Managing Impacts on air quality by carbon capture with amine scrubbing

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Agenda

- Why are we concerned?
- Air pollutants from power plants
- Mitigating air quality impacts from Amine Scrubbing
  - Site selection
  - Process features of amine scrubbing
  - Mitigating amine aerosol
- Pilot plant results
- Conclusions
- Recommendations

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. will require emissions management that might not otherwise make sense.

Air Pollutants from Power Plants with Amine Scrubbing

[a]TLV - Threshold Limit Value for vapor exposure in workplace

[b]NAAQS – National Ambient Air Quality Standard - protect the most sensitive subgroups f

	2019 TLV[a] (ppmv) [(ACGIH]	NAAQS[b] annual ave (ppbv)	LD_{50} for Rodents mg/kg
$PM_{2.5}$ (particles < 2.5 μm)	NA	12.0 $\mu g/m^3$	
Ozone	0.05-0.20	70 (8-hr)	
NO_2/NO	0.2/25	100	
NH_3	25		350
Piperazine	0.03		2600
Ethanolamine	6		700
SO_2	0.25	140	
Acetaldehyde	25		1930

Only PM2.5 (and maybe ozone) may be out of compliance with NAAQS

- Practically all power plants are in regions that comply with all NAAQS.
- However, the current PM2.5 NAAQS (12 mg/m^3) may be reduced
  - EPA is proposing reduction to 9 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.
- PM2.5 results from reactions of acids and bases in the atmosphere
- Capture systems must not increase or appear to increase PM2.5
  - By increased ammonia and amine emissions

Carcinogenic emissions of amine scrubbing are not equal

Parent amine	Carcinogen	TD_{50} in rats (mg/kg)
Dimethylamine	N-Nitrosodimethylamine	0.096
	Dimethylnitramine	0.55
Most amines	Formaldehyde	1.4
Piperazine	N-Nitrosopiperazine	8.8
Most amines	Acetaldehyde	153

Carcinogenicity Results in CPDB (the Carcinogenic Potency Project, https://files.toxplanet.com/cpdb/index.html)

•Zeitschrift fuer Krebsforschung., 74(179), 1970 [PMID:4252983]

Current 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.

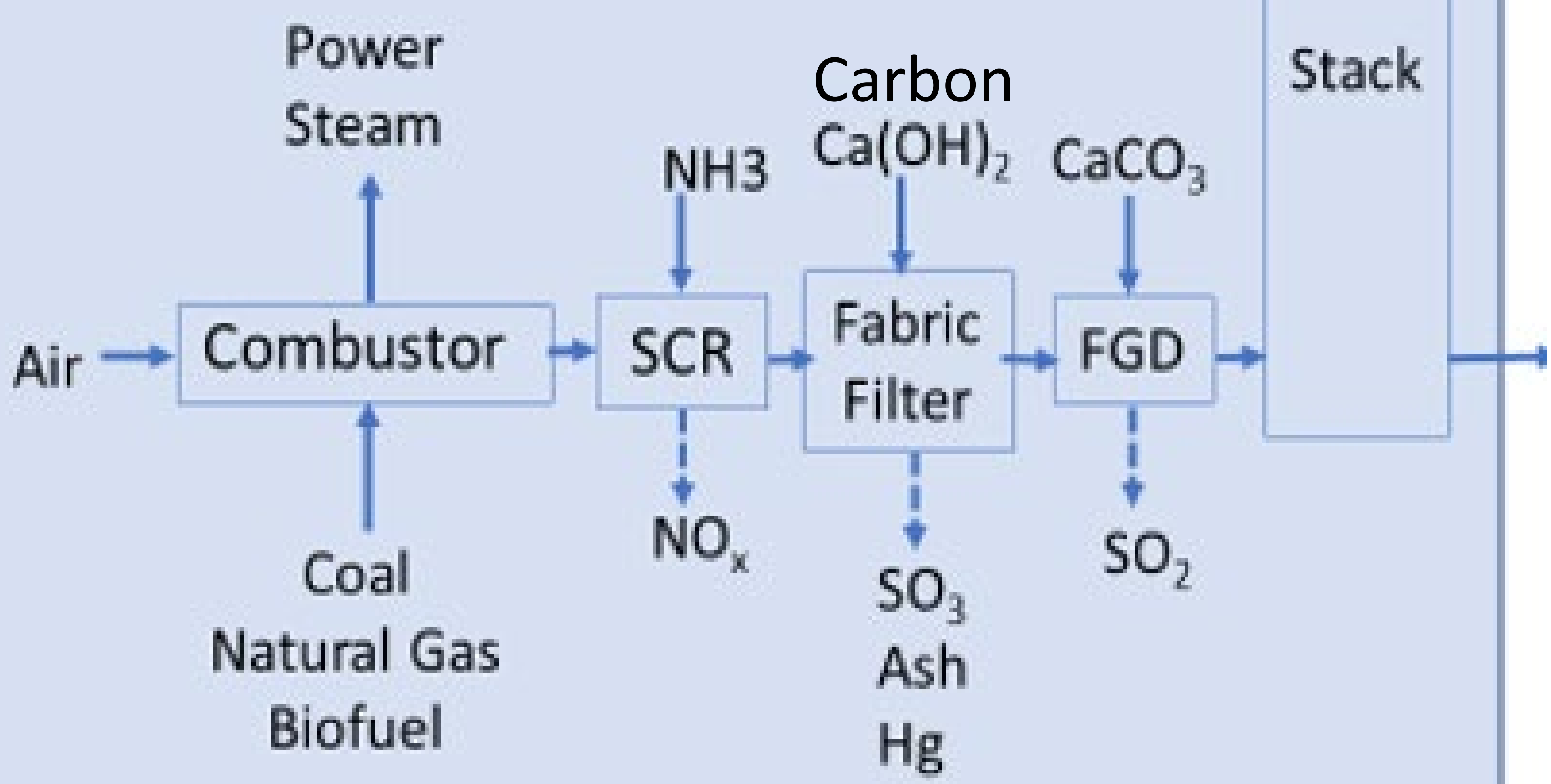
EPA should develop guidance to permit amine, ammonia, & nitrosamine emissions.

Liquid Waste from Amine Scrubbing

- Little or no water makeup or discharge from the solvent loop
- Spill management
  - Diking
  - Minimize nitrosamine, aldehydes, and other degradation products
  - The amine itself may be the primary concern
    - In rats given an increasing oral dose of solvent, with 1000 ppm MNPZ in 30 wt PZ, PZ is fatal at the same time that a tumor will develop.
- Reclaiming waste "non-hazardous" except?
  - Chromium from stainless steel corrosion
  - Unknown impacts of degradation products
  - Nitrosamine decomposed by heating

