Characterisation of Degraded Solvents from Amine Scrubbing

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Outline

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- Aims & Objectives
- Analytical methods
- Results
  - Degradation compounds
  - Comparison
    - Primary solvents
    - Mixed solvents
  - Techniques
- Summary

Factors affecting degradation

- Oxygen content in system- typically 5-12% in flue gas
- Metal- corrosion effects
- Temperatures- low temperature lead to oxidative degradation, high temperature leads to thermal degradation

Chakma, et al., Heat Recovery Systems & Chp, 1995, **15**, 231-240
Goff & Rochelle, Ind. Eng. Chem. Res., 2006, **45,** 2513-2521
Sexton & Rochelle, Ind. Eng. Chem. Res., 2011, **50,** 667-673

Major degradation products- MEA

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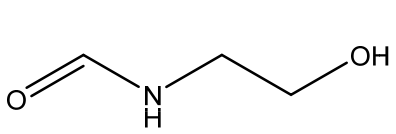
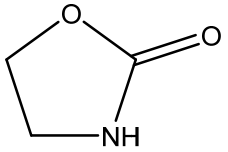
Oxidative

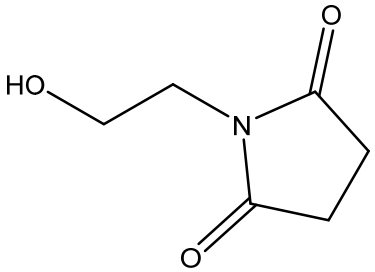
- Occurs in the absorber



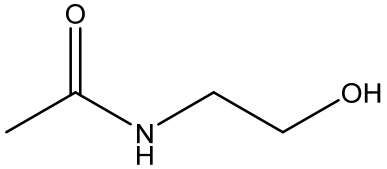
N-(2-hydroxyethyl) formamide (HEF) [2,3,6,8]



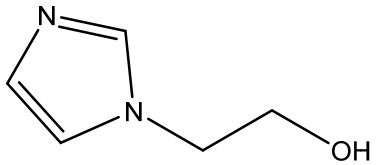
2-oxazolidone (OZD) [1,3,5,6]



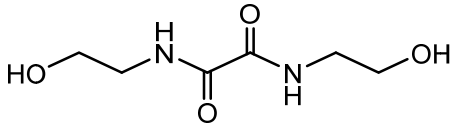
N-(2-hydroxyethyl) succinimide [2,8]



N-(2-hydroxyethyl) acetamide (HEA) [2,3,6,7,8]



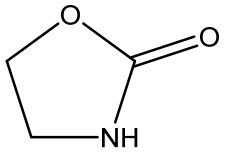
N-(2-hydroxycthyl) imidazole (HEI) [3,4]



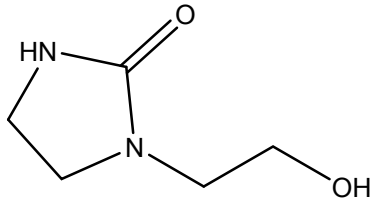
N,N'-bis(2-hydroxyethyl)oxalamide (BHEOX) [3,8]

Thermal

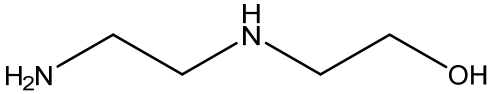
- Occurs in the stripper



2-oxazolidone (OZD) [1,3,5,6]



N-(2-hydroxyethyl)imidazolidin-2-one (HEIA) [1,3,4,5,7]



N-(2-hydroxyethyl) ethylenediamine (HEEDA) [1,3,7]

1. Lepaumier et al., *Ind. Eng. Chem. Res.*, 2009, **48**, 9061-9067.
2. Lepaumier et al., *Ind. Eng. Chem. Res.*, 2009, **48**, 9068-9075.
3. Lepaumier et al., *10th International Conference on Greenhouse Gas Control Technologies*, 2011, **4**, 1652-1659.
4. Sexton and Rochelle, *Ind. Eng. Chem. Res.*, 2011, **50**, 667-673.
5. Strazisar et al., *Abstracts of Papers of the American Chemical Society*, 2001, **223**, U569-U569.
6. Strazisar, R. R. Anderson and C. M. White, *Energy & Fuels*, 2003, **17**, 1034-1039.
7. Supap et al., *Ind. Eng. Chem. Res.*, 2006, **45**, 2437-2451.
8. Supap et al., in *10th International Conference on Greenhouse Gas Control Technologies*, eds. J. Gale, C. Hendriks and W. Turkenberg, 2011, vol. 4, pp. 591-598.

