Decomposition of nitrosamines through electrochemically-mediated reduction on carbon xerogel electrodes

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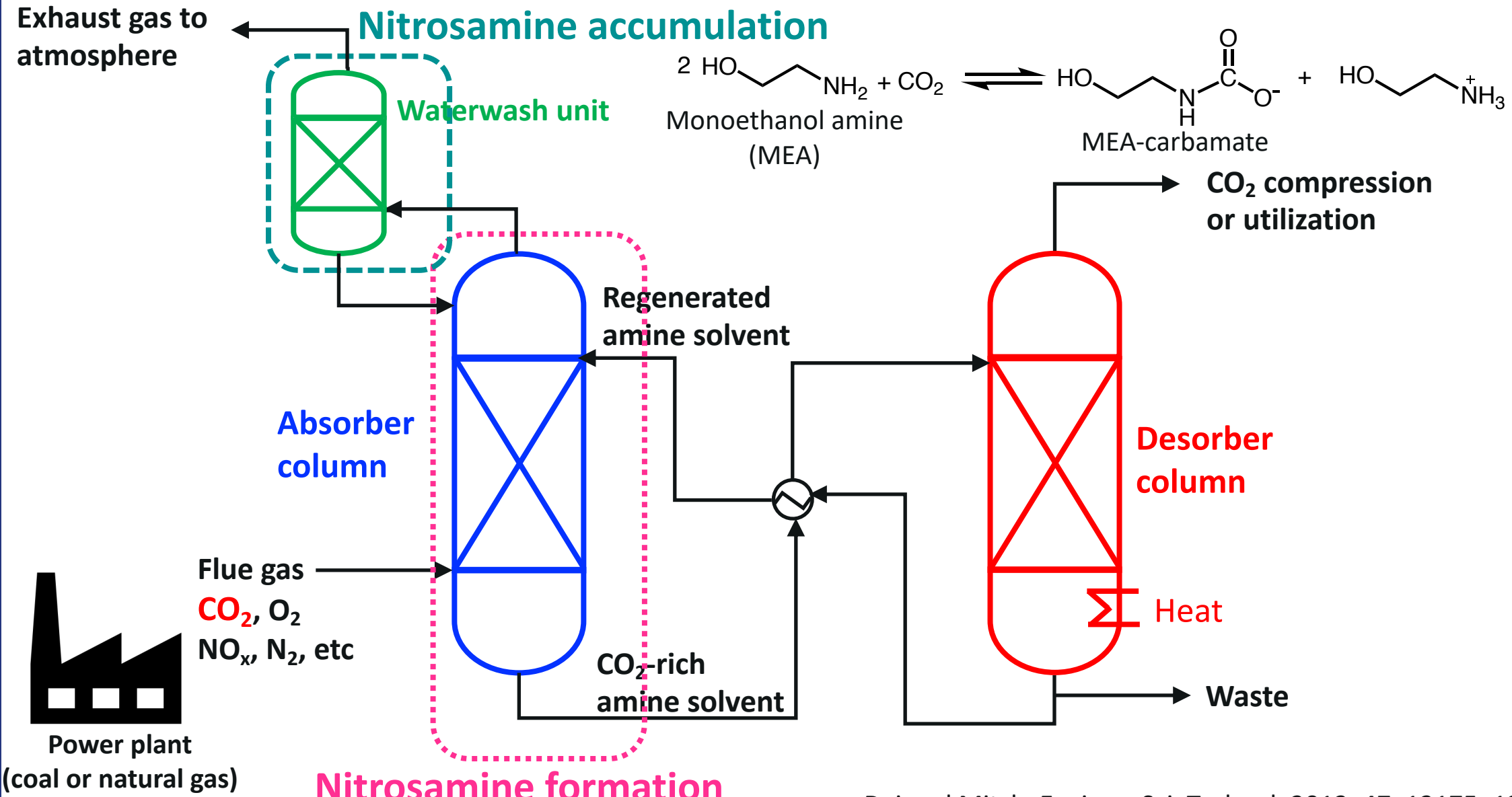
http://www.caer.uky.edu/powergen/home.shtml

Diagram of CO_2 capture system with waterwash unit



Dai and Mitch, Environ. Sci. Technol. 2013, 47, 13175−13183
Yu et al., Environ. Sci. Technol. 2017, 51, 11522−11536

General composition of waterwash solution from MEA-based CO_2 capture system

	Solvent	Water wash
pH	10 – 13	8 – 10
Amine concentration	2.5 – 8 M	~10 mM
Nitrite concentration	0.1 – 10 mM	100 – 20 μM
Nitrate concentration	20 – 200 mM	~20 μM
Aldehyde concentration	0.6 – 2 mM	150 – 200 μM
Nitrosamine concentration	50 – 300 μM	1 – 100 μM
Relative volume	1	<0.25
Temperature	Absorber: 40 – 60 ˚C Desorber: 100 – 140 ˚C	30 ˚C

Yu et al., Environ. Sci. Technol. 2017, 51, 11522−11536

Why we care about nitrosamines

- Harmful to both human health and the environment
  - **mutagenic**, **cytotoxic**, **genotoxic**, and **carcinogenic**
- Regulation by the US EPA to limit environmental nitrosamine levels in lakes and streams of NDMA: 0.69 ng/L (9.3×10^{-6} μM).
- Nitrosamines are generally polar and water soluble, so they are easy to trap in water wash

