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GDF SUEZ

Université de Liège

Optimal design of a CO_2 absorption unit and assessment of solvent degradation

Progress Review Presentation

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20th december 2012

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MEA degradation

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1. MEA semi-batch degradation

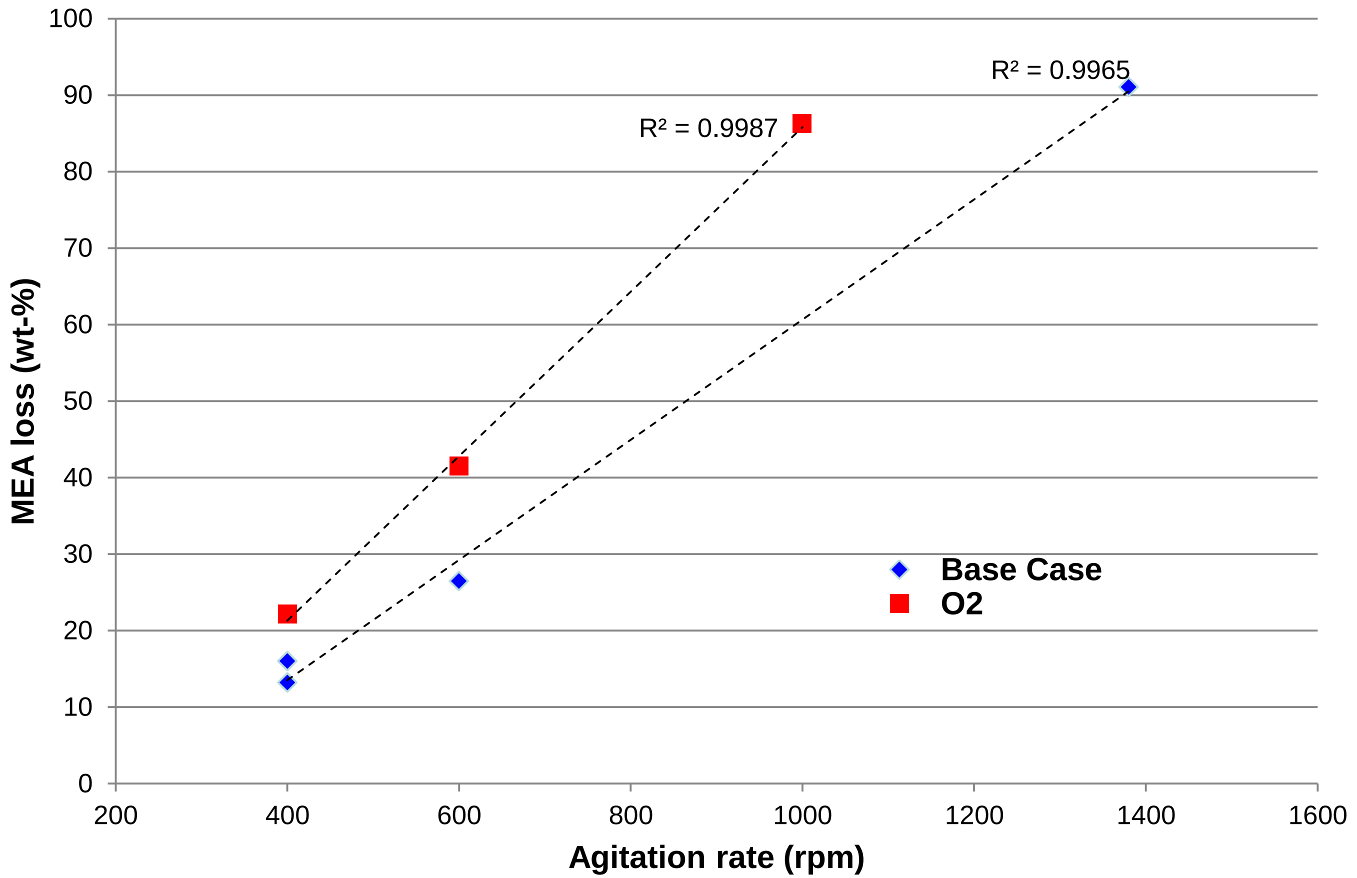
Experiment	Start	End	Time Days	Test	Agitation rpm	T [°C]	P_{tot} [bar]	P_{O2} [bar]	P_{CO2} [bar]	P_{N2} [bar]	Gas flow [mln/min]	Mass balance [%]	Solvent [wt% MEA]	Additives	Problems
17	31/07/12	7/08/12	7	**Base case at 600 rpm**	600	120	4	5	15	80	160	-1.33%	29.97	-	Crystal formation in the condenser
18	10/08/12	17/08/12	7	**O_2 at 600 rpm**	600	120	4	5	0	95	160	2.37%	29.99	-	-
19	21/08/12	28/08/12	7	**Temperature**	600	140	4	5	15	80	160	-4.82%	29.99	-	Crystal formation in the condenser
20	30/08/12	6/09/12	7	**Temperature**	600	55	4	5	15	80	160	2.17%	29.99	-	-
21	11/09/12	18/09/12	7	**Influence of SS metals**	600	120	4	5	15	80	160	-37.59%	29.98	Fe2+, Cr3+, Ni2+, Mn2+	Mass losses, crystal formation
22	19/09/12	26/09/12	7	**Influence of SS metals**	600	120	4	5	15	80	160	-1.07%	29.99	Fe2+, Cr3+, Ni2+, Mn2+	Crystal formation in the condenser
23	27/09/12	4/10/12	7	**Influence of Inh. A + SS**	600	120	4	5	15	80	160	-1.70%	30% (MEA from UT Austin)	SS metals + inh. A	Bad dissolution of metals
24	5/10/12	12/10/12	7	**Influence of DMTD + SS**	600	120	4	5	15	80	160	-1.17%	29.99	SS metals + DMTD	Bad dissolution of metals and inhibitor, power shortage (14h)
25	24/10/12	31/10/12	7	**Infl. of Inh.a + HEDP + SS**	600	120	4	5	15	80	160	-2.50%	30% (MEA from UT Austin)	SS metals + inh.A + HEDP	-

1. MEA semi-batch degradation

Experiment	Start	End	Time Days	Test	Agitation rpm	T [°C]	P_{tot} [bar]	P_{O2} [bar]	P_{CO2} [bar]	P_{N2} [bar]	Gas flow [mln/min]	Mass balance [%]	Solvent [wt% MEA]	Additives	Problems
26	1/11/12	8/11/12	7	**Influence of HEDP + SS**	600	120	4	5	15	80	160	-1.53%	29.99	SS metals + HEDP	Crystal formation in the condenser
27	9/11/12	16/11/12	7	**Influence of CO_2**	600	120	4	0	15	85	160	-3.83%	30.00	-	Power shortage (4h)
28	19/11/12	26/11/12	7	**Influence of O_2**	600	120	4	10	15	75	160	-1.50%	30.00	-	Crystal formation in the condenser
29	27/12/12	4/12/12	7	**Influence of CO_2**	600	120	4	5	30	65	160	-18.00%	30.02	-	Mass losses, crystal formation
30	5/12/12	12/12/12	7	**Influence of Temp**	600	100	4	5	15	80	160	-6.87%	30.00	-	Light Mass losses
31	13/12/12	20/12/12	7	**Influence of CO_2**	600	120	4	5	30	65	160	0.00%		-	

1.1 Agitation rate

- Linear dependence of the MEA loss on the agitation rate



1.1 Agitation rate

Further observations:

- More HEI when rpm rises
- Less HEPO when rpm rises (also less when under O_2 only)

=> HEI is formed when O_2 diffusion is not limited

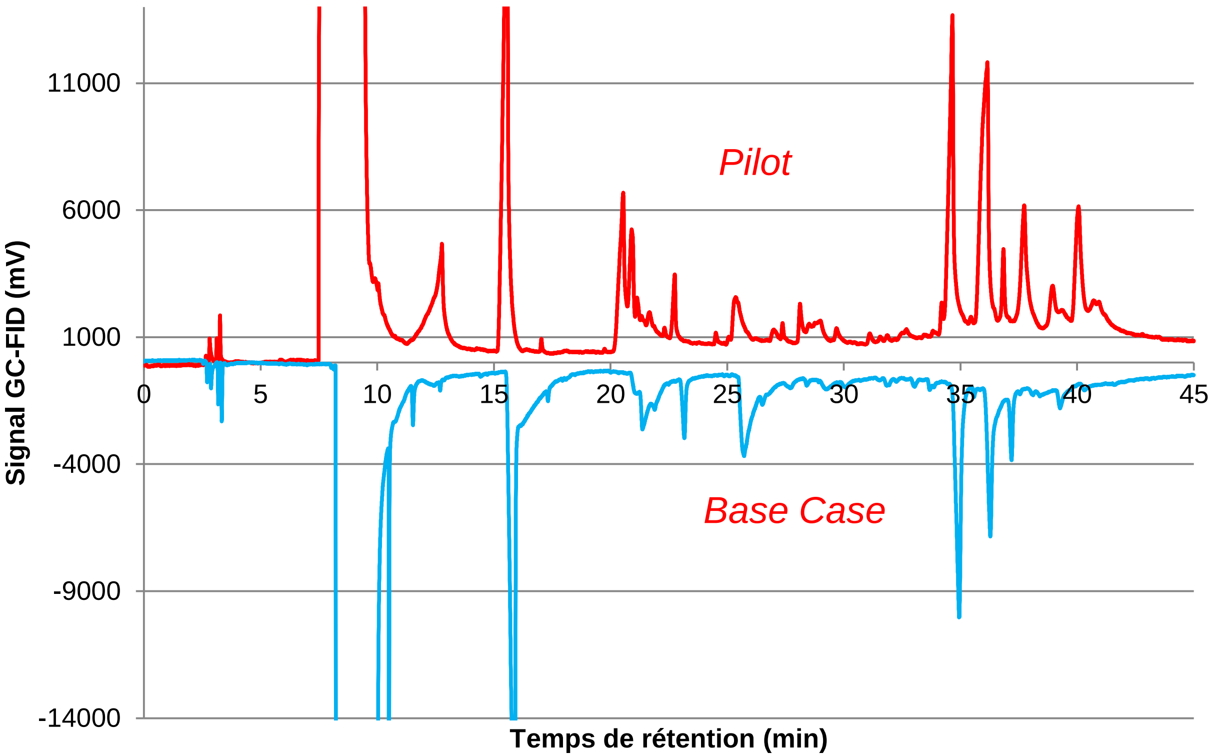
=> HEPO is formed when O_2 is less available

Base case Agitation rate	P10 400	P15 400	P17 600	P11 1380
MEA	22.17%	22.67%	20.09%	2.03%
OZD	0.0451%	0.0500%	0.0480%	0.1240%
HEI (Secondary axis)	0.1261%	0.0202%	0.1489%	3.9100%
HEPO	0.2555%	0.2757%	0.2555%	0.0697%

O2 Agitation rate	P16 400	P18 600	P13 1000
MEA	19.48%	12.64%	1.82%
OZD	0.0058%	0.0145%	0.1724%
HEI	0.0834%	0.4491%	3.2003%
HEPO	0.0558%	0.0868%	0.0918%