Mechanism of MEA degradation

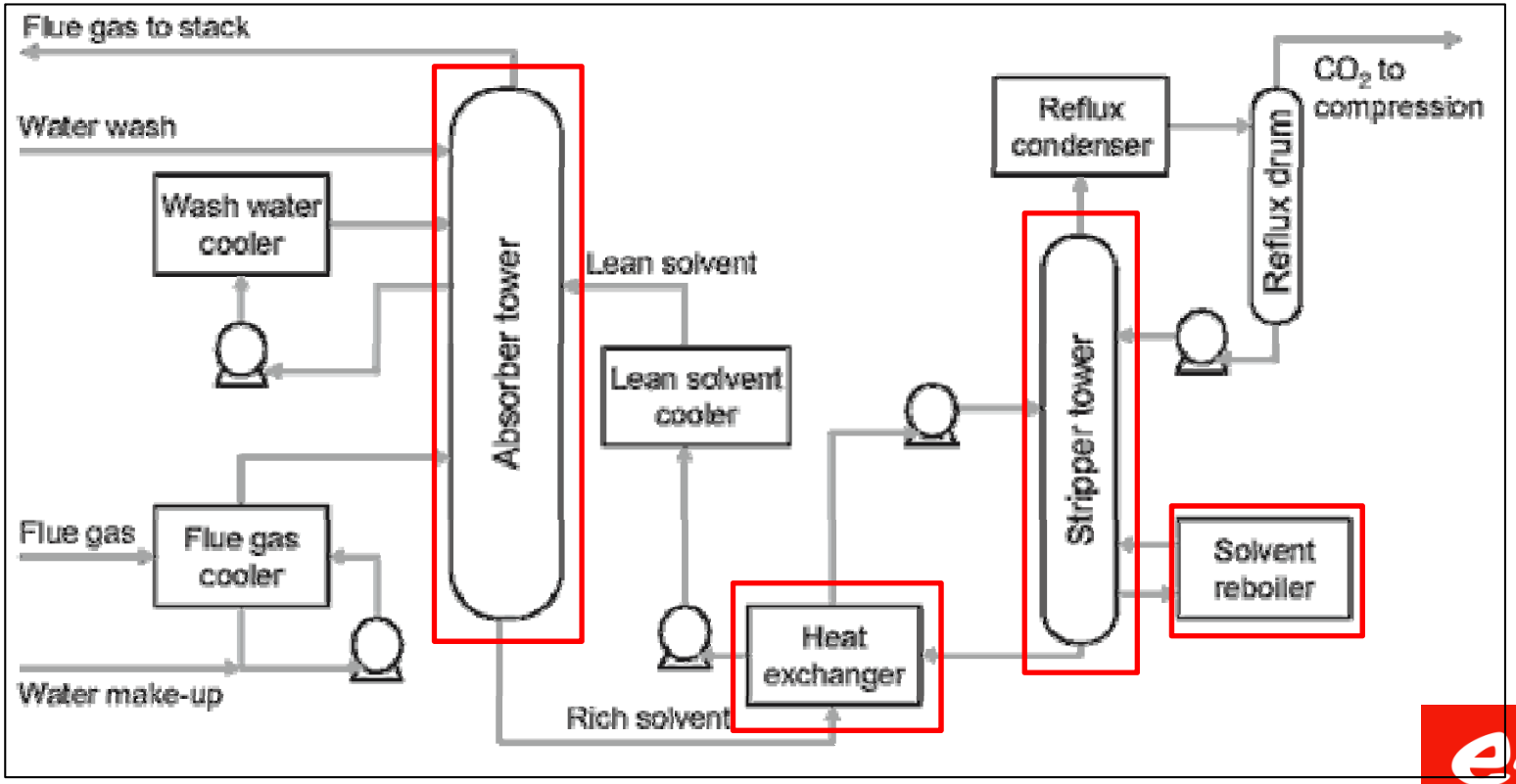
Oxidative degradation mechanism:

- Electron Abstraction
  - Lone pair on nitrogen atom
  - Uses free radicals e.g. Fe^{3+}
  - Products are aldehyde and ammonia
  - Only proven for tertiary amines
- Hydrogen Abstraction
  - From nitrogen, α-carbon or β-carbon atom
  - Uses free radicals
  - Five-membered cyclic hydrogen bonded conformation
  - Products are aldehyde and ammonia
  - Dominant mechanism for primary amines

Gofff & Rochelle, Ind. Eng. Chem. Res., 2004, **43**, 6400-6408
Chi & Rochelle, Ind. Eng. Chem. Res., 2002, **41**, 4178-4186.
[5] Bedell, 2009. In: Gale & Braitsch (eds.) GHGT 9
Bedell, International Journal of Greenhouse Gas Control, 2011, **5**, 1-6

Corrosion

- High level of O_2 thought to contribute to corrosive degradation products
- Uniform and localised corrosion observed- pitting, erosion, stress-corrosion cracking



Aims & Objectives

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- Characterise degraded solvents from pilot facilities using a variety of analytical techniques
- Correlate data from different analytical techniques
- Establish links between the degradation products and corrosion- effect of metals
- Identify the importance of specific factors in degradation

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Analytical Techniques

- GC-MS- identification major degradation products
- Anion IC- oxidation fragments (formate, oxalate, nitrate, nitrite)
- Cation IC- amine loss
- ICPMS- metal identification and quantification
- ^{13}C NMR spectroscopy- simple quantification of extent of degradation
- Electrochemical corrosion testing- corrosivity of solvent on stainless steels

Solvents Analysed

- Two different pilot plants- UK & Germany

- Primary amine, MEA
  - Operated under a range of conditions
  - With and without ion exchange to remove metals

- Mixed amine solvent
  - Operated under a range of conditions
  - 200-700 hours operation