➢Remove nitrosamines from waterwash prior to their emission to the environment

https://ntp.niehs.nih.gov/ntp/roc/content/profiles//nitrosamines.pdf

Nitrosamine decomposition techniques

- Photochemical (UV) Reduction and Ozone Treatment

  Dai and Mitch *Environ. Sci. Technol*. 2015, 49, 8878

- Membrane / Nanofiltration

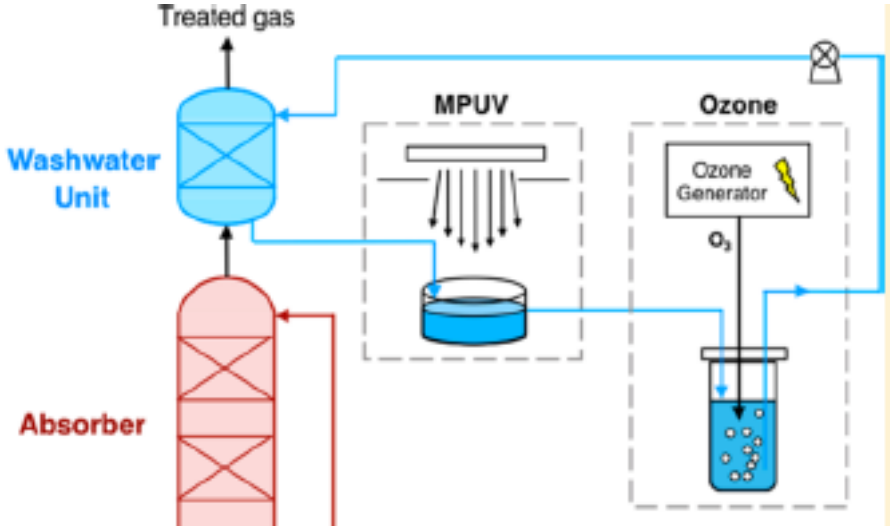
  Chon et.al. *Bioresource Technology* 2015, 190, 499

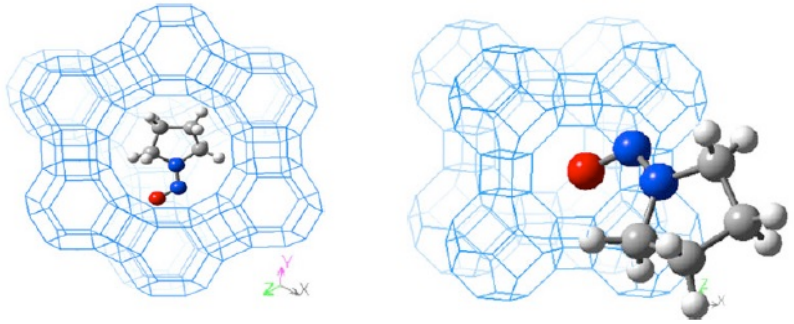
- Zeolite Membrane

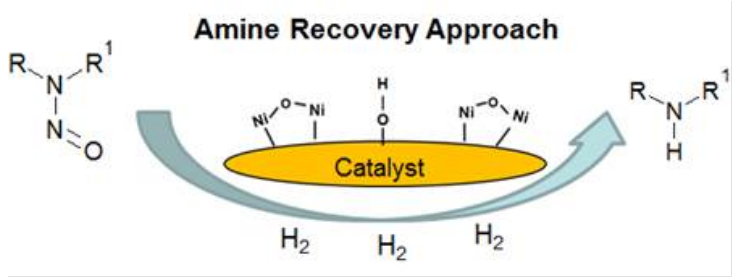
  Li et.al. *Environ. Chem. Lett.* 2014, 12, 139

- Catalytic Hydrogenation

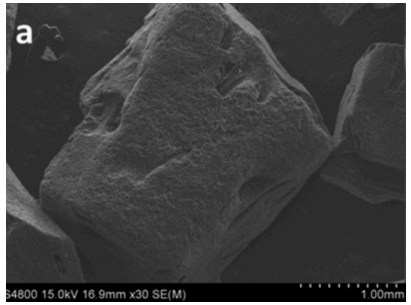
  Chandan et.al. *Int. J. Greenhouse Gas Control*. 2015, 39, 158

