Amine Solvent Reclaiming

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<u>Work in Progress and subject to change</u>

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- Why is Amine Solvent Reclaiming Important
  - Accumulated impurities require spent solvent disposition
  - Reclaiming concentrates impurities to facilitate environmentally acceptable disposal
  - Reclaiming recycles useful solvent
  - Reclaiming reduces cost of solvent disposition
    - Less material to dispose of
    - Less makeup of fresh amine

Outline

- Methods
- Impurities to be Reclaimed
- Economic Evaluation of Reclaiming
- Classification of Reclaimer Wastes
- Conclusions

Reference Cases

Coal – 900 MW, Gas – 810 MW

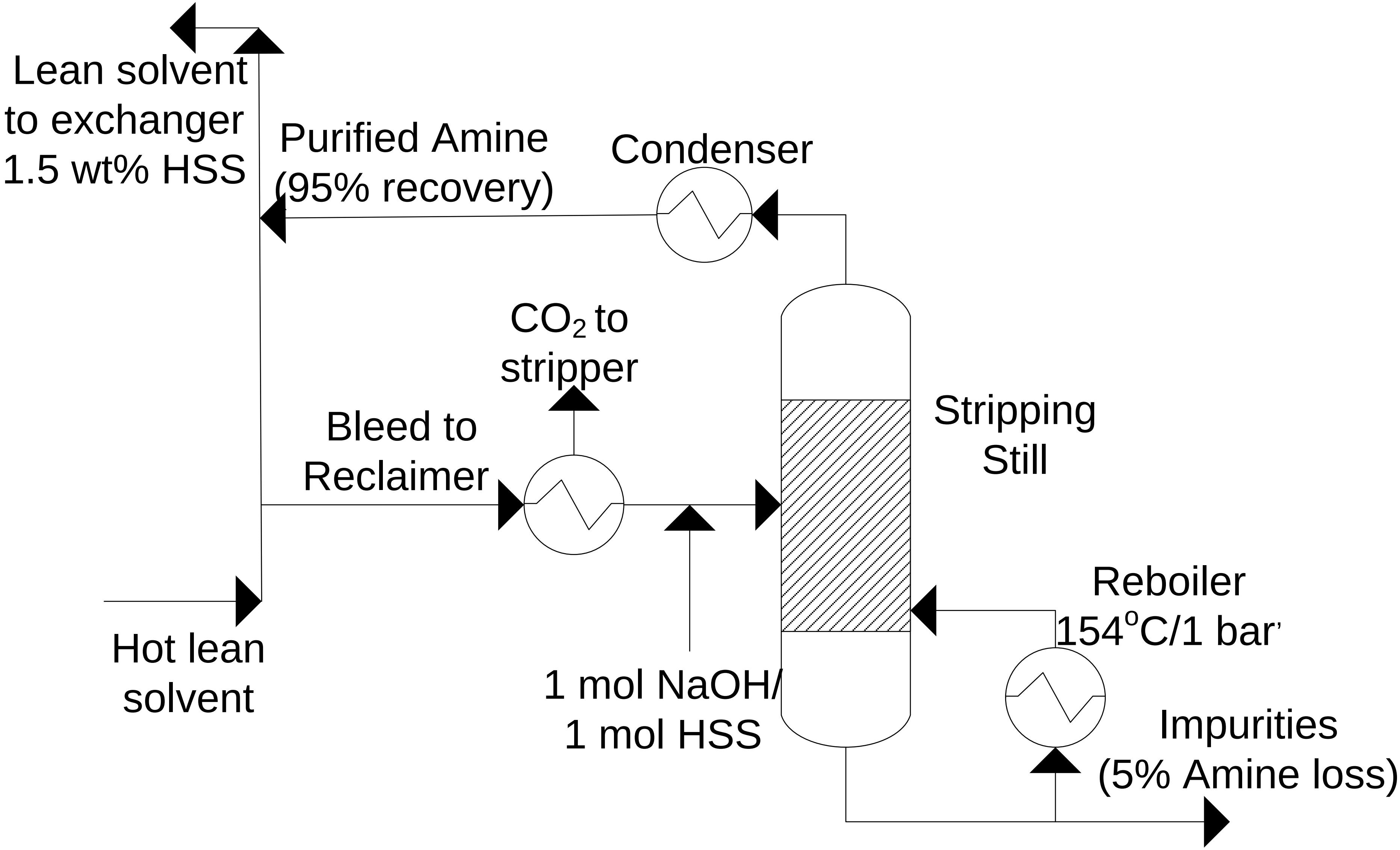
Solvent (Regen T)	**Flue Gas**	**CO_2 Gas (mol %)**	**CO_2 Loading (mol/mol total alkalinity)**		**Solvent (standard 1000 m^3/h)**
			Lean	Rich	
7 m MEA (120^oC)	Coal	11.8	0.12	0.51	10.7
	Natural Gas	4.1	0.12	0.49	5.1
8 m PZ (150^oC)	Coal	11.8	0.31	0.41	21.6
	Natural Gas	4.1	0.28	0.37	10.8
7 m MDEA /2 m PZ (135^oC)	Coal	11.8	0.11	0.25	26.7
	Natural Gas	4.1	0.11	0.25	12.1

