EVALUATION OF AMINE RECLAIMER OPERATION AND WASTE DISPOSAL FROM POST-COMBUSTION CO$_2$ CAPTURE

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ABSTRACT

An important environmental issue with respect to amine-based post-combustion CO$_2$ capture is the generation of degraded amine waste that must be mitigated or disposed of properly. The operation of an amine-based post-combustion CO$_2$ capture process will result in the formation of degradation products due to presence of impurities in the flue gas. These degradation products exhibit corrosive properties and reduce solvent CO$_2$ absorption characteristics. To control the concentration of these degradation products in the amine-based solvent, a slipstream of the solvent from the CO$_2$ capture unit is sent to a solvent reclaiming system; the recovered amine-based solvent is returned to the CO$_2$ capture unit while the waste from the reclaimer is discharged. This paper evaluates the environmental fate of reclaimer waste generated from three common amine-based solvents. For each solvent, a degradation model estimates solvent loss and degradation product accumulation expected in a commercial CO$_2$ capture unit. A techno-economic analysis of various reclaiming technologies (e.g., thermal and vacuum distillation, ion exchange, and electrodialysis) is conducted for each solvent. This techno-economic evaluation includes a breakdown of purchased equipment costs, total capital requirement, annualized operating costs, energy requirements, and cost of disposal.

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Introduction

With large scale carbon capture and sequestration (CCS) demonstration plants, post-combustion capture using aqueous amine based solvents is considered to be the most widely used technology. In the post-combustion capture amine unit, large amounts of degraded amine waste that requires disposal in an environmentally suitable manner can be generated. Amine solvents can degrade and form impurities in many different manners. The amine can degrade because of the presence of other gaseous species in the flue gas such as CO_2, SO_x, NO_x, O_2, halogenated compounds and other impurities. Some species react directly with the amine, while others (such as oxygen) are involved in a series of reactions to form a set of fragmented degradation products. At high temperature, the amine solvent can degrade to form high-molecular weight degradation products. Degradation products formed by amine based solvents can include heat stable salts (HSS), non-volatile organic compounds and suspended solids. These degradation products and heat stable salts can be corrosive and reduce solvent CO_2 absorption rates. Therefore, reclaiming is required to minimize the concentration of these degradation products in the capture solvent. Reclaiming recycles useful solvent to the main process, reduces the cost of solvent disposition (less material to dispose of and less makeup of fresh amine), and concentrates the impurities to facilitate environmentally acceptable disposal.

Typically, a slip stream of amine is sent to a reclaiming system, where part of the solvent is reclaimed and returned to the capture system. The waste remaining in the reclaimer is periodically discharged to prevent any accumulation of these impurities in the reclaimer. Literature values for generated reclaimer waste using monoethanolamine (MEA) varies from 1.2 kg/MWh$_{net}$ to 3.3 kg/MWh$_{net}$ for Natural Gas Combined Cycle (NGCC) and Pulverized Coal (PC) CO_2 capture cases, respectively [1]. This can result in a sizeable amount of reclaimer waste and, therefore, it is important to identify a sustainable method for disposal of these wastes.

This paper presents the results of a techno-economic study [2] to evaluate multiple solvent reclaiming technologies including: thermal reclaiming, ion exchange, and electrodialysis. The flue gases from pulverized coal (PC) and natural gas combined cycle (NGCC) applications were evaluated for use with monethanolamine (MEA), piperazine (PZ), and methydiethanolamine/piperazine (MDEA/PZ) amine solvents. Solvent losses and degradation

products were modeled to estimate the accumulation expected in a commercial CO_2 unit. The techno-economic evaluation includes a summary of the purchased equipment costs, total capital requirement, annualized operating costs, energy requirements, and cost of disposal for each of the cases. A sensitivity study is presented to demonstrate the impact of oxidation on the economics of the process. Finally, waste characterization, and disposal options and costs are also provided.

Design Basis

The technology feasibility evaluation was generated for two types of power plants: 1) a greenfield supercritical pulverized coal (PC) power plant with 90% CO_2 capture that produces 900 MWe of gross electrical power, and 2) a greenfield natural gas power plant (NGCC) with 90% CO_2 capture that produced 810 MWe of gross electrical power. A selective catalytic removal (SCR) unit was assumed upstream of the CO_2 capture unit for both the coal and natural gas power plants, and a wet flue gas desulfurization (FGD) unit and sodium hydroxide polishing unit were assumed to be located upstream of the CO_2 capture unit of the coal-fired power plant (to keep the SO_2 concentration to the capture unit < 10 ppmv). The capacity factor (or load factor) of the plant was assumed to be 85% for the economic analysis [3].

The resulting flue gas compositions for the coal and natural gas cases were taken from previous work [3]. The flue gas conditions are shown in Table 1.

Table 1 – Coal and Natural Gas Conditions

Parameter	Units	Pulverized Coal	NGCC
Gross power output	MW	900	810
Flue gas flow rate	Nm^3/hr	$3.89*10^6$	$5.04*10^6$
Temperature	C	54	109
Pressure	kPa	115.8	117.2
N_2	vol%	70.22	75.16
CO_2	vol%	11.78	4.09
H_2O	vol%	12.97	8.76
O_2	vol%	5.03	11.99
SO_x	ppmv wet	15	0.5
SO_3	ppmv wet	10	0
SO_2	ppmv wet	5	0.5
NO_x	ppmv wet	46.5	15.5
NO_2	ppmv wet	1.5	0.5
NO	ppmv wet	45	15
HCl	ppmv wet	1.85	0
HF	ppmv wet	0.075	0
Hg	$\mu g/Nm^3$ wet	1.8	0
Se	$\mu g/Nm^3$ wet	2.3	0
Fly ash	mg/Nm^3 wet	6	0
Other metals	$\mu g/Nm^3$ wet	5.5	0

Three amine-based solvents were evaluated: monoethanolamine (MEA), a blend of methyldiethanolamine promoted with piperazine (MDEA/PZ) and concentrated piperazine (PZ). The reference cases established by The University of Texas identified the lean/rich loadings and circulation rate of the solvents of interest, in addition to the operating conditions of the regeneration column (used to characterize thermal degradation rates). Table 2 shows general information on the reference cases as well as the approximate solvent circulation rates estimated to achieve 90% CO_2 capture. The solvent concentrations are shown in molality (moles of solvent/kilogram of water) and weight percent. The combination of flue gas cases and amine solvents results in six total cases for each reclaimer type (thermal reclaiming, ion exchange, and electrodialysis).

