Speciation of iron in MEA solutions: Solubility and Corrosion

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Outline

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- Motivation
- Methodology
- Results
- Conclusions

Introduction: Ideal Solvent

- Low degradation
- Low volatility
- Cheap
- High absorption rate
- High capacity
- Low corrosion rate

Introduction: Corrosion

- Corrosion is one of the main challenges in amine based PCCC
- The ideal solvent should have a minimum effect on corrosion
- Some iron compounds have a catalytic role in the degradation of solvents while others can increase the corrosion rate
- The target of this work is to examine an alternative, fast methodology for corrosion evaluation of solvents

Corrosion Evaluation: Overview

Weight loss technique with metal coupons is one of the most used for the calculation of the corrosion rate.

A number of electrochemical methods for corrosion measuring exist
Potentiodynamic polarization techniques are among the most popular

SEM- EDS : Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy

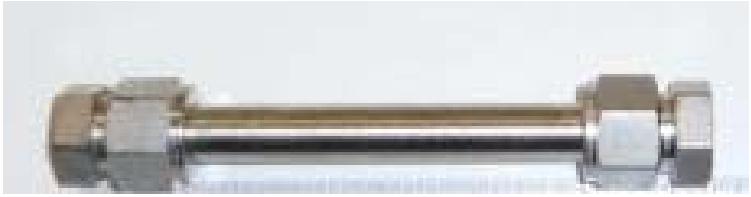
Surface morphology- Elemental Mapping (homogeneous corrosion or not)

ICP-MS : Inductively Coupled Plasma Mass

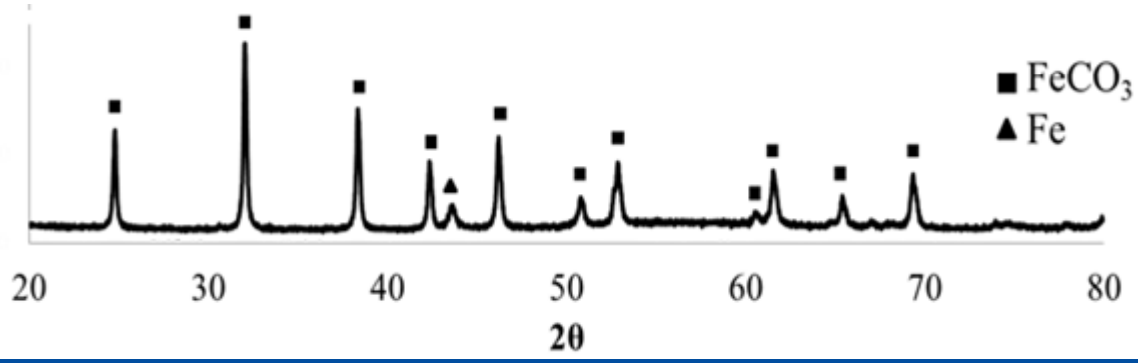
Total Metal Concentration in the liquid gives information about the relative corrosivity

