EVALUATION OF RECLAIMER SLUDGE DISPOSAL FROM POST-COMBUSTION CO_2 CAPTURE

Report: 2014/02

March 2014

INTERNATIONAL ENERGY AGENCY

The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme. The IEA fosters co-operation amongst its 28 member countries and the European Commission, and with the other countries, in order to increase energy security by improved efficiency of energy use, development of alternative energy sources and research, development and demonstration on matters of energy supply and use. This is achieved through a series of collaborative activities, organised under more than 40 Implementing Agreements. These agreements cover more than 200 individual items of research, development and demonstration. IEAGHG is one of these Implementing Agreements.

DISCLAIMER

COPYRIGHT

ACKNOWLEDGEMENTS AND CITATIONS

This report describes research sponsored by IEAGHG. This report was prepared by:

Trimeric Corporation USA; The University of Texas at Austin, USA & URS Corporation, USA

The principal researchers were:
Andrew J. Sexton (Trimeric Corporation)
Kevin S. Fisher (Trimeric Corporation)
Anne I. Ryan (Trimeric Corporation)
Paul Nielsen (The University of Texas at Austin)
Gary T. Rochelle (The University of Texas at Austin)
Eric Chen (The University of Texas at Austin)
Katherine Dombrowski (URS Corporation)
Jean Youngerman (URS Corporation)
William A. Steen (URS Corporation)
Douglas Orr (URS Corporation)

To ensure the quality and technical integrity of the research undertaken by IEAGHG each study is managed by an appointed IEAGHG manager. The report is also reviewed by a panel of independent technical experts before its release.

The IEAGHG manager for this report was:
Prachi Singh & John Davison

The expert reviewers for this report were:

- Max Ball, SaskPower, Canada
- Paul-Emmanuel Just & Mania Neisiani, Shell Cansolv, Canada
- Peter Moser, Sand Schmidt, RWE, Germany
- Bernd Schallert, E.ON, Germany
- Sven Unterberger, EnBW, Germany
- Erik Gjernes, Gassnova, Norway
- Ase Slagtern, The Research Council of Norway, Norway
- Espen Steinseth Hamborg, Statoil/TCM, Norway
- Andrew Botting, Ben Jackson, SEPA, UK
- Merched Azzi, CSIRO, Australia
- Segyu Jang, Kyungryoung Jang, Jang Kyung-Rong, KEPRI, South Korea

The report should be cited in literature as follows:

'IEAGHG, "Evaluation of Reclaimer Sludge Disposal from Post-Combustion CO_2 Capture", 2014/02, March 2014'

Further information or copies of the report can be obtained by contacting IEAGHG at:

IEAGHG, Orchard Business Centre,
Stoke Orchard, Cheltenham,
GLOS., GL52 7RZ, UK
Tel: +44(0) 1242 680753 Fax: +44 (0)1242 680758
E-mail: mail@ieaghg.org
Internet: www.ieaghg.org

EVALUATION OF RECLAIMER SLUDGE DISPOSAL FROM POST-COMBUSTION CO_2 CAPTURE

Key Messages

- For amine based solvents such as: monoethanolamine (MEA), piperazine (PZ), and methyldiethanolamine/piperazine (MDEA/PZ), oxidative degradation contributes more to solvent loss than thermal degradation or volatile losses.
- For coal based power plants, thermal reclaiming may be the preferred option whereas for natural gas based power plants an ion exchange and electrodialysis solvent reclaiming process is the preferred option.
- Based on US regulations the coal-fired thermal reclaimer waste is likely to be classified as hazardous due to the presence of metals, whereas thermal reclaimer waste from NGCC will be classified as non-hazardous.
- Under US regulations waste streams from the ion exchange and electrodialysis reclaiming process will not be classified as hazardous.
- In EU all type of reclaimer waste will be categorized as hazardous.
- There are sustainable ways available to dispose of reclaimer waste such as: by landfilling, combustion in a waste incinerator, firing in a cement kiln, co-firing at the power plant and handing in the waste water treatment plant.

EVALUATION OF RECLAIMER SLUDGE DISPOSAL FROM POST-COMBUSTION CO_2 CAPTURE

Introduction

Post combustion CO_2 capture using aqueous amine based solvents is considered to be the most widely used technology in large scale carbon capture and storage (CCS) demonstration projects. An important environmental issue with respect to post-combustion capture is the generation of considerable amounts of degraded amine waste that has to be mitigated or disposed of properly. Amine based solvents for CO_2 absorption can degrade due to the presence of gaseous species present in the flue gas such as CO_2, SO_x, NO_x, O_2, halogenated compounds and other impurities. Degradation products formed by amine based solvents can include heat stable salts (HSS), non-volatile organic compounds and suspended solids. Figure 1 shows the different mechanisms of amine based solvent loss.

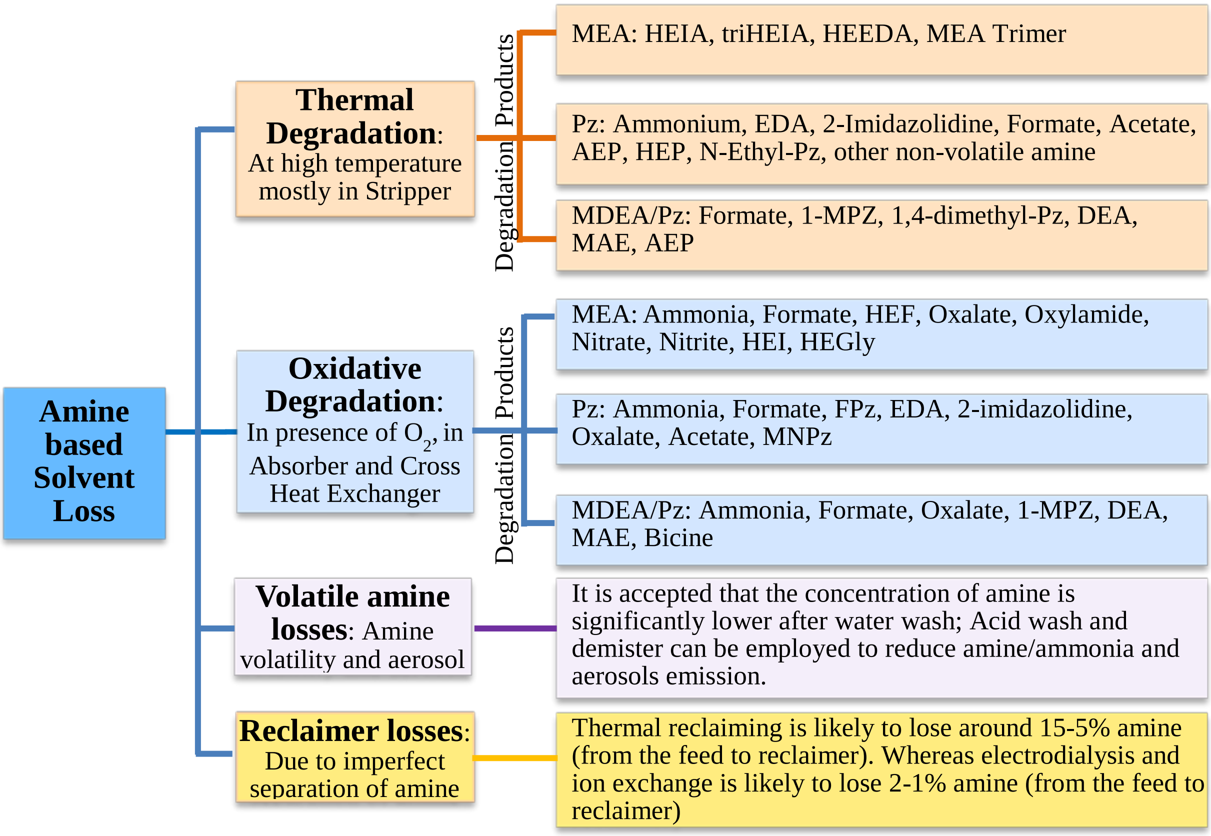


Figure 1 Amine based solvent loss by different mechanism and their degradation products. MEA (Monoethanolamine), MDEA (Methylenediethanolamine), Pz (Piperazine), HEIA (Hydroxyethylimidazolidone), triHEIA (Cyclic urea of the trimer), HEEDA (Hydroxyethylethylenediamine), EDA (Ethylenediamine), AEP (N-aminoethyl-PZ), HEP (N-hydroxyethyl-PZ), 1-MPZ (1-methyl-PZ), DEA (Diethanolamine), MAE (N-methyl-aminoethanol), AEP (Aminoethylpiperazine), HEF (Hydroxyethyl formamide), HEI (Hydroxyethylimdazole), HEGly (N-(2-hydroxyethyl)-glycine), FPz (N-Formyl-PZ), MNPz (N-nitroso-piperazine).

Another degradation compound nitrosamine will be formed by the absorption of NO_2 as a nitrite. This nitrite can react with secondary amine e.g. Pz and form carcinogenic nitrosamines e.g. MNPz. MnPz is thermally unstable and will decompose rapidly at stripper conditions. Other containments present in the flue gas such as mercury, selenium, arsenic and other metals will be also present in the amine based solvent.

Effect of degradation products on amine based solvent properties

Degradation products such as heat stable salts and larger polymers formed from solvent degradation are typically stable and non-volatile. These degradation products will accumulate in the circulating amine solvent at a constant rate. The following list shows the effects of these products on solvent properties:

- Increase of non-alkaline impurities such as formamide and amine sulphate increases the viscosity of the solvent. An increase in viscosity affects the heat transfer coefficient in the cross exchanger, diffusion coefficient, affecting mass transfer, which will result in an increased energy requirement of the process.
- The accumulation of amine degradation products, which will have different properties than the amine solvent, will degrade the kinetics of CO_2 absorption, heat of CO_2 absorption, and the operating CO_2 absorption capacity in most of the solvent cases.
- Based on lab-scale experiments and pilot plant tests, a clean amine based solvent is rarely seen to be foaming, but it is possible that foaming is probably a consequence of the presence of impurities.
- It is considered that corrosion is increased by degradation products which may serve as chelating agents and by dissolved salts that increase ionic conductivity. However, corrosion is also expected to increase oxidative degradation due to the accumulation of the dissolved metal catalysts.

Therefore, solvent reclaiming is necessary for the efficient operation of the process. In this study degradation of some of the conventional solvents for the CO_2 absorption process such as MEA, MDEA/Pz and Pz are evaluated for both coal and natural gas power plants. Different reclaiming technologies such as; thermal reclaiming, ion exchange and electrodialysis were evaluated based on different amine based solvents and economics. Furthermore different reclaimer waste disposal options such as: landfilling, cofiring in a boiler, using in a cement kiln and waste water treatment were also evaluated.

Study Approach

In this study different solvent reclaiming technologies were evaluated for two reference power plants: Supercritical Pulverised Coal (SCPC) and Natural Gas Combined Cycle (NGCC) at their respective gross power outputs (900 and 810 MW_e, respectively). A low sulphur Australian coal was used for SCPC case. A selective catalytic removal (SCR) unit is assumed upstream of the CO_2 capture unit for both the coal and natural gas power plants. In addition a wet flue gas desulfurization (FGD) unit and a sodium hydroxide polishing unit , is located upstream of the CO_2 capture unit in the coal-fired power plant thus reducing the SOx concentration to 10 ppmv or less .

Regarding the CO_2 capture process; first the flue gas is passed through a blower in order to increase the pressure to 110.3 kPa and a direct contact cooler to lower the temperature to 40°C. The cooled flue gas is sent to the absorber where CO_2 is absorbed at 40°C. The CO_2 lean amine solution from the stripper is cooled and sent to the top of the absorber, and the rich solution exits the bottom of the absorber. The treated flue gas exits from the top of the absorber and is sent to the stack. The CO_2 rich solution exchanges heat with hot CO_2 lean solution in a cross heat exchanger. This preheated CO_2 rich solution flows to the stripper where CO_2 desorbs from the solution. A steam-heated reboiler provides heat to the stripper column for CO_2 desorption and sensible heating of the liquid. The 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 vapour is cooled and water is condensed. The remaining CO_2 vapour then flows to a multi-stage compression train. It was assumed that the CO_2 exiting the capture plant was delivered at pipeline pressure of 11.0MPa and a temperature of 30°C for all cases.

The amine based solvents investigated in this study were 7Mole Monoethanolamine (MEA), 8Mole Piperazine (Pz) and 7Mole/2Mole Methyldiethanolamine (MDEA)/Pz. The required amine circulation rates were estimated from the optimized lean and rich solvent loadings for each of the six capture reference cases at 90% CO_2 capture rate. The CO_2 concentration in the flue gas was assumed to be 11.78 volume %, and 4.09 volume % for coal-fired and natural gas-fired power plants respectively. At their respective electric power outputs and flue gas rates, assuming 90% CO_2 removal, this equates to CO_2 removal rates of 810 tonne/hr and 365 tonne/hr for the coal-fired power and natural gas-fired power plants respectively.

For the solvent reclaiming, 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. The material balances assumes a 0.1% slipstream ratio of solvent feed to the reclaimer compared to the total circulation rate of amine within the capture process; this slipstream ratio is less than the 0.5% to 3% slipstream suggested by reclaiming vendors and given in literature, but this 0.1% slipstream was taken due to the requirement to keep solvent losses at acceptable levels. An overview of all three reclaiming technologies investigated in this study is presented in Table 1.

Table 1 An overview of different reclaiming technologies

Parameters	Thermal reclaiming	Ion Exchange	Electrodialysis
Process conditions	Atmospheric pressure, 149°C; For MDEA, 6.6-13.3kPa, 177°C	Atmospheric pressure, 40°C	Atmospheric pressure, 40°C
Amine recovery	85-95%	99%	96-98%
Heat Stable Salt removal	100%	90%	91.5%
Metal/Non-ionic product removal	100%	0%	0%
Waste characteristics	Semi solid	95% water	95% water
Equipment required	Gas-fired heater, cross exchanger, inlet separator, vapor scrubber, overhead accumulator, vacuum pump, reflux condenser, cooler and carbon filter	Neutralization and filtration (one micron pre-filter) required upstream of package ion exchange unit	Filtration, Feed pump, Membrane unit

In a Thermal reclaiming process, the process is a kettele type reboiler with a packed column. The amine fed to the reboiler and the liquid level is maintained several inches above the tube bundles. The amine and water are vaporized in the kettele and sent through a packed stripping column. The vapours (water, amine and CO_2) exit the top of the column to be condensed and sent to the lean solvent stream at the suction of the amine pump. The heavier boiling point and non-volatile impurities (heat stable salts, solids and dissolved metals) as well as a small fraction of amine based solvent and remining liquid is coming out as a thick sludge at the bottom of reclaimer and is periodically removed by a vaccum pump to a storage vessel or truck for transportation.

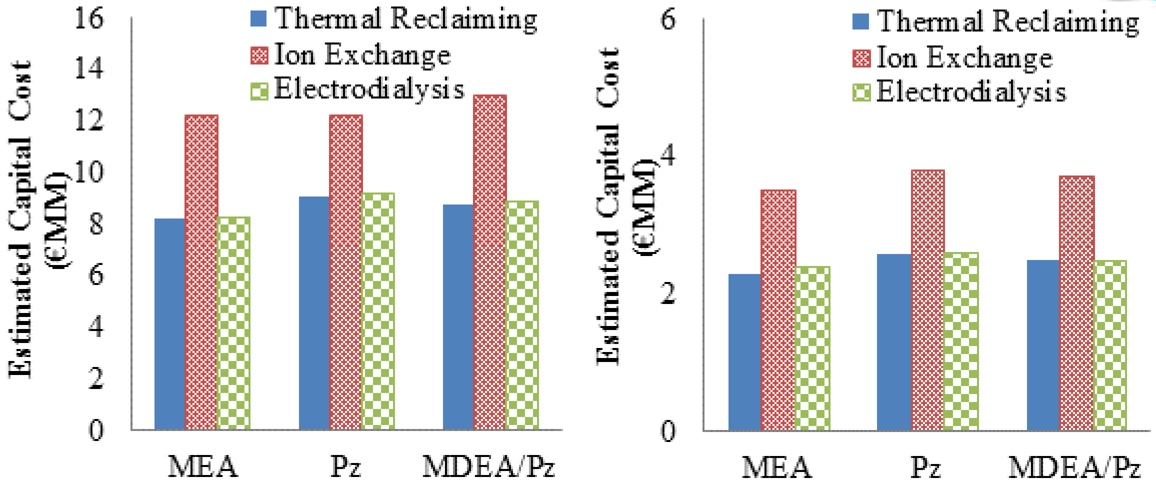
In Ion exchange solvent reclaiming process, the lean amine slipstream is fed into the cation exchange resin packed bed where the undesirebale cations bind to the resin and are removed from the amine stream. Then the amine is sent to the anion exchange resin bed where anion impurities are removed. The anion and cation resins are periodically regenerated by adding sulfuric acid and sodium hydroxide to the beds respecively. During this regeneration large amount of low concentration brine is produced, typically having 5% salt solution, NaOH and H_2SO_4.

Elecrodialysis solvent reclaiming process has a series of ion-selective membranes and electrodes. The amine stream is sent where cation moves towards negatively charged cathode and anion moves towards positively charged anode. A negatively charged cation exchange membrane between the anode and the waste stream prevent the anions from moving away from anode resulting in a concentrated anion waste stream. A positively charged anion exchange membrane is placed similarly between the second waste stream and the cathode to prevent the cations from moving further towards the cathode resulting in a cation waste stream.

Cost Estimation of Different Reclaiming Technologies

Different solvent reclaiming technologies were evaluated on the basis of their captial and operation costs. For the capital cost evaluation it was assumed that the concentration of heat stable salts (HSS) in the amine solution to the reclaimer is approximately 3 wt%. This figure was based on the information gathered from different literature sources which suggests that this is the approximate value of reported concentrations when amine solutions were subjected to batch reclaiming. When considering the turndown, the commercial reclaiming vendors have suggested having multiple units in parallel that can run at constant flow rates. Therefore, four parallel reclaiming units were assumed for each of the three reclaiming technologies in this study.

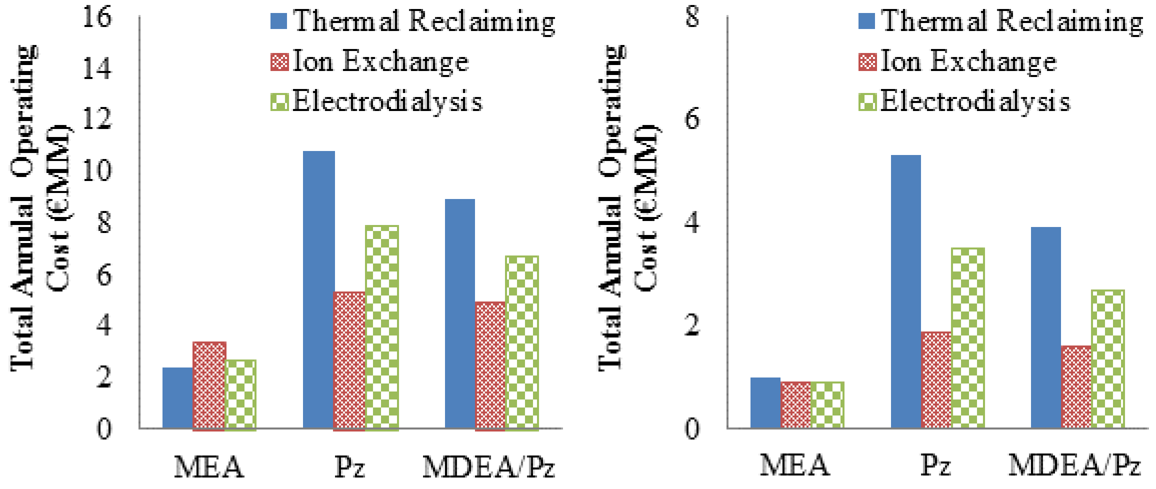
Figure 2 represents the coal and natural gas cases capital costs required for different reclaiming technologies for different reference solvents. It can be noticed that the costs of thermal and electrodialysis reclaiming are similar to each other for all solvents. Whereas the ion exchange reclaiming process is found to have a higher cost when compared to the other two reclaiming technologies. This is due to the higher purchased equipment cost which is manily due to the presence of six adsorption beds (two for adsorption, two for regenration and two for standby). As well the capital cost was influenced by the selection of stainless steel material for the adsorption bed and initial cost of cation and anion resins.



(a) Coal Case **(b) NGCC Case**

Figure 2 Estimated capital cost of different reclaiming technologies

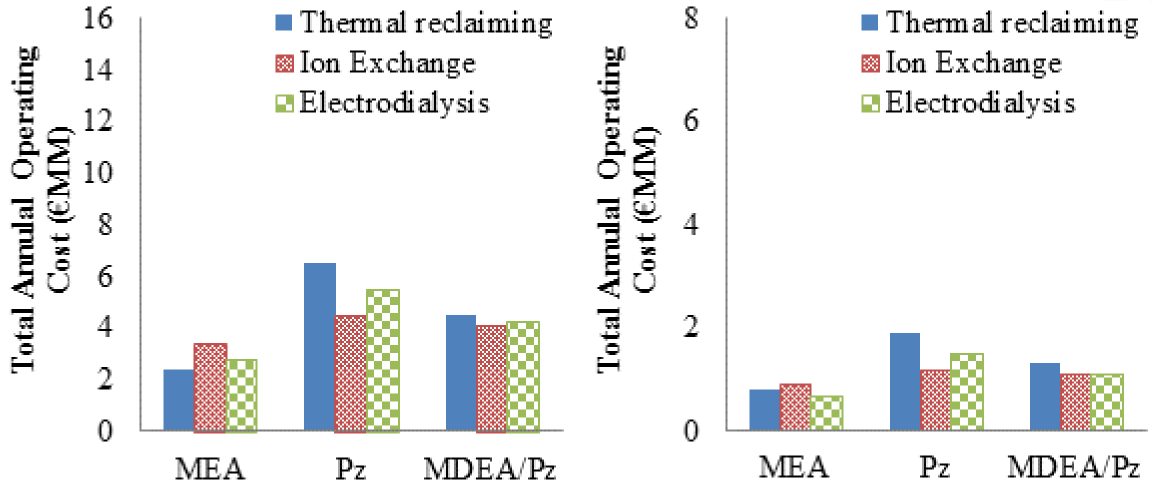
The operational cost for different reclaiming technologies depends on the maintinance and labor cost, electricity cost, solvent loss, consumables (soldium hydroxide for HSS neutralization, sulfuric acid, sodium hydroxide for ion exchange bed regeneration, demineralzied water) and for ion exchange and electrodilaysis replacement of resin and membranes respectively. Figure 3 shows the coal and natural gas case estimated annual operating costs fo the different reference solvents.



(a) Coal Case **(b) NGCC Case**

Figure 3 Estimated annual operating cost of different reclaiming technologies based on continous 0.1% slipstream ratio of solvent fed to the reclaimer

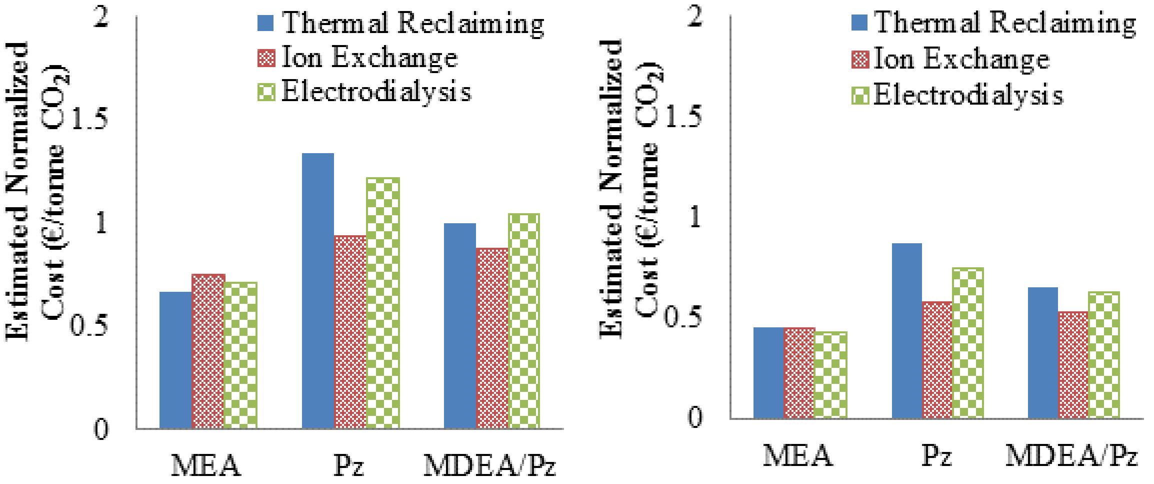
The solvent cost has an impact on the operational cost and solvents such as Pz ($5/kg) and MDEA/Pz ($2.42/kg) have higher operational costs compared to MEA ($1.91/kg). Moreover the formation of heat stable salts is found to be significantly lower for Pz and MDEA/Pz solvents when compared to that of MEA. On the basis of 5% solvent loss in the thermal reclaiming process for all reference solvents, Pz and MDEA/Pz, results in a higher operating cost for the coal and NGCC cases. The cost of solvent loss was noticed to be higher in electrodialysis process when compared to that of ion exchange process for coal and NGCC case



(a) Coal Case **(b) NGCC Case**

Figure 4 Estimated annual operating cost of different reclaiming technologies based on continuous <1.5 wt% heat stable salt concentration in the feed to the reclaimer

When considering the energy requirement for different reclaiming processes, thermal reclaiming was found to be the highest followed by ion exchange and electrodialysis. Hence from these results it is clear that it is important to adjust the reclaimer feed on the basis of heat stable salt formation for different solvents in order to reduce the solvent loss. Therefore, another evaluation was also performed in this study in which the <1.5wt% heat stable salt concentration was kept in the reclaimer feed.



(a) Coal Case **(b) NGCC Case**

Figure 5 Estimated normalized cost for different reclaiming technologies based on continous <1.5 wt% heat stable salt concentration in the feed to the reclaimer

Figure 4 shows that the annual operating cost is found to be lower when compared to the results shown in Figure 3, especially for the thermal reclaiming process where 5wt% solvent entering the reclaimer is assumed to be lost. The operational cost for ion exchange and electrodialysis is found to be lower with a constant heat stable salt concentration (<1.5wt%) feed to the reclaimer.

When considering the reclaiming cost on the basis of electricity requirement for the reclaimer it will account for 0.6 to 1.3% and 0.3 to 0.4% of total electricity demand from the CO_2 capture process for coal and NGCC cases respectively. Figure 5 shows the normalised cost '€/tonne CO_2 captured' for the coal and NGCC cases. It can be noticed that the reclaimer cost is found to be in range of 0.84 - 1.64 €/tonne CO_2 and 0.61 - 1.27 €/tonne CO_2 for coal and NGCC respectively.

Sensitivity analysis

In order to identify the effect of changes in process parameters such as increasing stripper temperature and changes in impurities concentration entering the CO_2 capture process, a sensitivity analysis for MEA and MDEA thermal reclaiming for coal case gives the following insights:

- Increasing CO_2 regeneration temperature from 120 to 150°C for MDEA case increases the higher molecular weight polymer degradation product formation, resulting in an increase in the operational cost.
- The NOx concentration change was found to be the parameter that is affecting most the normalised cost €/tone CO_2, for both MEA and MDEA solvents. This is because the NOx concentration is directly related to HSS formation as NOx react with amine to from HSS.
- The concentration of O_2 affects the oxidative degradation; hence by increasing O_2 to 10% in flue gas increases the cost of solvent reclaiming for both MEA and MDEA.
- Corrosion metals are an important parameter affecting degradation; hence when considering zero concentration of corrosion metals in the solvent, the reclaiming cost is lowered for both MEA and MDEA.

Reclaimer Sludge Characterization

The wastes generated from three evaluated reference solvents MEA, Pz and MDEA/Pz for different reclaiming technologies were characterized according to the current regulatory structures in the US and EU. This characterization was performed by evaluating the characteristics of the CO_2 capture solvent, the metals content and the nitrosamine content. Characteristics of the other minor constituents (e.g., HEIA, HEEDA, etc.) were not considered in this evaluation. The characterization was based upon the waste composition as determined by the model in the study; no real reclaimer waste was analysed for this purpose. In practice, the generated wastes need to undergo analytical testing to definitively characterize it as hazardous or non-hazardous.

US regulations:

- Thermal reclaimer wastes from coal-fired power plants may have mercury concentrations that exceed regulated limits. However, the model assumptions in this study took a conservative approach and may have overestimated mercury content in the waste. Furthermore, use of flue gas mercury controls should be capable of reducing mercury concentration in waste to levels below regulated limits.
- The reclaimer waste generated from MDEA thermal reclaiming process for the coal case shows that the waste is non-hazardous (and thus not corrosive) unless the metal concentration exceeds the toxicity characteristic leaching procedure threshold.
- Waste streams from ion exchange and electrodialysis reclaiming process were assumed to be non-corrosive due to their high (95%) water concentration and non-corrosive pH.

Table 2, Overview of reclaimer waste categorization based on EU regulations 2000/523/EC

Reclaimer waste	Waste Category	EU Waste Regulation
MEA, Pz & MDEA/Pz Thermal reclaiming Coal and NGCC w/o & w additional water	Irritant	If MEA, MDEA & Pz concentration is >10%
MEA, Pz & MDEA/Pz Thermal reclaiming Coal and NGCC	Harmful	If MEA, MDEA & Pz concentration is >25%
MEA Thermal reclaiming Coal w/o water addition; Pz & MDEA/Pz Thermal reclaiming Coal and NGCC	Toxic	If MEA, MDEA & Pz concentration is >5%
MEA, Pz & MDEA/Pz Thermal reclaiming Coal and NGCC	Corrosive	If MEA and Pz concentration is > 5%
Pz & MDEA/Pz Thermal reclaiming Coal and NGCC	Carcinogenic	Pz and MDEA/Pz will produce nitrosamine which will be >0.1%
Pz & MDEA/Pz Thermal reclaiming Coal and NGCC	Sensitizing	Pz is categorized as sensitizing (R42/43)
MEA, Pz & MDEA/Pz Thermal reclaiming Coal and NGCC	Ecotoxic	Can be Ecotoxic due to presence of metal

EU regulations:

Table 2 represents the categorization of the reclaimer waste generated by different solvents (MEA, PZ & MDEA/Pz) for different reclaiming technologies on the basis of EU regulations. It can be noticed that mainly thermal reclaiming waste from coal and NGCC case for all reference solvents falls into the category of Irritant, Harmful, Toxic, Carcinogenic, Corrosive, Ecotoxic. Whereas coal and NGCC case thermal reclaimer waste from Pz and MDEA/Pz is categorised as a sensitizer. This is because Pz is a categorized as sensitizer[1] (R42/43) and no minimum concentration of sensitizer was given to be characterized as hazardous. Hence, ion exchange and electrodialysis wastes from PZ and MDEA/PZ maybe categorized as sensitizing wastes.

For the MEA reclaimer waste to be characterized as carcinogenic there was no indication found in the safety data sheet for MEA of carcinogenicity. Substances are classified as carcinogenic when greater than 0.1%. Safety data sheet for PZ indicates no reports of carcinogenicity; however, thermal reclaimer wastes from PZ and MDEA/PZ processes will contain nitrosamines which are suspected carcinogens. Modelling work in the study predicted that these nitrosamines will be present in the thermal reclaimer wastes stream at a concentration above the threshold value of 0.1%.

---

[1] Sensitizing - A waste is considered sensitizing if it is a substance or preparation which, if it is inhaled, ingested or if it penetrates the skin, is capable of the following: Eliciting a reaction of hypersensitivity; and Such that on further exposure to the substance or preparation, characteristic adverse effects are produced.

Ion exchange and electrodialysis reclaimer waste which will contain up to 95% water were found to be not in the hazardous category. However, due to the categorization of Pz as sensitizing material these wastes may be hazardous when categorized as sensitizing wastes.

Disposal Options for Reclaimer Waste

The reclaimer waste generated from a post combustion capture process should be disposed of sustainably. Therefore, on the basis of waste categorization (non-hazardous and hazardous) the feasibility of reclaimer waste disposal options such as landfill, water incineration, cement kiln, cofiring in boiler, co-firing in NGCC HRSG, using as selective non-catalytic reduction (SNCR) reagent and power plant waste water treatment, were evaluated (see Figure 6). The following are some important information to consider for different reclaimer waste disposal options.

- Non-hazardous and Hazardous landfill will require the complete analytical data of the waste. The waste shall be in the solid form or solidified enough so that it does not threaten cap integrity. The thermal reclaiming waste from NGCC and coal fired power plants can be landfilled in the US but it does not meet the criteria to be landfill in the EU.
- Regarding the option of disposal in a cement kiln, the thermal reclaimer waste from MDEA/PZ coal case could provide up to 15% of the thermal input to the rotary kiln, while the coal-fired MEA reclaimer waste could only be used in very low quantities.
- The introduction of reclaimer waste especially with higher metal concentrations, sulphate or NaOH, would require an adjustment of the raw material to prevent influencing the resulting cement properties such as setting behaviour and strength development.

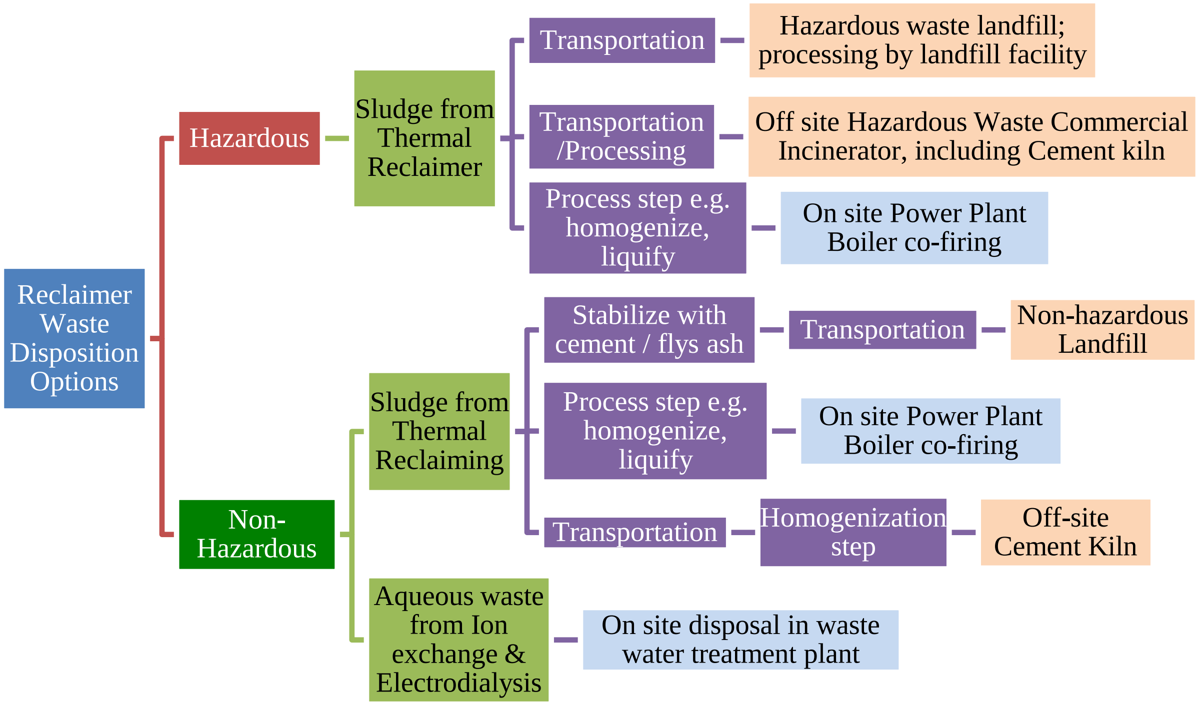


Figure 6 Disposition options for hazardous and non-hazardous reclaimer waste

- The addition of the amine sludge to a cement kiln would require additional testing to show that the kiln emissions would still comply with the applicable emission limits while using the sludge as fuel.

- When considering disposing of the reclaimer sludge in power plant boiler, the heating value is an important factor to be considered. The undiluted thermal reclaimer waste shows heating values equivalent to typical US and EU lignite coals, while the heating value of the diluted sludge is somewhat below the heating value for German lignite.
- Based on US regulation if the reclaimer waste is not classified as a legitimate fuel and it is non-hazardous, then a utility boiler co-firing the waste would be subject to Commercial and Industrial Solid Waste Incinerator regulation (CISWI), whereas when thermal reclaimer waste is considered a hazardous waste, then a boiler firing this material would be regulated as a hazardous waste combustor under 40 CFR 261.
- In EU co-firing any amount of reclaimer waste in the boiler furnace triggers the Waste Incinerator Directive (WID); and there is no minimum threshold. For hazardous wastes containing greater than 1% halogenated organic substances, the requirement is 2 seconds retention time at a temperature of 1100°C; for all other wastes the WID require to have at least a 2 seconds residence time at 850°C in the boiler.
- When co-firing in the boiler, there will be a slight increase in SO_2 and NOx concentration in the flue gas, which can be accommodated by flue gas desulfurization (FGD) and SNCR. Metal concentrations could increase as a result of reclaimer waste co-firing. Therefore, different emission control strategies shall be evaluated to determine the impact of the disposal of reclaimer waste.
- Reclaimer waste can also be used as a reagent in SNCR. This would require some additional consideration to be taken into account such as corrosion, which can occur due to the impurities present in reclaimer waste. The consistency of reclaimer waste concentration is very important for optimum performance, as well as the NOx concentration can also be increased.
- The reclaimer waste generated from ion exchange and electrodialysis are more suitable to be treated in waste water treatment plant at power plant. It would require additional units to a typical power plant wastewater treatment facility, such as an advanced oxidation system and bioreactor, in order to treat the amine present in the reclaimer waste.
- A plant-specific analysis would be required to determine if existing wastewater treatment facilities could handle the additional volume from the reclaimer waste. In the US, there are neither regulatory limits nor proposed regulatory limits specific to wastewater generated from CO_2 control technologies.

Expert reviewers' comments

In general most of the reviewers have found this study very comprehensive and an excellent resource for the industry and regulators summarising the latest information related to the environmental characterisation of major reclaimer waste pollutants. Reviewers suggested to include the model used to estimate the formation of degradation products, this has been taken into account and details of the model will be provided in the appendix. Reviewers have suggested including more information on the nitrosamine formation and counter measures to remove them. Information on nitrosamine formation from NO_2 and an estimated nitrosamine mass flow rate in reclaimer waste is included along with information on destruction of nitrosamine. One of the reviewers has emphasised that besides demonstration projects for post combustion capture processes it is also required to develop environmental standards and procedures for the post combustion capture plants.

Conclusions

This study gives an insight into the reclaimer waste generated by the conventional amine based solvents used for CO_2 post combustion capture processes, as well as characterizing the reclaimer waste based on US and EU regulation and identifying the most suitable reclaimer waste disposal options. It was noticed that for the solvents studied: monoethanolamine (MEA), piperazine (PZ), and methyldiethanolamine/piperazine (MDEA/PZ), oxidative degradation contributes more to the solvent loss than thermal degradation or volatile losses. In the NGCC cases higher formate concentration was found due to greater oxidation, but lower overall contaminant accumulation which is due to the lower concentration of SO_X and NO_X entering in the flue gas. For coal based power plants, thermal reclaiming may be the preferred option as it is the most robust solvent reclaiming method that will remove a majority of all types of degradation products and impurities from the amine solvent such as heat stable salts, high molecular weight polymeric products and transition metals. Whereas for natural gas based power plants ion exchange and electrodialysis solvent reclaiming process is more preferred as these technologies are most effective when extremely high incursion rates of heat stable salts are present.

Regarding to the reclaimer waste characterization, based on US regulation the coal-fired thermal reclaimer waste is likely to be classified as hazardous due to the presence of metals (from coal cases such as cadmium, lead, chromium, arsenic), whereas thermal reclaimer wastes from NGCC power plants do not contain metals and will not be classified as hazardous. In the EU the thermal reclaimer wastes from both the coal-fired and NGCC power plants would likely to be considered hazardous. The waste streams from the ion exchange and electrodialysis waste contain up to 95% water. In the US regulations these wastes will not be classified as hazardous, whereas in the EU due to Pz classified as sensitizing, the reclaimer waste from ion exchange and electrodialysis process for PZ and MDEA/PZ solvent may be classified as hazardous. Various reclaimer waste disposal options were investigated by looking into waste landfilling, combustion in a waste incinerator, firing in a cement kiln, firing at the power plant and handing in the waste water treatment plant. Thermal reclaimer waste has the potential to provide heating value (MDEA/Pz ~15% of total fuel heating value); hence this waste may be suitable for disposal in a cement kiln or co-firing in a power plant boiler. There will be regulation which will be required to be considered when disposing of reclaimer waste in a cement kiln or co-firing into the boiler at power plant. Moreover the impacts on emissions will also be looked into. Ion exchange and electrodialysis reclaimer waste is diluted waste hence, is most suitable to be disposed of in waste water treatment plant, which will require additional equipment to a standard power plant waste water treatment plant. Overall, it is considered that reclaimer wastes generated by different type of amine based CO_2 solvent can be disposed of sustainably.

Recommendations to Executive Committee

Based on the outcome from this study IEAGHG would like to highlight that the next step in the area of amine based solvent reclaimer waste will be to evaluate reclaimer waste from real pilot plants and based on that data identifying the most suitable disposal option. This type of work is however not part of IEAGHG main activities. Hence, IEAGHG would like to give recommendations to the researchers and engineers active in this area on some important areas for future work. During upset conditions the impurities in the solvent will be affected; hence solvent reclaiming should be evaluated under process upset conditions to identify the cost of reclaiming specifically for ion exchange and electrodialysis. There will be some nitrosamine present in the reclaimer waste; hence further work is required to reduce the nitrosamine in the reclaimer waste. This can be achieved by NO_2 and SO_2 polishing as well as by UV treatment for complete destruction of nitrosamine. Corrosion should be minimized in thermal reclaiming process by implementing cathodic protection.

It is important to develop technologies for the selective removal of impurities in order to remove transition metals together with heat stable salts. This can be achieved by implementing a combination of solvent reclaiming technology such as thermal reclaiming (for non-ionic compounds) in combination with ion exchange (for heat stable salts). IEAGHG would like to recommend that the characterization of reclaimer waste from a real plant is very important in order to determine the procedure for waste handling and identify the most suitable waste disposal options. This will also allow the plant operators to set up standards, procedures and communication required for environmental agencies.

Evaluation of Reclaimer Sludge Disposal from Post-Combustion CO_2 Capture

Prepared by
Andrew J. Sexton, Kevin S. Fisher and Anne I. Ryan
Trimeric Corporation

Paul Nielsen, Gary T. Rochelle and Eric Chen
The University of Texas at Austin

Katherine Dombrowski, Jean Youngerman, William A. Steen and Douglas Orr
URS Corporation

January 24, 2014

Prepared for:

IEA Environmental Projects Ltd.

Disclaimer: "This document contains the expression of the professional opinion of Trimeric Corporation (Trimeric), URS Corporation (URS), and the University of Texas (UT) as to the matters set out herein and it was prepared pursuant to an agreement dated November 9, 2012 between Trimeric Corporation and IEA Environmental Projects Ltd. Greenhouse Gas R&D Programme (IEAGHG) and the methodologies, assumptions and procedures stated therein. This document is written solely for the purpose stated in the agreement, and for the sole and exclusive benefit of IEAGHG, whose remedies are limited to those set out in the agreement. This document is not intended for the use of anyone other than IEAGHG, and anyone other than IEAGHG who elects to use and/or rely on this agreement, does so at its own risk."

Table of Contents

List of Figures

List of Tables

1 INTRODUCTION/BACKGROUND

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 that has to be mitigated or disposed of properly. 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 a series of reactions to form a set of fragmented degradation products; in addition, at high temperatures, 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.

Generally, a slip stream of amine is sent to a reclaiming system, where part of the solvent is reclaimed and returned to the capture process. The most commonly implemented reclaiming system involves thermal reclaiming; 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 for generated reclaimer sludge 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, per IEAGHG Report 2012-03 “Emissions of substances other than CO_2 from power plants with CCS”. Therefore it is important to identify a sustainable method for disposal of these wastes.

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 upon the composition of the waste stream. Therefore, IEAGHG has commissioned this study to evaluate the reclaimer sludge generated from various amine based solvents, and make assessments regarding sludge handling and disposal methods.

In the case of CO_2 capture for power plants and the reclamation of the solvents used, the processes are new. It is important to note that 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 disposition options.

Six major tasks are identified within the project scope specified by the IEAGHG, and they are listed below:

- Task 1: Develop CO_2 capture process reference cases
- Task 2: Identify degradation products and perform sensitivity analysis of solvent loss and formation of degradation components

- Task 3: Perform techno-economic evaluation of solvent reclaiming technology
- Task 4: Evaluate reclaimer sludge composition
- Task 5: Evaluate reclaimer sludge handling and disposal options
- Task 6: Propose future recommendations

The project team consists of Trimeric Corporation (prime contractor), URS Group Inc. and The University of Texas at Austin. Trimeric Corporation led Tasks 1 and 3, URS Group Inc. led Tasks 4 and 5, and The University of Texas led Tasks 2 and 6.

2 SUMMARY OF RESULTS

Analysis of Solvent Losses and Formation of Degradation Components

For monoethanolamine (MEA), piperazine (PZ), and methyldiethanolamine/piperazine (MDEA/PZ) CO_2 capture solvents, 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.

For a thermal reclaimer that removes all non-volatile components 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 approximately 0.5-2 wt% at steady-state conditions. This should not significantly affect solvent performance. The NGCC cases have a higher formate concentration due to greater oxidation, but lower overall contaminant accumulation due to a lower concentration of SO_X and NO_X entering in the flue gas.

Techno-Economic Evaluation of Amine Reclaiming Options

Process modeling and economic analysis were conducted for eighteen cases – three solvents of interest (MEA, MDEA/PZ and PZ) capturing CO_2 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).

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 electrodialysis 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, for the more expensive amine systems, it may be more advantageous to design a thermal reclaimer with a lower slip of amine to the waste stream.

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. Revision 2 (November 2010) of the DOE Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity lists a 30-yr average cost of electricity of 12.36 ¢/kWh (in 2012 dollars) for a supercritical coal power plant with the Fluor Economine® CO_2 capture technology, and a 30-yr average cost of electricity of 11.90 ¢/kWh (in 2010 dollars) for a NGCC power plant with the Fluor Economine® CO_2 capture technology.