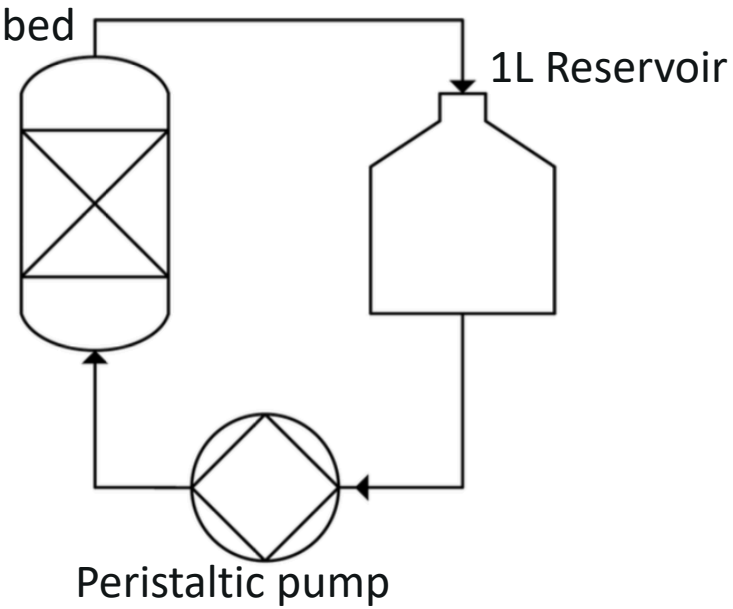




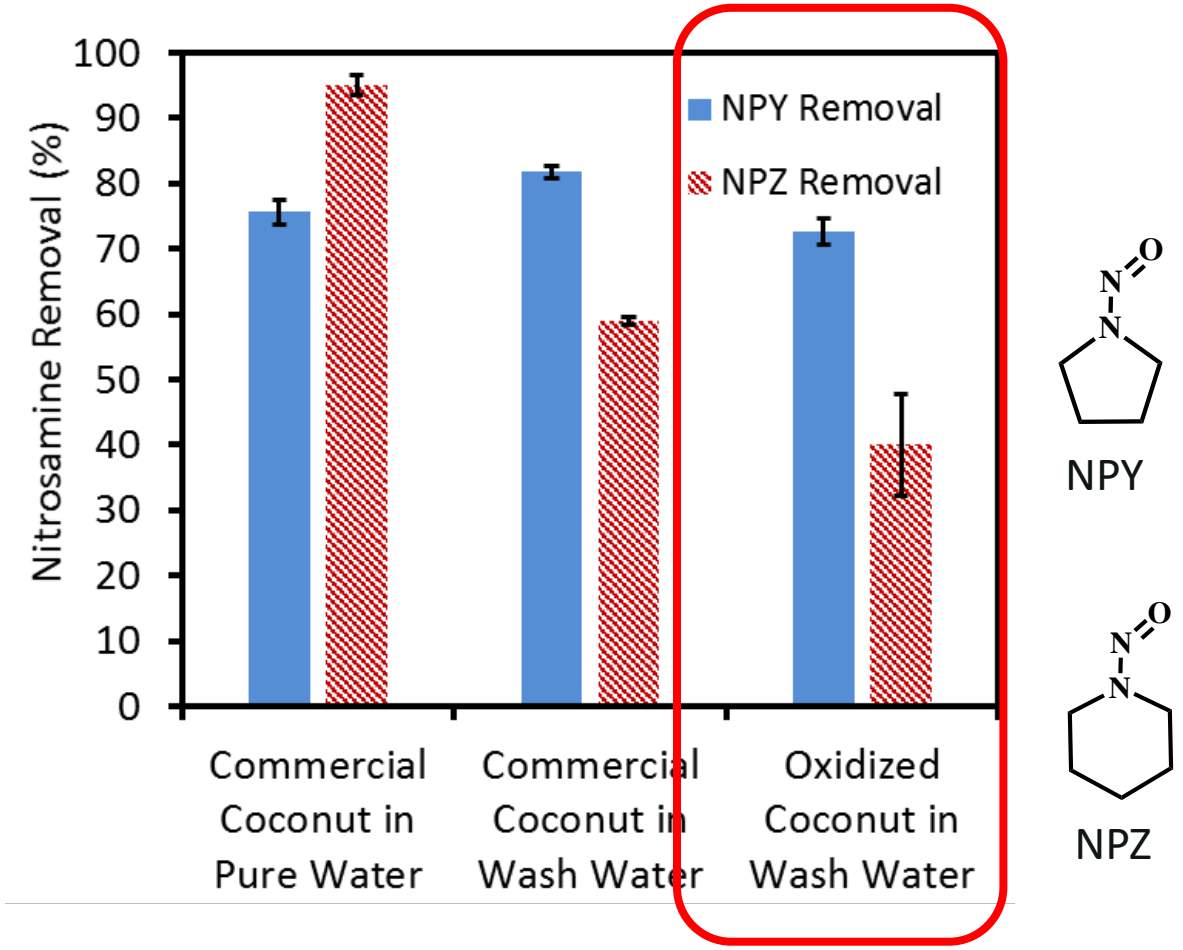


Previous study – using activated-carbon sorbents





With regenerated activated-carbon



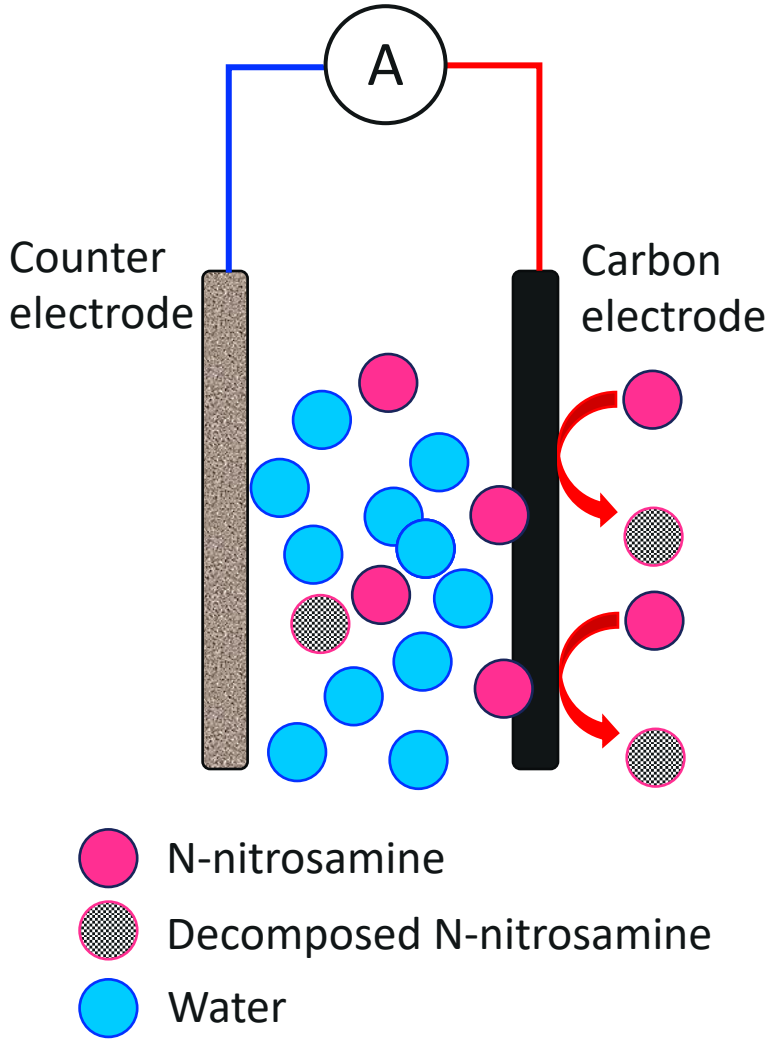
NPY

NPZ

Commercial coconut charcoal activated carbon has a high adsorption capacity and specificity towards nitrosamine (over the amine) in waterwash solutions (0.3 wt % MEA)

Widger, et.al., Environ. Sci. Technol. 2017, 51, 10913-10922

Our concept: remove nitrosamines from waterwash solution using a electrochemical approach

