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Evaluation of reclaimer sludge disposal from post-combustion CO₂ capture

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Abstract

An important environmental issue for amine-based post-combustion CO₂ capture is the generation of reclaimer sludge containing degradation products and impurities that must be disposed. This paper evaluated the environmental fate of reclaimer wastes generated from three amine-based solvents (monoethanolamine, piperazine, and a methyldiethanolamine/piperazine blend) used for CO₂ capture at a pulverized coal and a natural-gas combined cycle power plant (900 and 810 MW_e, respectively) with typical flue gas compositions. The solvent loss and impurities and degradation accumulation in the CO₂ capture units were modeled. A techno-economic analysis of different reclaiming technologies was conducted. The reclaimer sludge was classified based on US and EU regulations for hazardous waste, and alternative options for reclaimer sludge disposal were evaluated.

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1. Introduction

Post-combustion capture using aqueous, amine-based solvents is considered to be the most widely used technology in large scale carbon capture and sequestration (CCS) demonstration plants. An important environmental issue with respect to post-combustion capture is the generation of considerable amounts of degraded amine waste

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that has to be mitigated or disposed of in an environmentally suitable manner. Capture solvents can degrade due to the presence of other gaseous species present 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; in addition, at high temperature, the capture 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. Typically, these degradation products and heat stable salts exhibit corrosive properties and reduce solvent CO_2 absorption rates. Therefore, reclaiming is required to prohibit accumulation of these degradation products in high concentration in the capture solvent.

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 most commonly implemented reclaiming system involves thermal reclaiming (Figure 1). (Other reclaiming systems involve vacuum distillation, ion exchange, and electro dialysis.) In this process, amine vapors recovered from distillation are sent back to the CO_2 capture unit. The waste sludge remaining in the reclaimer bottoms is periodically discharged to prevent any accumulation of these impurities in the reclaimer. Literature values [1] for generated reclaimer sludge using monoethanolamine (MEA) varies from 1.2 $\text{kg/MWh}_{\text{net}}$ to 3.3 $\text{kg/MWh}_{\text{net}}$ for natural gas combined cycle (NGCC) and pulverized coal (PC) CO_2 capture cases, respectively. This can result in a sizeable amount of reclaimer sludge and, therefore, it is important to identify a sustainable method for disposal of these wastes.

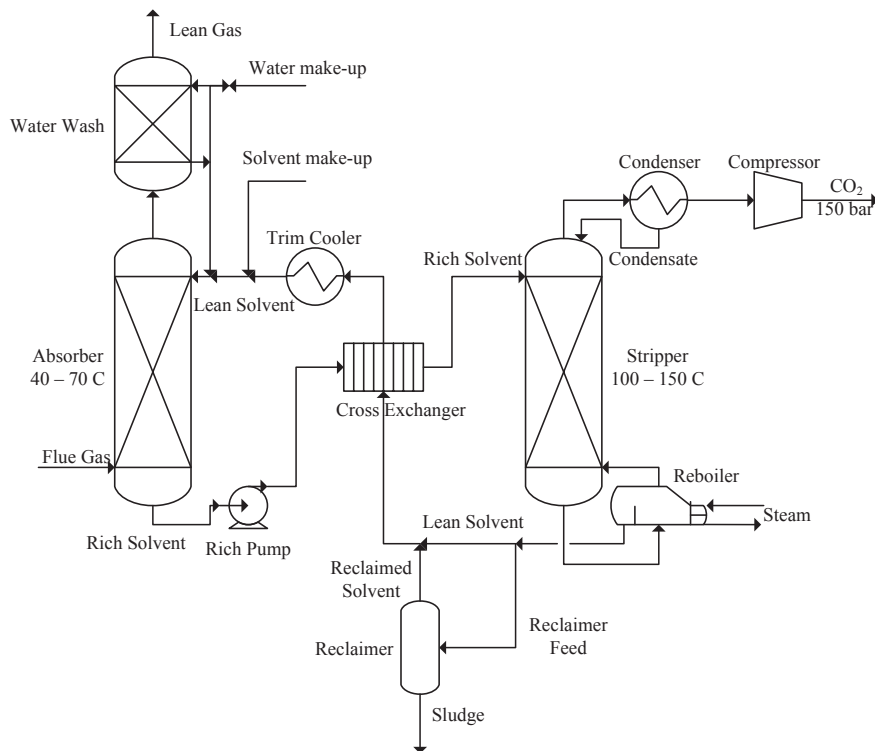


Fig. 1. Example amine scrubbing process flow diagram with thermal reclaiming.

Landfill disposal and incineration have been the traditional disposal methods for waste from amine reclaiming systems in the United States. Landfill disposal is not expected to be the long-term disposal option, and incineration has restrictions depending on the composition of the waste stream. Alternate disposal options may be required.

In the case of CO₂ capture for power plants and the reclamation of the solvents used, the processes are new. It is important to note that the reclaimer analysis presented here is based on information provided from a mathematical model of the reclaimer waste stream. No actual reclaiming waste streams were sampled or evaluated. Waste from an operating process will need to be analyzed to definitively classify the waste and identify disposal options.

This paper presents a summary of a study [2] performed for the IEAGHG research and development programme to evaluate the reclaimer sludge generated from various amine-based solvents, and make assessments regarding sludge handling and disposal methods. The reference cases that were developed for the CO₂ capture process in the study are discussed first, followed by a summary of the analysis of solvent losses and formation of degradation components in the system. The results of a techno-economic evaluation of amine reclaiming technology are presented next. The modeled composition of the reclaimer sludge is characterized and the resulting disposal options are presented. Lastly, future recommendations for the disposal of reclaimer sludge are made.