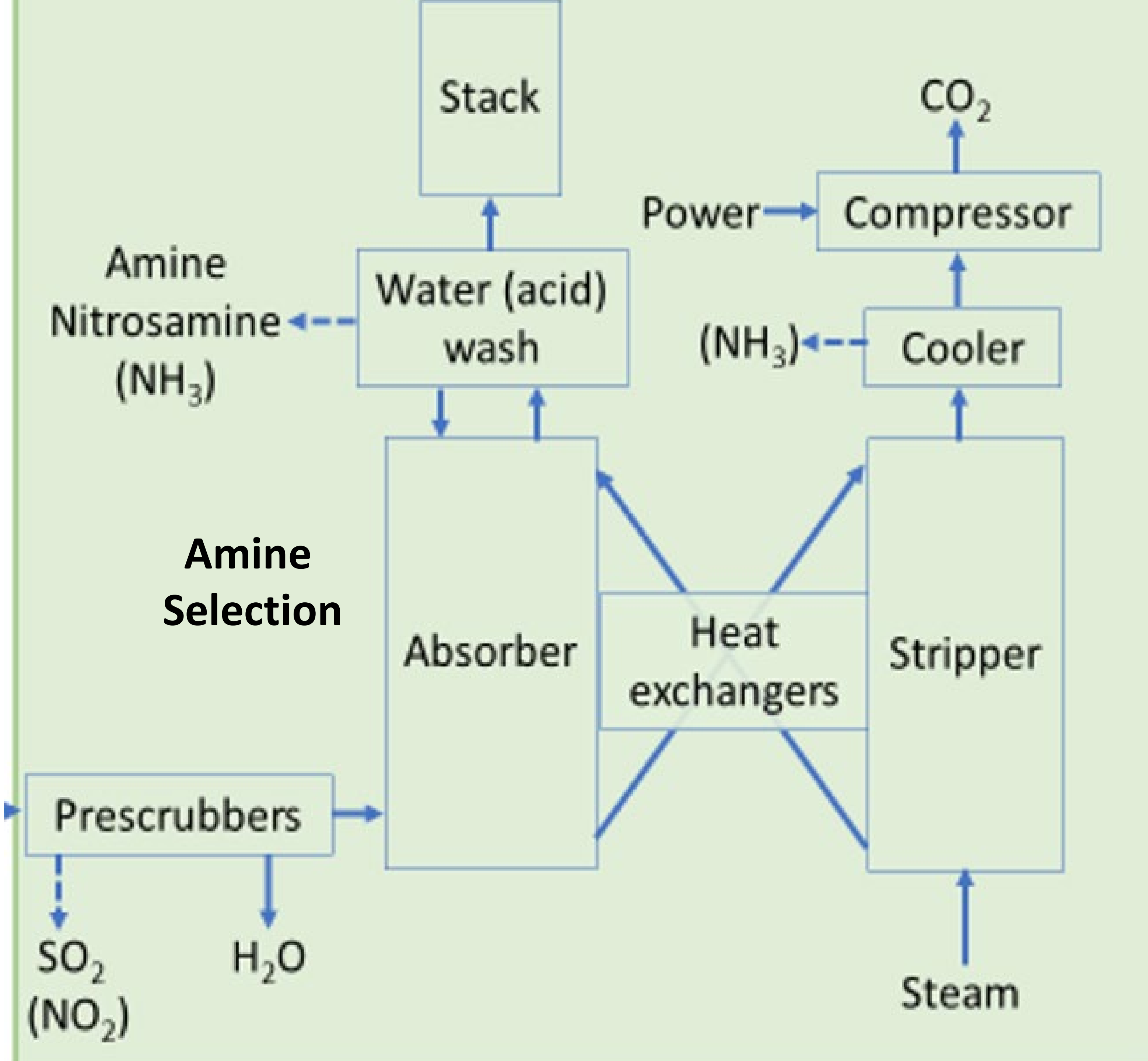
Mitigation

Site Selection will minimize impacts



Process features mitigate impacts

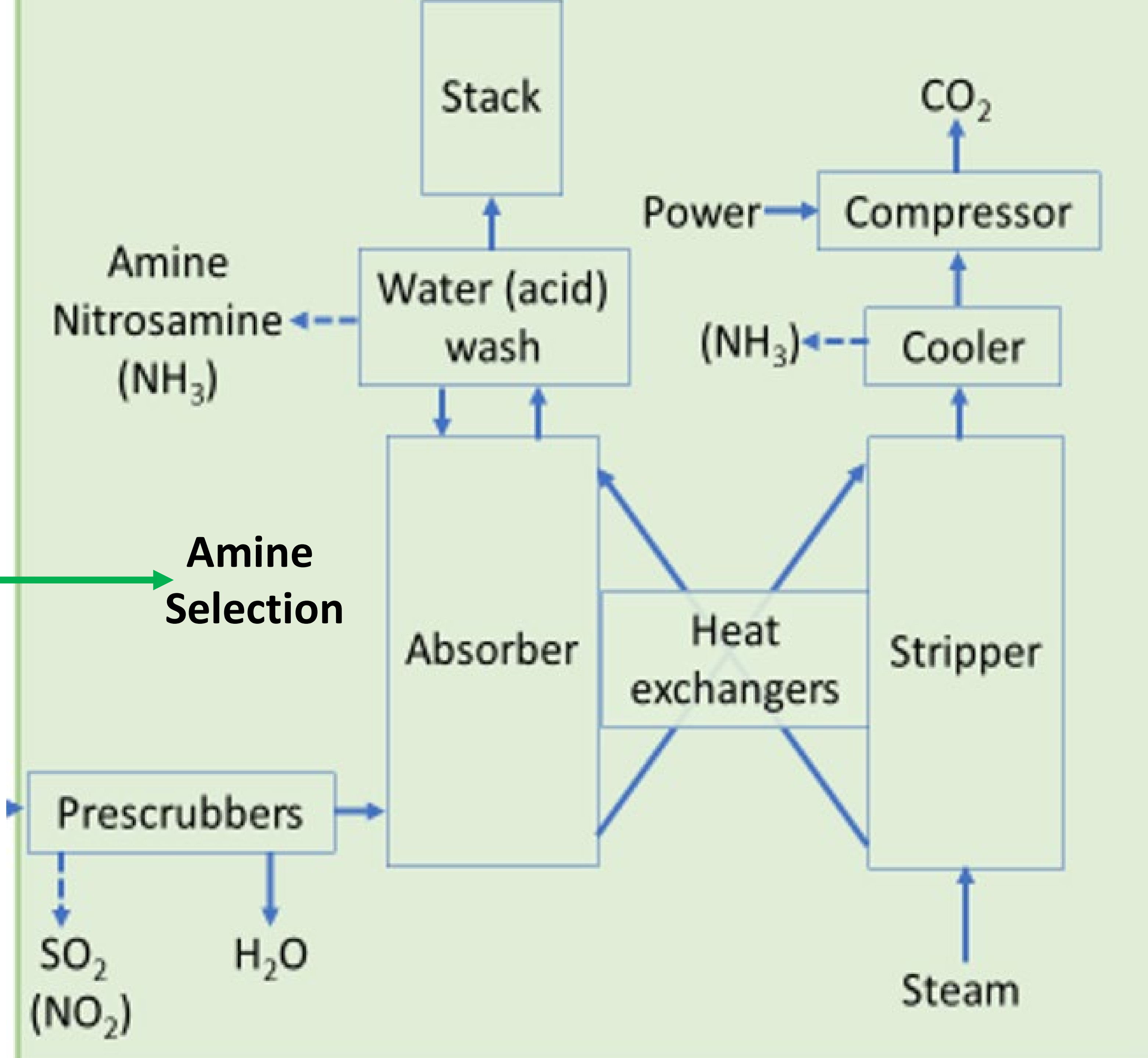
Prescrubbers remove all of SO_2 & NO_2 w Thiosulfate