Although these absolute cost of electricity numbers may be calculated 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 CO_2 capture, and only 0.3 to 0.4 percent of the total cost of electricity for natural gas plants with amine solvent CO_2 capture. These economics can also be expressed as \$0.90 to \$1.79/MT CO_2 captured (€0.67 to €1.34/ MT CO_2 captured) for the coal cases, and \$0.57 to \$1.16/MT CO_2 captured (€0.43 to €0.87/ MT CO_2 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 NO_2 in the inlet flue gas to the CO_2 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.

Sludge Composition, Handling and Disposal Options

The wastes generated from the various solvent reclaiming scenarios were characterized according to current regulatory structures in the US and EU. This characterization was performed by evaluating the characteristics of the CO_2 capture solvent, the metals content, and the nitrosamine content. Characteristics of the other minor constituents (e.g., HEIA, HEEDA, etc.) were not considered. The characterization was based upon the waste composition as determined by a model; no actual wastes were analyzed. 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 specifically listed or if it 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. No corrosivity data were available for these wastes; the wastes will have a non-corrosive pH, but they shall also meet 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. 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 TC (toxicity characteristic) 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; actual mercury concentrations in the solvent may be significantly lower. Furthermore, coal-fired power plants can reduce mercury loading to the solvent by operating flue gas mercury controls to achieve higher mercury removal upstream of the CO_2 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 electrodialysis 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 according to Annex III of Directive 2008/98/EC of 12 December 2008. 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 electrodialysis waste streams may be classified as hazardous if they are sensitizing wastes.

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 CO_2 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 presented here was based on the limited information provided from a mathematical model of the reclaimer waste stream. Waste from an operating process will need to be analyzed to definitively classify the waste and identify disposition options.

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 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 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 (for 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 a different set of 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.

Currently, most US electric generating power plants do not operate as hazardous waste incinerators.

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 reclaimer material's heating value 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 electrodialysis 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 existing 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 CO_2 control technologies. 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.

Recommendations

Although a substantial amount of information was documented within this report, several technical data gaps need to be addressed; the abbreviated recommendations list below attempts to identify these technical gaps and provide guidance in collecting information to address these gaps.

- Address technical gaps with data collected from pilot and full-scale plants
- Evaluate the feasibility of continuous ion exchange (or electrodialysis) reclaiming with batch off-site thermal reclaiming
- Perform reclaimer evaluations with vendor-leased equipment to optimize reclaimer operation
- Consider the return of spent solvent to amine supplier as a means for disposal
- Develop methods to selectively remove metals (ion exchange and electrodialysis reclaiming)
- Develop methods to minimize toxic impurities (nitrosamines in particular)
- Improve waste sludge handling (minimizing water content)
- Investigate waste characterization for unknown or non-characterized compounds, including development of a rocedure for characterization of a solvent as hazardous or not
- Develop a separate HSE program to handle toxicity evaluation of solvents, including communication with authorities on waste handling
- Address environmental standards and approval procedures with demonstration projects

3 CO_2 CAPTURE PROCESS REFERENCE CASES

The objective of Task 1 was to develop a design basis for greenfield coal and natural gas fired power plants, with the expectation of a high degree of process integration that will result in good fuel efficiency. These power plants were based upon reference plants detailed in the IEAGHG Report 2013-05 "Post Combustion CO_2 Capture Scale-Up Study", using electrical capacities in Table 3-1 of the study. The information on the reference coal and natural gas power plant is given in Appendix C.

Assuming 90% CO_2 capture for the supercritical PC and NGCC reference power plants at their respective gross power outputs (900 and 810 MW_e, respectively), required amine circulation rates were estimated from optimized lean and rich solvent loadings for each of the six reference cases; these loadings account for capital costs and energy requirements. It was assumed that CO_2 capture is 90% for all cases, and CO_2 exiting the capture plant was delivered at pipeline pressure of 11.0 MPa (1595 psia) and a temperature of 30°C (86°F). In addition, it was assumed that power produced by the reference plants are on the basis of gross output, and energy requirements from the CO_2 capture plant decreased the net power output. These power plants represent towards the upper end of the typical size ranges of modern large scale commercial power plants.

Detailed flue gas compositions are presented in the following chapter of this report. The CO_2 concentration in the flue gas for the coal-fired power plant was assumed at 11.78 volume %, and the CO_2 concentration in the flue gas for the natural gas-fired power plant was assumed at 4.09 volume %. At their respective electric power outputs and flue gas rates, assuming 90% CO_2 removal, this equates to CO_2 removal rates of 18,411 kmol/hr for the coal-fired power plant and 8,283 kmol/hr for the natural gas-fired power plant.

Figure 3-1 provides a reference diagram for an example CO_2 capture facility. Table 3-1 presents the estimated lean CO_2 loading (defined as kmol of CO_2 per kmol of total solvent alkalinity), rich CO_2 loading, and solvent circulation rates at standard conditions using 7 molal (m) monoethanolamine (MEA), 8 m piperazine (PZ) and 7 m methyldiethanolamine/2 m piperazine (MDEA/PZ) amine capture solvents for flue gas from coal-fired and natural-gas fired power plants; molality is defined as moles of solvent per kilogram of solute (water in this case). These solvent systems of interest were chosen because they are the most representative CO_2 capture systems that have the largest amount of publicly available data such that data is sufficient to make reasonable estimates of their performance in CO_2 capture and reclaiming systems.

Table 3-1 Amine Circulation Rates for CO_2 Capture from Coal and Natural Gas Combustion Flue Gases

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	Coal	0.12	0.51	10,719
	Natural Gas	0.12	0.49	5,083
PZ	Coal	0.31	0.41	21,641
	Natural Gas	0.28	0.37	10,818
MDEA/PZ	Coal	0.11	0.25	26,707
	Natural Gas	0.11	0.25	12,105

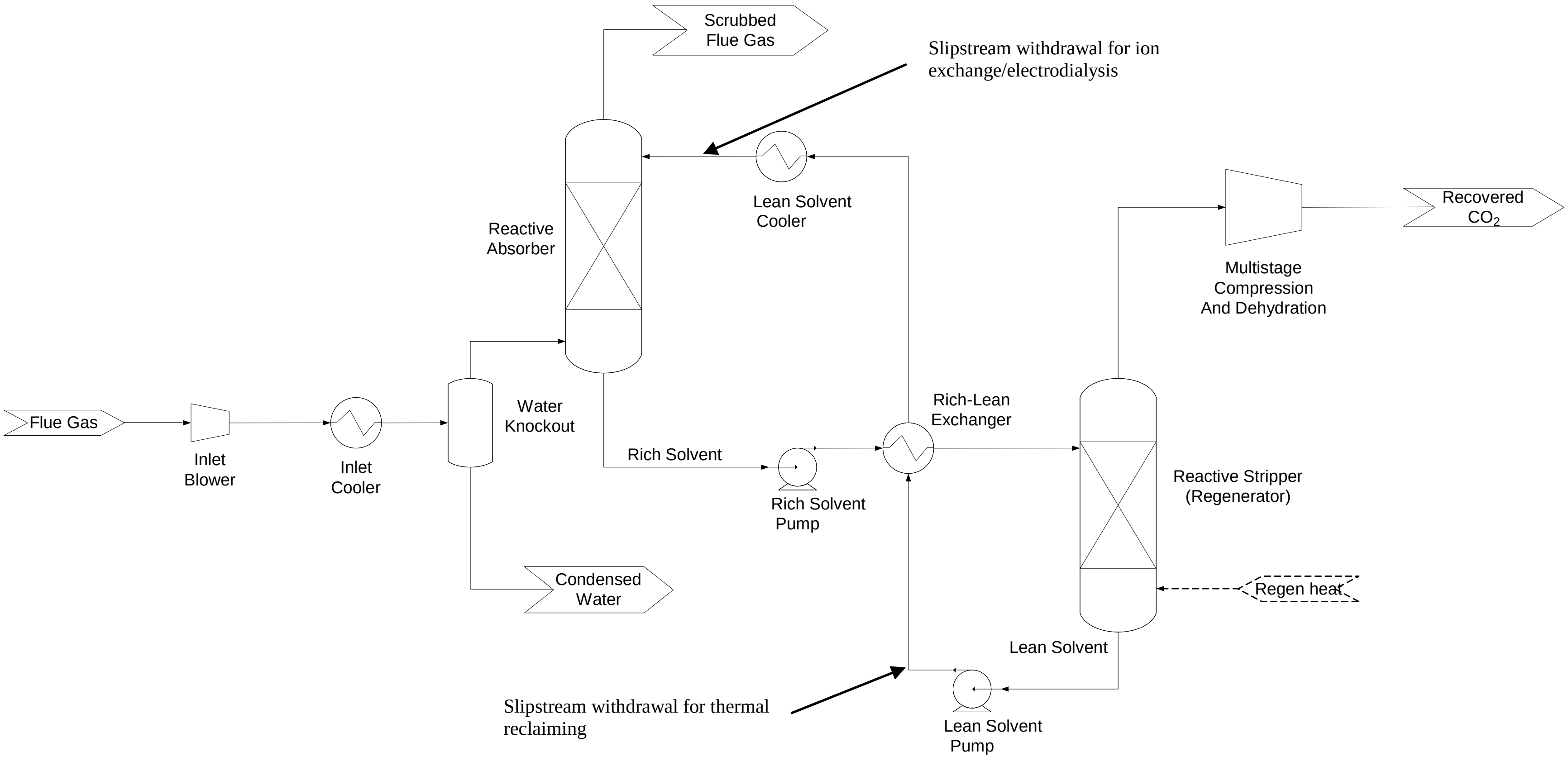


Figure 3-1 Example CO_2 Capture Process Flow Diagram.

4 IDENTIFICATION AND SENSITIVITY ANALYSIS OF SOLVENT LOSS AND FORMATION OF DEGRADATION COMPONENTS

4.1 Introduction

In order to estimate the flow rate and composition of the streams entering and exiting the reclaimer unit, the rate of solvent degradation and accumulation of flue gas contaminants within the circulating amine solvent was first determined. Figure 4-1 shows a typical process flow diagram (PFD) for the amine scrubbing process with thermal reclaiming. Flue gas enters the absorber and is contacted with the amine solvent which absorbs the CO_2 as well as SO_X, NO_2, and fly ash contaminants and a small proportion of the O_2 present in the flue gas. A water wash is employed to limit volatile amine emissions with the treated flue gas leaving the absorber. The solvent is cycled through a cross-exchanger to a stripper and reboiler to strip off the CO_2 for compression. The condensate produced by the stripper and compressor can be recycled back to the stripper or used as feed for the water wash in order to maintain a water balance around the system. The PFD also illustrates a thermal reclaimer, which heats a slipstream of lean amine from the stripper to flash off the amine, leaving nonvolatile contaminants in the reclaimer sludge. Alternatively, an ion exchange membrane or electrodialysis could be employed to remove polar contaminants.

Amine solvent loss can occur by thermal degradation of the solvent in the stripper, oxidation of the solvent in the absorber and cross exchanger, reaction of the amine with flue gas contaminants such as NO_2 to form the nitrosamine, loss of amine due to volatility and aerosol, and additional loss due to imperfect separation in the reclaimer. The buildup of degradation products and flue gas contaminants over time can impact solvent performance, reducing absorption rate and increasing solvent viscosity, toxicity, and corrosivity. This can be mitigated by using a solvent that is more resistant to degradation, such as piperazine (PZ) or methyldiethanolamine (MDEA), and by employing a reclaimer unit to remove the buildup of contaminants in the solvent. Operational strategies to keep the water inventory at a constant level in order to maintain a relatively constant concentration of amine and degradation products is not addressed in this study.

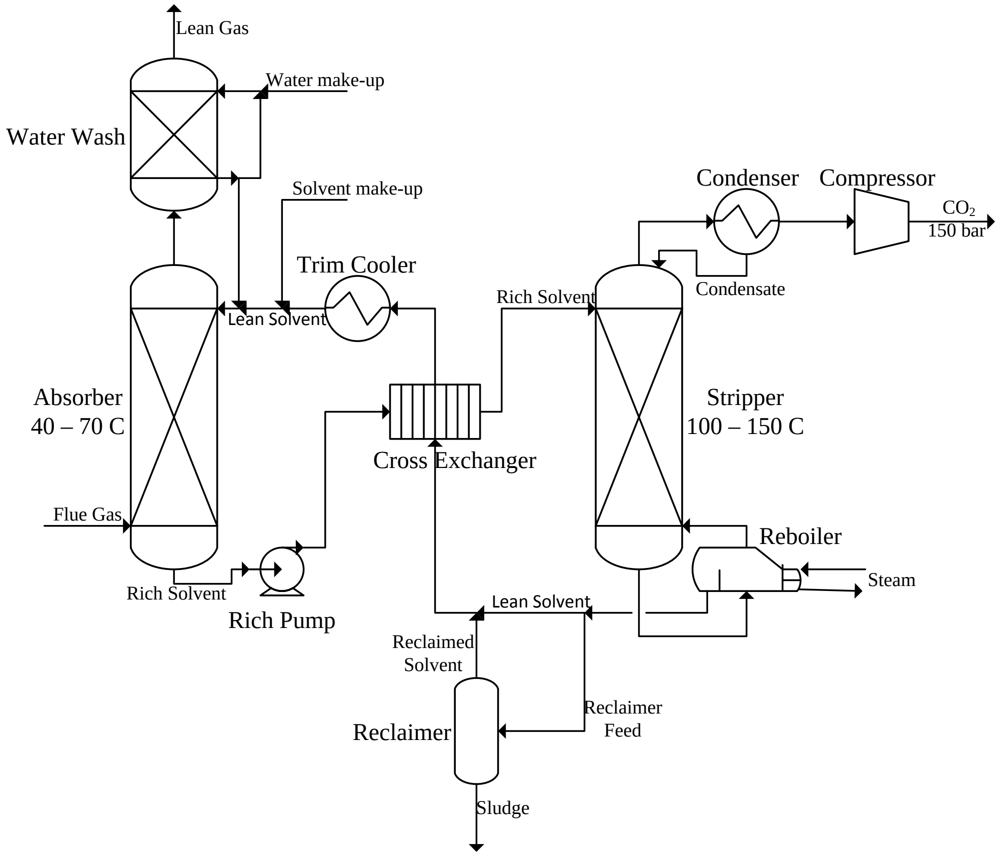


Figure 4-1 Example Amine Scrubbing Process Flow Diagram with Thermal Reclaiming

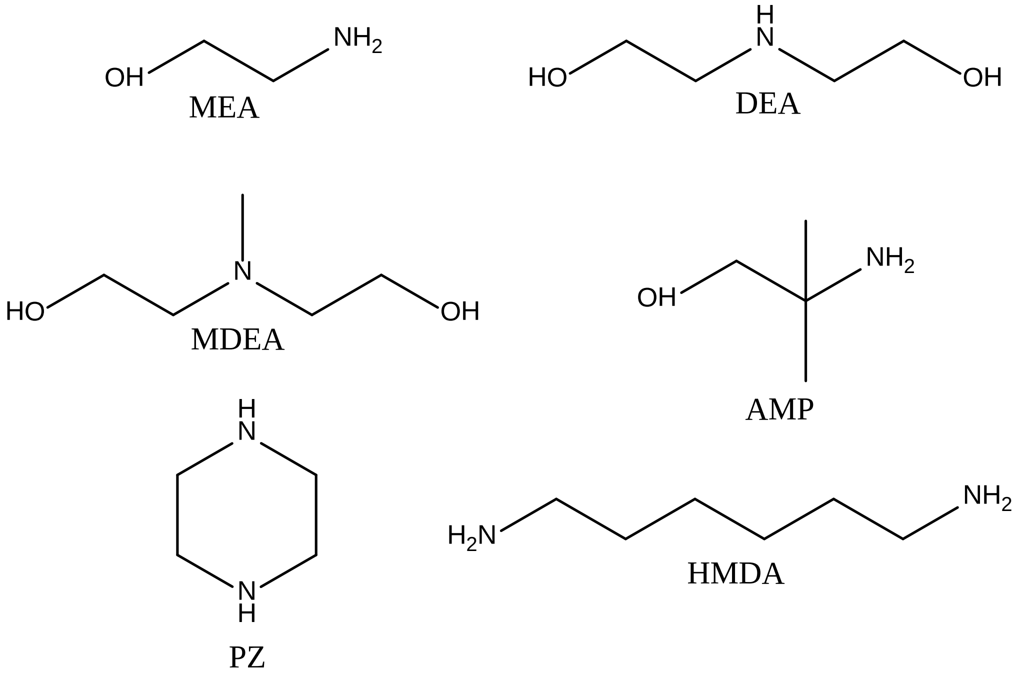


Figure 4-2 Select amine solvents for carbon capture: Monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino-2-methyl-propanol (AMP), piperazine (PZ), hexamethyldiamine (HMDA)

For three solvent systems (Figure 4-2) of interest (7 molal (m) MEA, 8 m PZ, and 7/2 m MDEA/PZ), a spreadsheet degradation model was created to model solvent loss and degradation product accumulation expected in a commercial CO_2 capture process.

The solvent loss model includes the following mechanisms:

1. Thermal degradation
2. Oxidative degradation
3. Nitrosamine formation from NO_2
4. Degradation product and flue gas contaminant accumulation
5. Volatile amine losses
6. Reclaimer losses

These 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.

Typical flue gas conditions used in this study for the coal and natural gas cases are shown in Table 4-1. Flue gas from NGCC combustion will be more dilute in CO_2 with higher oxygen content than flue gas from coal combustion due to the need for significant excess air to operate the gas turbine.

Table 4-1 Coal and Natural Gas Conditions

Parameters	Coal	NGCC
Gross power output (MW)	900.1	809.9
Flue gas flow rate (Nm^3/hr)	$3.89*10^6$	$5.04*10^6$
T (°C)	54	109
P (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 (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

4.2 Thermal Degradation

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 CO_2 vapor stream leaving the stripper increases, reducing work required for compression and lowering overall energy costs of the system. Davis determined that the optimized stripper temperature to balance energy requirements and amine loss is around 121°C for MEA [1]. The first order thermal degradation rate constant for MEA at this temperature is $2.9x10^{-8}$ s^{-1}. For comparison, the stripper operating temperature resulting in an equivalent thermal degradation rate constant is 163°C for 8 m PZ and 138°C for 7/2 m MDEA/PZ. Values for these and other solvents are shown in Table 4-2, with the stripper operating temperature labeled as T_{max}; T_{max} is estimated as a function of the thermal stability of the solvent. The activation energy (E_a) of MEA, PZ, and AMP are also shown. Other solvents have activation energies similar to either MEA or PZ, as listed in the table. The thermal degradation rates and activation energies of the solvents were determined by heating loaded solvent in sealed thermal cylinders at varying temperatures over a period of weeks to months [2].

In order to operate at regeneration temperatures greater than 150°C, more costly, higher quality steam will probably be required. The base case stripper operating temperatures were set at 120°C for MEA, 135°C for MDEA/PZ, and 150°C for PZ.

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 spreadsheet model calculates the amine loss rate in the sump of the stripper as well as in the packing, with the packing temperature accounting for the hot-side approach temperature of the cross exchanger and the temperature drop on 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 operating temperature.

Table 4-2 Optimal Stripper Operating Temperature for Amine Solvents ($k_1 = 2.9 \times 10^{-8}\ s^{-1}$) [2]

Solvent	Rich Loading (mol CO_2/mol alk.)[a]	T_{max} (°C)[b]	E_a kJ/mol[c]
8 m PZ	0.3	163 °C	184
8 m Hexamethyldiamine (HMDA)	0.3	160 °C	(~PZ)[d]
7/2 m MDEA/PZ	0.11	138 °C	(~PZ)
7 m 2-amino-2-methyl-propanol (AMP)	0.4	137 °C	112
4/6 m AMP/PZ	0.4	134 °C	(~PZ)
7 m MDEA	0.2	128 °C	(~MEA)
7 m MEA	0.4	121 °C	157
4 m Diethanolamine (DEA)	0.5	105 °C	(~MEA)[e]
Aqueous ammonia	Thermally stable		

[a] Loading is defined as total moles of CO_2 per mole of total alkalinity. MEA and MDEA have one mole of total alkalinity per mole of amine, while PZ has two moles of total alkalinity per mole of amine.
[b] T_{max} is stripper maximum operating temperature based on thermal degradation.
[c] E_a is activation energy.
[d] "~PZ" denotes equal to concentrated PZ
[e] "~MEA" denotes equal to MEA

4.2.1 Thermal Degradation Pathways and Products

MEA thermal degradation occurs by carbamate polymerization, as shown in Figure 4-3. Hydroxyethylimidazolidone (HEIA) and the cyclic urea of the trimer (triHEIA) will accumulate in significant amounts at a rate related to MEA loss. Hydroxyethylethylenediamine (HEEDA) and the trimer intermediates will also be observed in significant amounts, and will typically reach equilibrium with HEIA and triHEIA determined by the CO_2 loading of the solvent [1].

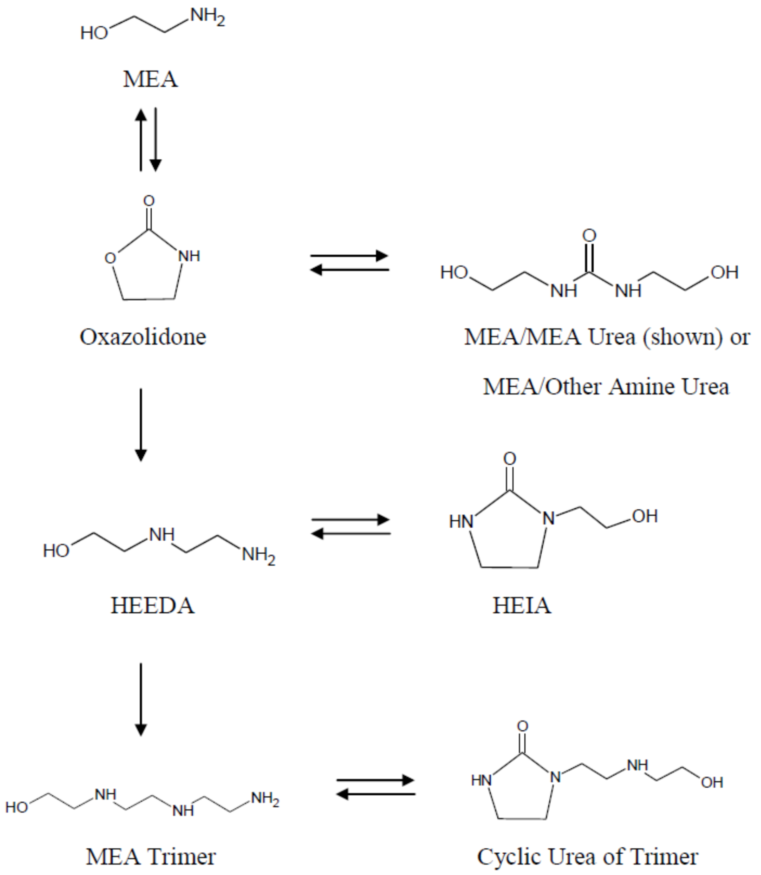


Figure 4-3 MEA Thermal Degradation Pathway [1]

PZ follows a different thermal degradation pathway. Typically, a PZ molecule will attack another protonated PZ molecule in an S_N2 nucleophilic substitution reaction, forming the compound AEAEPZ (Figure 4-4). AEAEPZ then reacts with PZ to form either N-aminoethyl-PZ (AEP) or ethylenediamine (EDA) and PEP (Figure 4-5), which can then decompose to form N-hydroxyethyl-PZ (HEP) (Figure 4-6). Formate and its constituent amide N-formyl-PZ are also produced [2].

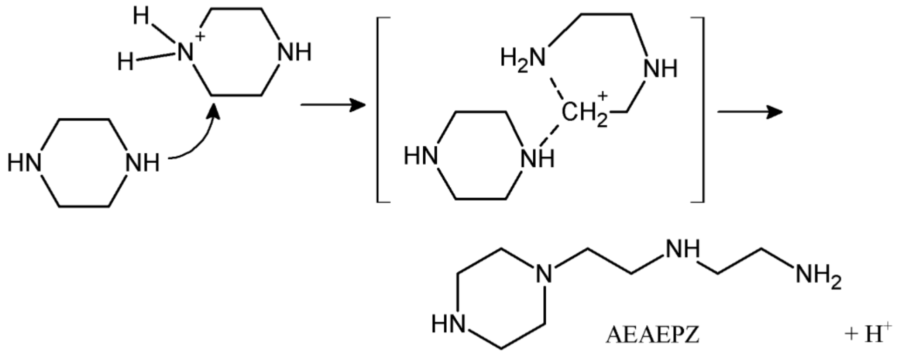


Figure 4-4 S_N2 Thermal Degradation Pathway for PZ to Produce AEAEPZ [2]

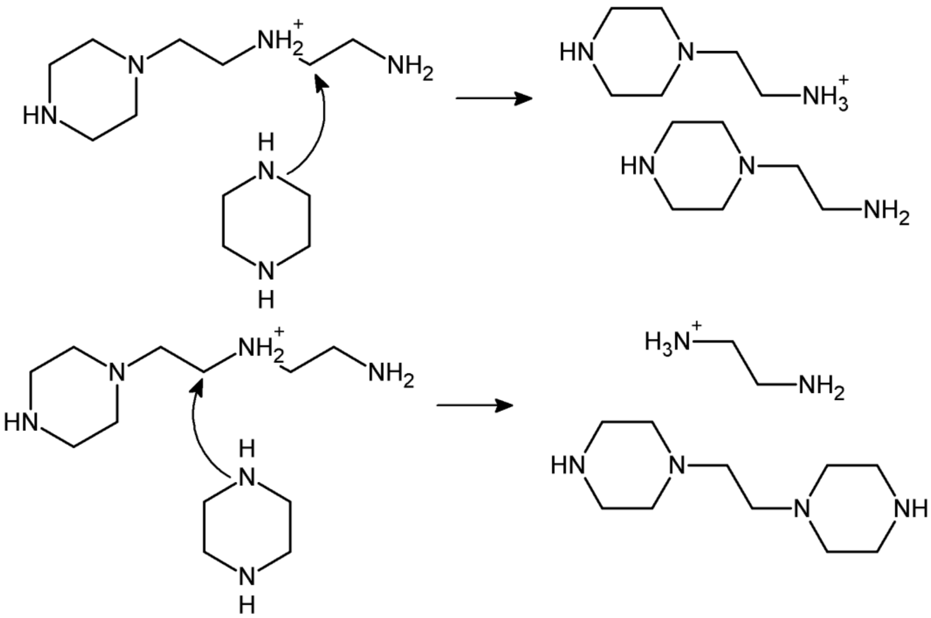


Figure 4-5 Formation of AEP, EDA, and PEP from AEAEPZ [2]

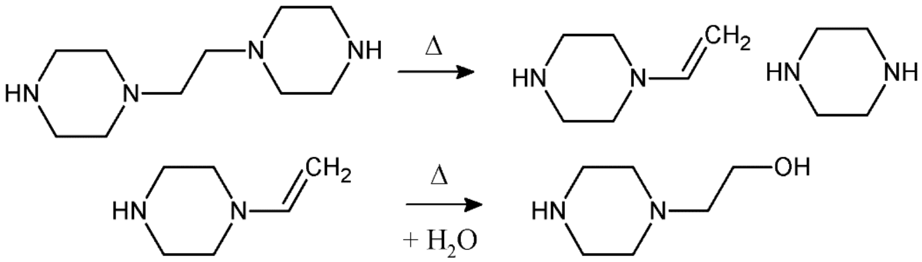


Figure 4-6 Formation of HEP from PEP [2]

MDEA/PZ degrades thermally at a higher rate than either MDEA or PZ alone due to the synergistic effects of the two components reacting with each other. A proposed S_N2 pathway for thermal decomposition is given below in Figure 4-7. A protonated PZ attacks the alpha carbon of MDEA, producing either 1-methyl-PZ (1-MPZ) and diethanolamine (DEA) or HEP and N-methyl-aminoethanol (MAE) depending on which arm of MDEA is attacked by PZ. DEA and MAE will likely undergo carbamate polymerization in the stripper sump, similar to MEA [22].

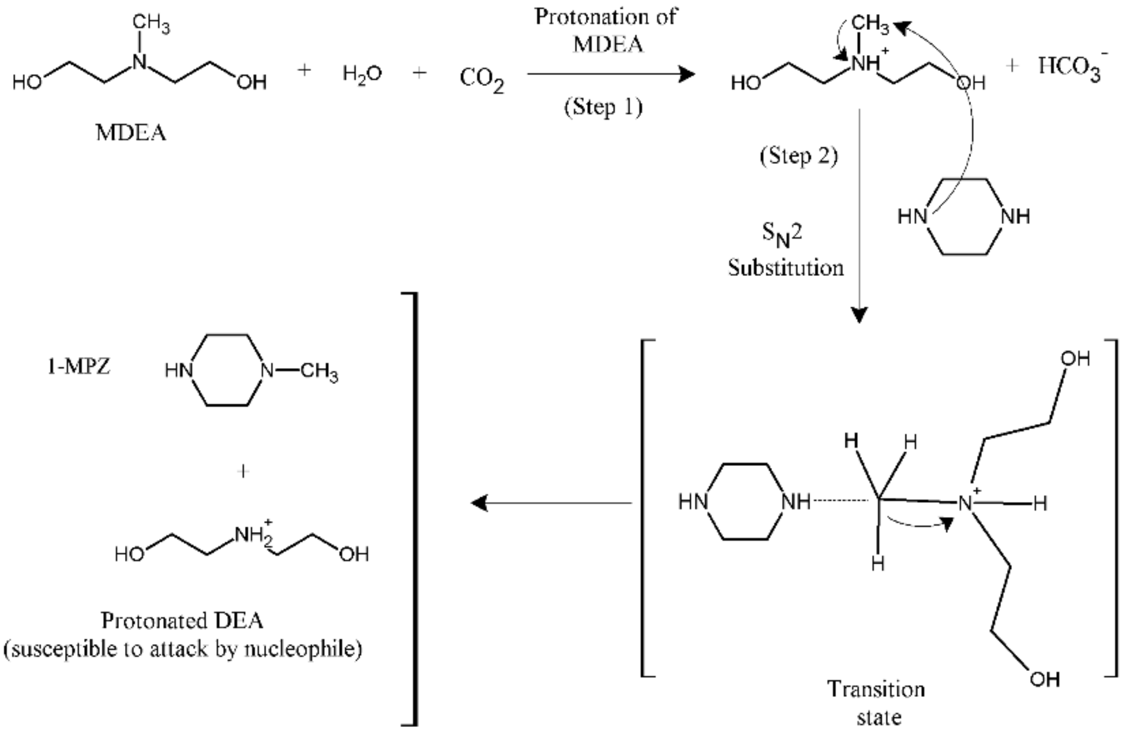


Figure 4-7 Thermal Degradation of 7/2 m MDEA/PZ [22]

Table 4-3 shows the major products quantified in bench-scale thermal degradation experiments, including a rough estimate of the amount produced of each product in moles per mole of amine degraded. For MEA thermal degradation, the HEEDA dimer and the MEA trimer are in equilibrium with HEIA and triHEIA respectively, determined by the CO_2 lean loading. The values from this table were used in the solvent loss models to estimate formation rates of these products as a function of thermal degradation rate.

Table 4-3 Stoichiometry of Products Produced per Mole of Amine Degraded

Product	Mole produced/mole amine lost
MEA [1]	
HEIA	0.2
triHEIA	0.05
HEEDA	in equilibrium w/ HEIA
MEA trimer	in equilibrium w/ triHEIA
PZ [2]	
Ammonium	0.29
EDA	0.03
2-Imidazolidone	0.06
Formate	0.06
N-Formyl-PZ (FPZ)	0.32
Total formate	0.39
Total acetate	0.02
AEP	0.07
HEP	0.04
N-Ethyl-PZ	0.03
Other nonvolatile amines	0.26
MDEA/PZ [22]	
Total formate	0.01
1-MPZ + 1,4-dimethyl-PZ	0.18
DEA + MAE	0.64
AEP	0.01

4.3 Oxidation

Early studies with MEA showed that it is very susceptible to oxidation at absorber conditions [3] and that amines react with oxygen to form hydroperoxides, which decompose in the presence of transition metals to produce free radicals [4]. MEA oxidation was shown to be catalyzed by transition metal ions and ammonia was observed as a major product [5,6]. Other observed oxidation products of MEA include heat stable salts [7], hydroxyethyl formamide (HEF), hydroxyethyl imidazole [8], hydroxyethyl glycine [9], and cyclic aldehydes [10]. Radical initiation by a ferric ion electron abstraction mechanism was proposed by Chi as the main pathway for MEA oxidation [11]. Table 4-4 lists the transition metal ions that have been tested at absorber conditions and their effectiveness as oxidation catalysts of MEA.

Table 4-4 Role of Transition Metals in MEA Oxidation [10]

Transition Metal	Role in MEA oxidation	Source
Iron	Catalyst	[12,13]
Copper	Catalyst	[6]
Manganese	Catalyst	[10]
Vanadium	No effect	[10]
Nickel	No effect	[10]
Molybdenum	No effect	[10]
Chromium	Catalyst	[10]
Cobalt	Catalyst	[10]
Tin	No effect	[10]

More recent studies have shown that most previous experimental setups were hindered by oxygen mass transfer limitations. However, oxidation in a real flue gas absorber is expected to be kinetically limited, and not mass transfer limited, due to the high contact area and turbulence in the absorber packing [14]. It has also been shown that cycling the solvent between an oxidation reactor at absorber conditions and a thermal reactor at stripper conditions increases the rate of oxidation due to either the carry-over of dissolved oxygen through the cross-exchanger into the high temperature stripper or possibly the cycling of oxidants such as dissolved metal ions and free radicals. This effect had not been previously observed in bench-scale experiments conducted at absorber conditions [10]. Results of pilot plant analyses show that oxidation will dominate over thermal degradation as a source of amine loss [9,15,16,18].

Other amines have been screened as potential replacements for MEA. At absorber conditions, diethanolamine (DEA) has been shown to oxidize at a similar rate to MEA. Hexamethyldiamine (HMDA) and aminoethylpiperazine (AEP) were also observed to oxidize, but at slower rates than MEA. Tertiary amines (MDEA), hindered amines (AMP), and cyclic amines (PZ) were all shown to be very resistant to oxidation at absorber conditions. Tertiary amines typically do not produce any ammonia as a degradation product. Piperazine and 1- and 2-methyl-piperazine were also observed to be resistant to oxidation, but oxidation and ammonia production could be catalyzed by the addition of iron or copper ions. Table 4-5 shows the results of amine oxidation screening at absorber conditions, with solvents ranked by relative resistance to oxidation.

Table 4-5 Screening Results of Solvent Oxidation at Absorber Conditions [10]

Solvent	Oxidizes in absorber?	Source
Glycine (Gly)	Yes, similar to MEA	[10]
MEA	Yes	[3]
DEA	Yes, similar to MEA	[8]
HMDA	Yes, less than MEA	[10]
Sarcosine (Sarc)	Yes, less than MEA	[10]
Aminoethylpiperazine (AEP)	Yes, less than MEA	[10]
AMP	Resistant, little NH_3 produced	[3,10]
All tertiary amines (MDEA)	Resistant, no NH_3 produced	[3]
PZ	Resistant, NH_3 produced with Fe, Cu	[2]
1-Methyl-PZ and 2-Methyl-PZ	Resistant, no NH_3 produced	[10]
Proline	Resistant, no NH_3 produced	[10]

The amino acids glycine (Gly), sarcosine (Sarc), and proline (Pro) have also been screened as potential MEA alternatives (Figure 4-8). Glycine has been shown to oxidize at absorber conditions at an equal or greater rate than MEA [10,21]. Sarcosine has been shown to be less susceptible to oxidation than MEA, but not fully resistant at absorber conditions. It will produce methylamine rather than ammonia when it oxidizes [10]. Proline has been shown to be the most resistant amino acid to oxidation, most likely due to its stable ring structure. It does not produce any observable volatile degradation products and only degrades in the presence of copper [10]. Sarcosine and proline are both secondary amines and will most likely form stable nitrosamines in the presence of NO_2.

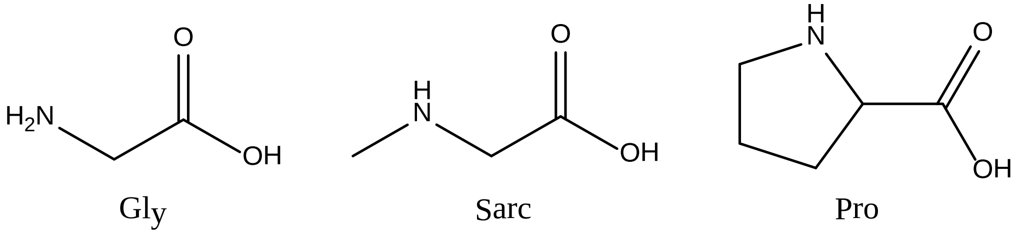


Figure 4-8 Glycine (Gly), Sarcosine (Sar), and Proline (Pro)

Recent progress in determining the details of amine oxidation has been made using the "Integrated Solvent Degradation Apparatus" (ISDA) and the "High Temperature Cycling System" (HTCS) [10,22]. These two cycling apparatuses mix the CO_2 capture solvent with air or oxygen in a low temperature oxidation reactor, then cycle the solvent to high temperature to simulate the temperature profile seen in an actual amine scrubbing process. Table 4-6 shows basic specifications for these two apparatuses. The HTCS uses an air-CO_2 mixture in a sparged high gas flow oxidative reactor while the ISDA uses an oxygen-CO_2 mixture in a stirred low gas flow oxidative reactor. The HTCS is also designed with a higher maximum operating temperature and an FTIR to measure the generation of volatile products such as ammonia and aldehydes. This gives the HTCS a more complete picture of solvent oxidation than the older ISDA apparatus.

Based on data gathered from these apparatuses, it has been shown that the amine oxidation rate is a strong function of temperature in the heated (regeneration) section of the capture process. The oxidation rate continues to rise above the point where all dissolved oxygen (DO) has been consumed due to the presence of organic peroxides and metal ion radicals acting as oxygen carriers. Solvent loss rates as well as formate and ammonia generation rates measured in the ISDA and HTCS are shown in Table 4-7 and Table 4-8 [10].

Transition metals, such as iron, manganese, and copper that accumulate in the solvent due to corrosion and flue gas contamination, are known to catalyze oxidation. In the absorber, oxygen dissolves into the solvent and can react at higher temperatures with amine in a metal-catalyzed radical reaction mechanism to form a hydroperoxide, which will then decompose to produce ammonia and formate. A synthetic mix of dissolved stainless steel metal ions (typically 0.4 mM Fe^{2+}, 0.1 mM Ni^{2+}, 0.1 mM Mn^{2+}, 0.05 mM Cr^{3+}) was added to all cycling apparatus experiments to replicate corrosion observed in pilot plant campaigns [17].

The spreadsheet solvent loss models use an oxidation rate constant calculated from experimental data collected in the HTCS and the ISDA. Oxidation rates and activation energies for 7 m MEA and 8 m PZ were taken from data collected in the HTCS apparatus (Table 4-8), while the oxidation rate and activation energy of 7/2 m MDEA/PZ was calculated from experiments conducted in the older ISDA apparatus (Table 4-7). Oxidation is assumed to be first-order with respect to the amine and oxygen content of the flue gas, and will occur chiefly in the heated section of the rich side of the cross exchanger and in the pipe downstream before entering the stripper. The residence time in this section is assumed to be on the order of 30 seconds in a typical amine scrubbing process. A 5°C hot-side approach temperature is assumed for the cross-exchanger. Therefore the maximum temperature reached in this section will be 5°C less than the operating temperature of the stripper sump. After the solvent enters the packed section of the stripper, any remaining DO will flash off, which will significantly slow the rate of solvent oxidation. Based on the observations from previous pilot plant campaigns [17], the base case for this study assumes a high metals content due to corrosion resulting in catalyzed oxidation rates similar to those observed in the ISDA and HTCS.

Table 4-6 Comparison of Solvent Cycling Apparatuses

Parameters	ISDA	HTCS
Total volume (L)	2	1.5
Oxidative reactor (L)	0.35	0.35
High temperature volume (L)	0.13	0.2
Solvent circulation rate (L/min)	0.2	0.2
Gas flow rate (L/min)	0.1	7.65
O_2 Partial Pressure in Flue Gas (bar)	0.98	0.2

Table 4-7 Solvent Oxidation Rates in the ISDA (55 – 120°C, 0.98 bar O_2) [10]

Solvents	Amine loss rate (mmol amine/kg solvent/hr)	Formate formation rate (mmol formate/kg solvent/hr)
4.8 m AMP	1.8 ± 0.32	0.022
8 m PZ	1.97 ± 0.18	0.223
7 m MDEA	5.1 ± 0.72	0.543
7/2 m MDEA/PZ	5 ± 0.4	0.907
7 m MEA	5.5 ± 0.34	0.702

Table 4-8 Solvent Oxidation Rates in the HTCS (0.2 bar O_2) [10]

Solvents	Ammonia formation rate (mmol NH_3/kg solvent/hr)	Amine loss rate (mmol amine/kg solvent/hr)	E_a (kJ/mol amine)	Ammonia formation rate @ 120 °C (mmol NH_3/kg solvent/hr)
4.8 m AMP (55 – 150°C)	1.16	10.7	110	0.15
4/4 m PZ/2-MPZ (40 – 150°C)	1.59	1.5	30	0.6
8 m PZ **(40 – 160°C)**	1.86	1.3	32	0.68
7 m MDEA (55 – 120°C)	0	1.3	N/A	0
7/3.4 m MEA/MDEA (55 – 120°C)	3.55	5.24/1.98	19	3.59
7 m MEA **(55 – 120°C)**	4.2	4.68	32	4.32

4.3.1 Oxidative Degradation Pathways and Products

Amine oxidation typically results in the production of ammonia and formate through a radical reaction pathway, with organic peroxides and aldehydes as intermediary products (Figure 4-9). Primary and secondary amines (MEA and PZ) typically produce 0.5 to 1 mole of ammonia per mole of amine loss. MDEA does not decompose into ammonia, but some ammonia will still be produced by PZ in the MDEA/PZ blend. Most amines will also produce 0.1 to 0.15 moles of formate per mole amine loss and smaller amounts of other heat stable salts, including oxalate, acetate, and glycolate. These salts will be in equilibrium with their constituent amides. There will also typically be smaller amounts of oxalate, and trace amounts of nitrate and nitrite produced. Oxidation will also produce some smaller amine fragments and imidazoles, such as hydroxyethylimdazole (HEI) from MEA and EDA from PZ. N-(2-hydroxyethyl)-glycine (HEGly) and 4-(2-hydroxyethyl)-piperazin-2-one (HEPO) have also been observed in significant quantities in MEA pilot plant studies [27]. The amino acid bicine has also been observed in oxidized MDEA/PZ [10].

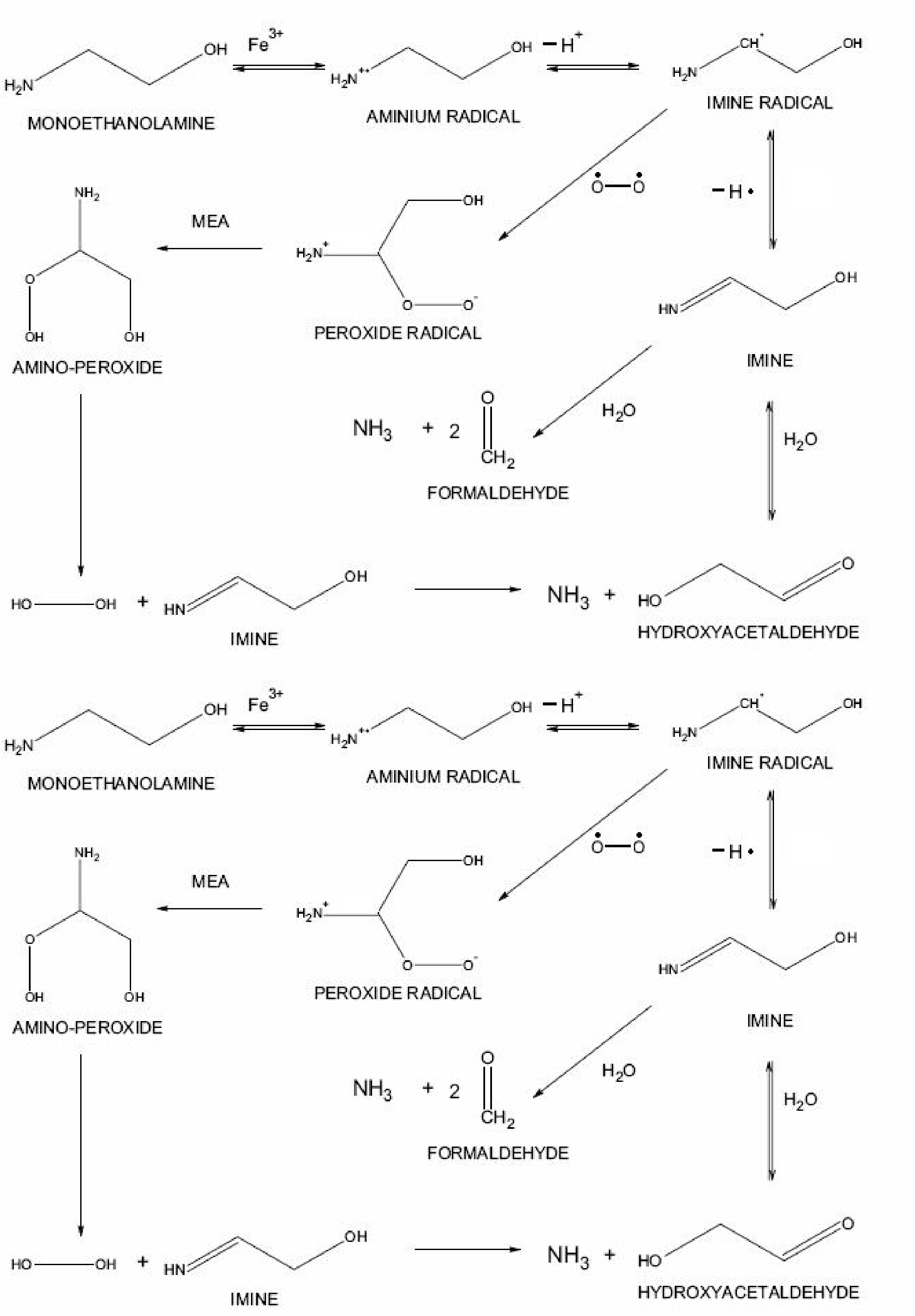


Figure 4-9 Electron Abstraction Mechanism for MEA Oxidative Degradation [11]

Table 4-9 shows the major products quantified in bench-scale cycling oxidation experiments, including a rough estimate of the amount produced of each product in moles per mole of amine degraded. The values from this table were used in the solvent loss models to estimate formation rates of these products as a function of oxidation rate.