2. CO₂ Capture Process Reference Cases

Reference cases were developed for the supercritical pulverized coal (PC) and natural-gas combined cycle (NGCC) power plants (900 and 810 MWe gross power output, respectively) with CO₂ amine-based capture facilities. Three amine-based solvents were evaluated: monoethanolamine (MEA), piperazine (PZ), and methyldiethanolamine/piperazine (MDEA/PZ). These solvent systems were chosen because they are the most representative CO₂ capture systems and have the largest amount of publicly available data on CO₂ capture performance and reclaiming systems.

A selective catalytic removal (SCR) unit is assumed upstream of the CO₂ capture unit for both the coal and natural gas power plants, and a wet flue gas desulfurization (FGD) unit and sodium hydroxide polishing unit are assumed to be located upstream of the CO₂ capture unit of the coal-fired power plant (to keep the SO_x concentration to the capture unit < 10 ppmv). For both cases, the inlet flue gas to the CO₂ capture unit will also pass through a blower to increase the pressure slightly and a direct contact cooler to lower the temperature to 40°C.

It was assumed that CO₂ capture is 90% for all cases, and CO₂ exiting the capture plant was delivered at pipeline pressure of 11.0 MPa and temperature of 30°C. It was also assumed that the power produced by the reference plants are on the basis of gross output, and the energy requirements from the CO₂ capture plant decreased the net power output. These power plants represent the upper end of the typical size ranges of modern, large-scale commercial power plants.

The flue gas conditions used in this study for the coal and natural gas cases are shown in Table 1. Flue gas from NGCC combustion will be more dilute in CO₂ (4.1 vol%) with higher oxygen content (12 vol%) than flue gas from coal combustion (11.8 and 5 vol%, respectively) due to the need for significant excess air to operate the gas turbine. The flue gas contaminant concentrations were determined after reviewing literature data [3] from coal-fired power generating units with similar pollution controls. The CO₂ removal rates are 18,411 kmol/hr for the coal-fired power plant and 8,283 kmol/hr for the natural gas-fired power plant at their respective electrical power outputs and flue gas rates (assuming 90% CO₂ removal).

The reference cases 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 provides some general information on the reference cases as well as the approximate solvent circulation rate estimated for each case to achieve 90% CO₂ capture. The solvent concentrations are shown in molality, which is defined as the moles of solvent per kilogram of solute (water in this case).

Table 1. Coal and natural gas conditions.

Parameter	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 ₂ O (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 (µg/Nm ³ wet)	1.8	0
Se (µg/Nm ³ wet)	2.3	0
Fly ash (mg/Nm ³ wet)	6	0
Other metals (µg/Nm ³ wet)	5.5	0

Table 2. Amine circulation rates for CO₂ capture from coal and natural gas combustion flue gases.

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

3. Analysis of Solvent Losses and Formation of Degradation Components

For each solvent system, a degradation model was developed to estimate solvent loss, impurities accumulation and degradation product accumulation expected in a commercial CO₂ capture unit. Amine solvent loss can occur by thermal degradation, oxidative degradation, amine volatility, reclaimer operation, nitrosamine formation from NO_x, and reactions with flue gas impurities. The standalone degradation models were then integrated with a material balance for different types of reclaiming systems to create a system-wide, steady-state material balance that provides compositions for the circulating amine capture solvent, reclaimer feed, and reclaimer waste streams. A description of the modeling basis is described below, followed by a summary of the modeling results for amine losses and reclaimer sludge composition.

3.1. Basis of Model

Thermal degradation occurs mostly in the stripper and is strongly dependent on the stripper operating temperature. As stripper temperature is increased, thermal degradation increases, raising solvent make-up costs. At the same time, the pressure of the CO₂ vapor stream leaving the stripper increases, reducing the work required for compression and lowering the overall energy costs of the system. The base case stripper operating temperatures were set at 120°C for MEA, 135°C for MDEA/PZ, and 150°C for PZ; these temperatures balance the system energy requirements and amine loss. The model assumes that amine degrades via a first-order mechanism, and that amine concentration will be kept constant through reclaiming and solvent make-up. The model estimates the amine loss rate in the sump of the stripper as well as the packing, with the packing temperature accounting for the hot-side approach temperature of the cross exchanger and the temperature drop due to flashing when entering the stripper. The base case stripper design assumes a stripper sump residence time of 5 minutes at the operating temperature, with an additional 3 minutes residence time in the packing at a temperature 10°C lower than the operating temperature.

Oxidative degradation losses were modeled as a function of oxygen concentration, dissolved metal ion concentration (known to catalyze oxidation) and rich loading of the amine-based solvent. The model uses an oxidation rate constant estimated from experimental data. Oxidation is assumed to be first-order with respect to the amine and oxygen content of the flue gas, and will occur mainly in the heated section of the rich side of the cross exchanger and in the piping downstream before entering the stripper. The residence time in this section is assumed to be 30 seconds. A 5°C hot-side approach temperature is assumed for the cross-exchanger. After the solvent enters the packed section of the stripper, any remaining dissolved oxygen will flash off, which will significantly slow the rate of solvent oxidation.

It should be noted that the thermal and oxidative degradation pathways and resulting products of formation are discussed in depth in the final report [2].

