

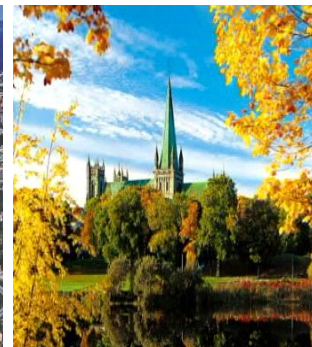
Oxidative degradation of amines using an open- and closed-batch reactor

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TCCS6



Outline

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 - Open batch system
 - Closed batch system
 - Comparison
- Summary

Introduction

- Amine degradation causes problems
 - Solvent loss
 - Corrosion
 - Fouling
 - Foaming
 - Emission of degradation compounds
- Literature describes three different oxidative degradation setups
 - Closed-batch reactor at elevated temperature and oxygen pressure¹
 - Open-batch reactor at 55 °C where the CO₂-loaded amine solution is sparged with a wet blend of CO₂ and air²⁻⁴
 - Integrated solvent degradation apparatus (ISDA)⁵

1) Lepaumier, H., et al. Ind. Eng. Chem. Res. (2009).**48**: 9068.

2) Chi, S., et al. Ind. Eng. Chem. Res. (2002).**41**: 4178.

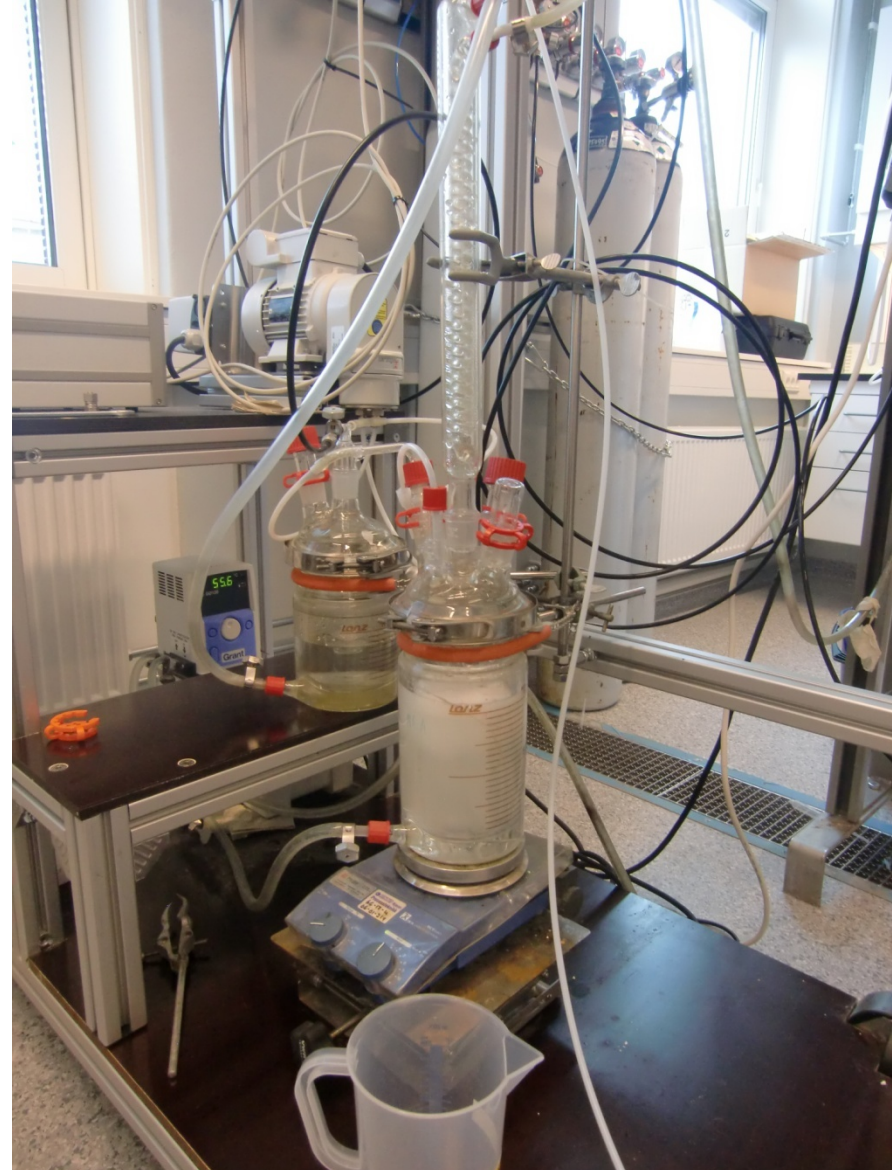
3) Goff, G.S., *Phd thesis*, in *Chemical Engineering*. 2005, University of Texas: Austin. p. 283.

4) Lepaumier, H., et al. Energy Procedia (2011) **4**, 1652.

5) Closman, F., et al. Energy Procedia (2011) **4**, 23.

Open batch

- Open batch glass reactor
- 30 wt% MEA
- Loaded with CO₂ ($\alpha = 0.4$)
- 0.35 L/min Air + 7.5 mL/min CO₂
- 55 °C for 3 weeks
- Liquid samples are taken out regularly from the reactor



Closed batch

- Closed batch glass reactor with Sulzer DX packing in SS316
- 30 wt% MEA
- Loaded with CO₂ ($\alpha = 0.4$)
- Circulation of gas (air) and liquid
 - Gas flow: 24.6 NL/min
 - Liquid flow: 0.91 L/min
- 50 – 55 °C for 3-4 weeks
- CO₂ and O₂ in the gas are logged
- Liquid samples are taken out from the liquid line regularly



