# MEA oxidation in $CO_2$ Capture

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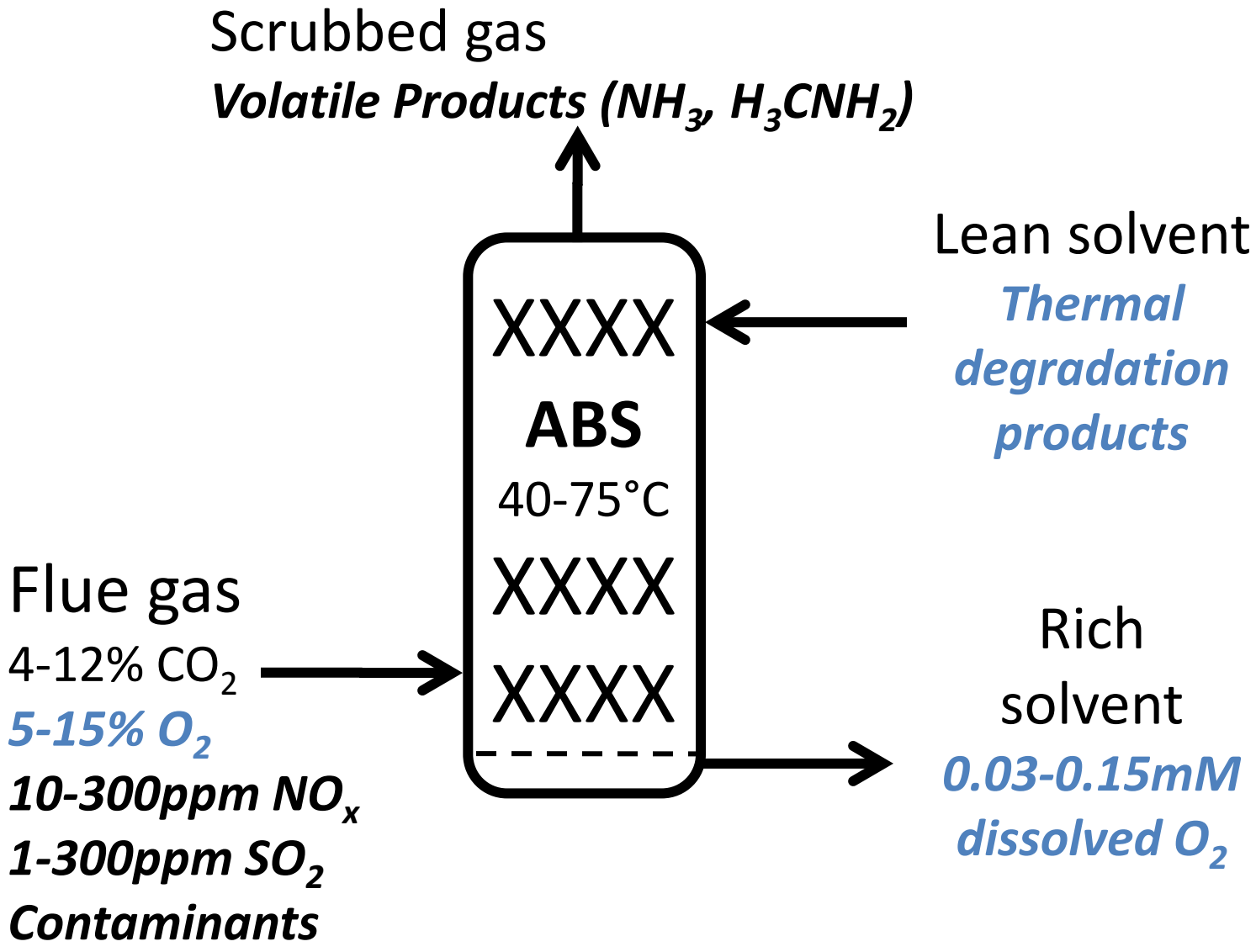
*Luminant Carbon Management Program*

