PM 2.5 and acetaldehyde

Potentially significant air quality impacts of amine scrubbing

Gary T. Rochelle
Texas Carbon Management Program
Department of Chemical Engineering
University of Texas at Austin

Presented to SPRINT

June 22, 2023

Agenda

- Why are we concerned?
- PM2.5
  - Perspective
  - Management
- Acetaldehyde
  - Perspective
  - Management
- Conclusions

Why should we manage air emissions?

- Professional Chemical Engineers shall “Hold paramount the safety, health and welfare of the public and protect the environment in performance of their professional duties.”

- The politics of Environmental Justice require that capture systems do not appear to degrade air quality.

- Legal requirements of AAQS, HAPS, etc. may require emissions management that might not otherwise make sense.

CCS must be responsive to the political realities of environmental justice

Center for International Law & 50 more oppose CCS

https://www.ciel.org/issue/carbon-capture-and-storage/

"CCS is not consistent with the principles of environmental justice."

"CCS makes dirty energy even more dangerous for frontline communities. Facilities equipped with carbon capture technology have to burn more fossil fuel to get the same energy output, resulting in increased emissions of toxic and hazardous pollutants, like fine particulates (PM2.5)."

Only PM2.5 may be out of compliance with NAAQS

- PM2.5 are particles < 2.5 microns
  - Directly emitted (but not from amine scrubbing)
  - Results from atmospheric reactions of acid and bases (NH_3,amines/HNO_3)
  - Epidemiology has quantified deaths as a primary health effect
- Practically all U.S. power plants are in regions that comply.
- However, the current PM2.5 NAAQS (12 mg/m^3) may be reduced
  - In Jan. 2023 U.S. EPA proposed to revise the annual standard to 8-10 mg/m^3.
  - World Health Organization (WHO) now recommends PM2.5 = 5 mg/m^3.
  - Extensive portions of U.S. would not comply with 9 or 5 mg/m^3.
- Capture systems must not increase or appear to increase PM2.5

Mitigating PM2.5 from amine scrubbing
Reduce Acid Emissions

- SO_2, SO_3, H_2SO_4
  - Prescrub SO_2 to protect solvent and eliminate emissions
  - Remove SO_3
    - Bag filter with $Ca(OH)_2$
    - Gas/Gas heat exchanger
    - Brownian diffusion filter

- NO_x- oxidizes to nitric acid - NO_2 catalyzes amine oxidation
  - SCR (by site selection, retrofit, or new build)
    - NO_2 is hard on solvents – Use SCR to protect solvent

Mitigating PM2.5 - Ammonia

- Water wash is ineffective
  - Ammonia is volatile and not completely removed
  - Ammonia recycles with wash water bleed to solvent
    - Accumulates in solvent until emission = production
- Minimize amine oxidation; which we want to do anyway
- Acid wash will remove ammonia
  - Must be implemented as a second stage wash
  - Cannot be returned to solvent loop
  - Waste water treatment required

Mitigate PM2.5 from amine scrubbing
Reduce amine emissions

- Amines – minimize economic loss or better
  - Water wash – single stage, 2-stage, (acid wash)
  - Avoid amine aerosol especially with coal

Required for water balance

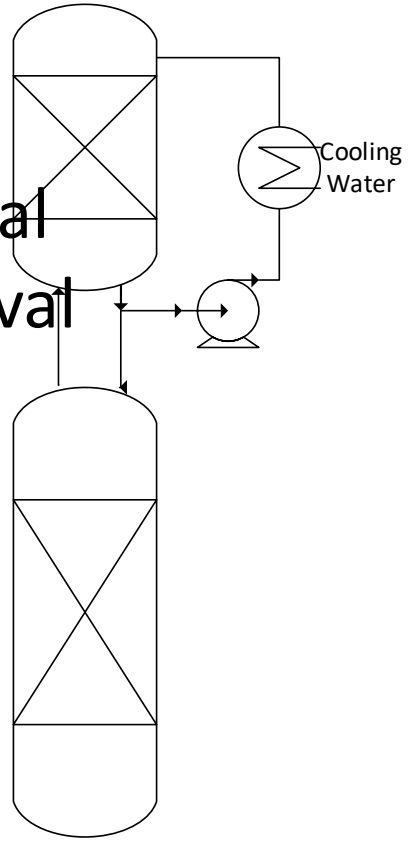
99+% removal of amine and nitrosamine with recycle to solvent

