Dissolved Oxygen and its Influence on Amine Degradation for Postcombustion CO_2 Capture

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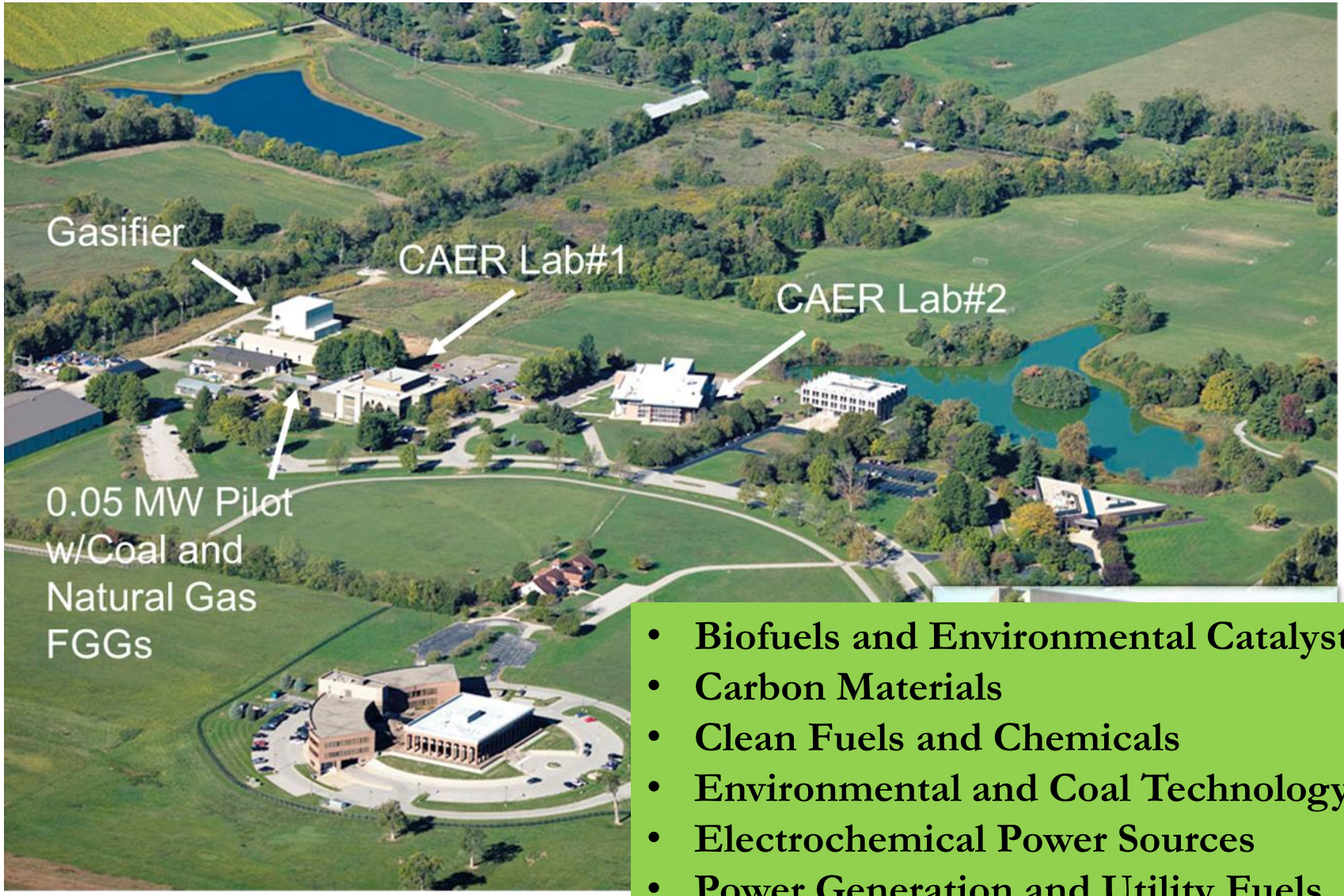


- Biofuels and Environmental Catalysts
- Carbon Materials
- Clean Fuels and Chemicals
- Environmental and Coal Technology
- Electrochemical Power Sources
- Power Generation and Utility Fuels

Areas of Research

Corrosion
- Non-metallic coating
- Inhibitors
- Localized effects

Conversion
- Gasification
- CO_2 utilization
- NG upgrading

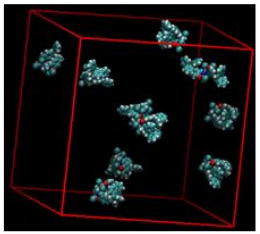
Pilot Plants
- Heat integration
- Hybrid processes
- Solvent & process testing