Process features mitigate impacts

Amine Selection

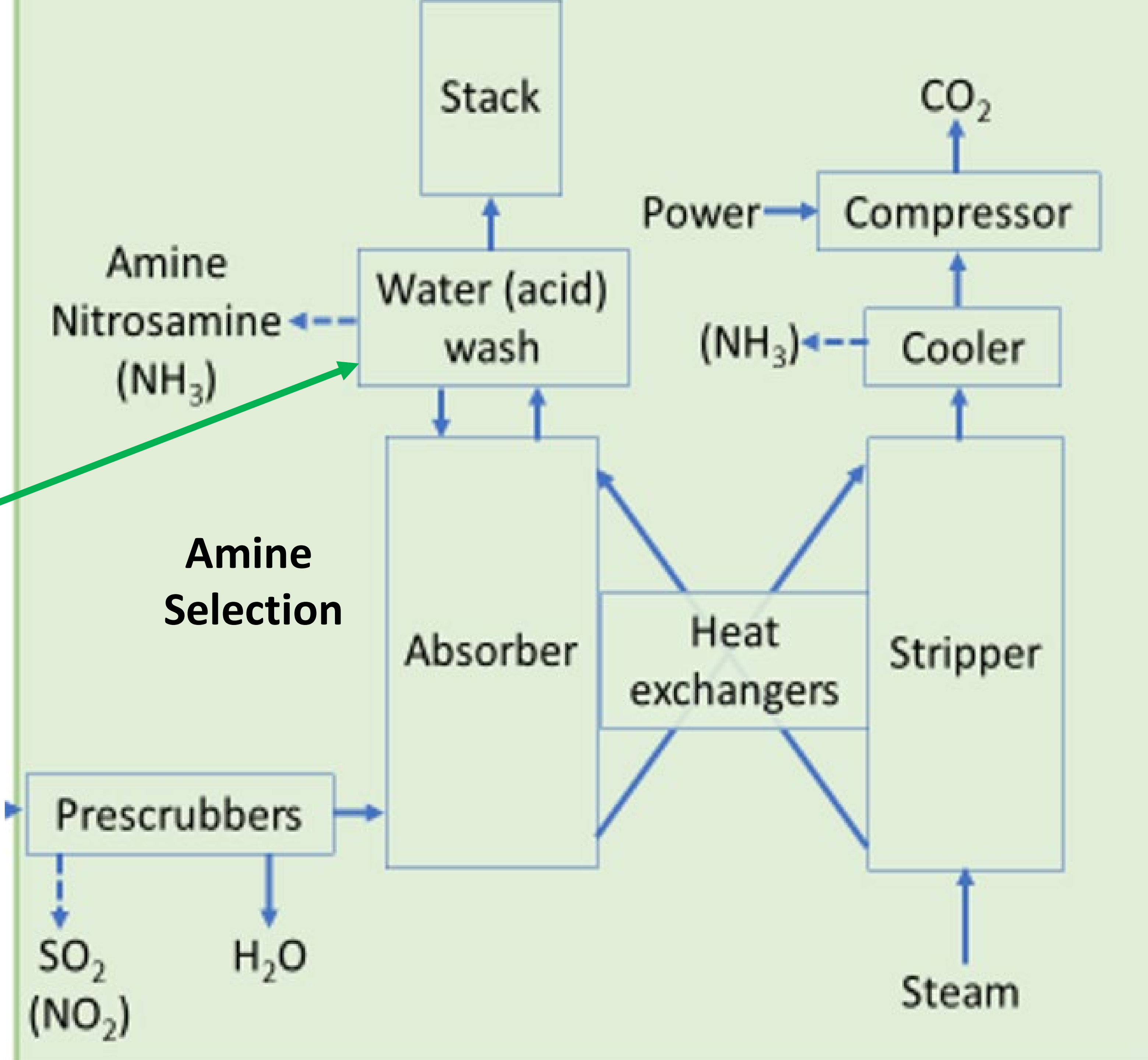
Minimize nitrosamine
Minimize volatility
Avoid oxidation
Avoid difficult degradation products



Process features mitigate impacts

Water Wash

Eliminates vapor amine emissions
With acid, eliminate NH_3
Removes most nitrosamines
Control amine aerosol
No makeup water