NO₂ will be absorbed in the flue gas as nitrite, which can react with secondary amines such as PZ to form carcinogenic nitrosamines such as N-nitroso-piperazine (MNPZ). MNPZ is thermally unstable and will decompose readily in the stripper. As a result, MNPZ will reach a steady-state concentration that will be a function of the stripper temperature and the flue gas NO₂ content as described in the literature [4]. Pure MEA and MDEA will not form stable nitrosamines. However, secondary amines present in degraded solvent will react to form nitrosamines. The formation of nitramines was not considered in this study.

In addition to degradation products, the capture solvent will accumulate contaminants from the flue gas, including sulfate and nitrate from SO_x and NO_x absorption. Coal flue gas will also contain trace amounts of chloride, fluoride, and fly ash. It was assumed that SO₂, HCl, and HF (90% removal) and NO₂ (100% removal) will be absorbed by the amine solvent and subsequently form heat stable salts. SO₃ and other NO_x compounds present in the flue gas will not be absorbed as readily. NO absorption as nitrate was conservatively estimated at 10% removal from flue gas. NO is relatively inert and not readily absorbed by amines, but low levels of nitrate accumulation have been observed in pilot plants operating with post-combustion coal flue gas. The absorption of the transition metals (via leaching of fly ash or absorption of gaseous mercury) into the solvent was conservatively assumed to be 50% removal.

Some amine will be removed from the solvent through the top of the absorber stack with the cleaned flue gas due to volatility, entrainment, aerosols, etc. However, it was assumed that a water wash will be used to limit emissions (the water wash is returned to the solvent). The model includes an estimation of amine loss as a function of the design specification of the water wash and an estimation of the concentration of ammonia leaving the absorber. The base case for all amines is 1 ppmv of amine in the flue gas leaving the water wash; the concentration of ammonia in the flue gas leaving the absorber is on the order of 2-5 ppmv.

In addition to the other causes of amine loss, some additional amine will be lost in the reclaiming process with the waste streams. Thermal reclaiming is likely to recover 95 wt% of the amine in the feed (with some loss due to additional thermal degradation) as well as 100 wt% HSS and metals/non-ionic removal. Electrodialysis and ion exchange should be of the order of 97 and 99 wt% amine recovery and 91.5 and 90 wt% HSS removal, respectively, but these processes will not remove polar contaminants [5].

3.2. Model Results for Amine Loss

For all three solvent systems, oxidation contributes more to solvent loss than thermal degradation or volatile losses. Estimated oxidation rates for NGCC cases are more than twice as much as the coal cases due to the higher oxygen 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.

Nitrosamine formation results in some additional loss of PZ in the 8 m PZ and 7/2 m MDEA/PZ cases. This is a strong function of the NO₂ concentration entering the absorber. Nitrosamines will also be formed in the 7 m MEA case, but through a reaction of NO₂ with secondary amine degradation products. It may be advantageous to remove the remaining NO₂ upstream of the capture unit to avoid solvent replacement costs.

In addition, for a thermal reclaimer that removes all non-volatile compounds with a continuous feed rate of 0.1% of the overall solvent circulation rate, the accumulation of non-volatile contaminants and degradation products will be on the order of 0.4-1.5 wt% at steady state conditions. This should not significantly affect solvent performance. The NGCC cases (1,010-1,235 ppmw) have a higher formate concentration than the PC cases (511-899 ppmw) due to greater oxidation. However, the overall contaminant accumulation for the NGCC cases (0.4-0.9 wt%) is lower than the PC cases (0.6 to 1.5 wt%) due to a lower concentration of SO_x and NO_x entering the flue gas. In PZ and MDEA/PZ, mononitrosopiperazine will reach a steady-state concentration of approximately 130-250 ppm, and fly ash transition metals will accumulate in the range of 100-300 ppb, well below regulated maximum concentrations for hazardous waste.

At a concentration of 1 ppmv amine exiting the water wash, the expected amine loss due to volatility is low. However, if the presence of aerosols with the exiting flue gas raises the amine concentration in the flue gas exiting the absorber, the losses could become very significant. Previous pilot plant campaigns have observed amine emissions as high as 50 ppmv due to aerosols, but such high levels are not expected in commercial plants.

Several other parameters involving solvent loss and degradation were evaluated, including: the effects of alternate process and operation conditions (CO₂ loading and absorber intercooling) on solvent loss, the effects of degradation products on the solvent (viscosity, other energy parameters, and foaming and corrosion), alternative stripper configurations, oxidation inhibitors, volatile emissions and aerosols and volatiles reclaiming processes. Details of these parameters can be found in the final report [2].

4. Techno-Economic Evaluation of Amine Reclaiming Systems

Process modeling and economic analyses were conducted for the three solvents of interest (MEA, MDEA/PZ and PZ) capturing CO₂ from two different types of flue gas (coal and natural gas combustion) and being reclaimed via three different technologies (thermal reclaiming, ion exchange and electrodialysis). A brief description of the reclaiming technologies is provided below, followed by details of the techno-economic evaluation and a qualitative comparison of the reclaiming technologies.

4.1. Amine Reclaiming Process Descriptions

A process flow diagram for a thermal reclaiming system is shown in Figure 2. A slipstream of lean amine is taken from the lean amine stream downstream of the regenerator and lean amine pump (and upstream of the cross-exchanger) and continuously fed to the reclaiming unit. A CO₂ pretreatment step occurs to reverse the reaction between CO₂ and amine that forms amine carbamate; one potential option involves heating at regeneration conditions to reverse the amine-CO₂ 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 flows to the thermal reclaimer where the impurities are removed; the stripper overheads are sent to a condenser and fed back into the main solvent circulation loop.