1.1 Agitation rate

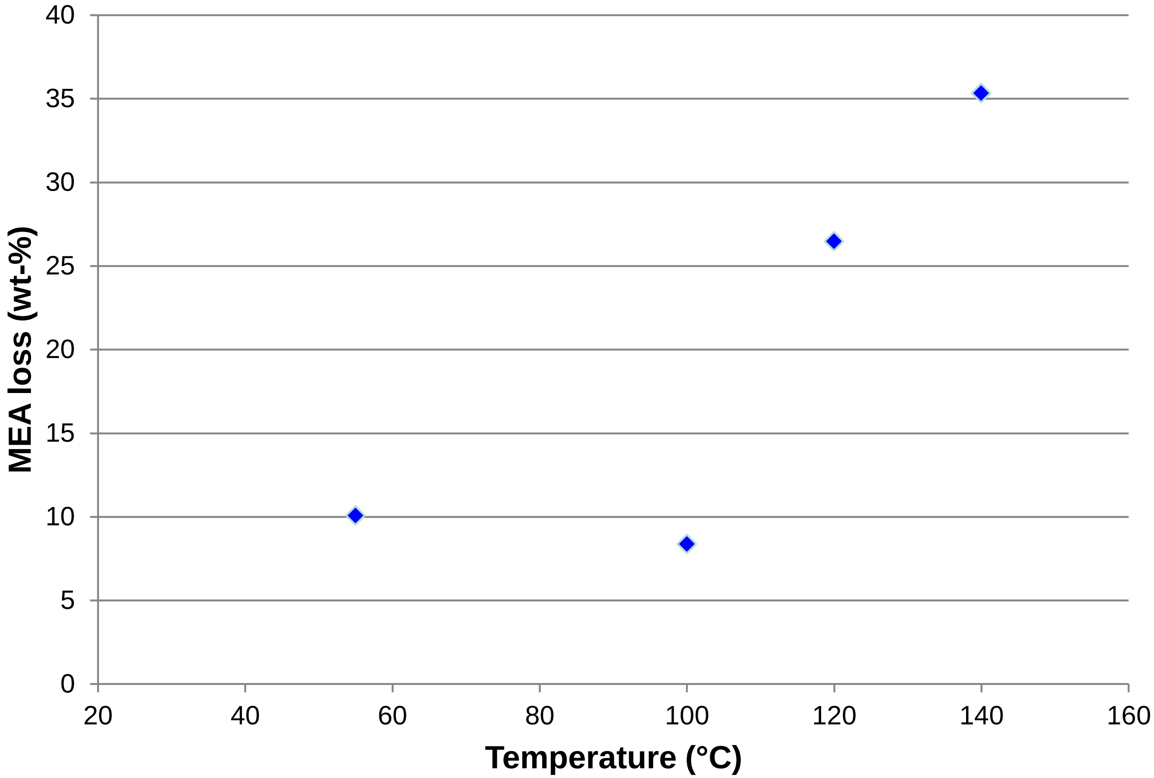
GC Comparison with pilot results => Experiment 17 has been chosen as base case



- 600rpm
- 120°C
- 4 bar
- 5% O_2, 15% CO_2, 80% N_2
- 160 mln/min
- 1 week

1.2 Temperature

- Higher temperature leads to higher MEA losses
- Experiment at 100°C gives unexpected results, maybe due to mass losses



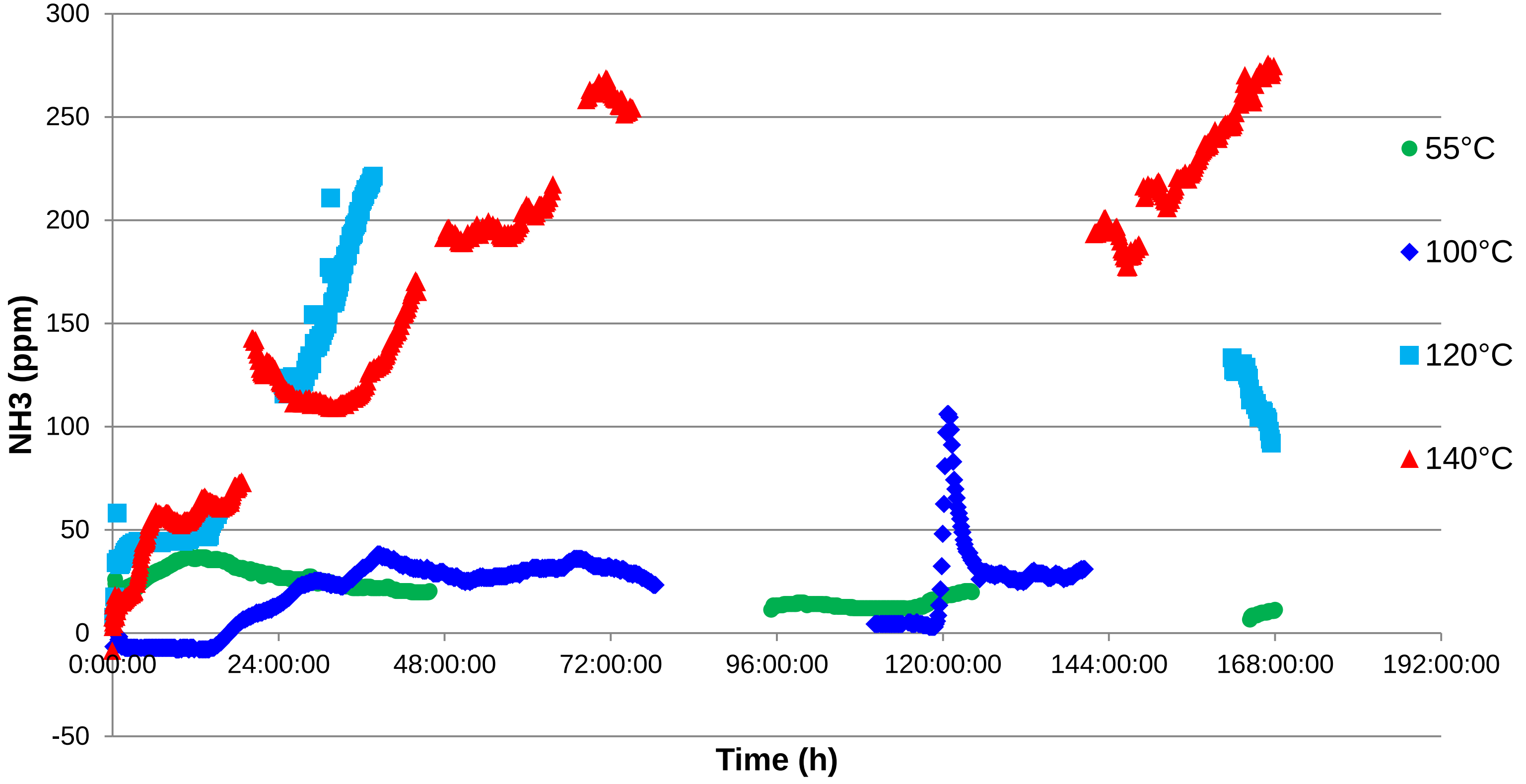
1.2 Temperature

- HEPO is formed at higher temperature, confirms a mechanism of cyclization
- HEI is less formed at higher temperature, maybe due to less Oxygen present in the liquid

	P20	P30	P17	P19
Temperature	55	100	120	140
MEA	23.66%	27.60%	20.09%	19.08%
OZD	0.0097%	0.0230%	0.0480%	0.0314%
HEI	0.0099%	0.3838%	0.1489%	0.0359%
HEPO	0.0315%	0.0507%	0.2555%	1.0057%