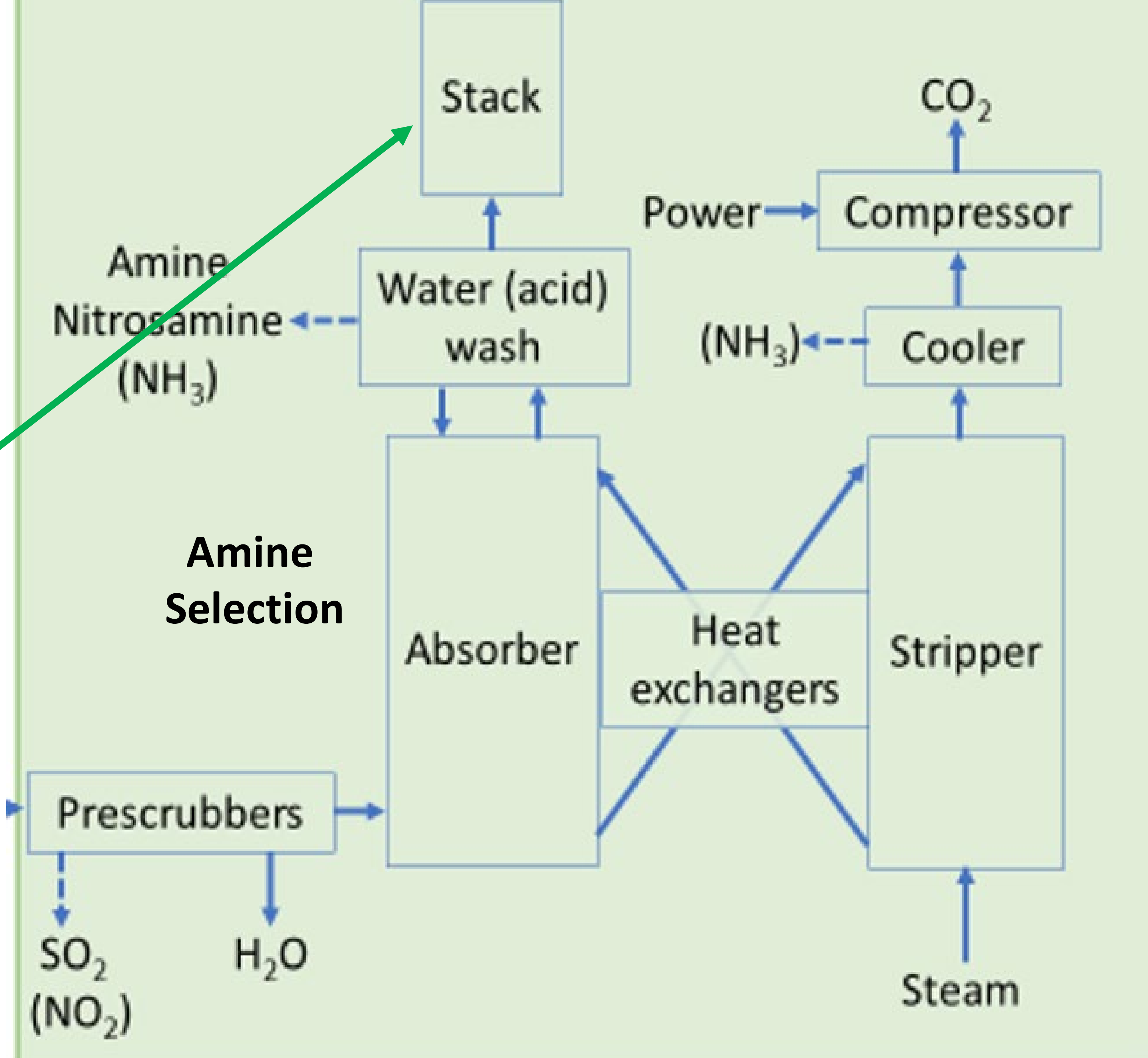
Process features mitigate impacts

Tall Stack + Atm Rxns

Disperses amine & resulting products
Provides time for atm degradation

<u>Half life in sunlight</u>

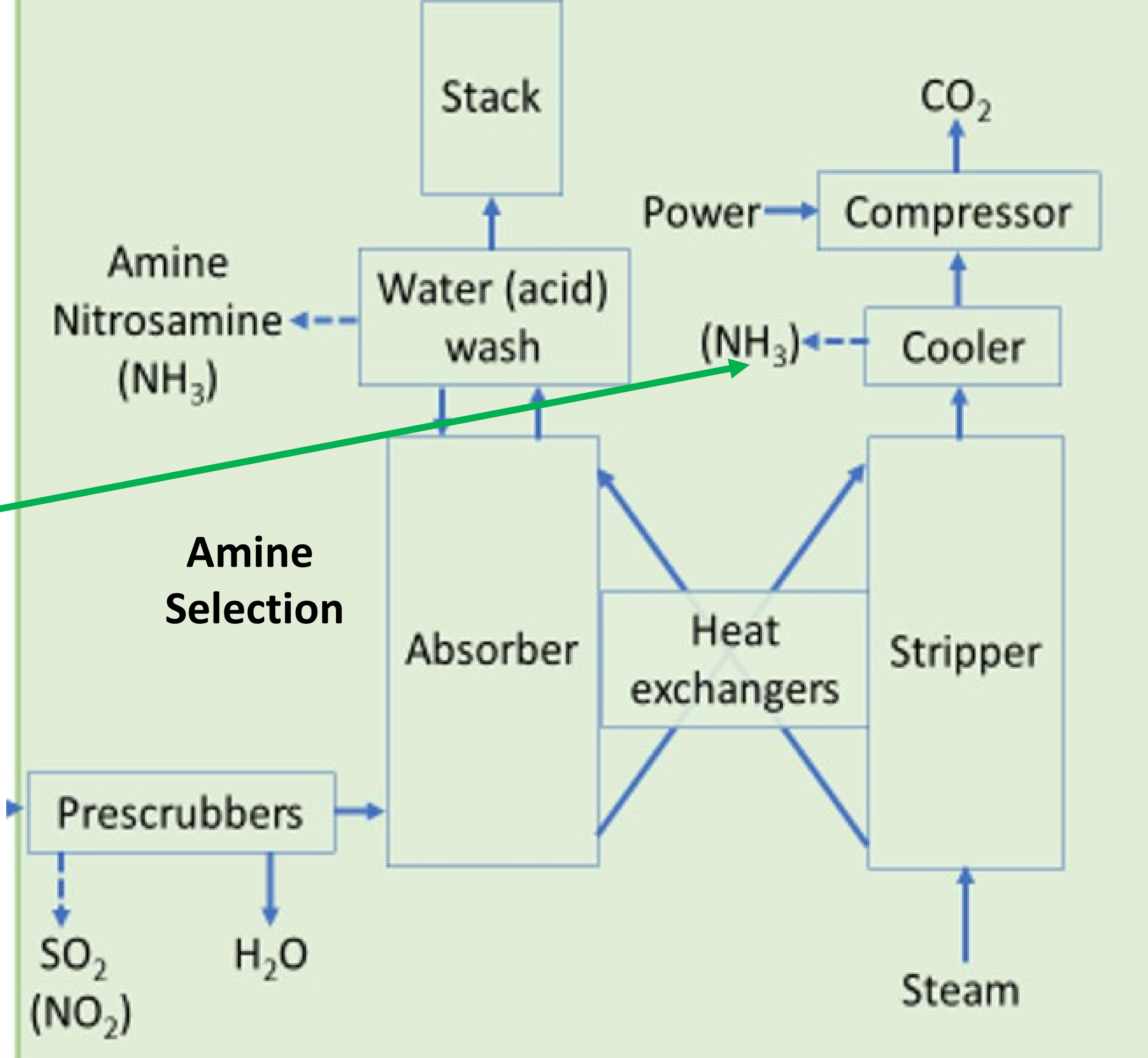
Piperazine - hrs
Nitrosopiperazine - hrs
Formaldehyde ~ 1 hr
Acetaldehyde ~ 1.6 weeks