Table 2 – Amine Circulation Rates for CO_2 Capture for PC and NGCC Cases

Solvent	Flue Gas	Lean Loading (mol CO_2 / mol total alkalinity)	Rich Loading (mol CO_2 / mol total alkalinity)	Circulation Rate (standard m^3/h)
MEA (7 m, 30 wt%)	Coal	0.12	0.51	10,719
MEA (7 m, 30 wt%)	Natural Gas	0.12	0.49	5,083
PZ (8 m, 40 wt%)	Coal	0.31	0.41	21,641
PZ (8 m, 40 wt%)	Natural Gas	0.28	0.37	10,818
MDEA/PZ (7/2 m, 50 wt%)	Coal	0.11	0.25	26,707
MDEA/PZ (7/2 m, 50 wt%)	Natural Gas	0.11	0.25	12,105

Process Description

A generic process flow diagram for an amine-based CO_2 capture system is shown in Figure 1. The inlet flue gas passes through a blower to increase the pressure to 110.3 kPa (16.0 psia) and a direct contact cooler to lower the temperature to 40°C (104°F). The gas enters the bottom of the absorber. Cooled, lean amine solution enters the top of the absorber, and rich solution exits the bottom of the absorber. Flue gas exits from the top of the absorber, through a water wash, and flows to the stack. Rich solution exchanges heat with hot lean solution. The preheated rich solution flows to the stripper where CO_2 desorbs from solution. A steam-heated reboiler provides heat to the stripper column for CO_2 desorption, water vaporization and sensible heating of the liquid. Hot lean solution exits from the bottom of the stripper and is cooled through cross exchange with the rich solution. Warm stripper overhead gas flows to a condenser where the vapor is cooled and water is condensed. The remaining CO_2 vapor then flows to a multi-stage centrifugal compression train to increase the pressure to 11.0 MPa (1595 psia). Dehydration takes place between the final compression stage and the centrifugal pump to deliver the dry CO_2 to its final pressure.

Tanks and pumps for makeup solution and water are required in addition to a cooling water system for the entire CO_2 capture unit. Finally, a reclaiming system is needed to remove degradation products as they accumulate in the solution over time. The reclaimer slipstream is taken on the discharge side of the lean solvent pump, and the reclaimed amine is returned on the suction side of the lean solvent pump; the lean amine is selected for reclaiming because of its
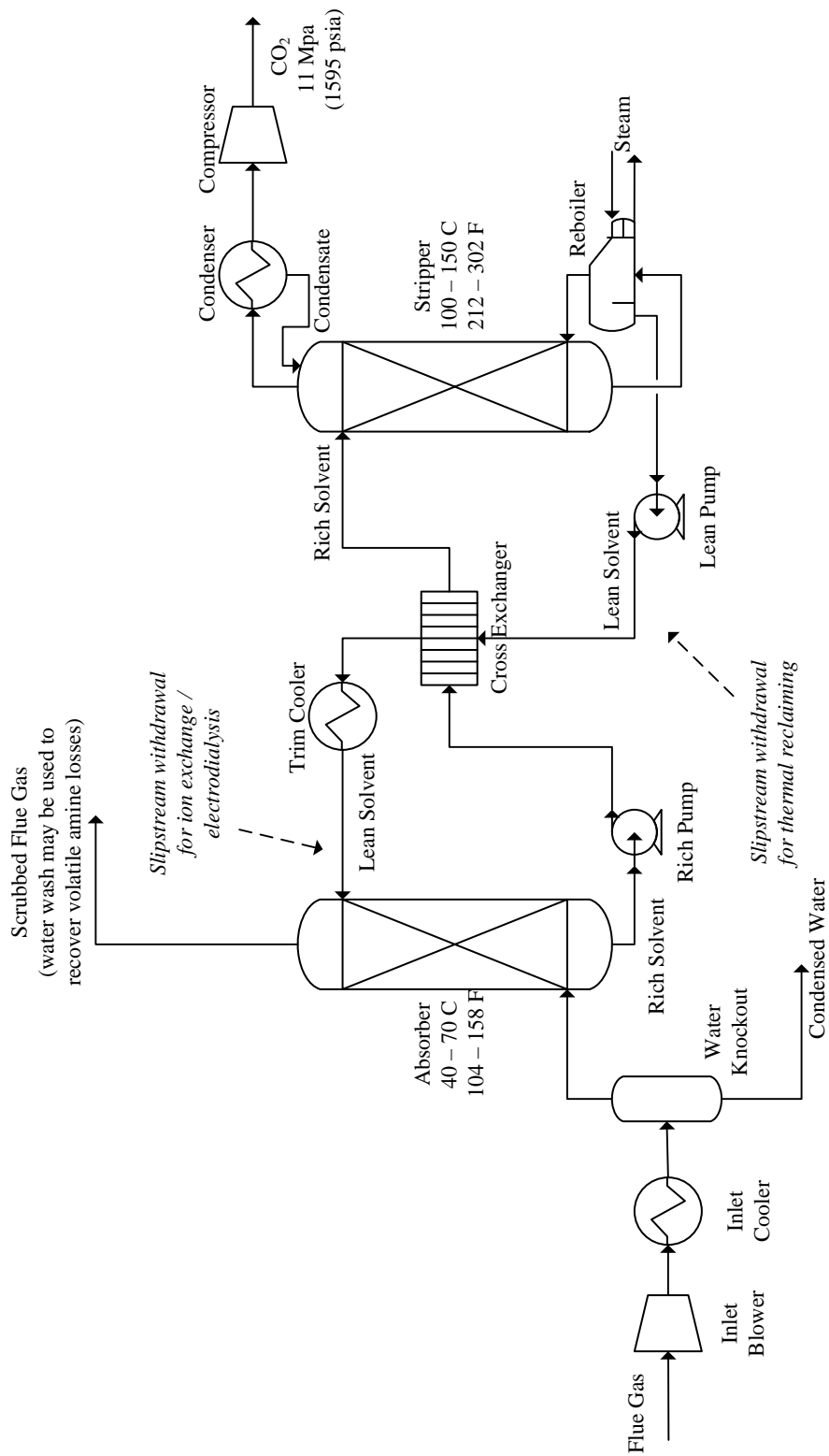
Figure 1 – Example CO$_2$ Capture Process Flow Diagram with Amine Reclaimer Slipstream Locations

Flue Gas

Inlet Blower

Inlet Cooler

Water Knockout

Condensed Water

Absorber
40 – 70 C
104 – 158 F

Rich Solvent

Rich Pump

Rich Solvent

Slipstream withdrawal
for thermal reclaiming

Scrubbed Flue Gas
(water wash may be used to
recover volatile amine losses)

Slipstream withdrawal
for ion exchange /
electrodialysis

Lean Solvent

Trim Cooler

Cross Exchanger

Lean Solvent

Lean Pump

Lean Solvent

Reboiler

Steam

Stripper
100 – 150 C
212 – 302 F

Condensate

Condenser

Compressor

CO$_2$
11 Mpa
(1595 psia)

lower CO_2 loading in solution. Alternatively, it may be preferable to take the slipstream for ion exchange or electrodialysis reclaiming downstream of the lean solvent cooler so that the stream has been filtered and cooled using the main solvent equipment loop. If the slipstream is taken on the discharge of the lean solvent pump, the reclaiming feed stream will have to be cooled and filtered with equipment dedicated to the reclaiming unit. For the purposes of this study, an integrated and continuous reclaiming system was assumed (as opposed to batch reclamation).

Overview of Degradation Model and Results

For each solvent system, a degradation model was developed to estimate solvent losses, impurities accumulation and degradation product accumulation expected in a commercial CO_2 capture unit. The classes of impurities that were considered in the model include: volatile products of oxidation from ammonia and amines as well as NO_x reactions to form nitrosamines. The non-volatile impurities include oxidation to heat stable salts (formate and oxalate), thermal degradation/carbamate polymerization to higher molecular weight products, reactions with flue gas impurities ($NO_x/SO_x/HCl$) to form heat stable salts, and dissolved metals.   More detailed information on the model and degradation pathways, products of formation, and other assumptions can be found in the final report [2].