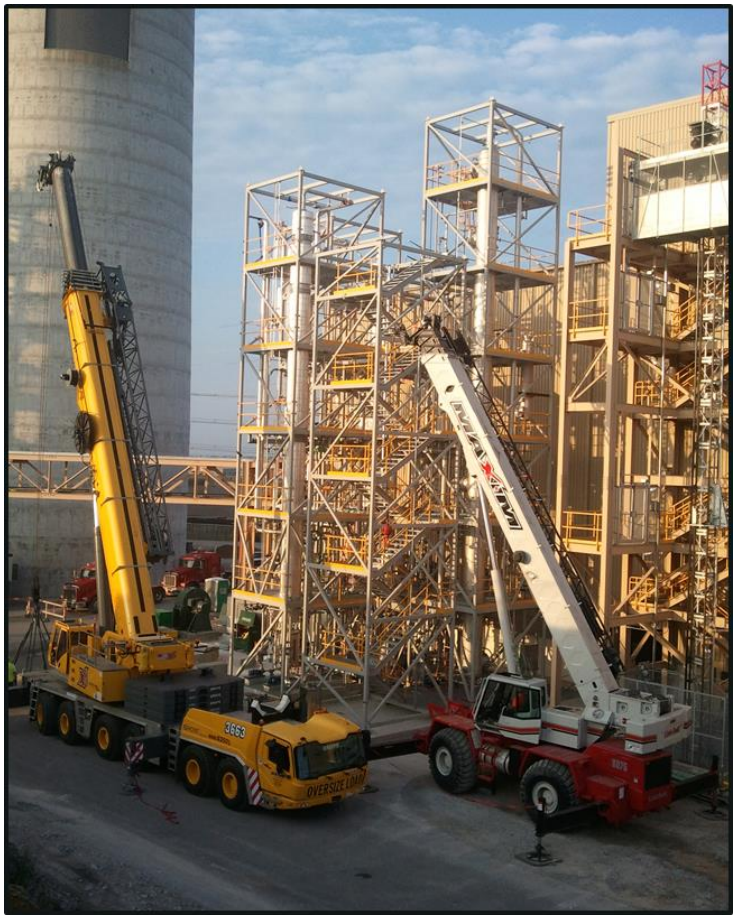
Membrane Separations
- Zeolite membranes
- Solvent enrichment

Solvents
- Chem/physical properties
- Emission
- Degradation

Chemical Looping
- Spouting fluidized bed
- Combustion/gasification
- Solid particle handling

Electrochemistry
- Water treatment
- Solvent enrichment





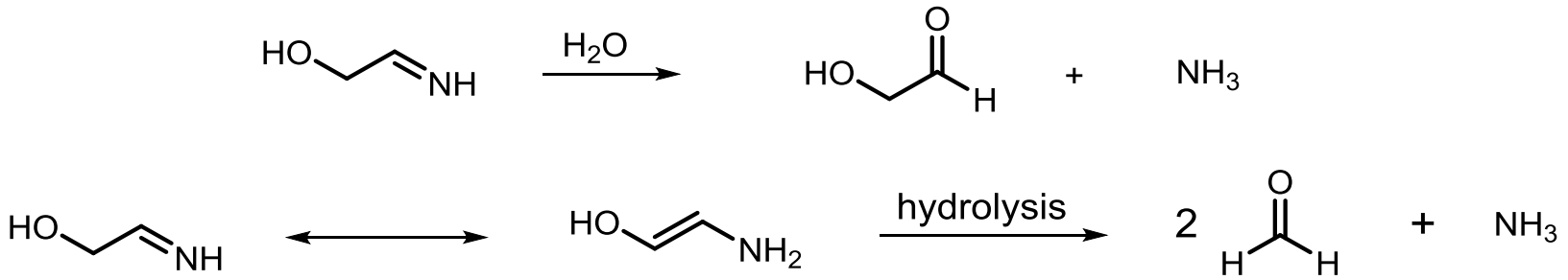
Oxidative Degradation

Under typical PCCC conditions, responsible for most of the amine degradation.

Proceeds via radical reactions.

Electron abstraction or proton abstraction results in an imine or amine radical.

End products include aldehydes, carboxylic acids, and ammonia.



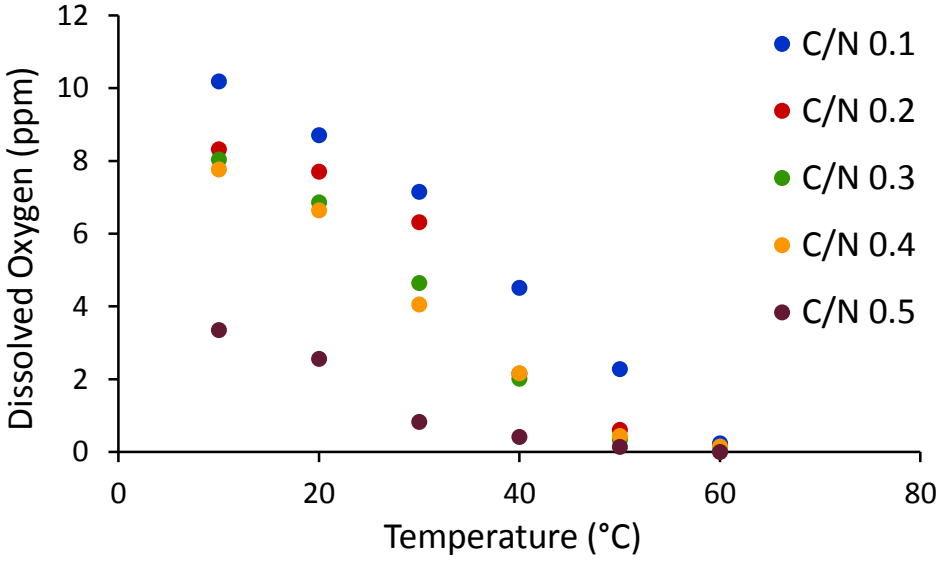
G. S. Goff, G. T. Rochelle. Monoethanolamine Degradation: O_2 Mass Transfer Effects under CO_2 Capture Conditions. *Ind. Eng. Chem. Res.* **2004**, *43* (20), 6400.

H. Lepaumier, D. Picq, P.-L. Carrette. New Amines for CO_2 Capture. II. Oxidative Degradation Mechanisms. *Ind. Eng. Chem. Res.* **2009**, *48* (20), 9068.

Background

Oxygen solubility data for 30 wt% MEA.