Results: Degradation products

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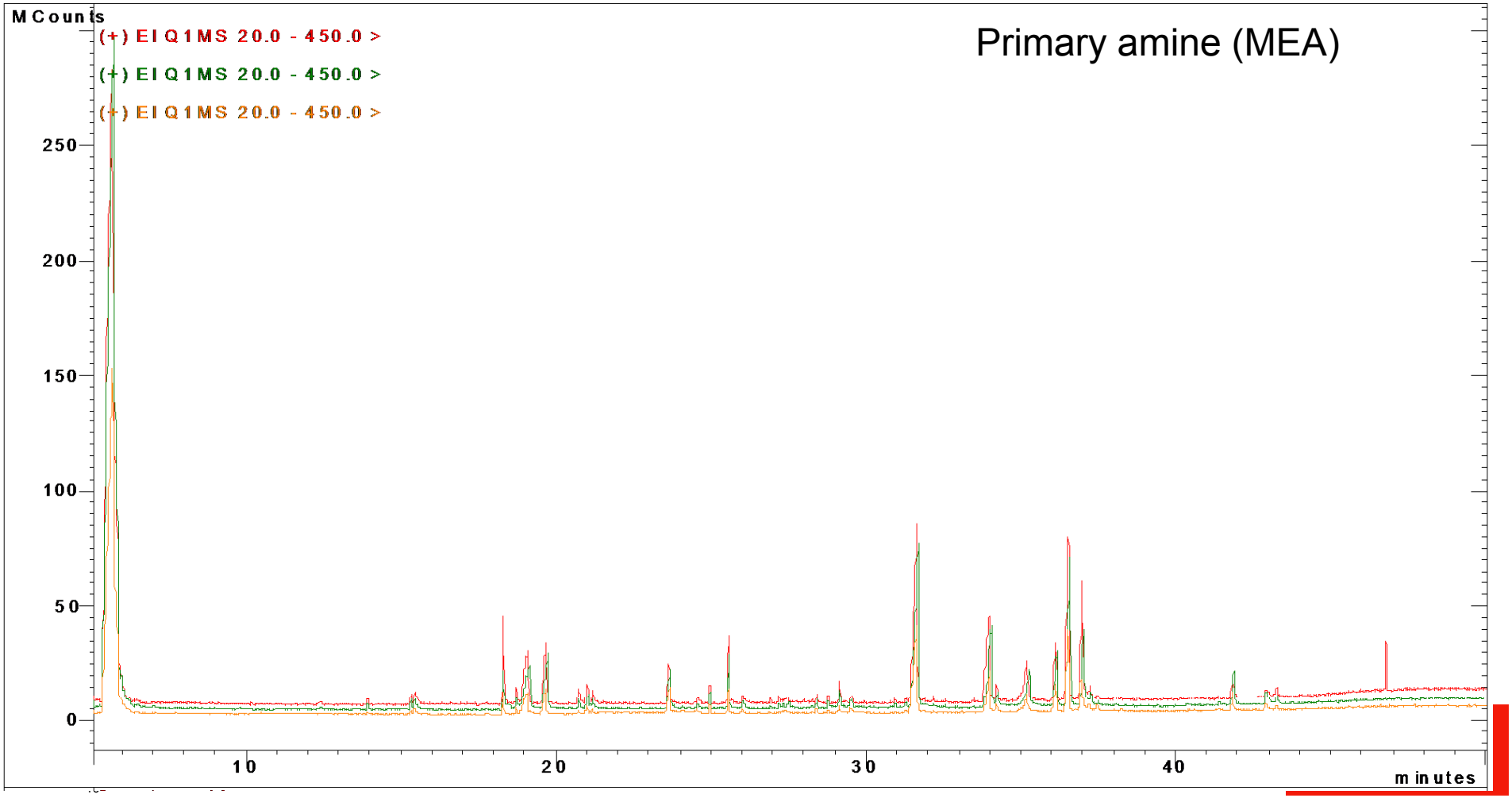
Identified degradation products (GC-MS)



Results: Metals

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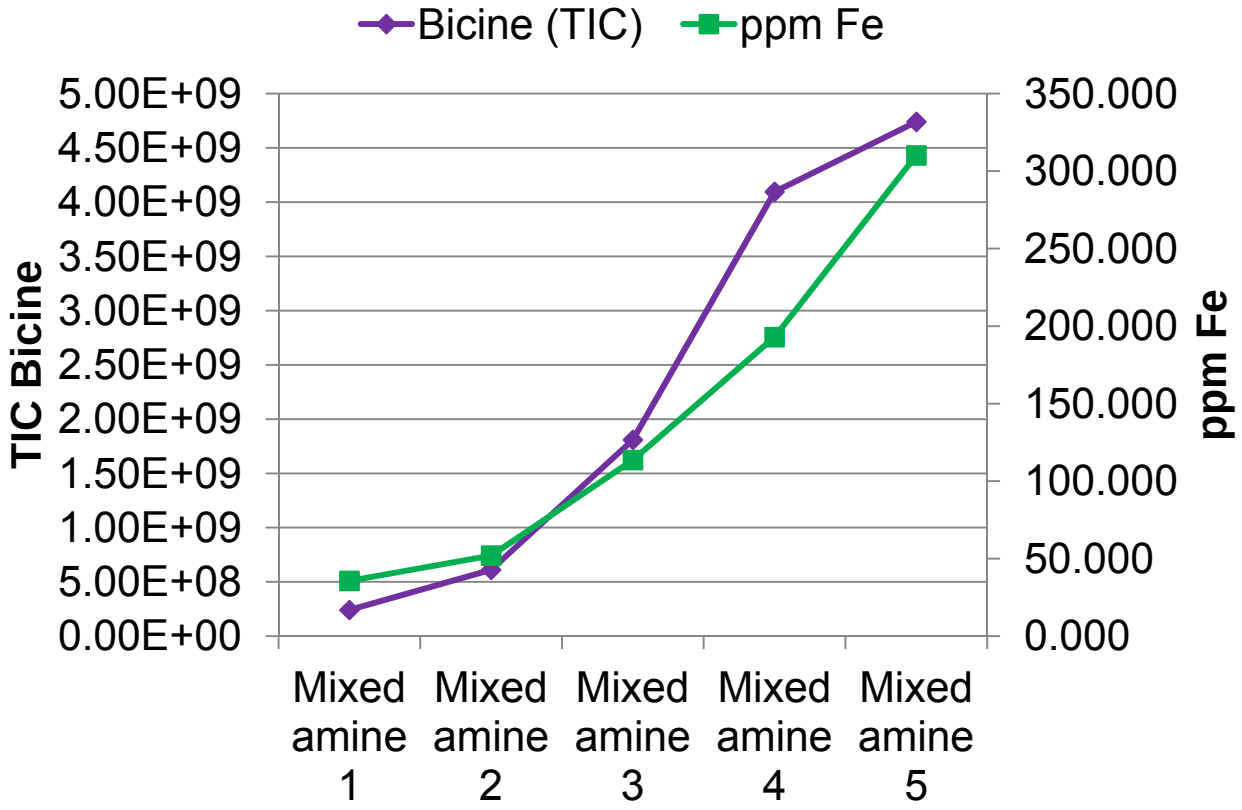
ICPMS