Oxidative degradation apparatus

Similarities

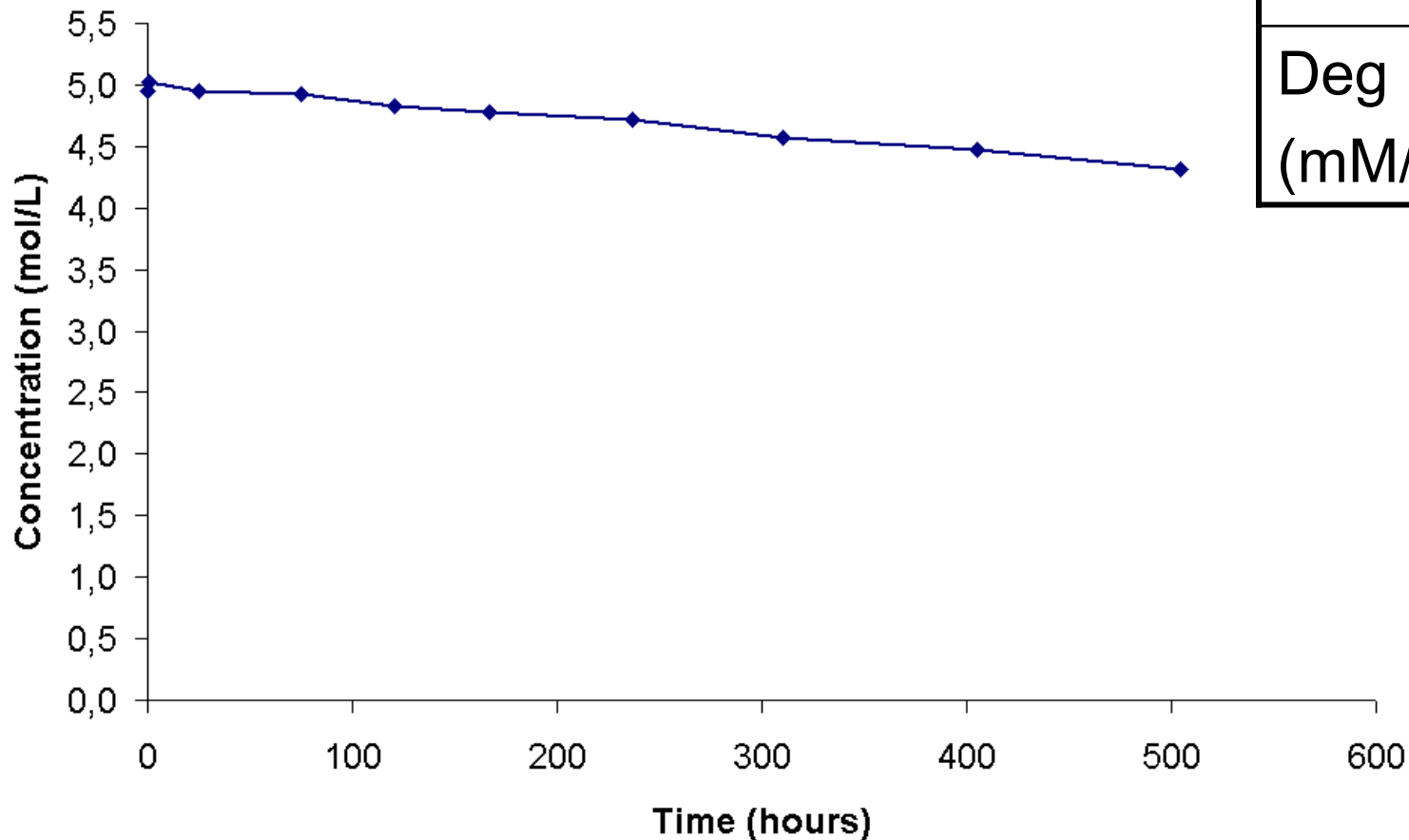
- An amine solution loaded with CO₂
- Glass apparatus

Differences (closed compared to open)

- Use structured packing instead of bubbling through the sump for mass transfer
- Recirculation of both gas and liquid
- Measure temperature in the sump and in the packing
- Temperature and gas (O₂, CO₂) composition are logged
- Higher gas flow through the system

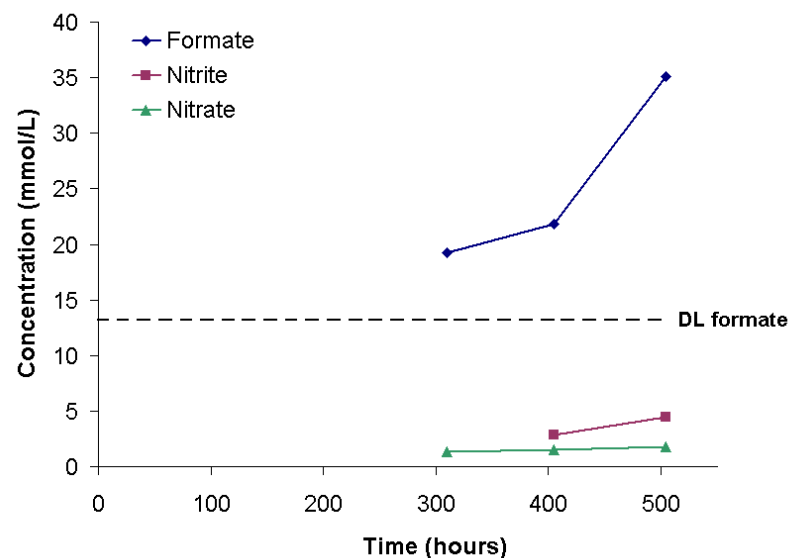
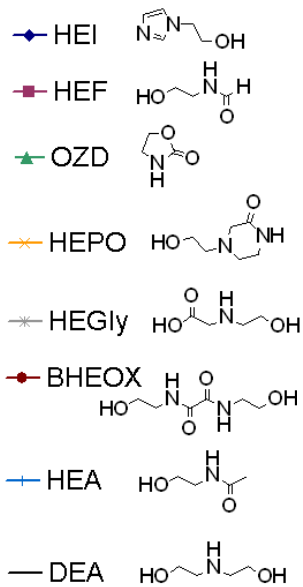
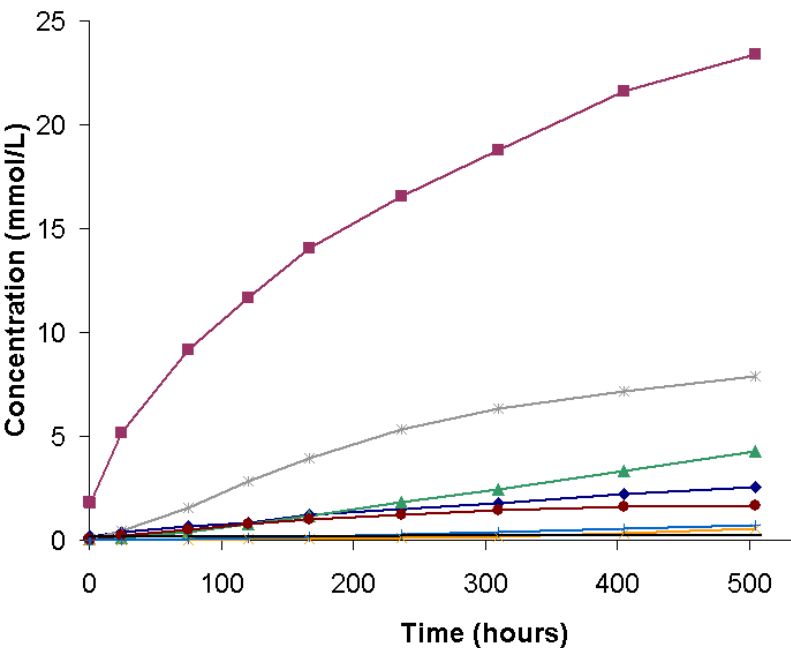
Results open batch

