Degradation inhibitors and metal additives: impact on solvent degradation

Littérature review

Grégoire Léonard

24th April 2012

Table of Content

LABORELEC
GDF SUEZ

Université de Liège

1. Introduction

24th April 2012

1. Introduction

Chemical reactions taking place during the CO_2 capture in Monoethanolamine (MEA):

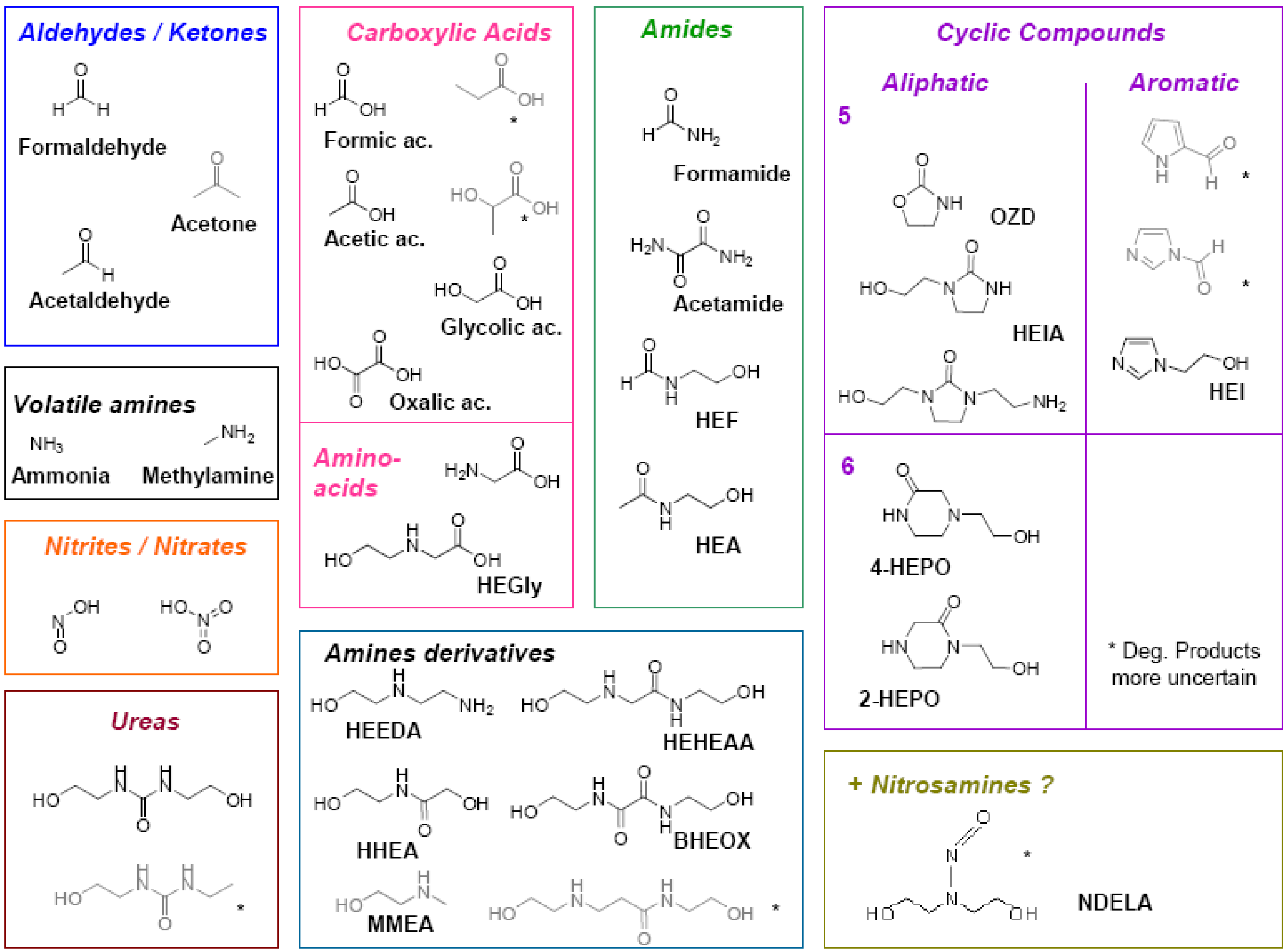
$2\ H_2O \leftrightarrow H_3O^+ + OH^-$
$C_2H_7NO + H_3O^+ \leftrightarrow C_2H_8NO^+ + H_2O$
$CO_2 + 2\ H_2O \leftrightarrow H_3O^+ + HCO_3^-$
$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$
$C_2H_7NO + HCO_3^- \leftrightarrow C_3H_6NO_3^- + H_2O$