For all three solvent systems, oxidation contributes more to solvent loss than thermal degradation or volatile losses, but contributes less than the formation of heat stable salts from the reaction between flue gas contaminants and solvent.

All other parameters being equal, the oxidation rate of PZ (on a mass rate) is approximately one-third the rate of the other two solvent systems (for both coal and NGCC cases). The estimated oxidative rates for NGCC are more than twice as much as the coal cases due to the higher oxidation content of the flue gas, and volatile solvent losses are approximately three times greater due to the greater flue gas rate relative to the absorber solvent feed rate.

Assuming an overall heat stable salt concentration of 1.5 wt% in the overall circulating solvent, contaminant removal is lower for the NGCC cases when compared to the PC cases due to lower concentration of SO_x, NO_x and halogens entering the flue gas that can react with the amine solvent to form heat stable salts. Relative to the circulation rate of amine for CO_2 capture, MEA experiences the highest rate of HSS incursion per kg of amine solvent.

Reclaiming Technology Background

Three different reclaiming technologies were evaluated: thermal, ion exchange, and electrodialysis. The reclaiming technologies were evaluated based upon the following criteria:

- Removal of non-ionic compounds
- Removal of ionic compounds (heat stable salts)
- Removal of dissolved metals/solids
- Amine loss rate
- Annual revenue requirement/normalized reclaiming cost
- Reclaimer waste profile
- Level of operator attention/operating reliability.

Table 3 shows the estimated amine recovery and degradation product removal for the three reclaiming technologies considered in this study. A brief description of the reclaiming technologies is presented below to facilitate discussions of the techno-economic results. The discussions of the reclaiming processes are generic representations of the technologies as many different versions exist and most of the information is proprietary to the specific vendors.

Table 3 – Reclaiming Technology Amine Recoveries and Degradation Product Removal

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

Thermal Reclaiming Process

A process flow diagram for a typical thermal reclaiming system is shown in Figure 2. A slipstream of lean amine is taken downstream of the regenerator and lean amine pump (and upstream of the cross-exchanger) and continuously fed to the reclaiming unit. A CO_2 pretreatment step occurs to reverse the reaction between CO_2 and amine that forms amine carbamate; one potential option involves heating at regeneration conditions to reverse the amine-CO_2 reaction (and vaporize a small amount of water). The contaminated amine is then pretreated with caustic to reverse the reaction between acid impurities (i.e., chlorine in the coal flue gas) and/or degradation products (i.e., formic acid) and the amine by adding sodium hydroxide. This reaction creates salts between sodium and the acid impurities/degradation products, and liberates the free amine. The pretreated amine is sent to the thermal reclaimer where the impurities are removed; the stripper overheads flow to a condenser and then to the main solvent circulation loop.
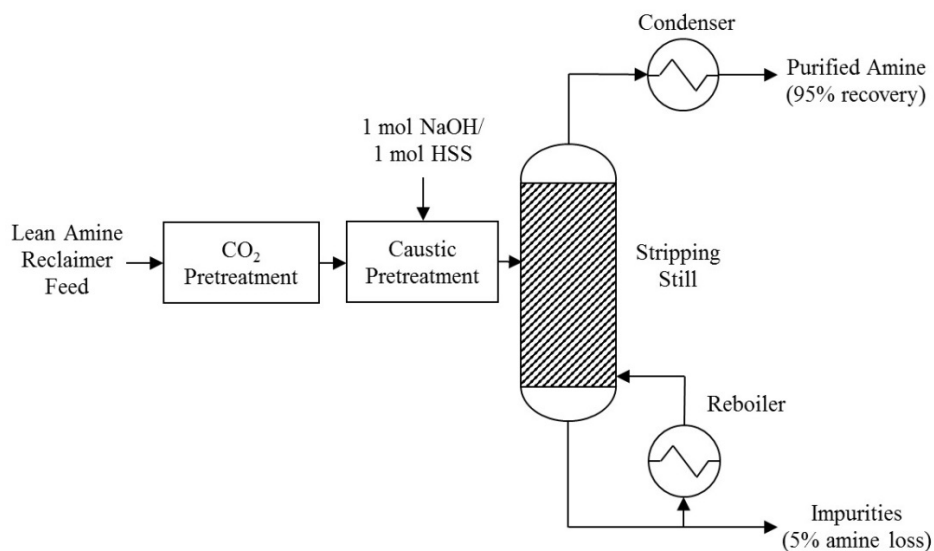

Figure 2 – General Thermal Reclaiming Process Flow Diagram

Ion Exchange Process

In a typical ion exchange reclamation process, a continuous slipstream of the lean amine can be taken from the same location as the thermal reclaimer or downstream of the lean solvent cooler before the absorber so that the stream has already been filtered and cooled. The ion exchange process (Figure 3) requires CO_2 pretreatment and caustic pretreatment similar to the thermal reclaiming process. Particulate filtration is also required. The contaminated amine is then sent through a cation exchange resin followed by an anion exchange resin where impurities are removed. The resin beds are periodically regenerated with sulfuric acid and sodium hydroxide solutions (using distilled, deionized water), respectively. During regeneration, large volumes of low concentration, aqueous brine are produced and can be sent to a wastewater treatment plant.
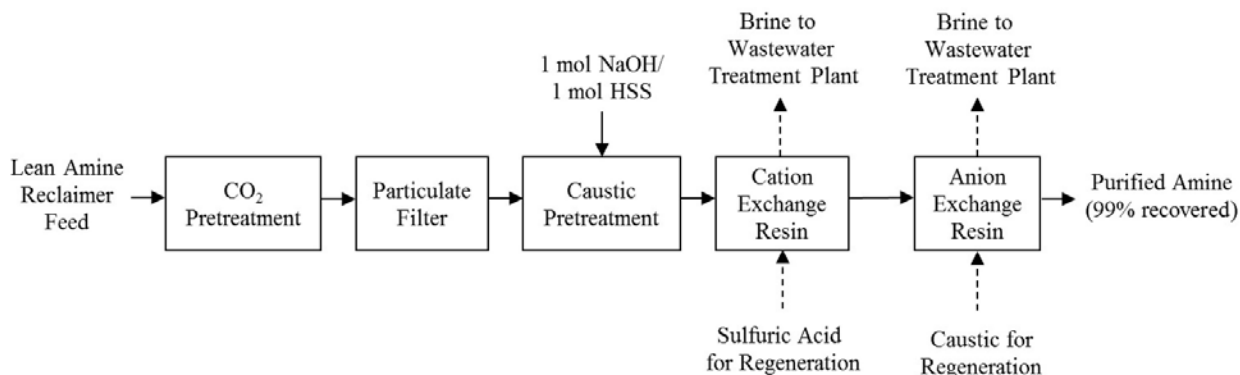