M. H. Wang, A. Ledoux, L. Estel. *J. Chem. Eng. Data* **2013**, *58*, 1117.



Degradation has also been correlated to dissolved oxygen.

$$r_{MEAdeg} = -5.35 \times 10^5 e^{-(\frac{41730}{RT})}[O_2]^{1.46}$$

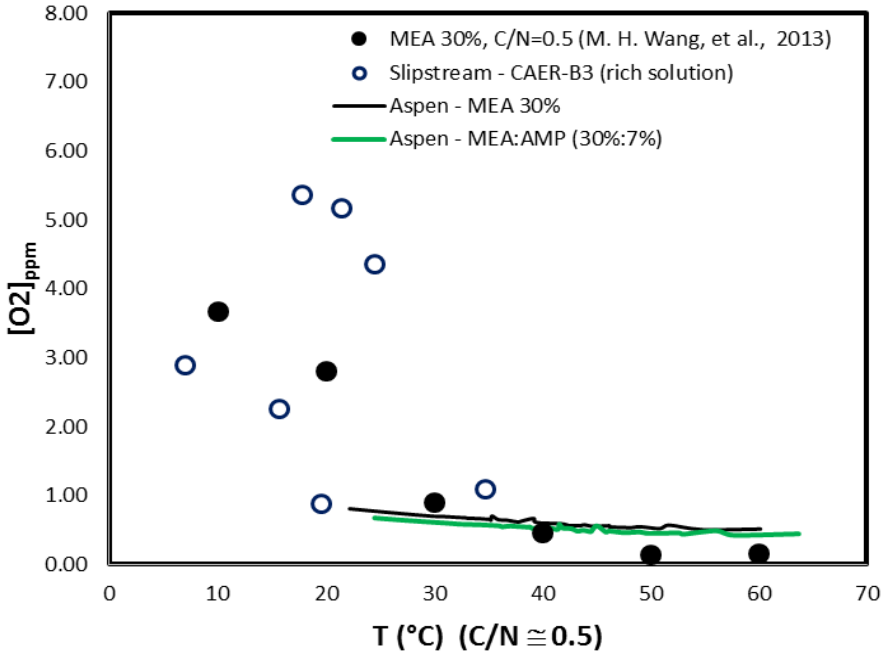
G. Leonard, D. Toye, G. Heyen. *Int. J. Greenhouse Gas Control* **2014**, *30*, 171.

$$r_{MEAdeg} = -2.5 \times 10^5 e^{-(\frac{66288.9}{RT})}[MEA][O_2]^{1.5}$$

T. Supap, R. Idem, A. Veawab, A. Aroonwilas, P. Tontiwachwuthikul, A. Chakma, B. D. Kybett. *Ind. Eng. Chem. Res.* **2001**, *40*, 3445.