10-20 feet of packing

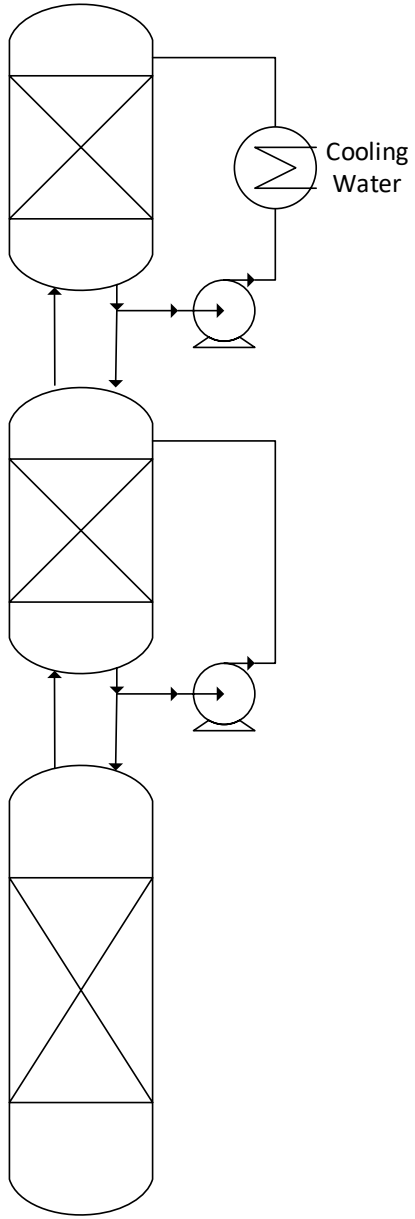
2-stage increases removal

Acid wash for NH_3 removal

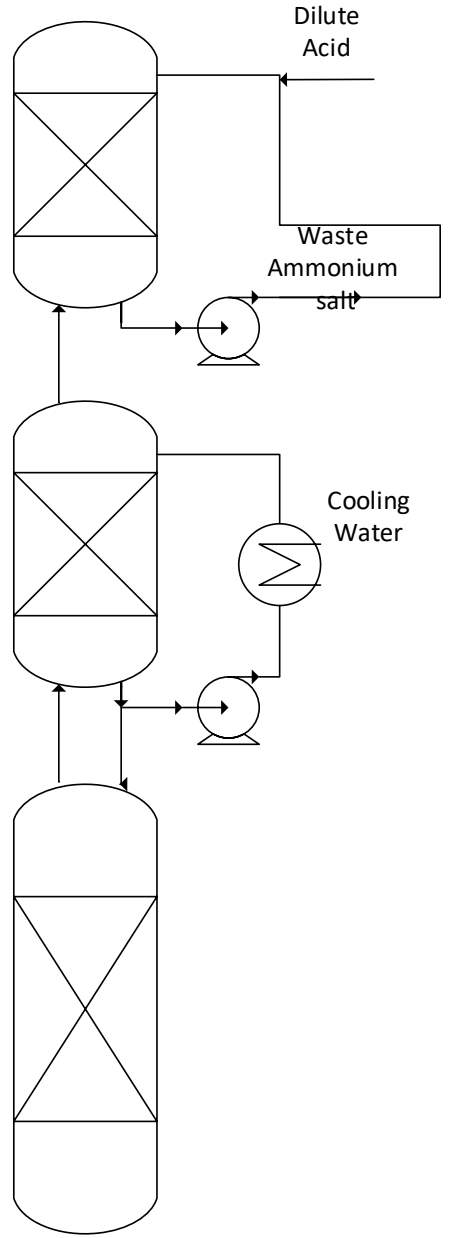
Wash Configurations



Single Stage
Water Wash
(default configuration)



2-Stage
Water Wash



Water Wash +
Acid wash

Current U.S. regulations for air toxics

Acetaldehyde and formaldehyde:

Listed Hazardous Air Pollutants

At 10 t/yr, will probably trigger New Source Review with MACT

1 ppm acetaldehyde = 20 t/y in Mustang FEED (460 MW NGCC)

EPA will develop guidance for MACT per legal requirements.