Background: Thermal degradation

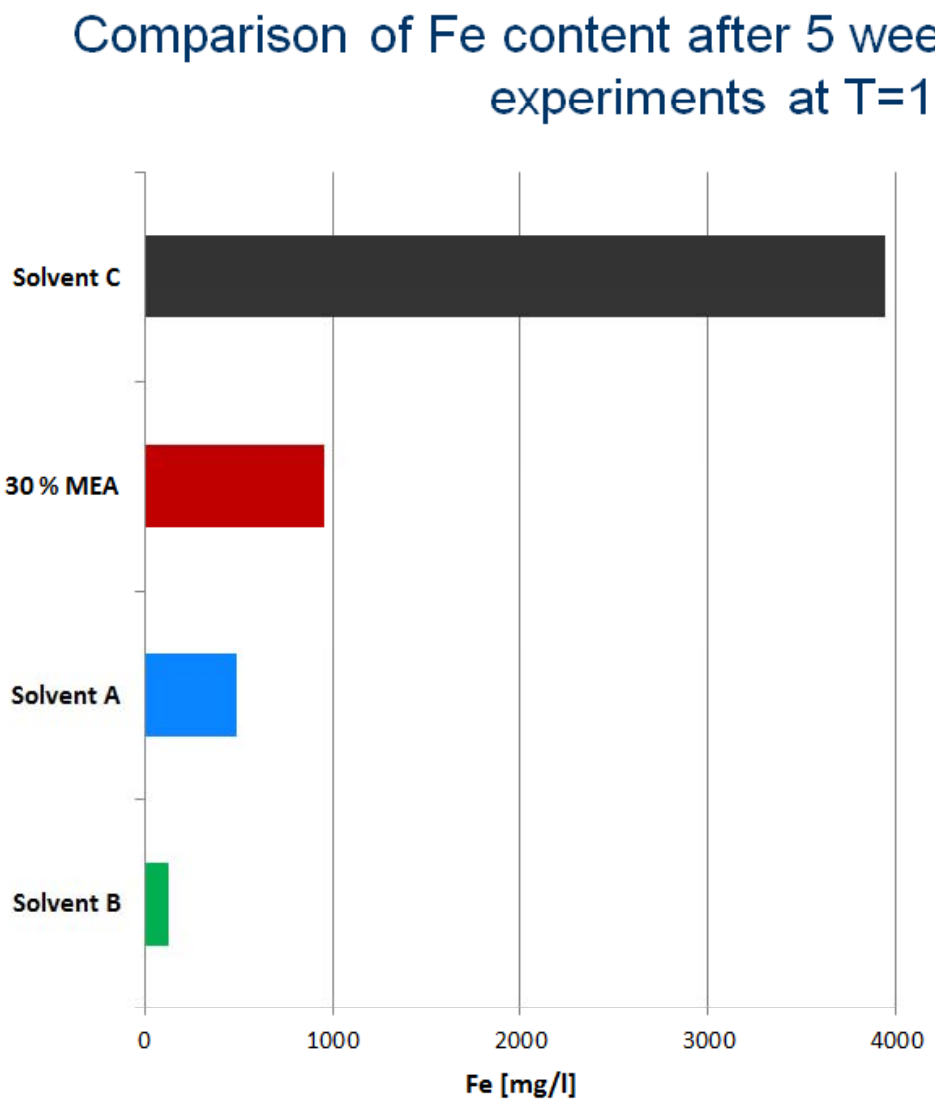
- Stainless steel cylinders (316 SS) equipped with Swagelok® end caps)

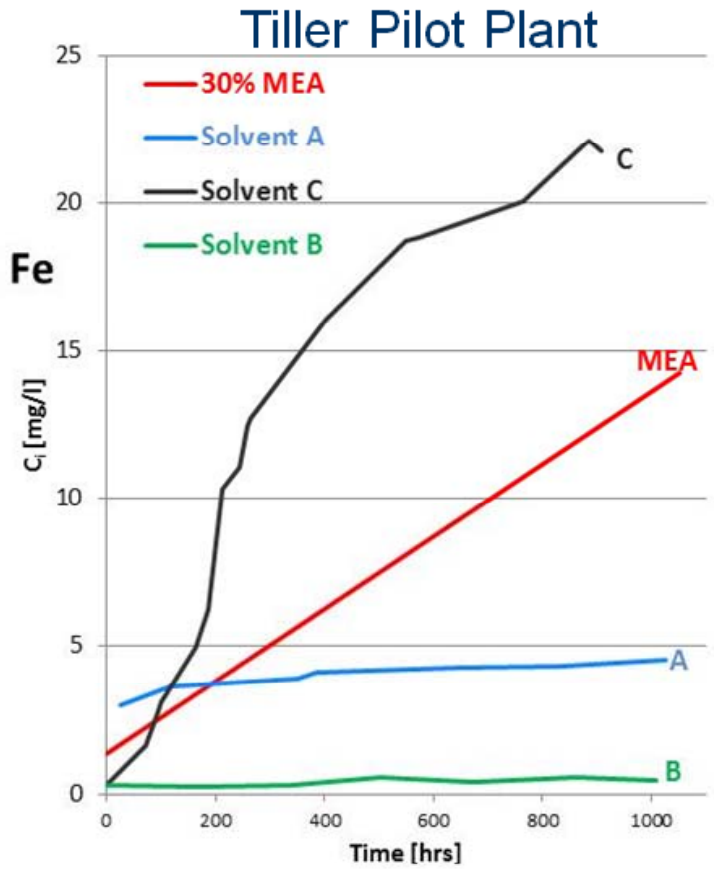


- 9 g of loaded solution of amine was injected into the cylinder
- Cell put in forced convection oven at 135 ^{o}C
- Experiments run for 5 weeks
- After thermal degradation experiments, we identify $FeCO_3$ on the steel surface with XRD



Background: ICP-MS





A. Grimstvedt, E.F. da Silva, K.A.Hoff: *Thermal degradation of MEA, effect of temperature and CO2 loading.* TCCS7, SINTEF Materials and Chemistry, 7465 Trondheim, 2013.