1. Introduction

4 main degradation types

- Oxidative
- Thermal
- CO_2
- SO_x and NO_x

1. Introduction



2. Metal effect

24th April 2012

2. Metal effect

Mechanism (oxidative degradation):

- $RH \rightarrow R^{\bullet} + H^{\bullet}$ Initiation
- $R\text{-}R \rightarrow 2\, R^{\bullet}$

- $R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ Propagation
- $ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$

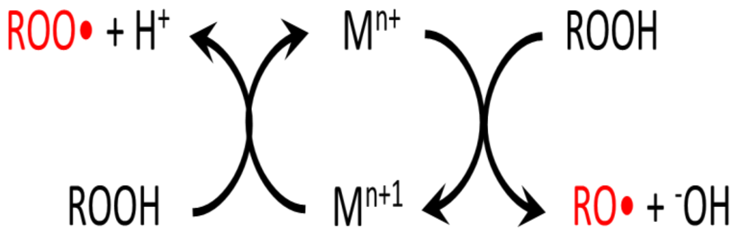
- $ROOH \rightarrow RO^{\bullet} + HO^{\bullet}$
- $2\, ROOH \rightarrow ROO^{\bullet} + RO^{\bullet} + H_2O$

- Termination

2. Metal effect

Metal catalyzed degradation reactions!

- $Fe^{2+} + O_2 \rightarrow Fe^{3+} + O^{\bullet}{}_2^{-}$
- $2H^+ + Fe^{2+} + O^{\bullet}{}_2^{-} \rightarrow Fe^{3+} + HOOH$

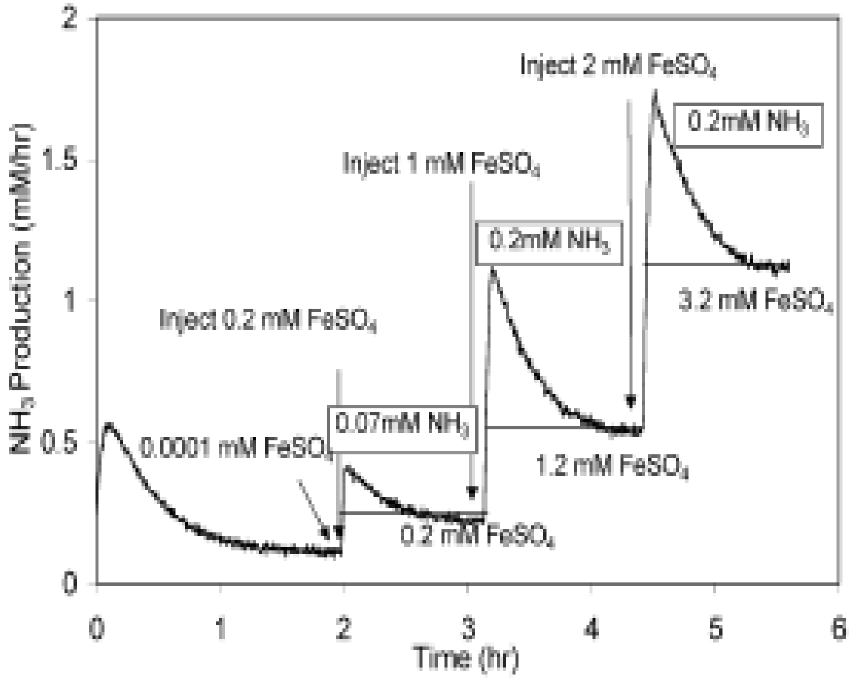


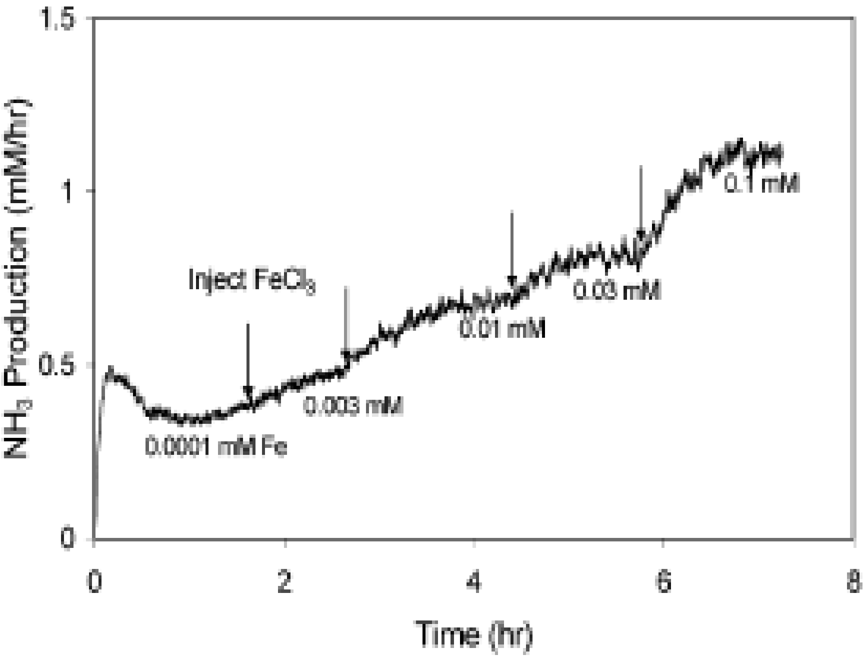
Metal have an essential catalytic effect:

- ***generation of free radical***
- ***initiation and propagation of chain reactions***

2. Metal effect: Fe

Effect of Fe^{2+} and Fe^{3+} on NH_3 evolution

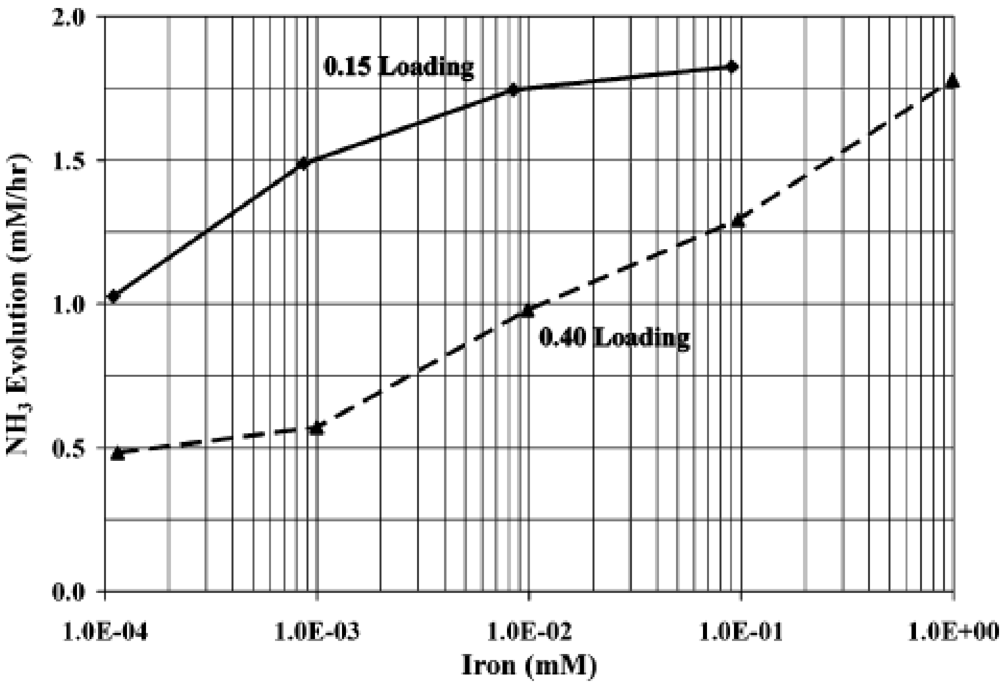




⇒ Fe^{2+} more active!