Emission of the lowest 18% in “existing” plants of a given class

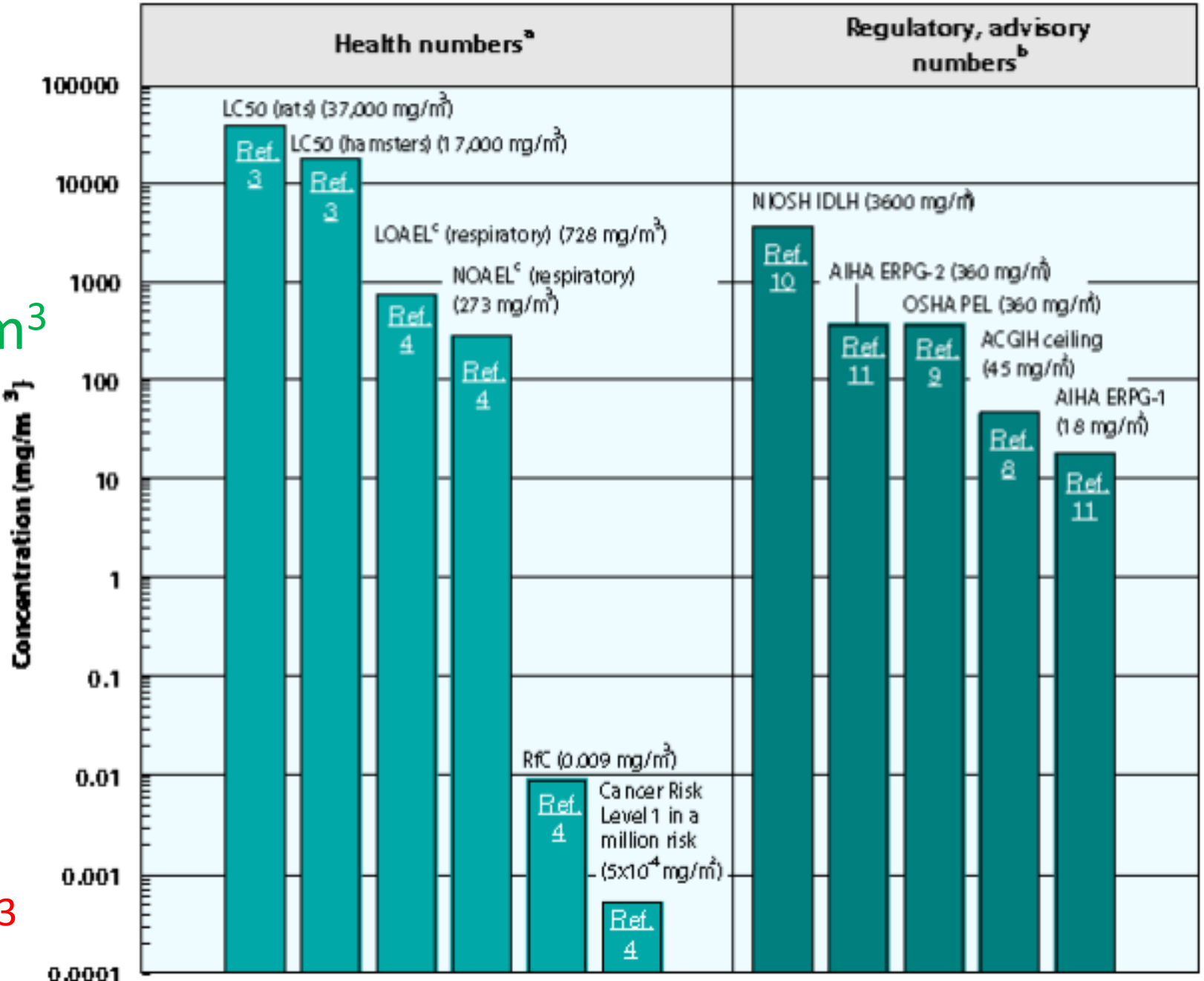
Perspective on acetaldeyhyde

- Annual US emissions – 27 million lbs (1995)
- 1 ppm acetaldehyde = 0.04 million lbs/yr in Mustang FEED (460 MW NGCC)
- Emissions from residential wood burning – 11 million lbs
  - 0.7 g/kg
- Ambient air concentrations average 5 $\mu g/m^3$
- 1220 μg/cigarette
- Common derivative from drinking alcohol
- US EPA Urban Air Toxics Strategy:
  - "[Acetaldehyde is] One of 33 hazardous air pollutants that present the greatest threat to public health in urban areas."
- Atmospheric half life may not be helpful
  - Daytime: 2-10 hour
  - Nighttime: 60 hr
  - [formaldehyde: 0.5 hr)