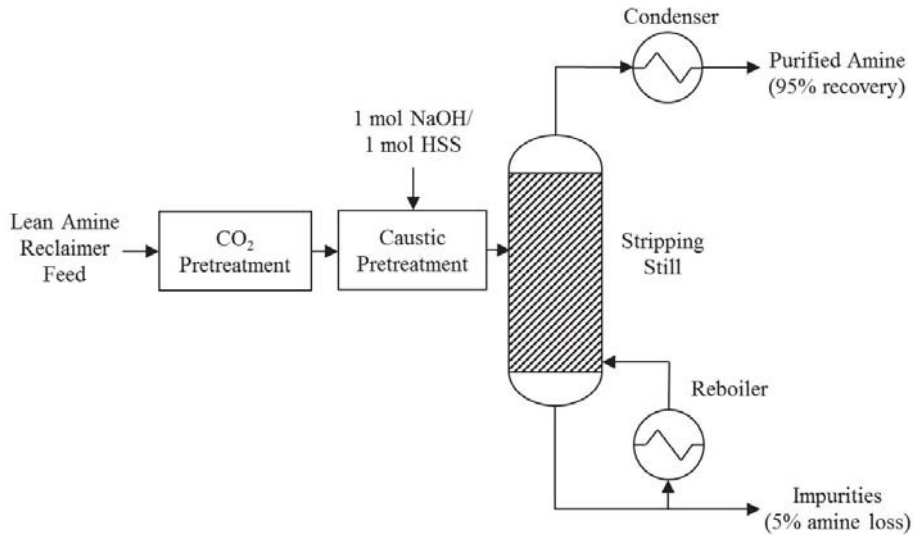


Fig. 2. General thermal reclaiming process flow diagram.

In the ion exchange 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.

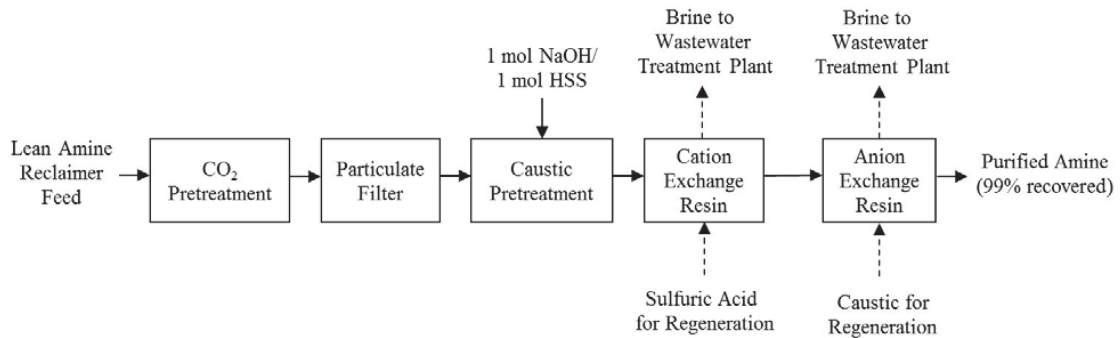


Fig. 3. General ion exchange reclaiming process flow diagram.

The potential slipstream locations to feed the electro dialysis process are the same as with ion exchange. The electro dialysis process (Figure 4) also requires CO₂ pretreatment, particulate filtration, and caustic pretreatment. The contaminated amine is then sent to an electro dialysis 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.

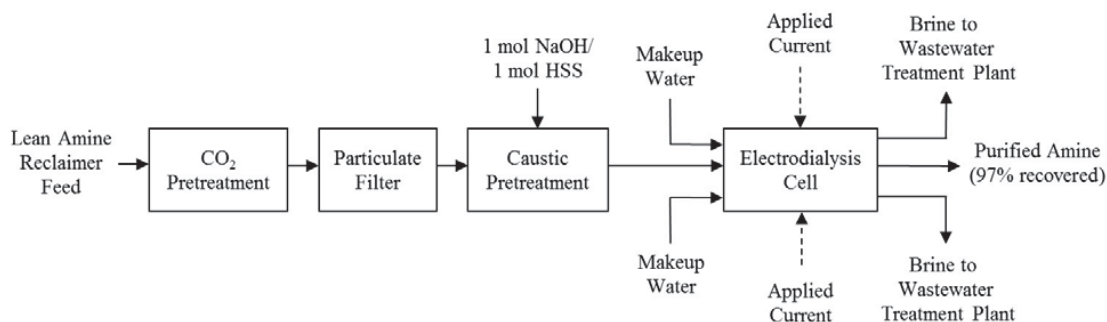


Fig. 4. General electro dialysis reclaiming process flow diagram.

4.2. Techno-Economic Evaluation

A literature review was conducted and communication with reclaiming vendors and oil and gas representatives were made to learn as much about the three reclaiming options as possible. Information obtained from this effort included: reclaimer conditions, amine recovery, amine degradation, HSS removal, capital costs, energy requirements, chemical requirements, and waste generation. The vendor capital costs were scaled using a 0.6 exponent based on amine throughput; operating data from vendors was used as appropriate.

Steady-state material balances were made around the reclaimer system assuming two different bases:

- A slipstream of 0.1% of the total solvent circulation rate is fed to the reclaiming unit. This slipstream ratio keeps the solvent losses at acceptable levels, but the heat stable salts (HSS) levels vary depending on the amine solvent.
- The reclaimer slipstream percentage is adjusted so that the steady-state concentration of HSS in the circulating amine solvent is 1.5 wt%.