# Factors Impacting Oxidation in $CO_2$ Capture



Low Gas Flow

0.1LPM

98 kPa $O_2$

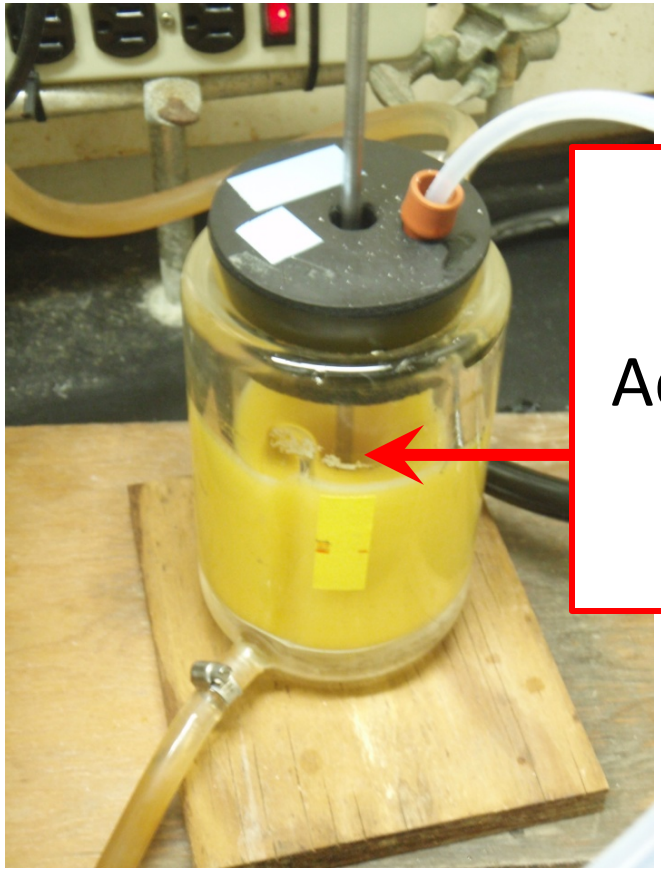
Liquid samples

High Gas Flow

7.5 LPM

21kPa $O_2$

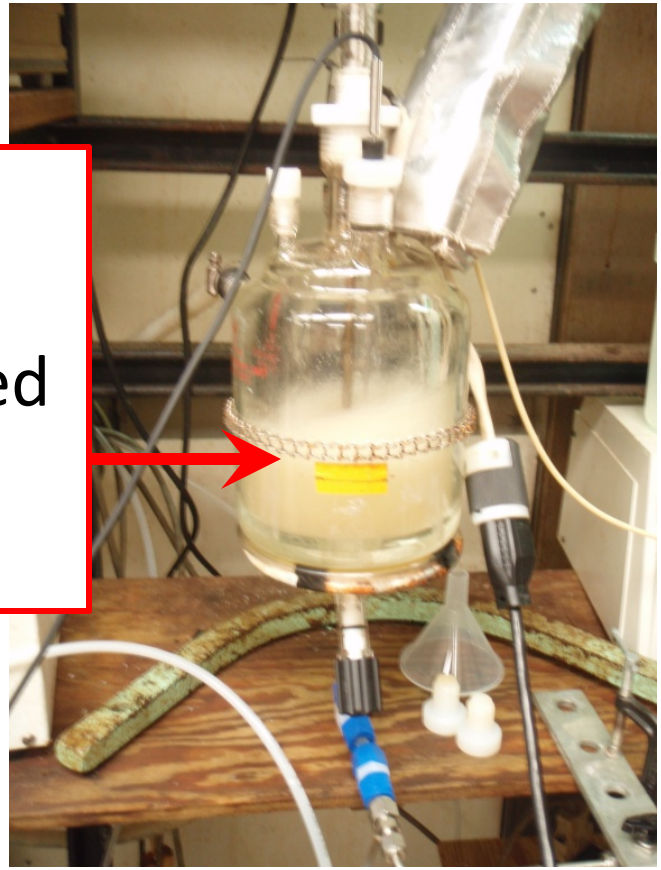
FTIR analysis ($NH_3$)



350mL

2kPa $CO_2$

Add dissolved metals & inhibitors

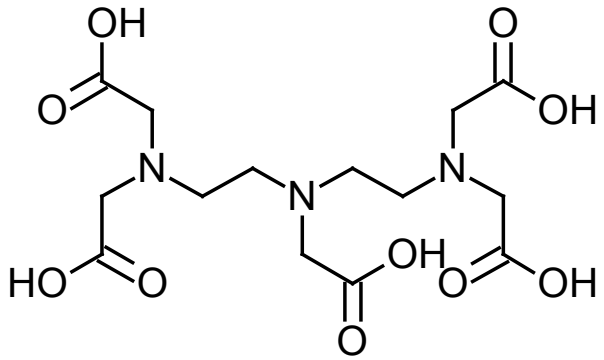


Semi-batch oxidation reactors

# Vapor Composition: Hot-Gas FTIR analyzer

# Identification of Catalysts and Inhibitors

- Tested 13 transition metals
  - Mn ≥ Cu >> Fe >> Cr
  - Vanadium was a mild inhibitor
  - No significant effect: Ti, Mo, Co, Ni, Sn, Se, Ce, Zn
- Tested >100 organic additives as inhibitors