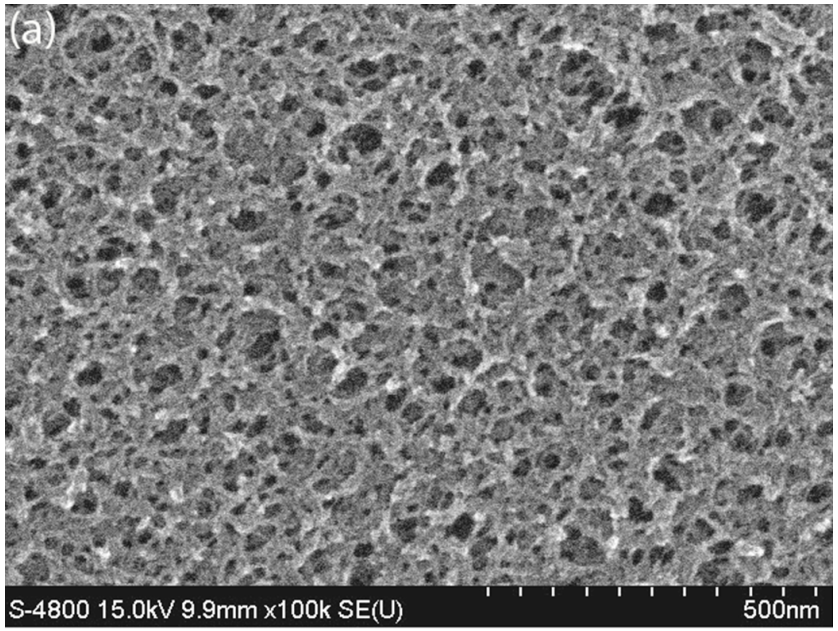


CO_2 Capture applications:

- Water wash to collect and decompose nitrosamines into less harmful compounds.
- No or low waste method
- Side benefit it does not impact amines (recovery)

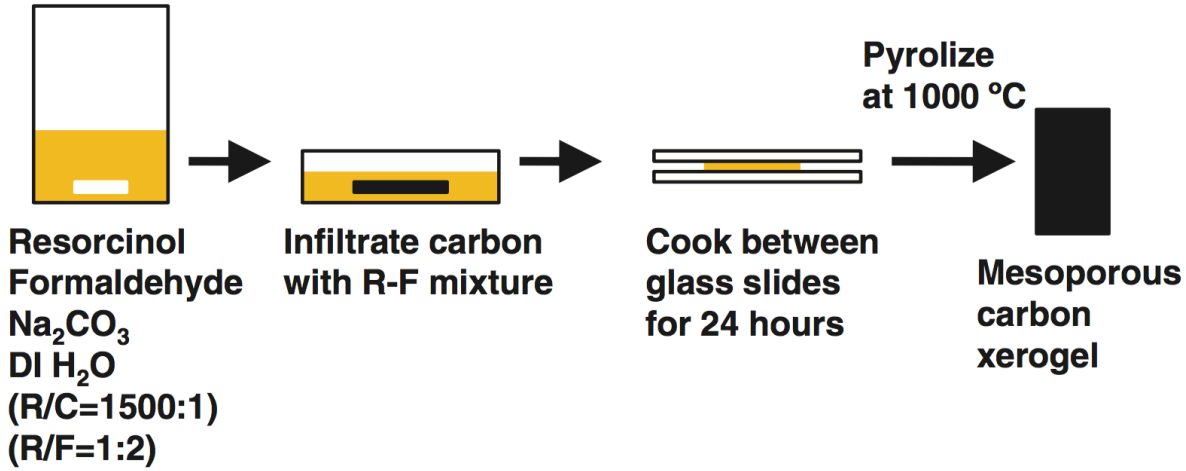
CX electrode - New effective system

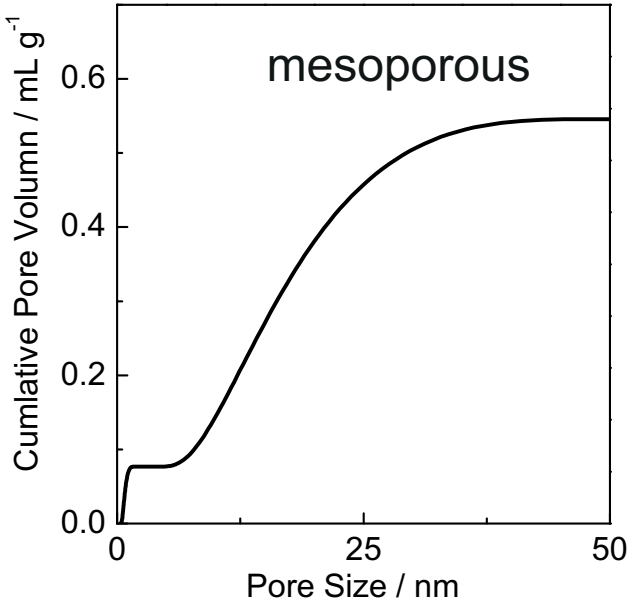
Carbon Xerogel (CX) material



Improved

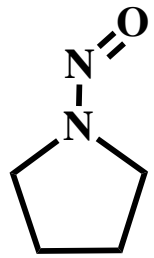
- Surface areas
- Chemical stability
- Conductivity
- Ion-adsorption capability
- Solvent wettability.