Process features mitigate impacts

Condensate Bleed

To Reduce emission of
Ammonia
Aldehyde
Volatile amine degradation products



Process features mitigate impacts

Mitigate Oxidation

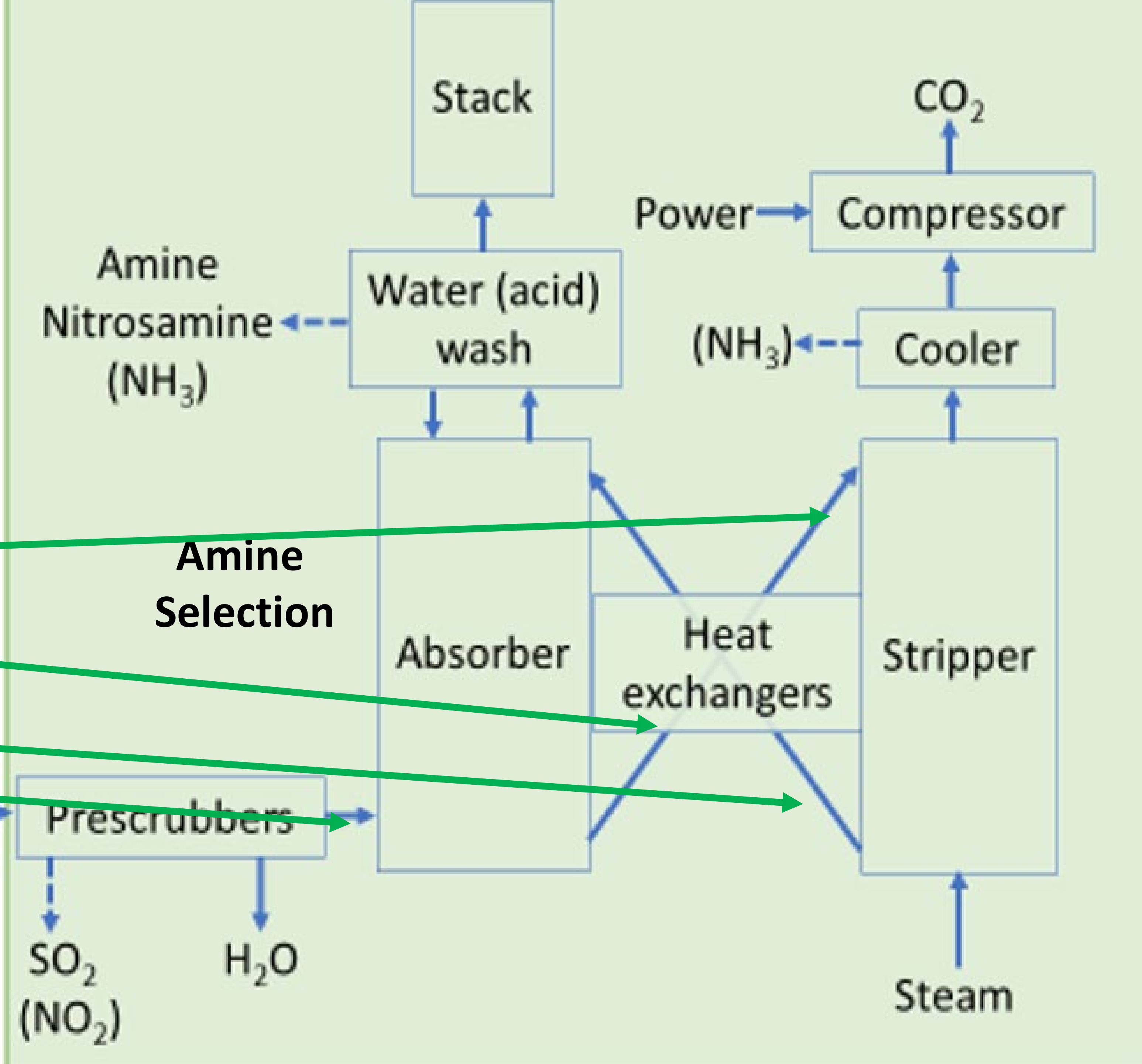
Reduce Time/T

N_2 sparging

Remove $Fe^{+2/+3}$

Continuous reclaiming

Avoid NO2



Aldehyde Management

Amine make-up at WW

Add sulfite to WW

Treat water wash or reflux

C Treating

Electrochemical oxidation

Other selective reactions

Selective mitigation of oxidation

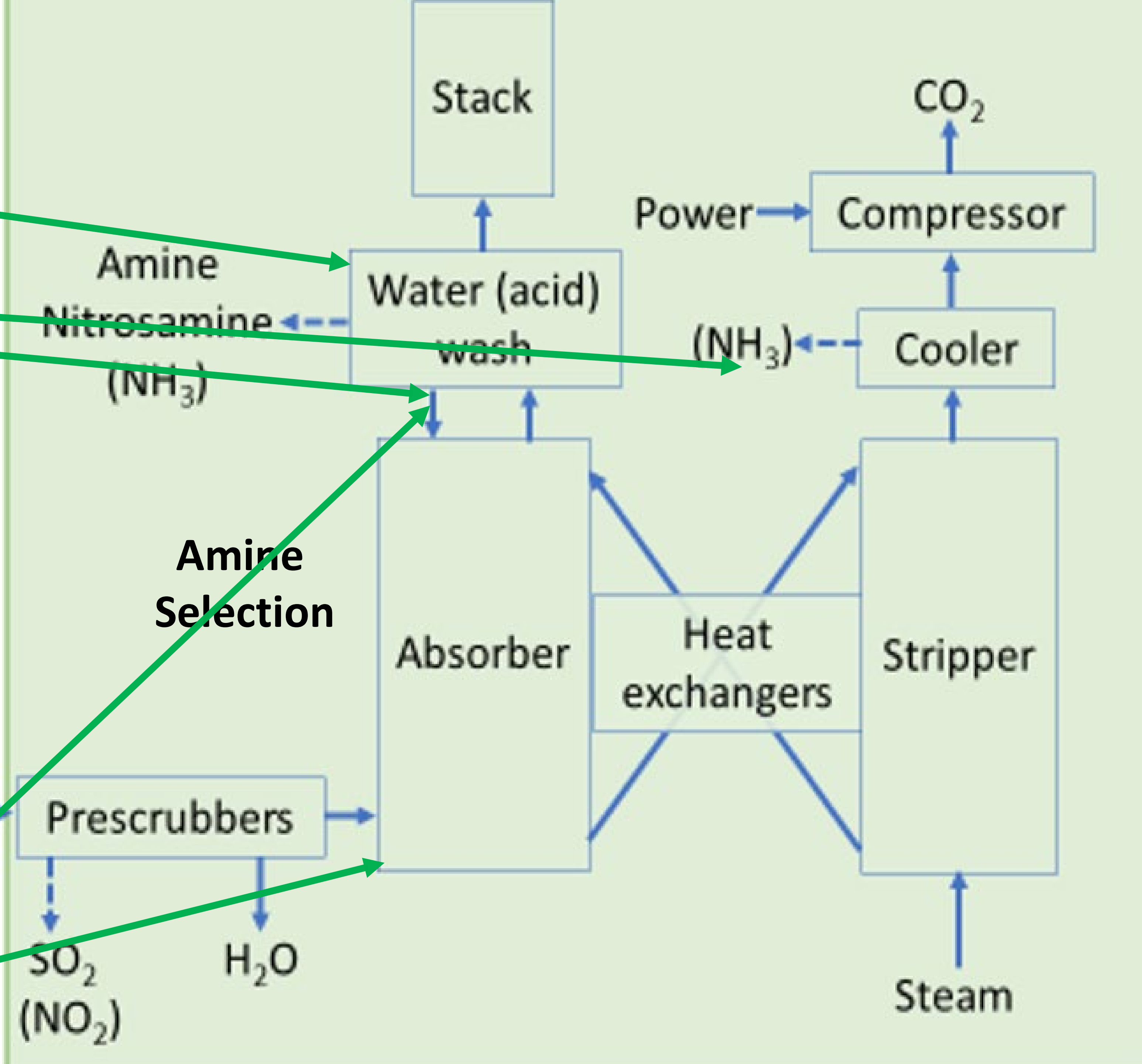
C treating

N_2 sparging

Selective catalysts

Bleed Water Wash

To absorber sump



Mitigating amine aerosol emissions avoids additional amine impacts

- Minimize aerosol nuclei in inlet flue gas
  - Select sites with < 10^5 particles/cm^3 nuclei in flue gas
  - Use fabric filter with added alkali to remove fine particulate & SO_3
    - Also appears to reduce NO_2 (with C for Hg removal)
  - Use flue gas exchanger to condense and remove SO_3 in inlet gas
  - Capture nuclei in Brownian filter
- Grow and capture aerosol
  - Use warm lean solvent to increase T at top of absorber
  - Add residence time (+ stage) in water wash
  - Use more volatile & less hydrophobic amine

Minimal emissions from Water Wash in Pilot Plants

amine	Amines (ppm)	Nitrosamine	NH_3 (ppm)	Acetald(ppmv)
MEA	0.05-0.3	ND	12-21	0.2-0.5
APBS	2.6-9.8 ppmw	ND	12-20	
CDRMax	<1		3	
APBS			1 – 6	1
KS-1			0.3-2	
S26	0.09-0.6 mg/Nm^3	<0.08 $\mu mol/Nm^3$	<0.01-8	
S26	1.8 mg/Nm^3	<0.04 $\mu mol/Nm^3$	2.6	1.5
DC-103	0.01-0.05		1.0	
Cesar-1	1.0/0.2 AMP 0 – 0.22 PZ	1-6 ppb		