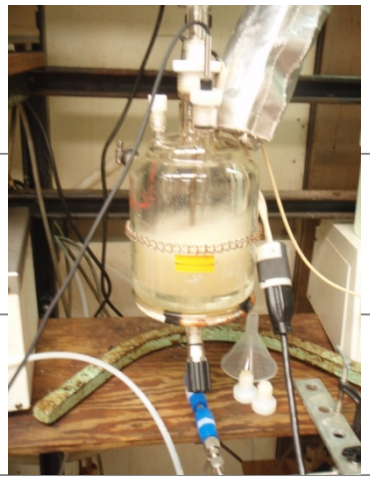



**Best inhibitor identified = Diethylene triamine pentaacetic acid 0.1 – 1%wt**

- Temperature effects, rates and products

# Temperature Dependence of $NH_3$ Production

9 m pilot plant MEA, 98 kPa air, 2kPa $CO_2$, 0.5mM Fe



69.6 C

63.4 C

55.9 C

NH3 Rate (mmol/kg/hr)

0 1 2 3 4 5 6

0 5 10 15 20 25 30

Time (hrs)

# Temperature Dependence

9 m pilot plant MEA, LGF, 98 kPa $O_2$, 2kPa $CO_2$

T = 55 C

$r_0$ = 24.8 mmol/kg/hr

T = 70 C

$r_0$ = 64.3 mmol/kg/hr

MEA Conc. (mmol/kg)

6000
5000
4000
3000
2000
1000
0

0
5
10
15
20

Exp. Time (days)

# Rates Summary

9 m pilot plant MEA, 2kPa $CO_2$

MEA loss ($r_0$)
Low gas, 98 kPa $O_2$

**$E_A$=55kJ/mol**

**$E_A$=57kJ/mol**

$NH_3$ rate
HG, 21 kPa $O_2$

100
10
1

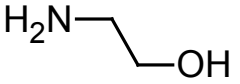
**Rate (mmol/kg/hr)**

56 C
63 C
70 C

Temperature (1/K)

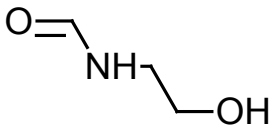
# Products and Analytical Methods

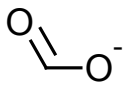
- Amines: cation chromatography

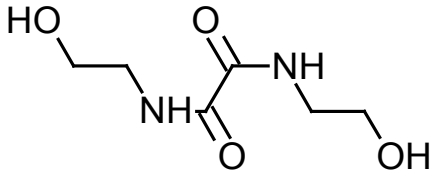


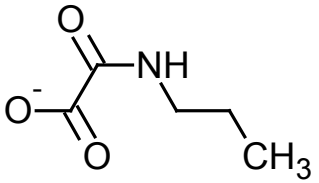


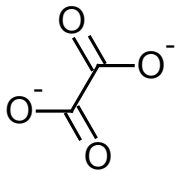
- Anions and amides (formate, etc.): anion chromatography