MEA loss

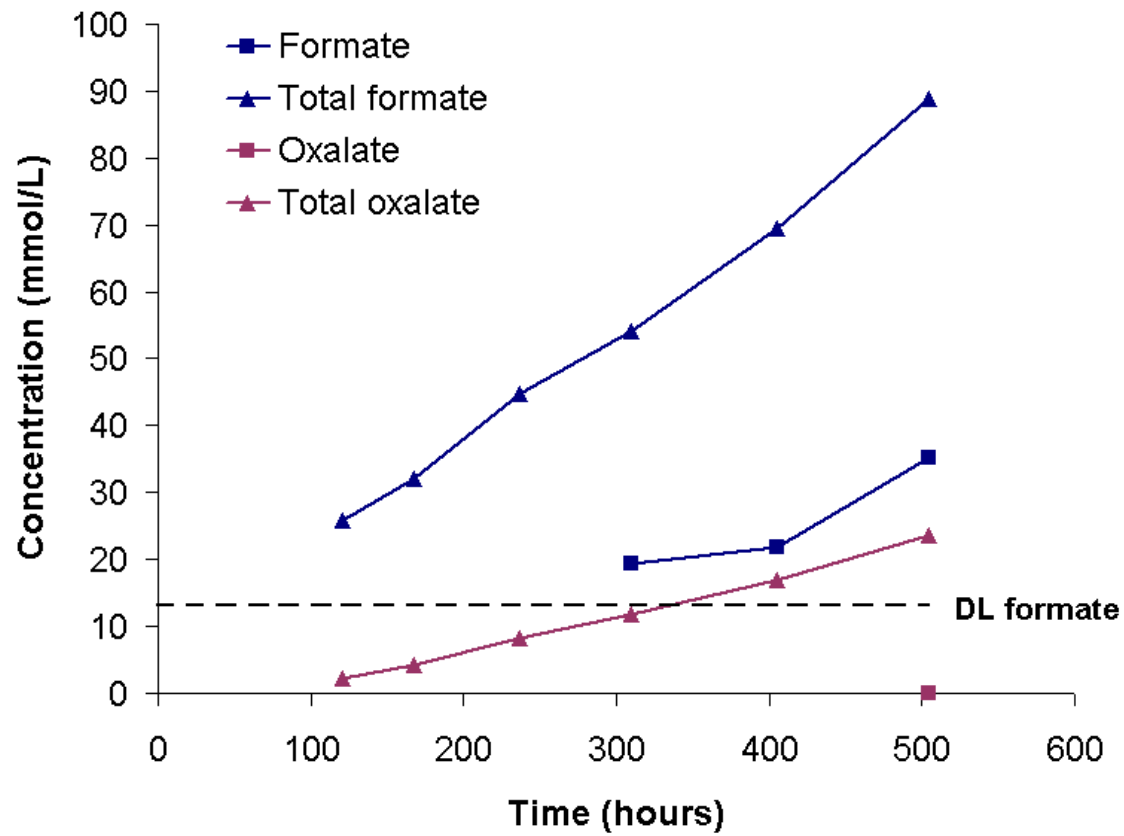


Abs degr (mol/L)	0.63
Rel degr	12.8 %
Deg rate (mM/h)	1.27

Degradation compounds



Degradation compounds – NaOH treatment*

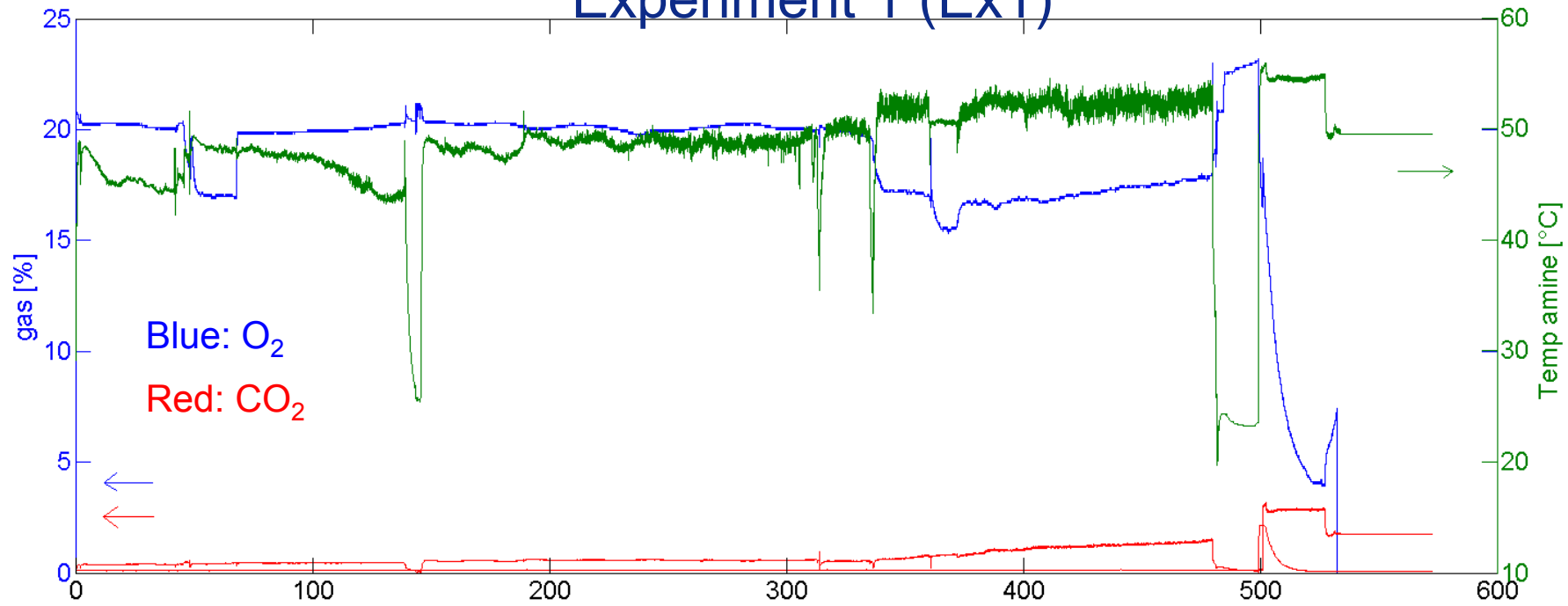


- 2.5 times more formate after NaOH treatment