Amine scrubbing on coal power plants will reduce PM2.5

Plants selected for CCS will have FGD, SCR, baghouse, Hg control, SO_3 control

Direct emissions of PM2.5 will be negligible

PM2.5 is formed from atm reactions of volatile acids & bases

Acids: $SO_2 \rightarrow H_2SO_4$ – polishing reduces SO_2 from 100 to 0.1 ppm

$NO_x \rightarrow HNO_3$ – minimized by SCR – <10-20 ppm

Bases: NH_3: 1-5 ppm SCR slip + 1-5 ppm amine oxidation

Amine: Only 0.01 – 1 ppm left after single stage water wash

Further mitigation is possible:

Add acid wash after water wash to reduce amine and NH_3 to <0.1 ppm

Develop methods to bleed ammonia as stripper condensate

Risks: Residual fine fly ash and SO_3/H_2SO_4 may create amine aerosol

Process upsets may disable mitigation measures

Gas power plants may make more PM2.5 with amine scrubbing

- NO_x starts at 15 ppm in existing gas-fired turbines w/o SCR
- Addition of SCR reduces NO_x to 1-3 ppm
  - Beneficial to minimize amine oxidation by NO_2
  - +1-2 ppm ammonia slip
- Amine scrubbing adds 1-5 ppm ammonia + 0.1-1 ppm amine
- Mitigate ammonia and amine with acid wash
  - Add one more section of 10 ft of packing to top of absorber
  - Adiabatic Pumparound loop at pH 4-6 with dilute H_2SO_4
  - Produce dilute waste water
- Mitigate ammonia with stripper condensate bleed?

Nitrosamine from amine scrubbing should be negligible

- Always use SCR to minimize NO_2 and NO (nitrosamines require NO_2)
- Water wash & optional acid wash with other features to remove all amine & nitrosamine emissions
- Careful amine selection to avoid volatile nitrosamine
- Process features to minimize nitrosamine accumulation in solvent
- Risks: Residual fine fly ash and SO_3/H_2SO_4 may create amine aerosol
  Process upsets may disable mitigation measures
  Atmospheric reactions may convert amine emissions to nitrosamine
    Minimized amine emissions will mitigate atmospheric reactions

Needs for Process Development

- Measure water wash perf w trickle bed, acid wash, & other confgs
- Test ammonia & aldehyde bleed in produced stripper condensate
- Develop & demonstrate mitigation for amine aerosol & oxidation
- Develop understanding & other mitigation for aldehydes
- Measure effects of fabric filters on NO_2, etc

Needs for atmospheric chemistry & modeling

- Atmospheric chemistry producing nitrosamine & nitramine
  - Especially in power plant plumes
  - Can nitrosamine/nitramine production be neglected?
  - Do tall stacks help?
- Contribution of ammonia/NO_x to PM 2.5
  - Marginal impact of more ammonia, especially in NO_x plume
  - How much ammonia can be tolerated?
  - (emissions from amine scrubbing should be small fraction of the total)
- Atmospheric chemistry degrading aldehydes
  - Do tall stacks help?

Regulations and emissions guidance needed

TD50 for more nitrosamines and nitramines

MACT for acetaldehyde, formaldehyde with amine scrubbing

Emissions guidance for ammonia, amines, nitrosamine, & nitramine

Recommendations

- Sensitive process and atmospheric gas monitoring (PTR-TOF-MS) to confirm insignificance of nitrosamine and aldehyde emissions.
- Amine scrubbing applications should consider SCR, fabric filters, and acid wash to reduce remaining effects on atmospheric reactions that may add to PM2.5 and nitrosamines.
- Process R&D should address:
  - Acid wash, mitigation of amine oxidation, and other process feature measures to reduce ammonia and aldehyde emissions.
  - Atmospheric chemistry experiments and modeling to quantify risk of PM2.5, aldehydes, and nitrosamine
- Great care should be exercised to avoid amine aerosol emissions from amine scrubbing applied to coal-fired power plants.
- EPA should develop guidance for permitting emissions of aldehydes, amines, and nitrosamine.

Conclusions

- It is most probable that CCS will reduce air quality impacts
- When amine scrubbing is applied to coal-fired power plants, it will significantly reduce PM2.5, primarily by eliminating SO_2 emissions.
- When amine scrubbing is applied to gas-fired power plants, it will reduce already low impacts to PM2.5, if SCR is added to reduce NO_x and an acid wash et al. is applied to minimize NH_3.
- Process features and amine selection will practically eliminate direct emissions of nitrosamine, and water wash will minimize amine emissions that may result in nitrosamine by atmospheric reactions.

Xtra Slides

Needs for additional stack & ambient measurements with more sensitive methods

Are nitrosamine emissions negligible? (as measured so far)

- Continuous FTIR provides amine and ammonia values >1 ppm at many sites
- Batch adsorbent tube sampling provides greater sensitivity for many components; most suppliers use this at NCCC
- Proton Transfer Reaction/Time Of Flight/Mass Spectrometry
  - Values >1 ppt can monitor ambient air for amines and nitrosamines
  - $600k/machine, several are available for ambient use in US
  - Used at TCM and other sites in Europe for source analysis by U Oslo
    - will be used at NCCC this summer.
  - PTR/TOF/MS should be used at all testing sites in U.S.

Mitigating Amine Oxidation

reduces emissions of ammonia and other degradation products

- Select amine that is resistant to oxidation
- Avoid reaction at elevated T with dissolved Oxygen
  - Strip oxygen from rich solvent with nitrogen or flashing
  - Reduce time/T of hot rich solvent after exchanger
- Minimize accumulation of degradation products & dissolved iron
  - Use thermal reclaiming of amine with useful volatility
    - Not possible with nonvolatile amine
  - Use ion exchange and carbon treating
  - Minimize corrosion by materials selection
- Avoid oxidation catalyzed by NO_2
  - Use SCR to minimize NO_x; retrofit if necessary
  - Remove NO_2 by sulfite prescrubbing

CCS must be responsive to political realities

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)."

The Environmental Defense Fund (letter to CEQ, 4/13/2022)

"impacts related to the presence and potential release of nitrosamines (a toxic carcinogen associated with the breakdown of amine solvents) may pose serious hazards to workers and the public near capture facilities utilizing certain amine solvents in post-combustion capture processes. ….this risk and its associated solutions are not well characterized in the literature."

Preferred Site Selection will minimize air quality impacts

Large coal plants with full environmental controls (2019)

	Rural	Large	SCR	FGD		Fabric Filter	
Power Stations	population	MW	Emissions (lbs/MWH)			Fabric	CO_2
with DOE FEEDs	within 3 mi		NO_x	SO_2	pm2.5	Filter	Mt/yr
Gerald Gentleman (NE)	20	1363	1.8	5.6	0.03	yes	8.7
San Juan (NM)	111	1848	2.8	0.6	0.01	yes	6.0
Large Plants in Texas							
J K Spruce (TX)	2644	1444	0.9	0.2	0.03	yes	7.5
Oak Grove (TX)	132	1796	1.2	1.9	0.20	yes	13.5

Indirect Air quality Impacts of Energy used by Amine Scrubbing: Site/grid specific

15-30% of the power plant output used by CCS must be replaced

- Most probable & best case – Incremental power mostly provided by new renewables
- Worst case – Incremental energy provided by increased load on other old coal plants with limited environmental controls, increasing emissions in sensitive areas.