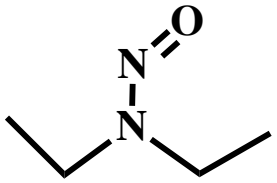
Landon et al., J. Electrochem. Soc., 159 (11) A1861-A1866 (2012)
Gao et al., J. Electrochem. Soc., 160 (9) E106-E112 (2013)

Proof of concept:



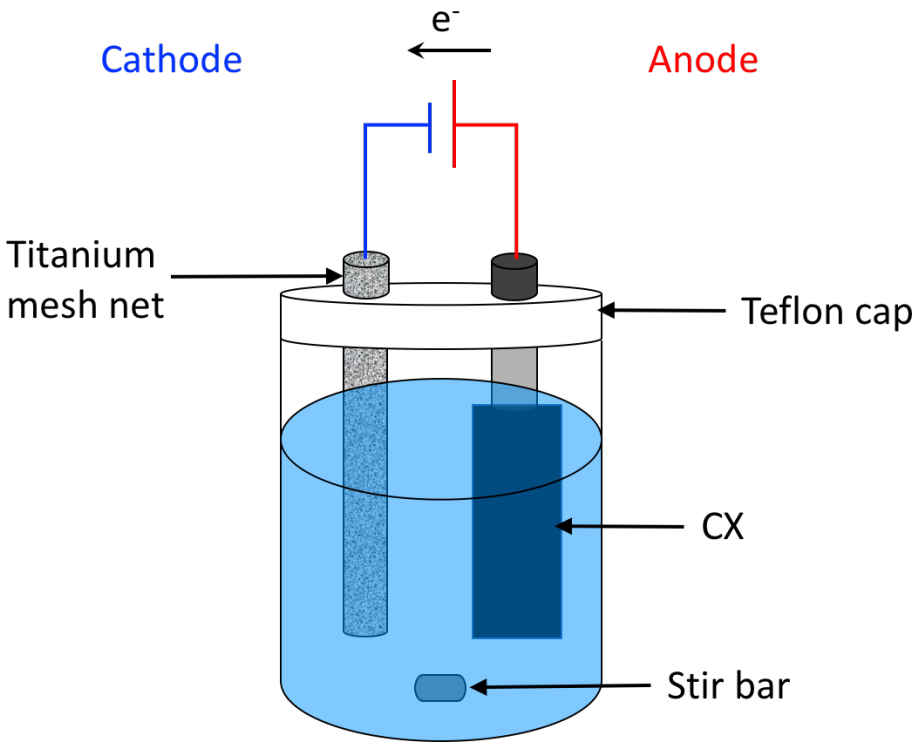
NPY

log $K_{o/w}$ = - 0.19



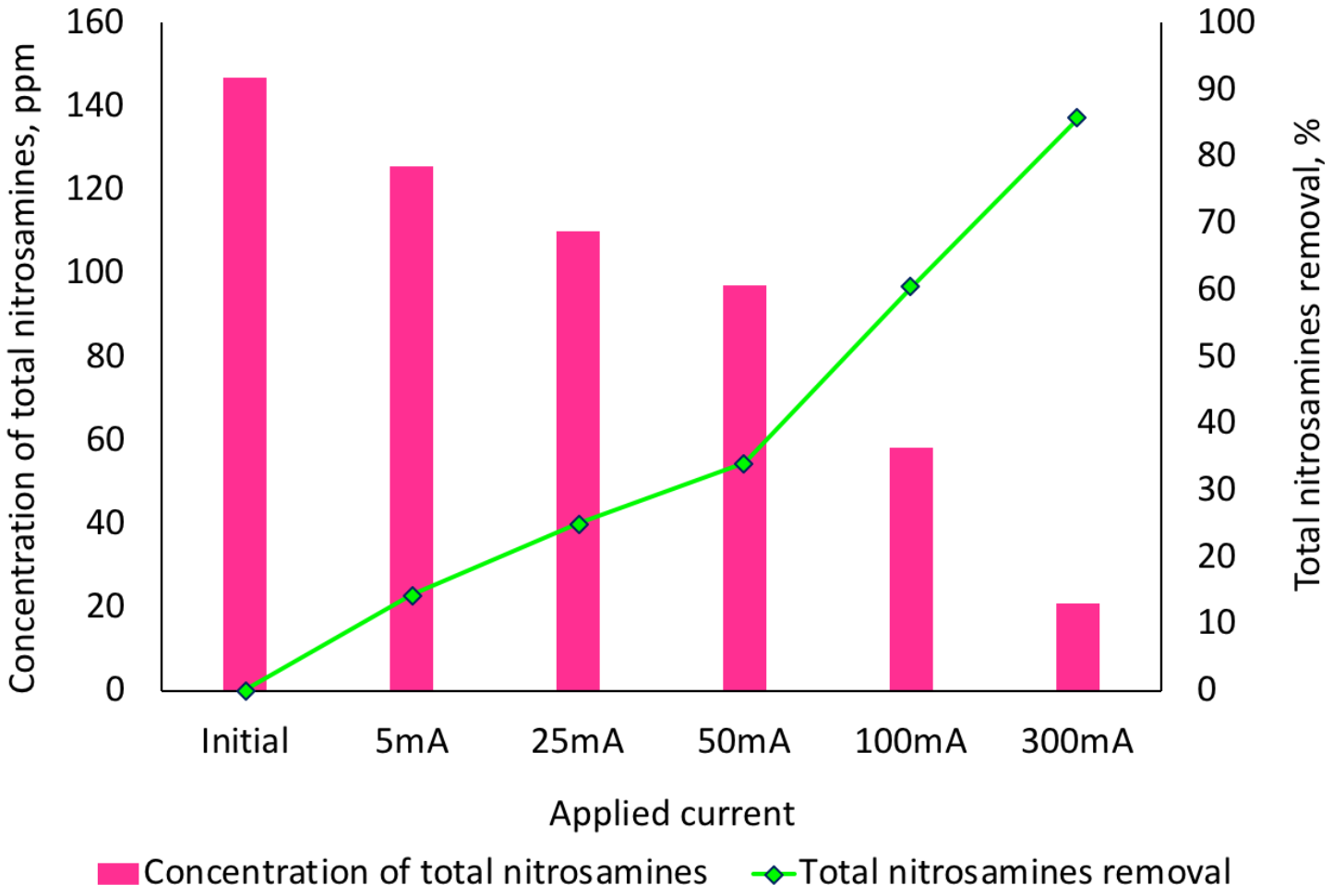
NDEA

log $K_{o/w}$ = 0.48



- Simulated waterwash solution was prepared with **1% MEA** and CO_2 loading.
- N-nitrosopyrrolidine (**NPY**) and n-nitrosodiethylamine (**NDEA**) were selected
- **Constant current** of 5 – 300 mA was passed through the cell
- Keep solution temperature at 25 ˚C using a temperature control hot plate.
- Changes in the nitrosamine concentration were monitored using **LC/MS** or UV-vis
- Degraded products of nitrosamine were explored using **IC**