- Iron is the predominant transition metal present in both the primary amine and the mixed amine solvent
- Iron in more soluble when bicine is present- increased corrosion risk



Results: Batch ion exchange

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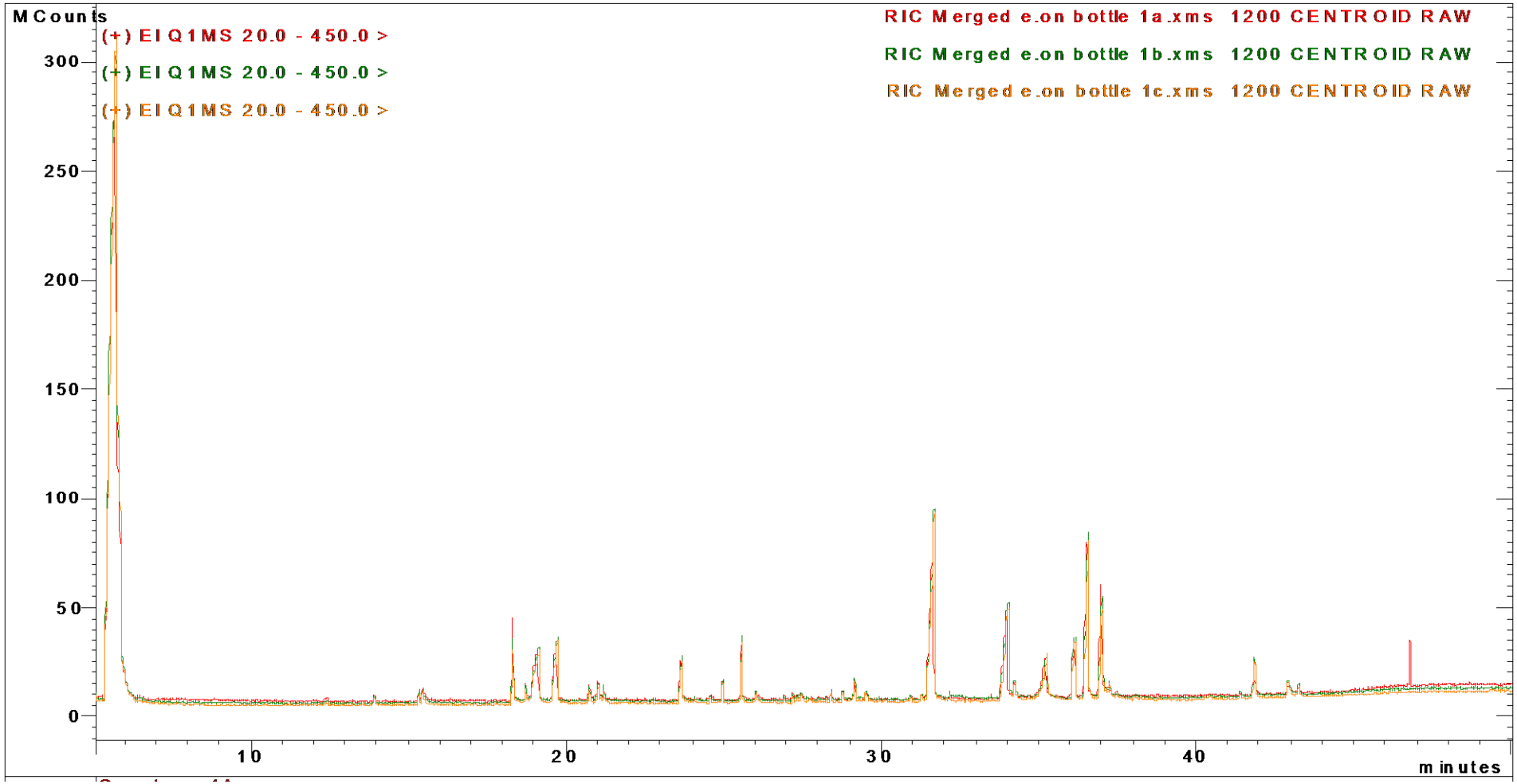
Effect of ion exchange- primary amine