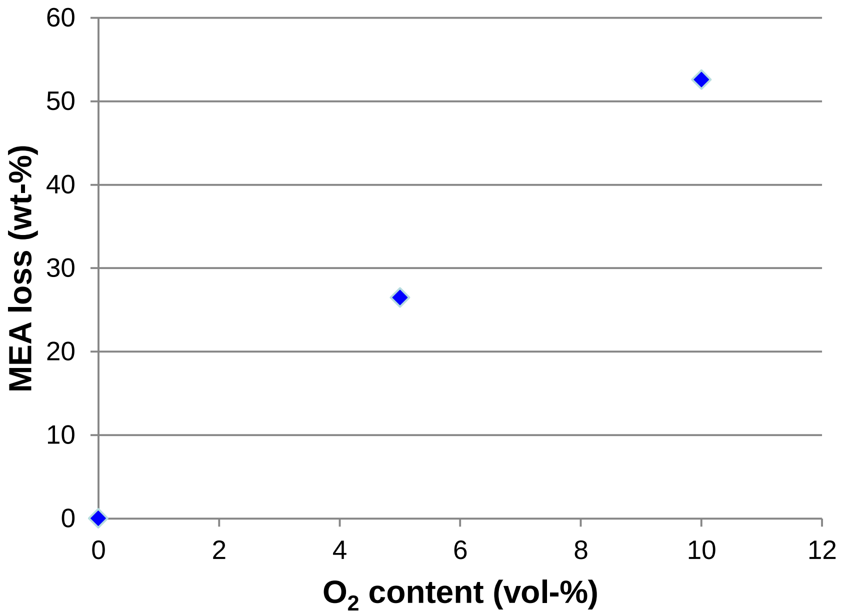
1.2 Temperature

- NH_3 emissions



1.3 Gas composition: O_2

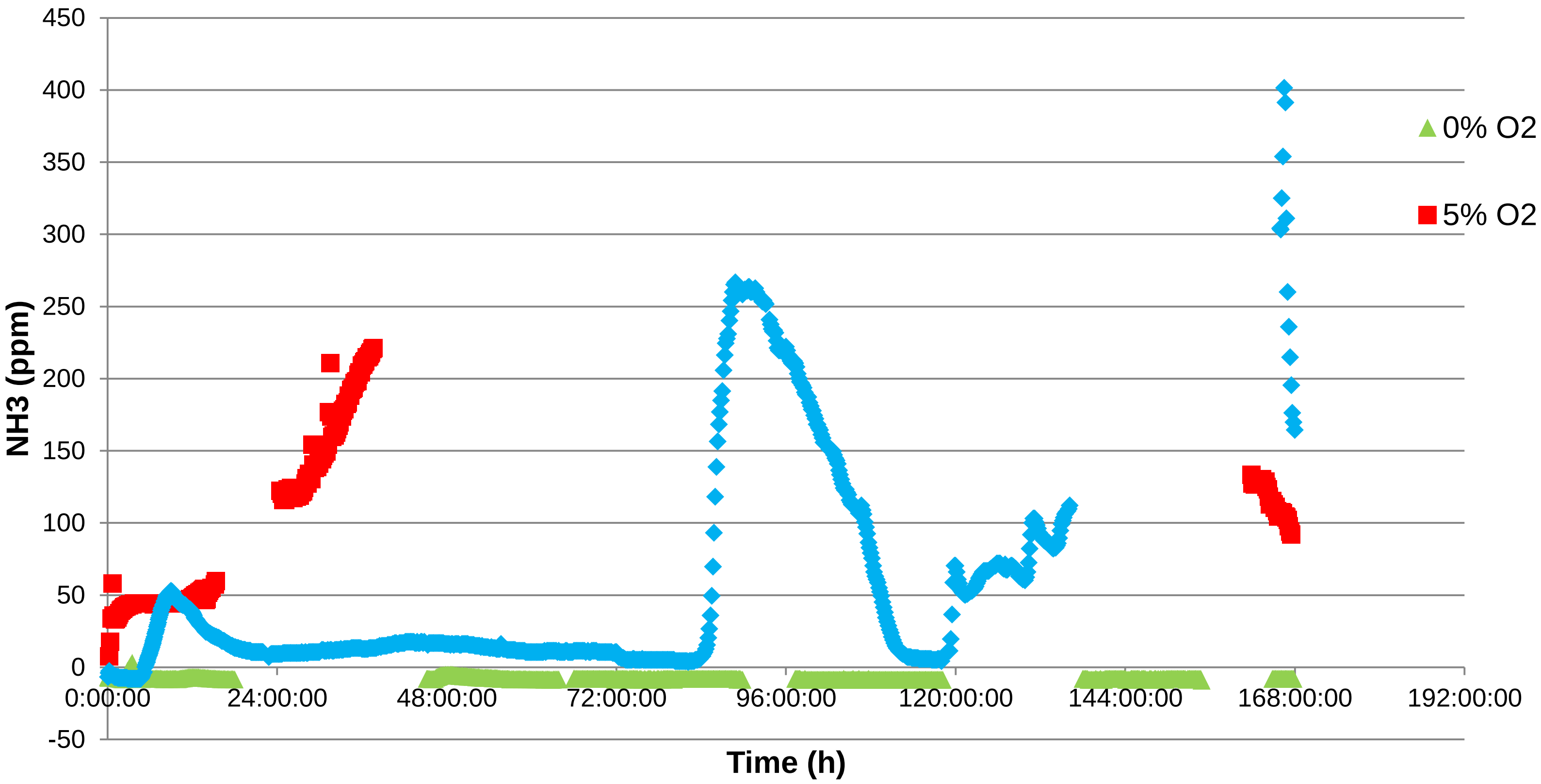
- The more oxygen, the more degradation
- More oxygen => more HEI and less HEPO
- In the absence of O_2, no degradation at 120°C



Vol-% Oxygen	P27 0	P17 5	P28 10
MEA	38.60%	20.09%	20.11%
OZD	0.0577%	0.0480%	0.0328%
HEI	0.0000%	0.1489%	0.3386%
HEPO	0.0000%	0.2555%	0.1002%

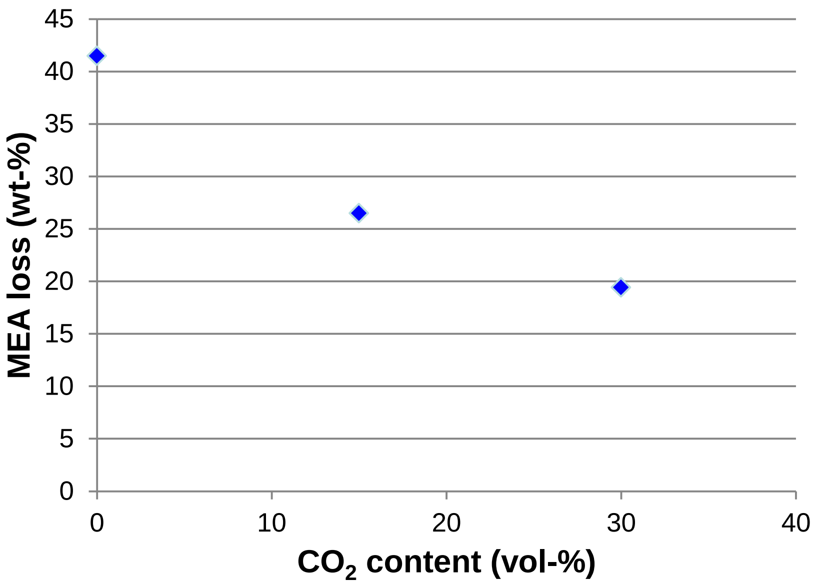
1.3 Gas composition: O_2

- NH_3 emissions



1.3 Gas composition: CO_2

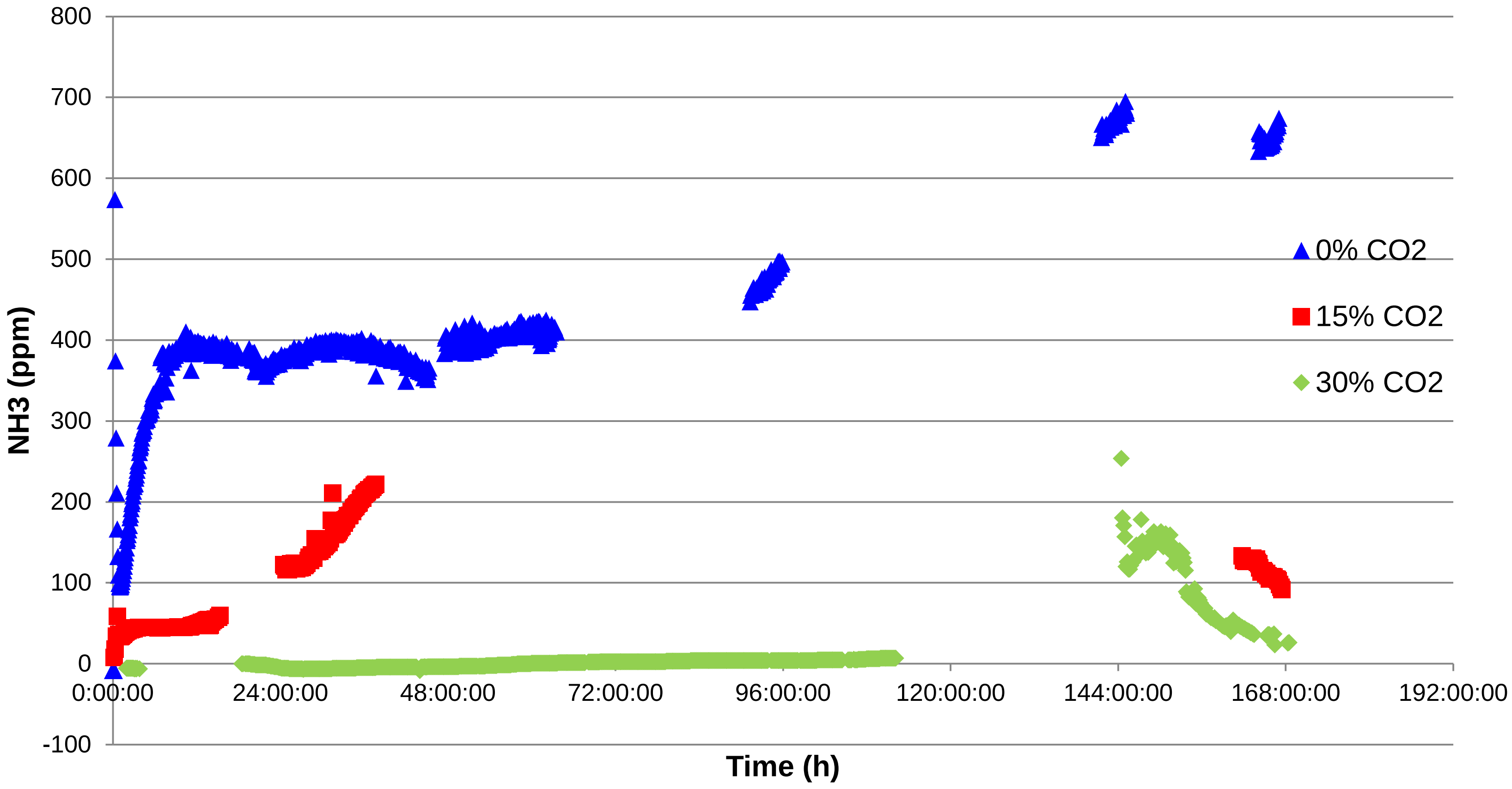
- The more CO_2, the less degradation
- Under-estimated effect
- 3rd point to be confirmed



	P18	P17	P29-P31
vol-% CO2	0	15	30
MEA	12.64%	20.09%	22.31%
OZD	0.0145%	0.0480%	0.0942%
HEI	0.4491%	0.1489%	0.3006%
HEPO	0.0868%	0.2555%	0.0000%

1.3 Gas composition: CO_2

- NH_3 emissions

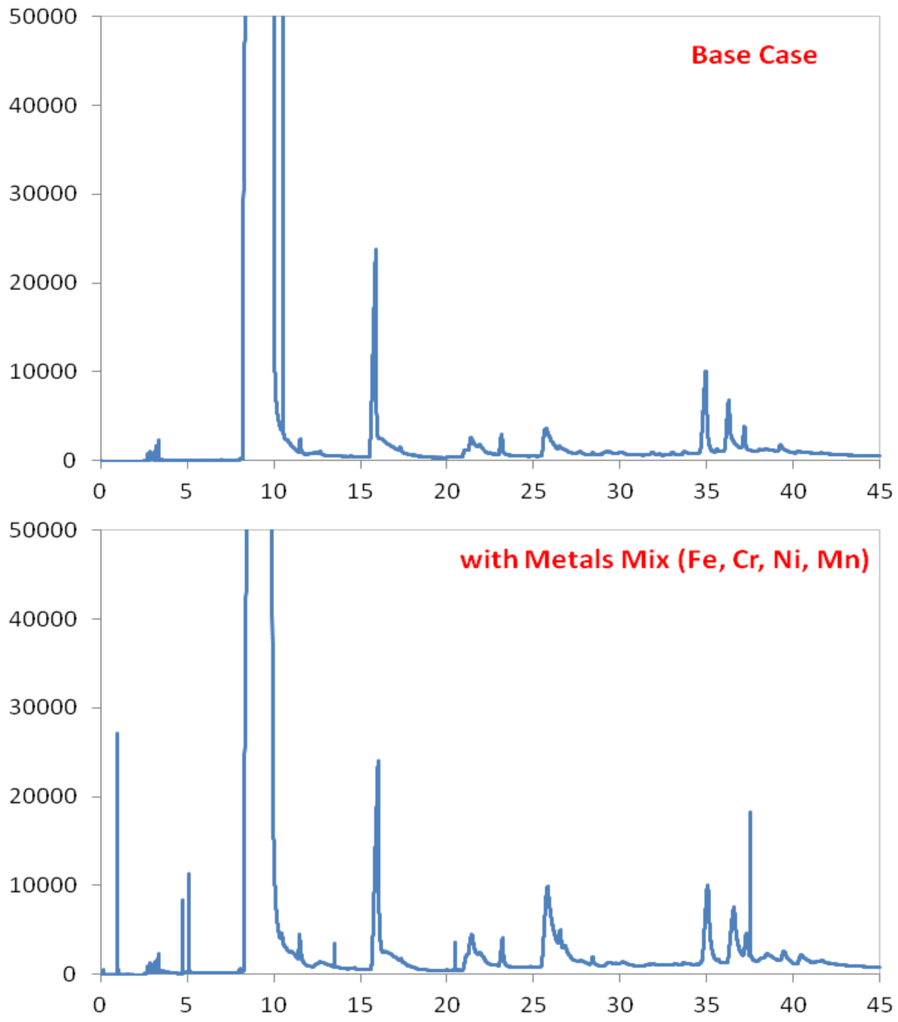


1.4 Metals

- Metals catalyze degradation:

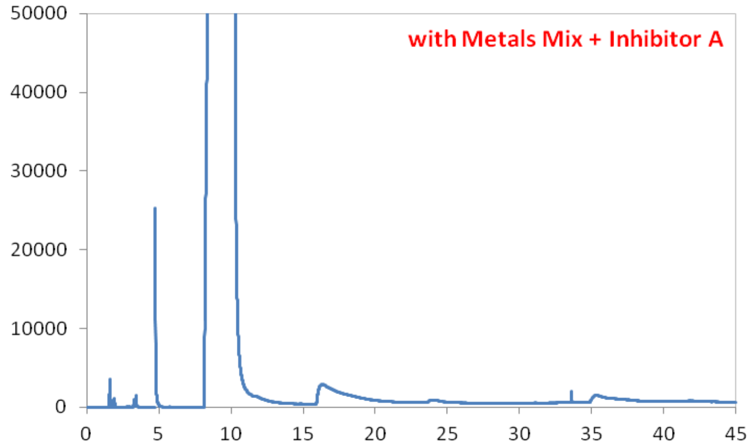
- $Mn^{7+} > Fe^{2+}/Cu^{2+} \geq Cu^{2+} > Cr^{3+}/Ni^{2+} > Fe^{2+} > Fe^{3+} > Cr^{3+} > V^{5+} >> $ Ti, Co, Mo, Ni, Sn, Se, Ce, Zn

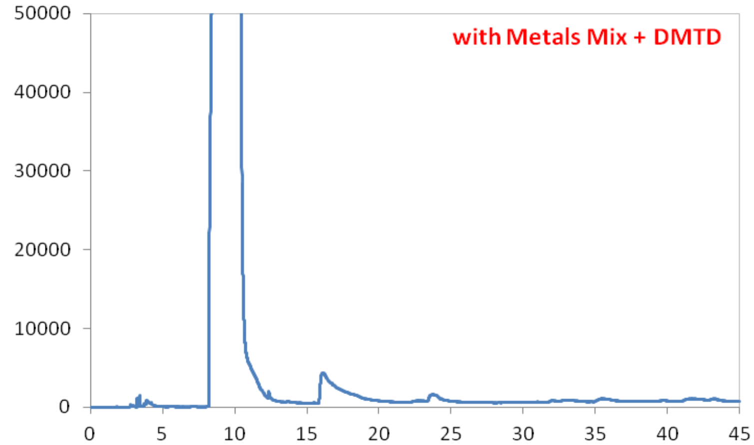
- 49% MEA loss instead of 32.5%!

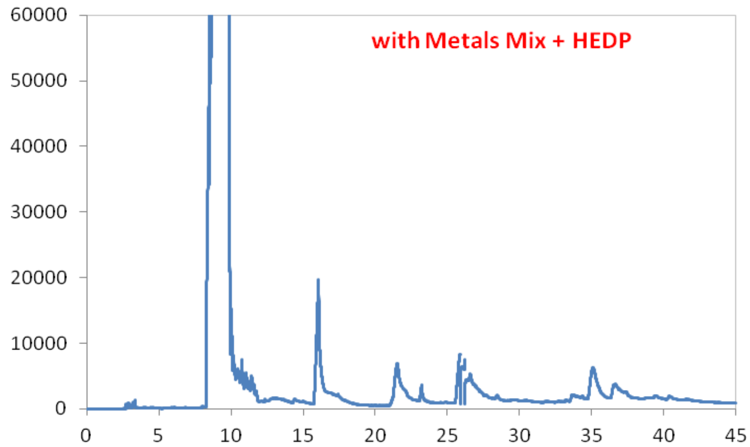


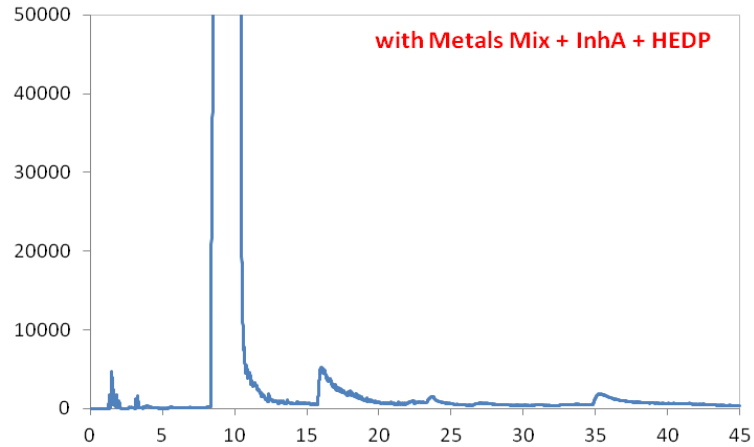
1.4 Metals and inhibitors

- Inh. A, DMTD, HEDP, Inh.A/HEDP



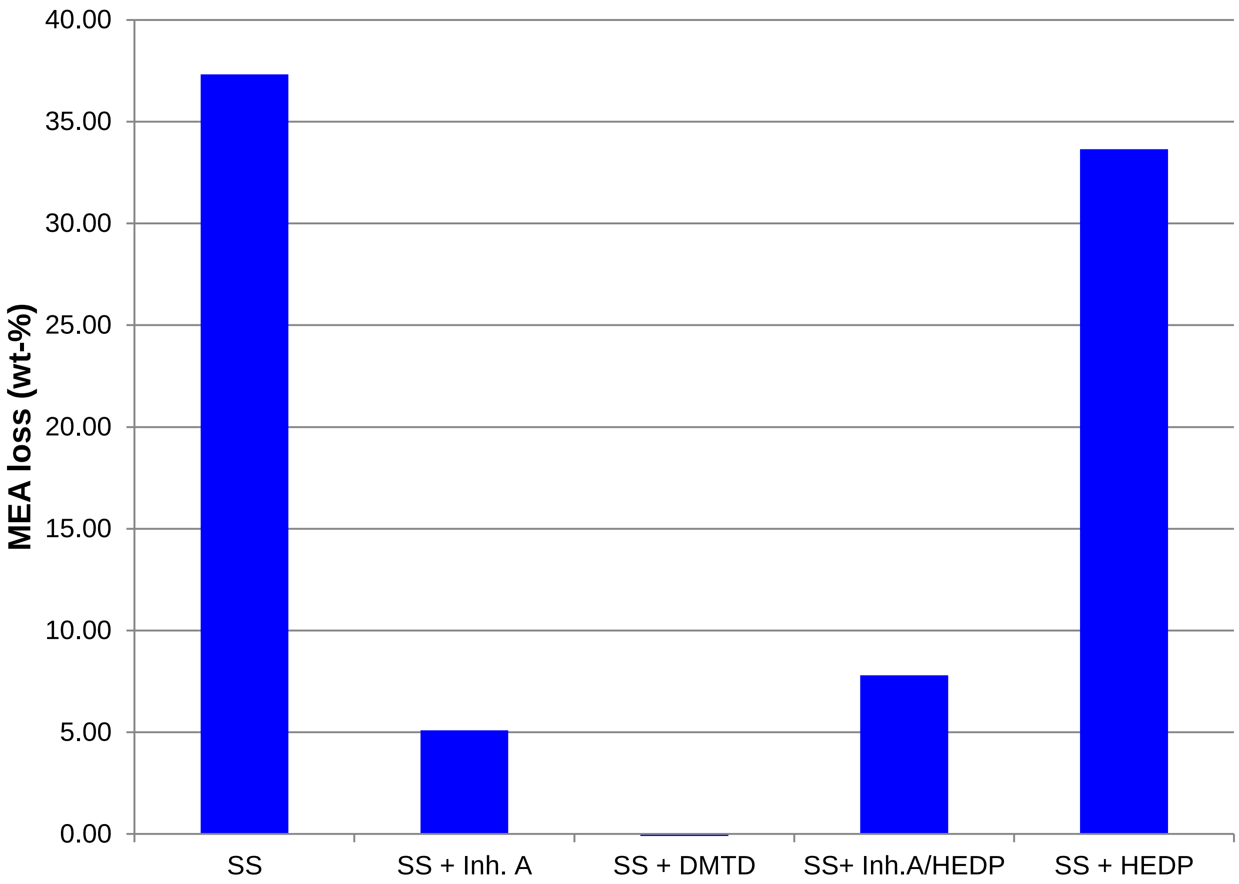






1.4 Metals and inhibitors

- Inh. A, DMTD, HEDP, Inh.A/HEDP



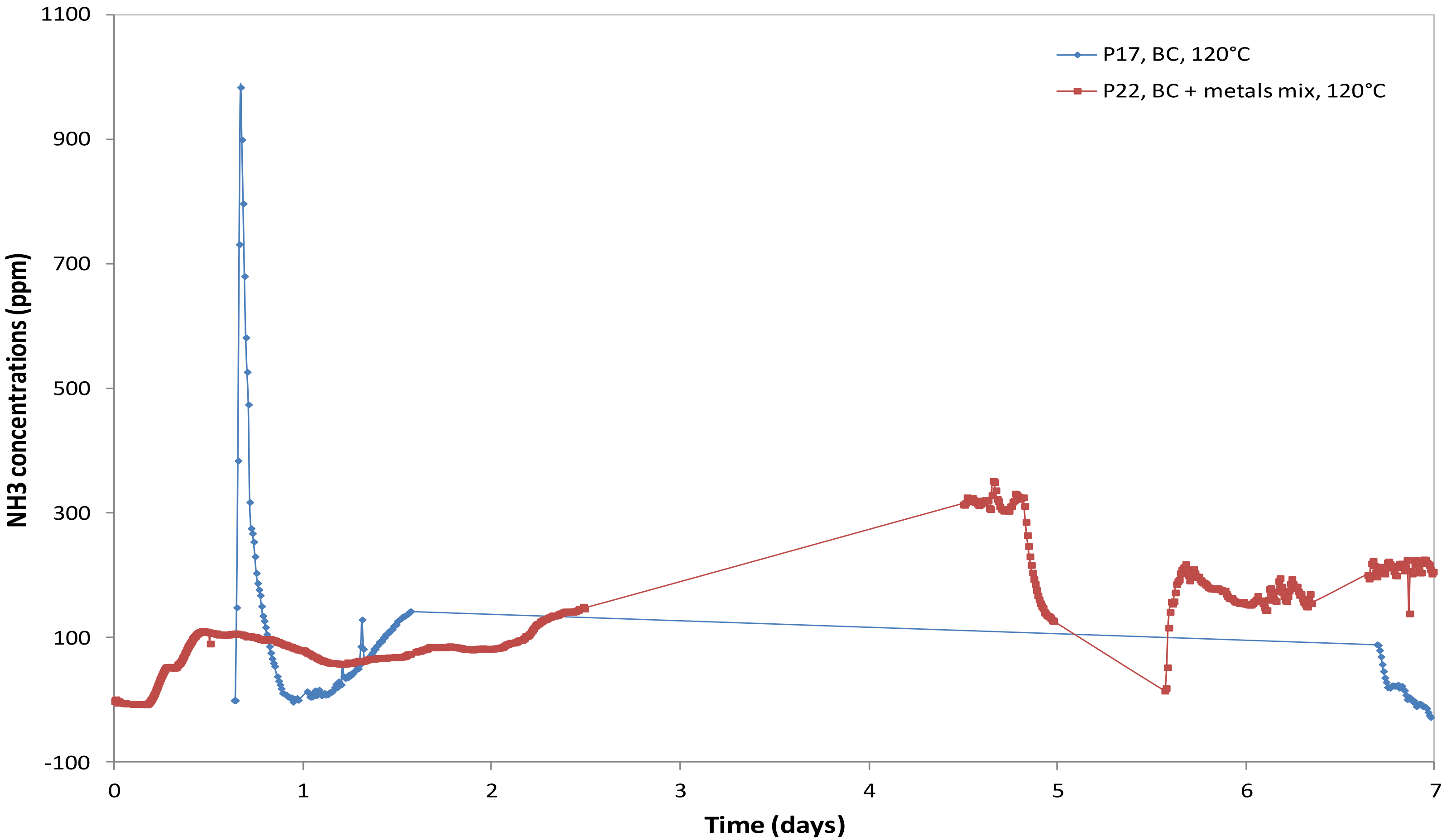
1.4 Metals and inhibitors

- Good inhibition of HEI formation with Inh. A, DMTD, Inh.A/HEDP, but not with HEDP alone
- HEPO formation is only inhibited by DMTD, but inthis case, more OZD