Acetaldehyde Inhalation Exposure

273 mg/m^3

0.5 µg/m^3



Oxidation pathway

- Piperazine + O_2 >> acetaldehyde $R_{PZ} = [PZ]\ f(O_2, Fe^{+2}, NO_2)$
- Acetaldehyde + O_2 > Acetic Acid $R_{acet} = [Acet]\ g(O_2, Fe^{+2}, NO_2)$
- $[Acet]_{ss} = [PZ]\ f(PZ, O_2, Fe^{+2}, NO_2) / g(Acet, O_2, Fe^{+2}, NO_2)$

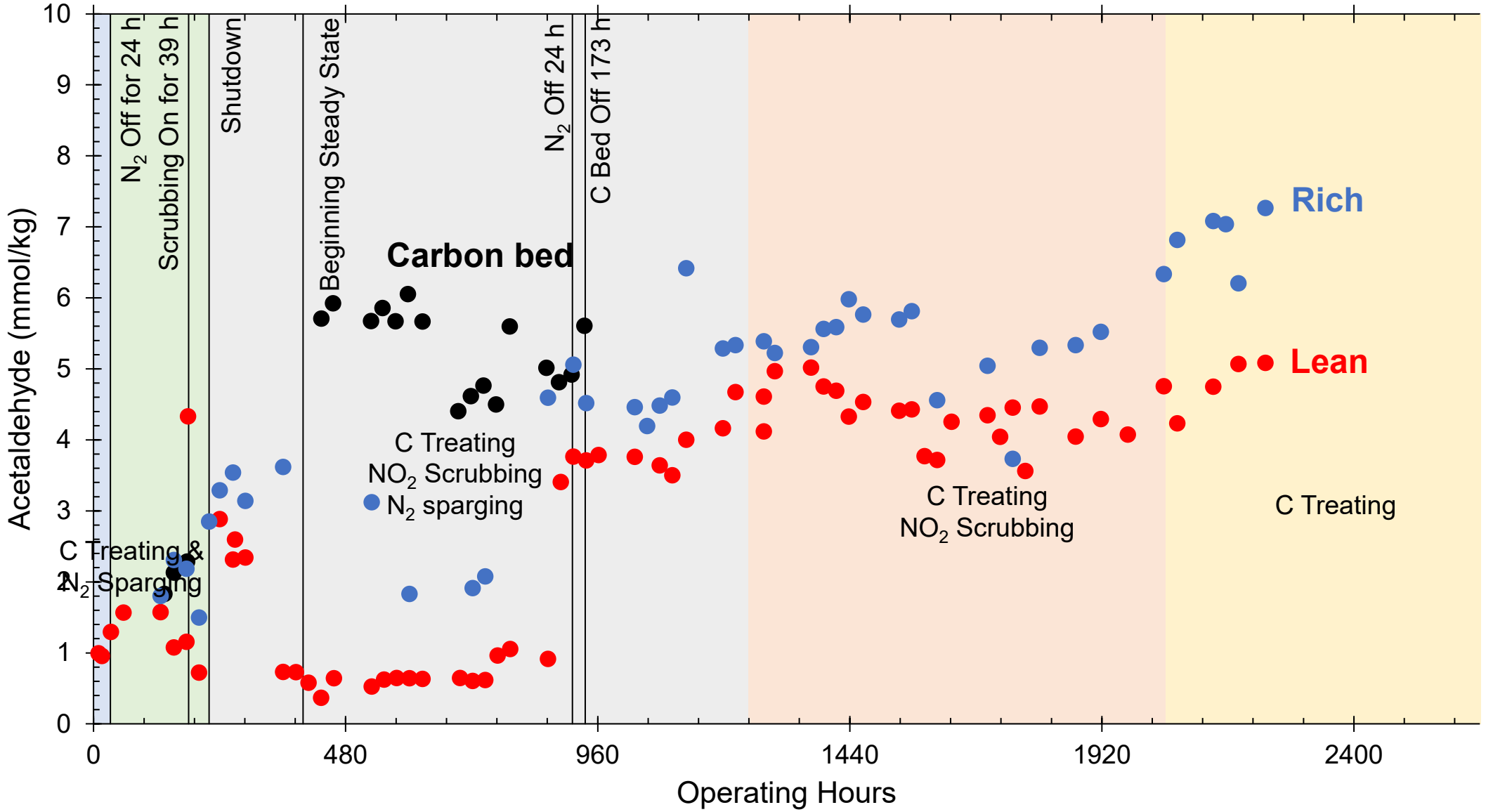
Therefore, maybe changes in oxidation routes can impact $[Acet]_{ss}$