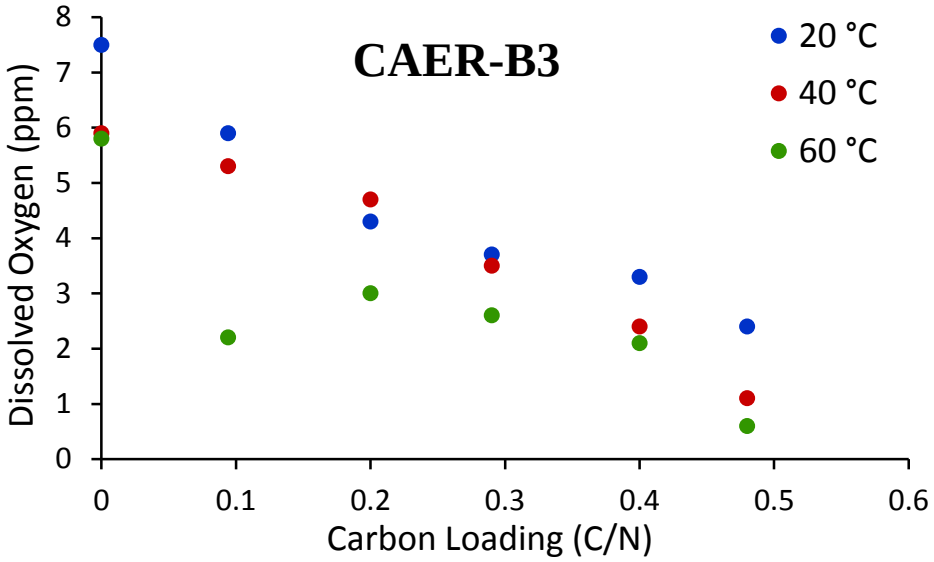
Motivation

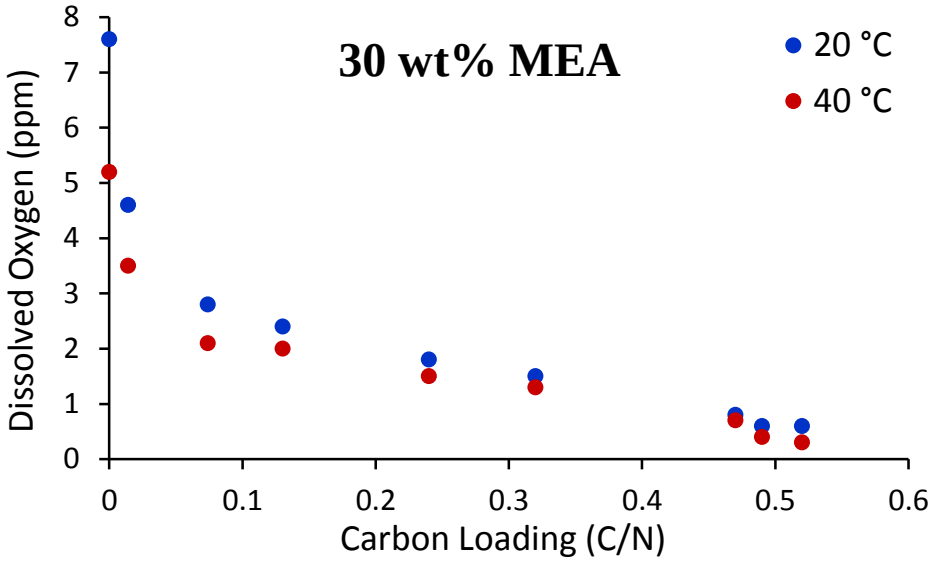
- Measure dissolved oxygen (DO) of our CAER-B3 solvent.
- Measure DO during CO_2 capture on a larger scale.
- Knowing how the oxygen content (and temperature) varies throughout the system helps to understand where degradation occurs.
- More measurements can be used to improve Aspen modeling.



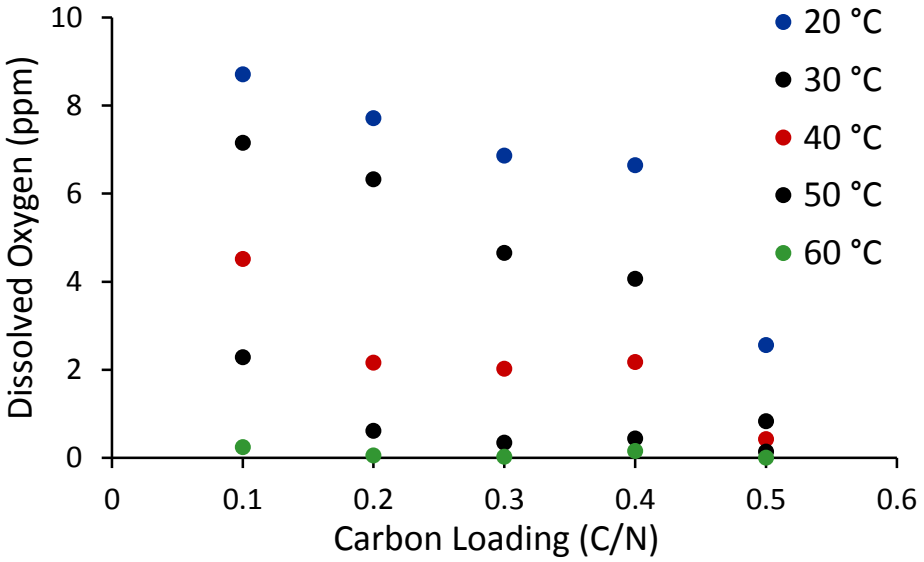
Aspen Plus® prediction and experimental dissolved oxygen in rich MEA 30 wt% and CAER-B3 solvents.

Lab Scale Measurements





Lab scale measurements were made with a handheld DO probe.



M. H. Wang, A. Ledoux, L. Estel. Oxygen Solubility Measurements in a MEA/H_2O/CO_2 Mixture. *J. Chem. Eng. Data* **2013**, *58*, 1117.

Pilot Scale Experiments

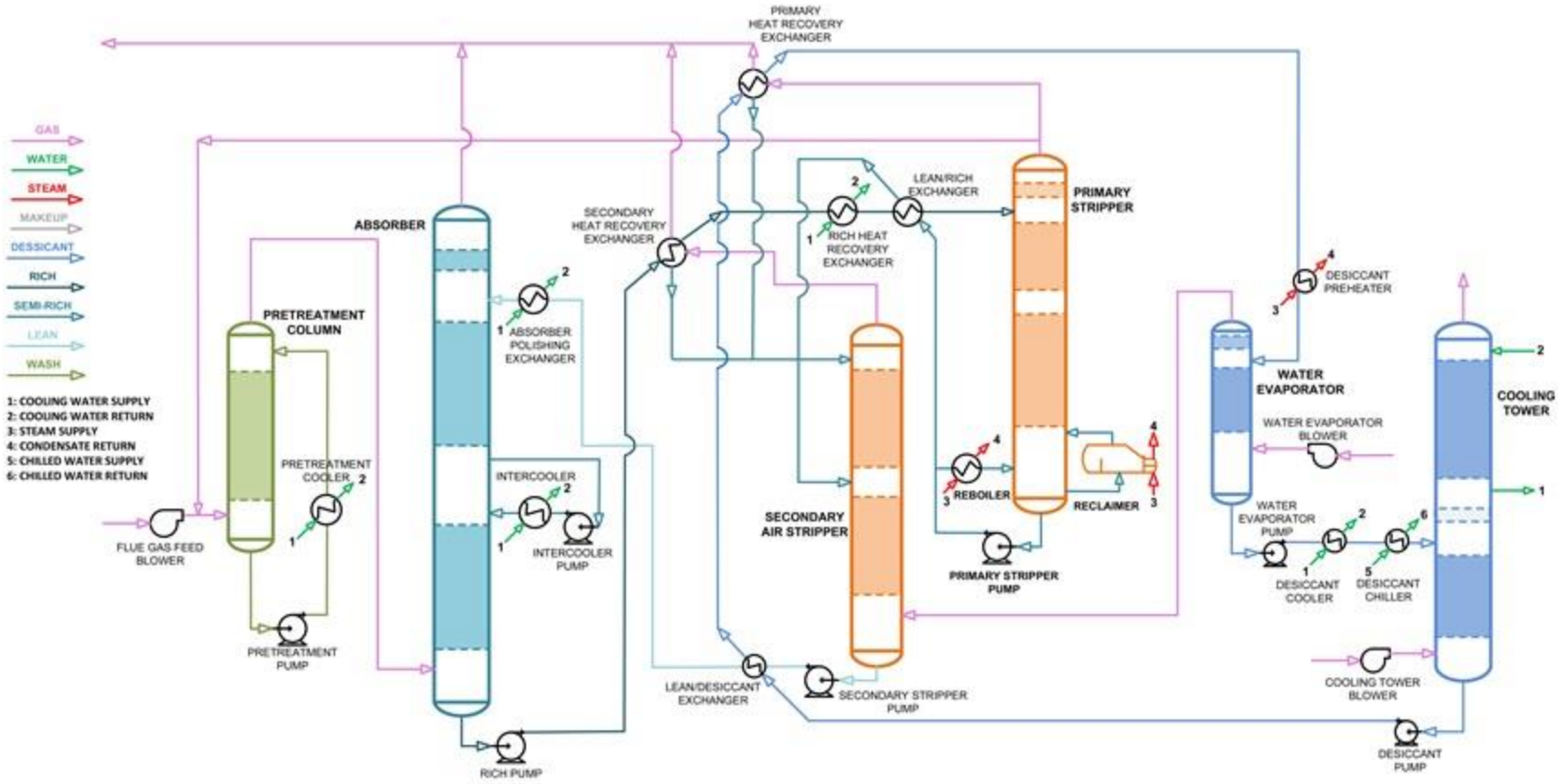
UKy-CAER 0.7 MWe small pilot scale CO_2 capture facility located at Kentucky Utilities E.W. Brown Generating Station in Harrodsburg, Kentucky. (Funded under DE-FE0007395).