Additives	P22 SS	P23 SS + Inh. A	P24 SS + DMTD	P25 SS+ Inh.A/HEDP	P26 SS + HEDP
MEA	14.44%	27.43%	26.72%	23.98%	14.96%
OZD	0.0546%	0.0393%	0.1253%	0.0439%	0.0442%
HEI	0.4095%	0.0000%	0.0000%	0.0000%	0.5027%
HEPO	0.2544%	0.1987%	0.0648%	0.1815%	0.2309%

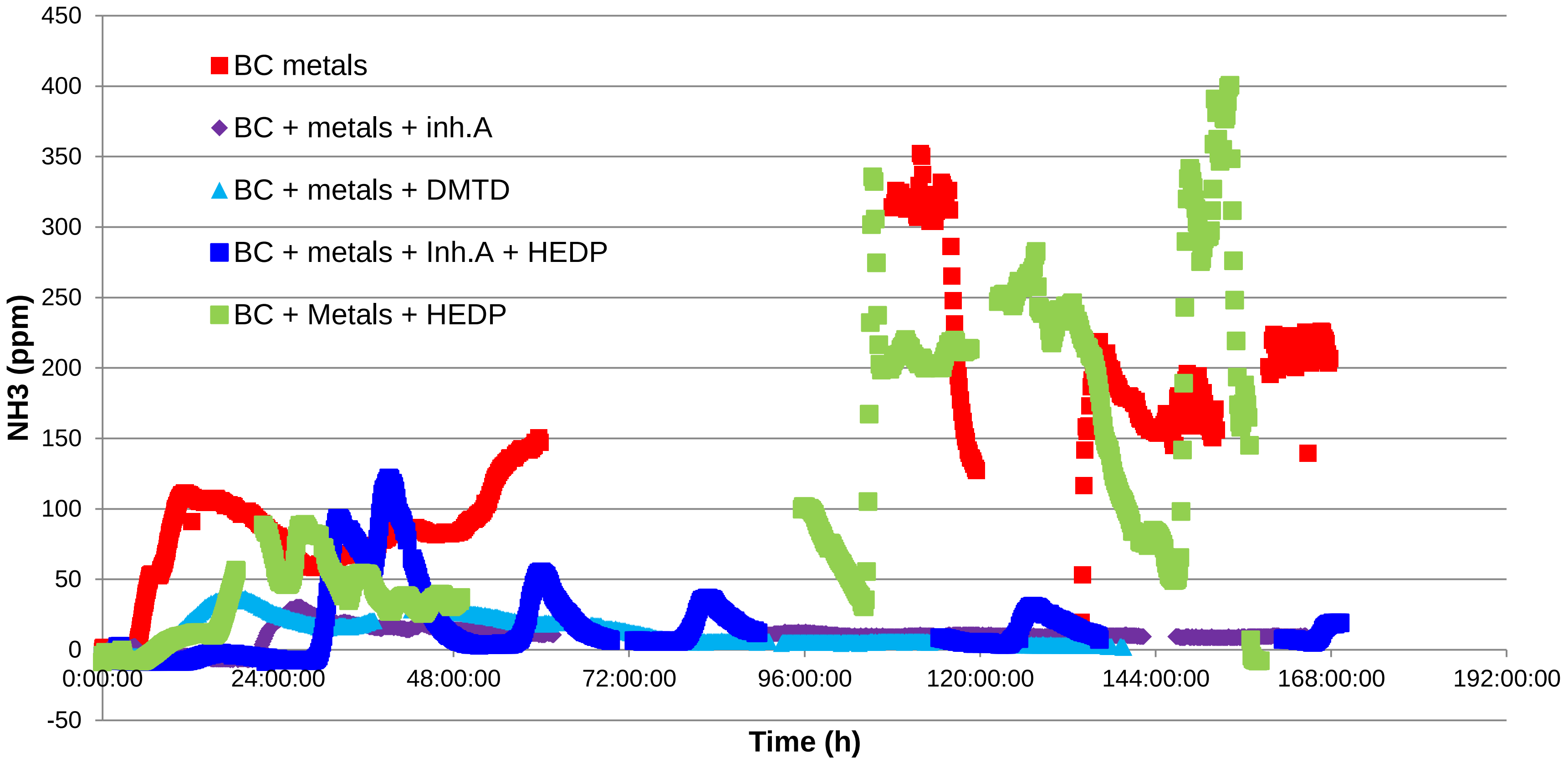
1.4 Additives

- NH_3 emissions: influence of metals?



1.4 Additives

- NH_3 emissions



1.5 Thermal degradation

- Objective is to test the stability of degradation inhibitors at high temperatures
- Stainless steel cylinders filled with amine solvents and set in an oven at 120 - 140°C
- Long-lasting tests: 3 weeks

1.5 Thermal degradation

- Objective is to test the stability of degradation inhibitors at high temperatures
- Tests at 120 and 140°C in stainless steel cylinders

P1 - 120°C	Start: 29/08/2012	**P2 - 140°C**	Start: 28/09/2012
Θ1	MEA 30% + CO_2	Θ1	MEA 30% + CO_2
Θ2	MEA 30% + CO_2 + inh.A	Θ2	MEA 30% + CO_2 + inh.A
Θ3	MEA from pilot + CO_2	Θ3	MEA from pilot + CO_2
Θ4	MEA from pilot + CO_2 + inh. A	Θ4	MEA from pilot + CO_2 + inh. A
P3 - 140°C	Start: 09/11/2012	**P4 - 140°C**	Start: 14/12/2012
Θ1	MEA + CO_2 + metal mix	Θ1	MEA
Θ2	MEA + CO_2 + HEDP	Θ2	MEA + metal mix
Θ3	MEA + CO_2 + DMTD	Θ3	MEA + CO_2 + TDE
Θ4	MEA + CO_2 + metal mix + HEDP	Θ4	MEA + CO_2 + DTPA
		Θ5	MEA + CO_2 + DTDP
		Θ6	MEA + CO_2 + inh. A + HEDP
		Θ7	MEA + CO_2 + metal mix + inh. A

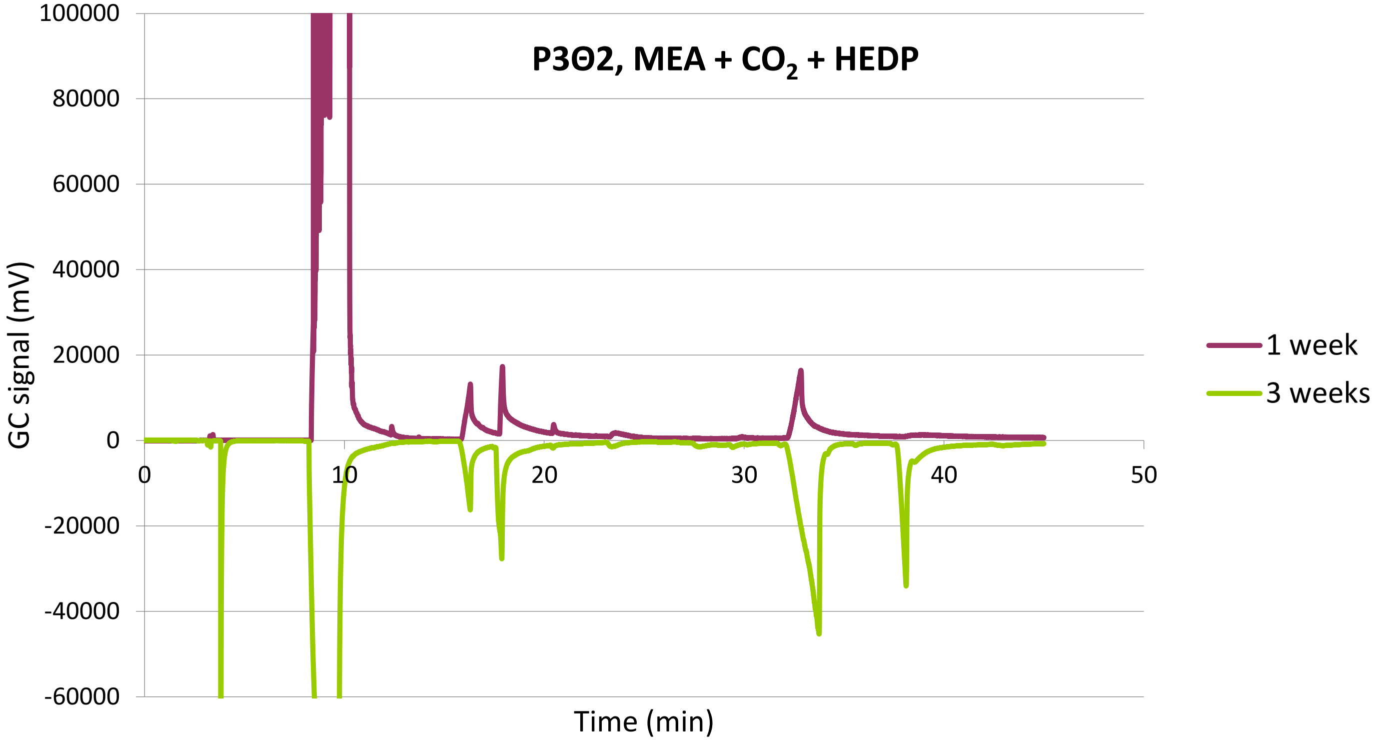
1.5 Thermal degradation

- Inh. A has few effect on thermal degradation
- DMTD is not stable at 140°C
- Thermal degradation is not catalyzed by metals

MEA loss (wt-%)	120°C	140°C
MEA/CO2	11.58	40.70
MEA/CO2 + inh.A	7.88	38.54
Degraded MEA/CO2	8.49	30.58
Degraded MEA/CO2 + inh.A	6.44	28.27
MEA/CO2 + SS		40.56
MEA/CO2 + HEDP		41.63
MEA/CO2 + DMTD		54.00
MEA/CO2 + HEDP + SS		42.90

