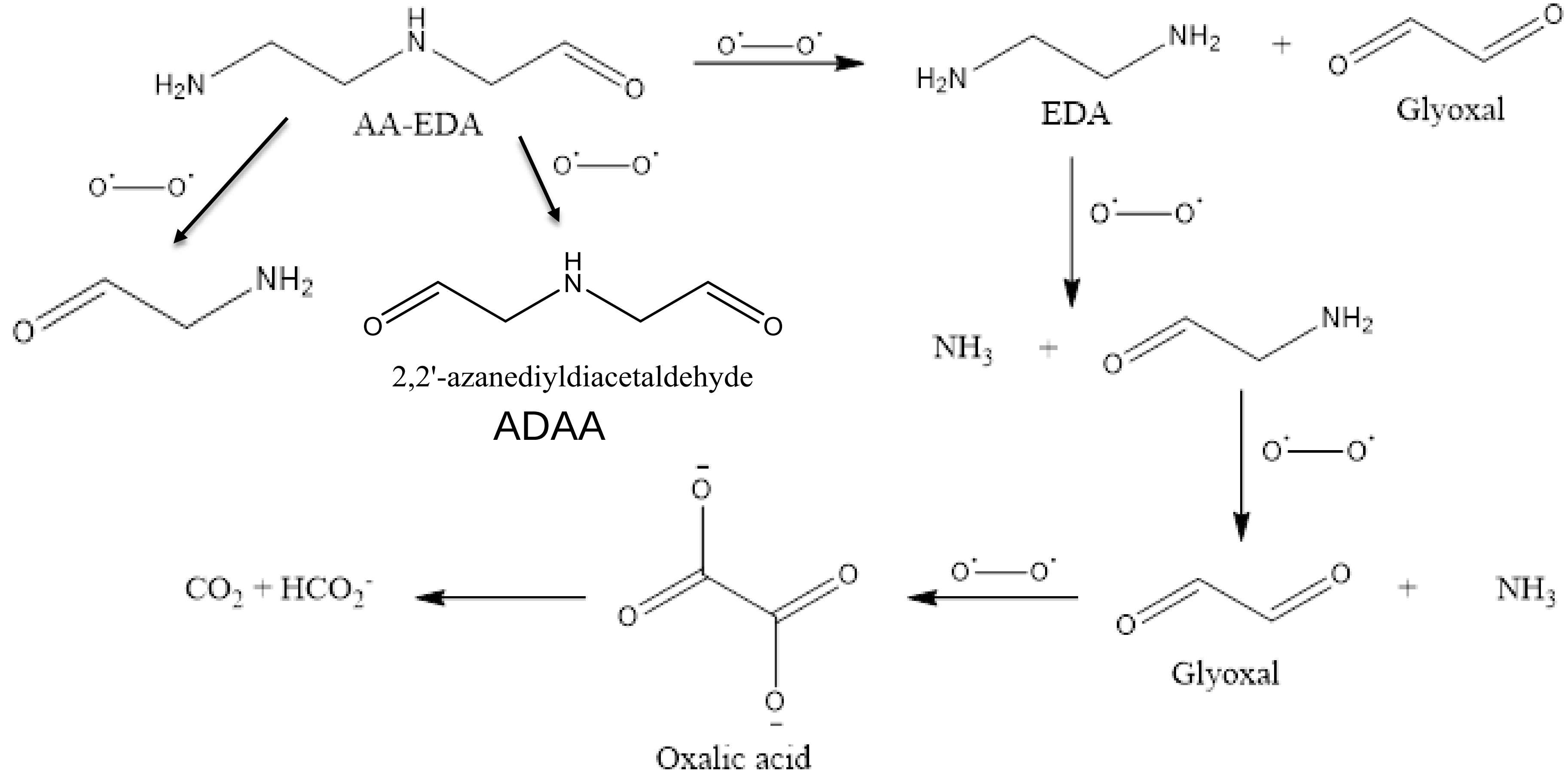


Sexton, 2008

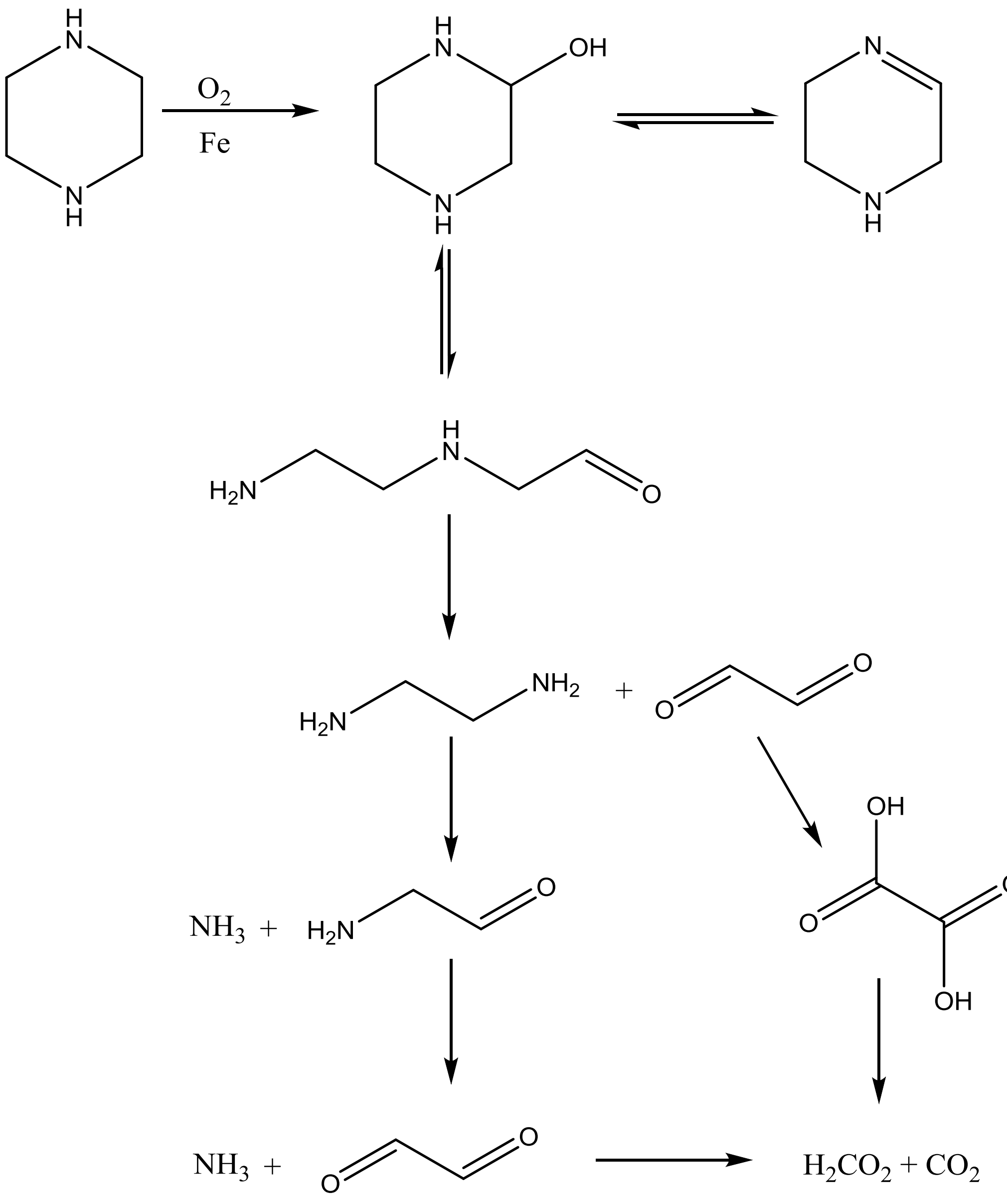
PZ Oxidation



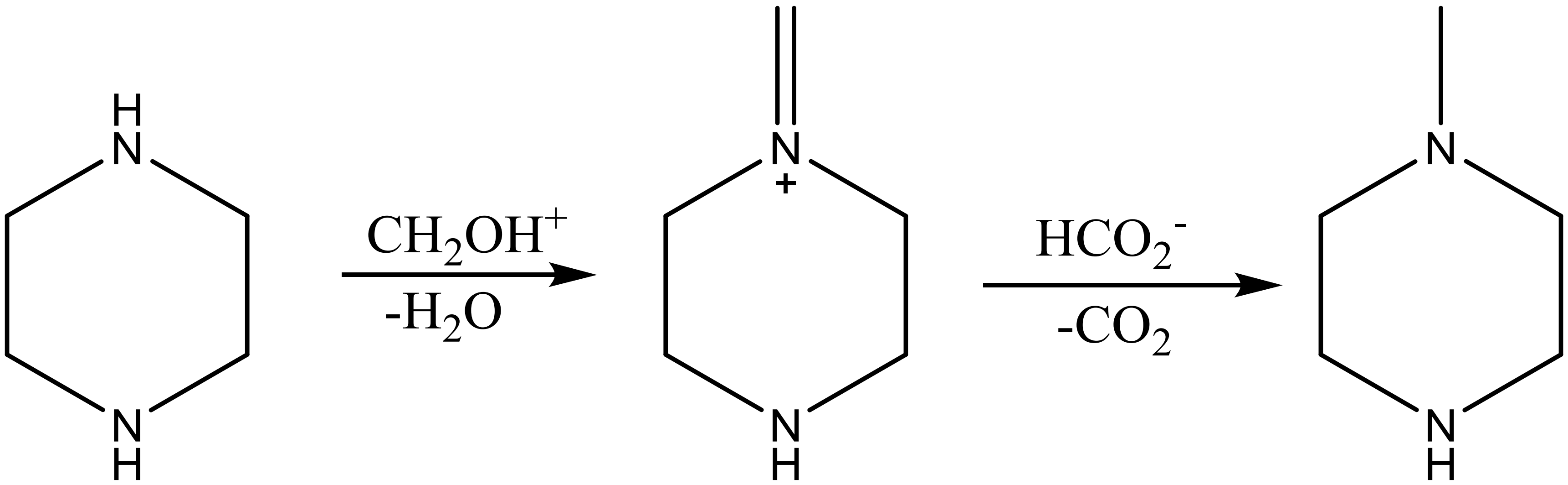
PZ Oxidation



PZ Oxidation



Formation of 1-MPZ: Eschweiler-Clarke



Amine reacts (S_N2) with protonated formaldehyde to form iminium salt, reduced to methylamine in presence of formate. Formate oxidized to CO_2

Requires oxidative environment to produce aldehyde, reducing environment to make methyl-PZ. Only forms in cyclic systems. In LGF: PZ + formaldehyde produces polymer foam

1-MPZ is significantly more volatile than PZ, may represent an emissions concern. MPZ:PZ 40x greater in water wash samples

Viscosity increase due to HSS accumulation