Stats/specs:
0.7 MWe
~1300 acfm flue gas

Main components

- Pretreatment tower
- Cooling tower
- Absorber column
- Stripping column
- Secondary air stripper
- Intercooler
- Reclaimer

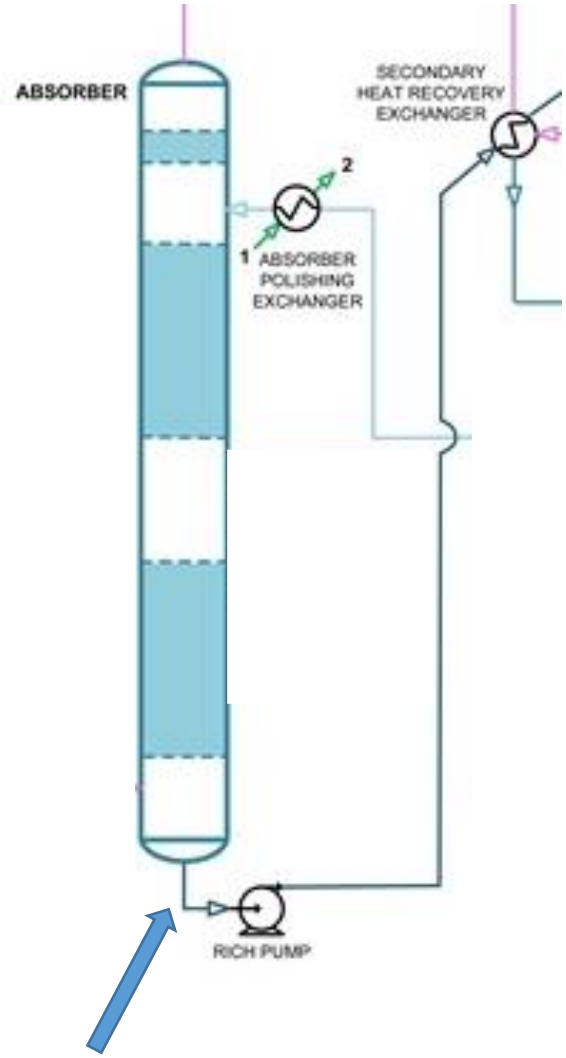
Process Overview



The temperature varies throughout the system.
CO_2 is also absorbed and desorbed.
The secondary stripper employs air (20% O_2).

How do these factors affect the DO?