- Oxalate only after NaOH treatment

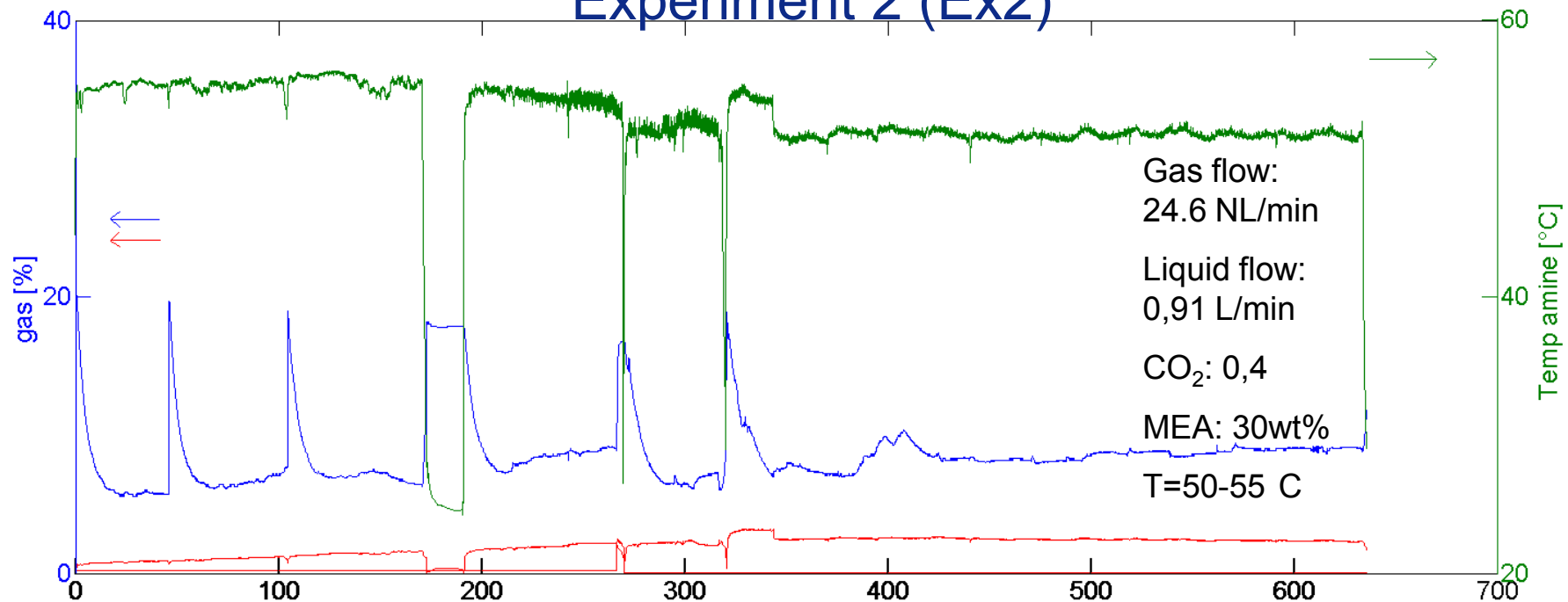
*Sexton, A.J., *Phd thesis: Amine oxidation in CO₂ capture processes*, 2008, The University of Texas: Austin. p. 262.

Results closed

Experiment 1 (Ex1)