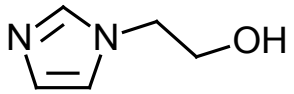



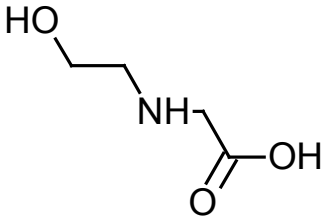




- Hydroxyethyl imidazole: HPLC-UV




- Amino acids: HPLC-ECD



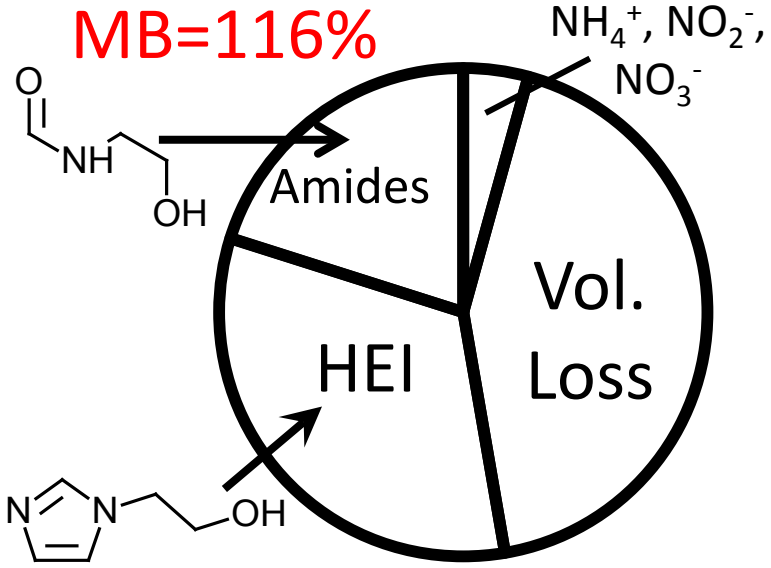

- Total material methods: TN, TOC, TIC, alkalinity

# Product Mix Comparison – N Balance

## 9 m pilot plant MEA, 70 C, 2kPa $CO_2$

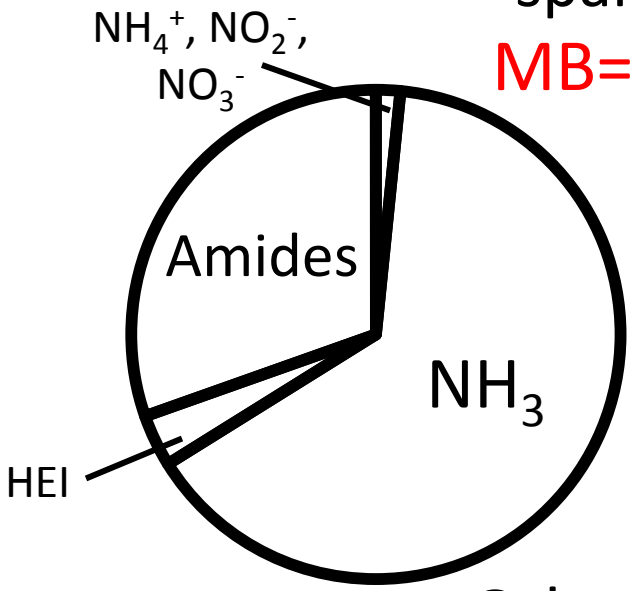
Low Gas Flow: 98kPa $O_2$, stirred cell

MB=116%

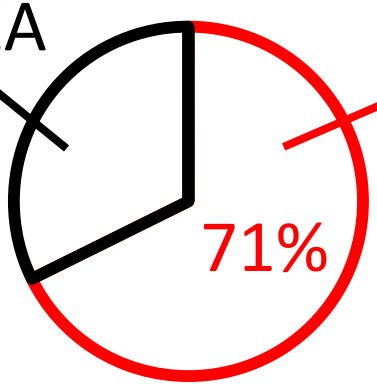



High Gas Flow: 21kPa $O_2$, sparged

MB=102%

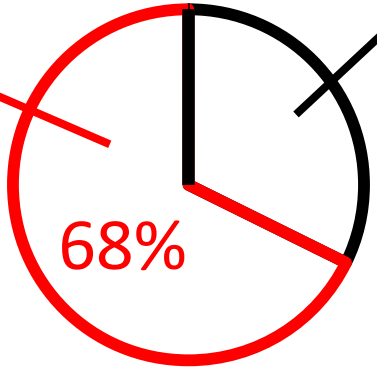