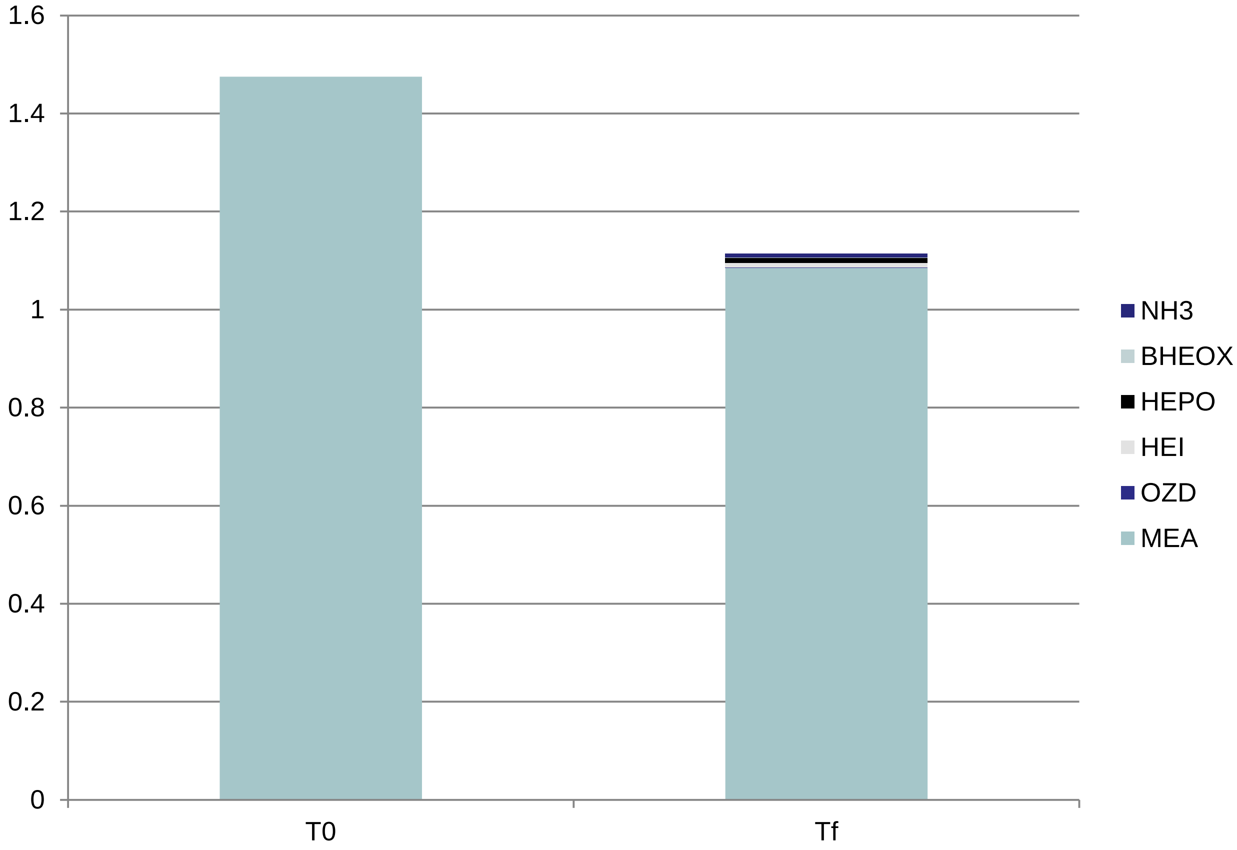
1.5 Thermal degradation

- No HEPO nor HEI in thermal degraded sample (120 – 140°C)
- But other products: HEIA and HEEDA ? Not quantified…



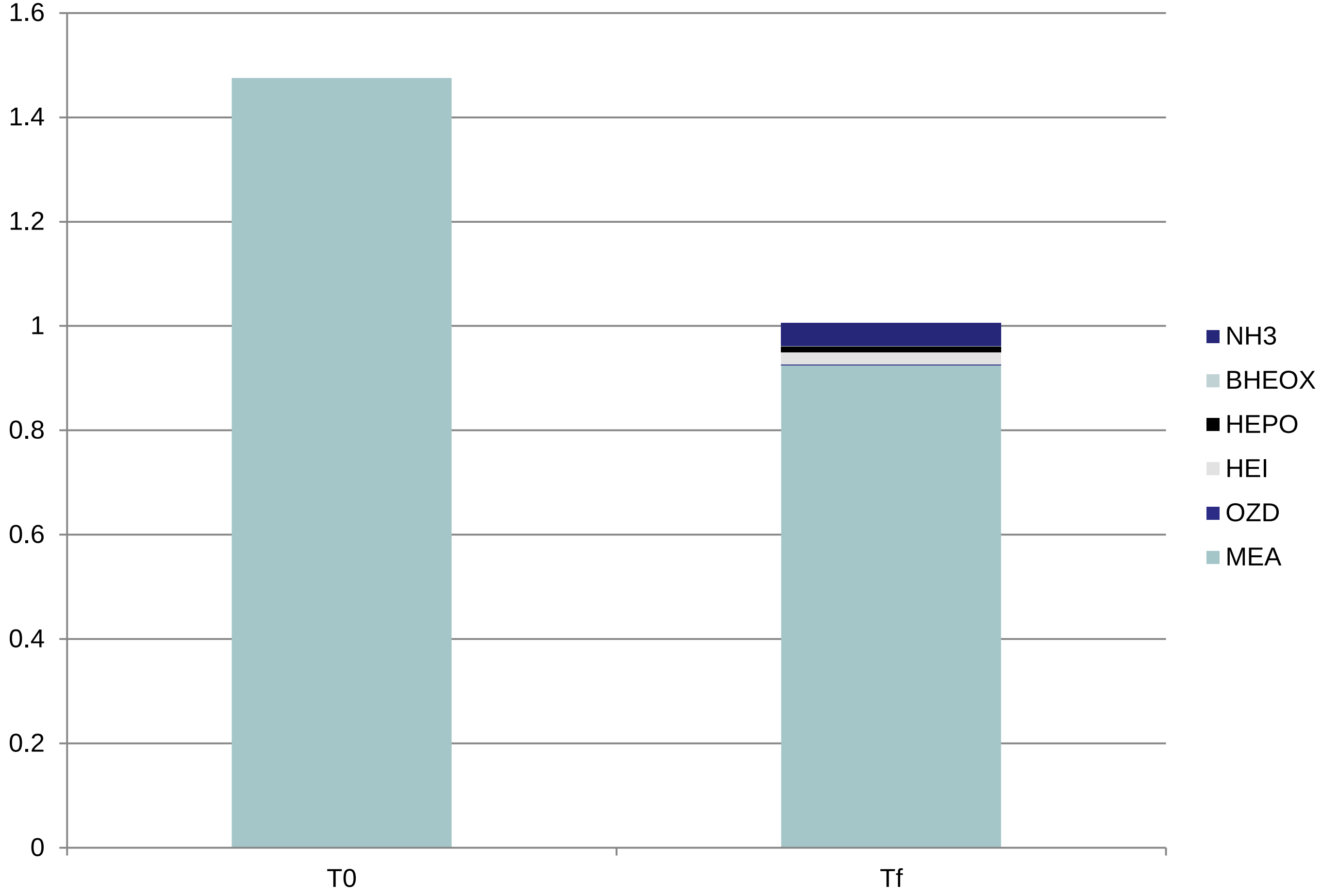
1. MEA degradation

- Nitrogen balance: P17



1. MEA degradation

- Nitrogen balance: P22



Degradation Modeling

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2. Degradation modeling

- 2 types de dégradation :
  - Dégradation oxydative
  - Dégradation thermique
- Expérimentation : 1/3 MEA disparaît en 4 mois

4) Dégradation : réaction et cinétique

Travail de Ségolène

- Equation :

$$MEA + \frac{3}{2} O_2 \rightarrow NH_3 + 2HCOOH$$

- Vitesse :

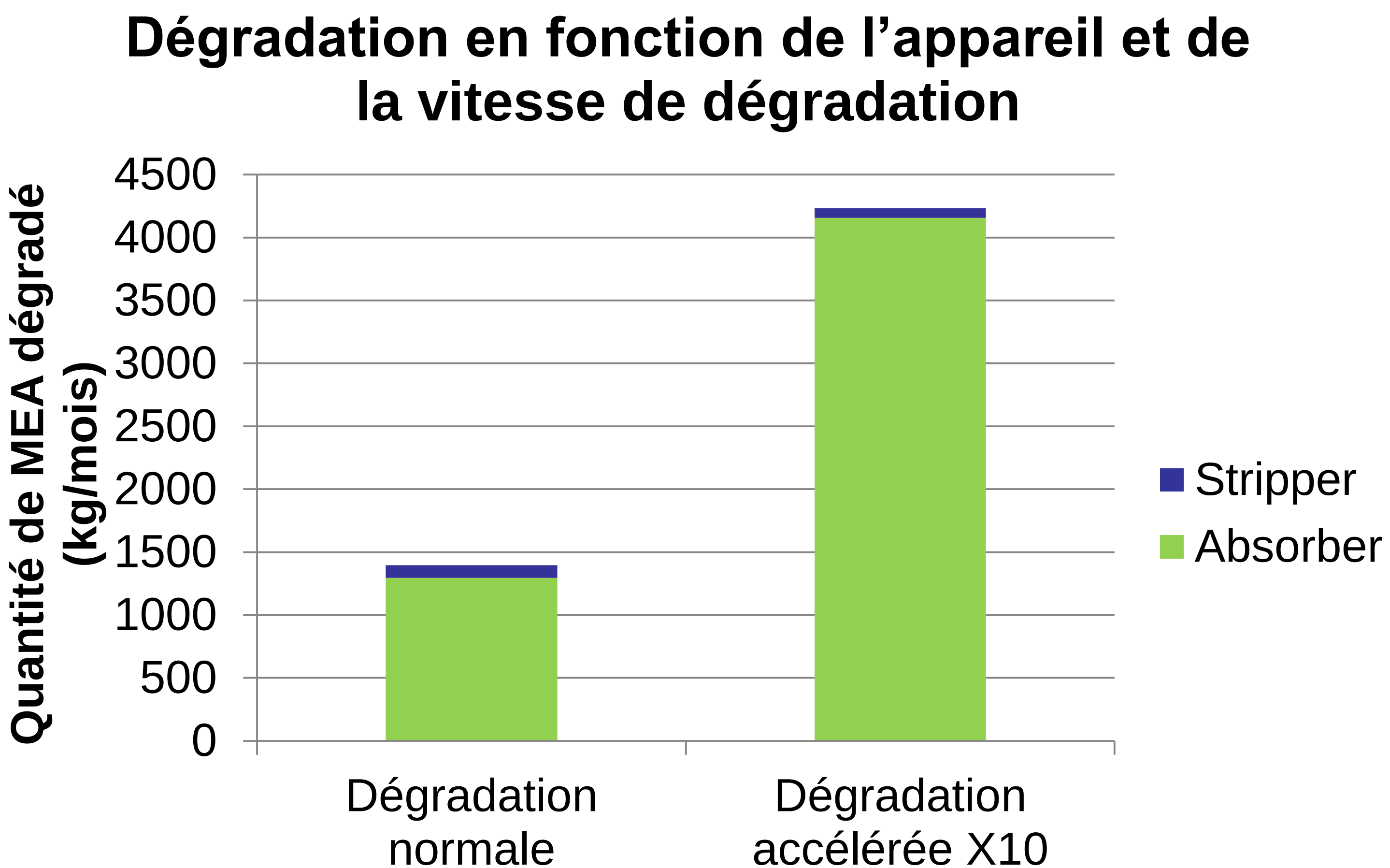
$$r = k' \, e^{-\frac{Ea}{RT}} [MEA]^{0.015} [O_2]^{2.91}$$