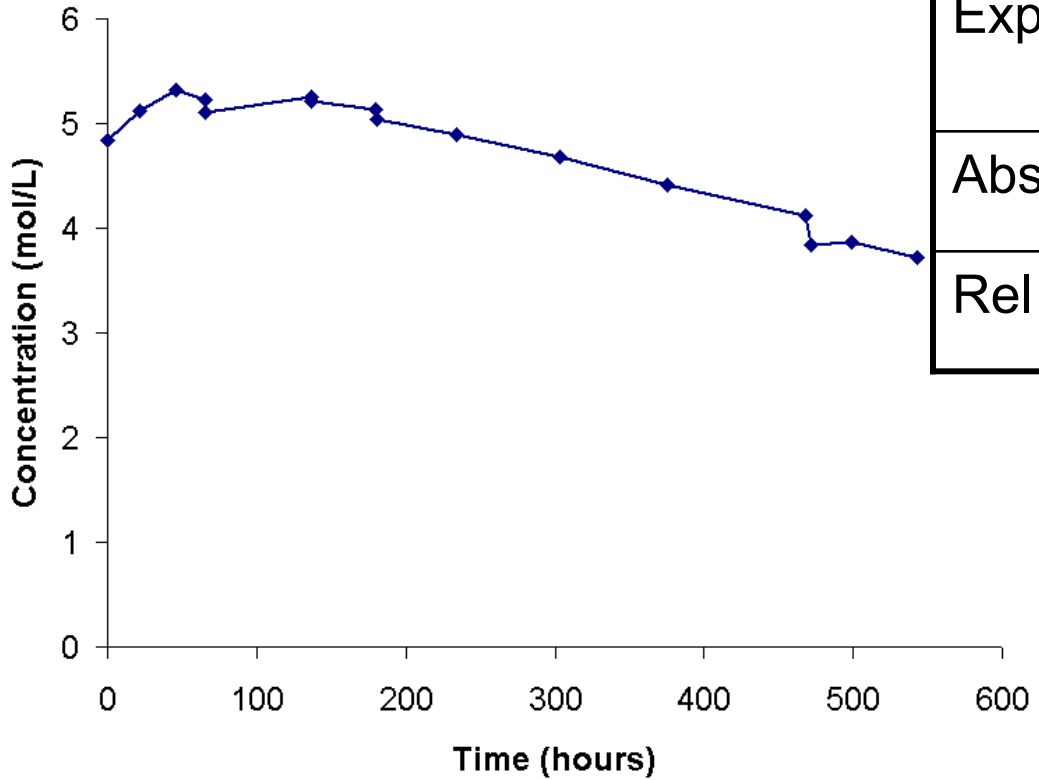


Experiment 2 (Ex2)



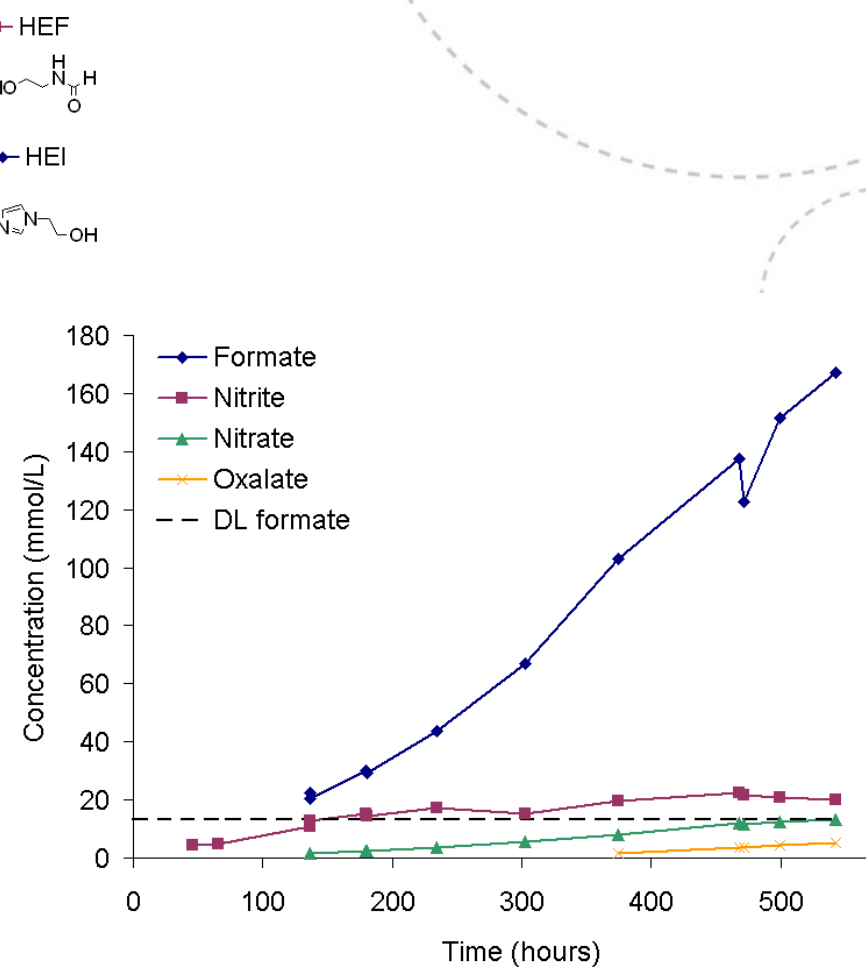
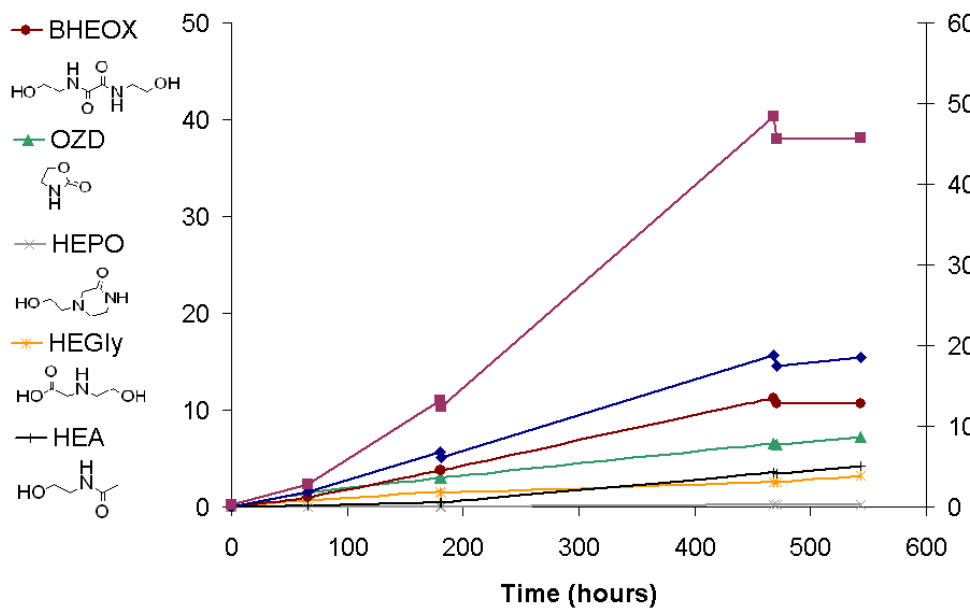
Amine loss