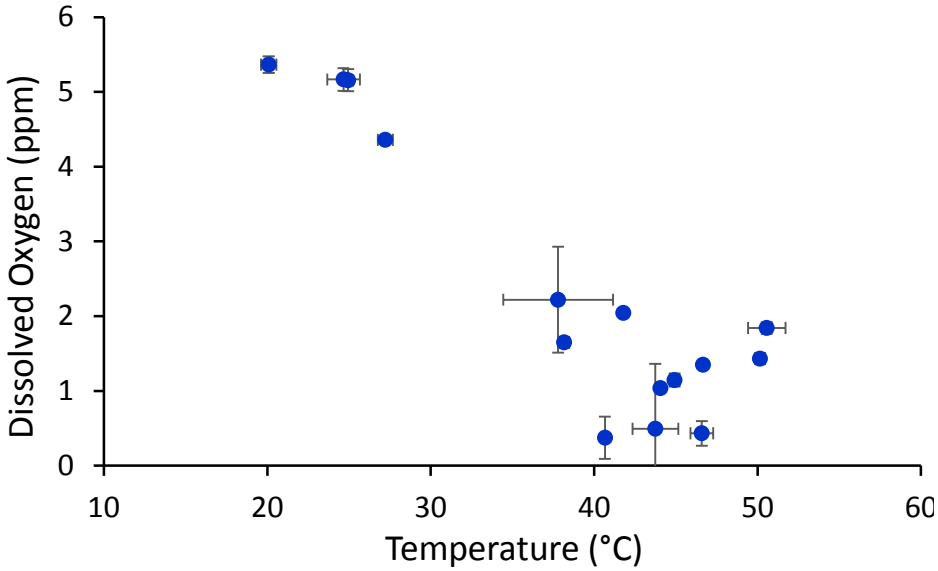
Dissolved Oxygen Measurements

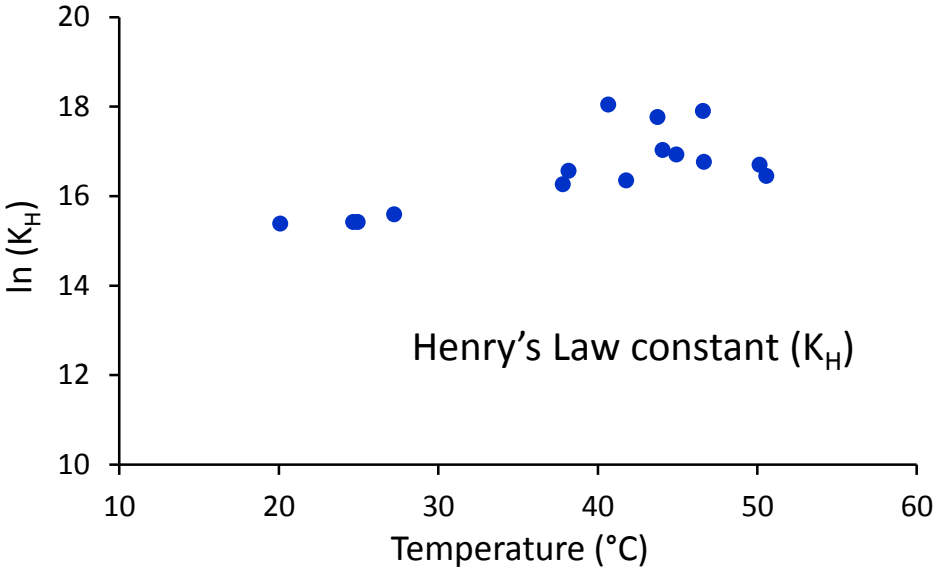


Sampling point

Rosemount 1056 Transmitter
and Hx438 DO sensor
Simultaneously measures DO and temperature
Automatic temperature correction

DO Temperature Dependence

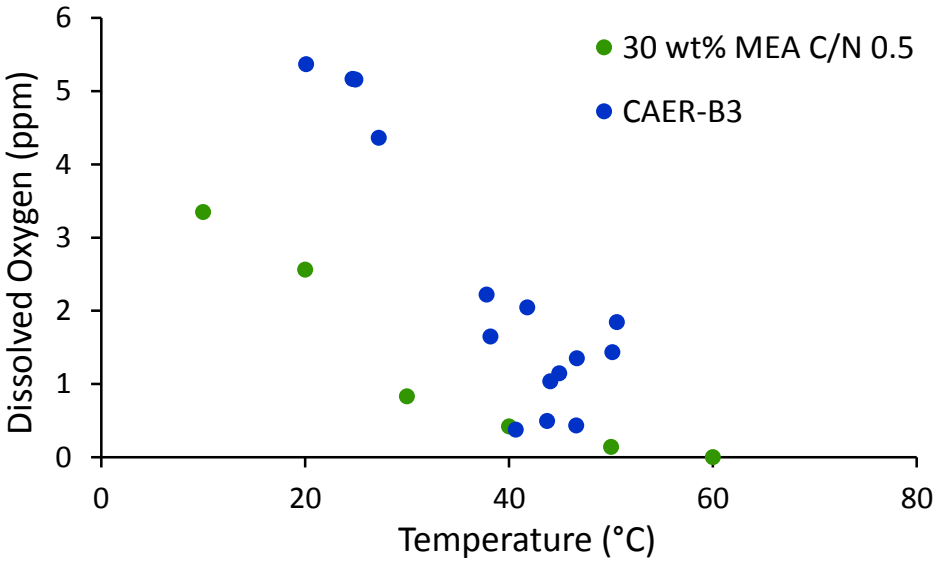




Dissolved oxygen in the rich amine as a function of the absorber temperature.

A simple correlation can be made based on these data.

$$DO\ (ppm) = -0.16T + 8.6$$



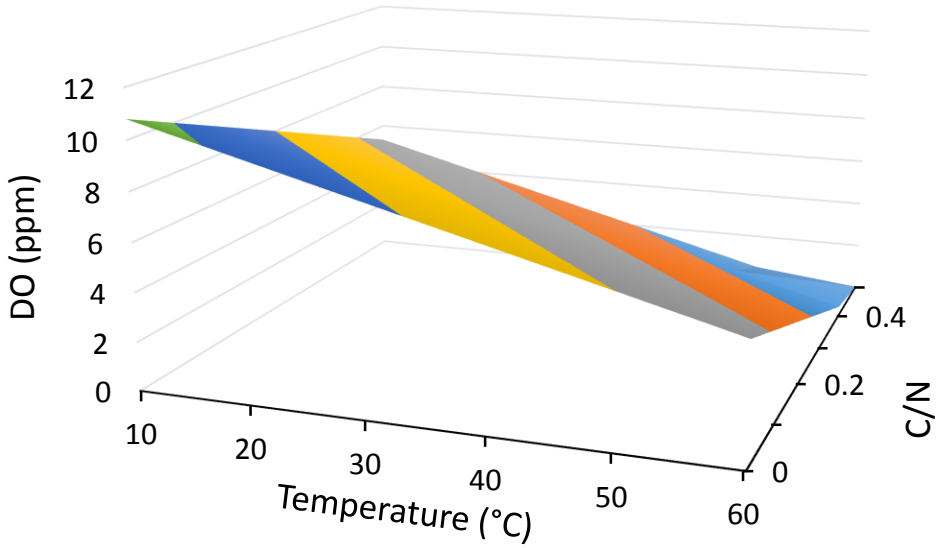
M. H. Wang, A. Ledoux, L. Estel. Oxygen Solubility Measurements in a MEA/H_2O/CO_2 Mixture. *J. Chem. Eng. Data* **2013**, *58*, 1117.