Table 4-9 Stoichiometry of Products Produced per Mole of Amine Degraded [24]

Product	Mole produced/mole amine lost
MEA	
Ammonia	0.67
Total formate + HEF	0.12
Oxalate + oxylamide	0.01
Nitrate	0.01
Nitrite	0.002
HEI	0.06
HEGly [28]	0.05
PZ	
Ammonia	1.0
Formate + FPZ	0.11
EDA + 2-imidazolidone	0.17
Oxalate + Acetate	0.03
MNPZ (from oxidation of amine)	0.005
MDEA/PZ	
Ammonia	0.22
Total formate	0.12
Total oxalate	0.01
1-MPZ	0.27
DEA + MAE	0.39
Bicine	0.05

4.4 Nitrosamine Formation from NO_2

NO_2 will be absorbed from 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, which will be a function of the stripper temperature and the flue gas NO_2 content as described in the following equations [23]. $MNPZ_{ss}$ is the steady-state concentration of the nitrosamine in the solvent in mmol/kg, $MNPZ_i$ is the initial value, MNPZ(t) is the current value for transient calculations, $y_{NO2,Flue}$ is the concentration of NO_2 in the entering flue gas in ppmv, k_d is the thermal degradation rate constant for MNPZ (determined by the stripper temperature) in s^{-1}, τ_{sump} is the residence time of the solvent in the stripper in seconds, V_{sump}/V_{total} is the ratio of solvent holdup in the stripper sump to the total solvent inventory, and G/L is the ratio of the flue gas flow rate in kmol/s to the solvent flow rate in kg/s.

$$MNPZ_{ss} = \frac{y_{NO2,Flue}}{k_d \tau_{sump}} * \frac{G}{L}$$

$$\frac{MNPZ(t) - MNPZ_i}{MNPZ_{ss} - MNPZ_i} = 1 - e^{-k_d \frac{V_{sump}}{V_{total}} t}$$

MNPZ decomposes into 2-piperazinol, which will eventually decompose into formate and ammonia, similar to PZ. As the temperature and holdup of the stripper is increased, the degradation rate of MNPZ increases, reducing the steady-state concentration in the solvent.

Pure MEA and MDEA will not form stable nitrosamines. However, secondary amines present in degraded solvent will react to form nitrosamines. In the case of MEA, N-hydroxyethyl-glycine (HEGly) and diethanolamine (DEA) are expected to be the most concentrated secondary amines, forming N-nitroso-HEGly and N-nitroso-diethanolamine (NDELA) respectively [27,28]. The formation of nitramines was not considered in this study.

4.5 Flue Gas Contaminants

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 fluoride, chloride, and fly ash. Table 4-10 shows a typical flue gas concentration range for major fuel contaminants, as well as the base case values used for the coal and NGCC base cases in this study; these values were chosen after reviewing data gathered by the United States Environmental Protection Agency (US EPA) in its 2010 Information Collection Request from coal-fired power generating units with similar pollution controls. The table shows the typical range of contaminants in coal flue gas (min – max) as well as the median values chosen for the coal and natural gas base cases. It was assumed that SO_2, NO_2, HCl, and HF will be absorbed by the amine solvent to some extent and subsequently form heat stable salts. However, SO_3 and other NO_X compounds present in the flue gas will not be absorbed as readily.

Table 4-10 Contaminant Concentrations in Flue Gas Entering the Absorber and Estimated Removal by Amine Scrubbing (dry, 3% O2)

Contaminant (wet basis)	Coal typical range	Coal base case	NGCC base case	% Removal from gas
SO_X (ppmv)	11 – 20	15	0.5	
SO_3 (ppmv)	10	10	0	0%
SO_2 (ppmv)	1 – 10	5	0.5	90%
NO_X (ppmv)	20 – 110	46.5	15.5	
NO_2 (ppmv)	1 – 5.5	1.5	0.5	100%
NO_X (ppmv)	19 – 104.5	45	15	10%
HCl (ppmv)	0.2 – 1.85	1.85	0	90%
HF (ppmv)	0.075	0.075	0	90%
Fly ash (mg/Nm^3)	1.5 – 45	6	0	50%
Hg (µg/Nm^3)	0.135 – 6	1.8	0	50%
Se (µg/Nm^3)	0.3 – 30	2.3	0	50%
Other metals (µg/Nm^3)	3 – 150	5.5	0	50%

NO_2 will be absorbed as nitrite, which will then react with PZ and other secondary amines to form nitrosamines. Sulfate, nitrate, chloride, and fluoride will be stable and nonvolatile, similar to the other heat stable salts formed by degradation. The other contaminants should not accumulate to a level where solvent performance is affected. However, mercury, selenium, arsenic, and other toxic components of the fly ash could potentially pose a health risk and result in the solvent or reclaimer waste being treated as a hazardous waste.

NO absorption as nitrate has conservatively been estimated at 10% removal from flue gas. NO is relatively inert and not readily absorbed by amines. However, nitrate accumulation has been observed in pilot plants operating with post combustion coal flue gas at up to the same order of magnitude as sulfate accumulation. Nitrate is a minor oxidation product, but the accumulation rates observed in these pilot plant studies are much higher than what would be predicted by solvent oxidation and show no dependence on operating temperatures. Thus nitrate is more likely to be from flue gas contamination than oxidation. The NO removal rate was specifically to give a nitrate accumulation rate similar to the sulfate accumulation rate. It has yet to be conclusively determined whether nitrate is a result of NO absorption or NO_2 absorption.

The absorption into the solvent of transition metals via leaching of fly ash or absorption of gaseous mercury has been conservatively estimated at 50% removal from the flue gas into the liquid. This is a conservative estimate meant to illustrate a worst-case scenario.

4.6 **Amine Loss Due to Volatility**

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 is assumed that a water wash will be employed to limit emissions. The water wash column treats the flue gas stream leaving the absorber, removing amine and other volatile contaminants by absorption into an aqueous phase, which is returned to the solvent. The model includes a calculation of amine loss as a function of the design specification of the water wash and a calculation 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 will be on the order of 2 to 5 ppmv (this is the estimated ammonia concentration before the water wash; it is expected that concentrations after the water wash will be significantly lower). An acid wash can also be employed to further reduce amine and ammonia emissions if necessary; acid-mist related emissions are not included in the model.

4.7 **Additional Loss of Solvent in the Reclaiming Process**

In addition to the other causes of amine loss, some additional amine will be lost in the reclaiming process with the waste streams. Perfect separation of the amine from the contaminants is thermodynamically unrealistic. Thermal reclaiming is likely to recover 85 to 95% of the amine in the feed, with some loss due to additional thermal degradation. Electrodialysis and ion exchange should be able to achieve a recovery closer to 98 to 99%, but will not remove non-polar contaminants [29].

4.8 **Base Case Model Results for Amine Loss**

It may be advantageous to remove the remaining NO_2 upstream of the capture unit to avoid the solvent replacement costs. Table 4-11 shows the required solvent make-up costs for the six base cases in \$/metric tonne of CO_2 removed, broken down by causes of solvent loss, as calculated by the spreadsheet models. Solvent prices were assumed to be \$1.92/kg for pure concentrated MEA, \$2.43/kg for MDEA, and \$5.00/kg for PZ. All cases assume 30 minutes of total residence time in the system to determine solvent inventory, 10 minutes residence time in the stripper (5 minutes in the sump, 5 minutes in the packing), and 30 seconds residence time in for high-temperature oxidation before the stripper. The flue gas leaving the water wash is assumed to have a maximum concentration of 1 ppmv of amine.

For all three solvent systems of interest, 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 per tonne of CO_2 captured 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 for both the 8 m PZ and 7/2 m MDEA/PZ cases. The cost of solvent makeup due to nitrosamine formation for these cases is expected to be on the order of 0.09 to 0.14 \$/MT of CO_2 captured, and is a strong function of NO_2 concentration entering the absorber. Nitrosamines will also be formed in the 7 m MEA case, but through the reaction of NO_2 with secondary amine degradation products. As these solvent losses are already accounted for in the amine degradation cost estimate, nitrosamine formation does not add to the cost of solvent makeup. NO_2 may also have a catalytic oxidative effect on all solvents, however this effect has not been confirmed or quantified and was not included in the model [10]. It may be advantageous to remove the remaining NO_2 upstream of the capture unit to avoid the solvent replacement costs.

Table 4-11 Sources of Amine Loss for Coal and NGCC Thermal Reclaiming Base Cases (30 min total residence time, 10 min stripper residence time, 30 sec residence time in hot side of cross exchanger and piping before stripper, 1 ppmv amine in flue gas leaving water wash, 0.1% continuous slipstream to reclaimer, 95% amine recovery in reclaimer feed)

Parameters	7 m MEA		8 m PZ		7/2 m MDEA/PZ	
Flue Gas	Coal	NGCC	Coal	NGCC	Coal	NGCC
Stripper operating temperature (°C)	120°C		150°C		135°C	
Loading range (mol CO_2/mol alkalinity)	0.12-0.51	0.12-0.49	0.31-0.41	0.28-0.37	0.11-0.25	0.11-0.25
Thermal degradation cost (\$/MT CO_2)	0.06	0.07	0.10	0.11	0.26	0.26
Oxidation cost (\$/MT CO_2)	0.13	0.33	0.28	0.72	0.43	1.02
Nitrosamine formation cost (\$/MT CO_2)	0	0	0.14	0.13	0.09	0.08
Volatile amine loss cost (\$/MT CO_2)	0.02	0.07	0.08	0.26	0.05	0.16
Total Amine Make-up (\$/MT CO_2 captured)	**0.22**	**0.45**	**0.60**	**1.23**	**0.83**	**1.53**
Total Amine Make-up (€/MT CO_2 captured)	**0.17**	**0.34**	**0.45**	**0.92**	**0.62**	**1.15**

Note: Cost of solvent loss = amine make-up cost

For a thermal reclaimer that removes all non-volatile components 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 approximately 0.5-2 wt% at steady-state conditions (Table 4-12).

This should not significantly affect solvent performance. In PZ and MDEA/PZ, MNPZ will reach a steady state of approximately 130 – 250 ppm, and transition metals leached from fly ash will accumulate in the range of 100 – 300 ppb. The NGCC cases have a higher formate concentration due to greater oxidation, but lower overall contaminant accumulation due to a lower concentration of SO_X and NO_X entering in the flue gas. The information on the model used is given in Appendix D.

A complete kinetic model for steady state concentration of nitrosamines in degraded MEA as a function of NO_2 concentration in the flue gas and stripper operating temperature and residence time has not been developed. Therefore no attempt was made to model nitrosamine concentration for the MEA cases. However, recent pilot plant results indicate that the concentration should be on a similar order of magnitude to the piperazine cases [23, 27].

Table 4-12 Composition of Solvents for the Coal and NGCC Base Cases with Reclaiming (30 min total residence time, 10 min stripper residence time, 30 sec residence time in hot side of cross exchanger and piping before stripper, 1 ppmv amine in flue gas leaving water wash, 0.1% continuous slipstream to reclaimer, 95% amine recovery in reclaimer feed)

Component	7 m MEA		8 m PZ		7/2 m MDEA/PZ	
	Coal	NGCC	Coal	NGCC	Coal	NGCC
Formate (ppmw)	511	1235	899	1010	772	1149
Sulfate (ppmw)	7647	2127	3822	999	3092	900
Nitrate (ppmw)	5009	4750	2469	2152	1997	1937
Chloride (ppmw)	1045	0	522	0	422	0
Flouride (ppmw)	23	0	11	0	9.2	0
Mercury (ppmw)	0.36	0	0.18	0	0.14	0
Selenium (ppmw)	0.46	0	0.23	0	0.18	0
MNPZ (ppmw)	N/A	N/A	113	110	221	215
All nonvolatile contaminants (wt%)	1.48 wt%	0.90 wt%	0.82 wt%	0.54 wt%	0.64 wt%	0.43 wt%

4.9 Effect of Alternate Processes and Operational Conditions

4.9.1 Effect of CO_2 Loading

The base case MEA model for coal and NGCC uses a relatively wide loading range of 0.12 to 0.51 moles CO_2/mole alkalinity. This minimizes solvent flow rate, reducing capital costs of the absorber and reboiler but increasing energy requirements. Alternatively, an MEA process optimized for minimum energy requirements but with higher capital costs would operate with a lean loading closer to 0.4 moles CO_2/mole alkalinity [1]. The results of changing this parameter, but leaving all other parameters constant, are shown below in Table 4-13. When normalized by the rate of CO_2 capture in MT/hour, the apparent rate of solvent degradation and flue gas contamination increases significantly. This is the result of a much larger solvent circulation rate relative to the rate of CO_2 capture, while the solvent inventory and holdups in the stripper are kept constant relative to the circulation rate. As a result, more degradation occurs per MT of CO_2 captured. Additional amine loss in the reclaimer also increases significantly relative to the carbon capture rate unless the reclaimer feed is set to maintain 1.5 wt% contaminants as opposed to being held constant at 0.1% of the solvent circulation rate.

Table 4-13 Effect of Lean Loading on Solvent Makeup Cost (30 min total residence time, 10 min stripper residence time, 120 °C stripper operating temperature, 30 sec residence time in heated section of cross exchanger and piping before stripper, 1 ppmv amine in flue gas leaving water wash, 95% amine recovery in reclaimer feed)

Loading range (mol CO_2/mol alkalinity)	0.12 - 0.51	0.4 - 0.51	0.4 - 0.51
Solvent circulation rate (MT/hr)	9628	34136	34136
Solvent inventory (MT)	4814	17068	17068
Reclaimer slipstream (%)	0.1	0.1	0.037
Wt% contaminants	1.5	0.57	1.5
Thermal degradation ($/MT CO_2)	0.06	0.22	0.22
Oxidation ($/MT CO_2)	0.13	0.48	0.48
Volatile loss ($/MT CO_2)	0.02	0.02	0.02
Additional loss in reclaimer ($/MT CO_2)	0.33	1.12	0.42
Total amine makeup cost ($/MT CO_2)	0.55	1.84	1.14
Thermal reclaimer feed rate (kg/hr)	9630	34140	12750
Thermal reclaimer sludge rate (kg/hr)	643	1476	882

Note: All other base case parameters kept constant except for lean loading (L/G) and reclaimer feed

4.9.2 Absorber Intercooling

By intercooling the absorber the temperature bulge caused by the heat released during CO_2 absorption is reduced, improving CO_2 mass transfer and solvent capacity. In-and-out intercooling (Figure 4-10) removes the solvent at the point in the column where the temperature bulge is expected to be the greatest and cools it back down to 40 °C before feeding it back to the column. Pumparound intercooling (Figure 4-11) uses a recycle loop between a middle section of packing. A coarser packing will be required in this middle section to accommodate the larger liquid flow rate. Employing in-and-out intercooling will slightly reduce oxidation in amines that readily oxidize in the absorber, such as MEA, due to the lower oxidation rate resulting from the reduction of the temperature bulge. The effect of pumparound intercooling will be more mixed due to the larger liquid holdup in the packing. However, neither configuration will have an effect on high temperature cyclic oxidation, where a majority of oxidation is expected to occur. Intercooling also should not affect amines that are resistant to oxidation at absorber conditions, such as MDEA and PZ.

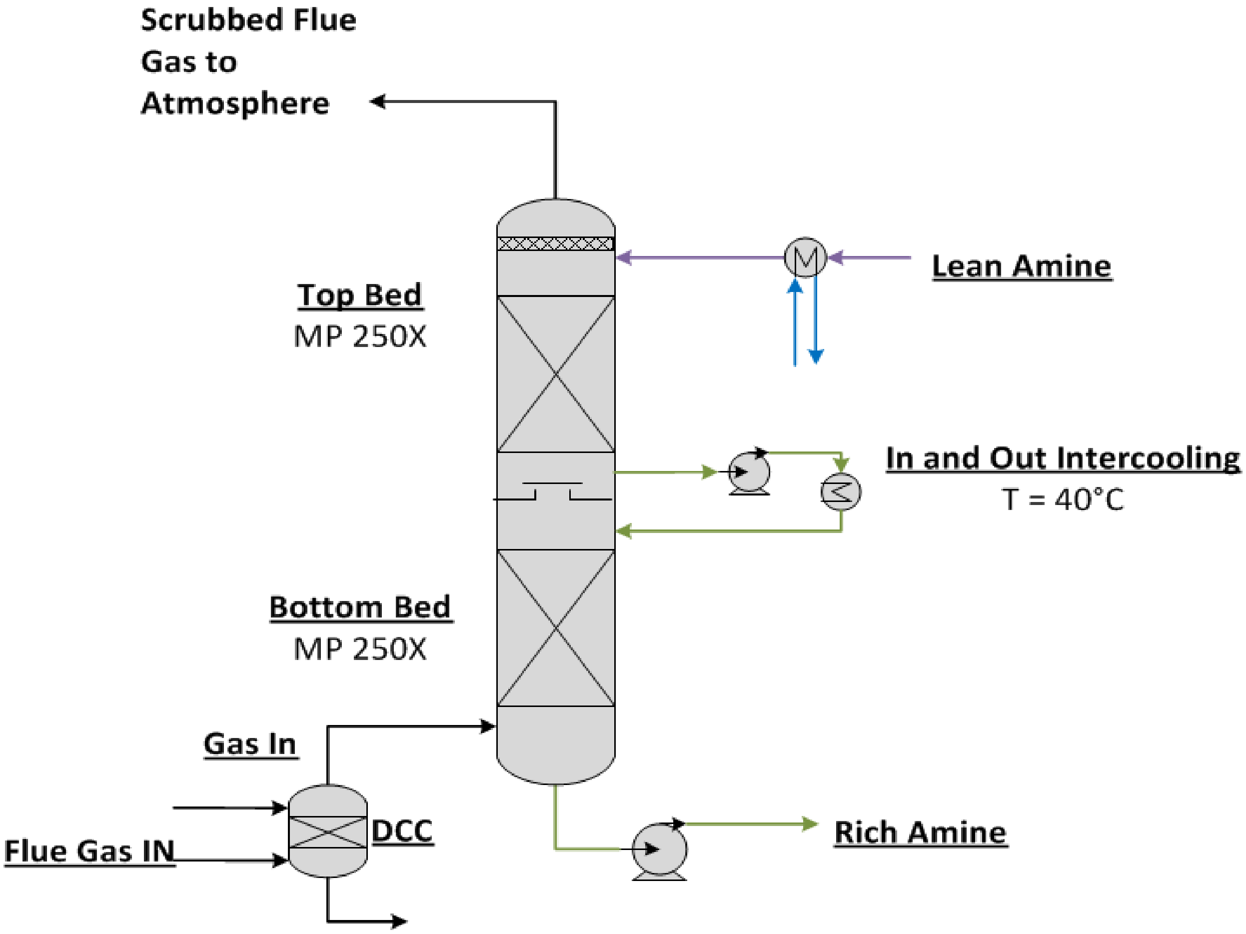


Figure 4-10 In-and-Out Intercooling Configuration

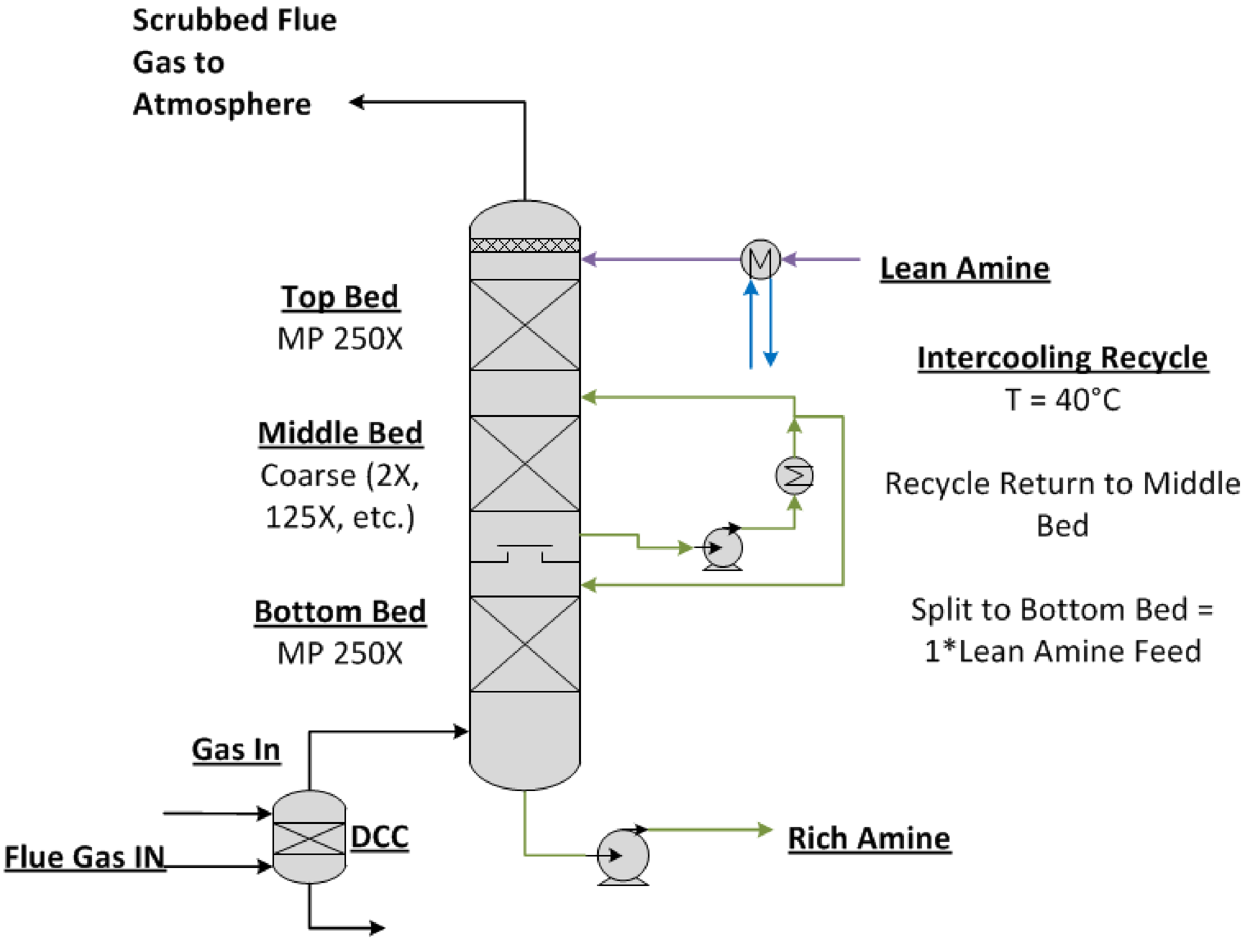


Figure 4-11 Pumparound Intercooling Configuration

4.10 Effects of Degradation Products on the Solvent

As a matter of process control, the water balance of pilot plants (and possibly commercial units) is frequently adjusted by the addition of water and parent amine to maintain a constant total alkalinity of amine. The heat stable salts and larger polymers formed from degradation are typically stable and non-volatile. These degradation products will accumulate in the circulating amine solvent at a fairly constant rate unless removed via reclaiming. Ammonia and other amine intermediates more volatile or more reactive than the parent amine of the solvent will reach a steady-state value determined by their vapor-liquid equilibrium or reaction kinetics. If a water wash is used to control volatile emissions, a strategy may need to be developed to intermittently purge volatile contaminants from the system. The following sections provide a brief qualitative assessment on the effect of degradation products on capture solvent properties. Physical properties such as heat capacity and density are not covered in this section, because these parameters are not expected to vary greatly at the concentrations of degradation products and impurities being assumed in this study, and there is a lack of information available to estimate any potential changes in these parameters.

4.10.1 Viscosity

As non-alkaline impurities such as formamide and amine sulfate accumulate, the viscosity of the solvent will increase. The heat transfer coefficient in the cross exchanger is inversely proportional to the square root of viscosity. Diffusion coefficients of CO_2 and amine products are also inversely proportional to the square root of viscosity, and as a result the associated mass transfer flux is also affected by viscosity to the 0.25 to 0.5 power. These effects become apparent in energy performance at an approximate accumulation of 3 to 10 wt% degradation product impurities in the solution.

4.10.2 Other Energy Properties

As the solvent is maintained at constant alkalinity, other amine degradation products, which have properties different from the parent amine, will accumulate in solution. Presumably the kinetics of CO_2 absorption, heat of CO_2 absorption, and operating CO_2 capacity may degrade, but in some cases the amine degradation products may result in superior energy properties.

For example, piperazine thermally degrades to aminoethylpiperazine (AEP). 6 m PZ/2 m AEP has been shown to have greater heat of absorption, somewhat lower capacity, and equivalent absorption kinetics to 8 m PZ [25]. In addition, the blended amine system has a broader range of solid solubility than PZ alone. However, a primary disadvantage of the blended amine system is that AEP will be removed by thermal reclaiming to convert the solvent back to 8 m PZ.

4.10.3 Foaming and Corrosion

Little is known about the effects of impurities on corrosion and foaming, but much has been speculated. Since clean solvents rarely seem to foam, it is possible that foaming is probably a consequence of impurities, but usually of unknown identity.

Chen et al. (2010) showed that foaming could be caused in 8 m loaded PZ with the addition of about 500 mM formaldehyde [26]. However, little if any foaming has been observed in pilot plant testing of piperazine and little formaldehyde has been found in pilot plant samples with more than 1500 hours of operation [17].

Corrosion has been speculated to be enhanced by degradation products that may serve as chelating agents and by dissolved salts that increase ionic conductivity. However, corrosion is also expected to increase oxidative degradation because of the accumulation of the dissolved metal catalysts, so it is difficult to separate cause and effect in operating systems.

4.11 Alternate Stripper Configurations

Several alternative stripper configurations have been proposed to reduce the energy requirements of solvent regeneration and CO_2 compression, usually by improving heat recovery. The energy requirements for three configurations using a combination of cold rich solvent bypass, a flash stripper, and interheating have been modeled by the University of Texas at Austin for 8 m piperazine. These configurations reduce the equivalent work requirements (reboiler duty and compression work) by approximately 10% relative to a base case model using a simple stripper with flashing allowed in the cross exchanger (Figure 4-12). This differs slightly from the base case model previously shown for PZ, which did not allow for flashing in the cross exchanger.

The flash stripper with rich exchanger bypass configuration (Figure 4-13) takes a slipstream of rich solvent from the absorber before the cross exchanger to recover heat from the stripper overhead vapor. The cross exchanger itself is split into two stages, and a second rich slipstream is taken between the exchangers and fed to the top of the stripper. The bulk of the rich solvent is then sent to a steam heater, in lieu of a reboiler, and fed to the bottom of the stripper where the CO_2 is flashed off. This design greatly reduces the packing requirement of the stripper and allows for a smaller sump as well, which will reduce thermal degradation. However, because the solvent is heated in a steam heater up to the stripper operating temperature for a longer residence time before dissolved oxygen is allowed to flash off in the stripper, the oxidation rate is approximately doubled.

The warm rich and cold rich exchanger bypass configuration (Figure 4-14) uses the same bypass configuration to recover heat from the stripper overhead, but feeds the bulk of the solvent into the stripper packing part of the way down the column. Compared to the base case simple stripper, with only a slight reduction in thermal degradation due to less holdup in the packing and slightly less oxidation due to some of the solvent the bypassing the high temperature oxidation section.

The interheated stripper with cold rich exchanger bypass configuration (Figure 4-15) still uses a cold rich solvent bypass to recover heat from the stripper overhead, but feeds this and the rest of the solvent to the top of the stripper at a moderately warm temperature. The solvent is then drawn off the column midway through the packing and heated in an additional cross exchanger by the lean solvent from the bottom of the stripper. Because dissolved oxygen will be flashed off at a lower temperature, oxidation will be significantly reduced.

A comparison of these configurations is shown in Table 4-14. The table shows the parameters used to model the configurations, the estimated energy requirements, and the cost of solvent makeup and reclaiming. Additional solvent loss in the reclaimer was fixed at 95% recovery from a reclaimer designed to maintain 1.5 wt% contaminants in the solvent. The flash stripper with rich exchanger bypass configuration resulted in the most degradation, while the interheated stripper had the least. However, all three designs are cheaper to operate than the base case simple stripper when energy savings are included. Because all three cases reduce the total solvent holdup at high temperature, the expected steady state nitrosamine concentration will increase.

Table 4-14 Comparison of Alternate Stripper Configurations with 8 m PZ

Configuration	Simple Stripper	Flash w/ Bypass	Rich Bypass	Interheated w/ Bypass
T_{sump}	150 °C	150 °C	150 °C	150 °C
τ_{sump}	5 min	4 min	5 min	5 min
$T_{packing}$	137 °C	121 °C	121/137 °C	119/138 °C
$\tau_{packing}$	5 min	2 min	1/1 min	1/1 min
Fraction solvent flow to packing	1	0.15	0.15/1	1/1
$T_{oxidation}$	137 °C	150 °C	137 °C	119 °C
$\tau_{oxidation}$	0.5 min	1 min	0.5 min	0.5 min
Fraction solvent in high temp ox	1	0.85	0.85	1
W_{eq} (kJ/mol CO_2)	31.9	29.0	28.8	28.9
W_{eq} (\$/MT CO_2) (\$50/MWh)	10.07	9.15	9.09	9.12
Thermal degradation (\$/MT CO_2)	0.10	0.06	0.08	0.08
Oxidation (\$/MT CO_2)	0.23	0.52	0.20	0.15
Total amine makeup (\$/MT CO_2)	1.56	1.82	1.50	1.45
Total + W_{eq} (\$/MT CO_2)	11.63	10.97	10.59	10.57
MNPZ (mmol/kg) (1.5 ppm_v NO_2)	1.0	1.9	1.4	1.4

$$W_{eq} = 0.75\left(\frac{T_{source} + \Delta 5 - 313}{T_{source} + \Delta 5}\right) Q_{reboiler} + W_{pump} + W_{compressor}$$

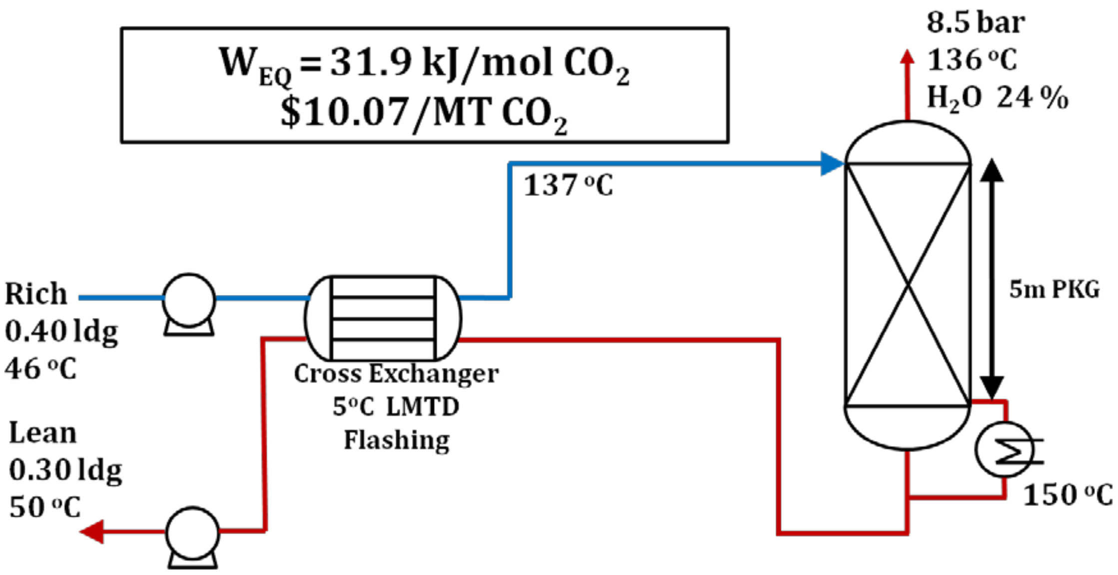


Figure 4-12 Simple Stripper with Flashing Cross Exchanger (Base Case)

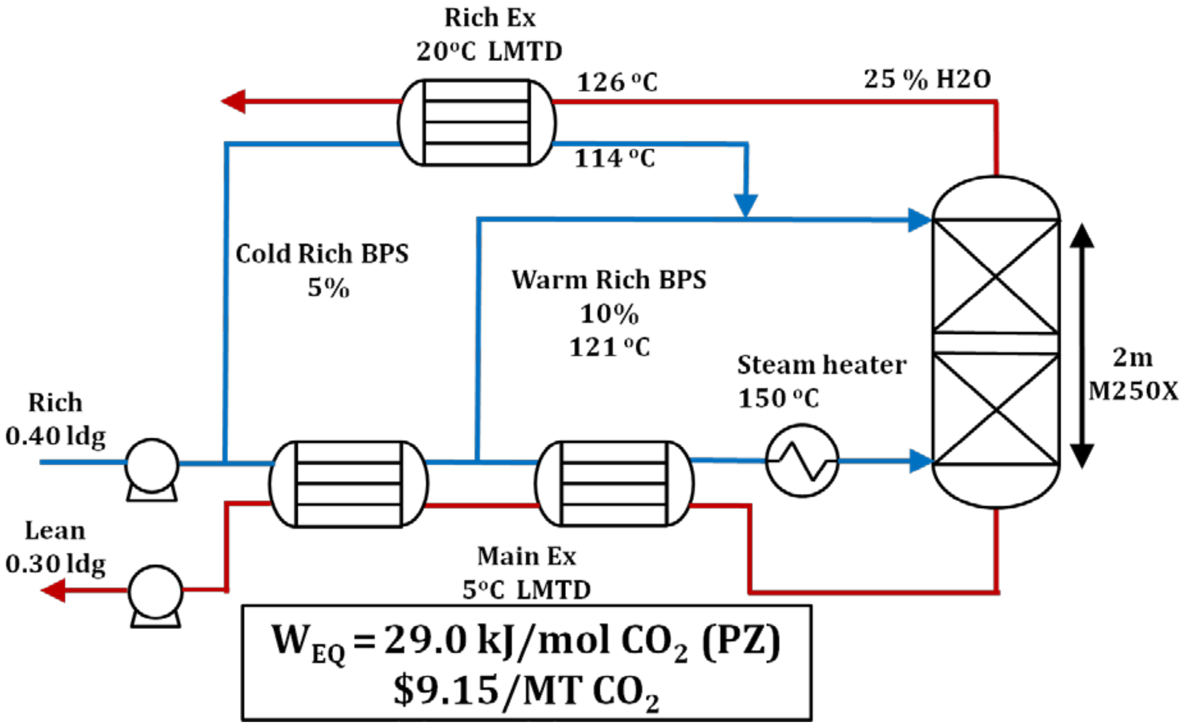


Figure 4-13 Flash Stripper with Rich Exchanger Bypass

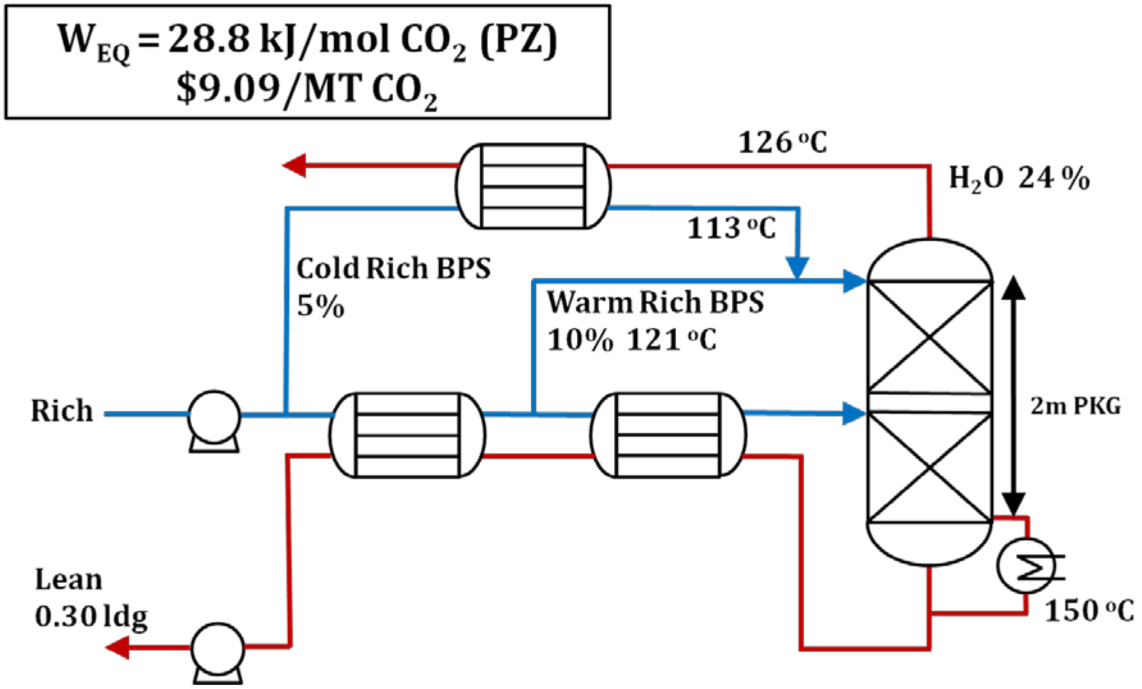


Figure 4-14 Warm Rich and Cold Rich Exchanger Bypass

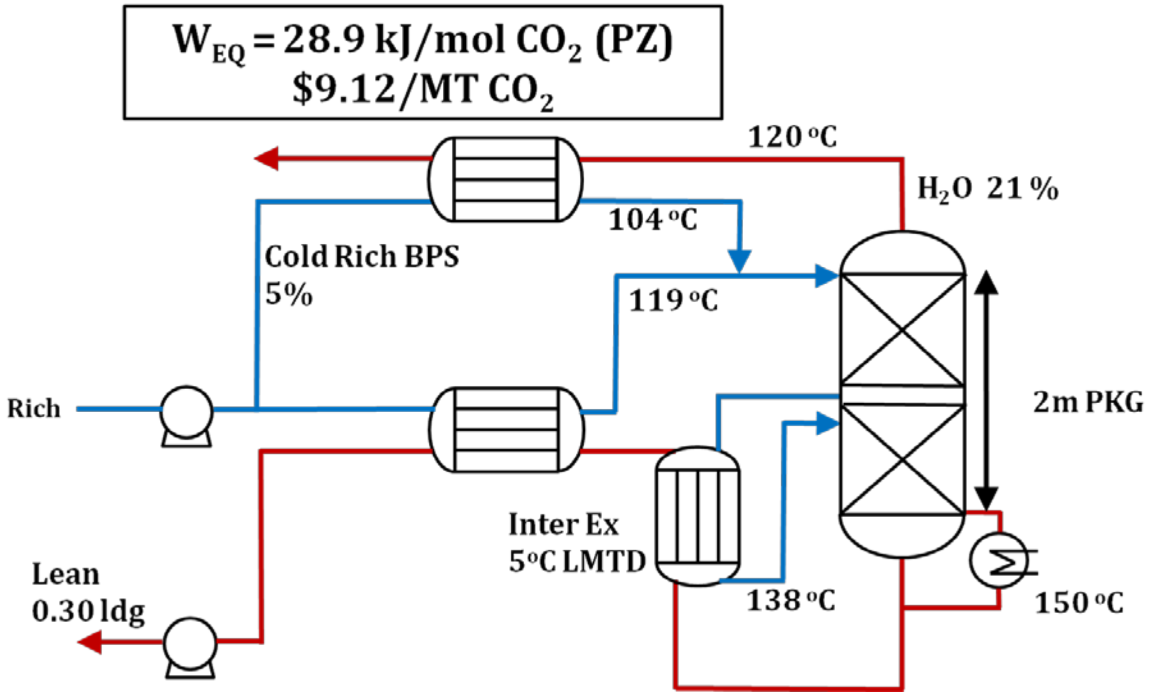


Figure 4-15 Interheated Stripper with Cold Rich Exchanger Bypass

4.12 Oxidation Inhibitors

Chelating agents, sulfur containing thiadozoles, free radical scavengers, and tertiary amines have all been shown to inhibit oxidation of MEA at absorber conditions, either by directly limiting oxidation or by inhibiting corrosion that would otherwise catalyze oxidation. A list of proposed oxidation inhibitors is shown in Table 4-15. However, none of the inhibitors were effective when cycled up to high temperatures in the ISDA and HTCS apparatuses, with most inhibitors either decomposing or showing no effect on the solvent oxidation rate [10].

Table 4-15 List of Oxidation Inhibitors [10]

Oxidation Inhibitor	Type	First Proposed
Ethylenediamine tetra(acetic acid) (EDTA)	Chelating agent	[6]
1-hydroxyethylidene-1,1-diphosphonic acid (HEDP)	Chelating agent	[18]
Diethylenetriamine penta(acetic acid) (DTPA)	Chelating agent	[10]
2,5-dimercapto-1,3,4-thiadiazole (DMcT)	Thiadiazole	[19]
Inhibitor A	Free radical scavenger	[14]
MDEA	Tertiary amine	[20]

4.13 Volatile Emissions and Aerosols

At a concentration of 1 ppmv amine exiting the water wash, amine loss due to volatility is on the order of \$0.02 to \$0.26 per metric ton of CO_2 removed. However, aerosols such as SO_3 could greatly increase the rate of amine emissions. Some previous pilot plants campaigns have observed amine emissions as high as 50 ppmv due to aerosols [30,31]. For the 8 m PZ coal case, this continuous concentration of amine exiting the absorber would cost \$4.13/MT CO_2 captured. Aerosols are therefore a very costly environmental and economic concern due to the loss of amine and emissions to the atmosphere. Most pilot plants are just now beginning to understand and address aerosols exiting the absorber stack; it is assumed a full-scale plant would install an impingement tray or Brownian demister unit (BDU) to capture aerosols, though either will result in a significant pressure drop for the flue gas, increasing blower operating costs. The exact cost of aerosol emissions has not been modeled.

4.14 Volatiles Reclaiming Processes

In addition to non-volatile degradation products, there may also be volatile degradation products such as ammonia and methyl-piperazine that will not be removed by thermal reclaiming. If a water wash is employed to control amine emissions, these volatile components will be captured as well and will accumulate in the solvent. One potential reclaiming concept is to treat the stripper condensate, which is where the volatile degradation products are expected to accumulate (Figure 4-16). A recent analysis of liquid samples from pilot plant campaigns using piperazine shows that ammonia and methyl-piperazine are concentrated by one to two orders of magnitude greater in the stripper condensate and water wash than in the solvent relative to the piperazine concentration [17]. Another reclaiming concept for addressing volatiles is to remove a slipstream of gas from the stripper middle and treat the condensed volatile degradation products.

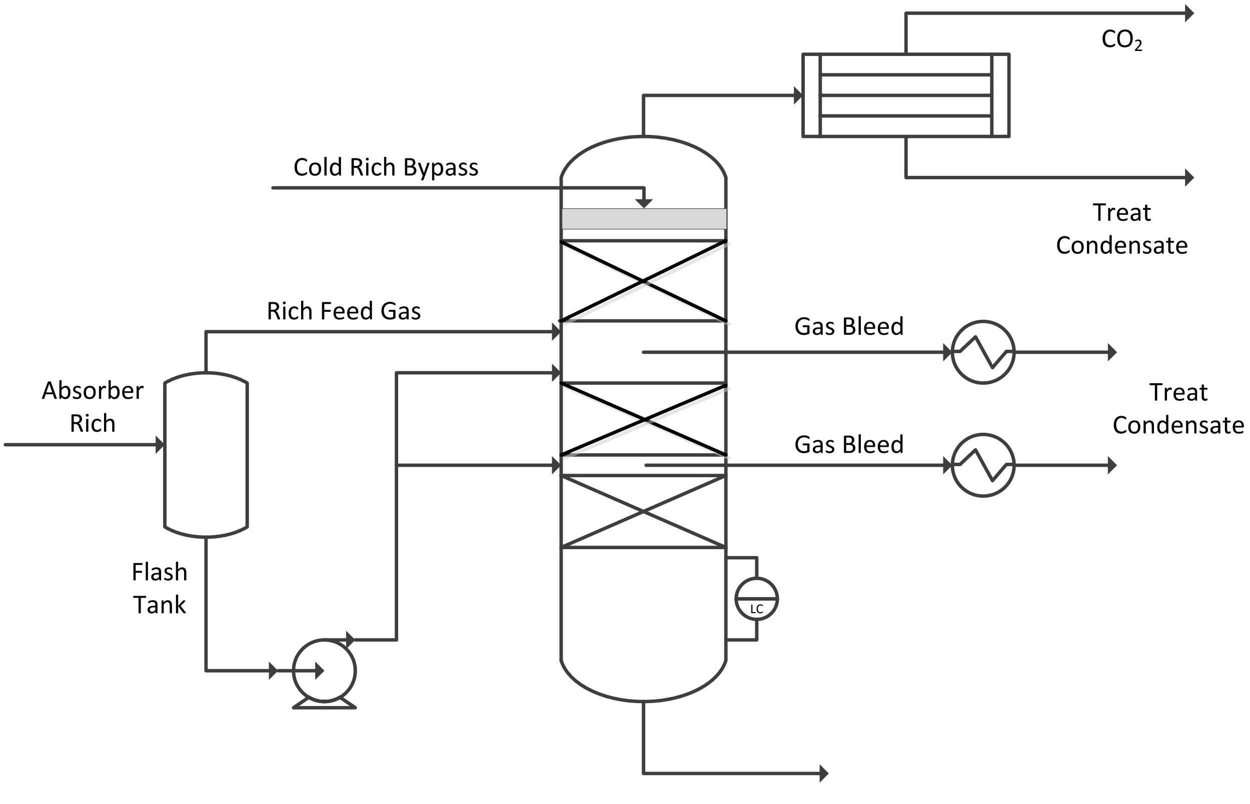


Figure 4-16 Volatiles Reclaiming by Treatment of Condensate from Overhead Gas and Gas Bleed from Stripper Middle

4.15 **Summary of Solvent Loss and Degradation Product Formation**

For monoethanolamine (MEA), piperazine (PZ), and methyldiethanolamine/piperazine (MDEA/PZ) CO_2 capture solvents, 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.