Experiment 1

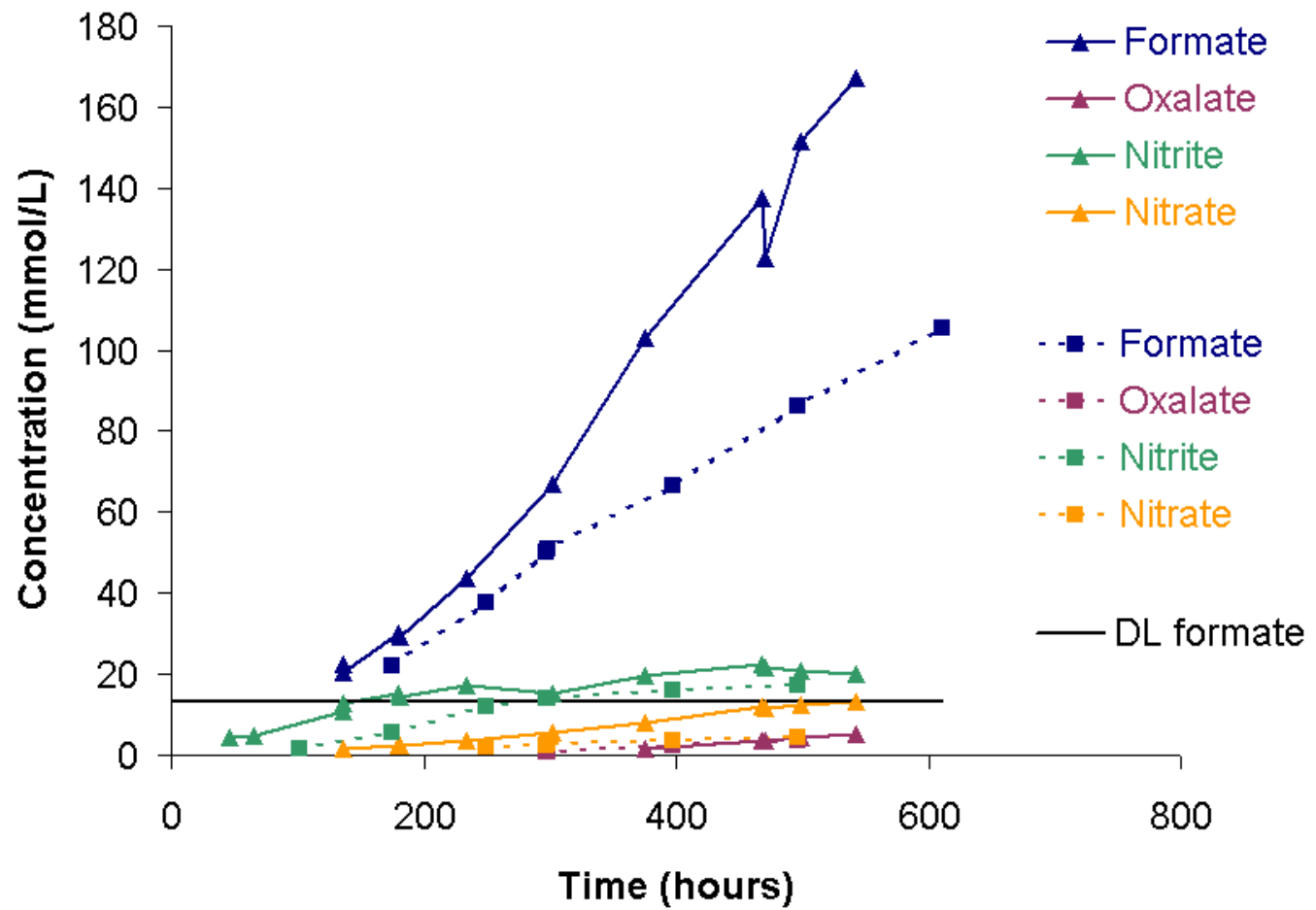


Experiment 1	Titration (mol/kg)	LC-MS (mol/L)
Abs degr	1.05	1.12
Rel degr	23.7	23.2
Deg rate (mM/h)		2.06
Experiment 2	Titration (mol/kg)	LC-MS (mol/L)
Abs degr	0.54	
Rel degr	12.5	