2. Metal effect: Fe^{2+}

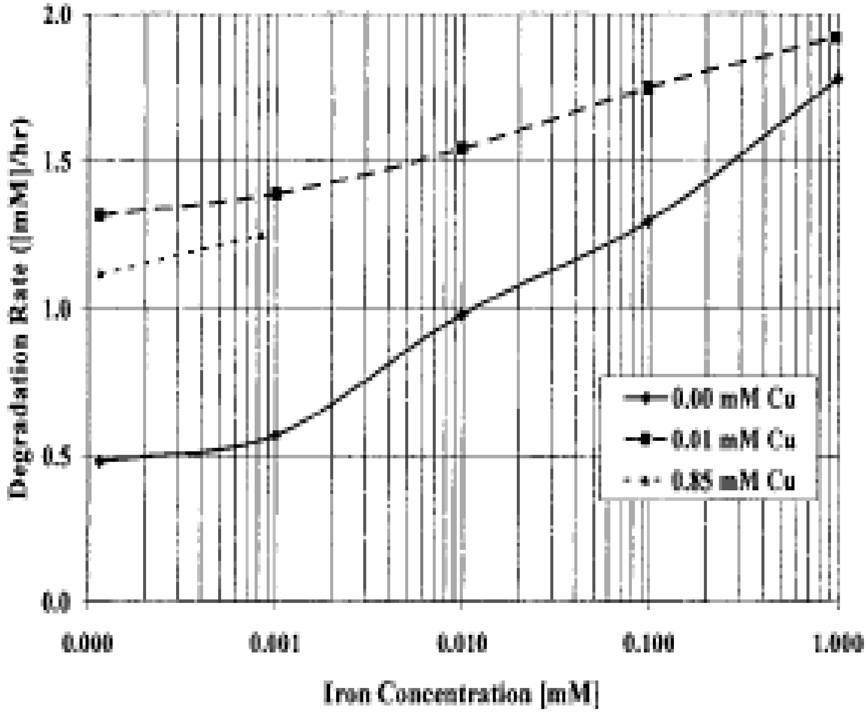
Effect of loading

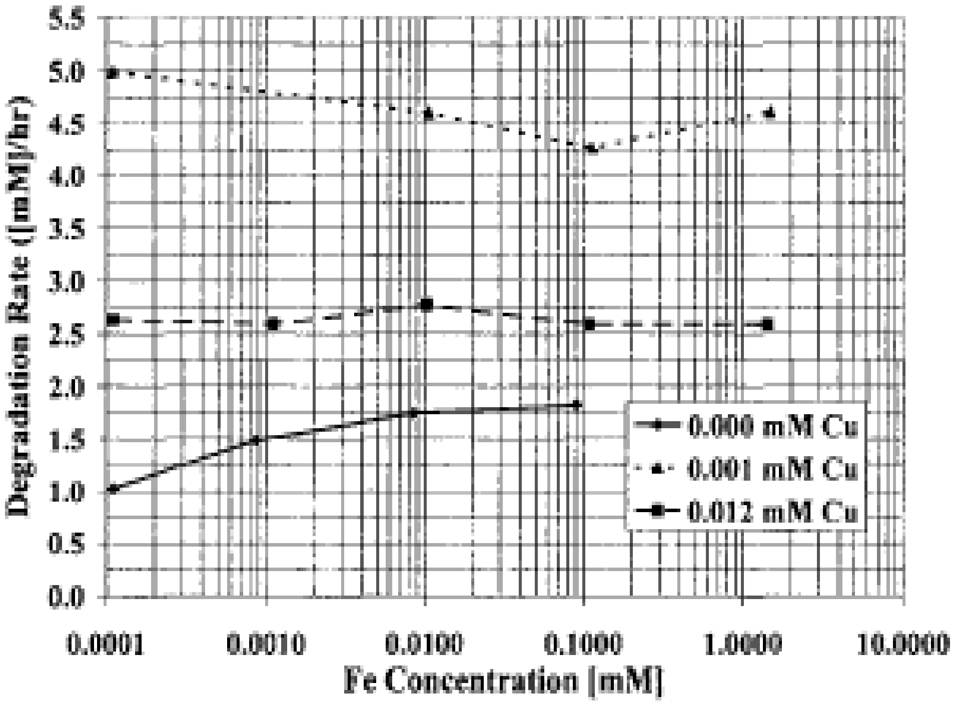


⇒ More degradation in loaded solutions!