Figure 3 – General Ion Exchange Reclaiming Process Flow Diagram

Electrodialysis Process

The potential slipstream locations to feed the electrodialysis process are the same as with ion exchange. The electrodialysis process (Figure 4) also requires CO_2 pretreatment, particulate filtration, and caustic pretreatment. The contaminated amine is then sent to an electrodialysis unit that uses a direct current and a series of ion-selective membranes to separate ionic species from the inlet solvent stream to waste streams located on the opposite sides of the membrane. Aqueous brine is sent to a wastewater treatment plant.
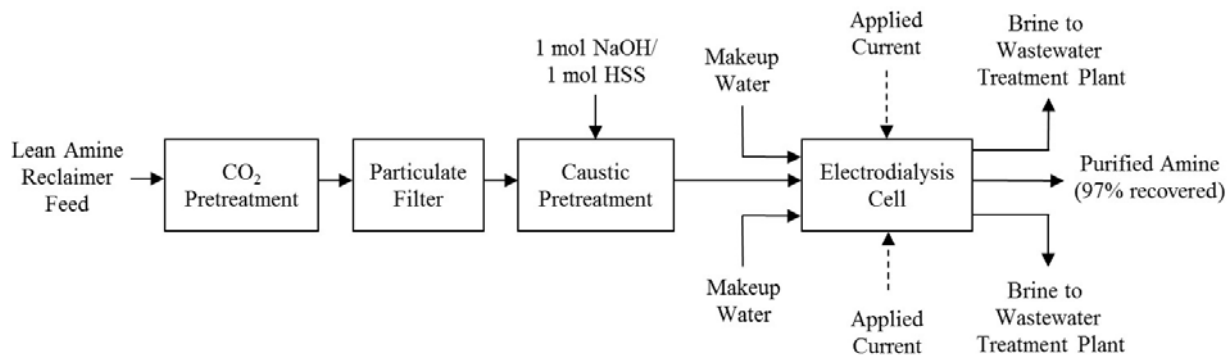

Figure 4 – General Electrodialysis Reclaiming Process Flow Diagram

Techno-Economic Results

A literature review was conducted and communications with reclaiming vendors and oil and gas representatives were made to obtain reclaimer information including: operating conditions, amine recovery and degradation, HSS removal, capital costs, energy and chemical requirements, and waste generation. Per data from the literature and vendors, the approximate normalized costs listed in Table 4 were used to estimate the capital costs for all cases in this analysis.

Table 4 – Normalized Capital Cost Estimates

Reclaiming Technology	Capital Costs (USD) per kg/hr of HSS
Thermal	$76,000
Ion Exchange	$101,000
Electrodialysis	$70,000

For the purposes of the techno-economic evaluation presented in this paper, a heat stable salt concentration of 1.5 wt% in the circulating amine solution was assumed. It is expected that plant operators would likely operate the reclaimer by adjusting the reclaimer feed to achieve a specified concentration of heat stable salts in the circulating amine solution rather than fixing the slipstream ratio and allowing the HSS concentration to vary. The 1.5 wt% concentration of HSS is within the range of practical limits given in the literature [4, 5]. The reclaimer slipstream percentage was adjusted so the HSS content in the circulating solution remained at this level. Table 5 shows the slipstream and flow rates to the reclaimers assuming 1.5 wt% HSS.

Table 5 – Slipstream Percentages and Flow Rates for 1.5 wt% HSS Content

Combustion Type/Solvent	Reclaiming Technology	Wt% Slipstream to Reclaimer, 1.5 wt% HSS	Flow to Reclaimer, kg/hr at 1.5 wt% HSS
Coal/MEA	Thermal reclaiming	0.100	9,810
	Ion exchange	0.111	10,912
	Electrodialysis	0.109	10,711
NGCC/MEA	Thermal reclaiming	0.060	2,774
	Ion exchange	0.066	3,055
	Electrodialysis	0.066	3,055
Coal/PZ	Thermal reclaiming	0.055	10,795
	Ion exchange	0.061	11,985
	Electrodialysis	0.060	11,786
NGCC/PZ	Thermal reclaiming	0.031	3,029
	Ion exchange	0.035	3,422
	Electrodialysis	0.034	3,324
Coal/MDEA/PZ	Thermal reclaiming	0.043	10,432
	Ion exchange	0.048	11,660
	Electrodialysis	0.047	11,414
NGCC/MDEA/PZ	Thermal reclaiming	0.027	2,948
	Ion exchange	0.030	3,280
	Electrodialysis	0.030	3,279

Purchased Equipment and Capital Costs

The estimated capital costs for the eighteen cases are shown in Figure 5. As shown in Figure 5, the capital costs of the ion exchange reclaiming technology is the highest for both the coal and natural gas cases; thermal reclaiming and electrodialysis capital costs are very similar. The capital costs for coal reclaiming are generally 3 to 3.5 times higher than the costs for natural gas reclaiming. This is because there is a larger reclaiming throughput for the coal cases than the natural gas cases to maintain the HSS at 1.5 wt%. Purchased equipment costs are roughly a factor of three less than the capital costs shown in Figure 5. The costs are shown in millions ($MM) of dollars.
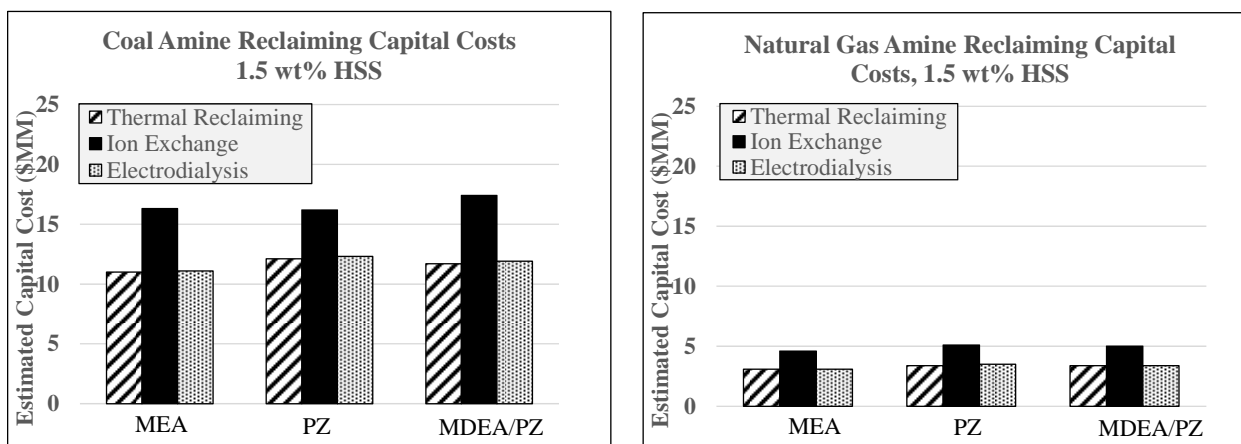

Figure 5 – Estimated Capital Costs for Coal and Natural Gas Amine Reclaiming

Energy Requirements

The energy requirements to operate the reclaiming unit are withdrawn from the main power facility either through electricity or steam. This decreases the net electrical output of the plant. The categories of electrical derating include:

- Lean solvent work pump (all cases) – It was assumed that the slipstream for solvent reclaiming is taken from the discharge of the lean solvent pump and returned to the suction of the lean solvent pump at operating pressure. Thus, the reclaiming system will require an incremental amount of pump power for this recycle amine loop.
- Reboiler thermal energy requirements (thermal reclaiming cases) – It was assumed that the reboiler thermal energy requirement is equivalent to the theoretical energy required to vaporize all the water and amine in the feed to the reclaiming system; no other inefficiencies were taken into account. A derating factor of 0.1211 hp-hr per lb of saturated steam required was used to convert the thermal energy requirement to an equivalent electrical derating.
- Vacuum pump work (MDEA/PZ thermal reclaiming cases) – It was assumed that electricity consumption for vacuum pumps are about 100 kW, and
- Applied current (electrodialysis cases) – Literature suggests that the electricity requirements for electrodialysis of amines is about 0.35 kWh per kg of amine fed to the reclaiming system [6].