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

For a thermal reclaimer that removes all non-volatile components 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 approximately 0.5-2 wt% at steady-state conditions. This should not significantly affect solvent performance. In PZ and MDEA/PZ, mononitrosopiperazine (MNPZ) will reach a steady state 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 nonhazardous waste. The NGCC cases have a higher formate concentration due to greater oxidation, but lower overall contaminant accumulation due to a lower concentration of SO_X and NO_X entering in the flue gas.

REFERENCES

1. Davis JD. *Thermal Degradation of Aqueous Amines Used for Carbon Dioxide Capture*. The University of Texas at Austin. Ph.D. Dissertation. 2009.

2. Freeman SA. *Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture*. The University of Texas at Austin. Ph.D. Dissertation. 2011.

3. Kindrick RC, Atwood K, Arnold MR. "The Relative Resistance to Oxidation of Commercially Available Amines." Girdler Report No. T2.15-1-30, in report: *Carbon Dioxide Absorbents.* Contract No. NObs-50023, by Girdler Corp., Gas Processes Division, Louisville, KY, for the Navy Department, Bureau of Ships, Washington, DC (Code 649P). 1950

4. Walling C. *Free Radicals in Solution*. John Wiley & Sons, Inc.: New York, NY. 1957

5. Johnson WW, McElwain RE, Lew M. *Stabilization of monoethanolamine with chelating agents*. Industrial Laboratory Mare Island Naval Shipyard Report No. 7116-59. 1960

6. Blachly CH, Ravner H. *The Stabilization of Monoethanolamine Solutions for Submarine Carbon Dioxide Scrubbers.* AD609888; NRL-6189; Naval Research Laboratory: Washington, D.C. 1964

7. Rooney PC, DuPart MS, Bacon TR. Oxygen's Role in Alkanolamine Degradation. *Hydrocarbon Processes, International Edition.* 77 (7): 109-113. 1998

8. Sexton AJ. *Amine Oxidation in CO_2 Capture Processes*. The University of Texas at Austin. Ph.D. Dissertation. 2008.

9. Lepaumier H, da Silva E, Einbu A, Grimstvedt A, Knudsen J, Zahlsen K, Svendsen H. "Comparison of MEA degradation in pilot-scale with lab-scale experiments." *Energy Procedia.* 4: 1652-1659. 2011

10. Voice AK. *Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing.* The University of Texas at Austin. Ph.D. Dissertation. 2013.

11. Chi S. *Oxidative Degradation of Monoethanolamine*. Masters Thesis, The University of Texas at Austin, Austin, TX. 2001

12. Chi S, Rochelle GT. "Oxidative Degradation of Monoethanolamine." *Industrial & Engineering Chemistry Research*. 41 (17): 4178-4186. 2002

13. Goff GS, Rochelle GT. "Oxidation Inhibitors for Cu Catalyzed Degradation of Monoethanolamine in CO2 Capture Processes." *Industrial & Engineering Chemistry Research.* 45 (8): 2513-2521. 2006

14. Goff GS. *Oxidative Degradation of Aqueous Monoethanolamine in CO_2 Capture Processes: Iron and Copper Catalysis, Inhibition, and O2 Mass Transfer*. Doctoral Thesis, The University of Texas at Austin. 2005

15. Hofmeyer BG, Scholten HG, Lloyd WG. "Contamination and Corrosion in Monoethanolamine Gas Treating Solutions." *Am. Chem. Soc., Div. Petrol. Chem., Preprints-Symposia.* 1 (2): 91-99. 1956

16. Strazisar BR, Anderson RR, White CM. "Degradation Pathways for monoethanolamine in a CO_2 capture facility." *Energy Fuels.* 17 (4): 1034–1039. 2003

17. Nielsen PT, Li L, Rochelle GT. "Piperazine Degradation in Pilot Plants" Poster manuscript, *GHGT-11*. Kyoto, Japan. November 19-23, 2012.

18. Elnan J. *Screening of inhibitors for amine degradation*. Master's thesis, Norwegian University of Science and Technology. 2012

19. Carrette PL, Delfort B. Absorbing solution containing a thiadiazole-derived degradation inhibitor and method for limiting the degradation of an absorbing solution. World patent WO2009/156619A2 2009c. 2009

20. Faucher JA. Process for inhibiting mono and diethanolamine degradation. US patent 4840777. 1989

21. Epp B, Fahlenkamp H, Vogt M. "Degradation of Solutions of Monoethanolamine, Diglycolamine and Potassium Glycinate in View of Tail-End CO2 Absorption." *Energy Procedia*. 4: 75-80. 2011

22. Closmann F. *Oxidation and Thermal Degradation of Methyldiethanolamine/Piperazine in CO_2 Capture*. The University of Texas at Austin. Ph.D. Dissertation. 2011.

23. Voice AK, Closmann F, Rochelle GT. "Oxidative degradation of amines with high-temperature cycling." Oral presentation, *GHGT-11*. Kyoto, Japan. November 19-23, 2012.

24. Fine NA, Goldman MJ, Nielsen PT, Rochelle GT. "Managing n-nitrosopiperazine and dinitrosopiperazine." Oral presentation, *GHGT-11*. Kyoto, Japan. November 19-23, 2012.

25. Du Y, Li L, Namjoshi O, Voice AK, Fine NA, Rochelle GT. "Aqueous piperazine/N-(2-aminoethyl) piperazine for CO_2 capture," poster manuscript for GHGT-11, Kyoto, Japan. November 19-23, 2012.

26. Chen X, Freeman SA, Rochelle GT, "Foaming of Aqueous Piperazine and Monoethanolamine for CO_2 Capture", *International Journal of Greenhouse Gas Control*. 2010; 4(5) 756-761.

27. da Silva EF, Lepaumier H, Grimstvedt A, Vevelstad SJ, Einbu A, Vernstad K, Svendsen HF, Zahlsen K. “Understanding 2-Ethanolamine Degradation in Postcombustion CO_2 Capture.” *Industrial & Engineering Chemistry Research*. 2012; 51:13329-13338.

28. Einbu A, da Silva EF, Haugen G, Grimstvedt A, Lauritsen KG, Zahlsen K, Vassbotn, T. “A new test rig for studies of degradation of CO_2 absorption solvents at process conditions: comparison of test rig results and pilot plant data for degradation of MEA.” *Energy Procedia*. 2013; 37:717-726

29. Kohl, A.; Nielsen, R. *Gas Purification*, 5th ed.; Gulf Publishing Co.: Houston, 1997.

30. Kamijo T, Kajiya Y, Endo T, Nagayasu H, Tanaka H, Hirata T, Yonekawa T, Tsujiuchi T. “SO_3 impact on amine emission and emission reduction technology.” *Energy Procedia*. 2013; 37:1793-1796

31. Khakharia P, Brachert L, Mertens J, Huizinga A, Schallert B, Schaber K, Vlugt TJH, Goetheer E. “Investigation of aerosol based emission of MEA due to sulphuric acid aerosol and soot in a Post Combustion CO_2 Capture process.” *International Journal of Greenhouse Gas Control*. 2013. 19:138-144

5 TECHNOECONOMIC EVALUATION

This chapter presents the results of a technology feasibility study, also known as a technoeconomic (TE) evaluation, of suitable reclaiming technologies for the designated solvents of interest. The reclaiming technologies evaluated include thermal and vacuum distillation, ion exchange and electrodialysis (it was assumed that "bleed-and-feed" was not viable option); these reclaiming technologies were evaluated for three solvent systems of interest: monoethanolamine (MEA), a blend of methyldiethanolamine promoted with piperazine (MDEA/PZ) and concentrated piperazine (PZ). In addition, rates of degradation and heat stable salt accumulation were evaluated for both coal-fired and natural gas-fired power plants.

The technology feasibility evaluation includes process descriptions, process flow diagrams, mass balances, utility requirements, energy requirements, and an economic evaluation of purchased equipment costs, capital costs, operating and maintenance costs, annualized cost of electricity and annualized cost per ton of CO_2 captured for the following power plant types:

- A greenfield supercritical pulverized coal (PC) power plant with 90% CO_2 capture that produces 900 MW of gross electric power; and
- A greenfield natural gas power plant with 90% CO_2 capture that produces 810 MW of gross electric power.

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

5.1 Design Basis and Process Description

The standard design for base case power plants for this evaluation are a 900 MW gross supercritical coal-fired power plant using Australian low-sulfur coal, and an 810 MW gross natural gas-fired power plant. A selective catalytic removal (SCR) unit is 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 are assumed to be located upstream of the CO_2 capture unit of the coal-fired power plant. The FGD and sodium hydroxide polishing units are expected to reduce SO_X concentration to the CO_2 capture unit to 10 ppmv or less. The resulting flue gas compositions for the coal and natural gas cases, taken from IEAGHG Report 2013-05 “Post-Combustion CO_2 Capture Scale-up Study”, are shown in Tables 5-1 and 5-2 [7]. A capacity factor of 85% was assumed for the economic analysis, and the CO_2 capture units were designed to remove 90% of the CO_2 from the flue gas stream. Greater detail on these flue gas streams is located in Chapter 4.

Table 5-1 Inlet Flue Gas Composition – SCPC Power Plant

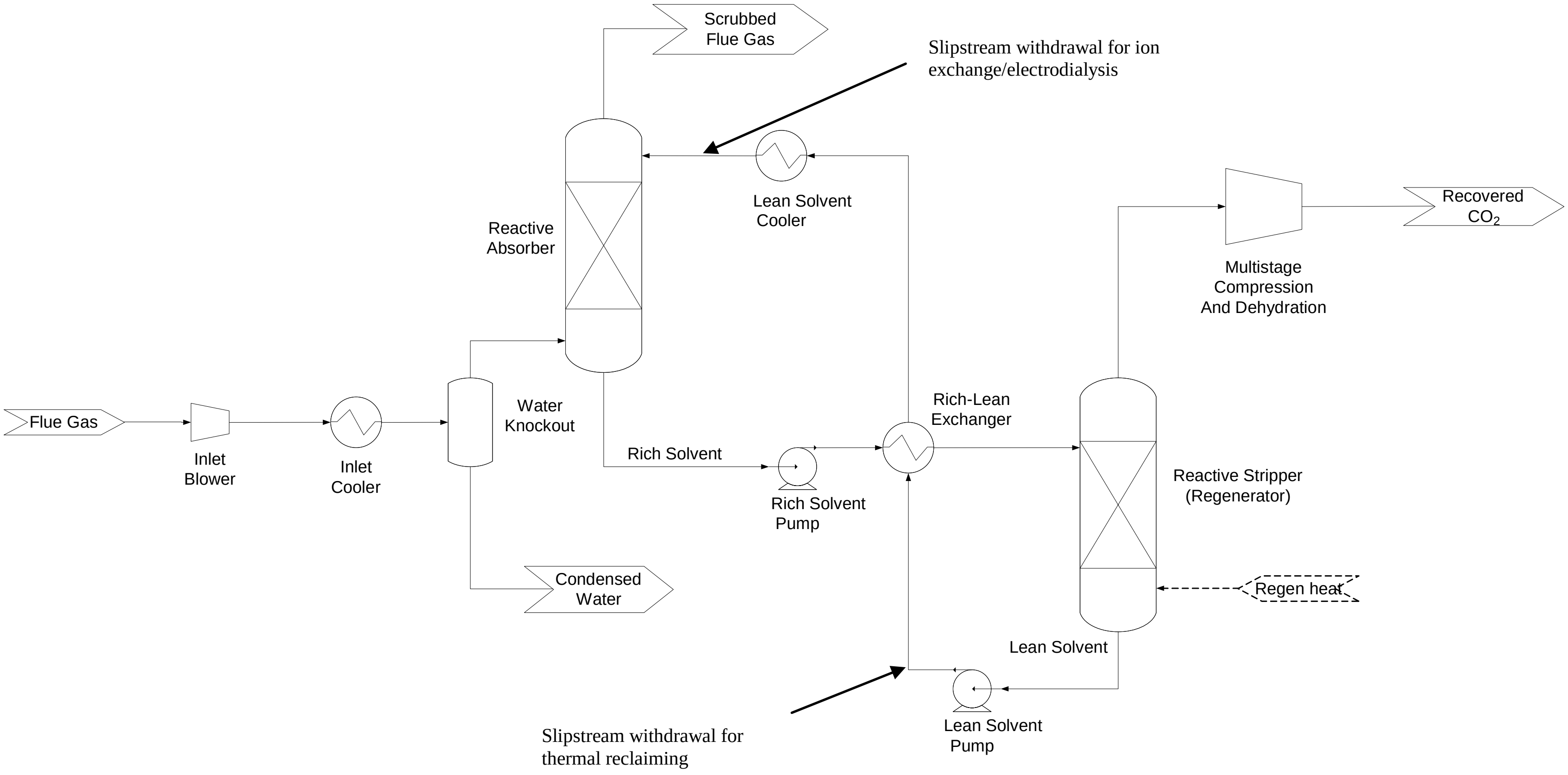
Composition	Mole %
CO_2	11.78
O_2	5.03
H_2O	12.97
N_2	70.22

Table 5-2 Inlet Flue Gas Composition – Natural Gas Power Plant

Composition	Mole %
CO_2	4.09
O_2	11.99
H_2O	8.76
N_2	75.16

5.1.1 CO_2 Capture Process Description

A generic process flow diagram for an amine-based CO_2 capture system is shown in Figure 5-1. 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 then 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 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 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 compression train.



Slipstream withdrawal for ion exchange/electrodialysis

Slipstream withdrawal for thermal reclaiming

Figure 5-1 Example CO_2 Capture Process Flow Diagram with Reclaimer Slipstream Locations.

The captured CO_2 is compressed to pipeline pressure of 11.0 MPa (1595 psia). The compressor train has multiple stages of centrifugal compression with interstage coolers and separators. A multistage centrifugal pump is used to pressurize the CO_2 to its final pipeline conditions. A dehydration unit is included between the final compression stage and the multistage centrifugal pump to dry the CO_2.

Tanks and pumps for makeup solution and water are required in addition to a cooling water system for the entire CO_2 capture unit (water is needed for the coolers in the process). Finally, a reclaimer 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 lower CO_2 loading in solution. Alternatively, it may be preferable to take the slipstream for ion exchange or electrodialysis reclaiming downstream of lean solvent cooler so that stream has been filtered and cooled using 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.

The intention of this study is to examine options for a dedicated, integrated and continuous reclaiming unit for a capture plant; batch reclaiming a solvent offline is a one-time cost that is performed using a mobile unit brought to the site by the reclaiming vendor. Determining the frequency and cost of this operation is solvent specific and outside of the scope of this study.

5.1.2 Reclaimer Process Descriptions

Thermal Reclaiming

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. The contaminated amine is pretreated with caustic to reverse the reaction between acid impurities (chloride in coal flue gas, for example) and/or degradation products (formic acid, for example) and the amine by adding about one mole of sodium hydroxide (NaOH) per mole of heat stable salts; this reaction creates salts between sodium and the acid impurities/degradation products, and liberates the free amine. In addition, the addition of NaOH to amides can reverse the amide formation reaction to liberate free amine and the heat stable salt.

Two example reactions of NaOH addition for amine liberation are given. The first shows the liberation of the amine cation from formate, and the second the liberation of the amine from chloride.

$$NaOH + R_3NH^+ + O_2CH^- \rightarrow R_3N + NaO_2CH + H_2O$$
$$NaOH + R_3NH^+ + Cl^- \rightarrow R_3N + NaCl + H_2O$$

Because of the appreciable concentration of CO_2 in the lean amine solvent in post-combustion capture processes, the reaction between CO_2 and amine that forms amine carbamate should be reversed before caustic pretreatment of the reclaimer feed. One potential option for pretreatment for CO_2 removal involves heating at regeneration conditions to reverse the amine-CO_2 reaction (and vaporize a small amount of water). Activated carbon filtration can also be utilized to remove impurities prior to thermal reclaiming.

This is not typical in conventional reclaiming processes for refining and gas processing applications because the CO_2 concentration in the lean solvent is negligible, but it is necessary for CO_2 capture reclaiming applications in post-combustion capture because of the significant quantities of CO_2 present in the lean amine feed to the reclaimer from the regenerator. Communication with reclaiming vendors revealed minimal additional information on this topic. This CO_2 pretreatment requirement is applicable to ion exchange and electrodialysis thermal reclaiming as well.

After both pretreatment for CO_2 removal (it is assumed this CO_2 is returned to the lean solvent) and caustic addition for heat-stable salt (HSS) conversion, the amine is then sent to a distillation column, where the amine and water product are vaporized by steam or hot oil. The reclaimer usually operates at amine regenerator pressure for monoethanolamine (MEA), atmospheric pressure for piperazine (PZ), and vacuum conditions for methyldiethanolamine (MDEA) (to keep temperature low enough to minimize thermal degradation in the reclaimer).

A traditional thermal reclaimer configuration is a kettle-type reboiler with a packed column. The amine is fed to the reboiler, where the liquid level is maintained several inches above the tube bundles. The amine and water are vaporized in the kettle and sent through a packed stripping column. The vapor product (water, amine and CO_2) exits the top of the column, is condensed and then recombined with the lean solvent stream at the suction of the lean amine pump.

Literature suggests that up to 95% of the amine is recovered in the vapor, with 5% of the amine (or greater) remaining in the liquid [4]; this is is a best-case assumption which assumes that reclaimer is designed and operated to maximize amine recovery and accelerated corrosion is likely to occur. Higher boiling point and non-volatile impurities (heat stable salts, solids, and dissolved metals), in addition to a small fraction of the amine solvent, remain in the liquid in the bottom of the thermal reclaimer. This thick sludge accumulates in the bottom of the reclaimer and periodically has to be removed by a vacuum pump to a storage vessel or truck for transport.

The CHEM Group Wiped Film Evaporator reclaimer unit utilizes mechanical removal of the sludge in order to simplify the process [8]. Once the feed enters the evaporator it is distributed by a rotating plate, which results in a thin film forming on the inside wall of the unit. A set of rotating wiper blades travels along the vessel to help ensure even film distribution. The liquid is heated by a jacket on the outside of the unit. The amine product and water are quickly vaporized and exits out the top of the evaporator, while the heavier components collect on the wall. Eventually these heavier components fall under the force of gravity, and rotating blades at the bottom of the unit mechanically force out the heavy materials. It is expected that the waste product from this process will have a low water content relative to a kettle-type reboiler. Flow diagrams of conventional and wiped film evaporators are given in Figures 5-2 and 5-3 below.

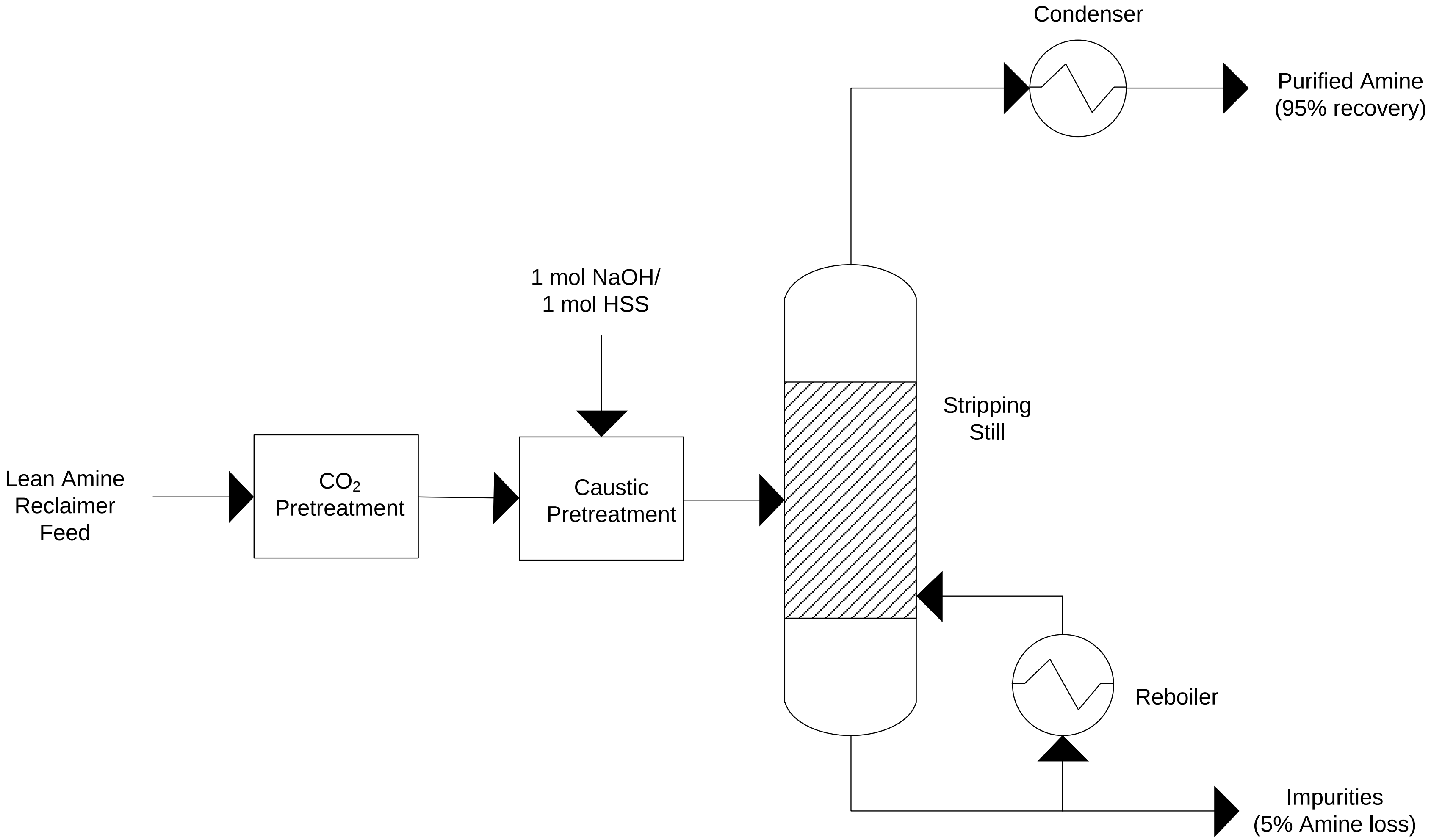


Figure 5-2 General Thermal Reclaiming Process Flow Diagram

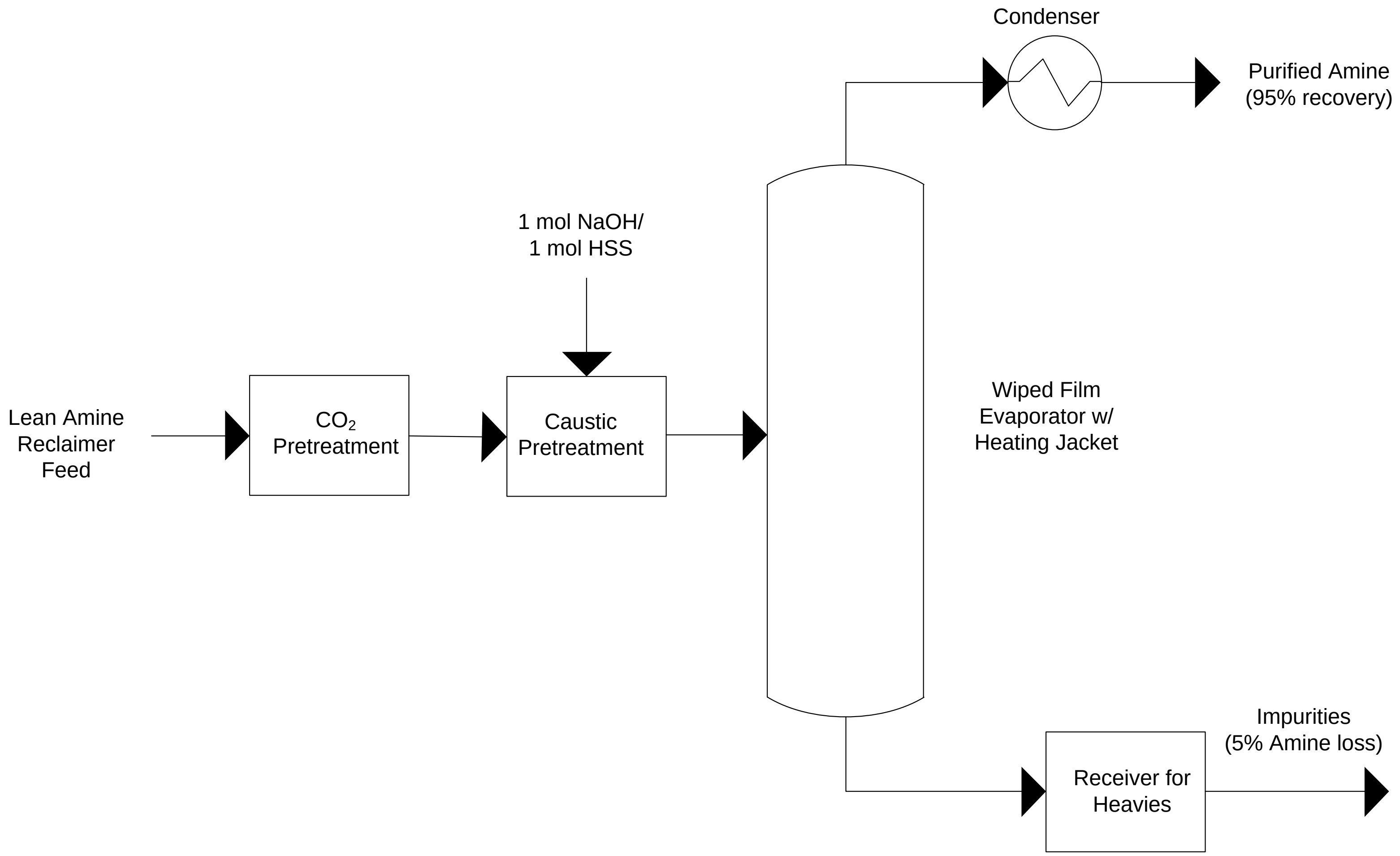


Figure 5-3 Wiped Film Evaporator Thermal Reclaiming Process Flow Diagram

Ion Exchange Reclaiming

In this technology 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. Alternatively, it may be preferable to take the slipstream for ion exchange reclaiming downstream of lean solvent cooler so that stream has been filtered and cooled using main solvent equipment loop.

The reaction between CO_2 and amine that forms amine carbamate should be reversed before caustic pretreatment of the reclaimer feed; this is similar to pretreatment for thermal reclaiming technology. Next, the contaminated amine is sent through a particulate filter and pretreated with caustic to reverse the reaction between acid impurities/degradation products and the amine salt by adding about one mole of NaOH per mole of heat stable salts; this reaction creates salts between sodium and the acid impurities/degradation products, and liberates the free amine.

The contaminated amine is then sent through a cation exchange resin. Undesirable cations bind to the resin and are removed from the amine stream, including the sodium cation from the NaOH added upstream of the resin beds. The amine is then sent to an anion exchange resin where anion impurities are removed. A typical ion-exchange resin is based on crosslinked polystyrene. Crosslinking is introduced via copolymerization of styrene and divinylbenzene; crosslinking is necessary to allow passage of ions and eliminate solbulity of the resin in water.

The cation and anion resins are periodically regenerated by adding sulfuric acid and sodium hydroxide to the beds, respectively. Sulfuric acid is used to regenerate the cation bed by flushing the sodium cations (Na^+) from the resin and replacing it with hydrogen cations (H^+), while sodium hydroxide is used to regenerate the anion bed by flushing the heat stable salt anions (HSS^-) from the resin and replacing them with hydroxide anions (OH^-). During regeneration large volumes of low concentration brine are produced, which are typically 5 wt% salt solution and include the NaOH and H_2SO_4 used to regenerate the beds. This brine can be sent to the wastewater treatment plant.

Up to 99% of the amine can be recovered during ion exchange reclamation [4,9,10]. However, this method is limited due to the fact that it can only remove ionic impurities and ionic degradation products, allowing non-ionic species to accumulate in the amine system. Additionally, transitional metals (Hg, As, Pb, Se, etc.) are only minimally removed by ion exchange, and transitional metals that are removed are likely to foul the exchange resin. This shortens the lifetime of the resins and consequently increases the frequency of bed changeouts. A flow diagram of ion exchange reclaiming is given in Figure 5-4 below.

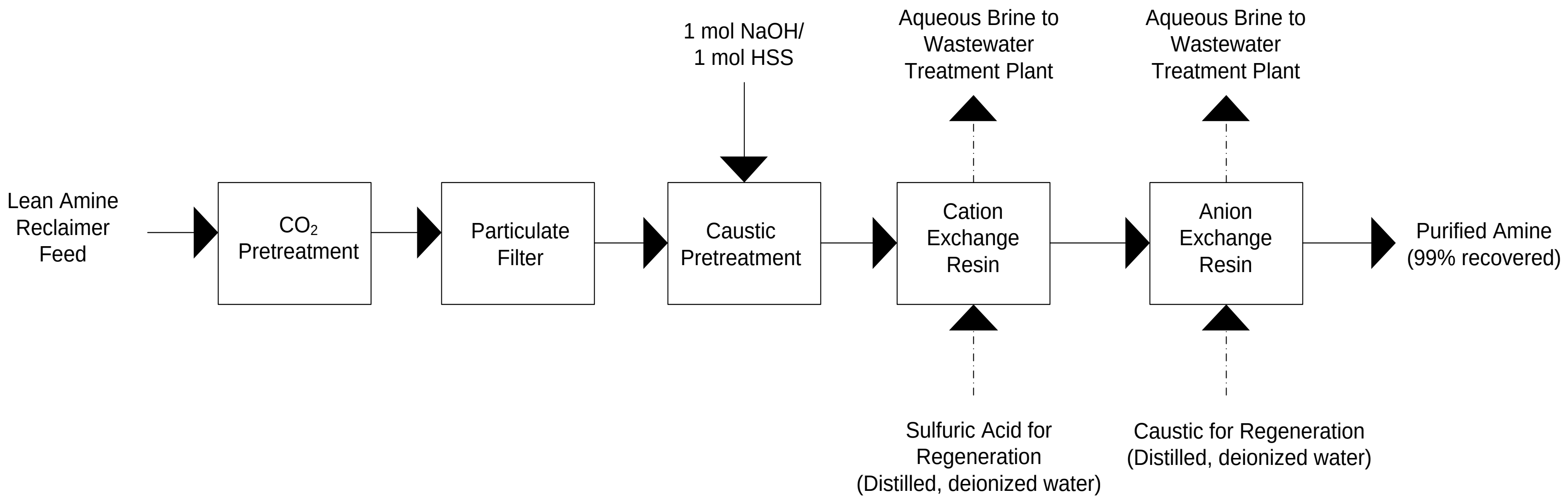


Figure 5-4 General Ion Exchange Reclaiming Process Flow Diagram

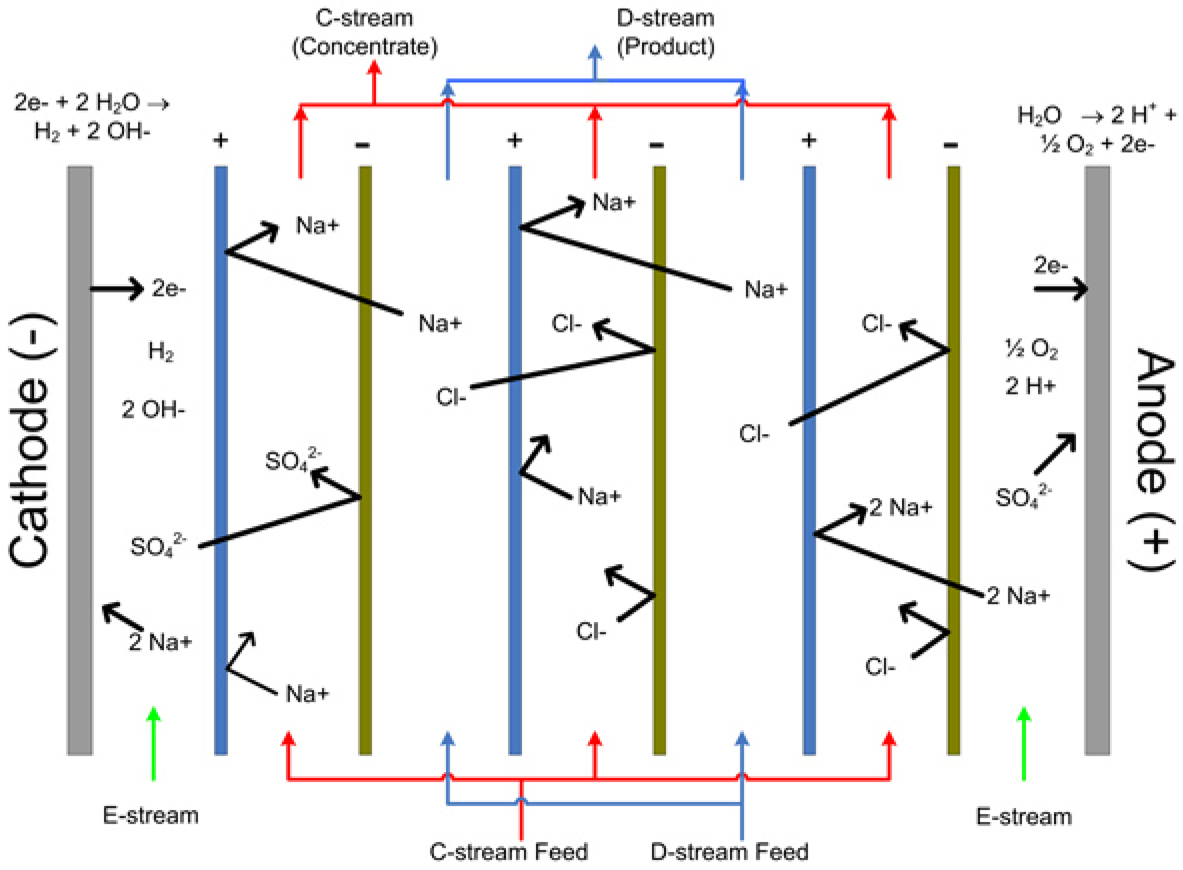
Electrodialysis Reclaiming

In electrodialysis technology 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. Alternatively, it may be preferable to take the slipstream for ion exchange reclaiming downstream of lean solvent cooler so that stream has been filtered and cooled using main solvent equipment loop.

The reaction between CO_2 and amine that forms amine carbamate should be reversed before caustic pretreatment of the reclaimer feed; this is similar to the method mentioned for the other two reclaiming technologies in the previous sections. Next, the contaminated amine is sent through a particulate filter and pretreated with caustic to reverse the reaction between acid impurities/degradation products and the amine salt by adding about one molar equivalent of NaOH per molar equivalent of heat stable salts; this reaction creates salts between sodium and the acid impurities/degradation products, and liberates the free amine.

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 (D-stream feed) to waste streams located on the opposite sides of the membrane (C-streams). A current is applied across the two electrodes, causing the cations to move toward the negatively charged cathode and the anions to move towards the positively charged anode. A negatively charged cation exchange membrane between the anode and the waste stream prevent the anions from moving further towards the anode, resulting in a concentration of the anions in the waste streams. A positively charged anion exchange membrane is placed similarly between the second waste stream and the cathode to prevent the cations from moving further towards the cathode. Ion permeable membranes used in electrodialysis are essentially sheets of ion-exchange resin (which were described in the previous section). The E-stream is an electrode stream that flows past each electrode in the stack to keep the anode and cathode wetted. Figure 5-5 provides an illustration of a typical electrodialysis cell (diagram supplied by EET Corporation).

In electrodialysis reclamation, up to 98% of the amine can be recovered, while the remaining amine passes through the membranes to the effluent streams where it cannot be recovered [4,9,10,11]. The electrodialysis process is limited to the removal of salts, allowing non-ionic impurities to accumulate in the system. Additionally, transitional metals (Hg, As, Pb, Se, etc.) are only minimally removed by electrodialysis. Transitional metals also foul membranes and the anode and cathode plates, shortening operating lifetime before membranes have to be replaced. A flow diagram of an electrodialysis reclaiming unit is given in Figure 5-6 below.



Courtesy EET Corporation
www.eetcorp.com

Figure 5-5 Illustration of Typical Electrodialysis Cell

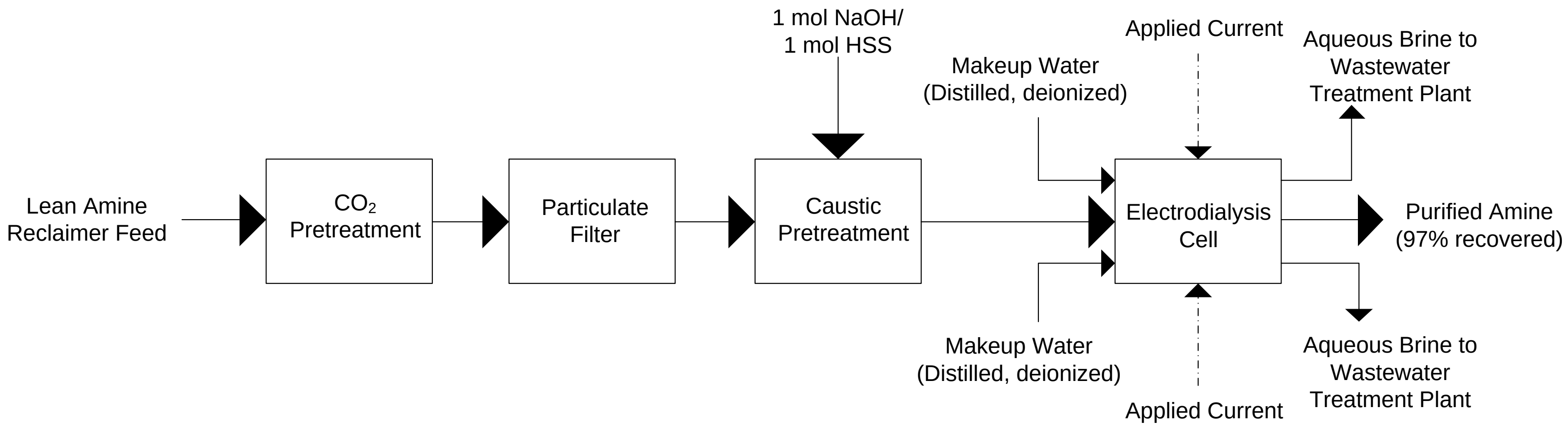


Figure 5-6 General Electrodialysis Reclaiming Process Flow Diagram

5.2 Literature Review

Trimeric conducted a literature search to identify as many publications as possible that would potentially provide information relevant to this study. Resources included conference proceedings, journal articles, patents, books and direct contacts with technology vendors and oil and gas representatives.

5.2.1 Reference Review

The literature search was based on the keyword searches “reclaimer” and “amine reclaiming” and ultimately resulted in 84 relevant publications which were reviewed by Trimeric for relevant content to develop assumptions for the reclaimer mass balances and economic analyses. The publications comprised 53 conference papers, 23 journal articles, 5 patents and 3 books. Information sought included rates of amine degradation, rates of amine recovery, equipment/energy/chemical requirements, cost information, rates of heat stable salt (HSS) removal, and waste generation.

A high level summary of the information found in the review is given in Table 5-3 and a detailed list of the publications reviewed and key content is given in Table A-1 in Appendix A.

Table 5-3 Summary of Key Information Obtained from Literature Review

	Electrodialysis	Ion Exchange	Distillation
Commercial Systems	UCARSEP (Dow)	HSSX (MPR), DOWEX (Dow), AmiPur (Eco-Tec)	CCR, MPR, CHEM Group
Reclaimer Conditions	40°C, atmospheric pressure	40°C, atmospheric pressure	MDEA: 50 - 100 mmHg (6.6-13.3 kPa) abs @ 350°F (177°C); MEA: atmospheric, 300°F (149°C)
Amine Recovery	96 to 98% recovery	99% amine recovery	85-95% recovery of 1-3% slipstream
Amine Degradation	1-2% amine losses	No degradation	3.4 - 5.6 mol amine loss/mol HSS (4-31 kg waste/ton CO_2 captured based upon multiple sources)
HSS Removal	86-97% removal	90% removal	Reduce HSS below 0.5 wt%
Cost Information	$130,000 capital costs to recover 2 lbmol/day (0.9 kmol/day) of MDEA; Operating costs of $0.28/lb ($0.62/kg) MDEA (utility, chemical costs)	Operating costs of $0.20 to $0.40/lb ($0.44 to $0.88/kg) MDEA (utility, chemical costs); capital costs of $175,000 to $200,000	MEA: $0.50/gal ($132/m^3), MDEA: $2.75/gal ($727/m^3) ($1.25/lb, or $2.75/kg, MDEA listed in another source); DGA:$8MM capital costs, $0.5MM operating costs for 50 gpm (11.4 m^3/h) unit (all costs in Canadian dollars)
Energy Requirements	$60/day power costs ($0.05/kWh); another source quotes 0.35 kWh/kg MEA for applied current (and another 0.35 kWh/kg MEA for pumping); third source quoted 4-18 kWh/1,000 gallons (1.1-4.8 kWh/m^3) for wastewater treatment	Draw downstream of lean solvent cooler and return at suction of lean amine pump	250 kW per gpm (1100 kW per m^3/h) of feed (DGA); 300,000 Btu/hr per gpm (387 kW per m^3/h) of amine (DGA); 150 psig (1034 kPa gauge) steam for MEA
Chemical Requirements	1 mol NaOH per mol HSS	1 mol NaOH per mol HSS; 1500 kg of acid and 500 kg of NaOH per cubic meter of resin	1 mol NaOH per mol HSS
Waste Generation	207-251 gal (0.8-1.0 m^3) waste generated per lbmol salt removed (~5 wt% salt solution); another source states 8.7 gal brine per gal amine	40-50% of inventory ends up as waste	5-15% of feed ends up as waste (0.8 gal, or 0.003 m^3, waste per ton CO_2)
Equipment List	Filtration, Feed pump, Membrane unit	Neutralization and filtration (one micron prefilter) required upstream of package ion exchange unit	Process requires gas-fired heater, cross exchanger, inlet separator, vapor scrubber, overhead accumulator, vacuum pump, reflux condenser, cooler and carbon filter

5.2.2 Communication with Reclaiming Vendors

Trimeric made contact with representatives from distillation, ion exchange, and electrodialysis reclaiming vendors with the intent of confirming information gathered during the literature review and gathering additional information that the literature review did not reveal, with the understanding that detailed process information would be kept confidential. Vendors commented that reclaiming costs for the different reclaiming options are often similar when all factors are considered, and technology selection may come down to operating costs and waste management preferences. For all reclaiming options, capital and operating costs can be reduced if the plant is designed around the reclaiming system, as opposed to installing an off-the-shelf unit that is not integrated into the process.

Vendors stressed that the incursion rate of heat stable salts is important when designing a reclaiming unit. As the concentration of heat stable salts entering the reclaimer decreases, it becomes more difficult to remove the contaminants – due to a lower driving force. It was also advised that for continuous, on-site reclaiming, multiple smaller units in parallel should be used for system turndown as opposed to one large reclaiming unit; the vendors suggested that the reclaiming units operate more reliabily at a constant feed rate to the reclaimer This allows the smaller units to run at full capacity and be turned on/off to deal with turndown as opposed to turning the rates for the single reclaiming unit up or down.

A representative from a reclaiming vendor with experience in on-site and off-site thermal reclaiming provided information on common distillation reclaiming practices. The typical targeted design removal is 95% of the non-volatile degradation products/metals and solids present in the amine slipstream, and the unit will run most efficiently when fed constant rates of solvent. The representative provided an equipment cost range of \$2.5MM +/- \$750,000 for a vacuum distillation unit processing approximately 4.9 gallons per minute (1.1 m^3/h) of amine solvent. However, most people lease reclaiming units as opposed to purchasing units – unless off-site reclaiming has to be performed three or more times annually, at which case it is recommended to install an on-site reclaimer.

Another contact familiar with the available options for reclaiming commented that MEA reclaimers have been successfully operated for years at atmospheric pressure. On the other hand, activated MDEA solvents behave much differently and require a vacuum distillation process in order to lower the vaporization temperature of the amine. It was suggested that vacuum distillation units have the most expensive capital equipment costs and largest energy usage (typically with hot oil or 200 psig [1,379 kPa gauge] steam used as a heat source), although operating costs are lower compared to ion exchange. Additionally, for thermal reclaiming on all types of solvents, erosion corrosion can occur at the bottom of the reboiler because of the high accumulated solids concentration.

A contact familiar with all the technologies stated that the higher contaminant removal can generally be achieved with ion exchange compared to thermal reclaiming, but in many cases it is the most expensive process to operate. Operating costs include large resin beds which will be replaced every few years, significant quantities of deionized water, and large volumes of wastewater disposal.

A representative from an ion exchange vendor also stressed that in order to minimize operating costs, it is important to optimize water usage; in some cases, it can be advantageous to regenerate the wastewater for reuse. It was cautioned that transition metals can potentially foul ion exchange beds, so if transition metals are of particular concern, thermal reclaiming could be the preferred option. However, if the incursion rate of heat stable salts in the primary concern, then ion exchange may be the preferred technology. The ion exchange vendor could not confirm reclaiming capital costs found in literature, but did state the operating costs found in literature are probably in the right range [16].

Trimeric also contacted an electrodialysis vendor. Representatives from the organization stated that wastewater generation is significantly lower than that of ion exchange. The typical average membrane lifetime is two years under normal operating conditions, and membrane cost is approximately \$250/m^2 for membranes in water treatment service.

The vendor could not confirm capital costs (including membrane costs), operating costs, energy performance, or waste generation rates found in literature for electrodialysis technology [16]. Transition metals can be removed from the amine to a certain extent, but at a significant concentration they may slowly foul the membranes and reduce the membrane performance and lifetime. A contact familiar with different amine reclaiming methods stated that the Union Carbide/Dow UCARSEP process, which is the most utilized electrodialysis reclaiming method, is typically only offered to UCARSOL amine customers. It has been claimed that electrodialysis gives superior performance compared to ion exchange, but significantly more operator attention is required to run an electrodialysis reclaiming unit.

5.2.3 Communication with Oil and Gas Representatives

After conducting the initial literature review and gathering additional information from reclaiming vendors, Trimeric contacted colleagues in the oil and gas industry to gain additional information and perspective on amine reclaiming in refinery service, with the understanding that detailed process information would be kept confidential. The contacts provided similar comments regarding the different reclaiming technologies. Corrosion is a serious concern associated with thermal reclaiming units and the majority of the units that suffered from failure due to corrosion were never replaced. In these cases of failed thermal reclaimers, bleed and feed is now practiced (sending a portion of the degraded amine to waste treatment and replacing it with fresh amine), and the waste amine is sent to the wastewater treatment plant. It was stressed that tube bundles in the heat exchanger should be stainless steel materials of construction; otherwise, if carbon steel is used, corrosion is likely to occur resulting in subsequent leaking. The vessel could be stainless or carbon steel but corrosion should be expected. The worst corrosion is usually observed at the gas/liquid interface of the reclaiming stills and is unavoidable.