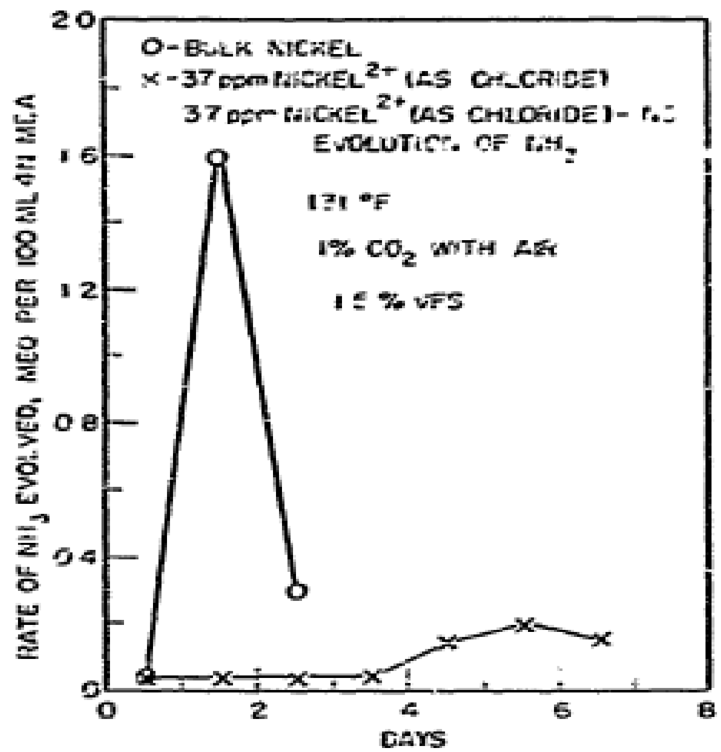
2. Metal effect: Cu^{2+}

Effect of loading



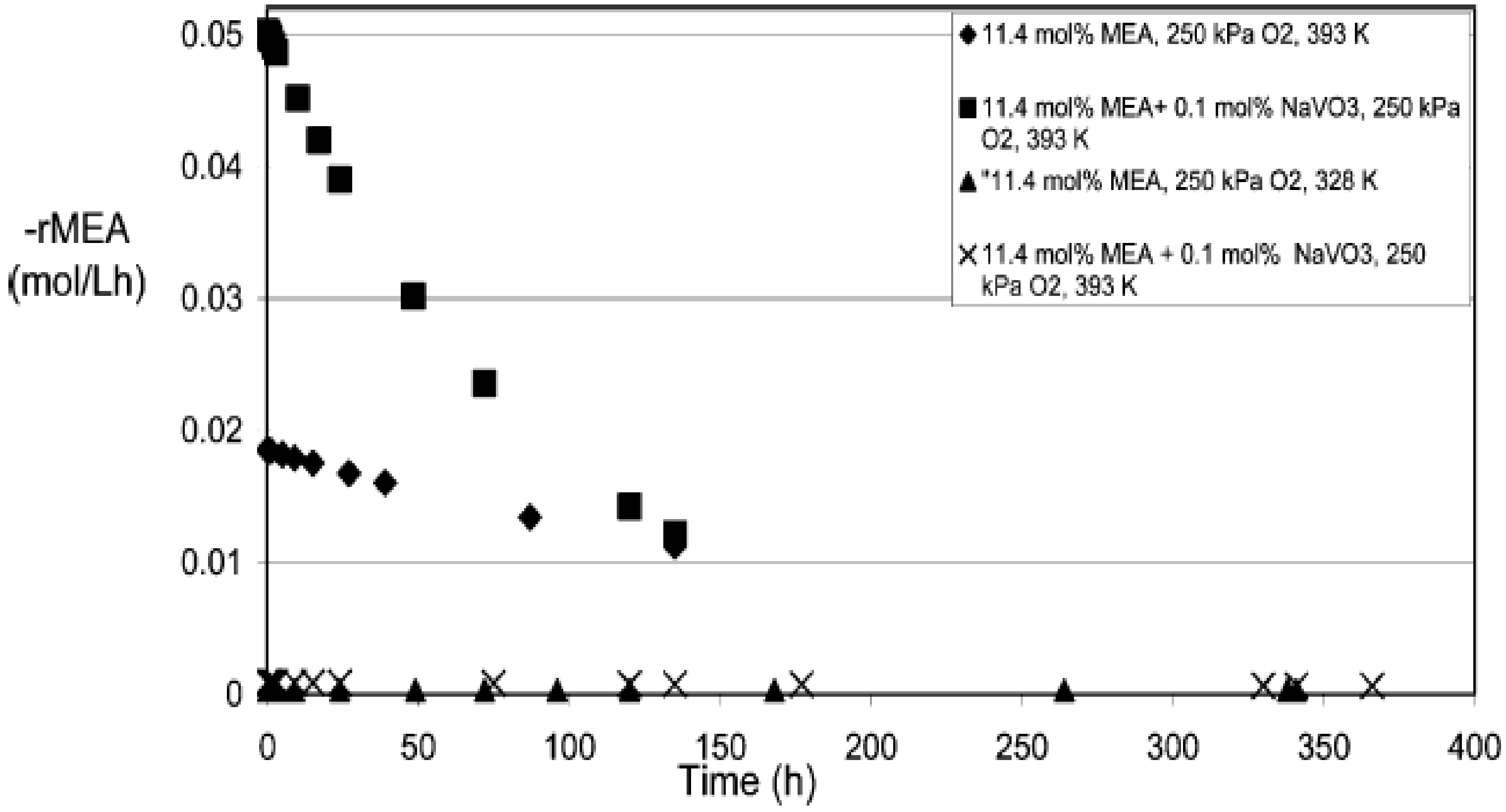


$\Rightarrow$ More degradation in loaded solutions!