Degradation compounds Ex1

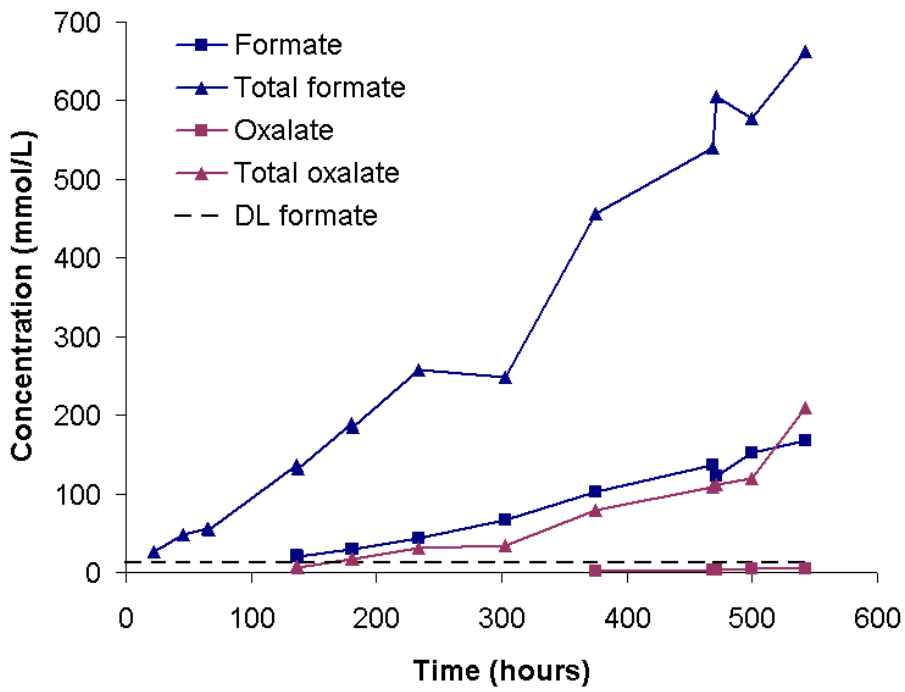


Degradation compounds Ex1 and Ex2

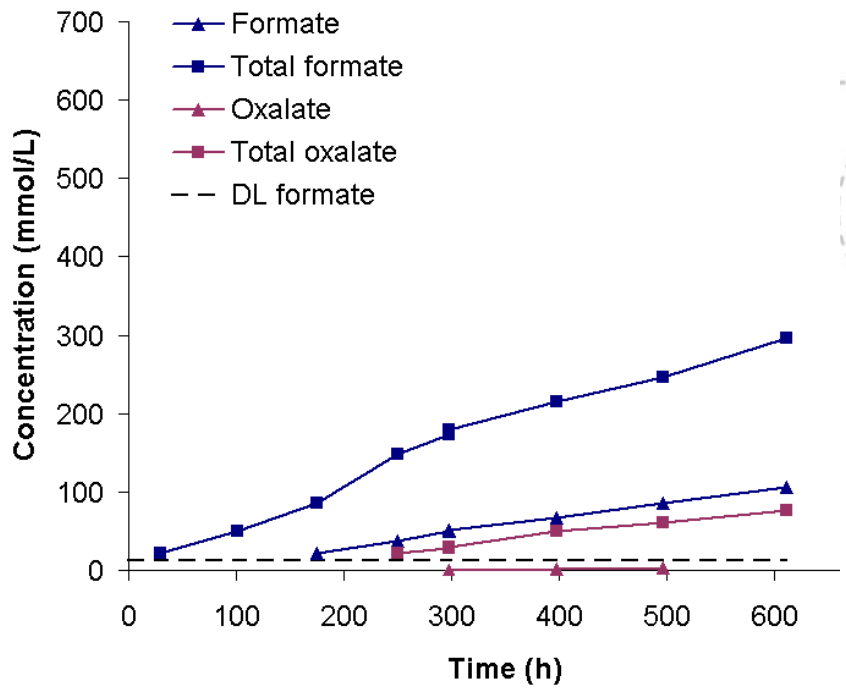


Degradation compounds – NaOH treatment*

Experiment 1



Experiment 2

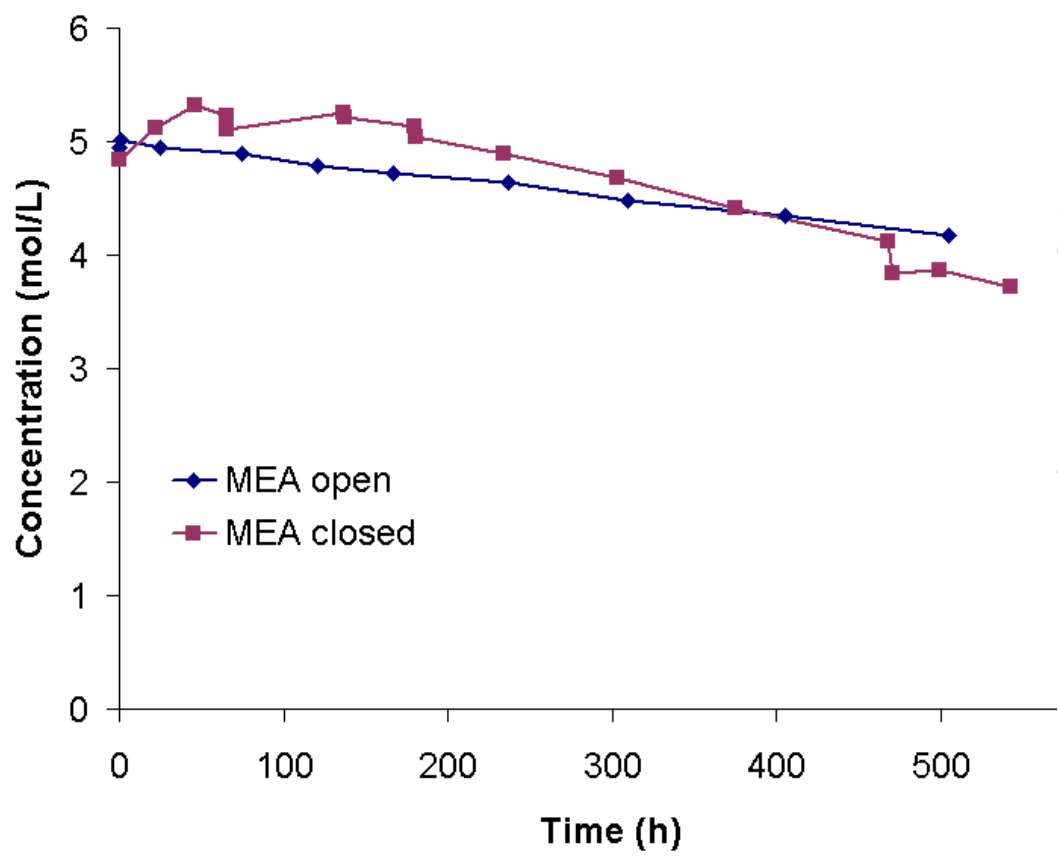


*Sexton, A.J., *Phd thesis: Amine oxidation in CO2 capture processes*, 2008, The University of Texas: Austin. p. 262.