One contact suggested that if a reclaiming unit is run correctly, corrosion is likely. Correct operation of a thermal reclaimer was described as running the reclaimer with a single liquid stream coming in and a single vapor stream coming out, with accumulation of salts in the reclaimer; those who run reclaimers correctly tend to corrode away the carbon steel quicker. Conversely, the same contact described running a thermal reclaimer incorrectly as running it with liquid entering and a vapor leaving but then also with a liquid stream leaving the reclaimer bottoms. In this case, the operator is just boiling off water and throwing away amine; those who run reclaimers incorrectly in this fashion tend to have less corrosion issues. Neither contact had much experience with vacuum thermal reclaiming, and one recommended that vacuum distillation only be used for MEA solutions when HSS concentration is extremely high (around 50 wt% or greater).

In refinery service, ion exchange appears to be preferred method for heat stable salt removal. A high percentage of amine is recovered, and the units require less operator attention and maintenance compared to thermal reclaiming. (It is noted that transitional metals are not contaminants in these applications, which are known to foul the ion exchange resin if present.) If occasional batch treating is required more than three times per year, then an on-site continuous unit is more economical than batch treating services. Leasing units has been preferred over purchasing units because of the operational support provided by reclaiming vendors. Anion resin regeneration involves first using a condensate to push the amine out of the resin and back into the amine system, followed by five caustic rinses and three condensate rinses. The caustic and condensate rinses are sent to the waste water treatment plant with an outfall, so no water returns to the system.

Both contacts had limited experience with electrodialysis, and could not comment on its use. Contaminant removal rates and operating costs are similar between electrodialysis and ion exchange, but ion exchange systems require much less operator attention.

5.3 **Material Balances**

The material balances developed by the University of Texas, as given in Chapter 4, are unsteady-state material balances where the rate of contaminants removed by the reclaiming unit is less than the rate of contaminants accumulated within the amine CO_2 capture system. Trimeric used the "first-hour" unsteady-state material balances developed by the University of Texas to create an "N^{th} hour" material balance, which represents a lean solvent composition into the reclaimer at steady-state conditions. The material balance was developed such that the rate of contaminants being removed from the reclaimer is equal to the rate of accumulation of contaminants and degradation products. The "N^{th}" hour is the number of hours of operation for the amine unit (without reclaiming) when sufficient concentration of impurities and degradation products have accumulated in the solvent so that when the reclaiming unit is turned on, the hourly rate of accumulation of degradation products and impurities from the reclaiming unit is equal to the hourly rate of removal of degradation products and impurities.

The material balances assume a 0.1% slipstream ratio of solvent fed to the reclaimer compared to the total circulation rate of amine within the capture process; this slipstream ratio is less than the 0.5% to 3% slipstream suggested by reclaiming vendors and given in literature, but it is required to keep solvent losses at acceptable levels [1,2,3,4,5]. Keep in mind that reclaiming continuously with a 0.1% slipstream is equivalent to batch reclaiming using a 1% slipstream for only 10% of the time. While the slipstream is lower than suggested literature values [4], the model calculated an acceptable level of heat stable salts in the circulating lean amine solvent for all cases evaluated (approximately 1.5 wt% or less HSS); suggested targeted concentrations vary but 1.5% HSS concentration is within the range of practical limits given in literature of about 1% [12] to 2.5% [13] up to 10% [14,15]. These ranges of HSS may be applicable to post-combustion capture processes as well; heat stable salts bind free amine and reduce the CO_2-carrying capacity of the solvent. The actual concentration of acceptable HSS concentration is specific to the individual application; ionic impurities from degradation and foaming inhibitors were not considered as a part of this study.

It is possible that full-scale post-combustion amine units are "first-of-a-kind" (FOAK) technology implementations where past suggested literature values for amine slipstream are not applicable [1,2,3,4,5]; another possibility to consider is that the model may be underpredicting the formation rate of degradation products in solution.

Table 5-4 below gives a breakdown of assumptions used for amine recovery by mass and the removal rate of impurities so that steady-state material balances can be developed. The amine that is not recovered overhead remains in the reclaimer waste stream as solvent loss. In all cases, 100% recovery of water and carbon dioxide was assumed.

These values were chosen for convenience for a first-pass analysis. In reality, a low level of transition metals and non-ionic, non-volatile products will be removed through the ion exchange resin and electrodialysis membranes. Similarly, a small percentage of volatile metals can potentially escape with the overhead water and amine in thermal reclaiming. Amine recovery rates were chosen based upon a review of existing literature; in reality, amine loss may be a function of the concentration of heat stable salts in the reclaimer feed [11,16].

Table 5-4 Amine Recovery and Contaminant Removal Assumptions for Reclaimer Material Balances

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

Figure 5-7 displays a block flow diagram of a generic reclaiming system which defines the streams in the material balance. The material balances for each of the eighteen base cases evaluated are given in Tables B-1 through B-18 in Appendix B. For the contaminants not removed by reclaiming (such as transition metals in the ion exchange cases), the values represent the product accumulation without reclaiming at the "Nth" hour; these contaminants will continue to accumulate in the system and will have to eventually be removed using batch thermal reclaiming.

For both the coal and natural gas combustion cases, the total rate of HSS generated is largest for the PZ cases, followed by the MDEA/PZ cases and the MEA cases; however, relative to the circulation rate of amine for CO_2 capture, MEA experiences the highest rate of HSS incursion per kg of amine solvent. For each individual solvent system, the rate of HSS generated by natural gas combustion is approximately three to four times less than coal combustion; this is because natural gas combustion flue gas does not contain as much NO_X, SO_2 and halogens that can react with the amine solvent to form heat stable salts. Rates of HSS generation for each of the eighteen base cases evaluated are given in Tables B-1 through B-18 in Appendix B.

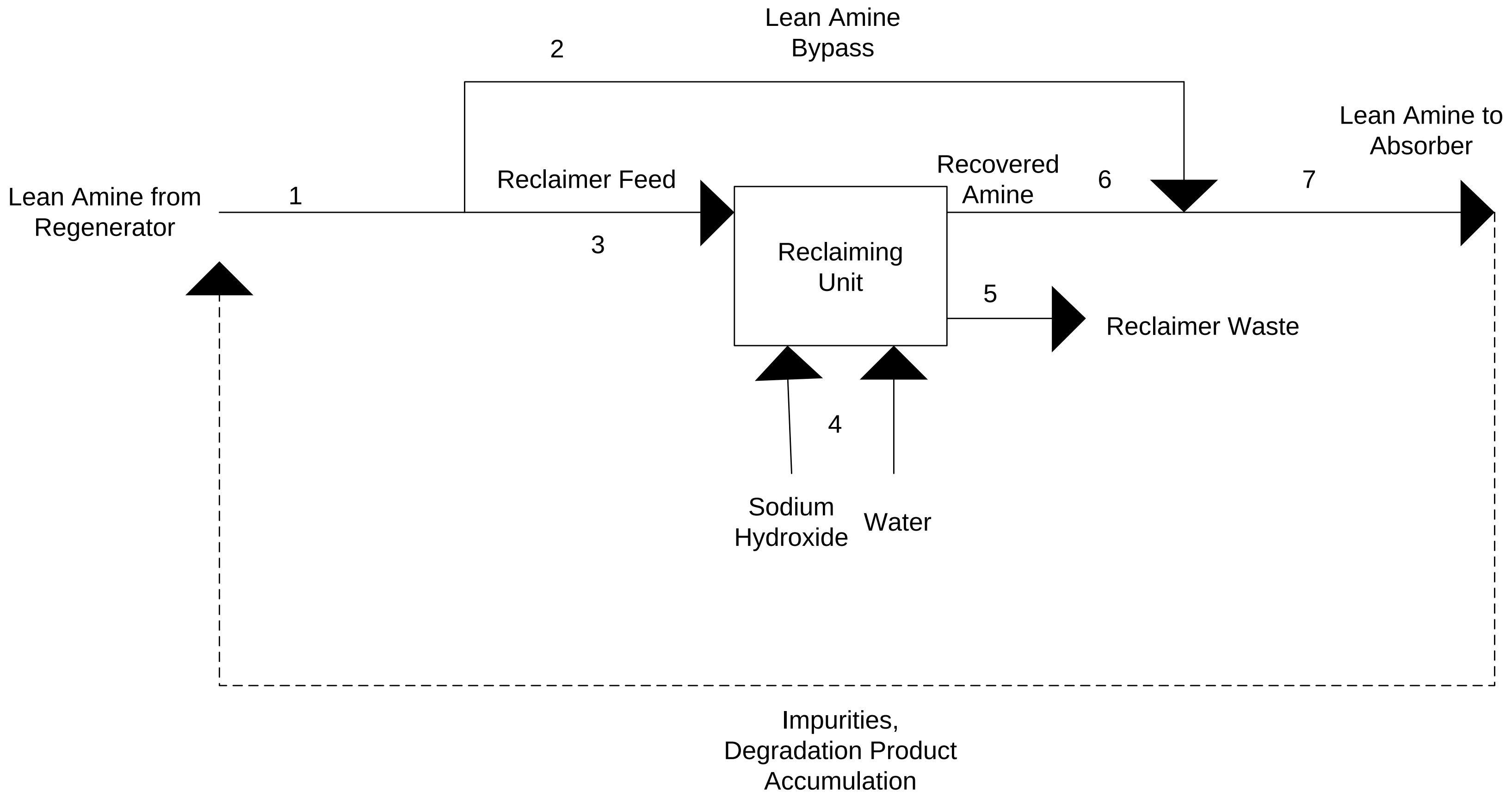


Figure 5-7 General Reclaiming System Diagram

5.4 Process Economics Evaluation

This section describes the approach used to estimate the capital and operating costs for the three reclaiming technologies for three solvent system of interest evaluated in this study at both coal and natural gas power plant operating conditions, resulting in eighteen overall cases for detailed comparison. In this section the equipment sizing and costing methodology is discussed first and then followed by a presentation of the results. The list below provides a matrix of cases that were evaluated within this technoeconomic evaluation.

- Flue gas types: coal, natural gas
- Amine solvents: MEA, PZ, MDEA/PZ
- Reclaimer types: thermal, ion exchange, electrodialysis
- Range of slipstream ratios: 0.027 to 0.111%
- Range of steady-state HSS concentrations: 0.40 to 1.65%

5.4.1 Capital Costs

As discussed in the literature review section of this chapter, amine reclaiming systems are typically sold as complete packaged units and not as individual pieces of equipment. In addition, there is a minimal amount of publicly available information regarding the capital costs of amine reclaiming systems.

In prior technoeconomic evaluations of CO_2 capture systems, the purchased equipment costs for amine reclaiming systems have been expressed as a percentage of the total purchased equipment costs for the entire capture system. Amine reclaiming vendors have suggested that this is a reasonable approach for estimating purchased equipment costs for continuous amine reclaiming units; these vendors believe that past experience has demonstrated that purchased equipment costs are similar for thermal reclaiming, ion exchange and electrodialysis, and that technology selection is based upon operating preferences and differences in annual operating costs.

A thermal reclaiming vendor provided total capital costs of $2.5MM USD (± $0.75MM USD) for a vacuum thermal distillation unit that processes approximately 4.9 gallons per minute (1.1 m^3/h) of amine solution. An evaluation provided by Bacon et al. (1988) provided total installed capital costs of $130,000 USD to recover two pound moles (0.9 kmol) per day of MDEA using electrodialysis, and total capital costs ranging from $175,000 to $200,000 USD to recover two pound moles (0.9 kmol) per day of MDEA using ion exchange (an average value of $187,500 USD was used) [16].

Assuming a 50 wt% MDEA solution, two pound moles per day of MDEA is equivalent to a flowrate of approximately 0.04 gpm (0.009 m^3/h) of amine solution; based upon these estimated flowrates, it is likely that the systems cited by Bacon were pilot-scale systems. However, in the absence of other available data from literature or reclaiming vendors, these data points were used as the capital cost basis for ion exchange and electrodialysis reclaiming systems [16]. Although the costs reported by Bacon are in 1988 dollars, a cost index was not applied to adjust the capital costs to 2013 dollars because it was assumed that present-day full-scale systems have lower unit costs (per kg of HSS processed) than the pilot-scale systems referenced by Bacon.

Assuming a cost-scaling exponent of 0.6 for capital costs based on amine throughput, it was estimated that total capital costs for an ion exchange reclaiming system processing 4.9 gpm (1.1 m^3/h) of amine are $3.35MM USD, and the total capital costs of an electrodialysis reclaiming system processing 4.9 gpm (1.1 m^3/h) of amine are $2.32MM USD.

It is assumed that the concentration of heat stable salts (HSS) in the amine solution to the reclaimer is approximately 3 wt%. This is based upon information gathered from a large number of literature sources listed in Appendix A that suggests that this concentration was in the approximate range of reported concentrations when amine solutions were subjected to batch reclaiming. A concentration of 3 wt% HSS in amine solution correlates to a mass flowrate of approximately 33 kg/hr of HSS to the reclaimer unit. This is the HSS flowrate that corresponds to the total capital costs mentioned in the prior two paragraphs in order to estimate a normalized capital cost of USD per kg/hr of HSS reclaimer feed for each reclaiming technology. These approximate normalized costs, listed in Table 5-5 below, were used as a basis for estimating capital costs for all cases detailed in this analysis.

Table 5-5 Normalized Capital Cost Estimates

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

Using these normalized costs and the rate of HSS entering the reclaimer as determined by the reclaimer material balance for each case, capital costs for each of the eighteen cases were estimated; these costs are shown in Table 5-6. An exchange rate of 1 USD to 0.75 EUR obtained on 6/17/13 was used as the exchange rate basis for this study.

Table 5-6 Estimated Capital Costs for Reclaiming Options with Assumed 0.1 wt% Slipstream

Combustion Type/Solvent	Reclaiming Technology	Estimated Capital Costs ($MM)	Estimated Capital Costs (€MM)
Coal/MEA	Thermal Reclaiming	11.0	8.2
	Ion Exchange	16.3	12.2
	Electrodialysis	11.1	8.3
NGCC/MEA	Thermal Reclaiming	3.1	2.3
	Ion Exchange	4.6	3.5
	Electrodialysis	3.1	2.4
Coal/PZ	Thermal Reclaiming	12.1	9.1
	Ion Exchange	16.2	12.2
	Electrodialysis	12.3	9.2
NGCC/PZ	Thermal Reclaiming	3.4	2.6
	Ion Exchange	5.1	3.8
	Electrodialysis	3.5	2.6
Coal/MDEA/PZ	Thermal Reclaiming	11.7	8.8
	Ion Exchange	17.4	13.0
	Electrodialysis	11.9	8.9
NGCC/MDEA/PZ	Thermal Reclaiming	3.4	2.5
	Ion Exchange	5.0	3.7
	Electrodialysis	3.4	2.5

Although specifications and costs for reclaiming systems are typically provided for packaged units (as opposed to individual components of the total system), a bottom-up purchased equipment cost estimate was constructed for coal combustion with MEA using the Aspen In Plant Cost Estimator and compared to the scaled packaged cost estimate for ion exchange reclaiming. A multiplier of three was used to scale bottom-up purchased equipment costs to total capital costs; this multiplier is a rule of thumb based upon construction of an Nth plant for a well-developed technology. This multiplier, sometimes referred to as a Lang Factor, can be as high as six for novel processes [21].

Estimated major purchased equipment costs for an ion exchange reclaiming system were based on initial quantities of ion exchange resin and stainless steel (assumed 316SS for costing purposes) vessels to house the resin. Commercial reclaiming vendors have suggested that it would be preferred to deal with turndown in reclaiming systems by having multiple units in parallel that run at constant flow rates, as opposed to having one large unit with a large turndown ratio; in this case, turndown can be achieved by turning units on or off. Four parallel units are assumed required for each of the three reclaiming technologies.

Stainless steel vessel costs were estimated using the Aspen In-Plant Cost Estimator, while initial resin cation and anion resin costs were estimated using information provided from ion exchange resin vendors. If it is assumed that six anion resin beds (two in absorption, two in regeneration and two on standby) and six cation resin beds are required for each parallel unit, and that there is sufficient resin in each bed so that the total cycle time (absorption and regeneration) per bed is approximately five hours, then the bottom-up capital costs of $16.7 MM (€12.6 MM) match the scaled package capital costs of approximately $16.3 MM (€12.2 MM) relatively closely.

In the absence of packaged capital costs information, capital costs can estimated from purchased equipment costs using a factored method reported in Version C-2 of the IEAGHG document "Criteria for Technical and Economic Assessment of Plants with Low CO_2 Emissions". The total of the purchased equipment costs and the installed costs is referred to as the purchased plant cost (PPC).

The total plant cost (TPC) is the installed cost of the plant including contingencies: engineering/home office, project contingency, and process contingency. These contingencies are expressed as a percentage of the purchased plant cost. Version C-2 of "Criteria for Technical and Economic Assessment of Plants with Low CO_2 Emissions" states that the default value for project contingency is 10% of the purchased plant cost, while process contingency and engineering are estimated at the discretion of the contractor. Per the U.S. Department of Energy (DOE)/National Energy Technology Labs (NETL) Systems Analysis Guidelines [17], process plant costs are increased by 10% to account for engineering and home office expenses and a process contingency of 5% is used for all of the cases since the amine reclaiming is a commercial process.

The total capital requirement (TCR) includes TPC, interest during construction, owner's costs, spare parts, working capital, start-up costs, and insurance/property taxes. These costs are covered in further detail below:

- The interest during construction is assumed to be the same as the standard IEAGHG discount rate (8% of the TPC); expenditure is assumed to take place at the end of each year.
- Owner's costs cover the costs of the feasibility studies, surveys, land purchase, permitting, arranging financing and other miscellaneous costs. Owner's costs are estimated to be 7% of the TPC.
- Spare parts are assumed to be 0.5% of the TPC; it is assumed that spare parts have no value at the end of the plant life due to obsolescence.
- Initial catalyst and chemical inventory is considered working capital, which includes all inventories of fuel and chemicals held in storage outside of the process plants. It is assumed that 30 days of working capital is required; this includes amine solvent, sodium hydroxide for HSS neutralization, deionized water (ion exchange and electrodialysis cases only) and sodium hydroxide/sulfuric acid for resin bed regeneration (ion exchange cases only).
- Start-up costs include 2% of the TPC, one month of chemicals costs, and three months of operating and maintenance labor costs.
- The total annual cost of insurance, local property taxes and miscellaneous regulatory and overhead fees is assumed to be 2% of the TPC.

Table 5-7 displays the estimated purchased equipment costs for the base cases, assuming a multiplier of three to scale bottom-up purchased equipment costs to total capital costs.

Table 5-7 Estimated Purchased Equipment Costs for Reclaiming Options with Assumed 0.1 wt% Slipstream

Combustion Type/Solvent	Reclaiming Technology	Estimated Purchased Equipment Costs ($MM)	Estimated Purchased Equipment Costs (€MM)
Coal/MEA	Thermal Reclaiming	3.7	2.7
	Ion Exchange	5.4	4.1
	Electrodialysis	3.7	2.8
NGCC/MEA	Thermal Reclaiming	1.0	0.8
	Ion Exchange	1.5	1.2
	Electrodialysis	1.0	0.8
Coal/PZ	Thermal Reclaiming	4.0	3.0
	Ion Exchange	5.4	4.1
	Electrodialysis	4.1	3.1
NGCC/PZ	Thermal Reclaiming	1.1	0.9
	Ion Exchange	1.7	1.3
	Electrodialysis	1.2	0.9
Coal/MDEA/PZ	Thermal Reclaiming	3.9	2.9
	Ion Exchange	5.8	4.3
	Electrodialysis	4.0	3.0
NGCC/MDEA/PZ	Thermal Reclaiming	1.1	0.8
	Ion Exchange	1.7	1.2
	Electrodialysis	1.1	0.8

5.4.2 Operating Costs

The major operating and maintenance (O&M) costs for reclaiming operations include solvent losses and other consumables, maintenance, and plant labor as shown in Tables 5-8 and 5-9. Byproduct credits and waste disposal costs are not included; they will be covered in Chapter 7 and merged with the costs covered in the TE study. The operating costs are based on a generic site location and should represent a reasonable average of those in various regions of the country.

The O&M cost factors, except for maintenance costs, were obtained from Version C-2 of "Criteria for Technical and Economic Assessment of Plants with Low CO_2 Emissions" provided by IEAGHG. The variable O&M costs were specific to the operation of the reclaiming system and depend on the capacity factor (or load factor) of the plant – which is assumed to be 85%.

The major operating and maintenance (O&M) costs are separated into two categories: fixed and variable operating costs. Fixed annual operating costs include maintenance costs and labor (operating and administrative/support). Per Version C-2 of "Criteria for Technical and Economic Assessment of Plants with Low CO_2 Emissions", maintenance costs are to be estimated independently by the study contractor. The DOE/NETL Systems Analysis Guidelines states that 2.2% of the TPC is representative of annual maintenance costs, so that factor was used for this study [17].

The 'fully burdened' cost of operating labor is assumed to be €60k (or $80k), and it is assumed that the equivalent of one operator will be required to monitor the reclaiming unit during normal operation. Administrative and support labor are assumed to be 30% of the operating and maintenance labor costs; maintenance labor is assumed to be 40% of the overall maintenance cost, hence the cost of administrative and support labor shall be 30% of the operating labor plus 12% of the total maintenance cost.

Variable operating 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 [11]. It was initially assumed that the solvent feed rate to the reclaimer is 0.1 wt% of the total lean amine circulation rate for each case. Solvent costs were assumed to be $0.87/lb ($1.91/kg) for MEA, $1.10/lb ($2.42/kg) for MDEA/PZ and $2.27/lb ($5/kg) for PZ. MEA costs were obtained from ICIS on 11/14/12 [18], MDEA costs were obtained from Oil & Gas Journal [19], and PZ costs were obtained from personal communication from the University of Texas. For the MDEA/PZ solvent, 65% of the costs attributed to solvent losses are for MDEA makeup, while the remaining 35% of the costs are for PZ makeup.

Consumables include sodium hydroxide ($0.31/lb, or $0.68/kg) for HSS neutralization, sulfuric acid ($0.03/lb, or $0.07/kg) and sodium hydroxide for regeneration of ion exchange beds (ion exchange cases only) and distilled, deionized water ($1.90/1,000 gallons, or $0.50/m^3) for resin bed flushing/regeneration for ion exchange reclaiming, and for removal of salts for electrodialysis reclaiming. Bulk sodium hydroxide costs were obtained from ICIS [18], bulk sulfuric acid costs were obtained from Fertilizer Week Market Analysis published on 9/19/12 [20], and distilled, deionized water costs were taken from Peters and Timmerhaus [21]. Table 5-8 details water usage for the ion exchange and electrodialysis technologies. For ion exchange reclaiming, water is used for rinsing the resin beds and for dilution of sulfuric acid and sodium hydroxide eluents; for electrodialysis reclaiming, water is used for creating the electrolyte streams and as makeup for the aqueous waste streams It was assumed that the minimum amount of water required would result in aqueous waste streams with a water concentration of 95 wt%.

Table 5-8 Estimated Water Usage for Reclaiming Options with Assumed 0.1 wt% Slipstream

Combustion Type/Solvent	Reclaiming Technology	Estimated Water Usage, gpm (m^3/hr)
Coal/MEA	Thermal Reclaiming	N/A
	Ion Exchange	28 (6.4)
	Electrodialysis	27 (6.1)
NGCC/MEA	Thermal Reclaiming	N/A
	Ion Exchange	9 (2.0)
	Electrodialysis	9 (2.0)
Coal/PZ	Thermal Reclaiming	N/A
	Ion Exchange	35 (7.9)
	Electrodialysis	40 (9.1)
NGCC/PZ	Thermal Reclaiming	N/A
	Ion Exchange	11 (2.5)
	Electrodialysis	15 (3.4)
Coal/MDEA/PZ	Thermal Reclaiming	N/A
	Ion Exchange	38 (8.6)
	Electrodialysis	51 (11.6)
NGCC/MDEA/PZ	Thermal Reclaiming	N/A
	Ion Exchange	13 (3.0)
	Electrodialysis	20 (4.5)

Ion exchange resin and electrodialysis membrane replacement costs were also categorized as variable annual operating costs. A rule of thumb for the capacity of ion exchange resins is approximately 1 m^3 resin required per kg-mol of HSS removed. This estimated capacity, along with an assumed total cycle time of five hours along with the assumption of 6 anion beds and 6 cation beds per parallel unit, help set the total resin requirements for the reclaimer system. Normalized resin costs for both anion and cation exchange resins were obtained from prior projects. Literature suggests that clean service resins can last up to five years for anion resins, and from five to ten years for cation resins. Based upon this literature information, it was assumed that ion exchange resins lasted five years for NGCC cases (“clean service”), and two and a half 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.). These intermediate resin costs were then normalized on an annual cost basis.

Literature suggests that chloralkali membranes have a total lifetime of five years in clean service [22]. Based upon this literature [22], similar assumptions to the ion exchange cases were made, in that electrodialysis membranes lasted five years for NGCC cases and two and a half years for coal cases. Electrodialysis membrane costs were not explicitly stated in literature that was reviewed in Appendix A, so it was assumed that the membrane costs were 25% of the total purchased equipment costs. These intermediate membrane costs were then normalized on an annual cost basis. Tables 5-9 and 5-10 display total annual operating costs (in addition to individual categories of costs) for each of the 18 base cases in both USD and EUR.

O&M costs associated with solvent losses are greatest for thermal reclaiming, followed by electrodialysis and ion exchange reclaiming. These costs are directly a function of the assumptions made in Table 5-4 for amine recovery. 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.

Table 5-9 Estimated Annual Operating Costs for Reclaiming Options (USD)

Reclaiming Technology	Total Annual Operating Costs ($MM)	Fixed O&M Costs ($MM)	Solvent Losses ($MM)	Other Consumables ($MM)	Resin or Membrane Replacement Costs ($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	3.6	0.8	1.2	0.5	1.1
MEA NGCC - Thermal Reclaiming	1.4	0.3	1.0	0.1	-
MEA NGCC - Ion Exchange	1.3	0.4	0.2	0.5	0.2
MEA NGCC - Electrodialysis	1.2	0.3	0.6	0.2	0.2
PZ Coal - Thermal Reclaiming	14.4	0.9	13.1	0.5	-
PZ Coal - Ion Exchange	7.1	1.1	2.6	1.9	1.4
PZ Coal - Electrodialysis	10.5	0.9	7.8	0.6	1.2
PZ NGCC - Thermal Reclaiming	7.1	0.3	6.6	0.1	-
PZ NGCC - Ion Exchange	2.5	0.4	1.3	0.5	0.2
PZ NGCC - Electrodialysis	4.6	0.3	4.0	0.2	0.2
MDEA/PZ Coal - Thermal Reclaiming	11.9	0.9	10.6	0.5	-
MDEA/PZ Coal - Ion Exchange	6.5	1.2	2.1	1.8	1.4
MDEA/PZ Coal - Electrodialysis	9.0	0.9	6.4	0.6	1.2
MDEA/PZ NGCC - Thermal Reclaiming	5.2	0.3	4.8	0.1	-
MDEA/PZ NGCC - Ion Exchange	2.1	0.4	1.0	0.6	0.2
MDEA/PZ NGCC - Electrodialysis	3.5	0.3	2.9	0.2	0.2

Table 5-10 Estimated Annual Operating Costs for Reclaiming Options (EUR)

Reclaiming Technology	Total Annual Operating Costs (€MM)	Fixed O&M Costs (€MM)	Solvent Losses (€MM)	Other Consumables (€MM)	Resin or Membrane Replacement Costs (€MM)
MEA Coal - Thermal Reclaiming	2.4	0.6	1.5	0.3	-
MEA Coal - Ion Exchange	3.4	0.9	0.3	1.2	1.0
MEA Coal - Electrodialysis	2.7	0.6	0.9	0.4	0.8
MEA NGCC - Thermal Reclaiming	1.0	0.2	0.7	0.1	-
MEA NGCC - Ion Exchange	0.9	0.3	0.1	0.4	0.1
MEA NGCC - Electrodialysis	0.9	0.2	0.4	0.1	0.1
PZ Coal - Thermal Reclaiming	10.8	0.7	9.8	0.4	-
PZ Coal - Ion Exchange	5.3	0.8	2.0	1.4	1.1
PZ Coal - Electrodialysis	7.9	0.7	5.9	0.4	0.9
PZ NGCC - Thermal Reclaiming	5.3	0.3	5.0	0.1	-
PZ NGCC - Ion Exchange	1.9	0.3	1.0	0.4	0.1
PZ NGCC - Electrodialysis	3.5	0.2	3.0	0.1	0.1
MDEA/PZ Coal - Thermal Reclaiming	8.9	0.7	7.9	0.3	-
MDEA/PZ Coal - Ion Exchange	4.9	0.9	1.6	1.4	1.0
MDEA/PZ Coal - Electrodialysis	6.7	0.7	4.8	0.4	0.9
MDEA/PZ NGCC - Thermal Reclaiming	3.9	0.2	3.6	0.1	-
MDEA/PZ NGCC - Ion Exchange	1.6	0.3	0.7	0.4	0.1
MDEA/PZ NGCC - Electrodialysis	2.7	0.2	2.1	0.1	0.1

5.4.3 Energy Requirements

The energy requirements to operate the reclaiming unit are withdrawn from the main power facility output either through electricity or steam. This decreases the net electrical output of the plant. Power requirements of electric motors (i.e., solvent pumps, vacuum pumps) translate directly to electrical derating (a decrease in MW_e); this applies as well for direct current required to electrically power electrodialysis reclaimer units.

As a conservative estimate, thermal energy demand is assumed to be the energy requirements for complete water and amine vaporization. CO_2 pre-treatment is a novel step specific to post-combustion capture from flue gas (for traditional acid gas treating, the lean CO_2 loading of the solvent entering the reclaiming unit is essentially zero). In this study, the energy demand for CO_2 pretreatment has been excluded (though it will be required for all reclaiming technologies).

Energy requirements that are supplied using steam, such as the heat requirements for thermal reclaimer reboilers, are converted into electrical derating by calculating the amount of electrical generating capacity that the steam would have supplied to the main power facility had the steam not been diverted to the CO_2 capture system. The low-pressure steam in a power plant is typically discharged from the low-pressure turbine (85% isentropic efficiency) at a pressure of 1 psia (6.9 kPa absolute). Based upon conversations with thermal reclaiming vendors, it was assumed that superheated steam was extracted at 200 psig (1379 kPa gauge); it may be preferable to use the same steam quality for the reboiler and the thermal reclaimer. The steam taken from the turbine will be de-superheated with steam condensate exiting the reboiler, so the superheated steam mass flow rate will be less than the saturated steam mass flow rate. This is taken into account in the reboiler derating calculations.

During the detailed design of a thermal reclaimer, there is opportunity for heat recovery with MEA thermal reclaiming at elevated pressures (i.e. regeneration pressure). If thermal reclaiming occurs at stripper pressure, vaporized water and amine can be returned directly to the regenerator; this reduces the energy requirement for the regenerator reboiler. PZ and MDEA/PZ thermal reclaiming will probably be operated at a pressure lower than regenerator pressure, so returning the vapor directly to the regenerator is not an option.

The categories of electrical derating are described below:

- Lean solvent pump work (all cases) – It is 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. Therefore, the reclaiming system will require an incremental amount of pump power for this recycle loop of amine.
- Reboiler thermal energy requirements (thermal reclaiming cases) – It is assumed that the reboiler thermal energy requirement is equivalent to the theoretical energy required to vaporize all water and amine in the feed to the reclaiming system. The value for heat of vaporization of water was assumed at 180°C (866 Btu/lb, or 2010 kJ/kg), while values for the standard heats of vaporization for MEA (360 Btu/lb, or 836 kJ/kg), PZ (320 Btu/lb, or 743 kJ/kg) and MDEA (200 Btu/lb, or 464 kJ/kg) were obtained from MSDS sheets. A derating factor of 0.1211 hp-hr per lb of saturated steam (0.1985 kW-hr per kg 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 is assumed that electricity consumption for vacuum pumps are approximately 100 kW.
- Applied current (electrodialysis cases) – Literature suggests that the electricity requirements for electrodialysis of amines if approximately 0.35 kWh per kg of amine fed to the reclaiming unit [23].

Table 5-11 provides normalized energy requirements for each of the base cases in terms of kWh per 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 ouput), 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.

Table 5-11 Estimated Energy Requirements for Reclaiming Options

Combustion Type/Solvent	Reclaiming Technology	Estimated Energy Requirements (MW_e)	Estimated Energy Requirements (kWh/kg HSS reclaimed)
Coal/MEA	Thermal Reclaiming	1.5	10.4
	Ion Exchange	0.015	0.1
	Electrodialysis	1.0	6.7
NGCC/MEA	Thermal Reclaiming	0.7	17.6
	Ion Exchange	0.012	0.3
	Electrodialysis	0.5	11.3
Coal/PZ	Thermal Reclaiming	2.5	15.4
	Ion Exchange	0.011	0.1
	Electrodialysis	2.4	15.0
NGCC/PZ	Thermal Reclaiming	1.3	27.7
	Ion Exchange	0.013	0.3
	Electrodialysis	1.2	26.9
Coal/MDEA/PZ	Thermal Reclaiming	2.9	19.1
	Ion Exchange	0.036	0.2
	Electrodialysis	4.0	26.0
NGCC/MDEA/PZ	Thermal Reclaiming	1.4	31.2
	Ion Exchange	0.016	0.4
	Electrodialysis	1.8	40.9

Annualized costs for energy requirements were estimated assuming that parasitic energy requirements (converted from MW of electricity to kWh/yr of electricity) cost 12 ¢/kWh. . Table 5-12 provides the annualized energy costs for each of the eighteen base cases.

Table 5-12 Estimated Annual Energy Costs for Reclaiming Options

Combustion Type/Solvent	Reclaiming Technology	Estimated Annual Energy Costs ($MM)	Estimated Annual Energy Costs (€MM)
Coal/MEA	Thermal Reclaiming	1.3	1.0
	Ion Exchange	0.01	0.01
	Electrodialysis	0.9	0.6
NGCC/MEA	Thermal Reclaiming	0.6	0.5
	Ion Exchange	0.01	0.01
	Electrodialysis	0.4	0.3
Coal/PZ	Thermal Reclaiming	2.2	1.7
	Ion Exchange	0.01	0.01
	Electrodialysis	2.1	1.6
NGCC/PZ	Thermal Reclaiming	1.1	0.8
	Ion Exchange	0.01	0.01
	Electrodialysis	1.1	0.8
Coal/MDEA/PZ	Thermal Reclaiming	2.6	2.0
	Ion Exchange	0.03	0.02
	Electrodialysis	3.6	2.7
NGCC/MDEA/PZ	Thermal Reclaiming	1.2	0.9
	Ion Exchange	0.01	0.01
	Electrodialysis	1.6	1.2

5.4.4 Economic Analysis and Results

This section uses the annualized cost summary to compare the cost of electricity and the cost of CO_2 captured for the eighteen base cases. The TCR, total O&M costs, and total annualized energy costs can be utilized to estimate the total annual revenue requirement (TRR).

TRR = (TCR * CRF) + Annual O&M Costs + Annual Energy Costs

The CRF is also known as the capital recovery factor, and it can be estimated via the following equation from Peters and Timmerhaus [21]:

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

In the above expression for CRF, *n* represents the plant life and *i* represents the discount rate. Per Version C-2 of "Criteria for Technical and Economic Assessment of Plants with Low CO_2 Emissions", the standard plant life of 25 years shall be used for economic assessments and the standard discount (interest) rate is 8%. Multiplying the capital recovery factor by the total capital requirements results in an estimate of the annualized capital costs. Tables 5-13 and 5-14 present the annualized capital costs and total revenue requirement for each of the base cases.

Table 5-13 Estimated Annual Revenue Requirements for Reclaiming Options (USD)

	Total Annual Operating Costs ($MM)	Annual Energy Costs ($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	0.013	1.5	6.0
MEA Coal -Electrodialysis	3.6	0.9	1.0	5.5
MEA NGCC - Thermal Reclaiming	1.4	0.6	0.3	2.3
MEA NGCC - Ion Exchange	1.3	0.011	0.4	1.7
MEA NGCC - Electrodialysis	1.2	0.4	0.3	1.9
PZ Coal - Thermal Reclaiming	14.4	2.2	1.1	17.8
PZ Coal - Ion Exchange	7.1	0.010	1.5	8.6
PZ Coal - Electrodialysis	10.5	2.1	1.2	13.8
PZ NGCC - Thermal Reclaiming	7.1	1.1	0.3	8.5
PZ NGCC - Ion Exchange	2.5	0.012	0.5	3.0
PZ NGCC - Electrodialysis	4.6	1.1	0.3	6.0
MDEA/PZ Coal - Thermal Reclaiming	11.9	2.6	1.1	15.6
MDEA/PZ Coal - Ion Exchange	6.5	0.032	1.6	8.2
MDEA/PZ Coal - Electrodialysis	9.0	3.6	1.1	13.7
MDEA/PZ NGCC - Thermal Reclaiming	5.2	1.2	0.3	6.8
MDEA/PZ NGCC - Ion Exchange	2.1	0.014	0.5	2.6
MDEA/PZ NGCC - Electrodialysis	3.5	1.6	0.3	5.5

Table 5-14 Estimated Annual Revenue Requirements for Reclaiming Options (EUR)

	Total Annual Operating Costs (€MM)	Annual Energy Costs (€MM)	Annualized Capital Costs (€MM)	Total Revenue Requirement (€MM)
MEA Coal - Thermal Reclaiming	2.4	1.0	0.8	4.2
MEA Coal - Ion Exchange	3.4	0.010	1.1	4.5
MEA Coal - Electrodialysis	2.7	0.6	0.8	4.1
MEA NGCC - Thermal Reclaiming	1.1	0.5	0.2	1.7
MEA NGCC - Ion Exchange	1.0	0.008	0.3	1.3
MEA NGCC - Electrodialysis	0.9	0.3	0.2	1.4
PZ Coal - Thermal Reclaiming	10.8	1.7	0.8	13.3
PZ Coal - Ion Exchange	5.3	0.008	1.1	6.4
PZ Coal - Electrodialysis	7.9	1.6	0.9	10.4
PZ NGCC - Thermal Reclaiming	5.3	0.8	0.2	6.4
PZ NGCC - Ion Exchange	1.9	0.009	0.4	2.2
PZ NGCC - Electrodialysis	3.5	0.8	0.2	4.5
MDEA/PZ Coal - Thermal Reclaiming	8.9	2.0	0.8	11.7
MDEA/PZ Coal - Ion Exchange	4.9	0.024	1.2	6.1
MDEA/PZ Coal - Electrodialysis	6.8	2.7	0.8	10.2
MDEA/PZ NGCC - Thermal Reclaiming	3.9	0.9	0.2	5.1
MDEA/PZ NGCC - Ion Exchange	1.6	0.011	0.4	2.0
MDEA/PZ NGCC - Electrodialysis	2.6	1.2	0.2	4.1

The cost of electricity attributed to reclaiming for each of the eighteen base cases was calculated using the following equation:

$$Cost\ of\ Electricity\ \left(\frac{¢}{kWh}\right) = \frac{TRR\ (\frac{\$}{yr})}{Annual\ Electric\ Output\ (\frac{kwh}{yr})} * (\frac{100¢}{1\$})$$

The cost of reclaiming per ton of CO_2 captured was calculated using the equation below. It is assumed that coal combustion emits 0.834 MT CO_2 per MWh of electricity and natural gas combustion emits 0.349 MT CO_2 per MWh of electricity generated [7]. 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.

$$Reclaiming\ Costs\ \left(\frac{\$}{ton\ CO_2\ captured}\right) = \frac{TRR\ (\frac{\$}{yr})}{Annual\ Elec.Output\ \left(\frac{kwh}{yr}\right) * {}^{MT\ CO_2}/_{MWh\ Elec.Output} * {}^{1\ MWh}/_{1000\ kWh} * 0.9}$$

Table 5-15 presents the cost of electricity attributed to reclaiming in ¢/kWh and €/kWh, and the cost of reclaiming per ton of CO_2 captured in both \$/ton and €/ton.

Table 5-15 Estimated Normalized Reclaiming Costs

	$/MT CO_2	¢/kWh	€/MT CO_2	€/kWh
MEA Coal - Thermal Reclaiming	1.11	0.08	0.84	0.0006
MEA Coal - Ion Exchange	1.20	0.09	0.90	0.0007
MEA Coal - Electrodialysis	1.10	0.08	0.82	0.0006
MEA NGCC - Thermal Reclaiming	1.23	0.04	0.92	0.0003
MEA NGCC - Ion Exchange	0.90	0.03	0.68	0.0002
MEA NGCC - Electrodialysis	1.01	0.03	0.75	0.0002
PZ Coal - Thermal Reclaiming	3.53	0.26	2.65	0.0020
PZ Coal - Ion Exchange	1.71	0.13	1.28	0.0010
PZ Coal - Electrodialysis	2.74	0.21	2.06	0.0015
PZ NGCC - Thermal Reclaiming	4.50	0.14	3.37	0.0011
PZ NGCC - Ion Exchange	1.58	0.05	1.19	0.0004
PZ NGCC - Electrodialysis	3.20	0.10	2.40	0.0008
MDEAPZ Coal - Thermal Reclaiming	3.11	0.23	2.33	0.0018
MDEA/PZ Coal - Ion Exchange	1.63	0.12	1.22	0.0009
MDEA/PZ Coal - Electrodialysis	2.71	0.20	2.04	0.0015
MDEA/PZ NGCC - Thermal Reclaiming	3.58	0.11	2.69	0.0008
MDEA/PZ NGCC - Ion Exchange	1.61	0.05	1.21	0.0004
MDEA/PZ NGCC - Electrodialysis	2.89	0.09	2.17	0.0007

5.5 Effect of Initial Assumptions

A brief examination of Tables 5-13 through 5-15 in the prior section reveals that the estimated total revenue requirement and normalized economics for the reclaiming cases using PZ and MDEA/PZ are significantly higher than the reclaiming cases using MEA solvent. This cost difference is more noticeable for the thermal reclaiming and electrodialysis cases; this difference can be attributed primarily to higher annual operating costs due to solvent losses, in addition to higher annual energy costs.

These differences are primarily a function of the initial assumptions that were made to fix the slipstream feed to the reclaimer as a percentage of the total lean solvent circulation, and to also fix amine losses as a percentage of the total slipstream feed. The implications of these assumptions can be illustrated in Table 5-16, which lists the concentration of heat stable salts in the steady-state recirculating lean amine solvent (which also happens to be the concentration of HSS in the reclaimer feed) when a slipstream of 0.1 wt% of the total solvent circulation rate is assumed. HSS removal efficiencies are consistent with values assumed in Table 5-4.

Table 5-16 Concentration of Heat Stable Salts in Reclaimer Feed with Assumed 0.1 Wt% Slipstream

Combustion Type/Solvent	Reclaiming Technology	Wt% HSS in Circulating Amine
Coal/MEA	Thermal Reclaiming	1.48
	Ion Exchange	1.64
	Electrodialysis	1.61
NGCC/MEA	Thermal Reclaiming	0.89
	Ion Exchange	0.98
	Electrodialysis	0.97
Coal/PZ	Thermal Reclaiming	0.82
	Ion Exchange	0.91
	Electrodialysis	0.89
NGCC/PZ	Thermal Reclaiming	0.46
	Ion Exchange	0.52
	Electrodialysis	0.51
Coal/MDEA/PZ	Thermal Reclaiming	0.64
	Ion Exchange	0.71
	Electrodialysis	0.69
NGCC/MDEA/PZ	Thermal Reclaiming	0.40
	Ion Exchange	0.45
	Electrodialysis	0.44

Table 5-16 shows that the concentration of HSS in the reclaimer feed is significantly lower for the PZ and MDEA/PZ cases compared to the MEA cases. For these PZ and MDEA/PZ cases, there are low concentrations of heat stable salts entering the reclaimer because there is too much additional amine solvent being carried through the reclaimer. While this does not affect the estimated purchased equipment costs (which are normalized relative the feed rate of HSS entering the reclaimer), feeding unnecessarily high rates of amine to the reclaimer results in high solvent losses (because an assumed fixed percentage of amine into the reclaimer is lost for each type of reclaiming) and high annual energy costs (because for thermal reclaiming all amine and water is vaporized, and for electrodialysis energy requirements are a function of the mass rate of amine entering the reclaimer).

It is important to clarify that the original assumption of a 0.1 wt% slipstream (mass rate of reclaimer feed relative to the mass rate of lean amine recirculating within the CO_2 capture system) is not necessarily the "optimum" slipstream. This assumption was made for all 18 base cases because this slipstream value reduced absolute solvent losses to acceptable levels from a cost standpoint (as opposed to assuming a 1 wt% to 3 wt% slipstream as suggested by literature) while keeping heat-stable salt concentrations at acceptable levels in the recirculating amine solvent [1,2,3,4,5]. As of right now, the assumption is that a HSS concentration less than 1.5 wt% in the reclaimer feed is acceptable; this is an arbitrary assumption based upon conversation with reclaiming vendors. This assumption also resulted in waste stream compositions that retained enough amine in the waste sludge to have a high enough heating value for co-firing, and also have metals concentrations that may avoid hazardous waste classification (for the thermal reclaiming cases).

In reality, the plant operator may want to fine tune the slipstream ratio in order to achieve a certain concentration of heat-stable salts in the circulating amine solution, to achieve a finite amount of amine losses from the reclaiming unit, or achieve a desired waste profile for a particular reclaiming process. Economics in Section 5.5 were explored further with the assumption that the slipstream ratio was adjusted for each case in order to achieve a HSS concentration of 1.5 wt% in the feed to the reclaiming unit; Table 5-17 displays the reclaimer slipstream necessary to achieve a HSS concentration of 1.5 wt% in the feed to the reclaiming unit. Table 5-18 provides a summary of normalized energy requirements, Tables 5-19 and 5-20 display a breakdown of annual operating costs with this alternative assumption, while Tables 5-21 through 5-23 display total revenue requirements and normalized economics.