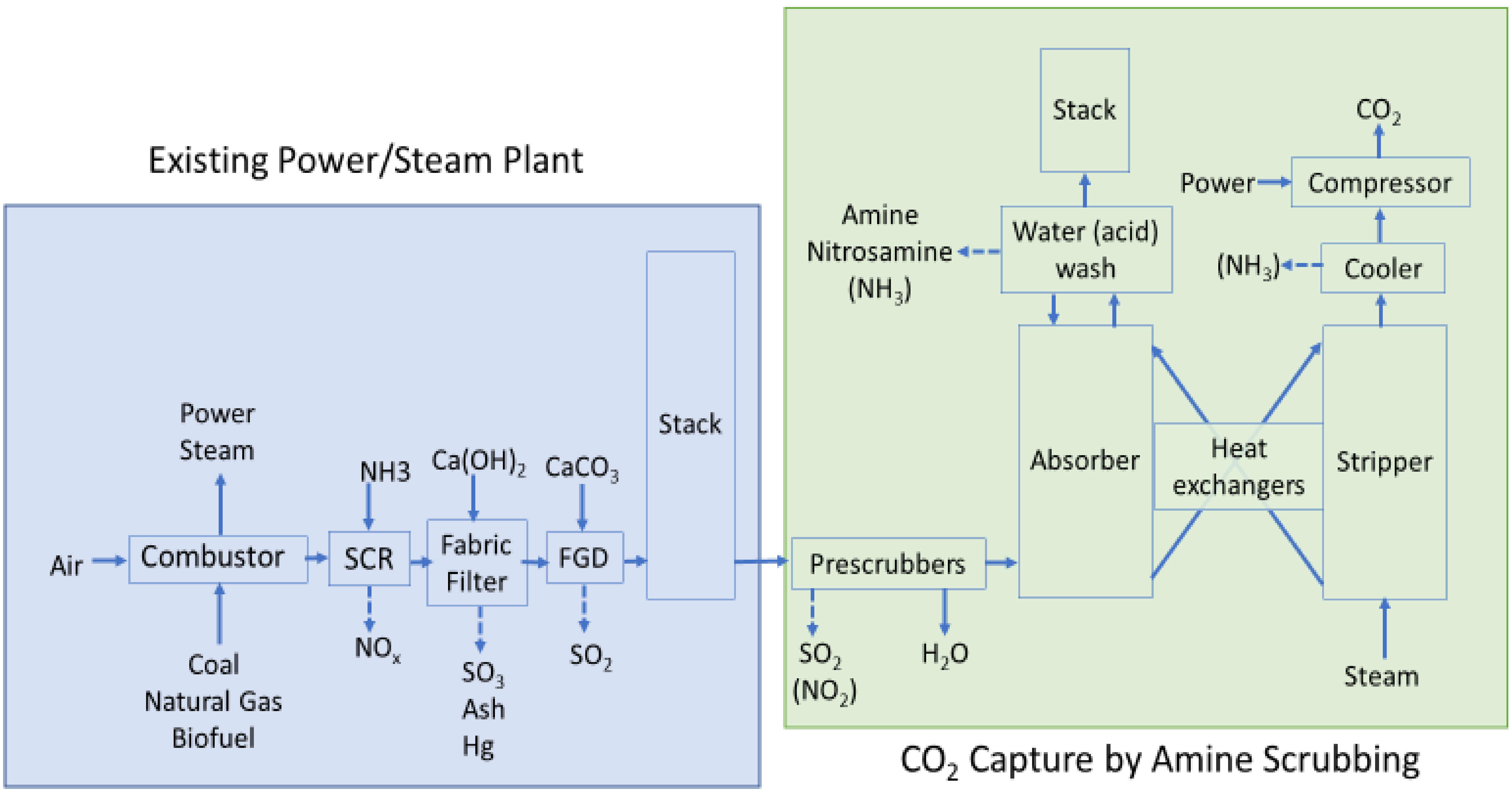
<u>Some more probable cases</u>

- Energy by new gas turbine with SCR & amine scrubbing
  - Add distributed air quality impacts from gas supply chain
- Energy by extraction from an existing underutilized coal-fired power plant
  - Add air quality impacts in proportion to already low emission levels
  - Add distributed air quality impacts from coal extraction and transport

Preferred Site Selection minimizes air quality impacts

Large, modern coal & gas plants with full environmental controls

- Flue gas desulfurization removes most of SO_2
- Selective catalytic reduction (SCR) greatly reduces NO_x
- Fabric filters remove fine particulate
  - Adding hydrated lime or sodium bicarbonate removes SO_3
  - Adding activated carbon removes mercury
  - Empirical results suggest NO_2 is also removed
- Rural location minimizes impacts of environmental justice
- Gas power plants with SCR reduce NO_2 (and NO)



Existing Power/Steam Plant
Air
Combustor
Power
Steam
Coal
Natural Gas
Biofuel
NH3
SCR
NO_x
$Ca(OH)_2$
Fabric Filter
SO_3
Ash
Hg
$CaCO_3$
FGD
SO_2
Stack
Prescrubbers
SO_2
(NO_2)
H_2O
Absorber
Heat exchangers
Stripper
Steam
Water (acid) wash
Amine
Nitrosamine
(NH_3)
Stack
Cooler
(NH_3)
Compressor
Power
CO_2
CO_2 Capture by Amine Scrubbing

Capture process features minimize air quality impacts

- Tall Stacks
- Prescrubbing
- Water wash
- Amine selection

Tall stacks disperse all emissions
Eliminating health effects of direct emissions

- Existing gas and coal-fired power plants comply with the U.S. NAAQS
  - Tall stacks disperse SO_2, NO_x, and particulate, dilute by 100-10,000 x
- With amine scrubbing the flue gas will usually bedischarged from somewhat shorter stacks added to the top of the absorber/water wash vessel.
  - Tall stacks will disperse ammonia emissions.
  - Tall stacks disperse and buy time to degrade amine emissions.
  - Tall stacks effectively disperse products of atmospheric reactions.

If greater dispersion is required, the clean flue gas can be redirected to the existing or new taller stack.

Prescrubbing removes SO_2 and reduces particulate

One-stage or two-stage prescrubbing reduces SO_2 <1 ppm

- NaOH for pH control
- 10 to 20 ft of structured packing
- [Na_2SO_4 waste solution must be managed.]

Prescrubbing cools flue gas and condenses water

- Provides better CO_2 removal and energy performance
- Required in coal plants to manage water balance
- Some configurations with gas plants may have no prescrubbing
- [Produced water can be recycled.]