NTNU

Motivation

- Tsuda et al. studied the effect of iron carbonate on the corrosivity of amine solutions in CO_2 removal units. They reported that corrosion was inhibited by the formation of $FeCO_3$ scale

- They correlated high corrosion with high solubility of $FeCO_3$

→ We will try to correlate the ferrous solubility with the solvent corrosivity

Tsuda, T., Takeda, M., Hosoya, K. Effect of iron carbonate on the corrosivity of amine solutions in CO2 removal units (2010) NACE - International Corrosion Conference Series, 9 p.

Solubility of Fe(II) in amine solutions

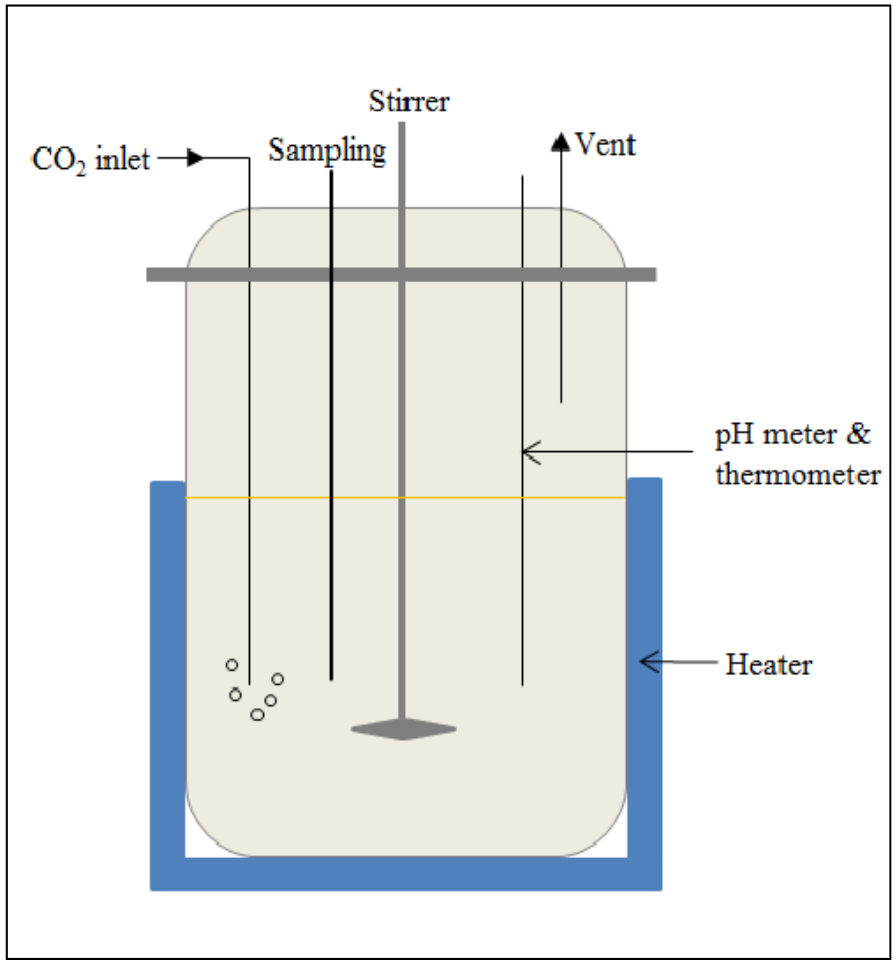
- Could this be a fast methodology to determine corrosivity?
- Is there a correlation between Fe(II) and amine corrosivity?
- Based on literature DETA is more corrosive than MEA and that MEA is more corrosive than MDEA