Table 5-17 Slipstream Ratio with Assumed HSS Reclaimer Feed Concentration of 1.5 wt%

Combustion Type/Solvent	Reclaiming Technology	% Slipstream to Reclaimer
Coal/MEA	Thermal Reclaiming	0.100
	Ion Exchange	0.111
	Electrodialysis	0.109
NGCC/MEA	Thermal Reclaiming	0.060
	Ion Exchange	0.066
	Electrodialysis	0.066
Coal/PZ	Thermal Reclaiming	0.055
	Ion Exchange	0.061
	Electrodialysis	0.060
NGCC/PZ	Thermal Reclaiming	0.031
	Ion Exchange	0.035
	Electrodialysis	0.034
Coal/MDEA/PZ	Thermal Reclaiming	0.043
	Ion Exchange	0.048
	Electrodialysis	0.047
NGCC/MDEA/PZ	Thermal Reclaiming	0.027
	Ion Exchange	0.030
	Electrodialysis	0.030

Table 5-18 Comparison of Estimated Energy Requirements for Reclaiming Based Upon Reclaimer Feed Assumptions

Reclaiming Technology	Estimated Energy Requirements (kWh/kg HSS reclaimed) – Assume Constant Slipstream %	Estimated Energy Requirements (kWh/kg HSS reclaimed) – Assume Constant HSS Conc.
MEA Coal - Thermal Reclaiming	10.4	10.4
MEA Coal - Ion Exchange	0.1	0.1
MEA Coal -Electrodialysis	6.7	7.3
MEA NGCC - Thermal Reclaiming	17.6	10.6
MEA NGCC - Ion Exchange	0.3	0.2
MEA NGCC - Electrodialysis	11.3	7.4
PZ Coal - Thermal Reclaiming	15.4	8.5
PZ Coal - Ion Exchange	0.1	0.04
PZ Coal - Electrodialysis	15.0	9.0
PZ NGCC - Thermal Reclaiming	27.7	8.6
PZ NGCC - Ion Exchange	0.3	0.1
PZ NGCC - Electrodialysis	26.9	9.3
MDEA/PZ Coal - Thermal Reclaiming	19.1	8.2
MDEA/PZ Coal - Ion Exchange	0.2	0.1
MDEA/PZ Coal - Electrodialysis	26.0	12.1
MDEA/PZ NGCC - Thermal Reclaiming	31.2	8.4
MDEA/PZ NGCC - Ion Exchange	0.4	0.1
MDEA/PZ NGCC - Electrodialysis	40.9	12.1

Table 5-19 Estimated Annual Operating Costs for Reclaiming Options for Alternate Case Assuming Constant HSS Concentration in Reclaimer Feed (USD)

Reclaiming Technology	Total Annual Operating Costs ($MM)	Fixed O&M Costs ($MM)	Solvent Losses ($MM)	Other Consumables ($MM)	Resin or Membrane Replacement Costs ($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

Table 5-20 Estimated Annual Operating Costs for Reclaiming Options for Alternate Case Assuming Constant HSS Concentration in Reclaimer Feed (EUR)

Reclaiming Technology	Total Annual Operating Costs (€MM)	Fixed O&M Costs (€MM)	Solvent Losses (€MM)	Other Consumables (€MM)	Resin or Membrane Replacement Costs (€MM)
MEA Coal - Thermal Reclaiming	2.4	0.6	1.5	0.3	-
MEA Coal - Ion Exchange	3.4	0.9	0.3	1.2	1.0
MEA Coal - Electrodialysis	2.8	0.6	1.0	0.4	0.8
MEA NGCC - Thermal Reclaiming	0.8	0.2	0.4	0.1	-
MEA NGCC - Ion Exchange	0.9	0.3	0.1	0.4	0.1
MEA NGCC - Electrodialysis	0.7	0.2	0.3	0.1	0.1
PZ Coal - Thermal Reclaiming	6.5	0.7	5.4	0.4	-
PZ Coal - Ion Exchange	4.5	0.8	1.2	1.4	1.1
PZ Coal - Electrodialysis	5.5	0.7	3.5	0.4	0.9
PZ NGCC - Thermal Reclaiming	1.9	0.3	1.5	0.1	-
PZ NGCC - Ion Exchange	1.2	0.3	0.3	0.4	0.1
PZ NGCC - Electrodialysis	1.5	0.2	1.0	0.1	0.1
MDEA/PZ Coal - Thermal Reclaiming	4.5	0.7	3.4	0.3	-
MDEA/PZ Coal - Ion Exchange	4.1	0.9	0.8	1.4	1.0
MDEA/PZ Coal - Electrodialysis	4.2	0.7	2.2	0.4	0.9
MDEA/PZ NGCC - Thermal Reclaiming	1.3	0.2	1.0	0.1	-
MDEA/PZ NGCC - Ion Exchange	1.1	0.3	0.2	0.4	0.1
MDEA/PZ NGCC - Electrodialysis	1.1	0.2	0.6	0.1	0.1

Table 5-21 Estimated Annual Revenue Requirements for Reclaiming Options for Alternate Case Assuming Constant HSS Concentration in Reclaimer Feed (USD)

Reclaiming Technology	Total Annual Operating Costs ($MM)	Annual Energy Costs ($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

Table 5-22 Estimated Annual Revenue Requirements for Reclaiming Options for Alternate Case Assuming Constant HSS Concentration in Reclaimer Feed (EUR)

Reclaiming Technology	Total Annual Operating Costs (€MM)	Annual Energy Costs (€MM)	Annualized Capital Costs (€MM)	Total Revenue Requirement (€MM)
MEA Coal - Thermal Reclaiming	2.4	1.0	0.8	4.2
MEA Coal - Ion Exchange	3.4	0.011	1.1	4.6
MEA Coal - Electrodialysis	2.8	0.7	0.8	4.3
MEA NGCC - Thermal Reclaiming	0.8	0.3	0.2	1.3
MEA NGCC - Ion Exchange	0.9	0.005	0.3	1.2
MEA NGCC - Electrodialysis	0.8	0.2	0.2	1.2
PZ Coal - Thermal Reclaiming	6.5	0.9	0.8	8.2
PZ Coal - Ion Exchange	4.5	0.005	1.1	5.7
PZ Coal - Electrodialysis	5.6	1.0	0.9	7.4
PZ NGCC - Thermal Reclaiming	1.9	0.3	0.2	2.4
PZ NGCC - Ion Exchange	1.2	0.003	0.4	1.6
PZ NGCC - Electrodialysis	1.5	0.3	0.2	2.0
MDEAPZ Coal - Thermal Reclaiming	4.4	0.9	0.8	6.1
MDEA/PZ Coal - Ion Exchange	4.1	0.012	1.2	5.3
MDEA/PZ Coal - Electrodialysis	4.2	1.3	0.8	6.3
MDEA/PZ NGCC - Thermal Reclaiming	1.3	0.2	0.2	1.8
MDEA/PZ NGCC - Ion Exchange	1.1	0.003	0.4	1.4
MDEA/PZ NGCC - Electrodialysis	1.1	0.4	0.2	1.7

Table 5-23 Estimated Normalized Reclaiming Costs for Alternate Case Assuming Constant HSS Concentration in Reclaimer Feed

Reclaiming Technology	\$/MT CO_2	¢/kWh	€/MT CO_2	€/kWh
MEA Coal - Thermal Reclaiming	1.11	0.08	0.84	0.0006
MEA Coal - Ion Exchange	1.21	0.09	0.90	0.0007
MEA Coal - Electrodialysis	1.13	0.08	0.85	0.0006
MEA NGCC - Thermal Reclaiming	0.89	0.03	0.66	0.0002
MEA NGCC - Ion Exchange	0.86	0.03	0.65	0.0002
MEA NGCC - Electrodialysis	0.82	0.03	0.61	0.0002
PZ Coal - Thermal Reclaiming	2.18	0.16	1.64	0.0012
PZ Coal - Ion Exchange	1.50	0.11	1.12	0.0008
PZ Coal - Electrodialysis	1.96	0.15	1.47	0.0011
PZ NGCC - Thermal Reclaiming	1.69	0.05	1.27	0.0004
PZ NGCC - Ion Exchange	1.10	0.03	0.83	0.0003
PZ NGCC - Electrodialysis	1.43	0.04	1.07	0.0003
MDEAPZ Coal - Thermal Reclaiming	1.63	0.12	1.22	0.0009
MDEAPZ Coal - Ion Exchange	1.41	0.11	1.05	0.0008
MDEA/PZ Coal - Electrodialysis	1.67	0.13	1.25	0.0009
MDEA/PZ NGCC - Thermal Reclaiming	1.26	0.04	0.94	0.0003
MDEA/PZ NGCC - Ion Exchange	1.01	0.03	0.76	0.0002
MDEA/PZ NGCC - Electrodialysis	1.21	0.04	0.91	0.0003

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 electrodialysis 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, for the more expensive amine systems, it may be more advantageous to design a thermal reclaimer with a lower slip of amine to the waste stream.

For MEA coal combustion, thermal reclaiming was found to be the least expensive reclaiming process, followed by electrodialysis, then ion exchange as the most expensive. Although ion exchange reclaiming presented the potential benefits of lower costs for solvent losses and lower annual energy costs when compared to thermal reclaiming and electrodialysis, these benefits were offset by the expected costs for periodic bed resin replacement and slightly higher annualized capital costs (primarily because of the low solvent costs for MEA).

For PZ and MDEA/PZ coal combustion, ion exchange was found to be the least expensive reclaiming process, followed by electrodialysis and thermal reclaiming. For solvents with higher costs, the benefits of lower costs for solvent losses and lower annual energy costs are greater than expected costs for periodic bed resin replacement and slightly higher annualized capital costs for ion exchange, compared to electrodialysis and thermal reclaiming.

For the ion exchange and electrodialysis cases, if the incursion rates of dissolved metals and and degradation rates of non-ionic impurities are significantly higher than the incursion rate of heat stable salts, the degraded amine solution may need to be replaced occasionally or be subjected to batch thermal reclaiming in order to reduce these metals and non-ionic contaminants back to acceptable concentrations.

Batch processing the solvent would require a plant outage in order to perform a batch reclaiming of the solvent using a mobile unit, and it may not be feasible to shut down the capture unit outside of normal outages for reclaiming. Conversations with reclaiming vendors have revealed that if batch reclaiming is required more than twice a year for non-ionic impurities, then a continuous system should be installed. These batch processing costs are not covered in this study, and they can readily be obtained from vendors.

In addition, the costs of media replacement for ion exchange reclaiming and membrane replacement for electrodialysis reclaiming are not trivial. Process upsets or excursions that could direct high concentrations of dissolved metals to the reclaimer could foul or poison resin beds and require costly bed changeouts. These costs are covered in this study.

For the natural gas combustion cases, ion exchange reclaiming was found to be the least expensive reclaiming process, followed by electrodialysis, then thermal reclaiming as typically the most expensive. The benefits of lower costs for solvent losses and lower annual energy costs slightly outweighed the disadvantages of costs of periodic bed resin replacement and slightly higher annualized capital 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. Revision 2 (November 2010) of the DOE Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity lists a 30-yr average cost of electricity of 12.36 ¢/kWh (in 2012 dollars) for a supercritical coal power plant with the Fluor Economine® CO_2 capture technology, and a 30-yr average cost of electricity of 11.90 ¢/kWh (in 2010 dollars) for a NGCC power plant with the Fluor Economine® CO_2 capture technology [6].

Although these absolute cost of electricity numbers may be calculated 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 CO_2 capture, and only 0.3 to 0.4 percent of the total cost of electricity for natural gas plants with amine solvent CO_2 capture. These economics can also be expressed as \$1.11 to \$2.18/MT CO_2 captured (€0.84 to €1.64/ MT CO_2 captured) for the coal cases, and \$0.82 to \$1.69/MT CO_2 captured (€0.61 to €1.27/ MT CO_2 captured) for the natural gas cases.

In addition to the overall process economics, the composition of the thermal reclaiming waste stream can be affected by the assumptions regarding the rate of amine fed to the reclaimer (as a function of HSS concentration in the feed) and the rate of amine loss to waste via thermal reclaiming. Tables 5-24 through 5-26 present the estimated thermal reclaiming waste profiles (on a water-free basis) using MEA, MDEA/PZ and PZ for coal and natural gas combustion using two sets of assumptions:

- The slipstream ratio is 0.1 wt% of the total amine circulation rate
- The slipstream ratio is adjusted until the concentration of HSS to the reclaimer feed is 1.5 wt% HSS.

Although we are currently assuming that the sludge is completely dehydrated using the CHEM Group wiped film evaporator for the purposes of the economic analyses, it is likely that there will be a finite amount of water in the sludge. Information regarding the amount of water within the reclaiming waste is not publicly available from reclaiming vendors and is going to be specific to the solvent and reclaiming operation.

Table 5-24 Estimated MEA Thermal Reclaiming Waste Stream Compositions

		Assume Constant Slipstream %		Assume Constant HSS %	
Concentration	**Units**	**MEA Coal**	**MEA NGCC**	**MEA Coal**	**MEA NGCC**
Flow Rate	kg/hr	406	150	406	123
MEA	wt%	34.6	44.5	34.6	32.5
NaOH	wt%	20.5	17.3	20.5	21.0
Formate	wt%	1.2	3.8	1.2	4.6
Other HSS	wt%	0.3	0.8	0.3	1.0
Sulfate	wt%	18.5	6.5	18.5	7.9
Nitrate	wt%	12.1	14.5	12.1	17.6
Nitrite	wt%	1.0	1.7	1.0	2.1
Chloride	wt%	2.5	0.0	2.5	0.0
Fluoride	wt%	0.1	0.0	0.1	0.0
HEIA	wt%	2.9	3.7	2.9	4.5
triHEIA	wt%	1.0	1.2	1.0	1.5
HEEDA	wt%	0.5	0.6	0.5	0.8
Trimer	wt%	0.2	0.2	0.2	0.3
HEI	wt%	1.6	4.8	1.6	5.9
Hg	ppm	8.6	0.0	8.6	0.0
Se	ppm	11.0	0.0	11.0	0.0
As	ppm	1.8	0.0	1.8	0.0
Cd	ppm	0.8	0.0	0.8	0.0
Cr	ppm	21.6	0.0	21.6	0.0
Pb	ppm	2.2	0.0	2.2	0.0
Fly ash	wt%	2.9	0.0	2.9	0.0
Fe + other SSM's (Corrosion Metals)	wt%	0.2	0.3	0.2	0.4

Table 5-25 Estimated PZ Thermal Reclaiming Waste Stream Compositions

		Assume Constant Slipstream %		Assume Constant HSS %	
Concentration	**Units**	**PZ Coal**	**PZ NGCC**	**PZ Coal**	**PZ NGCC**
Flow Rate	kg/hr	634	260	477	137
PZ	wt%	55.4	68.3	40.8	40.3
NaOH	wt%	14.8	11.0	19.8	20.8
Formate	wt%	2.8	3.8	3.7	7.2
Other HSS	wt%	1.4	1.9	1.8	3.6
Sulfate	wt%	11.8	3.7	15.7	7.1
Nitrate	wt%	7.6	8.1	10.2	15.3
Chloride	wt%	1.6	0.0	2.2	0.0
Fluoride	wt%	0.0	0.0	0.0	0.0
Non-Volatile PZ Polymers	wt%	2.0	2.5	2.7	4.8
MNPZ	wt%	0.4	0.4	0.3	0.2
Hg	ppm	5.5	0.0	7.3	0.0
Se	ppm	7.1	0.0	9.4	0.0
As	ppm	1.2	0.0	1.6	0.0
Cd	ppm	0.5	0.0	0.7	0.0
Cr	ppm	13.8	0.0	18.4	0.0
Pb	ppm	1.4	0.0	1.8	0.0
Fly ash	wt%	1.8	0.0	2.4	0.0
Fe + other SSM's (Corrosion Metals)	wt%	0.3	0.4	0.4	0.7

Table 5-26 Estimated MDEA/PZ Thermal Reclaiming Waste Stream Compositions

		Assume Constant Slipstream %		Assume Constant HSS %	
Concentration	Units	MDEA/PZ Coal	MDEA/PZ NGCC	MDEA/PZ Coal	MDEA/PZ NGCC
Flow Rate	kg/hr	951	419	616	225
MDEA	wt%	51.1	52.1	34.1	26.2
PZ	wt%	10.5	10.8	7.0	5.4
NaOH	wt%	9.7	6.9	15.0	12.9
Formate	wt%	2.0	3.0	3.0	5.5
Other HSS	wt%	0.2	0.3	0.3	0.5
Sulfate	wt%	7.9	2.3	12.2	4.3
Nitrate	wt%	5.1	5.0	7.9	9.3
Chloride	wt%	1.1	0.0	1.7	0.0
Fluoride	wt%	0.0	0.0	0.0	0.0
DEA + MAE + polymers	wt%	9.4	16.2	14.5	30.2
Bicine	wt%	1.1	2.6	1.7	4.9
MNPZ	wt%	0.6	0.6	0.4	0.3
Hg	ppm	3.7	0.0	5.7	0.0
Se	ppm	4.7	0.0	7.3	0.0
As	ppm	0.8	0.0	1.2	0.0
Cd	ppm	0.3	0.0	0.5	0.0
Cr	ppm	9.2	0.0	14.2	0.0
Pb	ppm	0.9	0.0	1.4	0.0
Fly ash	wt%	1.2	0.0	1.9	0.0
Fe + other SSM's (Corrosion Metals)	wt%	0.3	0.3	0.4	0.5

Assuming that the reclaiming systems will be operated with a constant concentration of heat stable salts entering the reclaimer (as opposed to a constant slipstream ratio of reclaimer feed to total lean amine circulation rate) has three major effects:

- The total amount of thermal reclaiming waste is reduced
- The concentration of amine (and subsequently the heating value of the waste stream) is reduced
- The concentration of potentially hazardous components in the waste stream is increased

One class of waste products of particular interest is nitrosamines. Nitrosamines are not removed from the reclaimer feed using ion exchange or electrodialysis reclaiming technologies because they are non-ionic species; in these systems, the nitrosamines will reach a steady-state concentration based upon temperature in the regenerator. However, for thermal reclaiming technologies, it is assumed that nitrosamines exit the system with the thermal reclaimer waste stream. The expected mass flow rate of nitrosamines entering the thermal reclaimer for each solvent system is listed in Table 5-27.

Table 5-27 Estimated Nitrosamine Mass Rate in Reclaimer Waste Assuming 0.1% Slipstream Ratio

Combustion Type/Solvent	Reclaiming Technology	Nitrosamine Rate in Waste (kg/hr)
Coal/MEA	Thermal Reclaiming	N/A
	Ion Exchange	N/A
	Electrodialysis	N/A
NGCC/MEA	Thermal Reclaiming	N/A
	Ion Exchange	N/A
	Electrodialysis	N/A
Coal/PZ	Thermal Reclaiming	2.2
	Ion Exchange	N/A
	Electrodialysis	N/A
NGCC/PZ	Thermal Reclaiming	1.0
	Ion Exchange	N/A
	Electrodialysis	N/A
Coal/MDEA/PZ	Thermal Reclaiming	5.4
	Ion Exchange	N/A
	Electrodialysis	N/A
NGCC/MDEA/PZ	Thermal Reclaiming	2.3
	Ion Exchange	N/A
	Electrodialysis	N/A

It is currently conservatively assumed that all of the nitrosamines that enter the thermal reclaiming unit exit with the waste stream. Depending upon the nitrosamine concentration and the location of the plant, hazardous waste classifications may be triggered - this is discussed in Chapters 6 and 7 in greater detail.

However, it is likely that a portion of the nitrosamines are destroyed in the thermal reclaiming unit before they exit with the waste stream. If the thermal reclaiming unit is operated at a temperature of 15°C above the regenerator temperature, it is expected that up to 60% of the nitrosamines in the feed to the thermal reclaimer would be thermally degraded; these percentages increase to 85% and 95% if the thermal reclaiming unit is operated at temperature 30°C and 50°C above the regenerator temperature.

For each individual solvent system, it will be important to evaluate the trade off between solvent thermal degradation and nitrosamine thermal destruction. Alternatives to thermal destruction of nitrosamines include UV treatment and addition of inhibitors to reduce the rate of nitrosamine formation.

5.6 **Sensitivity Studies**

The purpose of this section of the technoeconomic analysis is to assess sensitivities to particular economic parameters, and to also examine sensitivities to changes in flue gas composition and CO_2 capture plant operating conditions.

5.6.1 Effect of Plant Life, Discount Rate

Two relevant economic parameters that are assessed in this section of the report are the discount rate (interest rate) and plant life. The base case values for these parameters are 8% for the discount rate and 25 years for the plant life; the capital recovery factor estimated from these base case values, applied to the total capital requirement so that annualized capital costs can be calculated, is 0.094.

The discount rate was varied from 5 to 10%, and the plant life was varied from 25 to 40 years. The lowest potential capital recovery factor from these combinations will result from assuming the lowest discount rate and longest plant life (5% discount rate over 40 years of plant life), while the highest potential capital recovery factor will result from assuming the highest discount rate and the shortest plant life (10% discount rate over 25 years of plant life). The estimated capital recovery factors for these two cases are 0.058 and 0.110, respectively. Tables 5-28 and 5-29 demonstrate how these capital recovery factors impact the annualized capital costs and overall economics of reclaiming. Overall, the annual cost of reclaiming decreases by approximately 7% assuming a discount rate of 5% over a plant life of 40 years, and the annualized cost of reclaiming increases by 3% assuming a discount rate of 10% over a plant life of 25 years.

Table 5-28 Effect of Discount Rate and Plant Life on Reclaiming Economics (USD)

	Base Case Costs (8% Discount Rate, Plant Life = 25 years)		5% Discount Rate, Plant Life = 40 years		10% Discount Rate Plant Life = 25 years	
	Annualized Capital Costs ($MM)	$/MT CO_2	Annualized Capital Costs ($MM)	$/MT CO_2	Annualized Capital Costs ($MM)	$/MT CO_2
MEA Coal - Thermal Reclaiming	1.03	1.11	0.64	1.04	1.21	1.15
MEA Coal - Ion Exchange	1.53	1.21	0.95	1.09	1.79	1.26
MEA Coal - Electrodialysis	1.04	1.13	0.65	1.05	1.22	1.17
MEA NGCC - Thermal Reclaiming	0.29	0.89	0.18	0.83	0.34	0.91
MEA NGCC - Ion Exchange	0.43	0.86	0.27	0.77	0.51	0.90
MEA NGCC - Electrodialysis	0.30	0.82	0.18	0.76	0.35	0.84
PZ Coal - Thermal Reclaiming	1.14	2.18	0.70	2.09	1.33	2.22
PZ Coal - Ion Exchange	1.52	1.50	0.94	1.38	1.79	1.55
PZ Coal - Electrodialysis	1.15	1.96	0.71	1.87	1.35	2.00
PZ NGCC - Thermal Reclaiming	0.32	1.69	0.20	1.62	0.38	1.72
PZ NGCC - Ion Exchange	0.48	1.10	0.30	1.01	0.56	1.15
PZ NGCC - Electrodialysis	0.33	1.43	0.20	1.37	0.38	1.46
MDEA/PZ Coal - Thermal Reclaiming	1.10	1.63	0.68	1.54	1.29	1.66
MDEA/PZ Coal - Ion Exchange	1.63	1.41	1.01	1.28	1.91	1.46
MDEA/PZ Coal - Electrodialysis	1.11	1.67	0.69	1.58	1.30	1.71
MDEA/PZ NGCC - Thermal Reclaiming	0.31	1.26	0.19	1.19	0.37	1.29

	Base Case Costs (8% Discount Rate, Plant Life = 25 years)		5% Discount Rate, Plant Life = 40 years		10% Discount Rate Plant Life = 25 years	
	Annualized Capital Costs ($MM)	$/MT CO_2	Annualized Capital Costs ($MM)	$/MT CO_2	Annualized Capital Costs ($MM)	$/MT CO_2
MDEA/PZ NGCC - Ion Exchange	0.47	1.01	0.29	0.91	0.55	1.05
MDEA/PZ NGCC - Electrodialysis	0.32	1.21	0.20	1.15	0.37	1.24

Table 5-29 Effect of Discount Rate and Plant Life on Reclaiming Economics (EUR)

	Base Case Costs		5% Discount Rate, Plant Life = 40 years		10% Discount Rate Plant Life = 25 years	
	Annualized Capital Costs (€MM)	€/MT CO_2	Annualized Capital Costs (€MM)	€/MT CO_2	Annualized Capital Costs (€MM)	€/MT CO_2
MEA Coal - Thermal Reclaiming	0.77	0.84	0.48	0.78	0.91	0.86
MEA Coal - Ion Exchange	1.15	0.90	0.71	0.82	1.34	0.94
MEA Coal - Electrodialysis	0.78	0.85	0.49	0.79	0.92	0.88
MEA NGCC - Thermal Reclaiming	0.22	0.66	0.14	0.62	0.26	0.68
MEA NGCC - Ion Exchange	0.32	0.65	0.20	0.58	0.38	0.68
MEA NGCC - Electrodialysis	0.23	0.61	0.14	0.57	0.26	0.63
PZ Coal - Thermal Reclaiming	0.86	1.64	0.53	1.57	1.00	1.67
PZ Coal - Ion Exchange	1.14	1.12	0.71	1.04	1.34	1.16
PZ Coal - Electrodialysis	0.86	1.47	0.53	1.40	1.01	1.50
PZ NGCC - Thermal Reclaiming	0.24	1.27	0.15	1.22	0.29	1.29
PZ NGCC - Ion Exchange	0.36	0.83	0.23	0.76	0.42	0.86

	Base Case Costs		5% Discount Rate, Plant Life = 40 years		10% Discount Rate Plant Life = 25 years	
	Annualized Capital Costs (€MM)	€/MT CO_2	Annualized Capital Costs (€MM)	€/MT CO_2	Annualized Capital Costs (€MM)	€/MT CO_2
PZ NGCC - Electrodialysis	0.25	1.07	0.15	1.02	0.29	1.10
MDEA/PZ Coal - Thermal Reclaiming	0.83	1.22	0.51	1.16	0.97	1.25
MDEA/PZ Coal - Ion Exchange	1.22	1.05	0.76	0.96	1.43	1.10
MDEA/PZ Coal - Electrodialysis	0.83	1.25	0.52	1.19	0.98	1.28
MDEA/PZ NGCC - Thermal Reclaiming	0.23	0.94	0.14	0.90	0.28	0.96
MDEA/PZ NGCC - Ion Exchange	0.35	0.76	0.22	0.69	0.41	0.79
MDEA/PZ NGCC - Electrodialysis	0.24	0.91	0.15	0.86	0.28	0.93

5.6.2 Effect of Operating Conditions, Inlet Flue Gas Conditions

The sensitivities discussed in this section of the technoeconomic analysis include 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. These sensitivities are described below for two of the coal cases arbitrarily to show general trends, which should be applicable to all cases.

- The base case regeneration temperatures for the MEA and MDEA/PZ coal CO_2 capture cases are 120°C and 135°C, respectively. Sensitivities were examined that adjusted the regeneration temperature for MEA to 105°C and 135°C, and for MDEA/PZ to 120°C and 150°C.
- The base case oxygen concentration in the 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% for the MEA and MDEA/PZ cases.
- The base case NO_X concentration in the flue gas is 45 ppmv (with 1.5 ppmv consisting of NO_2). Sensitivities were examined that adjusted the NO_X concentration to 30 ppmv (1 ppmv NO_2) and 90 ppmv (3 ppmv NO_2) for the MEA and MDEA/PZ cases. It is assumed that the ratio of NO_X to NO_2 is 30:1, NO_2 removal from flue gas is 50%, and NO_X removal from flue gas is 10%.

- The base case fly ash concentration in the flue gas is 6 mg/Nm^3. Sensitivities were examined that adjusted the fly ash concentration to 3 mg/Nm^3 and 10 mg/Nm^3 for the MEA and MDEA/PZ cases. Altough we are assuming that fly ash is all captured in the reclaimer, it is possible some will be captured in in-line filtration systems and deposited in vessel sumps.
- The base case for both the coal and NGCC cases assumes corrosion rates that produce approximately 100 ppmv of dissolved iron (or stainless steel metals) in the solvent to accelerate oxidation; the corrosion rates that correspond to these arbitrarily assumed concentrations are unknown. Sensitivities were examined that assumed negligible corrosion rates and negligible concentrations of dissolved iron (or stainless steel metals) to accelerate solvent oxidation. Tables 5-30 and 5-31 detail how the concentrations of key constituents change as operating conditions and flue gas concentrations change – without adjusting the slipstream feed to the reclaimer.

Table 5-30 Effect of Operating Conditions on MEA Coal Thermal Reclaimer Feed Composition

	Overall HSS Concentration (wt%)	Concentration of High MW Polymer Products (wt%)	Fly Ash Concentration (wt%)
Base Case	1.48	0.25	0.12
105°C Regeneration Temperature	1.45	0.06	0.12
135°C Regeneration Temperature	1.51	1.21	0.12
10% Inlet O_2 Concentration	1.54	0.32	0.12
2.5% Inlet O_2 Concentration	1.44	0.22	0.12
90 ppm NO_X (3 ppm NO_2)	2.04	0.25	0.12
30 ppm NO_X (1 ppm NO_2)	1.31	0.25	0.12
10 mg/Nm^3 fly ash	1.48	0.25	0.20
3 mg/Nm^3 fly ash	1.48	0.25	0.06
0 ppm corrosion metals	1.41	0.23	0.12

Table 5-31 Effect of Operating Conditions on MDEA Coal Thermal Reclaimer Feed Composition

	Overall HSS Concentration (wt%)	Concentration of High MW Polymer Products (wt%)	Fly Ash Concentration (wt%)
Base Case	1.48	0.86	0.12
120°C Regeneration Temperature	1.43	0.28	0.12
150°C Regeneration Temperature	1.53	3.49	0.12
10% Inlet O_2 Concentration	1.53	1.27	0.12
2.5% Inlet O_2 Concentration	1.43	0.62	0.12
90 ppm NO_X (3 ppm NO_2)	2.06	0.86	0.12
30 ppm NO_X (1 ppm NO_2)	1.27	0.86	0.12
10 mg/Nm^3 fly ash	1.48	0.86	0.19
3 mg/Nm^3 fly ash	1.48	0.86	0.05
0 ppm corrosion metals	1.30	0.67	0.12

Process economics were also re-evaluated and compared to process economics presented in Section 5.6. Each sensitivity case was assumed to have the same concentration of HSS entering the reclaimer as the respective base cases (1.48 wt%). Annualized capital costs, solvent losses, consumables costs, and energy costs were updated to reflect the reclaimer feed slipstream rate required to achieve a concentration of HSS equivalent to the base case; note that for these cases the annualized capital costs were also updated because these sensitivities actually change the mass rate at which heat stable salts are incurred within the amine system. A summary of the economics for these sensitivity cases are shown in Tables 5-32 and 5-33.

Table 5-32 Effect of Operating Conditions and Inlet Flue Gas Conditions on MEA Coal Thermal Reclaimer Process Economics

	$/MT CO_2	¢/kWh	€/MT CO_2	€/kWh	% Change in Economics from Base Case
Base Case	1.11	0.08	0.84	0.0006	0.0%
105°C Regeneration Temperature	1.10	0.08	0.82	0.0006	-1.7%
135°C Regeneration Temperature	1.13	0.09	0.85	0.0006	1.7%
10% Inlet O_2 Concentration	1.15	0.09	0.86	0.0006	3.5%
2.5% Inlet O_2 Concentration	1.09	0.08	0.82	0.0006	-2.3%
90 ppm NO_X (3 ppm NO_2)	1.48	0.11	1.11	0.0008	32.4%
30 ppm NO_X (1 ppm NO_2)	1.00	0.08	0.75	0.0006	-9.8%
10 mg/Nm^3 fly ash	1.11	0.08	0.84	0.0006	0.0%
3 mg/Nm^3 fly ash	1.11	0.08	0.84	0.0006	0.0%
0 ppm corrosion metals	1.07	0.08	0.80	0.0006	-4.0%

Table 5-33 Effect of Operating Conditions and Inlet Flue Gas Conditions on MDEA Coal Thermal Reclaimer Process Economics

	$/MT CO_2	¢/kWh	€/MT CO_2	€/kWh	% Change in Economics from Base Case
Base Case	1.63	0.12	1.22	0.0009	0.0%
120°C Regeneration Temperature	1.58	0.12	1.19	0.0009	-2.8%
150°C Regeneration Temperature	1.67	0.13	1.25	0.0009	2.8%
10% Inlet O_2 Concentration	1.67	0.13	1.25	0.0009	2.8%
2.5% Inlet O_2 Concentration	1.58	0.12	1.19	0.0009	-2.8%
90 ppm NO_x (3 ppm NO_2)	2.19	0.16	1.64	0.0012	34.8%
30 ppm NO_x (1 ppm NO_2)	1.42	0.11	1.07	0.0008	-12.5%
10 mg/Nm^3 fly ash	1.63	0.12	1.22	0.0009	0.0%
3 mg/Nm^3 fly ash	1.63	0.12	1.22	0.0009	0.0%
0 ppm corrosion metals	1.45	0.11	1.08	0.0008	-11.1%

Tables 5-32 and 5-33 show that economic effects of regeneration temperature, inlet oxygen concentration in the flue gas and level of corrosion within the system are minor in comparison to the effect of the concentration of NO_X in the inlet flue gas. This results primarily because these contaminant concentrations directly impact the concentration of HSS within the circulating amine solvent because of the direct reaction between NO_X/ and the amine to form a heat stable salt. In contrast, the effects of regeneration temperature, O_2 concentration and corrosion all have an indirect effect on the level of HSS in solution.

5.7 Qualitative Discussion of Reclaimer Technologies (Advantages/Disadvantages)

Previous sections in this report have shown that for three solvent systems of interest (MEA, MDEA/PZ and PZ) evaluated for three different types of reclaiming technology (thermal reclaiming, ion exchange and electrodialysis), annualized reclaimer costs are relatively minor in comparison to costs for the entire power plant and CO_2 capture process. This section of the report will offer a brief commentary on the advantages and disadvantages of each type of reclaiming system, as these qualitative effects may have influence on reclaimer technology selection.

5.7.1 Thermal Reclaiming

Thermal reclaiming may be the preferred option for power plants with coal combustion because thermal reclaiming is the most robust reclaiming method that will remove a majority of all types of degradation products and impurities from the amine solvent – heat stable salts, high-MW polymeric products and transition metals. No off-site secondary reclaiming method should be required to periodically clean up the solvent. Thermal reclaimers have a successful track record of operation in industry.

However, thermal reclaiming using kettle-type reboilers also has a track record of incurring significant corrosion rates – especially within the reboiler tube bundle. Multiple industrial units have been abandoned in place because of corrosion issues. Building thermal reclaiming units with stainless steel materials of construction and wall thicknesses above the minimum required thickness would help to slow corrosion in the thermal reclaimer. In addition, the solvent loss rates from thermal reclaiming may make this option unattractive for novel, expensive solvents. Careful operation and advanced reclaimer designs may reduce the solvent losses with more expensive solvent.

Waste removal for thermal reclaiming using kettle-type reboilers is also a challenge. The waste sludge from thermal reclaiming operations has often been noted as having viscous tar-like qualities, and it has to typically be removed from the unit to a truck or storage vessel via a vacuum pump – which industry vendors have described as a challenging task. For some particular amine solvents, there is the potential for the reclaimer waste to solidify and lose its ability to flow. It is common to rinse the thermal reclaimer and reboiler waste with water to clean the system and allow the waste sludge to flow for disposal. However, rinsing the sludge with large quantities of water increases the volume of waste and decreases its heating value, creating challenges for disposal via landfill and incineration.

5.7.2 Ion Exchange

Ion exchange may be the preferred reclaiming option for power plants with natural gas combustion because ion exchange is most effective when the incursion of heat stable salts is the dominant amine impurity. Concentration of metals will be minimal in comparison to coal combustion (dissolved corrosion products from plant piping will likely be the only source of metals), and if the rate of formation of high-MW polymeric products is low compared to the rate of formation of HSS, then ion exchange is preferred. Ion exchange has been successful in the removal of HSS in industrial applications, and the dilute aqueous waste can be directed to wastewater treatment and then to outfall (or recycled). Another benefit of ion exchange reclaiming is that units can typically be run without continuous monitoring and oversight from operations.

However, even if the incursion rates of dissolved metals and non-ionic degradation rates and impurities are significantly lower than the incursion rate of heat stable salts, the degraded amine solution may need to be replaced occasionally or be subjected to batch thermal reclaiming to reduce these metals and non-ionic contaminants (particularly nitrosamines) back to acceptable concentrations. Additional UV treatment may be required for complete nitrosamine destruction; as an alternative, inhibitors may be added to reduce the rate of nitrosamine formation.

The cost of media replacement for ion exchange reclaiming is a fairly expensive operating cost. Process upsets or excursions that could direct high concentrations of dissolved metals to the reclaimer could foul or poison resin beds and result in costly bed changeouts.

In addition, large volumes of distilled, deionized water are required for ion exchange reclaiming. It may be necessary to recycle water from the wastewater processing facility on site if water supply is not abundant.

5.7.3 Electrodialysis

Electrodialysis may be another preferred option for power plants with natural gas combustion and extremely high incursion rates of heat stable salts. Electrodialysis technologies have been successfully demonstrated and installed in the wastewater industry, and the dilute aqueous waste can be directed to wastewater treatment and then to outfall (or recycled).

However, even if the incursion rates of dissolved metals and non-ionic degradation rates and impurities are significantly lower than the incursion rate of heat stable salts, the degraded amine solution may need to be replaced occasionally or be subjected to batch thermal reclaiming to reduce these metals and non-ionic contaminants (especially nitrosamines) back to acceptable concentrations. Additional UV treatment may be required for complete nitrosamine destruction; as an alternative, inhibitors may be added to reduce the rate of nitrosamine formation.

The cost of membrane replacement for electrodialysis reclaiming is a fairly expensive operating cost. Process upsets or excursions that could direct high concentrations of dissolved metals to the reclaimer that are atypical for steady-state operations could foul or poison membranes and require costly change outs.

Electrodialysis also requires continuous attention from operations to run successfully.
In addition, large volumes of distilled, deionized water are required for ion exchange reclaiming. It may be necessary to recycle water from the wastewater processing facility on site if water supply is not abundant.

Process support for electrodialysis may also be limited, as it is believed that Dow typically only offers support of the UCARSEP process for its UCARSOL amine customers.

REFERENCES

1. Wonder, D.; Blake, R.; Fager, J.; Tierney, J.; An Approach to Monoethanolamine Solution Control: Chemical Analysis and Its Interpretation, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1959.

2. Butwell, K.; Kubek, D.; Sigmund, P.; Primary Versus Secondary Amines - Characteristics in Gas Conditioning, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1979.

3. Huval, M.; Van de Venne, H.; Gas Sweetening in Saudi Arabia in Large DGA Plants, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1981.

4. Kohl, A.; Nielsen, R. *Gas Purification*, 5th ed.; Gulf Publishing Co.: Houston, 1997.

5. Maddox, R.; Morgan, D. *Gas Conditioning and Processing Volume 4,* 4th ed; Campbell Petroleum Series: Norman, 1998.

6. Department of Energy (DOE) National Energy Technology Laboratory (NETL). “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity”, Revision 2, November 2010, DOE/NETL 2010/1397.

7. IEAGHG, “Post-Combustion Capture Scale-up Study”, 2013/05, February 2013.

8. www.chem-group.com/Technologies.cfm

9. Dumee, L.; Scholes, C.; Stevens, G.; Kentish, S. Purification of aqueous amine solvents used in post combustion CO_2 capture: A review. *International Journal of Greenhouse Gas Control*, 10, 443-455, 2012.

10. Smith, G.D.; Tooley, N.; Cummings, A.L. Making Amine Systems Sing, GPA Europe Sour Gas Processing Symposium, Barcelona, Spain, May 13-15, 2009.

11. Burns, D.; Gregory, R.; The UCARSEP Process for On-Line Removal of Non-Regenerable Salts from Amine Units, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma 1995.

12. Street, D.; Alkanolamines: Operational Issues and Design Consideration, Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 1995.

13. Haws, R. Contaminants in Amine Gas Treating. 83rd Annual Gas Processors Association Annual Convention, San Antonio, Texas, March 14-17, 2004.

14. Nielsen, R.; Lewis, K.; Controlling Corrosion in Amine Treating Plant, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, 1995.

15. Bacon, T.; Amine Solution Quality Control Through Design, Operation, and Correction, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1987.

16. Bacon, T.; Bedell, S.; Niswander, R.; Tsai, S.; Wolcott, R.; New Developments in Non-Thermal Reclaiming of Amine, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1988.

17. Department of Energy (DOE) National Energy Technology Laboratory (NETL). "Carbon Capture and Sequestration Systems Analysis Guidelines", April 2005.

18. http://www.icispricing.com/il_shared/Samples/SubPage140.asp

19. Fouad, W. A.; Berrouk, A. S. Using mixed tertiary amines for gas sweetening energy requirement reduction. *Journal of Natural Gas Science and Engineering*, 11, 12-17, 2013.

20. http://fw.crugroup.com/fertilizer/dashboards/sulphuric-acid/reports/weekly-preview-reports/2012/9/192388/192391

21. Peters, M.; Timmerhaus, K.; West, E. R. *Plant Design and Economics for Chemical Engineers*. 2002

22. Sata, T. *Ion Exchange Membranes: Preparation, Characterization, Modification, and Applications*. Royal Society of Chemistry, 2004.

23. de Groot, M.T.; Bos, A.A.C.M.; Lazaro, A.P.; de Rooij, R.M.; Bargeman, G. Electrodialysis for the Concentration of Ethanolamine Salts, *Journal of Membrane Science*, 371(1), 75-83, 2011.

6 CLASSIFICATION OF WASTE STREAMS FOR DEMONSTRATION PLANTS

The scope of the number of solvents studied and the countries that were reviewed for waste regulations were agreed upon by the project team and IEAGHG during the proposal phase of the project; the matrix of cases studied and countries evaluated was adjusted to fit the project budget, with focus on solvents that have the most information and regulations focused on US and European perspectives.

6.1 Approach

Three solvents of interest, monoethanolamine (MEA), piperazine (PZ), and a mixture of methyl diethanolamine (MDEA) and PZ, are being evaluated as solvents for capturing carbon dioxide from coal-fired and natural gas-fired power plants. Each of these solvents can be reclaimed by thermal reclaiming, ion exchange, and/or electrodialysis. Thermal reclaiming produces a sludge which may or may not be mixed with up to 50% water, while the ion exchange and electrodialysis wastes are estimated to be 95% water. This chapter and the following chapter discuss the classification of these waste streams as hazardous or non-hazardous, and identify handling and disposal options and approximate costs for disposal. As discussed in the previous chapters, the volume and composition of waste streams from various reclaiming technologies and scenarios were estimated from modeling calculations (see Tables 5-22 through 5-24); still there is considerable uncertainty regarding the composition of these waste streams which is based upon the assumptions made for degradation of the different amine solvents, absorption of flue gas contaminants into the amine solvent, and operation of the reclaiming system. 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 the absence of analyses of actual wastes from these processes, these waste classifications cannot be considered definitive.

URS evaluated the waste disposal regulations from the United States (US) (40 CFR Part 261) [1], the European Union (EU) (Decision 2000/532/EC) [2], and from several other countries (Canada and Australia) to determine if the waste streams from the various reclaiming technologies were hazardous. Table 6-1 and Table 6-2 summarize the waste characterization results for the US and EU, respectively. The waste characterization was performed by evaluating the characteristics of the CO_2 capture solvent, the metals content, and the nitrosamine content. Characteristics of the other minor constituents (e.g., HEIA, HEEDA, etc.) were not considered. Details of the reclaiming technology waste classification evaluation are presented below.

6.2 Waste Classification

For each of the solvents of interest, the reclaimer waste was characterized with respect to hazardous waste regulations for the US (40 CFR Parts 260-282) [3] and the EU (*Annex III of Directive 2008/98/EC* [4]*; Decision 2000/532/EC establishing a List of Wastes as last amended by Decision 2001/573/EC)* [2]. The IEAGHG's reference plant for the techno-economic analysis is based in the Netherlands, which is subject to EU directives for hazardous waste. Definitions of characteristics of hazardous waste have been provided with a discussion of whether or not reclaimer waste from each solvent meets that characteristic; the listed wastes have been explained and their applicability determined. For the UK, Canada, and Australia, the pertinent regulation by major section have been referenced but a detailed drill-down has not been provided.

6.2.1 United States

Hazardous waste is a legal classification defined in the Resource Conservation and Recovery Act (RCRA) (1976) that governs the disposal of solid and hazardous waste. As shown in Figure 6-1, only a solid waste (i.e., any discarded material – EPA uses the term "solid waste" to officially describe solid, semi-solid, liquids or contained gaseous material) can be considered a hazardous waste. US Environmental Protection Agency (EPA) classifies industrial waste as hazardous if it is specifically listed (F, K, P, and U lists) or if it has any of the four characteristics (ignitable, corrosive, reactive, toxic) of a hazardous waste (40 CFR 261) [1]. If an industrial waste is not listed and does not exhibit hazardous characteristics, it is classified as non-hazardous. An entity is considered a large quantity generator (LQG) if it generates more than 1000 kg (2,200 lbs) of hazardous waste or more than 1 kg (2.2 lbs) of acute hazardous waste per calendar month. LQGs may only accumulate hazardous waste for less than 90 days without a hazardous waste permit, meet air emission standards, record the date that waste begins accumulating, and have preparedness and prevention plants, contingency plans, closure plans, training plans, and waste analysis plans. Currently, most power plants in the US are not LQGs. Acute hazardous wastes include dioxin and furan containing (F- listed) wastes and the P-listed wastes; the others are non-acute.