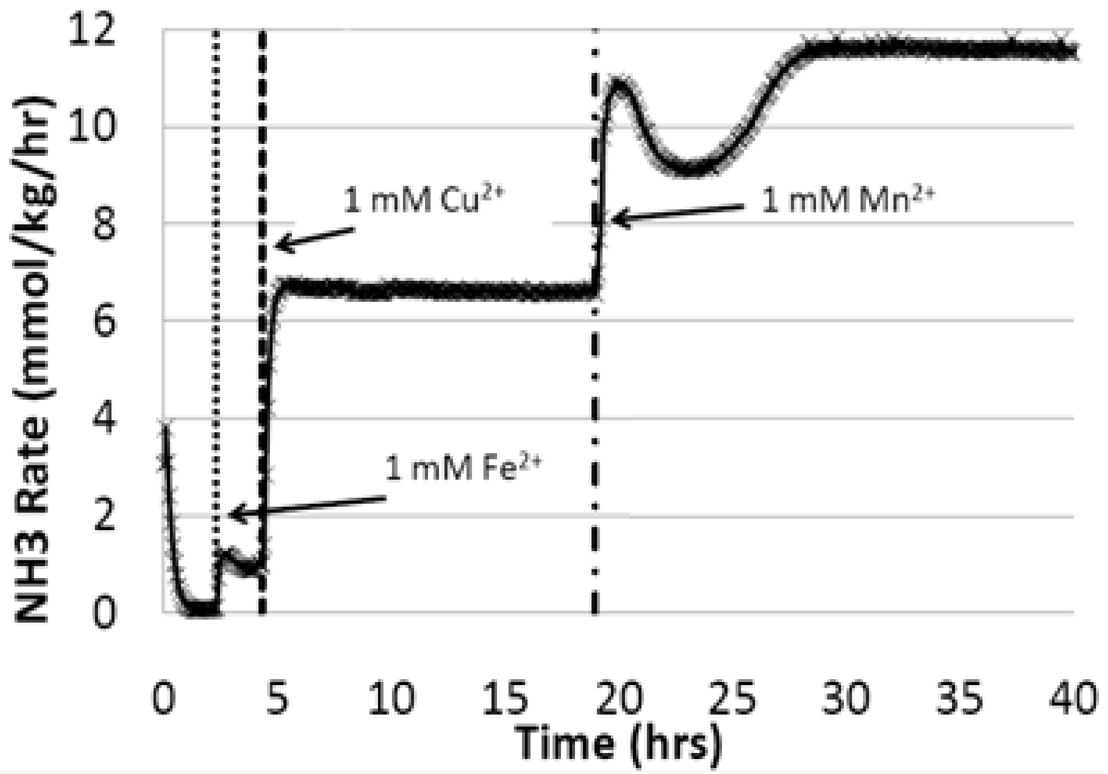


O-BULK NICKEL
×-37 ppm NICKEL2+ (AS CHLORIDE)
DAYS
0
2
4
6
8

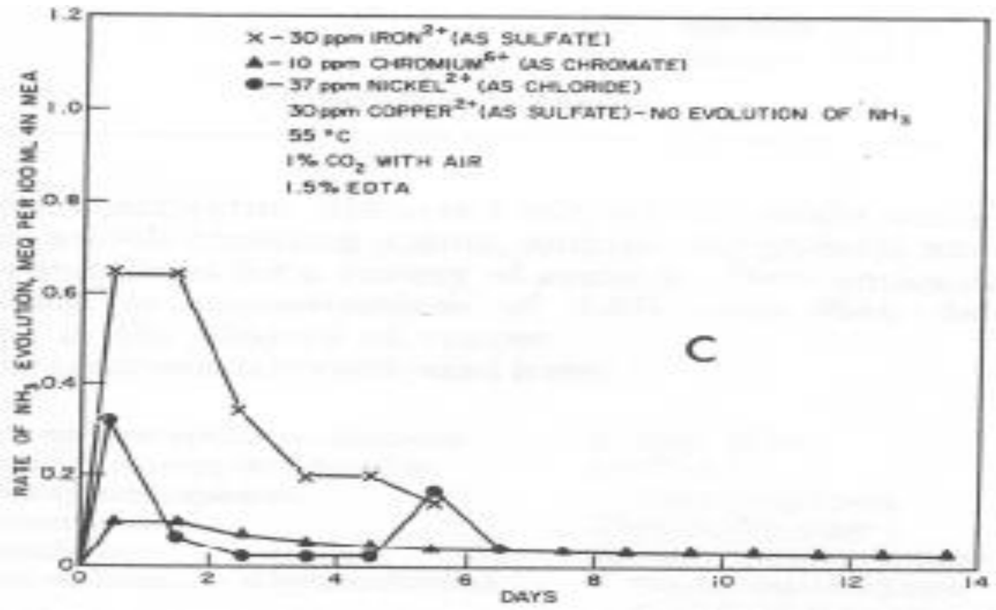
2. Metal effect: V^{5+}



2. Metal effect: Mn^{2+}



2. Metal effect: comparison



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

Moreover, the combination of different metals may increase their respective effect. Mn^{2+} is not listed since it is considered as a degradation inhibitor.