Material Balance Assumptions

Reclaiming Technology	Amine Recovery, wt%	HSS removal, wt%	Metals/Non-ionic products removal, wt%
Thermal Reclaiming	95	100	100
Ion Exchange	99	90	0
Electrodialysis	97	91.5	0

Reclaimer bleed adjusted
to get 1.5% nonvolatile solids in the solvent

Thermal Reclaiming



Major impurities with removal of 4.5 ppm SO_2

Generation rate

	PZ/Coal	MEA/Coal
	mmol/ kmol CO_2	mmol/ kmol CO_2
Nitrosamines (1.5 ppmv NO_2)	14	7.1
Ammonia	45	37
Total formate	11	6.9
Nonvolatile amines	4.1	11
Volatile amines	5.7	21
Sulfate (4.5 ppmv SO2)	42	42
Nitrate (4.5 ppmv NOx)	42	42
Chloride (1.8 ppmv HCl)	17	17

Amine Loss Rate with removal of 4.5 ppm SO2

	PZ/Coal	MEA/Coal
	mmol/ kmol CO_2	mmol/ kmol CO_2
Total Amine loss	194	221
Thermal degradation	10	24
Oxidation (5 kPa O_2)	28	56
Nitrosamine (1.5 ppmv NO_2)	14	7.1
Volatility (1 ppmv emitted)	8	8
Reclaimer loss (95% recovery)	132	124
Amine makeup (\$/MT CO_2)	**\$1.80/MT CO_2**	**\$0.55/MT CO_2**

Amine loss with better performance of prescrubber
Removal of 0.5 ppm SO_2 & NO in amine scrubber

	PZ/Coal	MEA/Coal
	mmol/ kmol CO_2	mmol/ kmol CO_2
Amine loss	78	129
Thermal degradation	10	24
Oxidation (5 kPa O_2)	28	56
Nitrosamines (0.5 ppmv NO_2)	4.8	2.4
Volatility (1 ppmv emitted)	8	8
Reclaimer loss (95% recovery)	27	39
Amine makeup cost	**\$0.77/MT CO_2**	**\$0.33/MT CO_2**
(with 4.5 ppm SO2)	**\$1.80/MT CO_2**	**\$0.55/MT CO_2**

Estimated Costs of Thermal Reclaiming (Not including disposal) (\$/ton CO_2 captured)

	Amine makeup etc.	Energy	Annualized Capital	Total
MEA Coal	0.53	0.18	0.17	0.90
MEA NGCC	0.38	0.11	0.11	0.60
PZ Coal	1.43	0.17	0.18	1.79
PZ NGCC	0.94	0.11	0.11	1.16

Costs of Reclaiming PZ w coal ($/ton CO_2 captured)

	amine makeup etc.	Energy	Annualized Capital	Total
Thermal	1.4	0.17	0.18	1.8
Ion Exchange	1.0	0.00	0.25	1.3
Electrodialysis	1.2	0.22	0.20	1.6

Qualitative Analysis of Reclaiming Options

- Thermal Reclaiming
  - Removes non-volatile impurities
  - Corrosion is an operational concern
  - Solvent losses are high with expensive solvents
- Ion Exchange
  - Does not remove non-ionic species or transition metals
  - Metals may foul media
  - Large volumes of wastewater
  - Minimal solvent losses
  - Minimal operator attention and maintenance
- Electrodialysis
  - Like ion exchange, but more operator attention
  - Greater solvent losses than ion exchange

Steady-state toxic impurities (ppm_w) Reclaimed to 1.5 wt% nonvolatiles

Component	7 m MEA		8 m PZ	
(ppmw)	Coal	NGCC	Coal	NGCC
Mercury	0.36	0	0.32	0
Selenium	0.46	0	0.42	0
Chromium	0.91	3.3	0.82	3.8
Nitrosamines	60	60	118	104

Metals in thermal reclaimer waste (coal) possibly “Hazardous” in the USA may be “Hazardous Waste Generator”

(ppmv)	TC limit	Solvent	Reclaimer	
			Total	Leachate (total/20)
Cr	5	0.90	21.6	1.1
Se	1	0.46	11.0	0.55
Hg	0.2	0.36	8.6	0.43