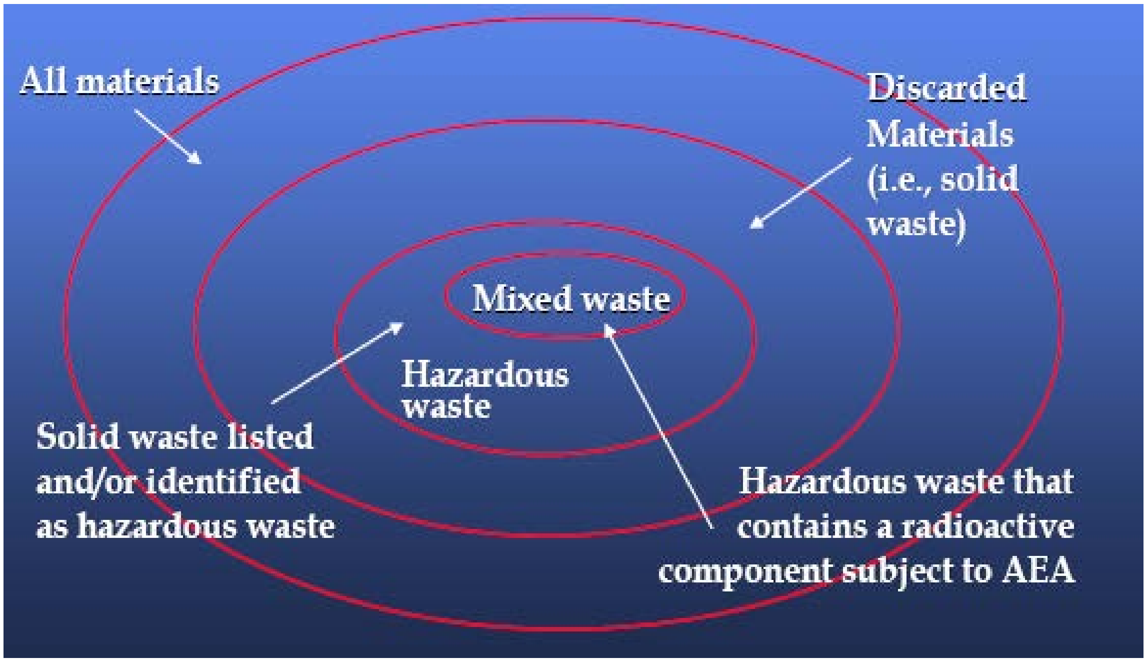


Figure 6-1 Hazardous Waste Classification for the US

A waste generator may use process knowledge and/or analytical testing to determine the status of the waste stream. In the case of CO_2 capture for power plants and the reclamation of the solvents used, the processes are new; therefore, analytical testing should be used to determine the status of the waste. For this study, the characterization of the reclaimer waste was based upon the chemical composition provided by the CO_2 capture and reclaiming process model; no samples of reclaimer waste were available for analysis.

Table 6-1 Summary of Hazardous Waste Characterization for United States of America, 40 CFR Part 261 [1]

Waste Stream	Ignitable	Corrosive	Reactive	Toxic	Listed
MEA, PZ, MDEA - PZ					
Coal-Fired Power Plant					
Thermal Reclaiming, No Water Addition	No	Unlikely[a]	No	Maybe[c]	No
Thermal Reclaiming, Water Addition	No	Unlikely[a]	No	Maybe[c]	No
Ion Exchange	No	No[b]	No	No	No
Electrodialysis	No	No[b]	No	No	No
Natural Gas Fired Power Plant					
Thermal Reclaiming, No Water Addition	No	Unlikely[a]	No	No	No
Thermal Reclaiming, Water Addition	No	Unlikely[a]	No	No	No
Ion Exchange	No	No[b]	No	No	No
Electrodialysis	No	No[b]	No	No	No

[a] The thermal reclaimer waste sludge is unlikely to be corrosive. The waste sludge will have non-corrosive pH (i.e., pH = 8 – 12); however, the waste must also not corrode steel at a rate greater than 6.35 mm per year. No corrosion measurements are available for these wastes. While the thermal reclaiming process does cause severe corrosion at elevated temperature at the bottom of the reclaimer at the gas/liquid interface, experience in the gas treating industry with reclaimed MDEA waste indicates that the waste is non-hazardous (and thus not corrosive) unless metals content exceeds Toxicity Characteristic Leaching Procedure threshold.

[b] Waste streams from ion exchange and electrodialysis were assumed to be non-corrosive due to high (95%) water content and non-corrosive pH.

[c] Thermal reclaimer wastes from coal-fired power plants may have mercury concentrations that exceed regulated limits, based upon the base case model assumptions. However, the model assumptions took a conservative approach and may have overestimated mercury content in the waste. Furthermore, use of flue gas mercury controls should be capable of reducing mercury concentration in waste to levels below regulated limits.

Table 6-2 Summary of Hazardous Waste Characterization for European Union, Decision 2000/532/EC [2]

Waste Stream	Explosive	Oxidizes	Ignitable	Irritant	Harmful	Toxic[a]	Carcinogenic	Corrosive	Infectious	Mutagenic[i]	Sensitizing	Ecotoxic	Listed
Coal-Fired Power Plant - MEA													
Thermal Reclaiming, No Water Addition	No	No	No	Yes[b]	Yes[c]	Yes	Maybe[e]	Yes[h]	No	No	No	Yes[k]	Yes[l]
Thermal Reclaiming, Water Addition	No	No	No	Yes[b]	Yes[c]	No	Maybe[e]	Yes[h]	No	No	No	Yes[k]	Yes[l]
Ion Exchange	No	No	No	No	No	No	No[g]	No	No	No	No	No	No[m]
Electrodialysis	No	No	No	No	No	No	No[g]	No	No	No	No	No	No[m]
Natural Gas Fired Power Plant - MEA													
Thermal Reclaiming, No Water Addition	No	No	No	Yes[b]	Yes[c]	No	Maybe[e]	Yes[h]	No	No	No	Yes[k]	Yes[l]
Thermal Reclaiming, Water Addition	No	No	No	Yes[b]	Yes[c]	No	Maybe[e]	Yes[h]	No	No	No	Yes[k]	Yes[l]
Ion Exchange	No	No	No	No	No	No	No[g]	No	No	No	No	No	No[m]
Electrodialysis	No	No	No	No	No	No	No[g]	No	No	No	No	No	No[m]
Coal-Fired Power Plant - PZ													
Thermal Reclaiming, No Water Addition	No	No	No	Yes[b]	Yes[c]	Yes[d]	Yes[f]	Yes[h]	No	No	Yes[j]	Yes[k]	Yes[l]
Thermal Reclaiming, Water Addition	No	No	No	Yes[b]	Yes[c]	Yes[d]	Yes[f]	Yes[h]	No	No	Yes[j]	Yes[k]	Yes[l]
Ion Exchange	No	No	No	No	No	No	No[g]	No	No	No	Maybe[j]	No	No[m]
Electrodialysis	No	No	No	No	No	No	No[g]	No	No	No	Maybe[j]	No	No[m]
Natural Gas Fired Power Plant - PZ													
Thermal Reclaiming, No Water Addition	No	No	No	Yes[b]	Yes[c]	Yes[d]	Yes[f]	Yes[h]	No	No	Yes[j]	Yes[k]	Yes[l]
Thermal Reclaiming, Water Addition	No	No	No	Yes[b]	Yes[c]	Yes[d]	Yes[f]	Yes[h]	No	No	Yes[j]	Yes[k]	Yes[l]
Ion Exchange	No	No	No	No	No	No	No[g]	No	No	No	Maybe[j]	No	No[m]
Electrodialysis	No	No	No	No	No	No	No[g]	No	No	No	Maybe[j]	No	No[m]
Coal-Fired Power Plant – MDEA/PZ													
Thermal Reclaiming, No Water Addition	No	No	No	Yes[b]	Yes[c]	Yes[d]	Yes[f]	Yes[h]	No	No	Yes[j]	Yes[k]	Yes[l]
Thermal Reclaiming, Water Addition	No	No	No	Yes[b]	Yes[c]	Yes[d]	Yes[f]	Yes[h]	No	No	Yes[j]	Yes[k]	Yes[l]
Ion Exchange	No	No	No	No	No	No	No[g]	No	No	No	Maybe[j]	No	No[m]
Electrodialysis	No	No	No	No	No	No	No[g]	No	No	No	Maybe[j]	No	No[m]
Natural Gas Fired Power Plant – MDEA/PZ													
Thermal Reclaiming, No Water Addition	No	No	No	Yes[b]	Yes[c]	Yes[d]	Yes[f]	Yes[h]	No	No	Yes[j]	Yes[k]	Yes[l]
Thermal Reclaiming, Water Addition	No	No	No	Yes[b]	Yes[c]	Yes[d]	Yes[f]	Yes[h]	No	No	Yes[j]	Yes[k]	Yes[l]

Waste Stream	Explosive	Oxidizes	Ignitable	Irritant	Harmful	Toxic[a]	Carcinogenic	Corrosive	Infectious	Mutagenic[i]	Sensitizing	Ecotoxic	Listed
Ion Exchange	No	No	No	No	No	No	No [g]	No	No	No	Maybe [j]	No	No[m]
Electrodialysis	No	No	No	No	No	No	No [g]	No	No	No	Maybe [j]	No	No[m]

[a] Toxic, Toxic for reproduction, or releasing toxic gases

[b] MEA, PZ, and MDEA in the waste stream are irritants. They are considered hazardous at a percentage greater than 10% of the waste stream (R41) or greater than 20% of the waste stream (R36, R37, R38).

[c] MEA, PZ, and MDEA are harmful. These are classified as harmful when greater than 25% of the total concentration. IE and ED streams are 95% water.

[d] MEA, PZ, and MDEA are not listed as toxic in CL Inventory; PZ is listed as R62, R63 (toxic for reproduction) and is present in concentration greater than 5% in the coal-fired and NGCC thermal reclaimer waste for PZ and MDEA/PZ.

[e] Safety Data Sheet for MEA indicate no reports of carcinogenicity for the solvent. Pure MEA will not form stable nitrosamines. However, secondary amines present in degraded solvent will react to form nitrosamines, which are suspected carcinogens. In the case of MEA, N-hydroxyethyl-glycine (HEGly) and diethanolamine (DEA) are expected to be the most concentrated secondary amines, forming N-nitroso-HEGly and N-nitroso-diethanolamine (NDELA) respectively. However, at this time, there is not enough information to quantify these constituents. Substances are classified as carcinogenic when greater than 0.1% of the substance is classified as carcinogenic, category 1 or 2.

[f] Substances are classified as carcinogenic when greater than 0.1% of the substance is classified as carcinogenic, category 1 or 2. Safety Data Sheet for PZ indicates no reports of carcinogenicity; however, thermal reclaimer wastes from PZ and MDEA/PZ processes will contain nitrosamines which are suspected carcinogens; modeling predicts these nitrosamines will be present in the thermal reclaimer wastes stream at concentrations above the threshold value of 0.1%.

[g] PZ and MDEA/PZ waste streams from ion exchange and electrodialysis are not expected to contain nitrosamines; therefore, these streams are not expected to be carcinogenic.

[h] MEA and PZ are classified as R34 in the CLP inventory; MEA and/or PZ are present at concentrations greater than 5% in the coal-fired and NGCC thermal reclaimer streams for the MEA, PZ, and MDEA/PZ solvents; therefore, these streams are corrosive.

[i] PZ, MEA, and MDEA are not classified as mutagens (R46 or R40) in the CL Inventory.

[j] PZ is a sensitizer (R42/43). The regulations do no list a minimum concentration of sensitizer to be characteristically hazardous, so all thermal reclaiming wastes from PZ and MDEA/PZ have been categorized as sensitizing wastes and all ion exchange and electrodialysis wastes from PZ and MDEA/PZ as “maybe” sensitizing wastes.

[k] The solvents themselves are not listed as ecotoxic; however, the coal-fired thermal reclaiming wastes contain metals which may be ecotoxic.

[l] The solvents themselves are not listed wastes. Mercury, selenium, arsenic, cadmium, chromium, and lead are present in the thermal reclaimer waste, and these metals are listed wastes as dangerous substances in the Annex to Decision 2000/532/EC. No minimum threshold concentration is provided for this classification.

[m] Assumed no metals removal by the ion exchange and electrodialysis processes. If in reality some metals are removed, then these streams could be listed waste due to metals content.

6.2.1.1 *Listed Waste*

A list of hazardous wastes is enumerated in 40 CFR Section 261Subpart D [1] and is divided into four category listings: F, K, P and U. The F list designates particular solid wastes from common industrial or manufacturing processes as hazardous. Because the processes producing these wastes can occur in different sectors of industry, the F list wastes are known as wastes from nonspecific sources. The K list designates particular solid wastes from certain specific industries as hazardous. K list wastes are known as wastes from specific sources. The P list and the U list are similar in that both list pure or commercial grade formulations of certain specific unused chemicals as hazardous. None of the materials in the reclaimer wastes being evaluated in this paper are listed.

6.2.1.2 *Characteristic Waste*

A waste is considered hazardous if it displays any of the four characteristics: ignitability, corrosivity, reactivity, or toxicity (40 CFR Section 261 Subpart C) [1]. This part of the regulations provides a screening mechanism that waste generators shall apply to all wastes from all industries.

Ignitability- A waste is considered ignitable if it meets any of the following criteria:

- Liquid wastes (other than those aqueous wastes containing less than 24 percent alcohol by volume) that have a flash point less than 60°C (140°F).
- Non-liquid wastes that under standard temperature and pressure are capable of causing fire through friction, absorption of moisture, or spontaneous chemical changes and when ignited, burn so vigorously and persistently that they created a hazard.
- Wastes that are considered an ignitable compressed gas.
- Wastes that are considered an oxidizer.

None of the identified reclaimer waste streams are expected to have a flash point below 60°C, nor are expected to burn spontaneously, nor are an ignitable compressed gas or an oxidizer. The individual solvents all have flash points >60°C. Therefore, the waste streams do not meet the hazardous characteristic of ignitability.

Corrosivity - A waste is considered corrosive if it meets any of the following criteria:

- Aqueous wastes with a pH of 2 or below or of 12.5 or above.
- Liquid wastes that corrode steel at a rate greater than 6.35 mm (0.25 inches) per year.

The thermal reclaimer waste sludge is unlikely to be corrosive. The waste sludge will have non-corrosive pH (i.e., pH = 8 – 10); however, the waste must also not corrode steel at a rate greater than 6.35 mm per year. No corrosion measurements are available for these sludges. Safety Data Sheets indicate that the solvents MEA and MDEA are corrosive, but no quantitative information is provided. While the thermal reclaiming process does cause severe corrosion at the bottom of the reclaimer at the gas/liquid interface, experience in gas treating industry with reclaimed MDEA waste indicates that the waste is not hazardous (and thus not corrosive) unless metals content exceed threshold.

Reactivity - A waste is considered reactive if meets any of the following criteria:

- It is capable of detonation or explosive decomposition or reaction at standard temperature and pressure, if subjected to a strong ignition source, or if heated under confinement.
- When mixed with water, it is potentially explosive, reacts violently, or generates toxic gases or vapors.
- If a cyanide or sulfide-bearing waste is exposed to pH conditions between 2 and 12.5, it can generate enough toxic gases, vapors, or fumes to present a danger to human health or the environment. (> 250 ppm reactive cyanides, >500 ppm reactive sulfides).
- It is normally unstable and readily undergoes violent changes without detonating.
- It is a forbidden explosive (49 CFR 173.51, Class A explosive 49 CFR 173.53) [5].
- It is a class B explosive (49 CFR 173.88) [5].

None of the identified reclaimer wastes are expected to be capable of detonation, or explosive detonation, or reaction at standard temperature and pressure, subjected to strong ignition source, or heated under confinement. When the waste streams are mixed with water, they are not potentially explosive anddo not react violently or generate toxic gases or vapor. Therefore, these reclaimer waste streams are not reactive.

Toxicity - A waste exhibits the toxicity characteristic (TC) if the extract obtained from the toxicity characteristic leaching procedure (TCLP) from a representative sample of the waste contains any of the TC constituents listed in 40 CFR 261.24 [1] at or above a concentration greater than or equal to the applicable regulatory level. Table 6-3 presents the TC contaminants and the concentration level at which the waste would be considered hazardous. Arsenic, cadmium, chromium, lead, mercury, and selenium may be present in some of the waste streams and are contained in the TC list. If the concentrations in the TCLP leachate from these waste streams are greater than the concentrations shown in Table 6-3, the waste is considered hazardous. In the absence of leaching test data, standard industry practice was followed by using total concentration data [21]. If a waste is 100% solid, then dividing the results of the total constituent analysis by twenty should give the maximum leachable concentration. This factor is derived from the 20:1 liquid-to-solid ratio employed in the TCLP. Alternately the regulatory levels were multiplied by 20 and compared to the total concentration results of the waste streams. The only TC contaminant to potentially exceed the regulatory limit was mercury. Mercury in the MEA coal and PZ coal thermal reclaimer waste streams exceeded 4 mg/L (i.e., 20 times the 0.2 mg/L TCLP limit). The mercury concentration in the MDEA/PZ coal thermal reclaimer waste stream was very close to 4 mg/L and may exceed this level depending on the variability of the CO_2 capture process conditions. As discussed in previous chapters, there is significant uncertainty in the estimated mercury concentration in the reclaimer sludge. It is very likely that mercury absorption into the solvent may in reality be much lower or can be controlled to lower levels via flue gas mercury controls. The concentration of metals in the solvent is linearly related to the concentration of solvent in the flue gas entering the CO_2 absorber and linearly related to the percent of uptake of the metal by the CO_2 capture process.

The thermal reclaimer waste stream may be diluted by half with water to facilitate transport of the waste. Although the concentrations of arsenic, cadmium, chromium, lead, mercury, and selenium in the diluted thermal reclaimer waste streams were below the TC limit, they would be considered as hazardous if the leachate from the undiluted stream exceeded the TC limit. Although it is allowable for a waste to be effectively diluted to facilitate removal from equipment, it is not allowable to dilute a waste solely to lower the concentration of the hazardous contaminants.

The metals concentrations in the ion exchange and electrodialysis reclaimer waste streams were assumed to be zero for this analysis, but in reality these streams will have some small finite concentration of metals.

Table 6-3 TC Contaminants and Regulatory Limits for US

Contaminant	Regulatory Level (mg/L)
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
Cresol	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor (and its epoxide)	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0

Contaminant	Regulatory Level (mg/L)
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

6.2.1.3 *Non-hazardous Waste*

Non-hazardous wastes are divided into industrial and non-industrial wastes. In general, industrial wastes are from the operation of industry, manufacturing, mining, or agriculture. Non-industrial wastes are mainly from schools, hospitals, churches, dry cleaners, service stations, and laboratories serving the public.

In the state of Texas, for example, non-hazardous industrial wastes are further subdivided into three classes (30 TAC Sections 335.505-08) [6]. Class 1 waste is considered potentially threatening to human health and the environment if not properly handled. Class 2 wastes include waste-activated sludge from biological wastewater treatment. Class 3 waste includes materials that are insoluble, do not react with other materials, and do not decompose. Class 2 and Class 3 wastes are generally acceptable for conventional (e.g., non-hazardous) landfill disposal.

A waste has to contain regulated asbestos-containing material, polychlorinated biphenyls, or petroleum substances to be considered a Class 1 waste. The solvent reclaimer waste stream does not meet those criteria. If the solvent reclaimer waste stream is considered non-hazardous (i.e., the natural gas-fired power plant wastes and the ion exchange and electrodialysis streams from the coal fired power plants), it would be classified as a Class 2 industrial waste which could be disposed of in a landfill.

6.2.1.4 *Other Considerations*

The reclaimer wastes contain sodium hydroxide, ethylenediamine (EDA) and metals; these compounds are on the list of hazardous substances in 40 CFR Table 302.4 [7]. This does not mean that materials containing these compounds are always hazardous; analytical characterization of the waste as well as process knowledge would be required to make that determination.

N-methylaminoethanol (MAE), EDA, and diethanolamine (DEA), degraded products or breakdown products, are also regulated in drinking water in the United States. This means that if the liquid wastes are disposed in a wastewater treatment plant, the effluent and wastewater discharge permit shall address these compounds.

Non-hazardous waste may be used as part of the process for producing energy.

6.2.2 EU

The legal classification of waste is provided in Directive 2008/98/EC of 19 November 2008 [4] on waste and repealing certain previous Directives. This Directive clarifies and rationalizes EU legislation on waste. As such, it clarifies the meaning of waste, recycling and recovery and it applies a new waste hierarchy. More stringent waste reduction and waste management targets are provided for Member States as requirements and should be reflected in the content of their waste management plans. Table 6-2 summarizes the information for all solvents and reclaiming technologies investigated in this study.

6.2.2.1 *Hazardous Waste*

Wastes are defined as substances which the holder discards, intends to discard, or is required to discard. Wastes are classified as hazardous if they fulfill one of these two criteria:

- They are included in the list provided in Decision 2000/532/EC of 3 May 2000 [2] and are marked as hazardous in this list;
- They display one or more of the characteristics of hazardous properties listed in Annex III of Directive 2008/98/EC of 12 December 2008 [4].

These two documents are explained below.

Listed Waste: Decision 2000/532/EC [2] last amended by Decision 2001/573/EC [9], and Directive 67/548/EEC [10]

A list of wastes is enumerated in Decision 2000/532/EC [2]. The Decision provides in Annex III a classification of waste according to the type of process, industry, etc. and a coding system is provided so that each waste type is coded. Several codes may apply in one case. The list also takes into account the origin and composition of the waste and the limits for which substances are considered hazardous are also provided. For some waste types, the code is followed by a * symbol, indicating that the waste class is hazardous. This Decision was last amended by Decision 2001/573/EC of 23 July 2001. Substances are hazardous if they are classified as such in Directive 67/548/EEC of 27 June 1967. Substances classified hazardous are considered to display one or more of the properties listed in Annex III to Directive 91/689/EEC on hazardous waste which has been repealed by Directive 2008/98/EEC [4]. It may be decided, in exceptional cases and on the basis of documentary evidence, that a waste listed in Decision 2000/532/EC [2] and normally considered hazardous does not display any of the properties listed in Annex III to Directive 91/689/EEC which has been repealed by Directive 2008/98/EEC [4]. In such case, this shall be decided by the Member State and communicated to the European Commission on a yearly basis.

According to the type of waste produced and the process involved in the production of waste, the following may apply:

- Wastes resulting from organic chemical processes are classified under coding section 07 of the list of waste. Subsection 07 07 concerns waste from manufacture, formulation, supply and use of fine chemicals and chemical products not otherwise specified. Most of the subcategories of 07 07 are *de facto* classified as hazardous waste.

- Inorganic wastes from thermal process are classified under coding section 10 01, wastes from power stations and other combustion plants. The subcodes include 10 01 08, *other sludges from gas treatment* and 10 01 99, *wastes not otherwise specified* [2]. While this waste code targets the appropriate industry, the reclaimer waste is an organic waste.
- Wastes containing heavy metals, such as antimony, arsenic, cadmium, copper, lead, mercury, nickel, selenium, thallium, and tin are classified as dangerous substances because they display properties listed in Annex III of Directive 2008/98/EEC [4].
- If the concentrations of those substances are such (i.e., percentage by weight) that it does not present one or more of the properties listed in Annex III to Directive 91/689/EEC which has been repealed by Directive 2008/98/EEC [4], it may be decided by the Member State, in exceptional cases and on the basis of documentary evidence, that those substances are not hazardous.

Several inorganic substances included in the waste stream (e.g., mercury, selenium, lead) are listed as hazardous in Directive 67/548/EEC [10] referred to in Decision 2000/532/EC [2].

Organics present in the waste stream are not directly cited in the abovementioned list of hazardous waste. However, these compounds are hazardous if they have one or more of the hazardous waste characteristics, as described below.

Characteristic Waste: Directive 2008/98/EC [4]
A waste is considered hazardous if it displays any of the following characteristics: explosive, oxidizing, ignitable, irritant, harmful, toxic (itself, or toxic for reproduction, or releasing toxic gases), carcinogenic, corrosive, infectious, mutagenic, sensitizing and ecotoxic. Wastes capable of yielding after disposal another substance with properties included among the properties of hazardous waste are also classified as hazardous. Toxic waste, waste toxic for reproduction and waste releasing toxic gases are separate categories under Directive 2008/98/EC [4].

Waste may be classified as hazardous if it meets one or more of the characteristics provided in Annex III to Directive 2008/98/EC [4]. In order to know if the waste has one or more of the characteristics, the waste should be evaluated. For the purpose of this report, the waste has been evaluated based on the characteristics and concentration of the amine solvent in each waste stream. Characteristics for each solvent were determined from the Safety Data Sheets (SDS) and from the Classification and Labelling (CL) Inventory from the European Chemicals Agency (ECHA). The CL Inventory lists the risk phrases (also known as R phrases), denoted by R##, assigned to each chemical to classify the hazard of the substance according to quantifiable metrics. For example, R35 is for substances causing severe burns, which is defined as destruction of full thickness of healthy, intact skin tissue in up to three minutes exposure or pH ≤ 2 and ≥ 11.5, while R34 is for substances casing burns, which is defined as destruction of skin tissue in up to four hours exposure.

Decision 2000/532/EC [2] classifies waste as hazardous when it displays one or more properties listed in Annex III to Directive 91/689/EC repealed by Directive 2008/98/EC [4] and contains one or more substances classified as hazardous at a concentration greater than specified in Decision 2000/532/EC [2]. Each of these hazardous characteristics was analyzed for the various reclaimer waste streams. The diluted thermal reclaimer wastes stream was given the same classification as the undiluted stream. Section 1.1.3.1 of Annex I of Regulation (EC) No 1272/2008 [22] states that if a mixture is diluted with a substance (in this case, water) with a lower hazard category classification, then the new mixture shall be classified as equivalent to the original mixture.

Explosive - A waste is considered explosive if it meets any of the following criteria:

- It may explode under the effect of flame; and
- It is more sensitive to shocks or friction than dinitrobenzene.

None of the reclaimer waste streams are expected to explode under flame or to be sensitive to shock. Therefore, the waste streams do not meet the hazardous characteristic of explosives.

Oxidizing - A waste is considered oxidizing if it exhibits highly exothermic reactions in contact with other substances. This is particularly the case for contact with flammable substances.

None of the reclaimer waste streams are an oxidizer. Therefore, the waste streams do not meet the hazardous characteristic of oxidizing waste.

Ignitability - A waste can be considered ignitable (flammable) or highly ignitable (highly flammable).

- It is considered flammable if it has a flash point equal to or greater than 21°C and less than or equal to 55°C;
- It is considered highly flammable if it meets any of the following criteria, applicable for substances and preparations of substances;
  - Liquid waste with a flash point below 21°C;
  - Solid waste which may readily catch fire after brief contact with a source of ignition and which continue to burn or to be consumed after removal of the source of ignition;
  - Gaseous waste flammable in air at normal pressure; and
  - Waste which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.

None of the reclaimer waste streams are expected to have a flash point below 60°C, are expected to burn, and are an ignitable compressed gas or an oxidizer. Therefore, the waste streams do not meet the hazardous characteristic of ignitability.

Irritant - A waste is considered an irritant if it is a non-corrosive substance or preparation which can cause inflammation in contact with the skin or mucous membrane in any of the following cases:

- Immediate contact;
- Prolonged contact; and
- Repeated contact.

Irritants are present at a total concentration of 10% and greater to be classified as hazardous under the code R41, or at a total concentration of 20% and greater to be classified hazardous under the code R36, R37 and R38. MEA and PZ are corrosive substances, so they are not classified as irritants. MDEA is classified as R36, irritant to the eyes. MDEA is present at a concentration greater than 20% in the thermal reclaiming streams for coal-fired and NGCC power plants. Therefore these streams are hazardous.

Harmful - A waste is considered harmful if it may involve limited health risks if it is inhaled, ingested or if it penetrates the skin. Harmful constituents are present at a total concentration of 25% and greater to be classified as hazardous. The SDS for MEA [11], PZ [12], and MDEA [13] state that they may be harmful. MEA, PZ, and/or MDEA are present at concentrations greater than 25% in their respective thermal reclaimer wastes. Therefore, these streams are hazardous.

Toxic - A waste is considered toxic if it is a substance or preparation which, if it is inhaled, ingested or if it penetrates the skin, may involve the following risks for health:

- Serious;
- Acute; or
- Chronic potentially leading to death.

Wastes containing one or more substances classified as very toxic at a total concentration of 0.1 % are classified as hazardous, or wastes containing one or more substances classified as toxic at a total concentration of 3% and greater are classified as hazardous. None of the three solvents (PZ, MDEA, MEA) are classified as toxic according to the CL Inventory.
Reproductive toxicity of a substance is classified separately. A waste is considered toxic for reproduction if it may induce non-hereditary congenital malformations or increase their incidence. A waste is considered toxic for reproduction if one or more substances toxic for reproduction of category 1 or 2 classified as R60, R61 at a total concentration greater than or equal to 0.5%, or if it contains one or more substances toxic for reproduction of category 3 classified as R62, R63 at a total concentration greater than 5%. Reproductive toxicity is not indicated in the CL Inventory for MEA or MDEA. The CL Inventory for PZ indicates that it is suspected of damaging fertility or the unborn child (hazard statement code H361fd) and has been assigned risk phrases R62 and R63. PZ is present in the PZ and MDEA/PZ thermal reclaimer streams at concentrations exceeding 5%; therefore, these streams are toxic for reproduction.

Waste which releases toxic or very toxic gases in contact with water, air or acid are toxic (hazardous) waste classified separately. Review of SDS does not indicate that the solvents will release toxic gases in contact with water.

Carcinogenic - A waste is considered carcinogenic if it is a substance or preparation which, if it is inhaled, ingested or if it penetrates the skin, may result in the following:

- Induce cancer; and
- Increase its incidence.

Wastes containing one or more substances known to be carcinogenic of category 1 (known/presumed carcinogens) or 2 (suspected carcinogens) at a total concentration of 0.1 % and greater are classified as hazardous. Categories of carcinogenicity are provided by the Global Harmonized System applicable in the European Union. Category 1 is further subdivided on whether evidence is mostly from human or animal data. Review of the SDS indicated there are no reports of carcinogenicity for MEA, MDEA, or PZ; however, thermal reclaimer wastes from PZ and MDEA/PZ processes will contain 1-nitrosopiperzaine which is a suspected carcinogen; modeling predicts this nitrosamine will be present above the threshold value of 0.1%. Pure MEA and MDEA will not form stable nitrosamines. However, secondary amines present in degraded solvent will react to form nitrosamines. In the case of MEA, N-hydroxyethyl-glycine (HEGly) and diethanolamine (DEA) are expected to be the most concentrated secondary amines, forming N-nitroso-HEGly and N-nitroso-diethanolamine (NDELA) respectively. However, at this time, there is not enough information to quantify these constituents for the MEA thermal reclaimer waste streams. MEA, PZ and MDEA/PZ waste streams from ion exchange and electrodialysis are not expected to contain nitrosamines; therefore, these streams are not expected to be carcinogenic.

Corrosive - A waste is considered corrosive if it is a substance or preparation which may destroy living tissue on contact.

Waste containing one or more corrosive substances classified as R35 (causes severe burns) at a concentration of 1% and greater, or waste containing one or more corrosive substances classified as R34 (causes burns) at a concentration of 5% and greater are classified as hazardous.

MEA and PZ are classified as R34 in the CLP inventory; MEA and/or PZ are present at concentrations greater than 5% in the coal-fired and NGCC thermal reclaimer streams for the MEA, PZ, and MDEA/PZ solvents; therefore, these streams are corrosive.

Infectious - A waste is considered infectious if it is a substance or preparation containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms.

None of the reclaimer waste stream is expected to contain viable micro-organisms or their toxins. Therefore, the waste streams do not meet the hazardous characteristic of infectious waste.

Mutagenic - A waste is considered mutagenic if it is a substance or preparation which, if it is inhaled, ingested or if it penetrates the skin, may result in the following:

- Induce hereditary genetic defects; and
- Increase their incidence.

Wastes containing one or more mutagenic substances of category 1 or 2 classified as R46 at a total concentration of 0.1% and greater, or wastes containing one or more mutagenic substances of category 3 classified as R40 at a total concentration of 1% or greater are classified as hazardous. The CL Inventory does not classify MEA, PZ, nor MDEA as mutagenic substances. Therefore, the waste streams do not meet the hazardous characteristic of mutagenic waste.

Sensitizing - A waste is considered sensitizing if it is a substance or preparation which, if it is inhaled, ingested or if it penetrates the skin, is capable of the following:

- Eliciting a reaction of hypersensitivity; and
- Such that on further exposure to the substance or preparation, characteristic adverse effects are produced.

The SDS [12] and CL Inventory for PZ indicates that it is a sensitizer (R42 via inhalation and R43 via skin). No minimum concentration of sensitizer is listed for rendering a hazardous classification, so all thermal reclaiming wastes from PZ and MDEA/PZ have been categorized as sensitizing wastes and all ion exchange and electrodialysis wastes from PZ and MDEA/PZ (which have lower PZ content) as “maybe” sensitizing wastes.

Ecotoxic - A waste is considered ecotoxic if it presents or may present immediate or delayed risks for one or more sectors of the environment.

The solvents themselves are not listed as ecotoxic in the CL inventory. However, coal-fired thermal reclaiming solvent waste will contain metals, such as mercury, that are ecotoxic. No minimum concentration of ecotoxic substance is listed for rendering a hazardous classification, so all coal-fired thermal reclaiming wastes have been categorized as ecotoxic wastes.

Waste capable of yielding another substance - Waste capable, by any means, after disposal, of yielding another substance, e.g., a leachate, or daughter product, which possesses any of the characteristics listed above, are also considered as hazardous waste.

Some of the waste streams considered in the above characteristics are degradation products yielded by the methods described (thermal reclaiming, ion exchange and electrodialysis). These are therefore already included in the above analysis.

6.2.2.2 *Non-hazardous Waste*

Non-hazardous waste may also be classified in accordance with this list of waste provided in Decision 2000/532/EC [2] and if the waste does not present the hazardous properties in given conditions as indicated in Annex III to Directive 2008/98/EEC [4]. Diluting or mixing an otherwise hazardous waste, resulting in a lower concentration, does not result in a waste classified as non-hazardous.

6.2.2.3 *Cost Associated with Disposal*

Wastes are mainly incinerated in the Netherlands, which is the assumed location of the base case EU plant. Based on URS experience, the cost for disposal by incineration in the Netherlands is approximately:

- 70 to 80 Euros per ton for non-hazardous waste; and
- 300 to 500 Euros per ton for hazardous waste.

The cost for landfilling is of the same order as incineration. Non-hazardous waste may be used in part for producing energy.

6.2.2.4 *Other Regulations*

Industrial Emissions in the EU: Directive 2010/75/EU [23]

One of the key pieces of EU legislation governing the emissions from the carbon capture plant (and associated re-claimer systems) will be Directive 2010/75/EU on Industrial Emissions. Any carbon capture plant that undertakes geological storage of the carbon dioxide represents a prescribed activity under section 6.9 of Annex 1 to the Directive. Installations undertaking such listed activities need to obtain a relevant operational permit. The Directive contains extensive requirements that must be enacted via the permit including setting emission limit values for emissions to air and water and governing waste generation. Limit values for emissions to water from aqueous re-claimer systems (if released from the same installation where the capture plant is operated) would be governed by such a permit which may impose emission limit values reflecting local circumstances as well as the requirements of the legislation noted in the sections below. The overarching premise of the Directive is that Best Available Techniques are adopted to ensure all appropriate preventative measures are taken against pollution. Specific statutory guidance on wastewater treatment plants and emissions to water would need to be taken into account. Similar provisions may relate to carbon capture plants that do not undertake geological storage as they may be considered to represent a directly associated activity to a combustion plant (as defined by Article 3(3) and Chapter III of the Directive). Chapter III and Annex V of the Directive impose specific provisions on the operation of combustion plant with capacities >50MWth input.

Landfill in the EU: Directive 1999/31/EC, last amendment by Directive 97/2011/EU [14]

Directive 1999/31/EC of 26 April 1999, last amendment by Directive 97/2011/EU is intended to prevent or reduce the adverse effects of landfills on the environment, in particular on surface water, groundwater, soil, air and human health. It defines the different categories of waste (municipal waste, hazardous waste, non-hazardous waste and inert waste) and applies to all landfills, defined as waste disposal sites for the deposit of waste onto or into land. Landfills are divided into three classes: landfills for hazardous waste, landfills for non-hazardous waste and landfills for inert waste. Landfill of non-hazardous and hazardous waste is authorized but waste is treated prior to disposal. The Directive sets up a system of operating permits for landfill sites.

The following wastes may not be accepted in a landfill: liquid waste, flammable waste, explosive or oxidizing waste, hospital and other clinical waste which is infectious, used tires (with certain exceptions) and any other type of waste which does not meet the acceptance criteria laid down in Annex II of Directive 1999/31/EC.

Therefore, the wet thermal reclaimer waste, ion exchange waste, and electrodialysis waste may not be landfilled without solidification.

Annex II provides the following information; acceptance in landfill also depends on waste characteristics:

- Inert wastes are defined in article 2e as waste that does not undergo significant physical, chemical or biological transformations and for which the total leachability and pollutant content is insignificant, and does not affect the environment's quality. Landfill sites for inert waste shall be used only for inert waste.
- Landfills for non-hazardous waste may be used for municipal waste and for non-hazardous waste.
- Hazardous wastes may not be accepted in a landfill without prior treatment if they exhibit total contents or leachability of potentially hazardous components that could present a short-term environmental risk and that would prevent waste stabilization in the landfill site.

Therefore, waste identified as non-hazardous according to Decision 2000/532/EC [2] referring to Directive 67/548/EEC [10], and Directive 2008/98/EC [4] may be accepted in landfill for non-hazardous waste. Waste identified as hazardous according to the same legal provisions may be accepted in hazardous landfill. All wastes, whether hazardous or non-hazardous, must be characterized prior to landfill. Wastes must be treated if they present short-term risks for the landfill site.

Waste characterization follows three steps called levels:

- Level 1: basic characterization of the waste with standardized analysis, emphasizing short- and long-term leaching behavior.
- Level 2: periodic testing to determine whether a waste complies with permit conditions and conditions as identified by level 1, basic characterization.
- Level 3: on-site verification to confirm that a waste is the same as subjected to compliance testing and described in the accompanying documents, a visual inspection before and after unloading at the landfill site.

Incineration of waste: Directive 2000/76/EC last amendment by Directive 2010/75/EU, and Decision 2011/632/EU [15]

This Directive applies to facilities intended for waste incineration and to "co-incineration" plants. All incineration or co-incineration plants shall be authorized. Permits will be issued by the competent authority and will list the categories and quantities of hazardous and non-hazardous waste which may be treated.

This Directive further provides technical information on incineration and related emissions destined to facilities intended for waste incineration and to "co-incineration" plants.

Directive 2010/75/EU revises and merges seven separate existing Directives related to industrial emissions into one single directive. It strengthens and adds certain provisions to ensure better implementation and enforcement of the legislation by national authorities, while at the same time it also simplifies the legislation and reduces administrative burdens. Chapters III to VI contain minimum technical requirements for waste incineration plants.

Decision 2011/632/EU establishes a questionnaire to be used for reporting on the implementation of Directive 2000/76/EC [2] on the incineration of waste.
Wastes from waste treatment, including incineration, are classified under coding section 19 of the list of hazardous wastes provided by Decision 2000/532/EC [2].

Provisions regarding water quality influencing pollution in wastewaters:
Directive 2000/60/EC, Directive 2006/118/EC and Directive 2008/105/EC [16]

Requirements concerning water quality may have an influence on limit values imposed for wastewater discharges. Requirements concerning water quality are covered by other legislation:

- Directive 2000/60/EC of 23 October 2000 establishing a framework for Community action in the field of water policy.
- Annex VI of Directive 2010/75/EU on the incineration of waste.
- Directive 2006/118/EC of 12 December 2006 on the protection of groundwater against pollution and deterioration.
- Directive 2008/105/EC of 16 December 2008 on environmental quality standards in the field of water policy.

Since 22 January 2013, Directive 2000/60/EC is the framework for water policy. The framework aims at the protection of inland surface waters, transitional waters, coastal waters and groundwater. It also provides measures regarding efficient and sustainable water use.
This framework states that a list of priority substances is published and reviewed by the European Commission. These substances may pose a significant risk for the aquatic environment.

A list of main pollutants is provided in Annex VIII of this Directive and below:

- Organohalogen compounds and substances which may form such compounds in the aquatic environment.
- Organophosphorous compounds.
- Organotin compounds.
- Substances and preparations, or the breakdown products of such, which have been proved to possess carcinogenic or mutagenic properties or properties which may affect steroidogenic, thyroid, reproduction or other endocrine-related functions in or via the aquatic environment.
- Persistent hydrocarbons and persistent and bioaccumulable organic toxic substances.
- Cyanides.
- Metals and their compounds.
- Arsenic and its compounds.
- Biocides and plant protection products.
- Materials in suspension.
- Substances which contribute to eutrophication (in particular, nitrates and phosphates).

- Substances which have an unfavorable influence on the oxygen balance (and can be measured using parameters such as biological oxygen demand [BOD], chemical oxygen demand [COD], etc.).

Metals and arsenic are present in the coal-fired power plant waste as a result of fly ash carryover from the coal combustion process.

Directive 2010/75/EU [23] also provides limit values for discharged wastewaters from the scrubbing of exhaust gases.

Directive 2006/118/EC [16] is designed to prevent and combat groundwater pollution. Its provisions include:

- Criteria for assessing the chemical concentrations in groundwater;
- Criteria for identifying significant and sustained upward trends in groundwater pollution levels, and for defining starting points for reversing these trends; and
- Preventing and limiting indirect discharges (after percolation through soil or subsoil) of pollutants into groundwater.

Member States shall set a threshold value for each pollutant identified in any of the groundwater within their territory considered to be at risk. At a minimum, Member States shall establish threshold values for ammonium, arsenic, cadmium, chloride, lead, mercury, sulphate, trichloroethylene and tetrachloroethylene. Member States shall establish a monitoring program. Entities will have to comply with the limit values for discharges into groundwater and surface waters as set by their national Authorities in the framework of this Directive.

Directive 2008/105/EC lays down environmental quality standards (EQS) for priority substances and certain other pollutants in the field of water policy. The EQS are included in Annex I. Member states are allowed to designate mixing zones adjacent to points of discharge. Concentrations for one or more substances listed in Annex I can exceed the EQS within such mixing zones if not affecting the compliance of the rest of the surface water body. Member states also have to establish an inventory, including maps, if available, of emissions, discharges and losses of all priority substances and pollutants listed in Annex I for each river basin district or part of a river basin district lying within their territory. As a result, limit values imposed will potentially have an influence on wastewater discharge authorized.

6.2.3 Canada and Australia

Hazardous waste is governed in Canada by the Canadian Environmental Protection Act, 1999 [19]. Hazardous waste is defined as dangerous goods that are no longer used for their original purpose if they meet the criteria for class 2, 3, 4, 5, 6, 8, or 9 of the Transportation of Dangerous Goods Regulations [19] or waste that is corrosive because it has a pH factor of less than 2.0 or greater than 12.5 measured directly when the waste is liquid. If the waste is toxic due to metals concentrations, the amount that can be generated on site monthly before becoming a registered generator is 1,000 L. Discharges of the waste to the environmental sewers are limited by the biochemical oxygen demand and concentrations of heavy metals.

Hazardous waste in Australia is governed by the Hazardous Waste Act of 1989 [20]. Hazardous wastes are explosive, flammable, poisonous, toxic, ecotoxic and or infectious substances and also wastes which contain certain compounds such as cadmium, mercury and lead. Currently, hazardous waste management differs by state and territory although there is movement to harmonize the framework of national and state model codes and regulations. Heavy metals are included in the hazardous substances that have an adverse effect on human health due to their physical, chemical, and biological properties.

6.3 Summary of Waste Characterization

The wastes generated from the various solvent reclaiming technologies and scenarios were characterized according to current regulatory structures in the US and EU. This characterization was performed by evaluating the characteristics of the CO_2 capture solvent, the metals content, and the nitrosamine content. Characteristics of the other minor constituents (e.g., HEIA, HEEDA, etc.) were not considered. The characterization was based upon the waste composition as determined by a model; no actual wastes were analyzed. 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 specifically listed or if it 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 reclaimer wastes did not contain ignitable or reactive constituents. No corrosivity data were available for these wastes; the wastes will have a non-corrosive pH, but they have to also meet 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. 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 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; actual mercury concentrations in the solvent may be significantly lower. Furthermore, coal-fired power plants can reduce mercury loading to the solvent by operating flue gas mercury controls to achieve higher mercury removal upstream of the CO_2 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 electrodialysis streams contain up to 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 according to Annex III of Directive 2008/98/EC of 12 December 2008 [4]. The exceptions were the waste streams from the solvents containing piperazine. Piperazine is a sensitizing material; the EU regulations contain no minimum thresholds for concentration of sensitizing materials. Therefore, the PZ and MDEA/PZ ion exchange and electrodialysis reclaimer waste streams may be classified as hazardous if they are sensitizing wastes.

REFERENCES

1. US Code of Federal Regulations, Part 261. http://www.ecfr.gov/cgi-bin/text-idx?c=ecfr&tpl=/ecfrbrowse/Title40/40cfr261_main_02.tpl
2. European Union, Decision 2000/532/EC, List of Wastes.
3. US Code of Federal Regulations, Part 260-282.
4. Directive 2008/98/EC of 19 November 2008.
5. US Code of Federal Regulations, 49 CFR 173, Shippers.
6. 30 TAC Sections 335, Subchapter R, Industrial Solid waste and Municipal Hazardous Waste, Waste Classification.
7. US Code of Federal Regulations, 40 CFR Table 302.4. Designation of Hazardous Substances.
8. Closure and Post-Closure Care Cost Estimating Software, Version 6.0, CostPro 6.0, United States Environmental Protection Agency; TetraTech EM, Inc, 2009.
9. Decision 2001/573/EC.
10. Directive 67/548/EEC, approximation of laws, regulations and administrative provisions relating to the classification, packaging and labeling of dangerous substances.
11. Huntsman Chemical, Material Safety Data Sheet, Monoethanolamine, 3/27/2000.
12. Science Lab.com, Material Safety Data Sheet, Piperazine, anhydrous. June 9, 2012.
13. The Dow Chemical Company, Product Safety Assessment, N-methyldiethanolamine, 3/24/2010.
14. Directive 1999/31/EC, last amended by Directive 97/2011/EU, Landfill of waste
15. Directive 2000/76/EC last amendment by Directive 2010/75/EU, and Decision 2011/632/EU, the Incineration Directive.
16. Directive 2000/60/EC, Directive 2006/118/EC and Directive 2008/105/EC, Establishing a Framework for Community action in the field of water policy.
17. The Hazardous Waste (England and Wales) Regulations 2005, Statutory Instrument 2005 No. 894.
18. The List of Wastes (England) Regulations 2005, Statutory Instrument 2005 No. 895.
19. http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=D44ED61E-1, CEPA Environmental Registry.
20. http://www.environment.gov.au/settlements/chemicals/hazardous-waste/tg/index.html, Australian Government, Department of Sustainability, Environment, Water, Population and Communities.
21. TCLP Questions. http://www.epa.gov/osw/hazard/testmethod/faq/faq_tclp.htm, accessed 03 May 2013.
22. Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.
23. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control)

7 DISPOSITION OPTIONS FOR RECLAIMER WASTE

Based on US and EU regulations, reclaimer waste from different solvents were classified as either non-hazardous or hazardous waste.