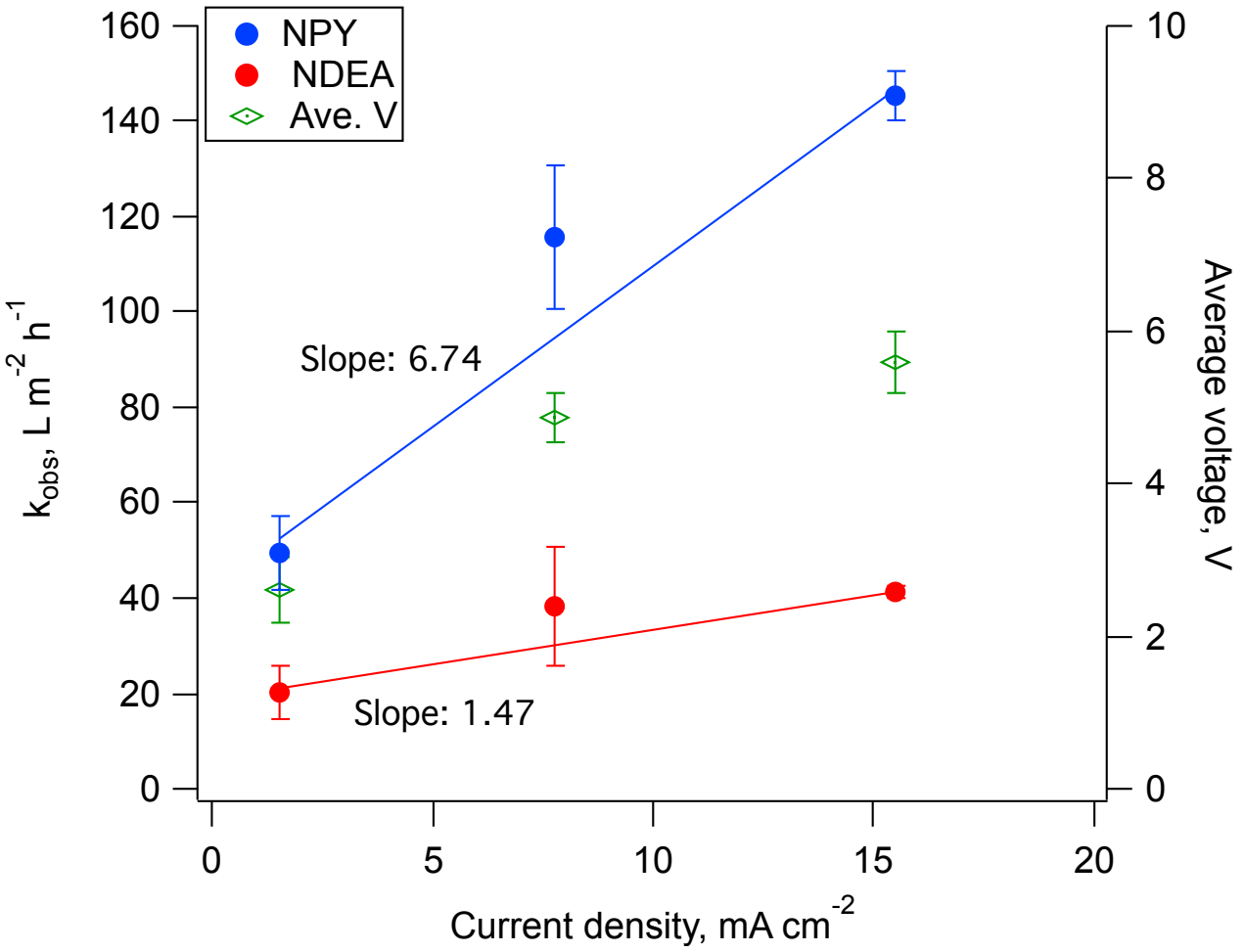
Removability of nitrosamines from simulated waterwash solution



- Total nitrosamines (NPY+NDEA) level in waterwash solution decreased as function of total charge passed. The removal achieved 86 % using an applied current up to 300 mA.
- Each current was charged for 1 hour. The pH of solution with CX before and after charging were around 9.0.
- Calculated Faradaic efficiency of total nitrosamines degradation: 0.8–6.9%.
- Observed voltage: 6–9 V

Thompson et al., *Int. J. Greenhouse Gas Control.* 83 (2019) 83–90

Normalized observed removal rate constants of nitrosamines with applied current density

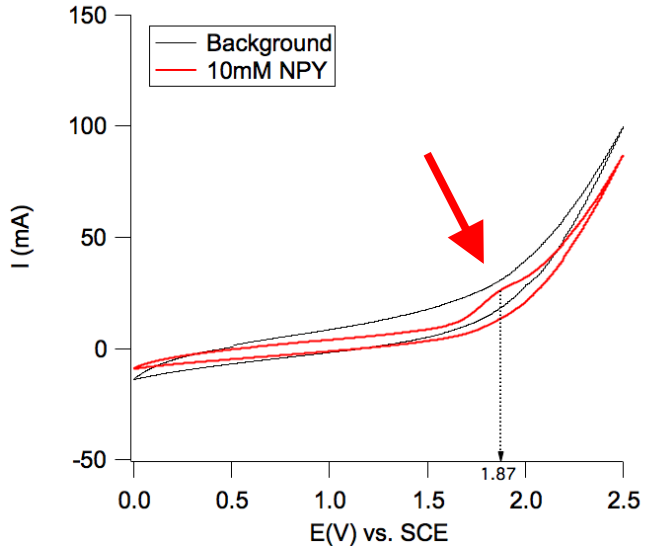


- We tentatively assumed k was as pseudo first-order and each nitrosamine dopes two electrons in accordance with Chaplin et al. (2009 and 2010).
- The k_{obs} is normalized with the geometric size of CX electrode and solution volume.
- Error bar for nitrosamine indicates the standard deviation of slope which indicates k by plotting $-\ln(C/C_0)$ vs. time.