Figures 5 and 6 show the estimated normalized reclaiming cost for the coal and natural gas CO₂ capture systems. The costs were estimated assuming an 8% discount rate and a plant life of 25 years [6]. The process 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 both MDEA/PZ and PZ-based capture systems, with PZ-based capture systems having the highest estimated annualized reclaiming costs. This annualized cost difference is attributed to annual costs from solvent losses and energy consumption for the thermal reclaiming and electro dialysis cases; based upon the assumptions made in the study, annual operating costs attributed to solvent losses will be greater for more expensive amines. This is especially true for thermal reclaiming cases, where it is assumed that 5 wt% of amine entering the reclaimer is lost with the waste stream.

In addition, the concentration of amine in the neat solvent is higher for both the MDEA/PZ (50 wt% amine) and PZ solvents (40 wt% amine) than for the MEA solvent (30 wt% amine); MEA is also a less expensive amine than both the PZ and MDEA/PZ solvents. The simplifying assumption that 5 wt% of the total amine is lost with the reclaimer waste penalizes the more concentrated and expensive amines; for an actual detailed plant design, with a more expensive amine system, it may be more advantageous to design a thermal reclaimer with a lower slip of amine to the waste stream.

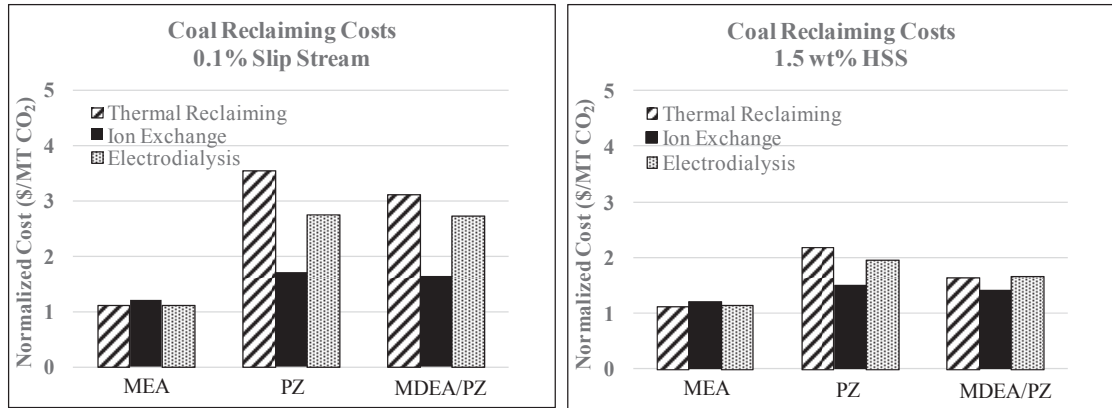


Fig. 5. Estimated coal reclaiming costs (\$/MT CO₂) for (a) 0.1% slip stream and (b) 1.5 wt% HSS.

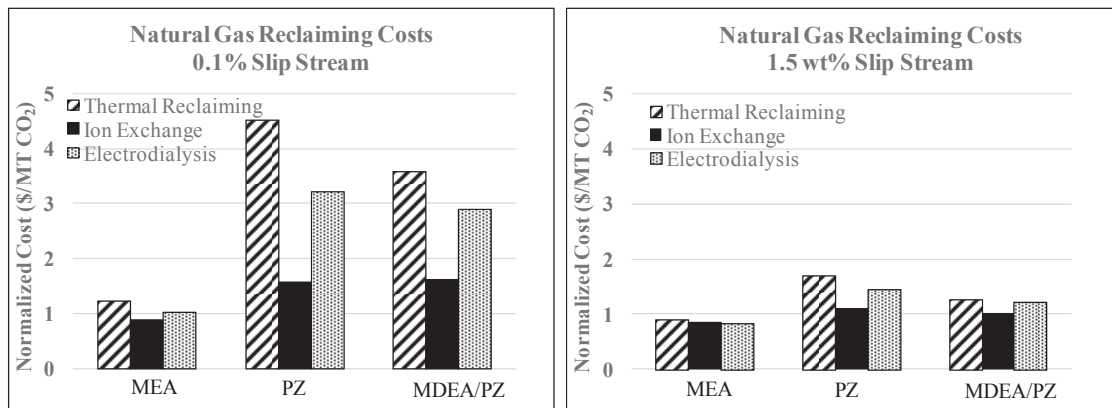


Fig. 6. Estimated natural gas reclaiming costs (\$/MT CO₂) for (a) 0.1% slip stream and (b) 1.5 wt% HSS.

For MEA coal combustion, thermal reclaiming was found to be the least expensive reclaiming process, while for PZ and MDEA/PZ ion exchange was the least expensive. For natural gas combustion, ion exchange was the least expensive reclaiming process for all the amines except for MEA with 1.5 wt% HSS, where electro dialysis had a slightly lower cost. It should also be noted that for coal and natural gas combustion, the assumption of keeping the HSS at a constant 1.5 wt% resulted in lower overall reclaiming costs.