Avec $$k' = \frac{k}{1 + k_0 [CO_2]^{0.18}}$$

=> k, E_a et ordre de O_2

=> Ordre de CO_2 et de MEA

Comparaison de vitesses de réaction (1)



Comparaison de vitesses de réaction (2)

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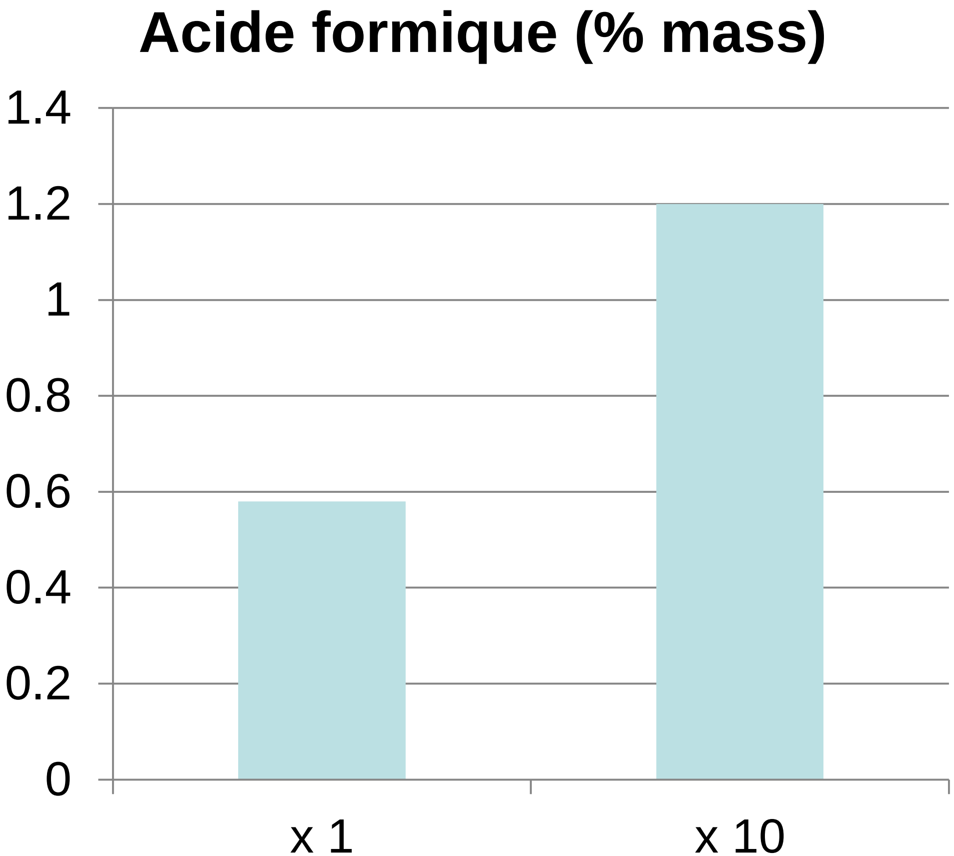
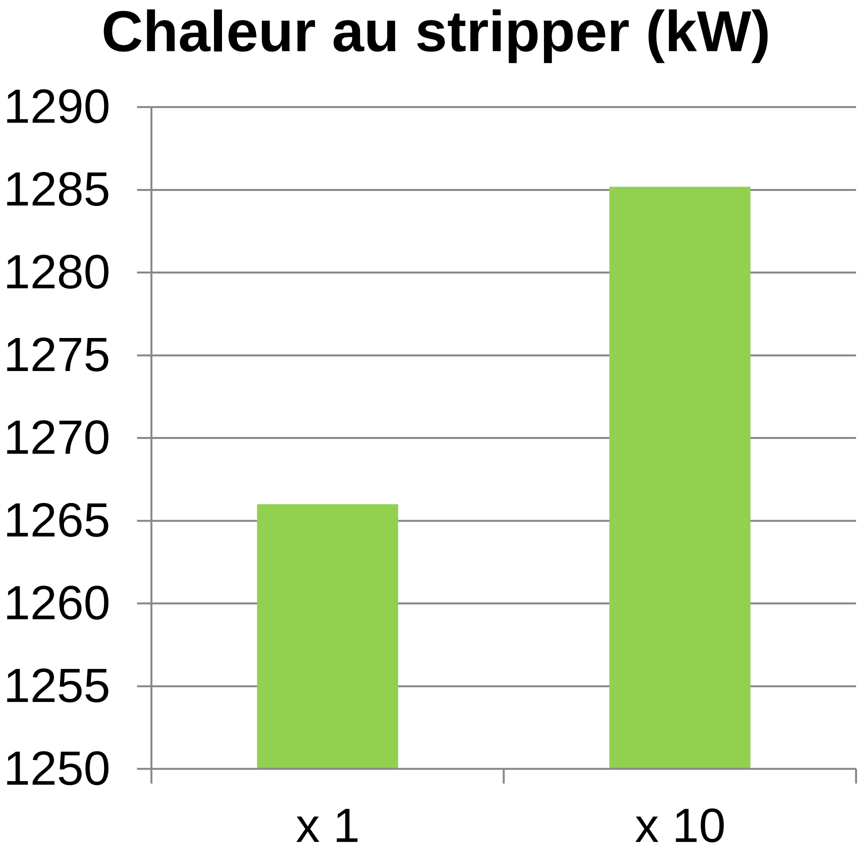
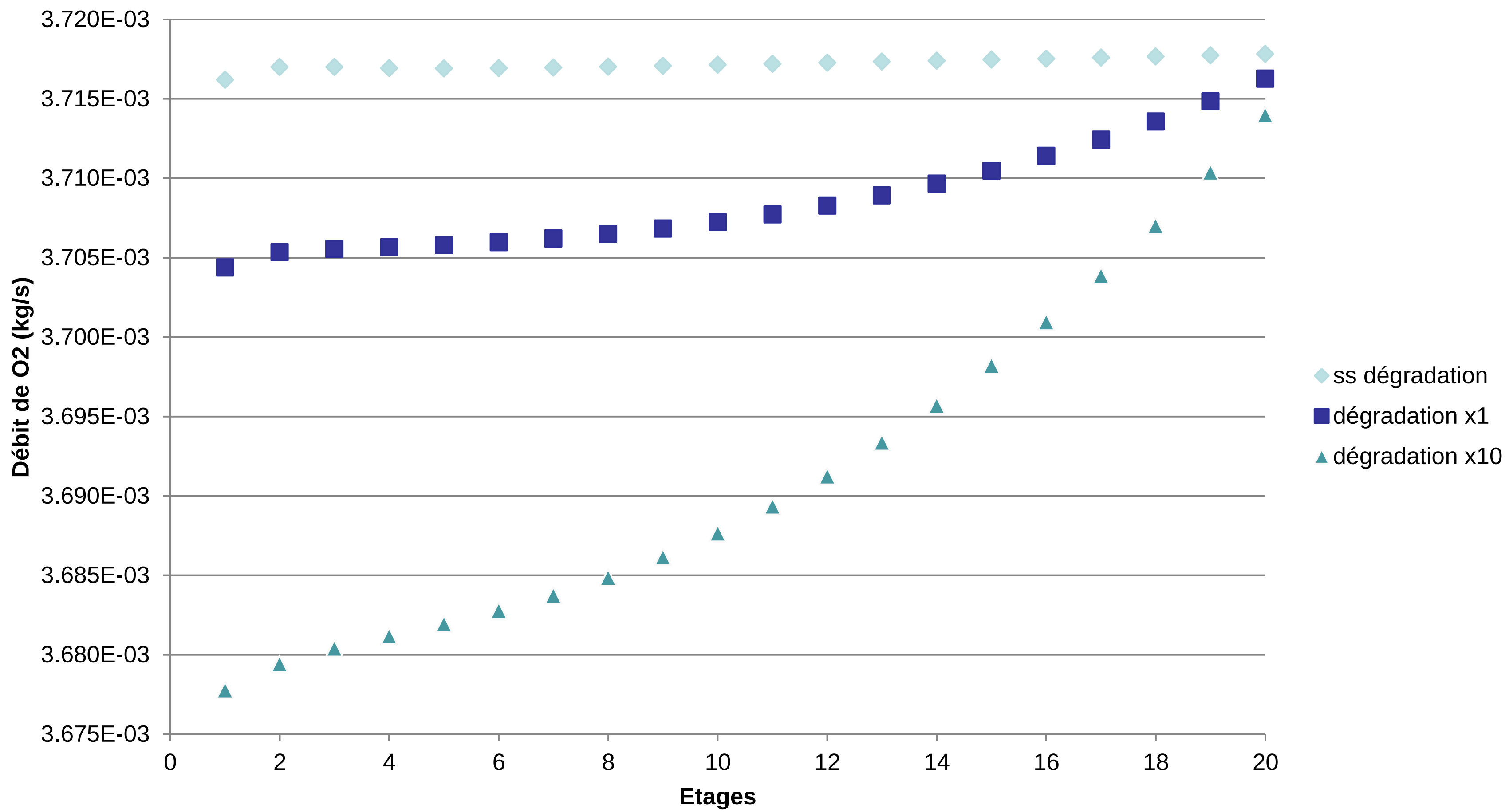
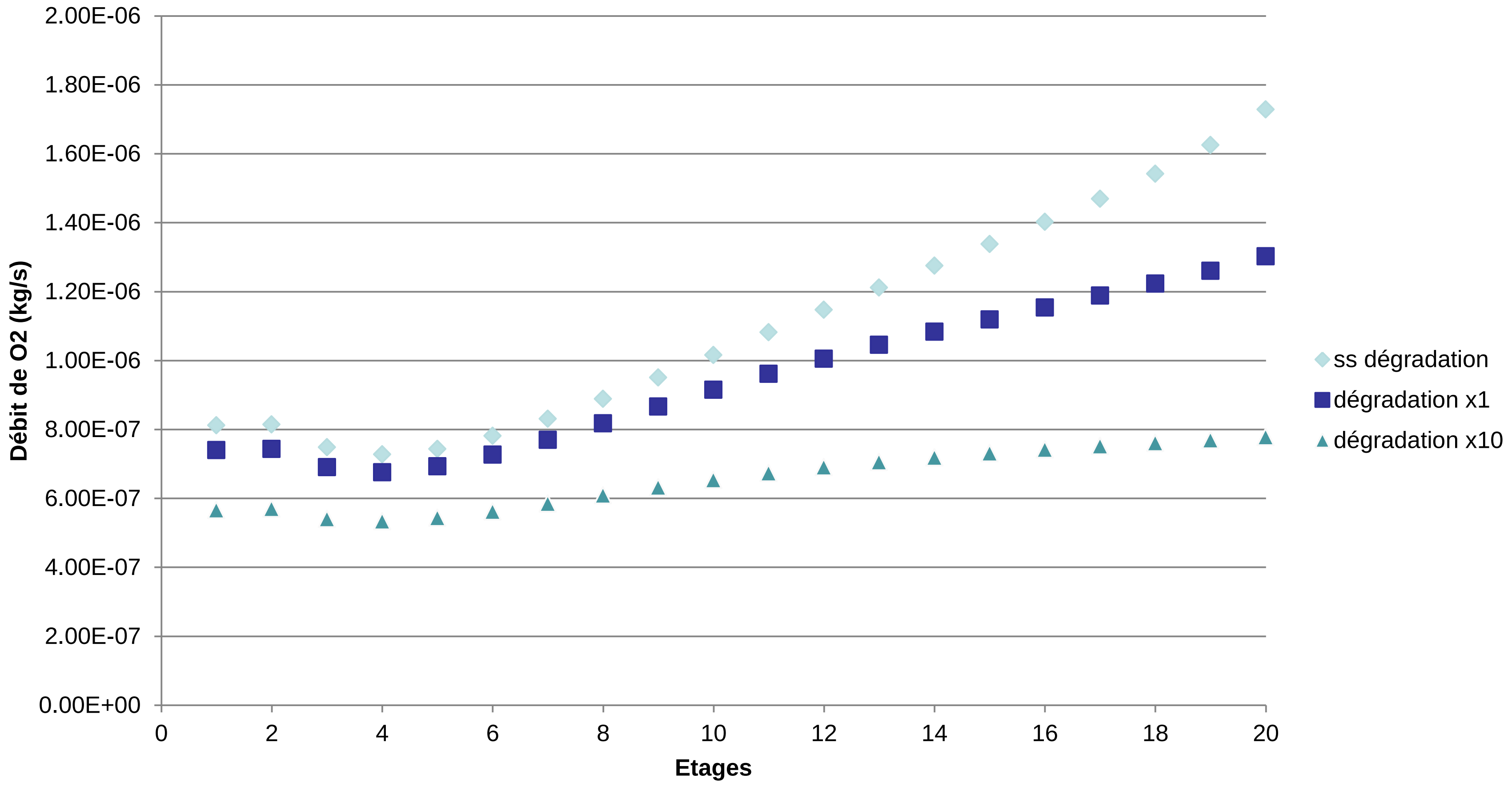