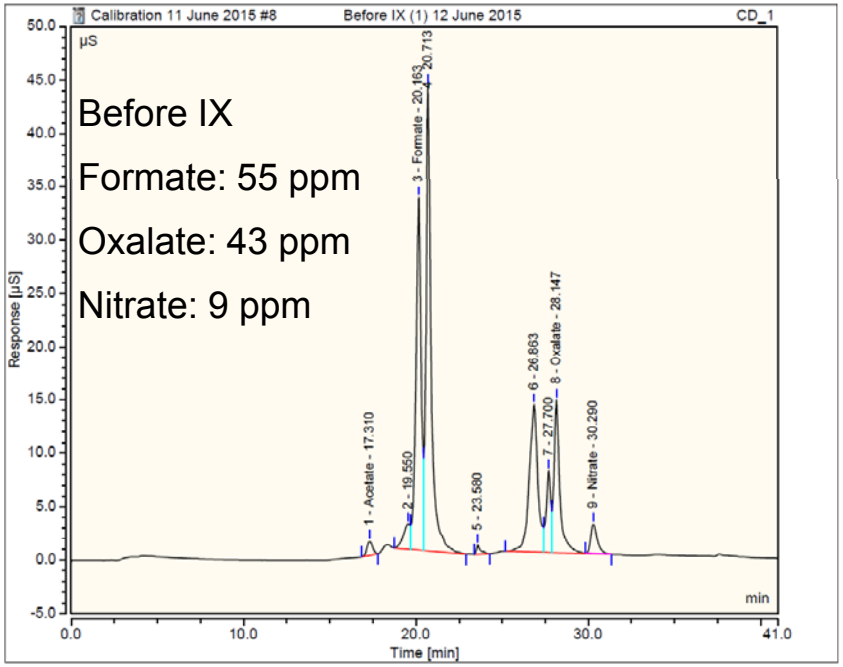
Batch ion exchange

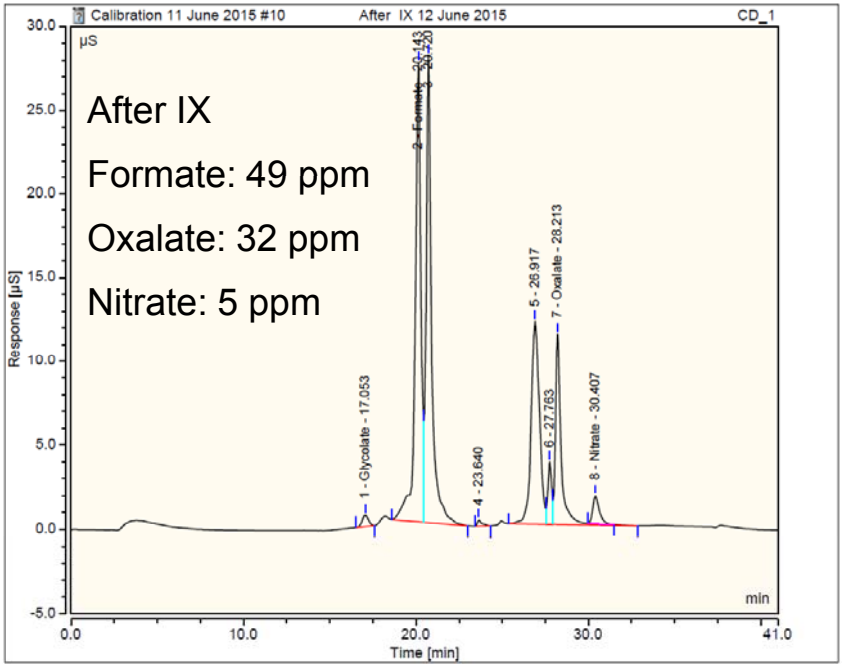


Results: Ion Chromatography

Anion IC- effect of batch ion exchange; primary amine

- Acetate and glycolate difficult to separate
- Peak after formate likely to be HEOX- precursor to known degradation product BHEOX





Cation IC- effect of batch ion exchange; primary amine

- Little effect on number of degradation products

Results: Continuous ion exchange

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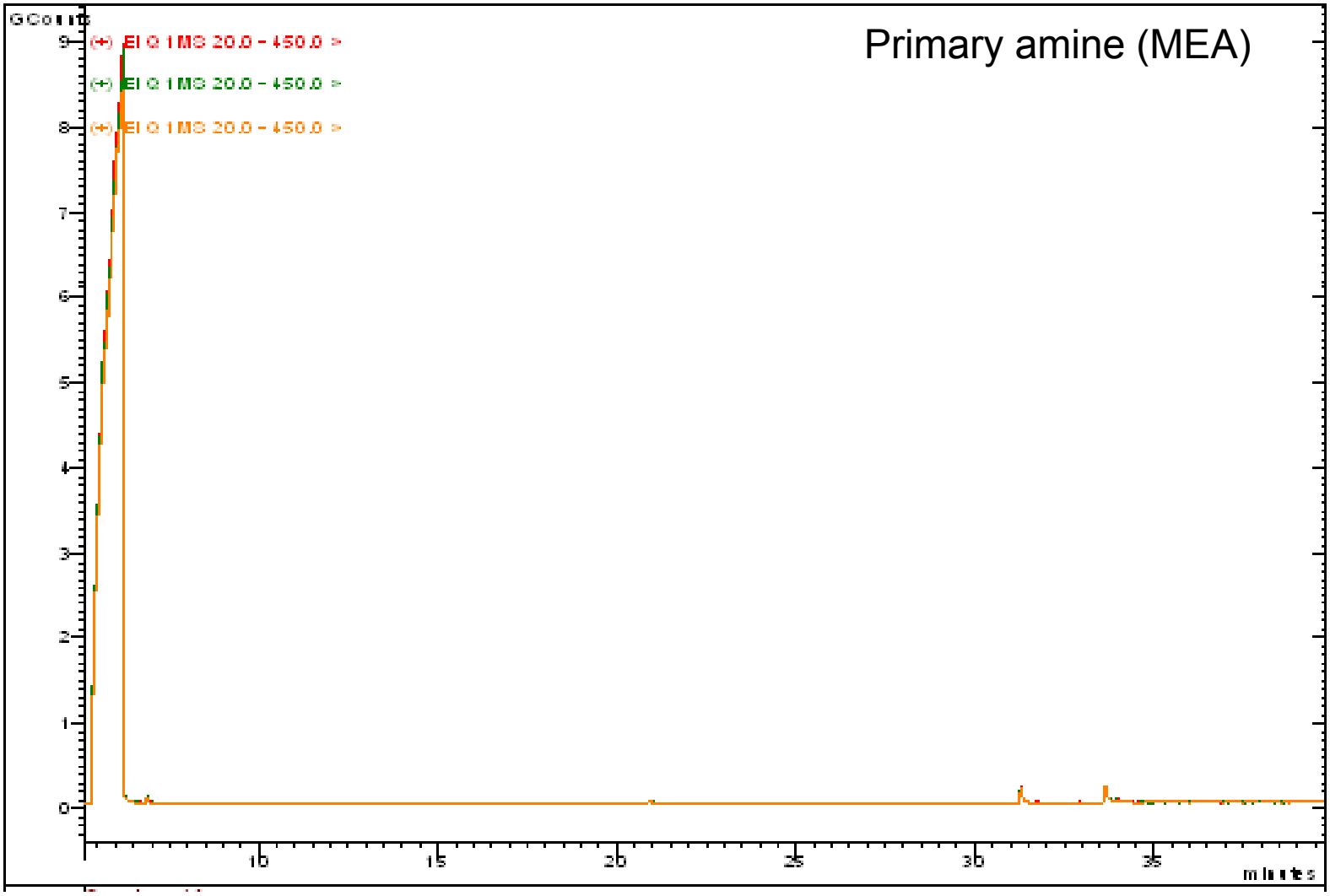
Continuous ion exchange- primary amine