Overall, the estimated cost of electricity attributed to reclaiming ranged from 0.08 to 0.16 ¢/kWh (0.0006 to 0.0012 €/kWh) for the coal combustion cases, and 0.03 to 0.05 ¢/kWh (0.0002 to 0.0004 €/kWh) for the natural gas combustion cases (for the fixed 1.5 wt% HSS case). A literature report [7] lists a 30-yr average cost of electricity of 12.36 ¢/kWh (in 2012 dollars) for a supercritical coal power plant with state-of-the-art amine CO₂ capture technology, and a 30-yr average cost of electricity of 11.90 ¢/kWh (in 2010 dollars) for a NGCC power plant with state-of-the-art amine CO₂ capture technology.

Although these absolute cost of electricity numbers may be on slightly different bases, this comparison demonstrates that amine reclaiming may only account for 0.6 to 1.3 percent of the total cost of electricity for coal plants with amine solvent CO₂ capture, and only 0.3 to 0.4 percent of the total cost of electricity for natural gas plants with amine solvent CO₂ capture. These economics can also be expressed as \$1.11 to \$2.18/MT CO₂ captured

(€0.84 to €1.64/ MT CO₂ captured) for the coal cases, and \$0.82 to \$1.69/MT CO₂ captured (€0.61 to €1.27/ MT CO₂ captured) for the natural gas cases.

A sensitivity study was performed to examine the effects of regeneration temperature, oxygen concentration in the inlet flue gas, NO_x concentration in the inlet flue gas, fly ash concentration in the inlet flue gas, and the concentration of stainless steel metals from corrosion for the MEA and MDEA/PZ coal thermal reclaiming cases. Overall, this high-level sensitivity study suggests that minimizing the concentration of NO₂ in the inlet flue gas to the CO₂ capture system appears to offer the most direct benefit to reducing the concentration of HSS in the amine solvent, thus reducing the requirements (and costs) of the reclaiming system.

Because the economics for a majority of the studied options are within a similar range of costs, metrics such as level of required operator attention and waste handling preferences may determine technology selection.

4.3. Qualitative Comparison

In general, thermal reclaiming may be the preferred option for power plants with coal combustion because thermal reclaiming is robust and can remove the majority of all types of degradation products and impurities from the amine solvent (HSS, transition metals, high-molecular weight polymeric products). Corrosion issues in the kettle reboilers have been reported and need to be taken into consideration.

Ion exchange may be preferred for power plants with natural gas combustion because it is most effective when the metals concentration is low, and the formation of high-molecular weight polymeric products is low compared to the rate of HSS formation. Even if this is the case, the degraded amine may need to be occasionally replaced or subjected to batch thermal reclaiming to reduce metals and nitrosamines back to acceptable levels. Ion exchange units can usually be run without continuous monitoring. Media replacement cost can be expensive.

Electrodialysis may be another preferred reclaiming option for power plants with natural gas combustion and high incursion rates of heat stable salts. The electrodialysis process has been installed in the wastewater industry. Process upsets or excursions that could direct high concentrations of dissolved metals to the reclaimer could poison the membranes. This technology also requires significant attention from operations to run successfully, and membrane replacement cost can be expensive

5. Classification of Reclaimer Sludge Waste

The wastes generated from the various solvent reclaiming scenarios were characterized according to current regulatory structures in the United States (US) and European Union (EU). This characterization was performed by evaluating the characteristics of the CO₂ capture solvent, the metals content, and the nitrosamine content. Characteristics of the other minor degradation constituents were not considered. The characterization was based upon the waste composition determined by the model discussed previously; no actual wastes were analyzed. For this reason, the waste classifications offered here should be used to identify *potential* issues associated with the selection of reclaiming methods and process conditions and their effect on waste disposal options. In practice, the generated wastes need to undergo analytical testing to definitively characterize it as hazardous or non-hazardous.

The US EPA classifies industrial waste as hazardous if it is 1) specifically listed or 2) has any of the four characteristics (ignitable, reactive, corrosive, toxic) of a hazardous waste. None of the waste components in any of the reclaiming scenarios were listed wastes. The wastes did not contain ignitable or reactive constituents. Corrosivity data were not available for these wastes. Although the wastes will have a non-corrosive pH, the waste would need to be tested to determine that it meets the corrosion rate limits for steel. While the thermal reclaiming process encounters severe corrosion in the bottom of the reclaimer, experience from one gas-treating facility operating a reclaimer for MDEA indicates that the reclaimer waste is not characteristically corrosive. Thus, this study indicates that the likely trigger for hazardous classification would be the metals content of the coal-fired thermal reclaimer waste; the thermal reclaimer wastes from NGCC power plants do not contain metals. Under the base case assumptions, the thermal reclaimer waste from coal-fired power plants may be classified as hazardous in the United States due to mercury above the toxicity characteristic (TC) limits; the model results indicated other toxic metals would be below the TC limits. Conservative assumptions for mercury capture by the solvent were used in the base case model, and actual mercury concentrations in the solvent may be significantly lower. Also, coal-fired

power plants can reduce mercury loading to the solvent by operating flue gas mercury controls to achieve higher removal upstream of the CO₂ capture system.

The EU uses several additional metrics to classify industrial waste. The thermal reclaimer wastes from both the coal-fired and NGCC power plants would likely be considered hazardous. Each of the thermal reclaimer waste streams contain a significant fraction of the solvent, which safety data sheets indicate meets one or more of the EU's characteristics of a hazardous waste (e.g., harmful, corrosive); the presence of metals in the coal-fired thermal reclaimer waste streams make the stream a listed waste. The waste streams from the ion exchange and electro dialysis streams are 95% water. The modeled streams were assumed to have no metals content; if these streams indeed contained some low level of metals, they would be classified as hazardous waste due to the presence of those metals. In general, the solvent content was not high enough to trigger hazardous classification [8]. The exceptions were the waste streams from the solvents containing piperazine. Piperazine is a sensitizing material; minimum thresholds for concentration of sensitizing materials could not be located in the EU regulations. Therefore, the PZ and MDEA/PZ ion exchange and electro dialysis waste streams may be classified as hazardous if they are sensitizing wastes.