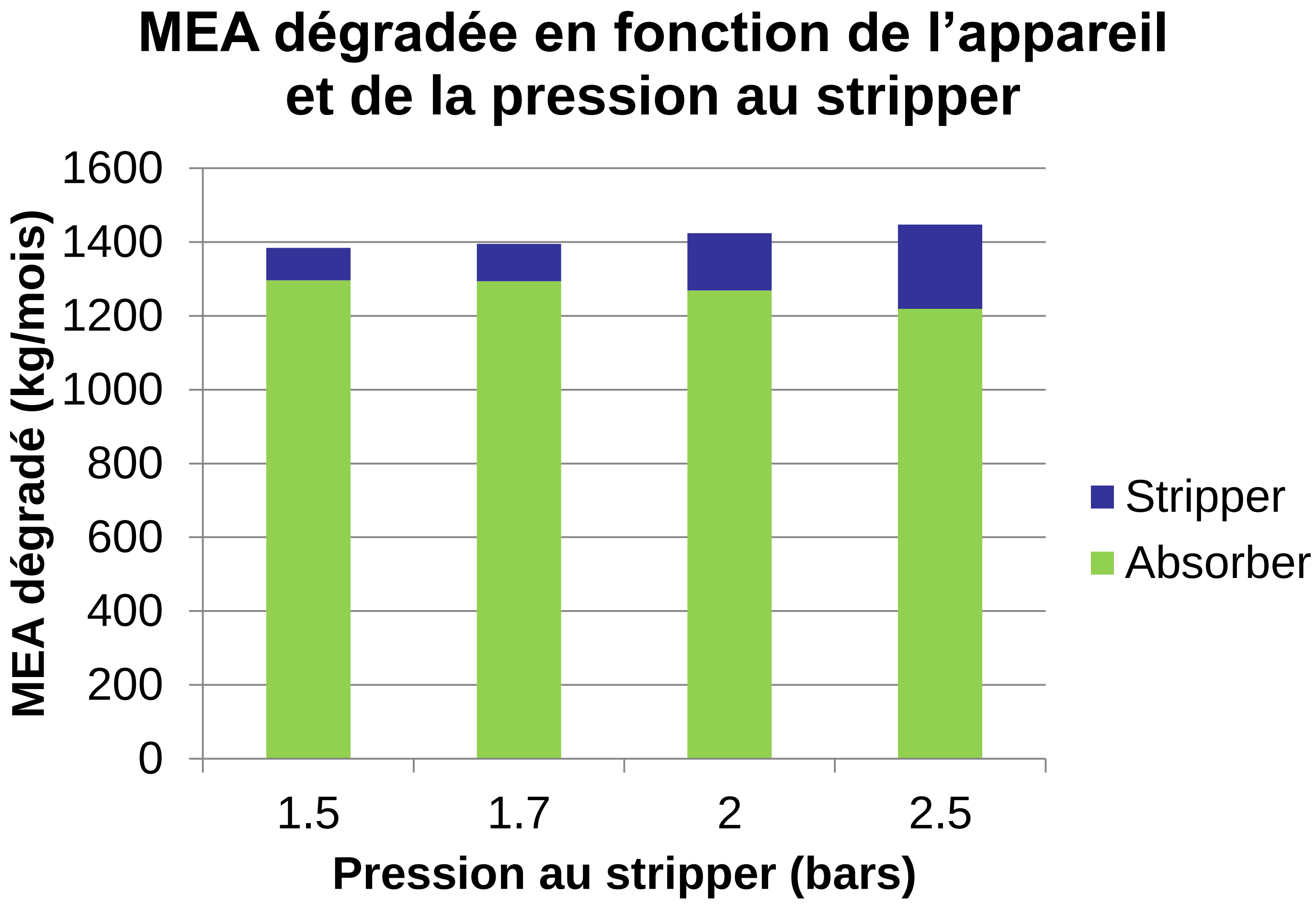
Profil de O2 vapeur dans l'absorber



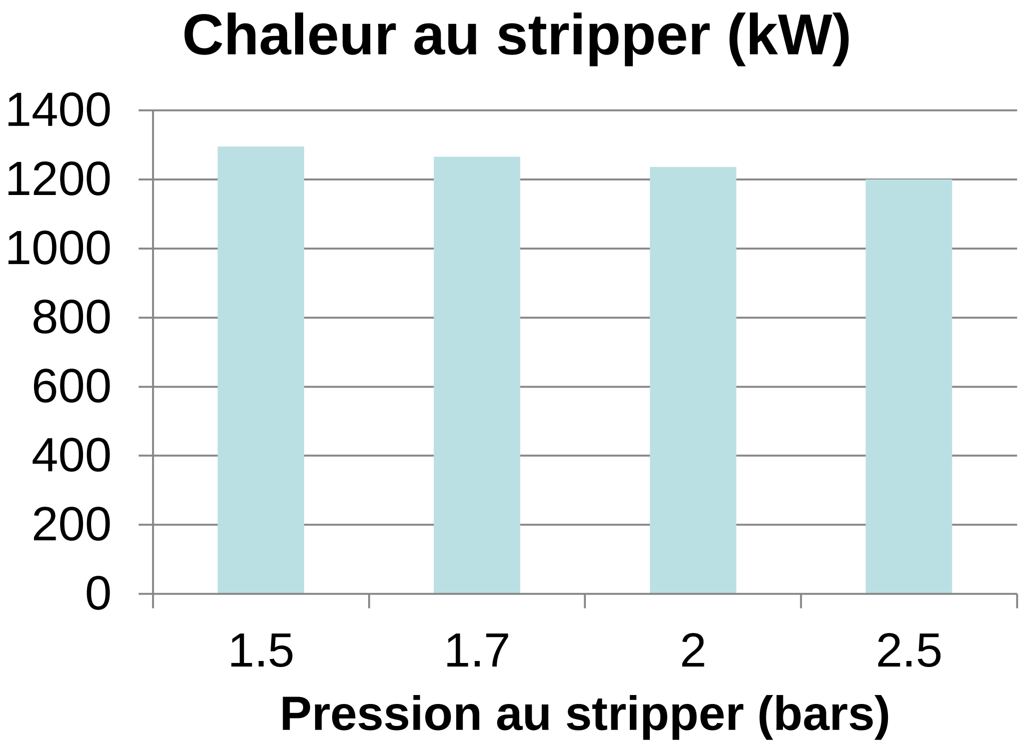
Profil de O2 liquide dans l'absorber

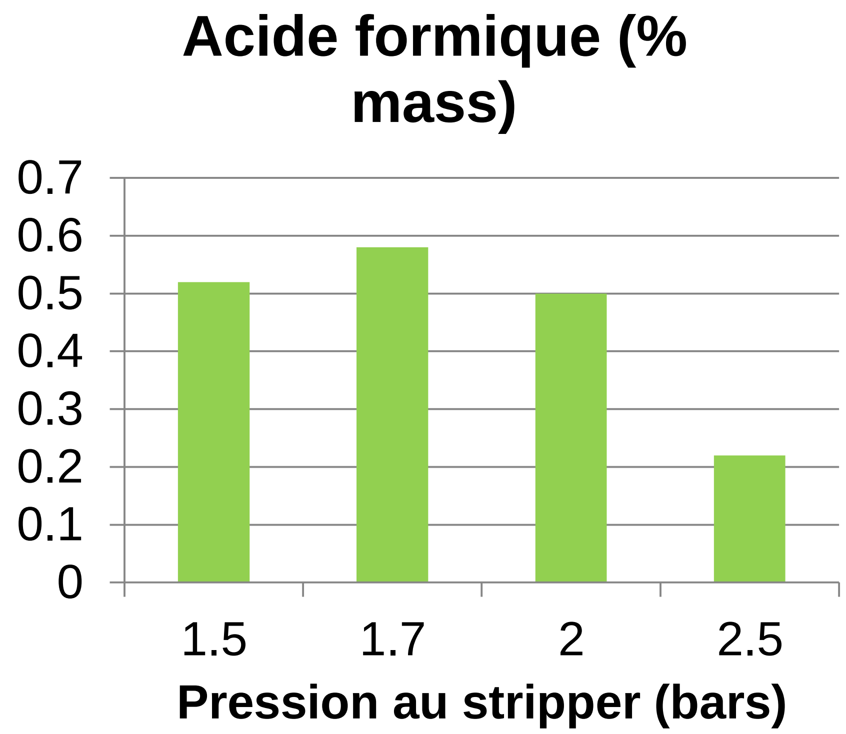


Influence de la pression au stripper (1)



Influence de la pression au stripper (2)





Perspectives

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3. Perspectives

- January 2013 : last experiments
  - Repetition of failed experiment
  - O_2 and CO_2
  - Limit: FTIR availability
- February 2013 : Model building and exploitation
- March 2013 : Beginning of the redaction
- Mai 2013 : End of the redaction
- June-July 2013 : Public defense

Thank you for your attention!

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