2. Metal effect: comparison

- ***Influence on the degradation products***

Experiment	12/2004	09/2005
Distinguishing Conditions	0.2 mM Cu	0.2 mM Cu and Fe
Acetate/Glycolate (mM/hr)	0.26	0.34
Formate (mM/hr)	0.33	0.64
Oxalate (mM/hr)	0.03	0.03
Nitrate (mM/hr)	0.07	0.20
Nitrite (mM/hr)	0.18	0.26
EDA (mM/hr)	N/A	N/A

2. Metal effect

- ***Metal don't have any influence on degradation with CO_2***

- ***The influence of metals on thermal degradation has not been studied so far.***

- ***The influence of metals on degradation with SO_x and NO_x has not been studied so far.***

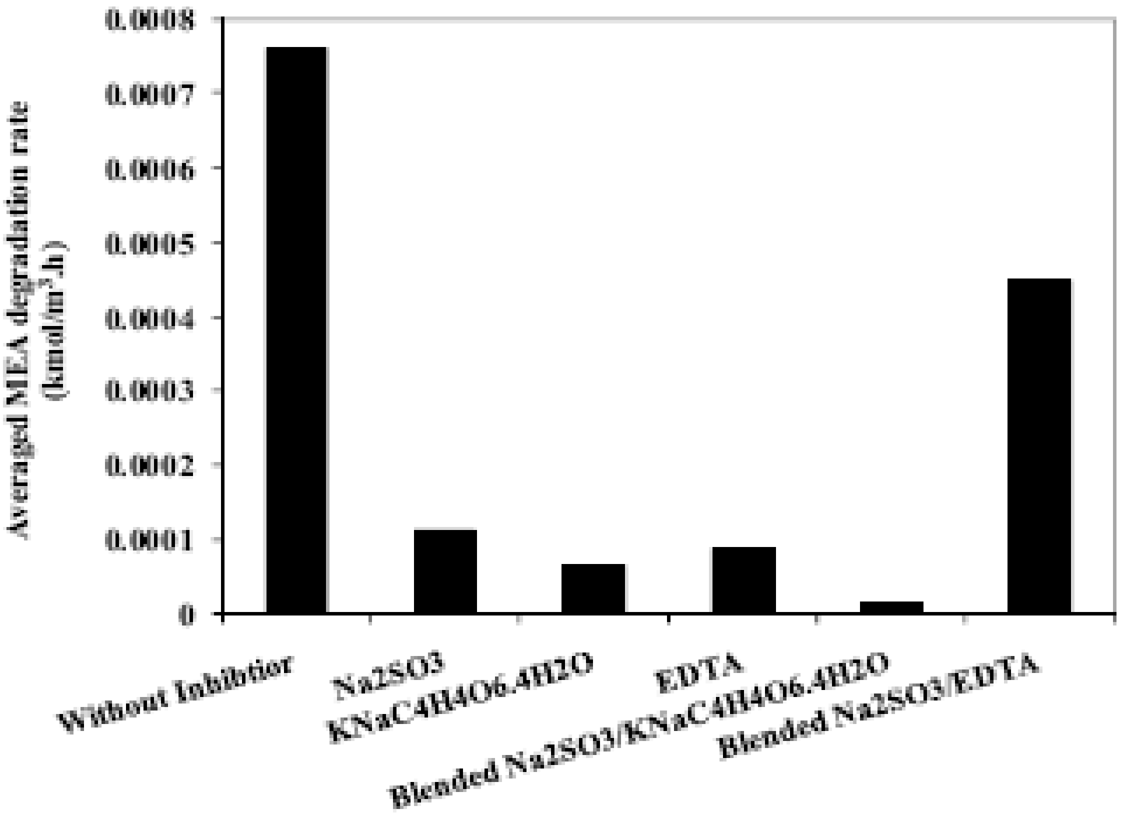
3. Inhibitor effect

- Chelating agents
  - Bicine is not stable with Cu^{2+}
  - EDTA is slowly oxidized with Fe^{2+}
  - HEDTA, TEA, gluconate still require more studies

- Potassium-sodium tartarate presents very interesting properties, especially in combination with Na_2SO_3. This has to be confirmed by further studies.
- HEDP also seems very promising, especially in combination with DTPA.
- Citric acid and NTA seem less interesting