With 2 stages and SO_2, thiosulfate can be added to get 80-95% removal of NO_2

Amine selection reduces amine, nitrosamine, and ammonia emissions

- Use principal amine with moderate volatility (1-20 ppm)
  - Requires molecules with ≥ 2 hydrophobic groups
  - Degradation products must not have greater volatility
- Avoid volatile secondary amines to minimize nitrosamine emissions
  - Use stable secondary amines such as PZ at greater stripper T (150^{o}C)
  - Avoid principal amines that degrade to secondary amines
- Select amines that resist thermal and oxidative degradation

Features that Mitigate air quality impacts

- Site selection to minimize NOx and aerosol nuclei in feed gas
- Tall stacks to disperse nitrosamine precursors, amine, & aldehydes
- Prescrubbing to remove SO_2 (and maybe NO_2)
- Water wash (w acid?) to remove amine and ammonia
- Amine selection
- Process features to minimize amine oxidation
- Process features to minimize amine aerosol emissions

Possible Important air quality impacts of amine scrubbing

- Of the priority pollutants:
  - PM2.5 resulting from NH_3, amine, and NO_x
- Of the hazardous air pollutants:
  - Nitrosamine resulting from principal amine emissions
  - Nitrosamine from emissions of amine degradation products
  - Acetaldehyde (because it is listed as a HAP)

Nitrosamine accumulation in solvent is manageable.

- Nitrosamine accumulation may pose a risk of spill or employee exposure.

  But it should be less significant that the amine itself

  Piperazine LD_{50} = 2600 mg/kg

  Mononitrosopiperazine TD_{50} = 8.8 mg/kg

  Equivalent toxicity 5 m PZ == 5*8.8/2200 = 0.02 m MNPZ

In pilot plant testing MNPZ < 0.002 m, so amine toxicity is more significant.

These will be "chemical" plants with accepted administrative controls, engineering controls, and personal protective equipment to reduce risk of exposure.

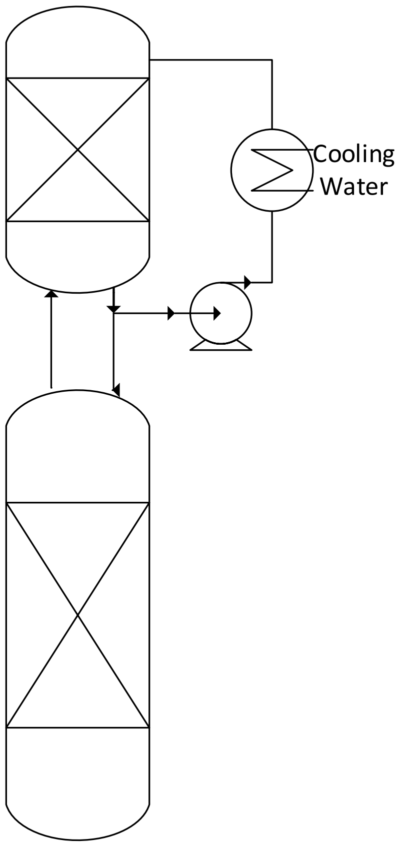
Water Wash

Provides Water Balance

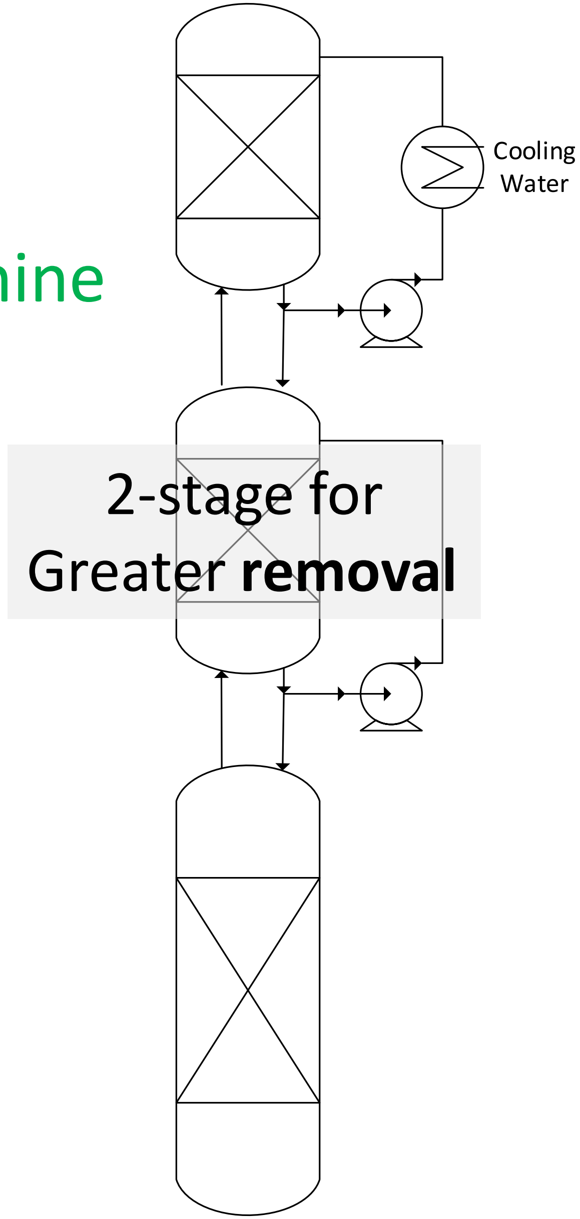
Does not use or produce water

99+% removal of amine & nitrosamine

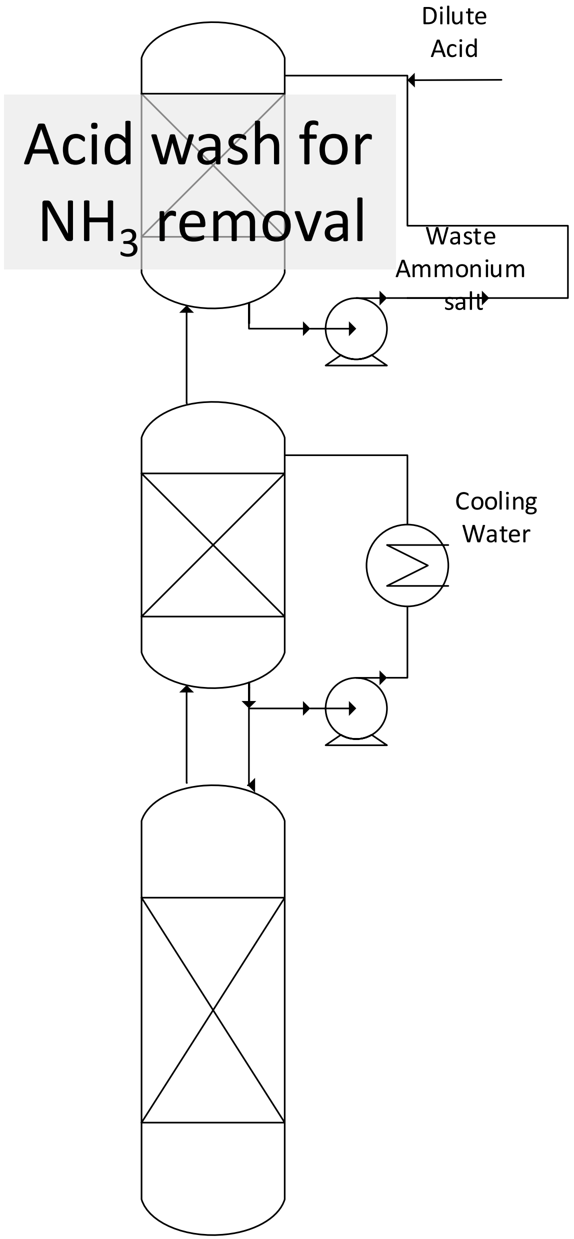
Recycled to solvent



Single Stage
Water Wash
(default configuration)



2-Stage
Water Wash



Water Wash +
Acid wash