The estimated energy usage is shown in Figure 6 in terms of kWh/kg of HSS reclaimed. Overall, the energy requirements for the thermal reclaiming cases are attributed to thermal energy for the reclaimer reboiler (converted to an equivalent electrical output), the energy requirements for the ion exchange cases are attributed directly to electric pump power, and the energy requirements for the electrodialysis cases are attributed directly to electric current.

The estimated energy requirement is highest for electrodialysis with MDEA/PZ in both the coal and natural gas cases (12 kWh/kg HSS). The energy requirements generally decrease for electrodialysis reclaiming from MDEA/PZ to PZ (9 kWh/kg HSS) and MEA (7 kWh/kg HSS). Thermal reclaiming energy requirements are highest for MEA (10 kWh/kg HSS) followed by PZ (8.5 kWh/kg HSS) and then MDEA/PZ (8.3 kWh/kg HSS). The pump energy requirement for ion exchange is minimal. The normalized estimated energy usage is similar for both the coal and natural gas cases. The annualized costs for energy requirements were estimated assuming that reclaimer energy requirements (converted from MW of electricity to kWh/yr of electricity) cost 12 ¢/kWh.
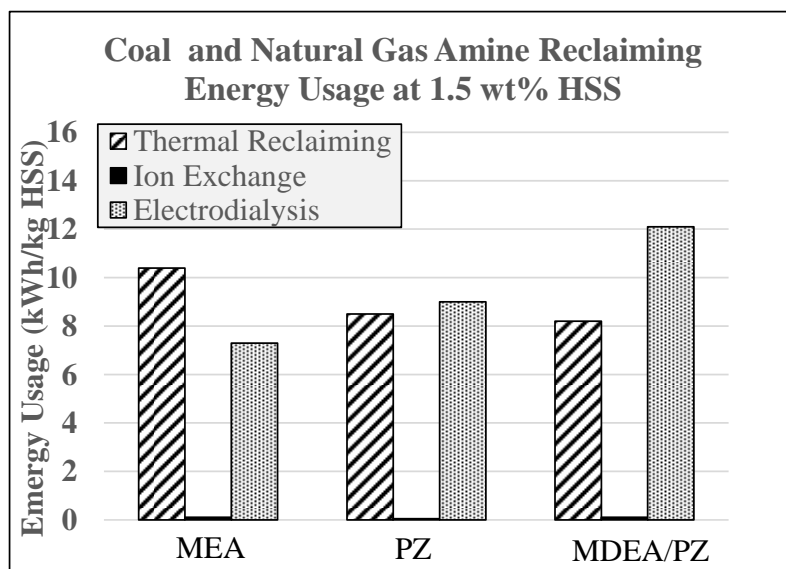

Figure 6 – Estimated Energy Requirement (kWh/kg HSS reclaimed)

Annual Operating Costs

The estimated major operating and maintenance (O&M) costs are separated into two categories: fixed and variable costs. Fixed annual operating costs include maintenance costs and labor (operating and administrative/support). Variable costs include solvent losses, consumables, and for the ion exchange and electrodialysis cases, replacement of ion exchange media and electrodialysis membranes. Solvent losses were assumed to be 5% of the inlet amine to the reclaimer for thermal reclaiming, 3% for electrodialysis, and 1 % for ion exchange; these values are based upon ranges of solvent losses supplied in literature [7]. Solvent costs were assumed to be $0.87/lb for MEA, $1.10/lb for MDEA/PZ, and $2.27/lb for PZ. Consumables include sodium hydroxide (0.31/lb) for HSS neutralization, sulfuric acid ($0.03/lb), and sodium hydroxide ($1.90/1,000 gallons) for regeneration of the ion exchange beds and distilled/deionized water for resin bed flushing/regeneration for ion exchange reclaiming, and for removal of salts for electrodialysis reclaiming. Replacement of the resin bed for ion exchange and membranes for

electrodialysis is also included. It was assumed that ion exchange resins lasted 5 years for NGCC cases ("clean service") and 2.5 years for coal cases ("dirty service" created by the presence of high molecular weight, non-ionic compounds and transition metals such as Hg, As, Pb, etc.). The anion ion exchange resin cost was $21/ft^3 and the cation ion exchange resin was $11/ft^3. Similar assumptions were made for the electrodialysis membrane lifetime; the electrodialysis membrane costs were assumed to be 25% of the total purchased equipment costs. Table 6 shows the estimated annual operating costs (not including waste disposal) for a constant HSS concentration in the reclaimer feed. Waste disposal costs are discussed later in the paper.

Table 6 – Estimated Annual Operating Costs for Constant HSS Concentration in Amine Reclaimed Feed

Reclaiming Technology	Annual Operating Costs ($MM)	Fixed O&M Costs ($MM)	Solvent Losses ($MM)	Other Consumables ($MM)	Resin or Membrane Replacement ($MM)
MEA Coal – Thermal Reclaiming	3.2	0.8	2.0	0.4	-
MEA Coal – Ion Exchange	4.5	1.1	0.4	1.7	1.3
MEA Coal – Electrodialysis	3.7	0.8	1.3	0.5	1.1
MEA NGCC – Thermal Reclaiming	1.0	0.3	0.6	0.1	-
MEA NGCC – Ion Exchange	1.2	0.4	0.1	0.5	0.2
MEA NGCC – Electrodialysis	1.0	0.3	0.4	0.2	0.2
PZ Coal – Thermal Reclaiming	8.6	0.9	7.2	0.5	-
PZ Coal – Ion Exchange	6.0	1.1	1.6	1.9	1.4
PZ Coal – Electrodialysis	7.4	0.9	4.7	0.6	1.2
PZ NGCC – Thermal Reclaiming	2.5	0.3	2.1	0.1	-
PZ NGCC – Ion Exchange	1.6	0.4	0.5	0.5	0.2
PZ NGCC – Electrodialysis	2.0	0.3	1.4	0.2	0.2
MDEA/PZ Coal – Thermal Reclaiming	5.9	0.9	4.6	0.5	-
MDEA/PZ Coal – Ion Exchange	5.4	1.2	1.0	1.8	1.4
MDEA/PZ Coal – Electrodialysis	5.6	0.9	3.0	0.6	1.2
MDEA/PZ NGCC – Thermal Reclaiming	1.7	0.3	1.3	0.1	-
MDEA/PZ NGCC – Ion Exchange	1.4	0.4	0.3	0.6	0.2
MDEA/PZ NGCC – Electrodialysis	1.5	0.3	0.8	0.2	0.2

As shown in Table 6, O&M costs associated with solvent losses are greatest for thermal reclaiming, followed by electrodialysis and ion exchange. These costs are directly a function of the assumptions made in Table 3 for amine recovery; higher amine recovery can be achieved at the expense of greater equipment corrosion. Higher temperatures are required to recover more amine, which results in higher corrosion rates at the gas/liquid interface in the column. O&M costs associated with consumables are greatest for ion exchange reclaiming due to sodium hydroxide and sulfuric acid consumption required for resin bed regeneration.