Other MEA loss



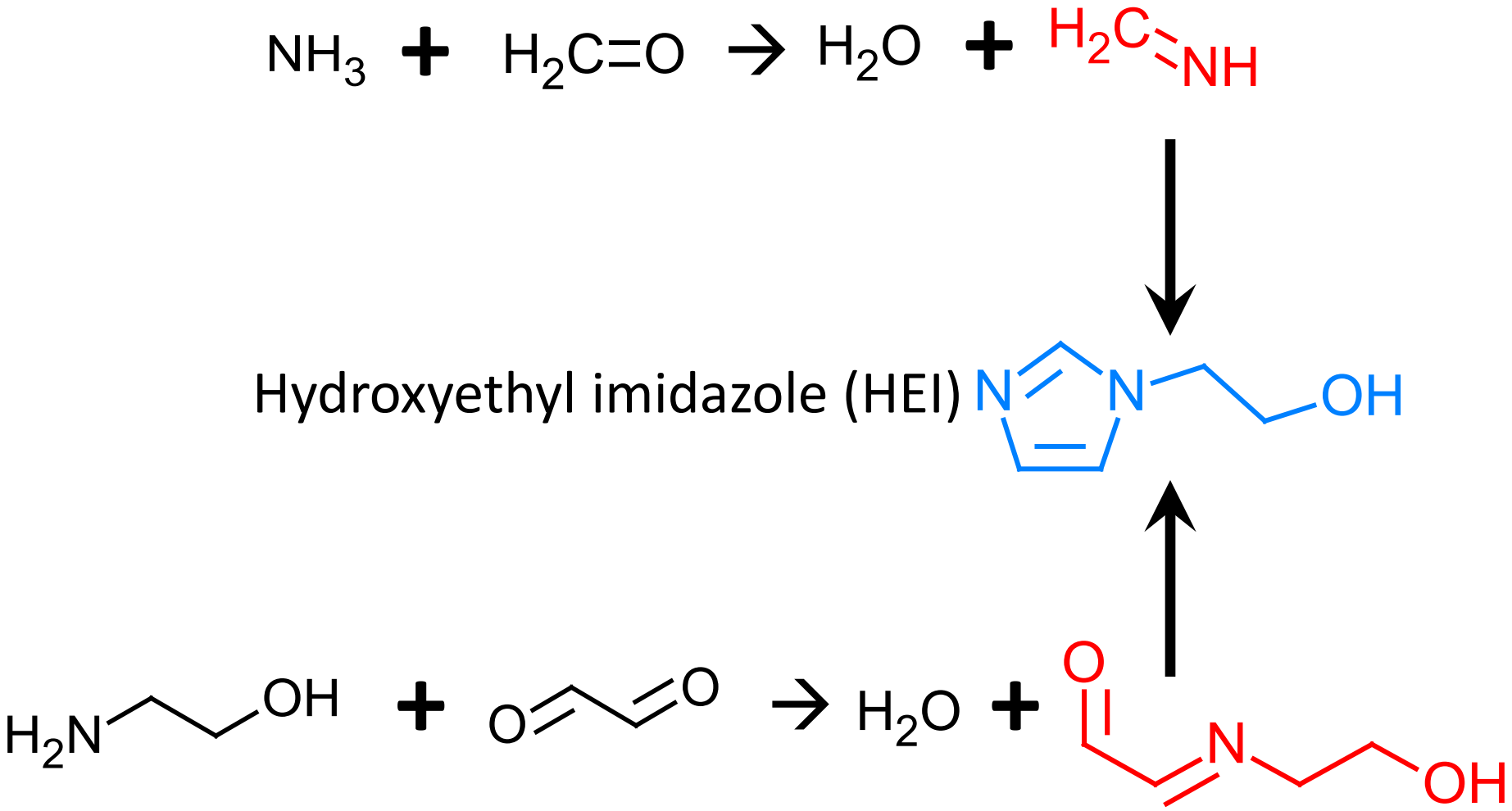

$NH_3$ prods

$NH_3 + 0.5*HEI + NH_4^+$




Other MEA loss

# Pathway for HEI Production



# Presence of Thermal Degradation Products

*7 m MEA, 98kPa $O_2$, 2kPa $CO_2$, 55 C*

7 m MEA, neat

$r_0$ = 8.8 mmol/kg/hr

**Therm. deg.**

**2 weeks, 135 C**

**$r_0$ = 14.0 mmol/kg/hr**

**7 m MEA, thermally degraded**

**MEA Conc (mol/kg)**

5000

4000

3000

2000

1000

0

5

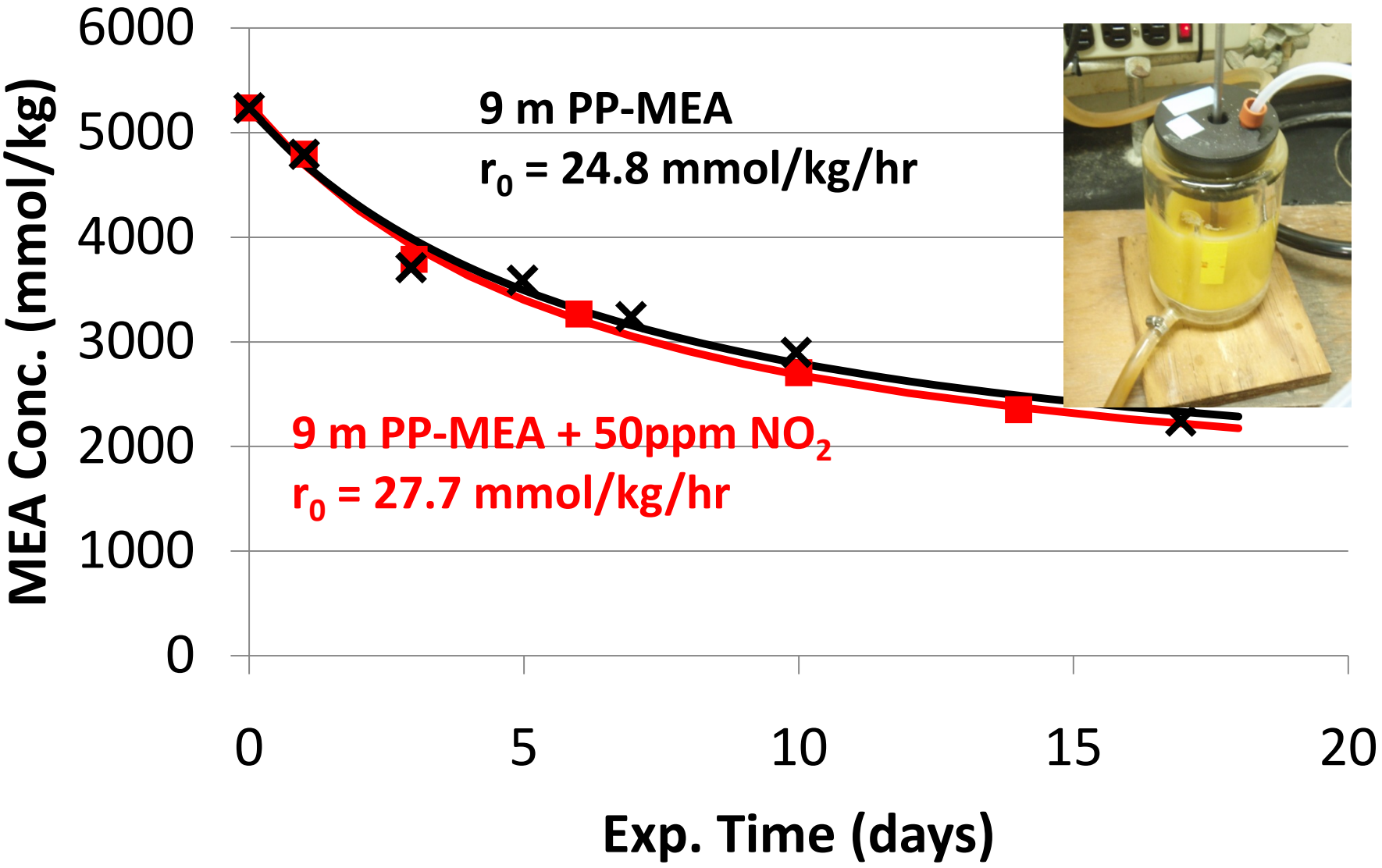
10

15

**Oxidation Time (days)**

# Effect of the presence of $NO_2$

*9 m PP-MEA, 98kPa $O_2$, 2kPa $CO_2$, 55 C, 0.5mM Fe*



# Summary of Factors Impacting MEA Oxidation

| Variable | Conditions | % Change (basis) |
|---|---|---|
| $Fe^{2+}$ | 0 → 1 mM | +1200 ($NH_3$) |
| $Cu^{2+}$, $Mn^{3+}$ | 0 → 1mM | +500-1000 ($NH_3$) |
| Temperature | 55 → 70 C | +160 (MEA) |
| $O_2$ | 20 → 92 kPa | +290 (MEA) |
| Inhibitor | 0 → 1.5% | -90% ($NH_3$) |
| $NO_2$• | 0 → 50ppm | +<10% |
| Thermal degradation | 2 weeks 135 C | +59% |

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