Results: Ion Chromatography

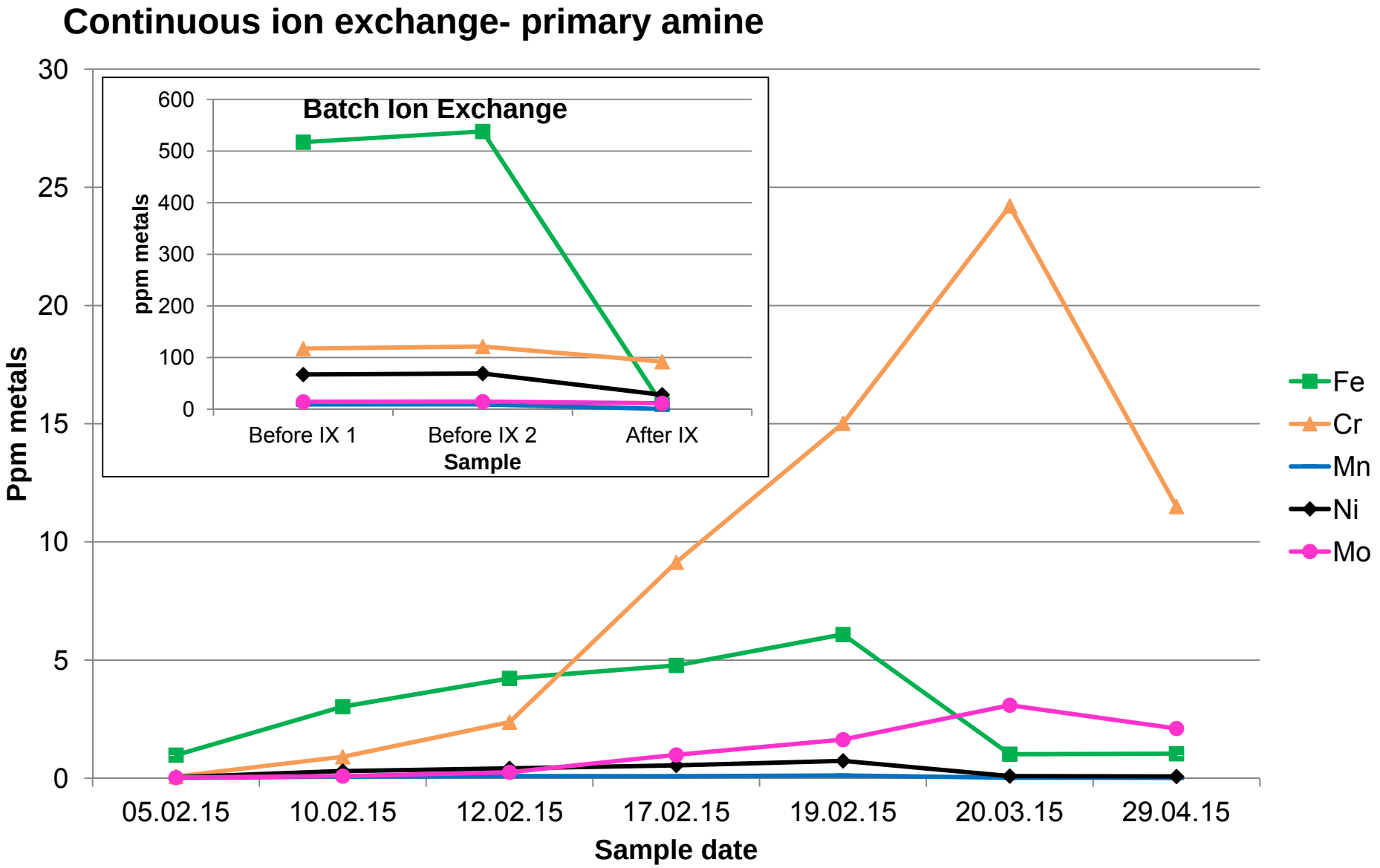
Anion IC- effect of continuous ion exchange; primary amine