Revenue Requirements

Table 7 shows the estimated annual revenue requirements for the reclaiming options. The total annual revenue requirement (TRR) is calculated from the total capital requirement (TCR), total O&M costs, and total annualized energy costs in Equation 1. The CRF is also known as the capital recovery factor, and it can be estimated via Equation 2. A standard plant life of 25 years was used and the standard discount (interest) rate is 8%.

TRR = (TCR * CRF) + Annual O&M Costs + Annual Energy Costs $\qquad$ (Equation 1)

$$CRF = \frac{i*(1+i)^n}{(1+i)^n - 1} \qquad \text{(Equation 2)}$$

Table 7 – Estimated Annual Revenue Requirements for Amine Reclaiming Options

Reclaiming Technology	Annual Operating Costs ($MM)	Annualized Energy Costs ($MM)	Annualized Capital Costs ($MM)	Total Revenue Requirement ($MM)
MEA Coal – Thermal Reclaiming	3.2	1.3	1.0	5.6
MEA Coal – Ion Exchange	4.5	0.014	1.5	6.1
MEA Coal – Electrodialysis	3.7	0.9	1.0	5.7
MEA NGCC – Thermal Reclaiming	1.0	0.4	0.3	1.7
MEA NGCC – Ion Exchange	1.2	0.007	0.4	1.6
MEA NGCC – Electrodialysis	1.0	0.3	0.3	1.5
PZ Coal – Thermal Reclaiming	8.6	1.2	1.1	11.0
PZ Coal – Ion Exchange	6.0	0.006	1.5	7.5
PZ Coal – Electrodialysis	7.4	1.3	1.2	9.8
PZ NGCC – Thermal Reclaiming	2.5	0.3	0.3	3.2
PZ NGCC – Ion Exchange	1.6	0.004	0.5	2.1
PZ NGCC – Electrodialysis	2.0	0.4	0.3	2.7
MDEA/PZ Coal – Thermal Reclaiming	5.9	1.1	1.1	8.2
MDEA/PZ Coal – Ion Exchange	5.4	0.015	1.6	7.1
MDEA/PZ Coal – Electrodialysis	5.6	1.7	1.1	8.4
MDEA/PZ NGCC – Thermal Reclaiming	1.7	0.3	0.3	2.4
MDEA/PZ NGCC – Ion Exchange	1.4	0.004	0.5	1.9
MDEA/PZ NGCC – Electrodialysis	1.5	0.5	0.3	2.3

Normalized Amine Reclaiming Costs

The cost of electricity attributed to the amine reclaiming cases was calculated using Equation 3:

$$Cost\ of\ Electricity\ \left(\frac{\cent}{kWh}\right) = \frac{TRR\ \left(\frac{\$}{yr}\right)}{Annual\ Electric\ Output\ \left(\frac{kwh}{yr}\right)} * \left(\frac{100\cent}{1\$}\right) \qquad \text{(Equation 3)}$$

The cost of reclaiming per ton of CO_2 captured was calculated using Equation 4. The total annual revenue requirement (TRR) is estimated from Equation 1 and the parameters in the denominator were based on information specified in the literature [3]. It is assumed that coal combustion emits 0.834 MT (metric tonnes) CO_2 per MWh of electricity and natural gas combustion emits 0.349 MT CO_2 per MWh of electricity generated [3]. 90% CO_2 capture is assumed for all cases. At an annual capacity factor of 85%, approximately 6.7 billion kWh/yr of electricity is generated for the coal cases and 6.0 billion kWh/yr is generated for the NGCC cases.

$$Reclaiming\ Costs\ \left(\frac{\$}{ton\ CO_2\ captured}\right) =$$

$$\frac{TRR\ \left(\frac{\$}{yr}\right)}{Annual\ Elec.Output\ \left(\frac{kwh}{yr}\right) * {MT\ CO_2}/{MWh\ Elec.Output} * {1\ MWh}/{1000\ kWh} * 0.9} \qquad \text{(Equation 4)}$$

Figure 7 shows the estimated normalized reclaiming cost for the coal and natural gas CO_2 capture systems. The economics suggest that for both coal and natural gas combustion, annualized reclaiming costs for MEA-based capture systems could be lower than annualized reclaiming costs for PZ and MDEA/PZ systems. PZ-based capture systems have the highest estimated annualized reclaiming costs. The difference in annualized cost is attributed to annual costs from solvent losses and energy consumption for the thermal reclaiming and electrodialysis cases. Based on the assumptions made in the study, annual operating costs due to solvent losses will be greater for more expensive amines. This is especially true for thermal reclaiming, where it was assumed that 5 wt% of amine entering the reclaimer is lost with the waste stream. The concentration of amine in the neat solvent is higher for both MDEA/PZ (50 wt% amine) and PZ solvents (40 wt% amine) than for the MEA solvent (30 wt% amine). MEA is also less expensive than the other two solvents considered in this study. The assumption that 5 wt% of the total amine is lost with the reclaimer waste penalizes the more concentrated and expensive amines.

For MEA coal and natural gas combustion, similar costs are obtained for ion exchange, electrodialysis, and thermal reclaiming. For PZ coal and natural gas combustion, thermal reclaiming had the highest cost. Electrodialysis and ion exchange were the next to least expensive alternatives, respectively. For MDEA/PZ coal combustion, ion exchange was the least expensive followed by thermal reclaiming and electrodialysis. For natural gas combustion with MDEA/PZ, ion exchange was also least expensive followed by electrodialysis and then thermal reclaiming.

Overall, the estimated cost of electricity due to reclaiming ranged from 0.08 to 0.16 ¢/kWh for the coal combustion cases and from 0.03 to 0.05 ¢/kWh for the natural gas combustion cases. Literature [8] data shows a 30-yr average cost of electricity of 12.36 ¢/kWh (2012 dollars) for a supercritical coal power plant with state-of-the-art amine CO_2 capture technology and another unit at 11.90 ¢/kWh (2010 dollars) for a NGCC power plant with state of the art amine CO_2

capture technology. This suggests that the cost of amine reclaiming may be on the order of 0.6 to 1.3% of the total cost of electricity for coal plants with amine solvent CO_2 capture and only 0.3 to 0.4% for natural gas plants. The economics can also be expressed as $1.11 to $2.18/MT CO_2 captured for the coal cases, and $0.82 to $1.69/MT CO_2 captured for the natural gas cases.
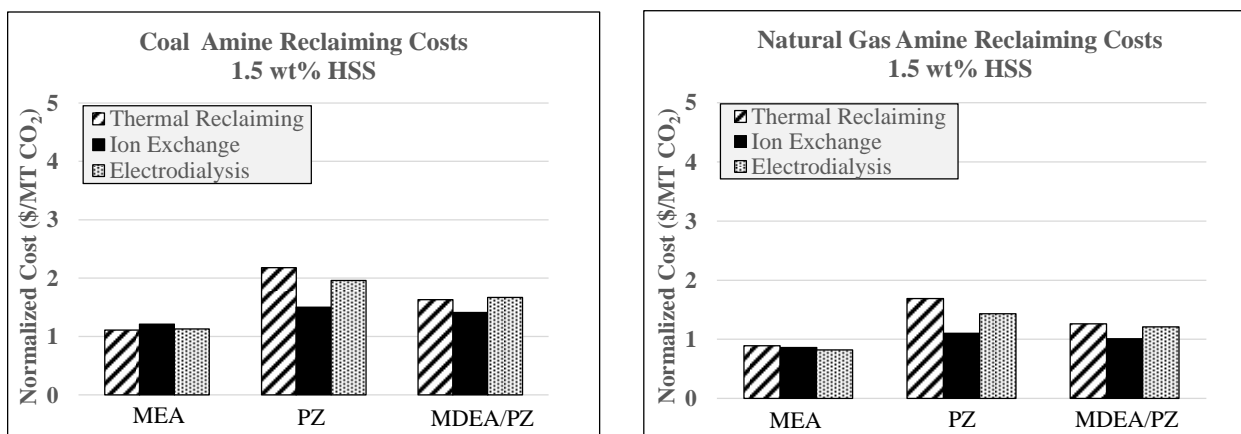