Chaplin et al., Environ. Sci. Technol., 43, 8302-8307 (2009)
Chaplin et al., Environ. Sci. Technol., 44, 4264-4269 (2010)

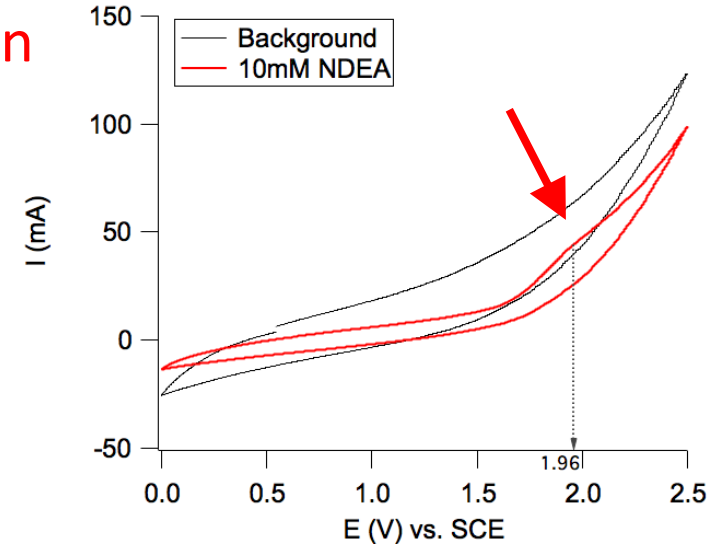
Half-cell: Cyclic voltammogram of nitrosamines in alkaline solution