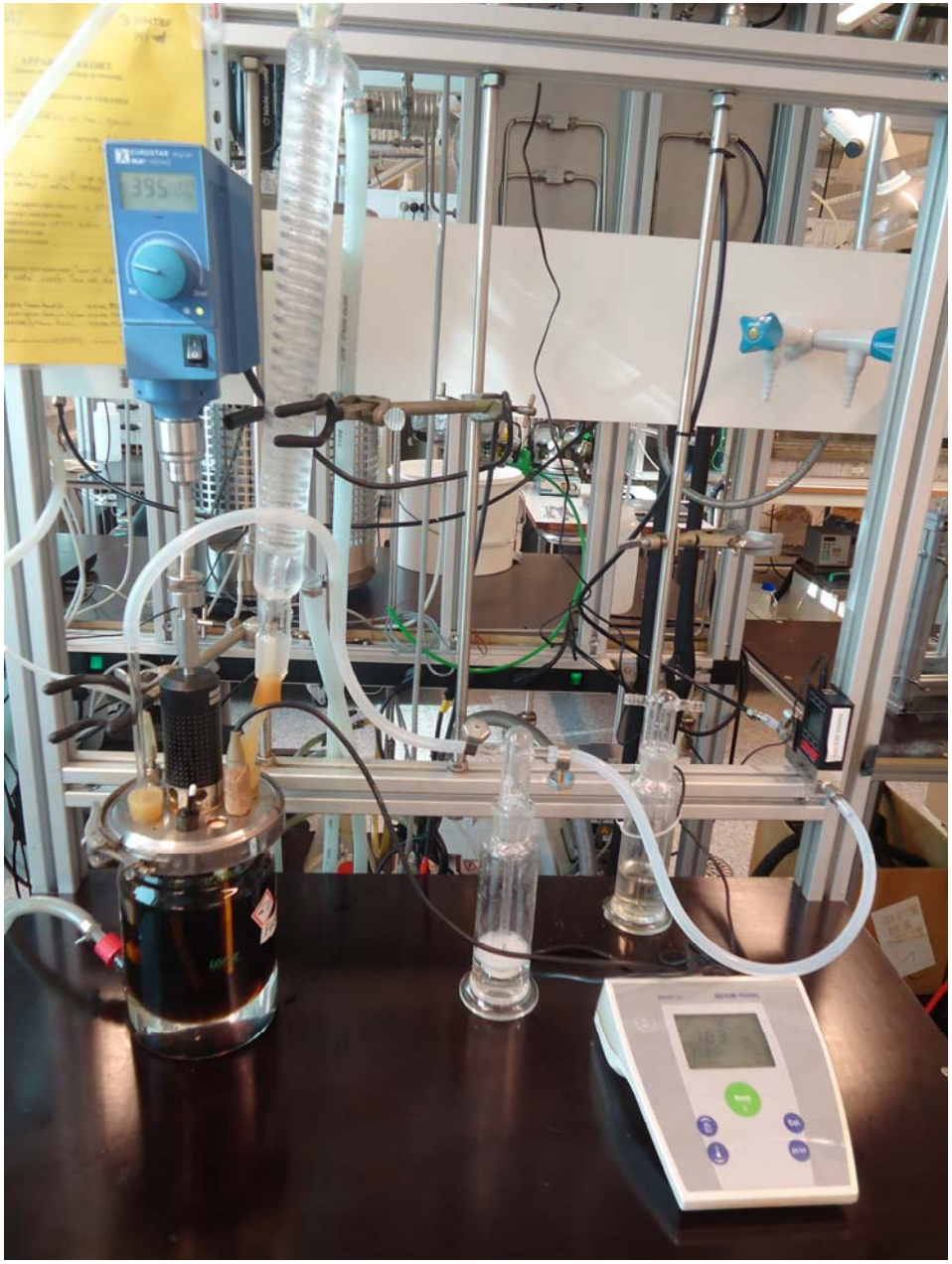
*A. L. Cummings ,S. W. Waite, and D. K. Nelsen. MPR Services Inc., Dickinson Texas.
Corrosion and Corrosion Enhancers in Amine Systems. The Brimstone Sulfur Conference Banff, Alberta, April 2005

Methodology

We measured the solubility of ferrous in 30wt% amine solution with 0.4 CO_2 loading

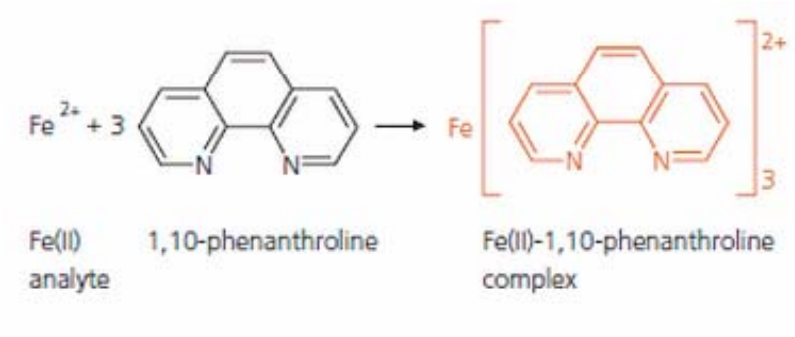
- $FeSO_4$ is added gradually
- Three temperatures were tested:
- 25 ^oC, 40 ^oC and 60 ^oC
- Amines tested: MEA, MDEA, DETA