Results open versus closed

Amine loss

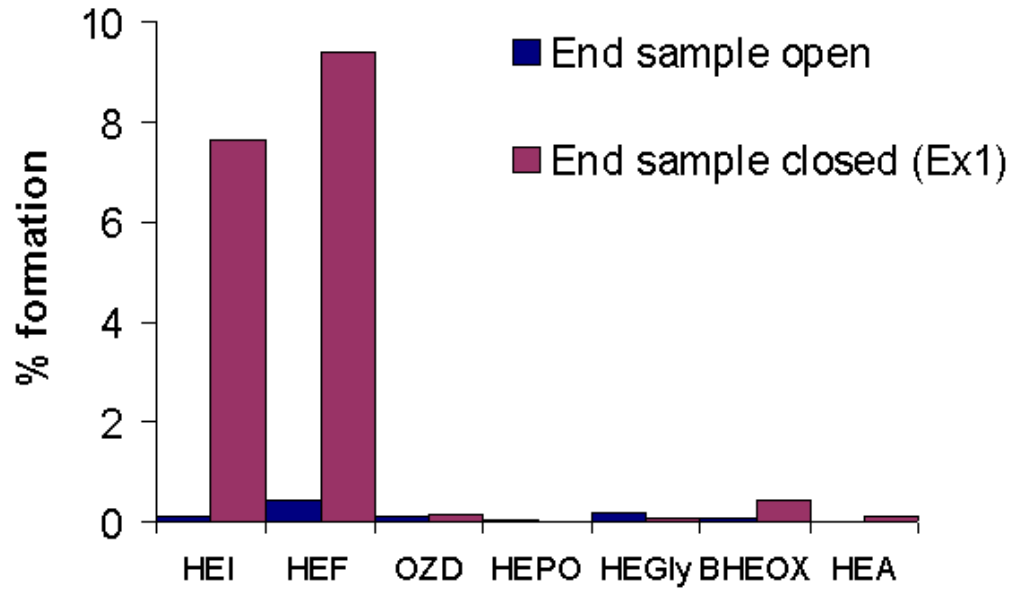
	Method	
Experiment	LC-MS	Titration
Open (blue)	12.8	13.9
Closed Ex1 (purple)	23.2	23.7
Closed Ex2 (green)	-	12.5

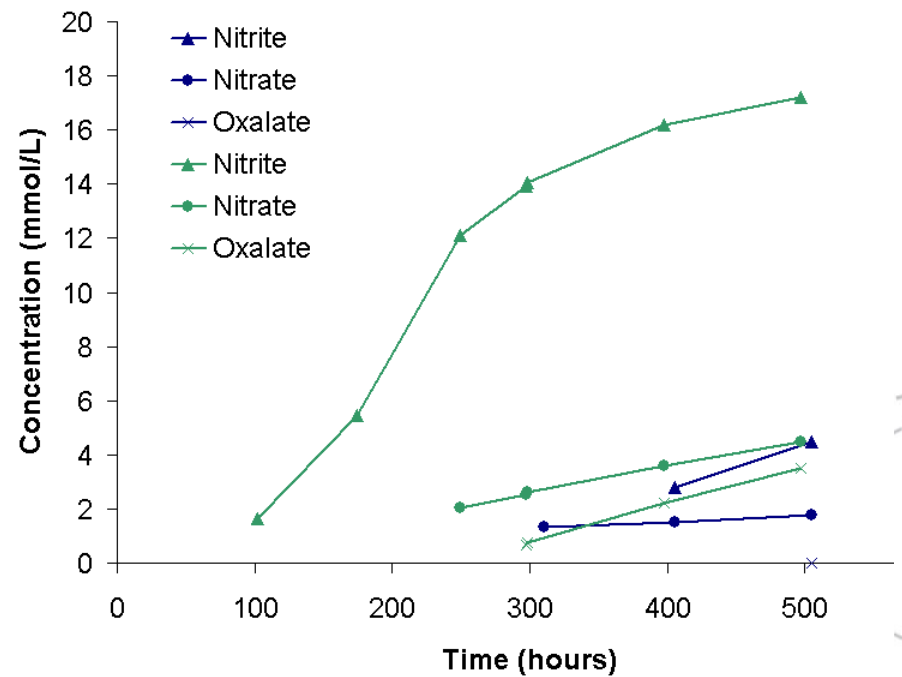
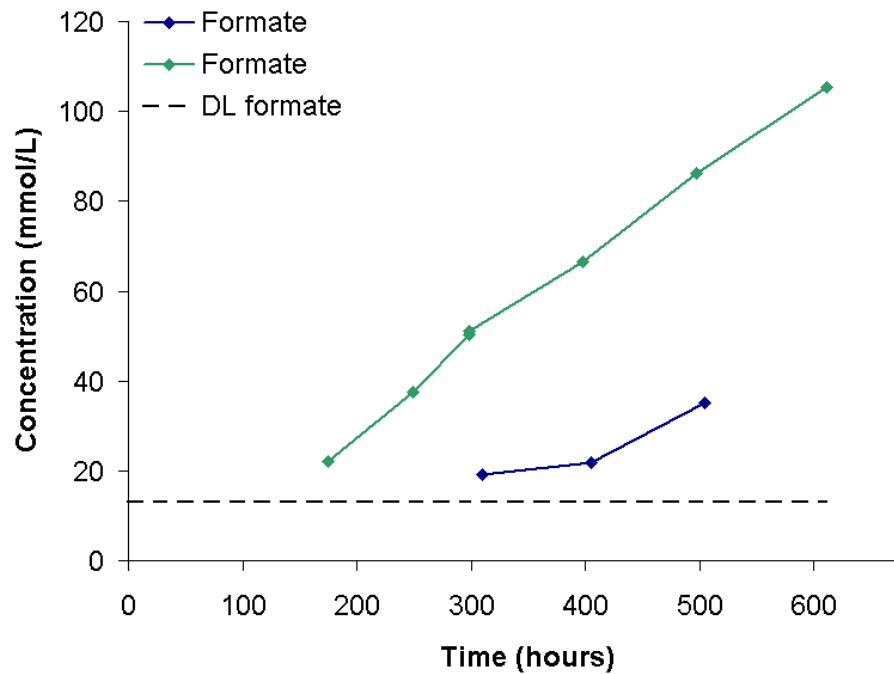


Degradation compounds

Open: HEF > HEGly > OZD > HEI > BHEOX > HEA > HEPO
 Closed Ex1: HEF > HEI > BHEOX > OZD > HEA > HEGly > HEPO

Deg cpd	End sample – % formation	
	Open	Closed (Ex1)
HEI	0,10	7,64
HEF	0,44	9,40
OZD	0,09	0,15
HEPO	0,02	0,01
HEGly	0,16	0,06
BHEOX	0,07	0,44
HEA	0,01	0,09





Ex	Time (hours)	Concentration (mmol/L)			
		Formate	Nitrite	Nitrate	Oxalate
Open	505	35	4	2	<0.60
Closed Ex1	499	151	21	12	4
Closed Ex2	497	86	17	4	3

Summary

- Mainly the same degradation compounds discovered in both setups
- The order of the degradation compounds seems to be different
 - Presence of packing in closed setup is likely the reason
- The nitrogen balance still not closed

Acknowledgement



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Thank you