Amines react reversibly with aldehydes to increase solubility

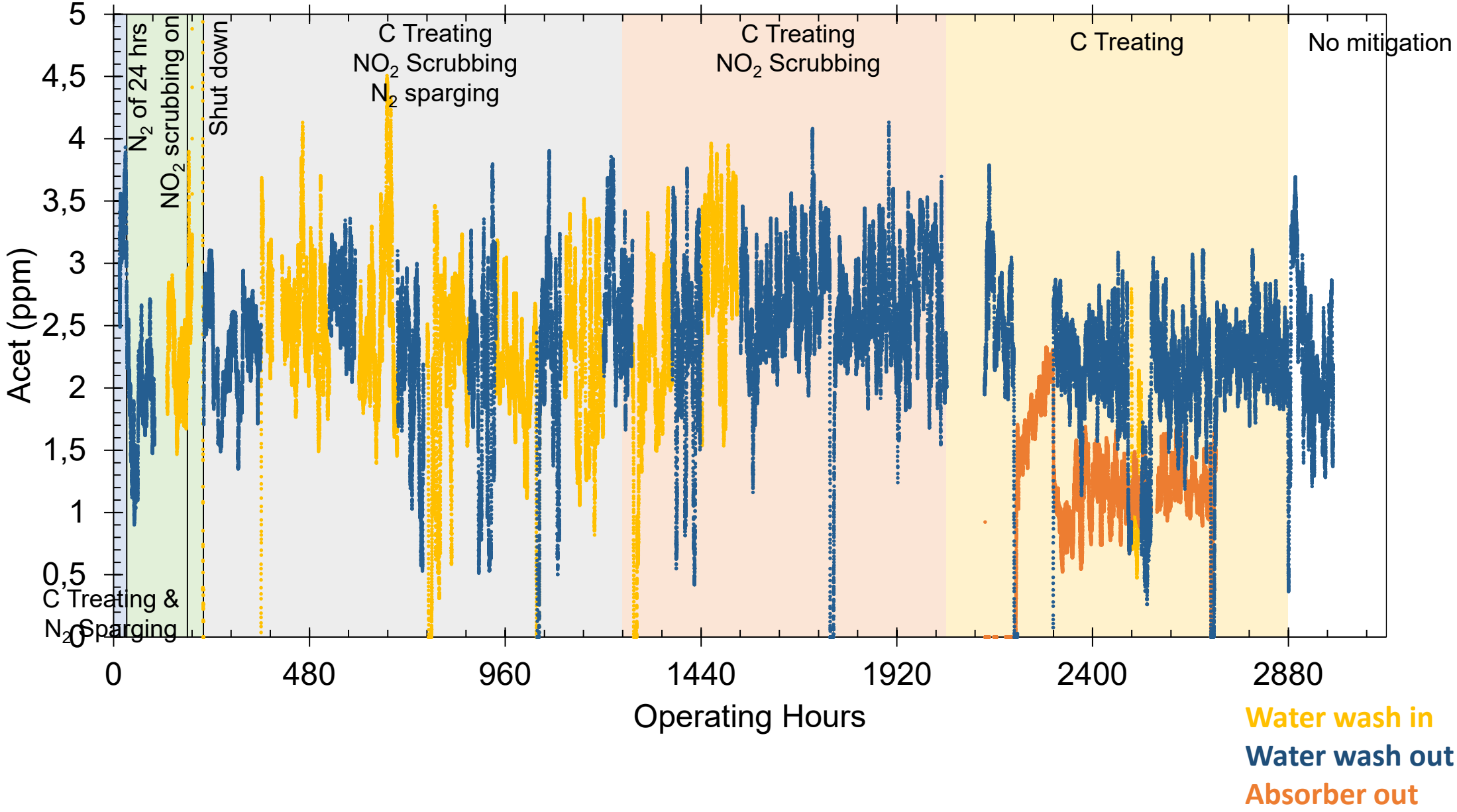
$$RNH_2 + O{=}CH_2\text{-}CH_2 \leftrightarrow RNH\text{-}CHOH\text{-}CH_2$$