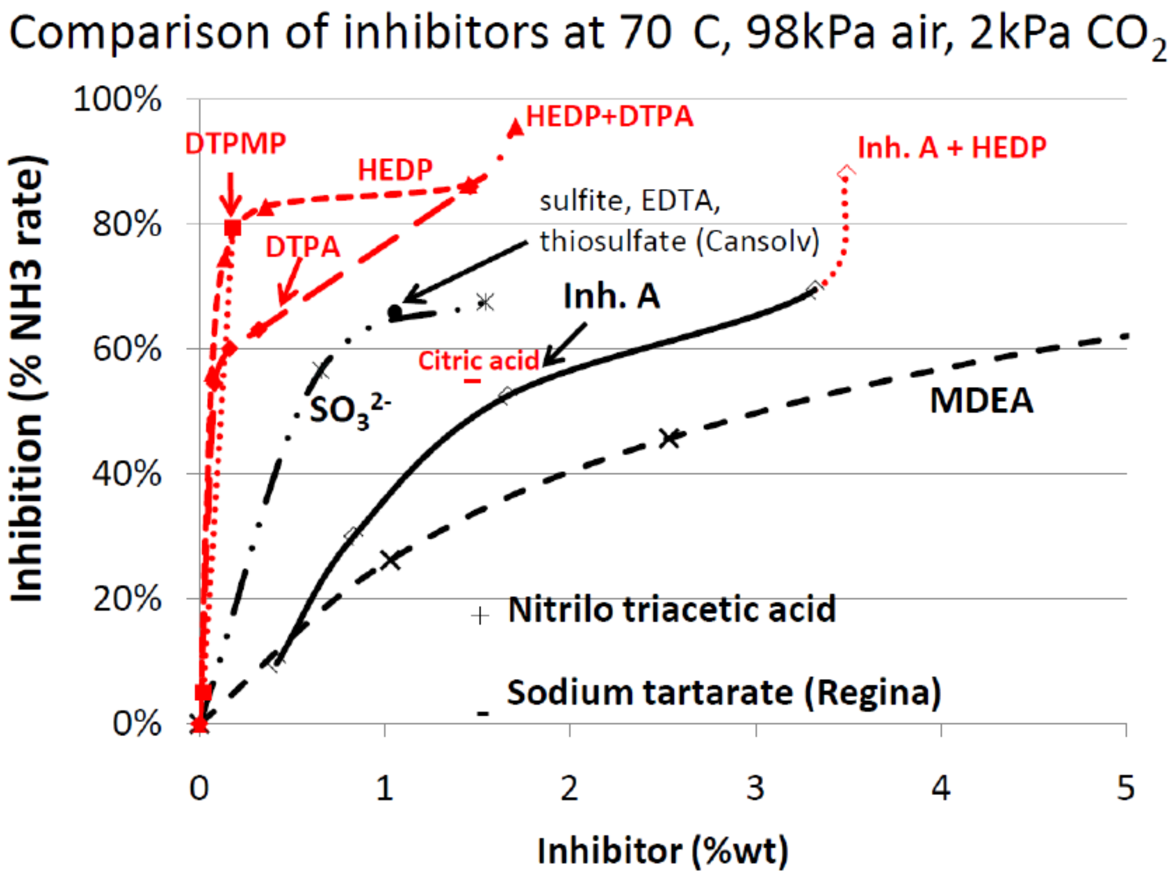
3. Inhibitor effect

- Chelating agents

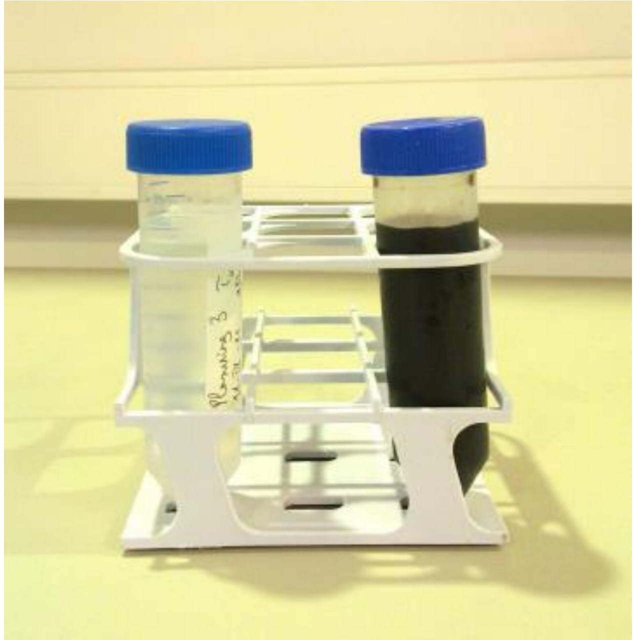


3. Inhibitor effect

- Radical and O_2 scavengers



Thanks for your attention!



24th April 2012