- Formate, nitrite, oxalate and nitrate- all below 5 ppm

Cation IC- effect of continuous ion exchange; primary amine

- Maintains low levels of degradation throughout

Results: Continuous ion exchange



Results: Corrosion

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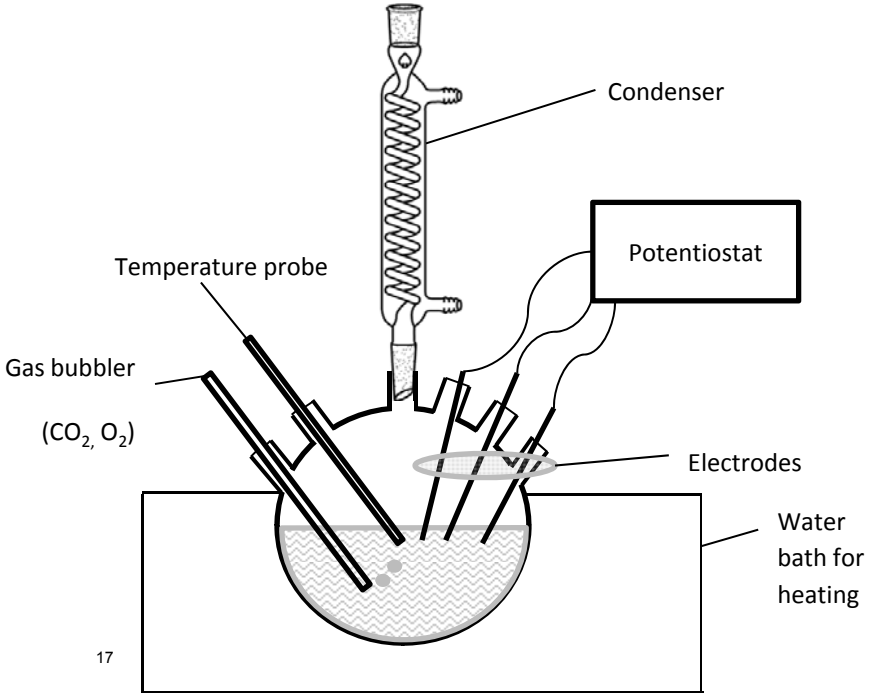
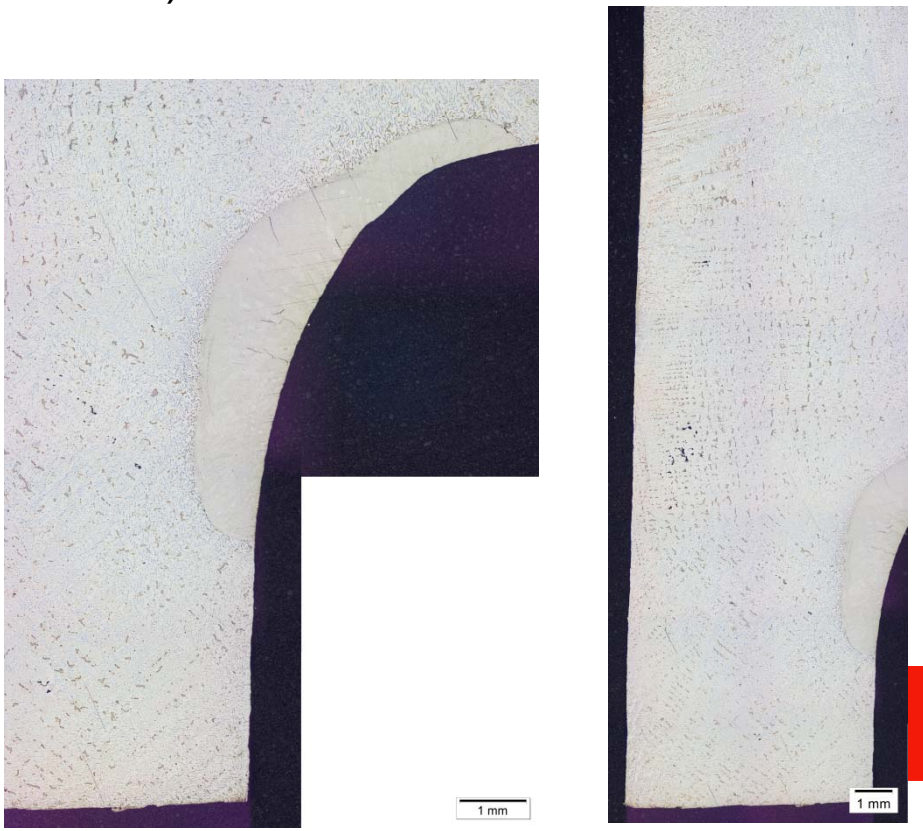
Electrochemical testing- 316 stainless steel, clean unloaded MEA

- Both amine concentration and ion exchange appear to have little effect on corrosion in the short term (~200 hours)
- Low temperature long term tests (~700 hours) shows little corrosion effect- some etching of 316 steel observed