Figure 7 -- Estimated Coal and Natural Gas Amine Reclaiming Costs ($/MT CO_2) for 1.5 wt% HSS

Qualitative Analysis of Reclaiming

Since thermal reclaiming removes all species (HSS, transition metals, and high-MW products), it may be the preferred option for coal combustion power plants that have more contaminants and degradation routes. However, corrosion is an operational concern as well as solvent losses, especially for the novel, expensive amines.

Ion exchange does not remove non-ionic species and batch reclamation may be required to periodically remove these species. The technology is not practical for removal of transition metals and produces large volumes of wastewater. However, the solvent losses are minimal and the process generally requires minimal operator attention and maintenance. Ion exchange may be preferred for power plants with natural gas combustion when the metals concentration is typically low.

Electrodialysis is similar compared to ion exchange, but requires significant operator attention to run properly. It also has greater solvent losses than ion exchange. It may be another reclaiming choice for natural gas combustion power plants.

Oxygen Sensitivity of Techno-Economic Results

A sensitivity study was conducted for the pulverized coal case to look at the impact of oxygen concentration for MEA and MDEA/PZ systems. The base case oxygen concentration in the inlet flue gas is approximately 5 mol%. Sensitivities were examined that adjusted the oxygen concentration by a factor of two to 2.5 mol% and 10 mol%, and these results were extrapolated for a case assuming no oxygen. The results of this study are shown in Table 8. As shown in the table, decreasing the coal inlet flue gas oxygen content by a factor of two (2.5% O_2) also decreases the overall costs by 2.3 to 2.8% for MEA and MDEA/PZ, respectively. Increasing the coal O_2 content in the flue gas by a factor of 2 (10% O_2), increases the costs by 3.5% for MEA

and 2.8% for MDEA/PZ. Extrapolating the data to 0% oxygen gives values of $1.07/MT for MEA and $1.54/MT for MDEA/PZ.

Table 8 – Oxygen Concentration Sensitivity Study Results

Case	Overall HSS Concentration Wt%	High MW Polymers Wt%	Fly Ash Wt%	$/MT CO_2	¢/kWh	% Change from Base
MEA Base (5% O_2)	1.48	0.25	0.12	1.11	0.08	0
MEA 10% O_2	1.54	0.32	0.12	1.15	0.09	3.5
MEA 2.5% O_2	1.44	0.22	0.12	1.09	0.08	-2.3
MEA 0% O_2 (extrapolated)	1.42	0.19	0.12	1.07	0.08	-3.9
MDEA/PZ Base (5% O_2)	1.48	0.86	0.12	1.63	0.12	0
MDEA/PZ 10% O_2	1.53	1.27	0.12	1.67	0.13	2.8
MDEA/PZ 2.5% O_2	1.43	0.62	0.12	1.58	0.12	-2.8
MDEA/PZ 0% O_2 (extrapolated)	1.42	0.43	0.12	1.54	0.12	-5.6

Waste Disposal Characterization and Costs

The selection of the reclaiming technology may be based on the economics of the process as well as the waste management preferences. Disposal of the wastes may be dependent on whether they are considered to be hazardous according to current regulatory structures. The classification of the reclaimer wastes in this study relied on the degradation modeling results and took into consideration the solvent characteristics, metals content, and nitrosamine content. Since no actual wastes were tested, the classifications reported in this paper are not definitive.

This paper focuses on the waste disposal options based on U.S. regulations; however, disposal options dependent on the European Union, Canadian, and Australian regulations were also covered in the main report [2]. The U.S. EPA classifies industrial waste as hazardous if it is specifically listed or has any of the four characteristics of a hazardous waste (ignitable, reactive, corrosive, and toxic). Table 9 shows a summary of the U.S. hazardous waste classification for the thermal reclaiming technologies in this study.

Table 9 – U.S. Hazardous Waste Classification

Classification Category	Thermal Reclaiming Waste (Coal)	Thermal Reclaiming Waste (NGCC)	Ion Exchange and Electrodialysis (Coal, NGCC)
Listed	No	No	No
Ignitable	No	No	No
Reactive	No	No	No
Toxic	Maybe	No	No
Corrosive	Unlikely	Unlikely	No

As shown in the table, the reclaimer wastes may only potentially trigger hazardous waste classification for toxicity with thermal reclaiming in coal combustion power plants. A waste is considered toxic if extract from the toxicity characteristic leaching procedure (TCLP) contains a toxic constituent at a concentration above the regulatory level. Coal amine thermal reclaimer waste was predicted to contain metals that are potentially hazardous including: chromium, selenium and mercury. The predicted levels of these compounds in 7 m MEA and 8 m PZ, respectively, are: 8 and 5.5 ppmw mercury, 10.2 and 7.1 ppmw selenium, and 20 and 13.8 ppmw chromium. Nitrosamines ranged up to 330 ppmw for MEA and 3,500 ppmw for PZ. The NGCC cases do not contain any mercury, selenium, or chromium; however, the nitrosamines ranged up to 850 ppmw for MEA and 3,800 ppmw for PZ. These values are on a water-free basis.

While thermal reclaimers do have issues with corrosion in the bottom of the reclaimer and at the liquid/vapor interface, the reclaimer waste would not likely be considered characteristically corrosive. The NGCC amine thermal reclaimer waste will not contain metals and is not hazardous. The ion exchange and electrodialysis processes likely produce non-hazardous wastes since the streams are mostly water and the processes are not expected to transfer metals to the waste.

Several options exist for the disposal of the reclaimer wastes depending on whether they are considered to be hazardous or not as shown in Figures 8 and 9. Figure 8 shows the disposal options for hazardous reclaimer wastes. The hazardous waste can be 1) sent to a hazardous waste landfill, 2) fired in a hazardous waste incinerator or in a cement kiln licensed to fire hazardous waste, or 3) fired at the power plant.