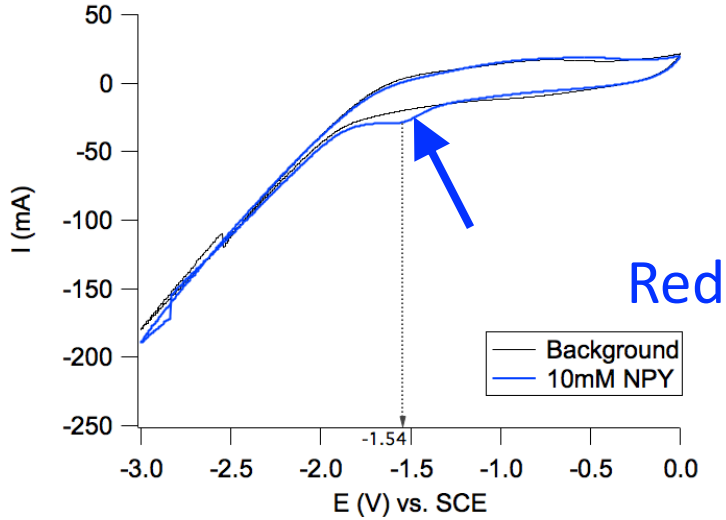
NPY



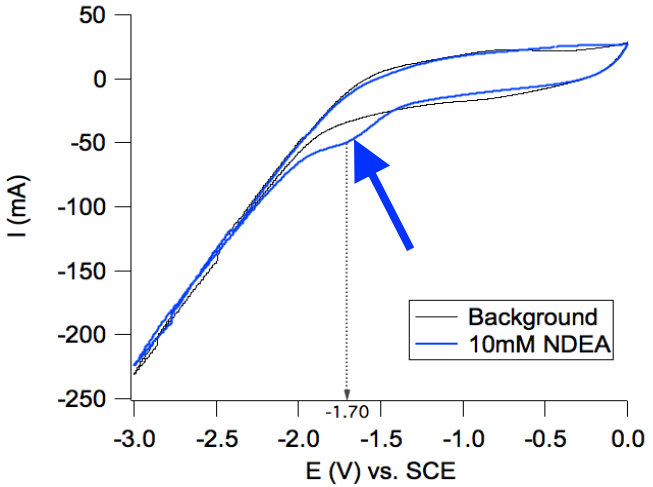
Oxidation

NDEA





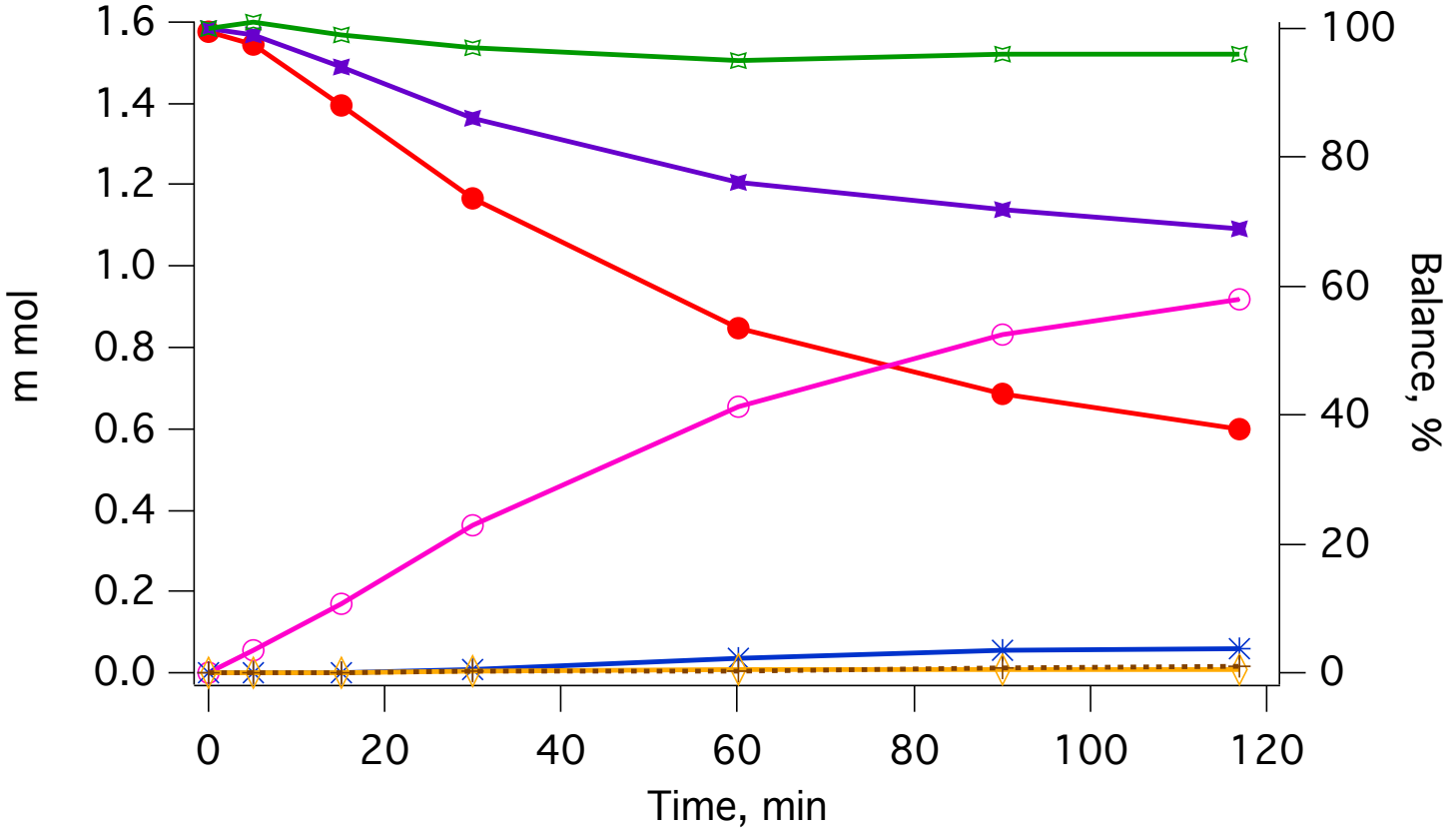
Reduction

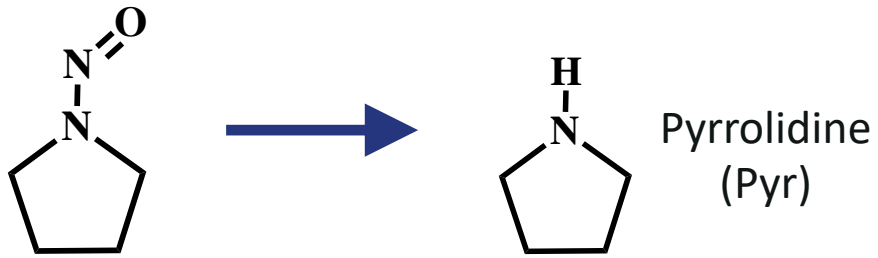


- NPY and NDEA react at anode and cathode.
- Compared to NDEA, NPY requires less energy to drive reaction due to less voltage at the peak current.

Working electrode: 40mm^2 CX, Counter electrode: graphite, Scan rate: 100 mV/s, 1M Na_2SO_4 background electrolyte (+NaOH), pH: 8-9 at 25 °C

NPY degradation and products as a function of time





Hybrid reactions of anode and cathode

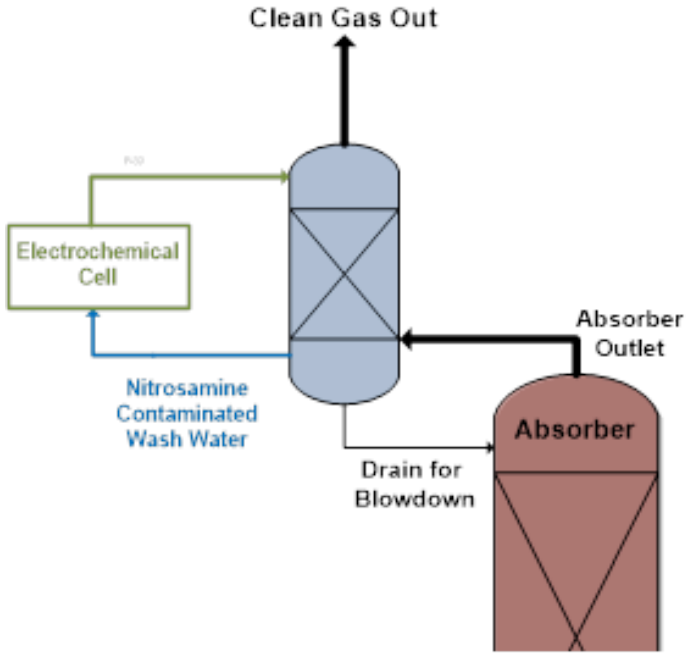
Initial solution conditions: 2000 ppm NPY in 50 mM Na_2SO_4 background electrolyte. The pH was adjusted to 8.54. 100 mA was charged.

Note:NH_4^+ was not analyzable using IC due to abundant of Na^+ from supporting electrolyte.

Current and future work

Funded in part by DOE-NETL (DE-FE0007395)

- Optimization and fabrication of a larger electrochemical cell and testing with waterwash solutions from the UKy-CAER Advanced 0.7 MWe small pilot CCS



Thank You

- The Carbon Management Research Group (CMRG) Members: Duke Energy, Electric Power Research Institute (EPRI), and Louisville Gas & Electric (LG&E) and Kentucky Utilities (KU) – financial support during the preliminary development stage.

- This research is currently supported by US DOE-NETL (DE-FE0031661).

- UKy-CAER Analytical Team, Ayokunle Omosebi, and Roger Perrone