Carbon Loading Dependence

DO measurements in the pilot plant from both absorber and secondary stripper columns.

	DO (ppm)	Temp (°C)	C/N
rich	1.1	44.9	0.52
	1.0	44.1	0.50
	1.6	38.2	0.56
	5.2	24.9	0.44
	5.4	20.1	0.41
	2.0	41.8	0.43
	1.4	50.2	0.42
	1.8	50.6	0.44
	1.3	46.7	0.45
lean	2.0	76.3	0.22
	1.7	76.2	0.22
	0.5	69.6	0.22
	0.5	69.8	0.22

- DO of the amine in the primary stripping column could not be measured.
- Temperature has a larger effect than carbon loading (up to C/N 0.5).
- The oxygen levels in the two columns are not drastically different.



An expression for DO can be written as a function of carbon loading and temperature.

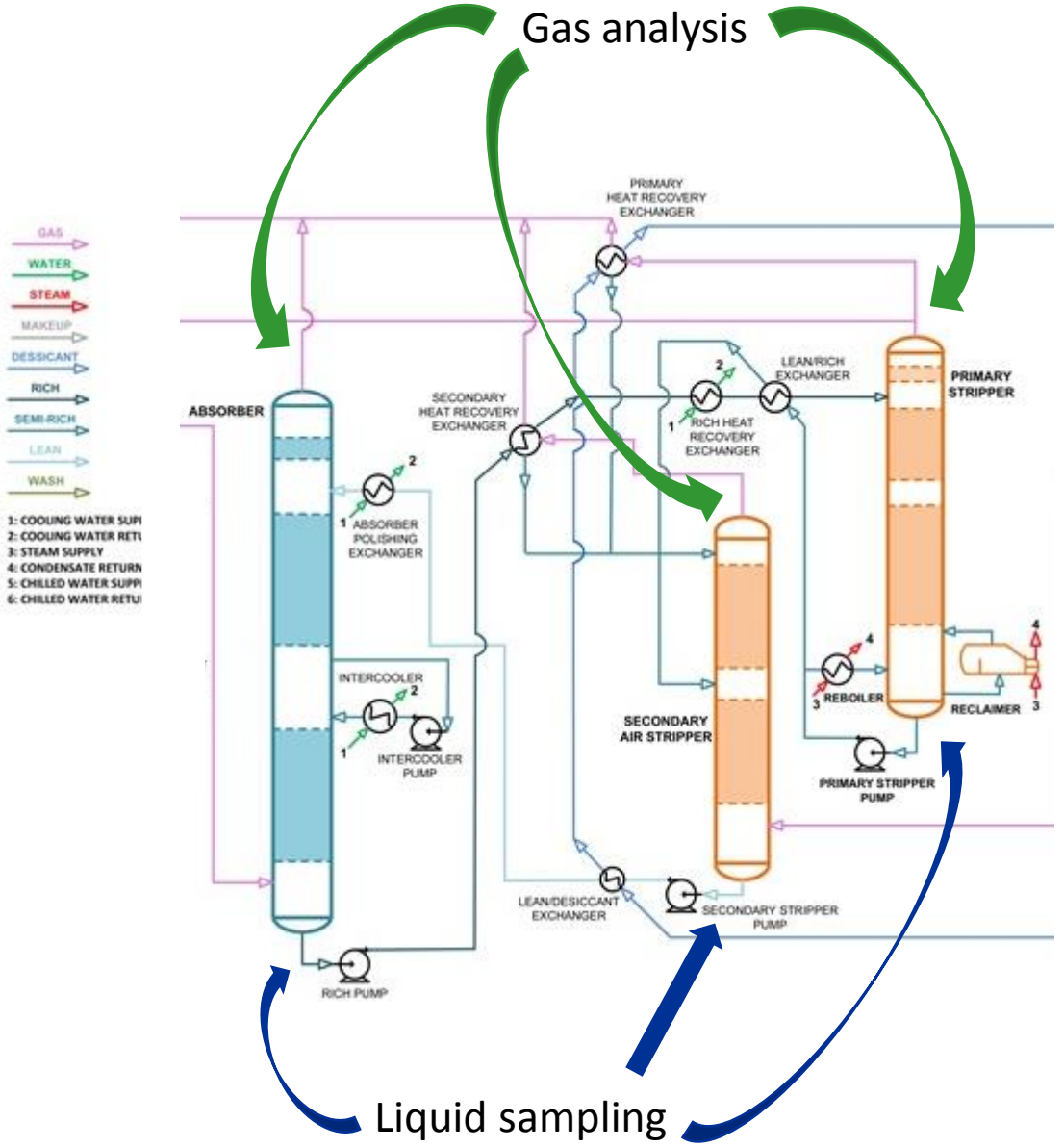
$$DO\ (ppm) = -0.12T - 11\alpha + 12$$

Future Work

We are currently measuring DO at different points in the system (liquid sampling points).