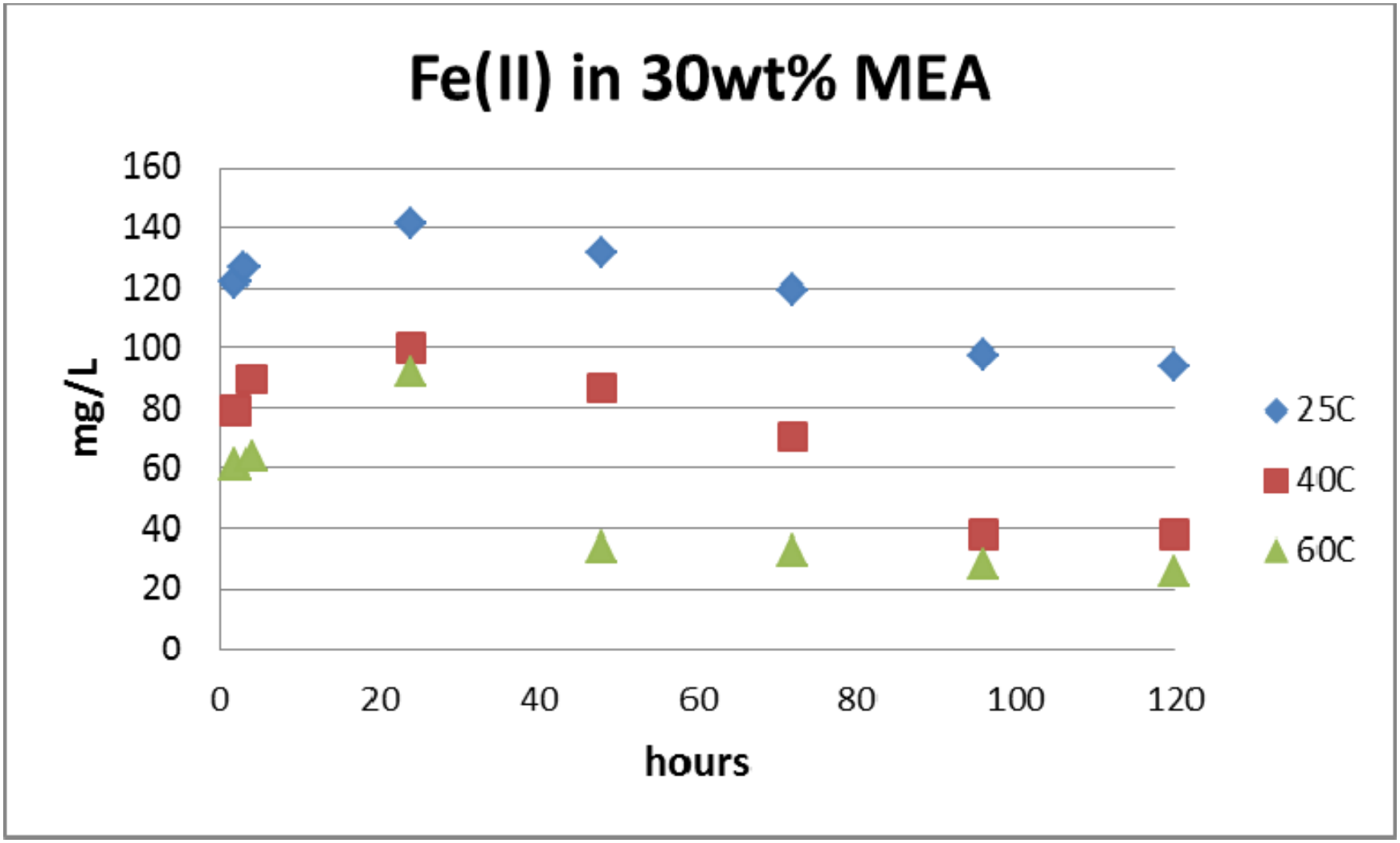
Spectrophotometric Determination of Fe^{2+}

Fe^{2+} + 3phen → $(phen)_3Fe(II)$



For quantitative analysis, the wavelength λ_{max}=508nm is chosen

Results


Fe(II) in 30wt% MEA
160
140
120
100
80
60
40
20
0
mg/L
0
20
40
60
80
100
120
hours
25C
40C
60C

Comparison of Fe^{2+} values (mg/L)

60 °C

TIME	MDEA	MEA	DETA
3 h	59	64	91
24 h	16	92	136
48 h	6	34	175

45 °C

TIME	MDEA	MEA	DETA
3 h	71	90	200
24 h	47	100	200
48 h	29	87	200

Conclusions

- The measured Fe(II) solubility in an amine solution was correlated with the corrosivity of the solvent
- Corrosivity: DETA>MEA>MDEA
- Our results are in good agreement with literature data from pilot and industrial plants
- Based on the current results, it seems the Fe(II) solubility could be used to predict corrosivity. However further tests will take place to confirm this correlation.

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Thank you for your attention