Preliminary measurements of acetaldehyde in PZ solvent at NCCC pilot plant by DNPH/HPLC (UV)

9uv



Acetaldehyde in gas out with 5 m PZ at NCCC pilot



Aldehyde Management

Amine make-up at WW

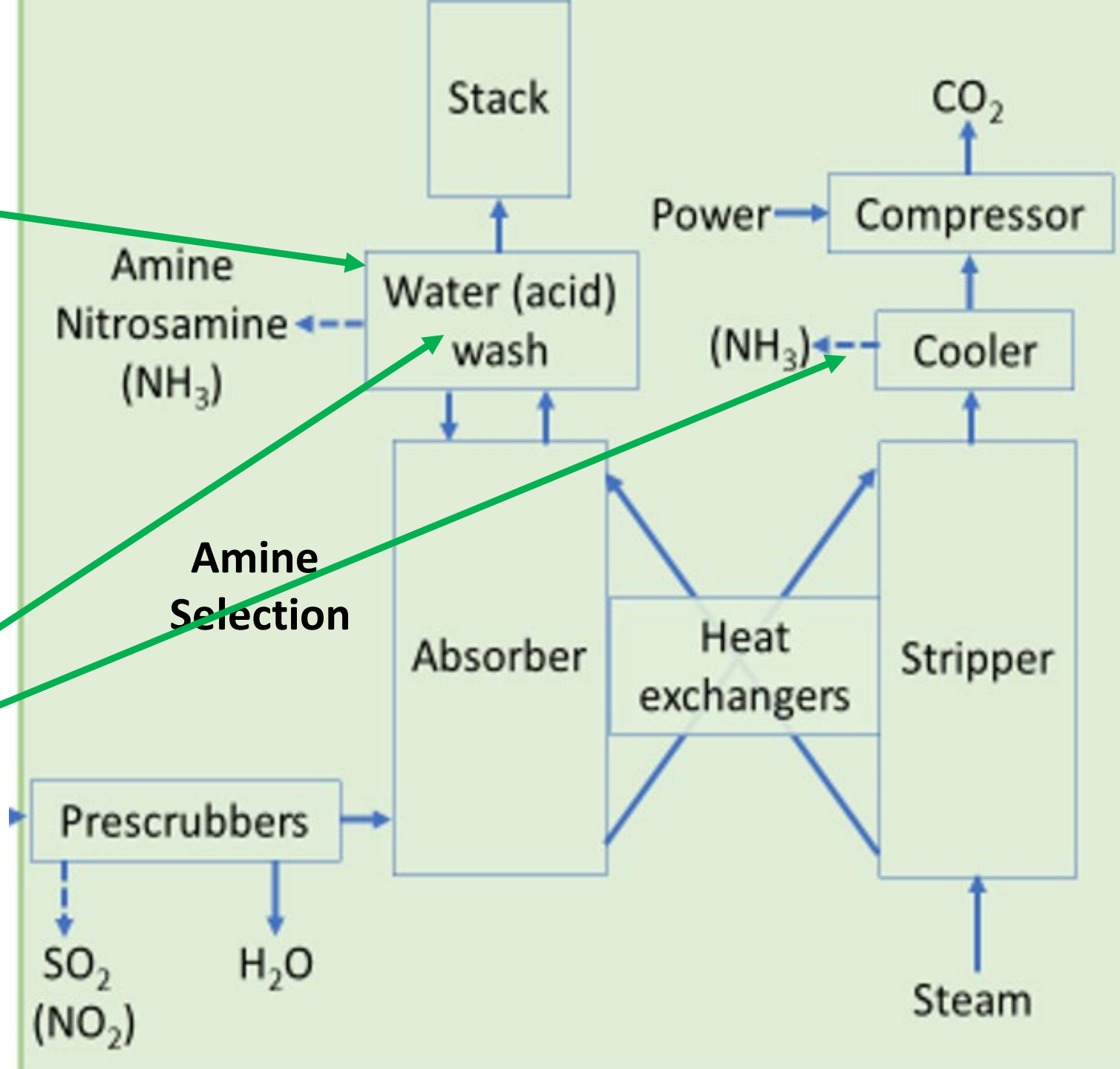
Add sulfite to WW

Treat water wash or reflux

C Treating

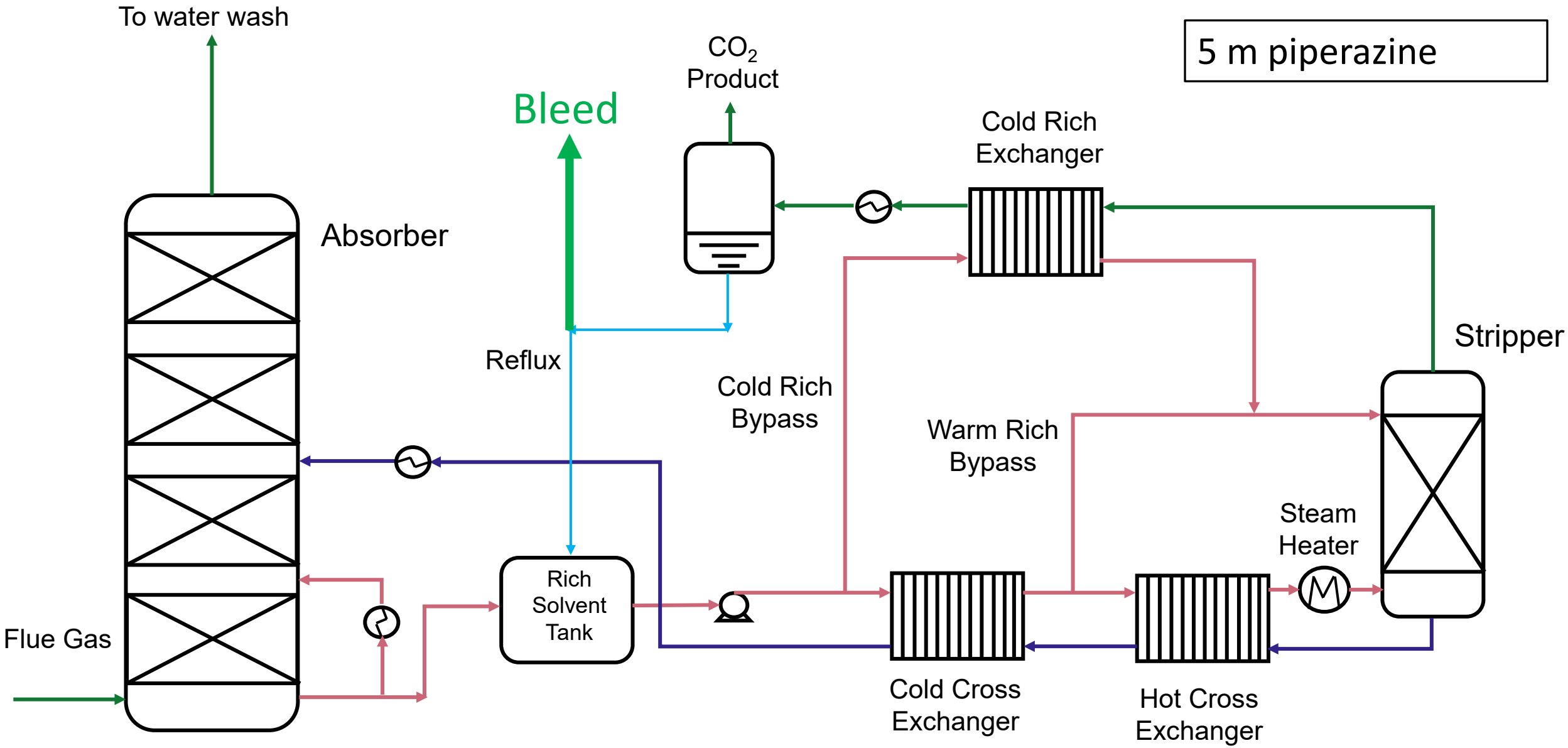
Electrochemical oxidation

Other selective reactions



PZAS™ process

Condensate bleed to reduce NH_3 and aldehyde emissions



Conclusions

- PM2.5 will be the most significant priority pollutant
  - Documented health effects
  - Formed by atmospheric reactions of nitric acid with ammonia and amine
  - Reduce NO_x emissions (use efficient SCR)
  - Reduce ammonia and amine emissions

- Acetaldehyde will the most significant hazardous air pollutant
  - It may cause cancer by inhalation
  - It is not readily eliminated by atmospheric reactions
  - Manage oxidation mechanisms
  - Treat or bleed water wash or stripper reflux to decompose or remove