Disposal options for non-hazardous wastes are shown in Figure 9. The thermal reclaimer waste has the potential to be classified as non-hazardous waste. If so, the disposal options include non-hazardous landfill, firing in the power plant boiler, or firing in a cement kiln. The aqueous waste stream produced by the ion exchange and electrodialysis processes is best suited for disposal via waste water treatment plants. In the U.S., there are no regulatory limits nor proposed regulatory limits specific to wastewater generated from CO_2 control technologies. The cost of different wastewater treatment systems will be highly dependent on the characteristics of the reclaimer wastewater, the required effluent composition, and the combination of technologies selected.
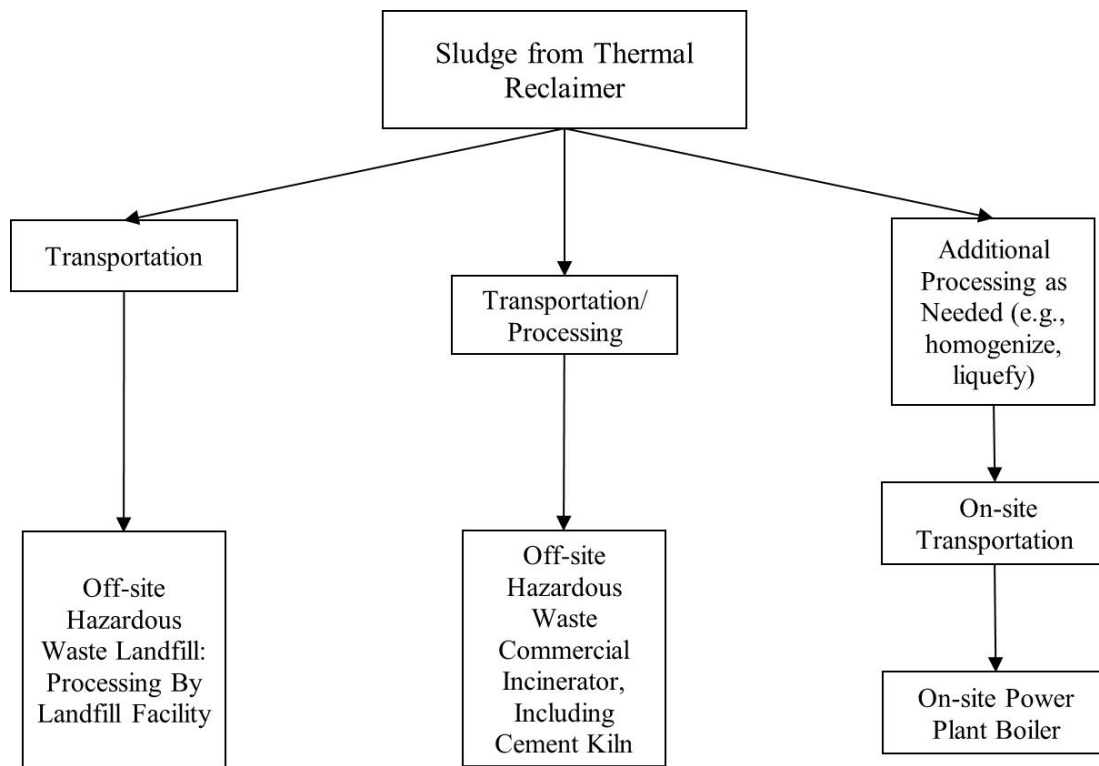
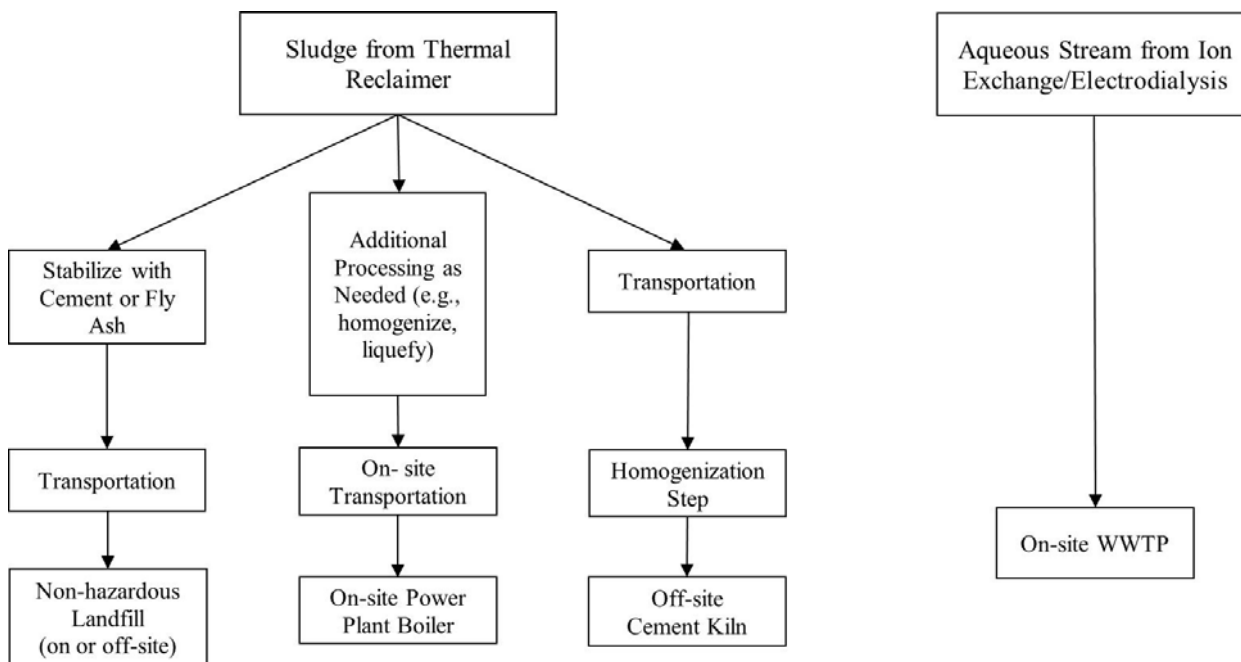**Figure 8** – Disposition Options for Hazardous Reclaimer Wastes

Figure 9 – Disposition Options for Non-Hazardous Reclaimer Wastes

The selection of the reclaiming process must consider the implications of waste classification on the disposal costs. Waste disposal costs were not included in the aforementioned economics. Table 10 shows the estimated cost of disposal for the thermal amine reclaimer option.

Table 10 – Estimated Thermal Amine Reclaimer Disposal Costs

Disposition Option	Reclaiming Case	Cost Added to Annualized Reclaimer Operations
Non-hazardous landfill	NGCC thermal reclaimer waste (US)	15 – 30%
Hazardous landfill or incinerator	Coal thermal reclaimer waste (US)	~ 100%

Costs for wastewater treatment processes needed at power plants to handle ion exchange and electrodialysis streams are very case specific as additional unit operations such as advanced oxidation systems and bioreactors may be required.

Conclusions

The cost of reclaiming and solvent makeup will be less than \$2/MT CO_2; however, the disposal costs could make it as high as \$4/MT CO_2. When the reclaimer design is set by the flue gas contaminants, expensive solvents will be less attractive; the cost of thermal reclaiming with PZ is the highest of all the options considered in the study. Reclaiming on pulverized coal flue gas is more expensive (25 to 40% higher) than with natural gas. The effect of inlet oxygen concentration in the flue gas was also examined; from 0 to 10 mol% O_2 in the flue gas, the cost of CO_2 capture only varied by \$0.10/MT and has a negligible effect.

The thermal reclaiming waste may be "hazardous" in the U.S. because of the metals content in coal-fired flue gas. Ion exchange and electrodialysis reclaimer wastes are not expected to trigger hazardous classification. However, it should be noted that the classification of the reclaimer waste was based on modeled results to identify potential issues. Regulations will also differ for other countries. Finally, the waste generator's preferences for waste management and operability may dominate the decision-making process.

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