Oxygen in the solvent is emitted in the exhaust gas or consumed in degradation reactions.

Measuring the gas phase oxygen (gas analysis points) provides more data on where degradation is occurring.



Acknowledgments

Host site: LG&E/KU
Lynn Brickett and José Figueroa, DOE NETL [DE-FE0007395]
CMRG Members: LG&E and KU, EPRI, Duke

Outline

- Degradation is bad. Oxidative degradation in particular, as it is responsible for most of it.
- Oxidative degradation is called such because it relies on oxygen. It works as shown here
- Previous works have quantified degradation rates and the dependence on oxygen concentration
- Other work has measured the oxygen concentration in amine solutions.
- Our intent is to carry such work over to the larger scale and under actual process conditions
- At the pilot plant capture unit at E. W. Brown to be exact
- We start with the temperature dependence in the absorber column, as this is where it is expected to degrade the most (add literature support)
- We next test the C/N dependence by sampling the other columns (stripper and secondary stripper)

Literature Models

Fitting Equations for Dissolved Oxygen in 30 wt% MEA

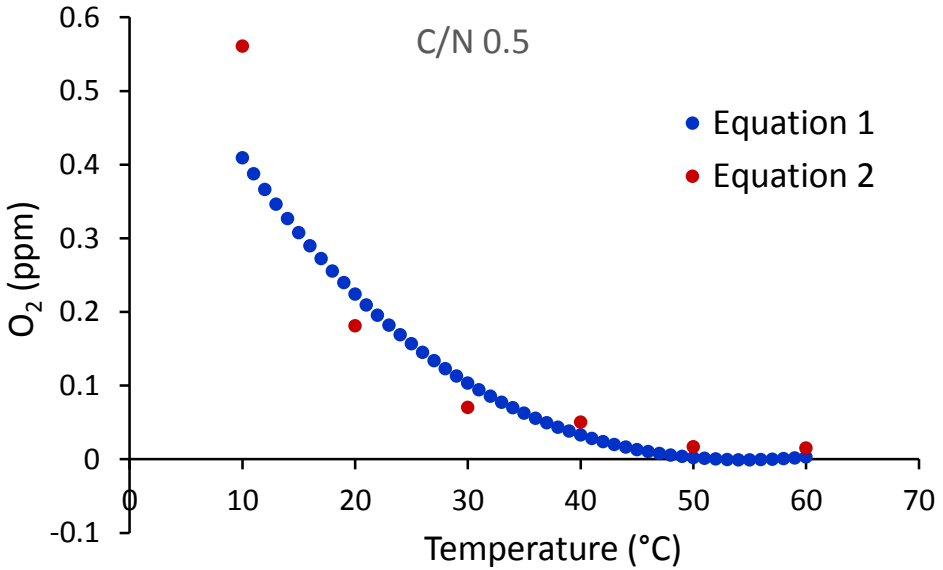
$[O2] = a_0 + a_1.a/T + a_2/T^2 + a_3/T^3 + a_4.a^2$ (1)

$[O2] = a_0 + a_1/a + a_2/a^2$ (2)

a_0, a_1, a_2, a_3, and a_4 are fitting parameters (Table 1), T is the temperature, and a is the C/N ratio.

	a_0	a_1	a_2	a_3	a_4		
Eq. (1)	1.309E-04	-3.450E-02	-4.014E+01	9.384E+03	1.154E-04	10°C ≤ T ≤ 60°C	$0 < \alpha \leq 0.5$
Eq. (2)	-2.381E-05	2.293E-05	-1.529E-06			T= 10°C	$0 < \alpha \leq 0.5$
Eq. (2)	-2.666E-05	1.835E-05	-1.223E-06			T= 20°C	$0 < \alpha \leq 0.5$
Eq. (2)	-2.803E-05	1.618E-05	-5.811E-07			T= 30°C	$0 < \alpha \leq 0.5$
Eq. (2)	-2.765E-05	1.678E-05	-1.119E-06			T= 40°C	$0 < \alpha \leq 0.5$
Eq. (2)	-6.879E-06	4.246E-06	-2.830E-07			T= 50°C	$0 < \alpha \leq 0.5$
Eq. (2)	7.199E-08	2.081E-07	-1.387E-08			T= 60°C	$0 < \alpha \leq 0.5$

Reference?



Initial experiments

EDO cell. Visually observed that the amine solvent degrades.
But not when you take out the oxygen

Minimizing DO

Use of MBT. What effect does it have in the lab scale on DO?
What are the kinetics of MBT degradation?
And how does this align with degradation rate? Any explanations for the discrepancy?

Extra

4 pilot plant study: Problems with the 95% number
Shoddy methodology? (not yet able to follow)
Assumptions go too far (100% of degradation occurs in the sump and the HEX. And this assumption is not even listed as one of their 4 assumptions)
Did they measure the dissolved oxygen concentration?
They state (in the same paragraph) that the parameters are regressed from the pilot plant data and then proceed to calculate the degradation using a model based on laboratory-scale experiments.
Other problems
The ammonia data are all over the place with no explanation why.

Future Work

Further investigation into oxidative degradation

- Effect of temperature and carbon loading
- How much degradation can we expect at different points in the system

$$r_{MEAdeg} = -5.35 \times 10^5 e^{-(\frac{41730}{RT})}[O_2]^{1.46}$$

G. Leonard, D. Toye, G. Heyen. *Int. J. Greenhouse Gas Control* **2014**, *30*, 171.

Predicts 2.5X the degradation at 70 °C compared to 50 °C