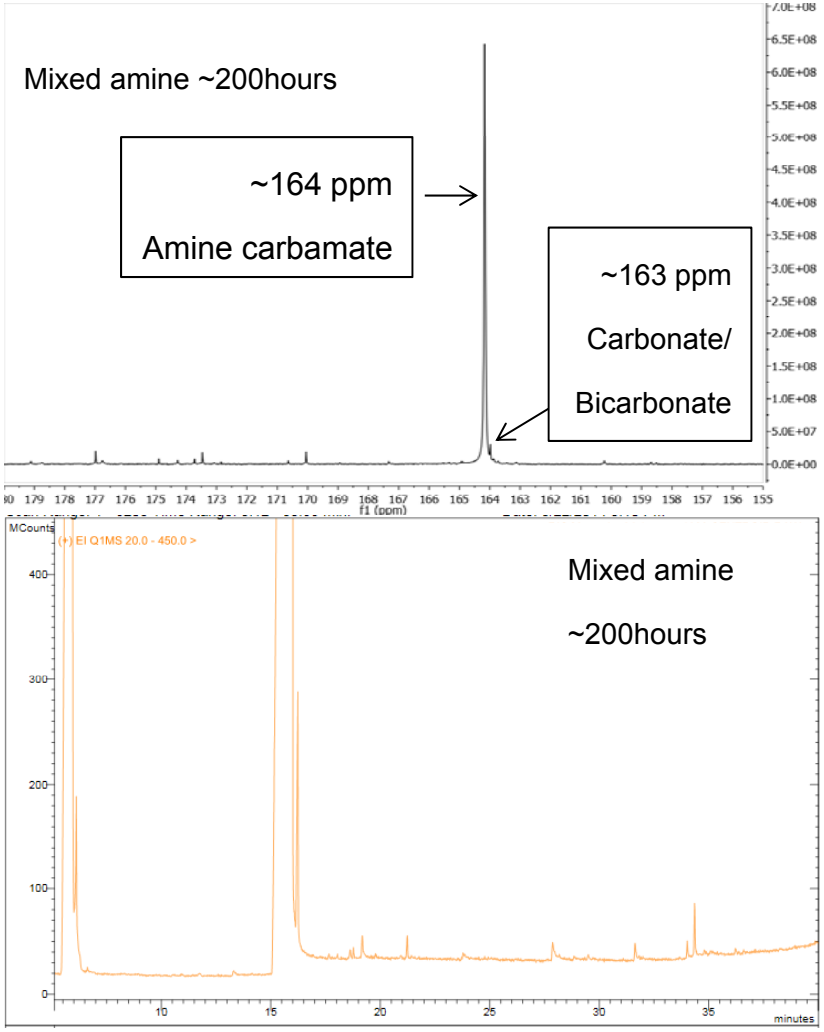


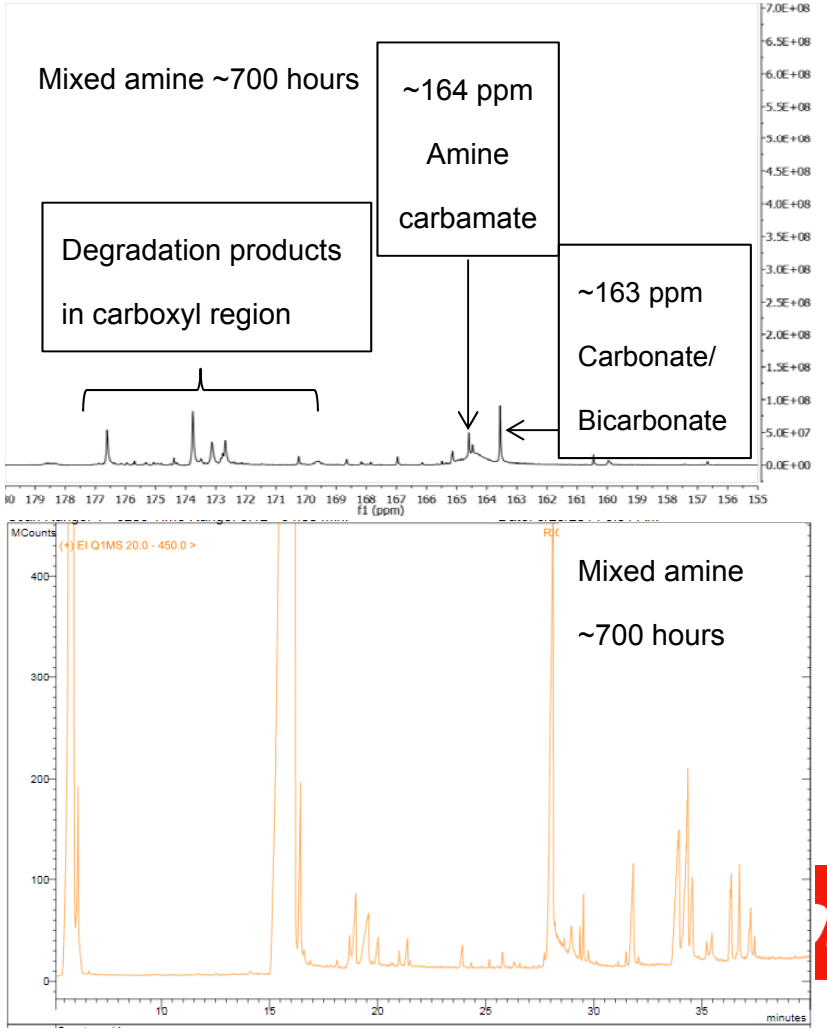


Results: NMR

^{13}C NMR- mixed amine

- Proved useful in observing the extent of degradation





Summary

- Iron is the predominant transition metal in both solvents
  - Possible link to bicine
- Continuous ion exchange appears maintain low levels of degradation- unclear as to how it effects corrosion
- Combining several analytical techniques provides a clear picture of the extent of degradation
  - GC-MS provides identification of degradation products
  - ICP-MS for monitoring levels of metals, particularly iron
  - IC shows the anions present which are from heat stable salts- contribute to corrosion
  - ^{13}C NMR analysis is a useful tool for analysing the extent of degradation
- Link between degradation and corrosion needs more investigation

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