6. Reclaimer Sludge Disposal Options

Disposition options for the waste streams generated by the various reclaiming scenarios were considered. The available disposition options depend upon the characteristics of the waste (e.g., heating value) and the regulatory strictures that might apply. The analysis presented here was based upon current regulations; if CO₂ capture at power plants is widely deployed, it is possible that industry specific rules could be created for the classification and treatment of the reclaimer waste. The analysis is also based on a mathematical model of the reclaimer waste. Waste from an operating process will need to be analyzed to definitively classify the waste and identify disposition options.

Figure 7 shows the disposal options for hazardous reclaimer wastes. For thermal reclaimer waste that is classified as hazardous waste, the disposition options for the US are as follows: send to a hazardous waste landfill, fire in a hazardous waste incinerator, fire in a cement kiln licensed to fire hazardous waste, or fire at the power plant. The options for the EU are limited to the incineration options; the corrosivity and organic carbon content appear to make the waste ineligible for a hazardous waste landfill. The compositional consistency of the waste will be a challenge to its disposal in a cement kiln and the power plant; however, this may be overcome by packaging the waste with other materials. While firing the waste in a coal-fired boiler appears technically feasible, firing in the HRSG (heat recovery steam generator) of an NGCC requires more investigation. A literature search [9] identified at least one example in the US of using in-duct firing in the HRSG to dispose of gas-phase volatile organic waste; further studies are needed to determine if the solid thermal reclaimer sludge would be sufficiently destroyed (US) or achieve sufficient time and temperature combustion requirements (EU) as well as meet air emissions requirements. In both the US and EU, power plants would be subject to different regulatory obligations if they fire hazardous waste in their coal-fired boilers; in the EU, the power plant will have to comply with various additional regulations at a cost. Most US electric generating power plants do not operate as hazardous waste incinerators.

Disposition options for non-hazardous waste are shown in Figure 8. In the US the thermal reclaimer waste has the potential to be classified as non-hazardous waste. If so, disposal options include non-hazardous landfill, firing in the power plant boiler, or firing in a cement kiln. Depending on the heating value of the reclaimer material and how it is processed and handled, it may or may not be considered a solid waste. If the thermal reclaimer material meets legitimacy criteria, it may be exempt from classification as a solid waste and the power plant might remain under its current regulatory structure. If it is a solid waste, the power plant would be subject to a new regulatory structure for solid waste incinerators.

The aqueous waste stream produced by the ion exchange and electro dialysis processes is best suited for disposal via wastewater treatment plants. Most US power plants do not currently have wastewater treatment plants; German power plants with FGD will have wastewater treatment plants on-site, and other German power plants have access to wastewater treatment facilities through municipal services off-site. The amine content of the waste stream would require additional unit operations (e.g., advanced oxidation systems, bioreactors) beyond what is typically found at a power plant wastewater treatment facility. A plant-specific analysis would be required to determine if the existing

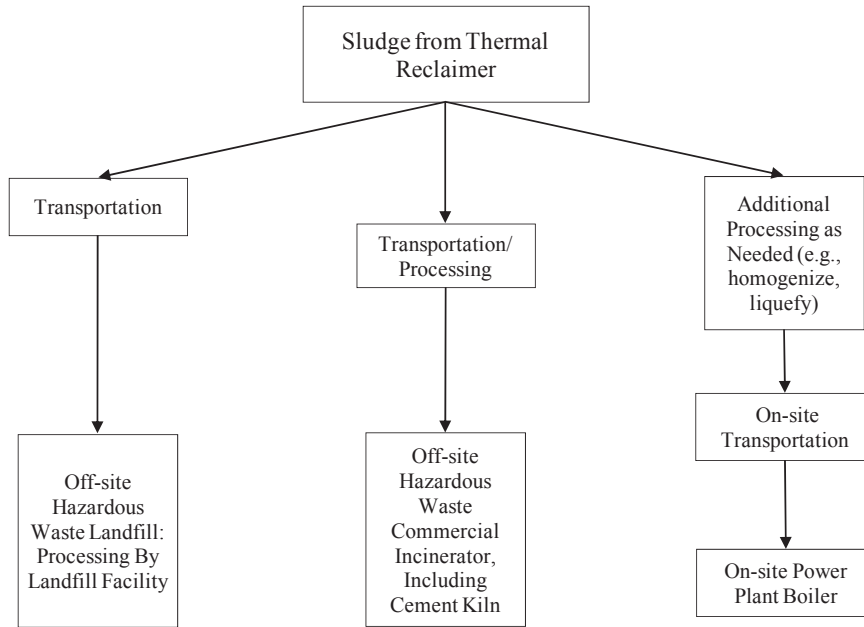


Fig. 7. Disposition options for hazardous reclaimer wastes.