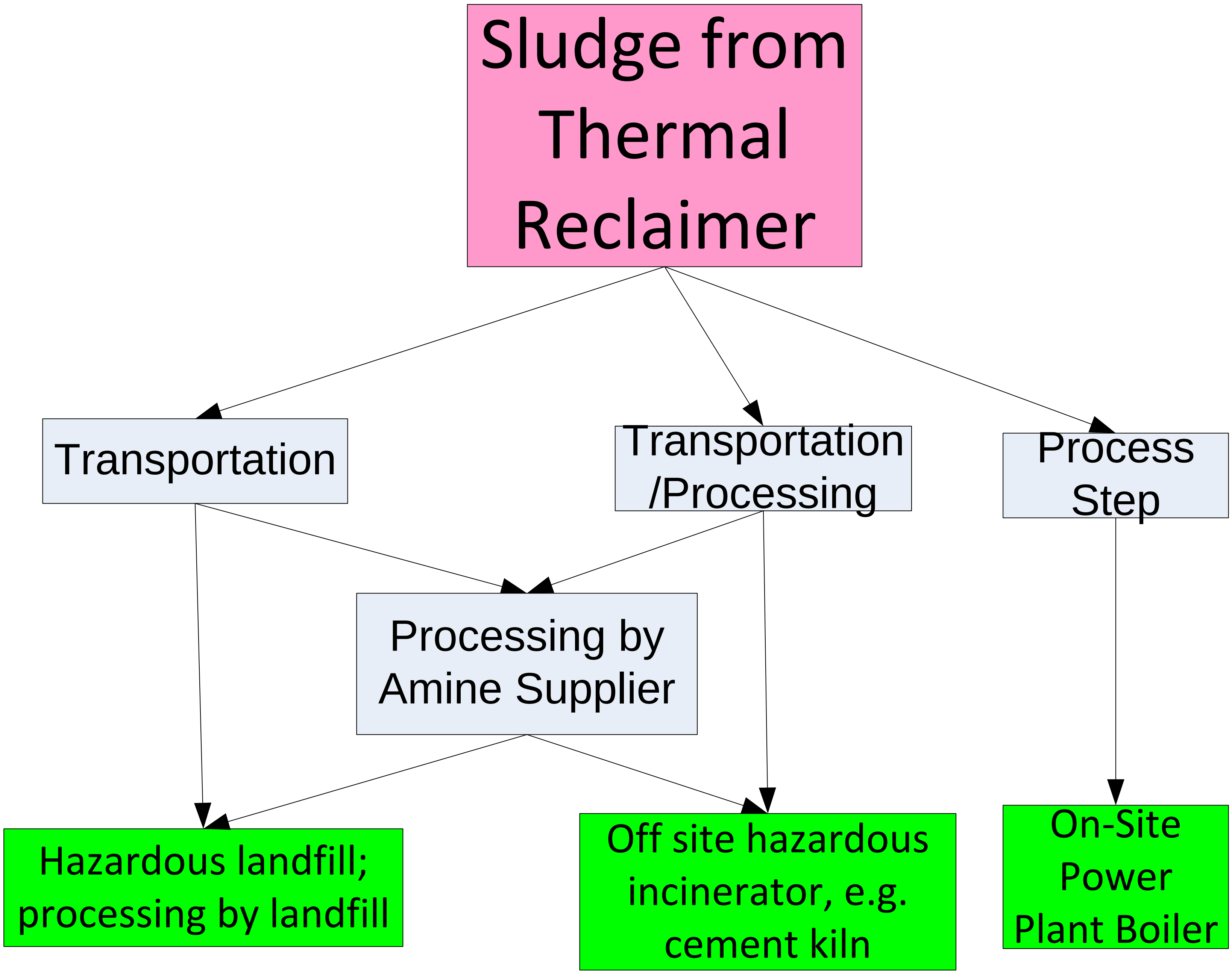
In EU, all thermal reclaimer wastes are likely "Hazardous"

- Solvents in the reclaimer waste are hazardous
  - Irritant
  - Harmful
  - Corrosive
- Metals in reclaimer waste are hazardous
  - Ecotoxicity
  - Listed waste
- PZ containing wastes may add issues with
  - Carcinogenicity (nitrosamines)
  - Sensitizing
  - Perceived ReproductiveToxicity

Ion Exchange & Electrodialysis Probably Non-hazardous

- Low solvent concentration < thresholds for irritant, harmful, toxic, etc.
- No minimum threshold for sensitizing components, so PZ wastes may be hazardous
- If metals are removed, then waste streams could be listed hazardous wastes

Disposition Options for Hazardous Waste



Costs of Disposal

Disposition Option	Reclaiming Case	Annual Cost Added
Non-hazardous landfill	NGCC (US)	15 - 30%
Hazardous landfill or incineration	Coal (US)	~ 100%

Conclusions

- Cost of reclaiming and solvent makeup will be less than \$2/MT $CO_{2,}$ but disposal could make it \$4/MT CO_2.
- When reclaiming bleed is set by sulfate, etc., Even if more stable, expensive solvent solvents will be less attractive.
- Thermal reclaimer waste will possibly be "hazardous"
  - U.S.: Cr, Se, or Hg.
  - Europe: amine, nitrosamine, metals

Conclusions

- The uncertainties in cost, quantities, and environmental impact of solvent degradation and reclaiming are large & require additional research.

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