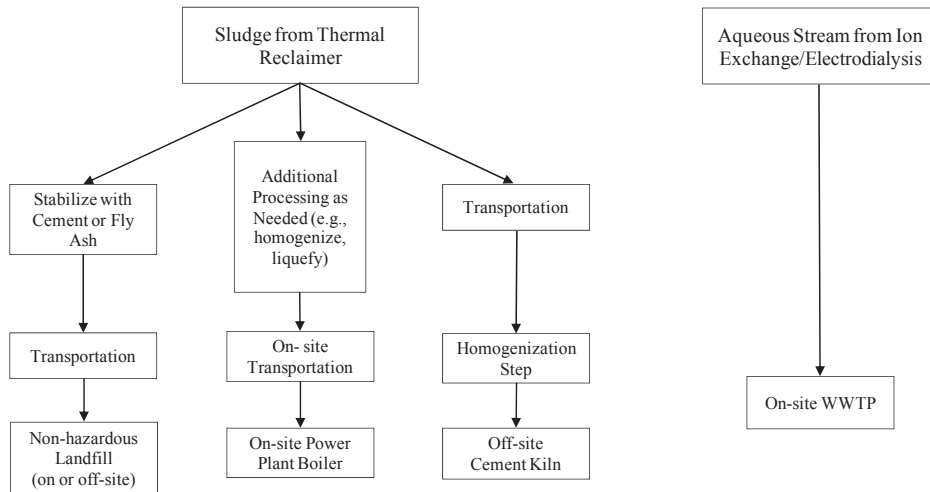


Fig. 8. Disposition options for non-hazardous reclaimer wastes.

wastewater treatment facility could handle the additional volume from the reclaimer waste. In the US, there are no regulatory limits nor proposed regulatory limits specific to wastewater generated from CO₂ 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.

It should be noted that the annualized costs for operating the reclaimer process presented in Section 4 of this paper did not include the cost of waste disposition. The annual cost for hazardous waste disposal for each solvent is either similar to or greater than the annualized cost of operating the reclaiming process. The non-hazardous waste landfill cost for NGCC thermal reclaimer sludge was estimated to range from €0.16 to €1.2MM/yr (\$0.21 to \$1.6MM/yr), while hazardous waste disposal (landfill/incineration) for a coal-fired power plant varied from €1.9 to €11.4 MM/yr (\$2.5 to \$15.1 MM/yr). This is a significant expense; therefore, selection of a reclaimer process should carefully consider the type of waste generated and associated costs of disposing that waste.

7. Recommendations for Future Work

Although a significant amount of information was documented on amine-based CO₂ capture reclaimer sludge in the final report that this paper is based on, there were some areas where additional data or development would be useful. For example, technical data gaps from information collected from pilot and full-scale programs will need to be addressed. Actual reclaimer sludge could be collected and analyzed for waste characterization. Reclaimer operation can be optimized and reclaimer technologies combined where it makes sense (e.g., continuous ion exchange reclaiming with batch off-site thermal reclaiming). Methods can be developed to selectively remove metals and minimize toxic impurities. Finally, demonstration projects can be used to address issues with environmental standards and approval procedures.

8. Summary of Results

Reference cases were developed for three amine solvents (monoethanolamine, piperazine, and a methyldiethanolamine/piperazine blend) used for CO₂ capture at a pulverized coal and a natural-gas combined cycle power plant (900 and 810 MWe gross power output, respectively) with typical flue gas compositions.

A mathematical model was developed to estimate solvent losses and impurity/degradation accumulation in the amine-based CO₂ capture system. Oxidation contributes more to solvent losses than thermal degradation or volatile losses. Oxidation rates are higher for the natural gas cases than coal because of the higher oxygen content in the flue gas. The accumulation rate of non-volatile contaminants and degradation products is expected to be low and should not affect solvent performance (0.1% slipstream ratio).

Annual reclaiming costs appear to be lower for MEA-based capture systems than for PZ and MDEA/PZ systems. The cost of electricity from amine reclaiming is expected to be only a small portion (0.3 to 1.3%) of the total cost of electricity for coal and natural gas plants with amine solvent CO₂ capture.

Based on modeled reclaimer sludge compositions, it appears that the metals content of the thermal reclaimer waste could potentially trigger a hazardous waste classification in the US. This could impact coal-fired thermal reclaimer waste since natural gas systems do not contain metals. Based on the conservative assumptions in this study, mercury was above the toxicity characteristic limit, while other toxic metals were below the limit. Measures could be made to lower the mercury content of the inlet flue gas with proper control technology. In EU, the thermal reclaimer wastes from both the coal-fired and NGCC power plants would likely be considered hazardous material.

If the ion exchange and electro dialysis streams contained low level of metals, they would be classified as hazardous. The solvent content of the waste streams was not high enough (95% water) to trigger hazardous classification. However, piperazine is a sensitizing material and could potentially cause these streams to be hazardous (minimum thresholds for sensitizing material could not be located in EU regulations).

It should be noted that the classification of reclaimer waste is based on modeled results and should only be used to identify *potential* hazardous waste issues. Sampling and analytical on actual reclaimer waste streams will need to be conducted to verify these findings.

Disposal options vary depending on the classification of the reclaimer waste. Hazardous thermal reclaimer waste can be transported to an off-site waste landfill, transported and processed in an off-site commercial incinerator, or

require additional processing and transportation to on-site power plant boiler. Non-hazardous thermal reclaimer waste can be stabilized and sent to a landfill, require additional processing and transported to on-site power plant boiler, or transported/homogenized and sent to an off-site cement kiln. The aqueous stream from ion exchange and electro dialysis reclaiming will be treated at an on-site waste water treatment plant.

Recommendations were made for future work, including additional data development, optimizing operation of current reclaimer technologies, and developing methods to selectively removal metals and other contaminants from the sludge.

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