Figure 7-1 and Figure 7-2 show possible disposition options for non-hazardous and hazardous reclaimer wastes, respectively.

- **Non-hazardous Thermal Reclaimer Waste:** Disposition options are similar for the US and EU and include non-hazardous landfill, firing in a cement kiln, and firing in the on-site power plant furnace. Waste stabilization with fly ash prior to landfilling is common industrial practice.
- **Hazardous Thermal Reclaimer Waste:** Hazardous waste disposition options for the US include landfilling, off-site incineration, and firing in the on-site power plant furnace. Options for the EU include off-site incineration and firing in the on-site power plant furnace/boiler.
- **Ion Exchange and Electrodialysis Waste:** The ion exchange and electrodialysis process wastes are >95% water. The composition of the balance constituents can be found in the tables in Attachment 2 of this chapter. In the US and EU, these aqueous streams are subject to wastewater effluent guidelines. These liquid waste streams can be treated in either an on-site water treatment plant (WWTP), or pre-treated on-site prior to discharge to an off-site publically owned treatment works (POTW) for additional treatment.

Each of the disposition options is discussed below, including an evaluation of the suitability of the waste for that option and an estimate of disposition costs.

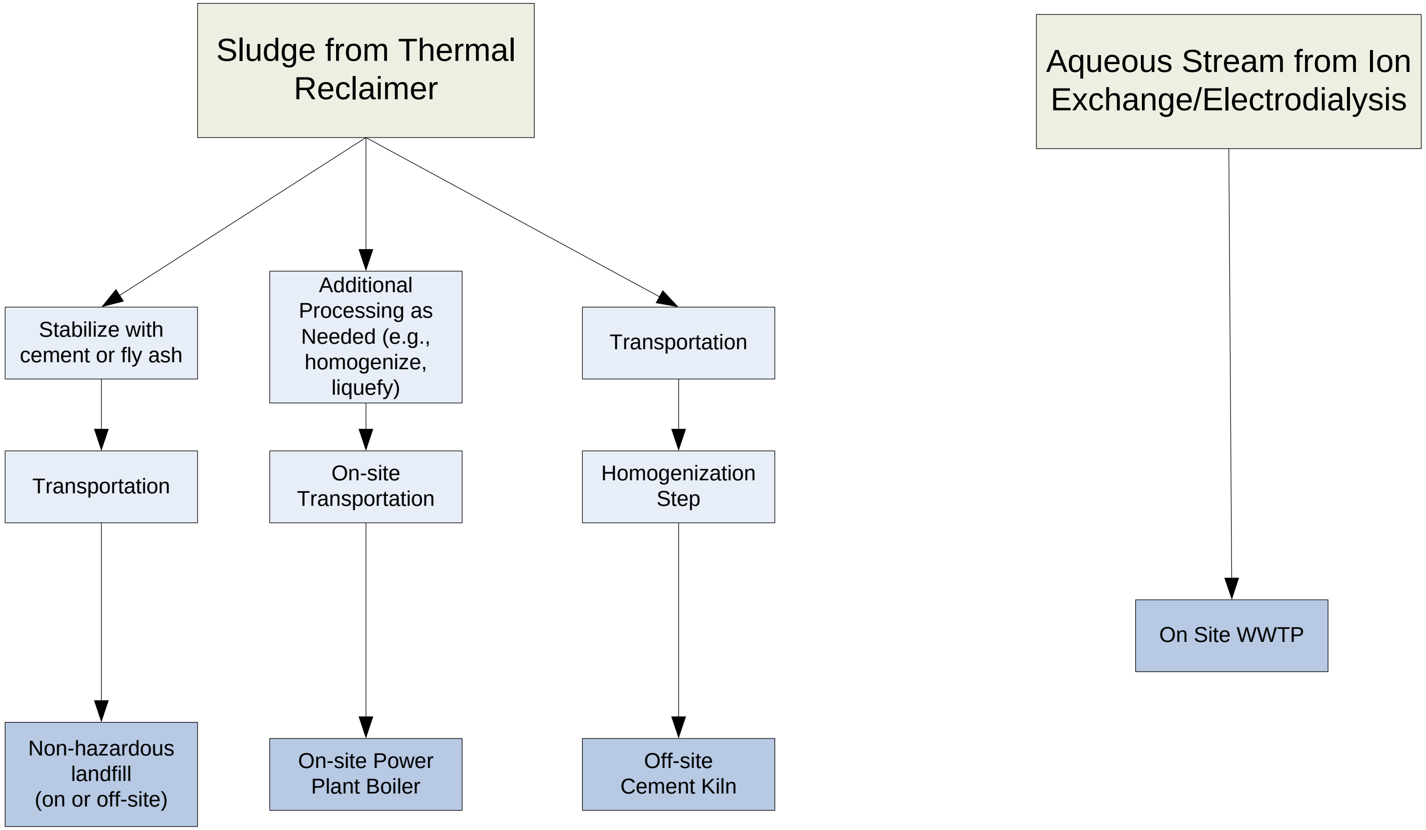


Figure 7-1 Disposition Options for Non-Hazardous Reclaimer Wastes in US and EU

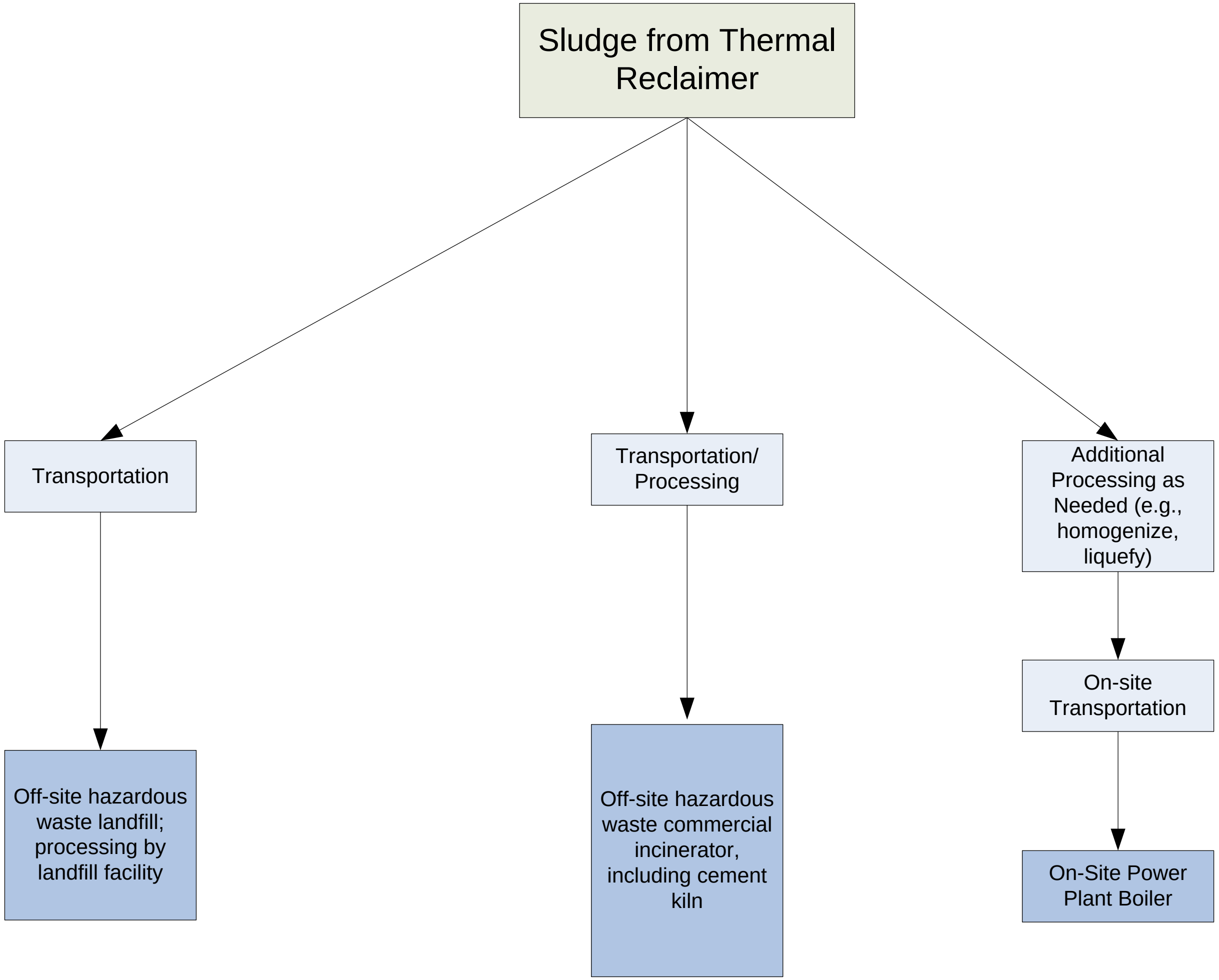


Figure 7-2 Disposition Options for Hazardous Reclaimer Wastes in US and EU

7.1 **Non-hazardous Waste Landfill**

The non-hazardous reclaimer wastes may be disposed of in a commercial non-hazardous landfill; in the US, thermal reclaiming waste from NGCC power plants and possibly the thermal reclaimer waste from coal-fired power plants might be eligible for disposal in a non-hazardous landfill. In the EU neither the coal-fired nor NGCC power plant wastes are eligible for disposal in a non-hazardous landfill. The ion exchange and electrodialysis waste streams are 95% water and more suited for disposal via WWTP than a landfill.

Each landfill has its own acceptance criteria based upon its permit. Typically, the landfill requests analytical data to demonstrate that the waste is not hazardous and that the waste is mostly solid. The data are used to build a waste "profile" which is updated as the process changes or at the request of the facility (usually annually). There were 1,645 landfills in the US as of 2005 [1]. In 2008, 135 million tons of non-hazardous waste was landfilled in the US; the US currently has 20 years of capacity. [2]

7.1.1 Waste Handling

It is likely that only dry, non-hazardous thermal reclaimer waste will be accepted by a commercial landfill. With a wiped film evaporator type thermal reclaimer, the sludge may be removed without dilution by water. With other thermal reclaiming systems, dilution by water is used to remove the sludge. Based on conversations with users of these processes, dilution with water by as much as 50% may be needed to recover the sludge from the reclaimer. This stream would need to be solidified prior to landfill disposal.

7.1.2 Costs

Transportation and disposal costs for disposing of the non-hazardous NGCC thermal reclaiming waste in a non-hazardous landfill were estimated using US EPA's Cost Spreadsheet, CostPro [3]; these are the thermal reclaiming wastes most likely to be non-hazardous. The costs shown in Table 7-1 include labor costs to package the waste, solidification costs, transportation to the landfill, and disposal of the non-hazardous waste in a solid waste landfill. The costs assume that the water addition wastes are transported as liquid in tankers and solidified off-site. The costs assume that the no water added wastes are solidified on-site and transported in boxes. The disposal costs ranged from $171,000 to $478,000 annually for the thermal reclaimer sludge removed from the reclaimer without water addition; diluting the stream to 50% water increases the disposal cost to $510,000 to $1,420,000 annually. Costs from CostPro 6.0 are presented in 2007 dollars; these costs were scaled to current dollars using the overall Chemical Engineering Plant Cost Indicies (CEPCI) and then converted to Euros assuming 1 USD = 0.75 EUR. The costs as presented in EUR/year do not represent an estimation of landfill costs for the EU. Landfill costs are highly location specific due to availability of landfill sites and local regulation. Within the US, landfill costs can vary widely from the east coast (expensive) to the less populated areas in the west (less expensive). Furthermore, costs developed for the US cannot be used to infer disposal costs for other countries. The annualized costs for operating the reclaimer process presented in Chapter 5 did not include the cost of waste disposition. The annual costs associated with disposing of the non-hazardous waste from the NGCC power plants (US only) represent 15 to 30% of the annualized cost of the reclaimer process.

Table 7-1 Estimated Costs for Disposing of Non-Hazardous Waste Sludge Generated by the Thermal Reclaimer from NGCC Power Plant in the US

Waste Stream from NGCC Power Plant	Non-hazardous Waste Landfill $/year	Non-hazardous Waste Landfill €/year
MEA Thermal Reclaiming – No Water Added	208,000	156,000
MEA Thermal Reclaiming – Water Addition	567,000	425,000
PZ Thermal Reclaiming – No Water Added	369,000	277,000
PZ Thermal Reclaiming – Water Addition	981,000	736,000
MDEA – PZ Thermal Reclaiming – No Water Added	581,000	436,000
MDEA – PZ Thermal Reclaiming – Water Addition	1,582,000	1,187,000

7.2 Hazardous Waste Landfill and Hazardous Waste Incineration

Hazardous wastes are disposed of in an approved treatment, storage, or disposal facility such as a hazardous waste landfill, hazardous waste incinerator, or on-site boiler. Waste may need to be treated by solidification by the treatment, storage, or disposal facility prior to disposal.

In the US, a hazardous waste landfill will require a profile of the waste which will need to be updated as the process changes or as required by the landfill. The waste shall be in a solid form or solidified enough so that it does not threaten cap integrity. Most hazardous waste landfills have the capability to solidify liquid hazardous waste at an additional charge. Wastes placed in a hazardous waste landfill have to be able to meet land disposal restrictions. There are 21 commercial hazardous waste landfills in the United States [2].

The EU has restrictions on the types of hazardous material that can be landfilled, as communicated by a representative of the Scottish Environment Protection Agency [46]. Flammable, oxidizing, and corrosive materials cannot be landfilled. Only hazardous materials that have undergone some sort of pretreatment (unless not technically possible) and that meet leachability limits are eligible for a hazardous waste landfill. These limits were derived by an EU Technical Advisory Group. In addition to limits for metal contamination and key organic anions, the waste should have less than 10% loss on ignition and total organic carbon content less than 6%. The modeled waste from the thermal reclaimer does not meet several of these criteria (e.g., corrosivity, organic carbon content), therefore, the waste is ineligible for disposal in a hazardous waste landfill.

In the US, a hazardous waste incinerator will require a profile of the waste which will include how much energy will be generated when the waste is burned. The water content of the waste may require additional fuel. There are 22 facilities permitted to incinerate hazardous waste in the United States [2]. The hazardous waste could also be fired in a cement kiln; this option will be discussed in Section Firing in Cement Kiln. The hazardous waste could be fired in the on-site power plant furnace; this option will be discussed in Section Firing in On-site Power Plant Furnace.

A dedicated waste incinerator could be built at the power plant site for the purpose of disposing of the amine sludge waste. Additional support fuel would be required to maintain stable combustion, due to the high water content of the amine waste sludge. Alternately, the sludge could be incinerated in a fluidized bed furnace without support fuel, so long as the waste did not cause bed agglomeration or de-fluidization. This option is likely to be very expensive because it would require its own flue gas cleaning technologies and flue gas monitoring so that the emissions source meets the permit requirements of its locale. It is unlikely power plants would choose this option, so it was not considered further for this study.

7.2.1 Costs

Cost estimates for disposal of hazardous waste were made using US EPA's cost spreadsheet, CostPro 6.0 [8]. Table 7-2 presents the costs associated with disposing of the hazardous wastes. The following assumptions (generally defined by the program) were made to generate the cost estimate:

- The flow rates developed by the waste model in Chapter 5 were used to develop the waste volume for each stream.
- The costs included the labor and materials to collect the waste and transfer it to the disposal facility, the cost to solidify liquid waste (landfill) or homogenize the waste (incinerator), and the cost to dispose of the waste. The approximate contribution to costs for each of these steps is as follows: removal (5-10%), transporation (10-15%), solidificaiton (5-10%), and treatment/disposal (70-80%).
- The cost to solidify the waste for landfilling or to homogenize for incineration was assumed as €49/m^3 (\$50/$yard^3$). Both types of thermal reclaiming waste ("no water added" and "water addition") include solidification/homogenization costs.
- The distance to the hazardous waste landfill or incinerator was kept to 483 km (300 miles); this value is the default distance in the EPA cost model.
- The cost to treat and dispose of the waste off-site was assumed to be at the high end of the cost range in the model's database (i.e., €387/m^3 or \$395/yd^3 for solid waste (i.e., no water added waste); €0.60/liter or \$3.04/gal for liquid waste (i.e., water addition waste)). The default model assumptions used the same unit costs for treatment and disposal for the landfill and incinerator options.
- The costs were based on a 7 day week/24 hour/day operation at 85% capacity of the power plant.

Table 7-2 Estimated Costs for Disposing of Hazardous Wastes Generated by Thermal Reclaimer, either by Landfill or Incinerator, in the US

Waste Stream from Coal-fired Power Plant	Hazardous Waste Disposal $/year	Hazardous Waste Disposal €/year
MEA Thermal Reclaiming – No Water Added	2,531,000	1,898,000
MEA Thermal Reclaiming – Water Addition	6,395,000	4,796,000
PZ Thermal Reclaiming – No Water Added	3,963,000	2,972,000
PZ Thermal Reclaiming – Water Addition	10,103,000	7,577,000
MDEA – PZ Thermal Reclaiming – No Water Added	5,945,000	4,459,000
MDEA – PZ Thermal Reclaiming – Water Addition	15,152,000	11,364,000

The annualized costs for operating the reclaimer process presented in Chapter 5 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. These waste disposal costs are applicable to waste solvent profiles for the coal thermal reclaiming cases in Tables 5-22 through 5-24 in Section 5.6 using the initial assumption of a slipstream of 0.1 wt% of the total circulation rate. The annualized total revenue requirement (includes capital costs, operating and maintenance costs, and energy requirements) for these cases are €4.1MM/yr for MEA, €13.1MM/yr for PZ, and €11.5MM/yr for MDEA/PZ. In Section 5.7, analysis demonstrated that solvent losses via reclaiming were reduced when it was alternately assumed that the concentration of heat stable salts entering the reclaimer was 1.5 wt%; although the waste disposal costs were not explicitly calculated for this alternate assumption, it is expected that waste disposal costs would decrease if the mass flow rate of waste being disposed decreases. Therefore, selection of a reclaimer process should carefully consider the type of waste generated and associated costs of disposing of that waste.

7.3 Firing in Cement Kiln

Firing in a cement kiln is a potential disposition option for the amine sludge from the thermal reclaimer, and is applicable whether the amine waste classified is hazardous or non-hazardous. In the United States, a wide variety of wastes, both hazardous and non-hazardous, are currently fired in cement kilns, including liquid wastes such as paint sludges and waste solvents, slurried wastes such as residual sludge from pulp and paper production, and solid waste such as tires. In the EU, major alternative fuels for cement kilns include refuse-derived wastes, plastics, commercial wastes, communal wastes, animal meal, sewage sludge, and tires. These wastes are added with the fuel to the cement kiln.

7.3.1 Cement Kiln Process

A cement kiln is a rotating, slightly inclined from horizontal, cylindrical furnace lined with refractory brick that is used in the production of cement. The kiln is typically fired with coal, petroleum coke, or oil; some cement production facilities replace some of the fossil fuel with alternate fuels. Both the fuel and the raw materials used in cement production naturally contain halogens, metals, and organic compounds. The hot kiln gases run countercurrent to the raw feed materials and carries particulate matter to downstream air pollution control devices (e.g., gas cyclones, electrostatic precipitators, and fabric filter baghouses).

The major raw materials are limestone and clay or shale. Other raw materials may be used to provide the correct mix of metals needed to produce cement. The raw materials are ground to a fine powder and may be fed to the kiln as a water based slurry (wet process) or as a dry powder (dry process.) Most of the dry process kilns have a separate preheater and/or precalciner section that begin the heating process. Sintering takes place in the kiln.

As the limestone decomposes in either the precalciner or the kiln, CO_2 is driven off from the solid matrix. The raw material then continues to heat and react under oxidizing conditions to form clinker which is primarily composed of calcium oxide; oxides of silicon, aluminum, and iron are also present. Upon exiting the kiln, the clinker is cooled and mixed with gypsum to make the final cement product [4].

In the kiln the feed materials can reach temperatures as high as 1450°C (2640°F), with the gas temperature typically no greater than 2000°C (3600°F).

The particulate matter collected from the air pollution control device(s) is termed cement kiln dust (CKD) and is typically returned to the kiln with the raw feed. Some portion of the CKD is purged to prevent the buildup of alkali salts and semi-volatile metals in the process; the purged CKD can be used as a lime substitute, to stabilize wastes, etc., or it can be landfilled. With some exceptions, CKD is not generally classified as a hazardous waste in both the US and EU.

The cement manufacturing process does not generally employ any direct contact water for washing or cooling such that a liquid waste stream is generated. Water fed to the kiln in the wet process is completely evaporated and is discharged into the air.

7.3.2 Regulatory Framework – US

Cement kilns operating in the US are potentially subject to several different environmental regulations that limit air emissions of various constituents. The applicability of the individual regulations is based on the construction or modification date of the kiln and the type(s) of fuel used. The New Source Performance Standards (NSPS) for cement kilns [5] applies to all kilns constructed after June 2008 or kilns that have been modified, regardless of fuel. The National Emission Standards for Hazardous Air Pollutants (NESHAP) from the Portland Cement Manufacturing Industry [6] applies to all cement kilns that do not burn hazardous waste, while the Hazardous Waste Combustor MACT Standards [7] apply to kilns that do burn hazardous waste. The NSPS Regulations for Commercial and Industrial Solid Waste Incinerators (CISWI) [8] apply to cement kilns that burn non-hazardous secondary materials (NHSM). NHSM are defined in the Resource Conservation and Recovery Act (RCRA) [9] regulations as those materials that are not hazardous waste, but are also not considered as fossil fuels or equivalent to fossil fuels [10].

Table 7-3 summarizes these regulations and presents the emission limits of the regulated constituents. Because the impurities present in the amine sludge will at least be partially volatilized in a cement kiln and will likely be emitted into the air, the potential applicability of these regulations is important to understand how they may influence the ability of a cement kiln to accept the amine sludge.

All of the described regulations have undergone several iterations of proposal, promulgation, and legal challenge. In mid-2013, all of these regulations are final and in effect and desribed in the table. However, these limits may change over time if additional legal challenges occur. In addition, because the CISWI limits were only promulgated in February 2013, those limits will only become effective for existing cement kilns three years after the states amend their state implementation plan or by February 2018 under a federal plan.

In addition to the emission limits presented in Table 7-3, cement kilns have to develop various operating limits, use continuous emission monitors, perform process monitoring, conduct periodic emission testing, and perform various recordkeeping and reporting functions to comply with these regulations. The addition of amine sludge as a fuel to a cement kiln that is already complying with the regulations may change or add to its compliance requirements or may require additional testing or monitoring to demonstrate compliance while using the amine sludge.

Table 7-3 Summary of US Air Emission Regulations Applicable to Cement Kilns

Regulation	New Source Performance Standards (NSPS) for Cement Kilns [11]	Portland Cement Maximum Achievable Control Technology Standards (MACT) [12]	NSPS for Commercial and Industrial Solid Waste Incinerators CISWI [13]	Hazardous Waste Combustion (HWC) MACT [14]
Applicability, based on Fuel Used	All	Fossil fuels and/or non-hazardous alternate fuels	Non-hazardous secondary material used as a fuel in a cement kiln	Hazardous Waste Fuels with or without Fossil Fuels
Particulate Matter (PM)	0.01 kg/metric ton (0.02 lb/ton) clinker (kilns constructed after 6/16/08); or 0.035 kg/metric ton (0.07 lb/ton) clinker (kilns that have undergone a modification).	0.035 kg/metric ton (0.07 lb/ton) clinker	4.6 mg/dscm@7% O_2	64 mg/dscm (0.028 grains/dscf) @7% O_2 and 20% opacity (Opacity not required with bag leak detection system)
Oxides of Nitrogen (NO_x)	0.75 kg/metric ton (1.50 lb/ton) of clinker (kilns constructed after 6/16/08) (Not applicable to kilns with alkali bypass duct).	None	630 ppmvd@7% O_2	None
Sulfur dioxide (SO_2)	0.2 kg/metric ton (0.4 lb/ton) clinker (kilns constructed after 6/16/08); or 90% SO_2 reduction across SO_2 control device.	None	600 ppmvd@7% O_2	None
Carbon Monoxide (CO)	None	None	110 ppmvd @7% O_2 (long kilns); 790 ppmvd @7% O_2 (preheater/precalciner kilns)	For kilns with a mid-kiln bypass duct or sampling system: 100 ppmvd @7% O_2 and 10 ppmv THC during DRE testing (at the mid-kiln; Or 10 ppmv THC at the mid-kiln. For kilns without a mid-kiln bypass or sampling system:
Total Hydrocarbons (THC) (measured as propane)	None	24 ppmvd@7% O_2	None	

Regulation	New Source Performance Standards (NSPS) for Cement Kilns [11]	Portland Cement Maximum Achievable Control Technology Standards (MACT) [12]	NSPS for Commercial and Industrial Solid Waste Incinerators CISWI [13]	Hazardous Waste Combustion (HWC) MACT [14]
				100 ppmvd @7% O_2 and 20 ppmv THC during DRE testing (at the main stack) or 20 ppmv THC in the main stack
Dioxins/Furans (D/F)	None	0.2 ng/dscm TEQ@7% O_2	0.075 ng/dscm TEQ@7% O_2	0.20 ng/dscm TEQ@7% O_2
Hydrogen chloride (HCl)	None	3 ppmvd@7% O_2	3 ppmvd @7% O_2	120 ppmv @7% O_2
Mercury (Hg)	None	27.5 kg/10^6 metric ton (55 lb/MM ton) clinker	0.011 mg/dscm @7% O_2	Average as-fired concentration of Hg in all hazardous waste no more than 3 ppmw and 120 µg/dscm @7% O_2
Lead (Pb)	None	None	0.014 mg/dscm @7% O_2	3.5E-04 kg (7.6E-04 lb) combined Cd &Pb/MMBTU attributable to the hazardous waste, and 330 µg combined Cd &Pb /dscm @ 7% O_2
Cadmium (Cd)	None	None	0.0014 mg/dscm @7% O_2	
Arsenic (As) , Beryllium (Be), and Chromium (Cr)	None	None	None	9.80E-06 kg (2.16E-05 lb) combined As, Be,& Cr/MMBTU attributable to the hazardous waste, and 56 µg combined As, Be, & Cr /dscm @ 7% O_2
Destruction and Removal Efficiency (DRE)	None	None	None	99.99% of specified organics.

Notes: dscm = dry standard cubic meter; dscf = dry standard cubic foot; TEQ = toxicity equivalents.

7.3.2.1 *Cement Kiln Dust*

Cement Kiln Dust (CKD) wasted from cement kilns that do not burn RCRA hazardous waste is currently categorized as a special waste by US EPA. It is temporarily exempted from being considered as a hazardous waste under the Bevill amendment. EPA is in the process of developing management standards for CKD under the non-hazardous, solid waste regulations (Sub-Title D) of the RCRA [15].

CKD wasted from cement kilns that do burn hazardous waste may or may not be considered as a RCRA hazardous waste under the waste residue provision [16] of the rule governing Hazardous Waste Burned in Boilers and Industrial Furnaces (BIF) [17]. If the cement kiln processes at least 50% by weight normal cement-production raw materials, and the owner demonstrates that the hazardous waste burned in the cement kiln does not significantly affect the residue by comparing either 1) the waste-derived residue with the normal residue, or 2) comparing the waste-derived residue with health-based limits, then the CKD is not subject to regulation as a hazardous waste. If these conditions are not met, then the CKD wasted from a hazardous waste-burning cement kiln is not excluded from being considered as a hazardous waste.

7.3.3 **Suitability of Reclaimer Waste for Firing in Cement Kiln**

The cement industry does not burn any waste that would compromise the quality of its cement. In the US cement shall meet performance standards set by the American Society for Testing and Materials (ASTM).

In addition to the product quality concerns, the impact of the reclaimer sludge on the CKD also needs to be considered. If the amine sludge is considered a RCRA hazardous waste, then its impact on the CKD generated and wasted from a cement kiln would need to be evaluated so that the kiln operator would know the regulatory determination of the CKD generated while burning the amine sludge.

7.3.3.1 *Energy Content*

Table 7-4 summarizes the energy contents for the modeled thermal reclaimer waste sludges. With a wiped film evaporator type thermal reclaimer, the sludge may be removed without dilution by water. With other thermal reclaiming systems, dilution by water is used to remove the sludge. Based on conversations with users of these processes, dilution with water by as much as 50% may be needed to recover the sludge from the reclaimer. While there is no lower energy content limit for hazardous waste to be used as a fuel, low energy content materials may not be accepted by hazardous waste burning facilities, or they may only be accepted at high cost. If the amine sludge is not a hazardous waste, it would most likely be considered a NHSM. Again, there is no minimum limit on energy content to be eligible as a NHSM, but facilities may have little interest in accepting low energy content material.

The substitution rate for coal by alternate fuels in Europe is approximately 30% on a weight basis. However, because of the lower specific heating content of the alternative fuels, the substitution rate is only approximately 12% on an energy basis. Because of the lower heating content of alternatives, a greater mass of those fuels are required to introduce an equivalent heat input. As a result, more combustion air is required to combust these materials, which also raises the overall gas flow and amount of heat wasted in the exhaust gas. The amount of alternate fuel that can be fed without negatively impacting the kiln system is therefore dependent on the heating value of the fuels and the energy efficiency of the plant. For example, it is expected that the coal-fired MDEA/PZ reclaimer waste could provide up to 15% of the thermal input to the rotary kiln, while the coal-fired MEA reclaimer waste could only be used in very low quantities. A high water content would cool the flame and retard ignition of the fuels and cause difficulties in burning the clinker.

Table 7-4 Energy Content of Thermal Reclaimer Waste Sludges

Modeled Case	Thermal Reclaiming, No Water Addition (kJ/kg)	Thermal Reclaiming, Water Addition to 50% H_2O Content (kJ/kg)
MEA – Coal	9731	4866
PZ – Coal	19600	9801
MDEA/PZ – Coal	20424	10212
MEA – NGCC	12506	6253
PZ – NGCC	24189	12094
MDEA/PZ - NGCC	22516	11256

7.3.3.2 *Organic Constituents*

Cement kilns are advantageous for firing liquid hazardous and non-hazardous waste fuel because of their long gas residence times in the combustion chamber and high firing temperatures. Cement kilns typically satisfy the thermal destruction benchmark for the complete destruction of organic compounds of a residence time of greater than two seconds at a temperature of greater than 1200°C [18]. Organic emissions are monitored to comply with applicable regulations by continuous measurement of carbon monoxide or total hydrocarbons. Dioxin/furan emissions are measured during periodic testing. For hazardous waste burning kilns, organic emissions are also minimized by demonstrating a minimum organic destruction and removal efficiency (DRE) of 99.99% [19]. The addition of the amine sludge to a cement kiln would require additional testing to show that the kiln emissions would still comply with the applicable emission limits while using the sludge as fuel.

7.3.3.3 *Metals Content*

Based upon modeling results, the waste sludges from the various solvents and reclaiming processes may contain anywhere from <1 ppm of various regulated metals to up to approximately 20 ppm chromium. These metal concentrations may be different and higher than the metals concentrations in the currently used fuels. The introduction of wastes with higher metal concentrations would require an adjustment of the raw material to prevent influencing the resulting cement properties such as setting behavior and strength development.

The volatile metal mercury (Hg) evaporates at approximately 250°C and may be emitted from the cement kiln system with the exhaust gases. Some Hg may re-condense with the CKD in the cooler portions of the system. Semi-volatile metals, such as cadmium (Cd) and lead (Pb), volatilize in the kiln, but at least partially re-condense in the cooler, downstream air pollution control device(s). These metals, along with chlorides, are often concentrated in the CKD. High melting point, refractory metals generally do not volatilize in the kiln and are discharged with the cement clinker product.

The content of aluminum and iron will have an effect on the type of formed clinker phase. For example, a higher content C3A (phase containing Al) will result in faster setting. Other clinker phases are less formed and could impair the strength development.

In general, the raw mix would need to be adjusted for the changes in metal concentration arising from the use of the amine wastes to ensure comparable clinker is produced. Wastes that have similar metals contents to the fuels currently used could be substituted at a higher substitution rate without affecting clinker quality.

During emission testing to demonstrate compliance with the regulations, cement kilns generally feed the maximum amount of metals and chlorine they can, while not affecting the quality of the cement, not affecting the CKD, and still meeting the emission limits. From these tests, the kilns develop maximum feed rate limits for each regulated metal and chlorine. If amine sludge were to be added to the fuel mix, the metals and chlorine content of the sludge would need to be considered and accounted for to stay within the established limits.

The NGCC-derived thermal reclaimer wastes are expected to have very low to no hazardous metals content. The coal-derived thermal reclaimer wastes have hazardous metals content up to 25 ppm. Both the NGCC- and coal-derived wastes have significant non-hazardous metals contents; the metals deriving from iron and other stainless steel metals range from 0.2 to 0.4 wt% in the reclaimer waste. Kilns that recycle CKD back to the kiln have the potential to increase the concentration of metals such as Hg and Cd in the kiln dust over time. Since the amine sludge waste from coal-fired units contains an appreciable metals content, the heavy metals equilibrium of the cement kiln would need to be considered and may affect the kiln's emissions compliance demonstration strategy.

7.3.3.4 *Chlorine Content*

The impact of firing the hazardous waste on recycled volatile elements such as chlorine, sulfur or alkalis has to be considered prior to burning. It is important that the introduction of these components does not affect the operation of the kiln [4]. Hydrogen chloride **(**HCl) is generated when chlorinated wastes are burned in a cement kiln. The NGCC-derived wastes have little to no chloride content. The chloride content of the undiluted coal-derived thermal reclaimer wastes ranged from 1.1 to 2.5 wt%, while typical chlorine contents for feed materials are 50 to 240 ppm for limestone and 15 to 450 ppm for clay/shale; typical coal chloride concentrations range from 20 to 1000 ppm.

A feed rate of the amount of 1000 kg/h of the reclaimer waste would amount to approximately 3% of thermal input of an average cement plant with 3,000 tons/day clinker production.

According to a cement kiln industry expert, a chlorine concentration of 1% in the waste would not add an excessive amount of chlorine to the overall system.

7.3.3.5 *Ash Content*

The amount of material from the amine reclaimer sludge that would be bound in the clinker depends on the ash content of the fuel used in the power plant. The various amine reclaimer sludges from coal-fired power plants may contain from approximately 0.5% to 3.0% fly ash. Fly ash is a common substitute material in cement kilns; therefore the presence of fly ash in the reclaimer sludges is likely to have no significant impact to the kiln operation.

7.3.3.6 *Sulfate Content and NaOH Content*

The sulfate concentration of the various waste stream ranges from <1% to 18.5%. These higher sulfate concentrations are quite high, and, depending on the other specifications of the power plant, may require the addition of a bypass system to remove the sulfate to not impact clinker quality. The same applies to sodium hydroxide.

7.3.4 Waste Handling

The amine sludge is conditioned prior to firing in a cement kiln. Typically, specialized companies collect the waste at the producing source and prepare it off-site for firing in a cement kiln. Often these companies are co-located at the cement kiln. Since the amine sludge product composition will vary over time, the waste will need to be analyzed, classified and then stored for stabilization purposes; a blend of the waste would be prepared to ensure continuity in the composition of the waste delivered to the cement kiln.

Due to the characteristics of the solvents in the thermal reclaimer sludge, the sludge will need to be handled in closed systems, with special measures taken to avoid release of the sludge (e.g., secondary confinement) and to avoid contact with humans, wildlife, and the environment. Cement kiln personnel will need to be trained in the handling of these substances.

7.3.5 Costs

Costs specific to incineration at a cement kiln are expected to be similar to the costs to incinerate at a hazardous waste facility, as provided in the previous section 7.2.1 Costs.

7.4 Firing in On-site Power Plant Furnace

One potential disposition option is to fire the reclaimer waste in the facility’s boiler furnace. Supercritical pulverized coal (SCPC) power plants fire coal as the primary fuel source, but some facilities have also been retrofit to accommodate firing tire waste or biomass. Biomass can include municipal solid waste, agricultural waste, animal factory waste, construction/demolition (wood) debris, and even energy crops such as switchgrass [20]. Power plant furnaces typically use oil and/or gas as a start-up fuel. The reclaimer waste could be introduced through an existing oil gun or with an alternative fuel stream. While it may not seem likely that a viscous or high water content waste stream could be co-fired with natural gas in a NGCC, options may exist for disposing the reclaimer sludge in the heat recovery steam generator (HRSG). Firing the amine sludge serves to destroy the waste while adding heating value to the boiler. This approach is viable even if the amine waste is classified as hazardous, though extra regulatory requirements would be introduced.

Additional regulatory requirements to co-firing hazardous waste in both the US and EU will be addressed below. The suitability of the reclaimer sludge as an alternative fuel for coal fired units, including the additional heat value of the waste, will then be discussed. The viability and impact of using the waste in the HRSG of a NGCC will be addressed, following by a discussion on the impact of emissions on a SCPC. Because of the high amine content, the amine waste may be useful as part of a NO_X control scheme. The possibility of using the amine waste to augment the reagent used for either selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) will be explored. This section will conclude with reclaimer waste handling issues and a high level assessment of the cost of co-firing in the on-site power plant furnace.

7.4.1 Regulatory Framework – US

The Clean Air Act (CAA) defines EPA's responsibilities for protecting and improving the nation's air quality. The last major amendments to the Act were made in 1990. Title I of the Act sets out requirements for EPA to set emission standards for new sources and to regulate sources of hazardous air pollutants (HAP).

New Source Performance Standards (NSPS) regulate new and modified sources by the type of emission unit. These standards are codified in 40 CFR 60. National Emission Standards for Hazardous Air Pollutants (NESHAPS), also referred to as MACT (Maximum Achievable Control Technology Standards), apply to all sources in a specific industry sector and are codified in 40 CFR 63.

There are currently 187 regulated hazardous air pollutants. The Act also requires EPA to regulate air emissions from waste combustion.

7.4.1.1 *Classification of Thermal Reclaimer Waste per the CAA*

The air quality regulations that apply to firing of thermal reclaimer waste in a utility boiler depend on whether the reclaimer waste is a RCRA hazardous waste or a non-hazardous waste. If it is considered a RCRA hazardous waste, then, since 1991, firing it in a boiler makes that boiler subject to the RCRA Boiler and Industrial Furnace (BIF) Rule (40 CFR 266, Subpart H). However, since 2005, the emission and operating limits in these standards have been superseded, and emissions from combustion of hazardous waste are now regulated at 40 CFR 63, Subpart EEE, National Emission Standards for Hazardous Air Pollutants (NESHAPs) from Hazardous Waste Combustors.

Therefore, it would be important to test the thermal reclaimer waste prior to firing to prove that it is not characteristically hazardous. The frequency with which this test would be conducted would depend on the expected variability of the waste composition.

Recent regulatory changes appear that even the co-firing of non-hazardous waste in a coal-fired boiler may soon be subject to the regulations meant for commercial and industrial solid waste incinerators (CISWI). This is discussed in more detail in the section below.

7.4.1.2 *RCRA NHSM Rules Related to the CAA*

In March 2011, EPA promulgated the “Non-Hazardous Secondary Materials (NHSM) that are Solid Waste” definition rule under RCRA at 40 CFR 241. Revisions to the rule were finalized in

December 2012 were published in the Federal Register on February 7, 2013. The rule codifies requirements and procedures that identify whether the definition of solid waste applies to non-hazardous secondary materials burned as fuels or used as ingredients in combustion units (cement kilns). A “secondary material” is any material that is not the primary product of a manufacturing or commercial process, and can include post-consumer material, off-specification commercial chemical products or manufacturing chemical intermediates, post-industrial material, and scrap (codified in § 241.2). “Non-hazardous secondary material” is a secondary material that, when discarded, would not be identified as a hazardous waste under 40 CFR. The NHSM definition rule is used when combustion sources (e.g., boilers) burn materials other than “traditional fuels” (e.g., clean biomass, fuel oil, coal, natural gas) to determine if the combustion unit is burning a fuel and can be regulated as a boiler or is burning a non-hazardous waste and is regulated as a solid waste incinerator.

7.4.1.3 *Legitimacy Criteria*

In the March 2011 NHSM rule, EPA specified the criteria to be used to determine if NHSM are solid wastes. Amendments finalized in December 2012 were intended to provide clarification and assist in the implementation of the rule as originally intended. For purposes of the CAA, NHSM used as fuels that remain with and are combusted within the control of the generator and that meet the legitimacy criteria are not solid wastes. In order to be considered a legitimate fuel, NHSM shall:

- be handled as a valuable commodity,
- have meaningful heating value,
- be used as a fuel in a combustion unit that recovers energy, and
- contain contaminants at levels comparable to those in traditional fuels.

Materials “handled as a valuable commodity” are either managed in a manner similar to comparable fuels or otherwise contained to prevent spill or leakage into the environment. NHSM with a heating value greater than 5,000 Btu/lb, as fired, would be considered to have meaningful heating value. However, NHSM with a heating value lower than 5,000 Btu/lb, as fired, may also be considered to have a meaningful heating value if the combustion unit can cost-effectively recover energy from combustion of these materials. NHSM will also have to be compared to contaminants in traditional fuels – contaminants being defined as constituents of NSHM that could results in emissions of Hazardous Air Pollutants (HAPs) listed under CAA Section 112(b) or the nine pollutants regulated under CAA section 129.

It is possible that the thermal reclaimer waste could meet all of the legitimacy criteria: the thermal reclaimer waste could be handled as a valuable commodity, the heating value is meaningful (as shown in Section Suitability of Reclaimer Sludge for Firing in Coal-Fired Furnace, it is within range of lignite coals), and it can be fired in a combustion unit that recovers energy. As will be discussed in this section, the concentrations of Hg and Se in the modeled reclaimer waste were approximately100 times the concentrations found in the coal; however, the predicted metals concentrations in the waste carry considerable uncertainty since they were based solely on modeling results. Actual reclaimer waste would need to be analyzed for a determination on contaminant levels.

7.4.1.4 *Commercial and Industrial Solid Waste Incinerator Regulations (CISWI)*

If the reclaimer waste is not classified as a legitimate fuel and it is non-hazardous, then a utility boiler firing the waste would be subject to CISWI. Existing units are regulated under state rules based on the Emission Guidelines located at 40 CFR 60, Subpart DDDD. New and modified units are regulated under the New Source Performance Standards located in 40 CFR 60, Subpart CCCC for units built after November 30, 1999.

In the March 21, 2011, revisions to the CISWI rules, EPA established a subcategory with emission limits for energy recovery units (boilers) burning NHSM. The CISWI rules were subsequently amended on February 7, 2013. Existing boilers burning NHSM are regulated under the emission guidelines, which states incorporate into their State Implementation Plan (SIP). States either incorporate the federal emission guidelines by reference or have a SIP rule that is updated to reflect the revised emission guidelines. The emission guidelines allow existing units 3 years to come into compliance. New/modified boilers burning NHSM will be regulated under the new source performance standards (NSPS) and shall comply upon startup.

The CISWI rules contain fairly stringent limits for hydrogen chloride, carbon monoxide, lead, cadmium, mercury, filterable particulate matter (PM), dioxin/furan, NO_x, SO_2, and opacity. The hydrogen chloride and dioxin/furan limits are extremely low. Rigorous monitoring, testing, recordkeeping, and reporting requirements are included in the CISWI rules. A waste management plan and operator training are also required. CISWI units can switch back to being regulated as boilers six months following the cessation of burning of solid waste.

7.4.1.5 *Hazardous Waste Combustor Regulations*

If the thermal reclaimer waste is considered hazardous waste under 40 CFR 261, then a boiler firing it would be regulated as a hazardous waste combustor.

Regulations at 40 CFR 63 Subpart EEE regulate emissions of dioxin/furan, mercury, cadmium, lead, arsenic, beryllium, chromium, PM, hydrogen chloride, chlorine, and either carbon monoxide or total hydrocarbon. The emission limits for PM and metals are more stringent than CISWI, but the emission limits for carbon monoxide (CO) and hydrochloric acid (HCl) are less stringent. Rigorous monitoring, testing, recordkeeping, and reporting requirements are included in Subpart EEE. Units that want to start burning hazardous waste would have to be in compliance with these regulations at start-up.

Boilers regulated under Subpart EEE also need a RCRA permit to operate. However, the RCRA permit only needs to address general facility standards, corrective action, closure, other hazardous waste management units (such as storage units), and other combustor-specific concerns such as materials handling.

7.4.1.6 *Utility Boiler Mercury and Air Toxics Standards (MATS)*

Hazardous Air Pollutants (HAPs) from combustion of coal and oil in utility boilers are regulated under the NESHAP for Coal and Oil-Fired Electric Utility Generating Units at 40 CFR 63, Subpart UUUUU, also referred to as the Mercury and Air Toxics Standards (MATS). This rule would not apply to a utility boiler firing thermal reclaimer waste; instead, as discussed above, either the CISWI rule or Hazardous Waste Combustor NESHAP would apply. However, both of these rules have provisions for moving back and forth between air quality standards that apply to waste combustion and fuel combustion, so a utility boiler could conceivably be regulated under the MATS rule as well as a waste combustion rule at different time periods depending on the fuels or wastes fired in the unit. The MATS rule was promulgated on February 16, 2012, and establishes emission standards for PM (or metals), hydrogen chloride (or SO_2), and mercury. Extensive monitoring and testing are required.

SO_2 emissions are covered in Section 7.4.5.6. From the standpoint of increased sulfur loading, the SO_3 increase is expected to be small. The sulfur loading to fuel only increases by 1% (i.e., if coal sulfur was 1.0 lb/MMBtu, it would now be 1.01 lb/MMBtu; and SO_2 to SO_3 converion is typically only 1-2%), so no measurable effect on acid dewpoint is expected.

7.4.1.7 *Other Considerations*

State-specific air toxics standards might also apply to the firing of thermal reclaimer waste in boilers. These programs may require air dispersion modeling of emissions of air toxics when combusting waste, in order to demonstrate that fence line concentrations are below established acceptable ambient levels. The acceptable ambient levels are generally established state-by-state and are based on health risk thresholds.

In the US, fly ash from coal-fired power plants is currently not classified as hazardous waste under the Bevill amendment. A regulatory analysis would be required to determine if firing of the amine waste would alter the non-hazardous status of the fly ash.

7.4.2 Regulatory Framework – EU

Regulatory requirements for firing the sludge in a power plant in the EU were addressed in a report by EON [21]. In summary, firing the sludge in the furnace is classified as waste incineration which is controlled by Directive 2000/76/EC (which has now been superceded by Directive 2010/75/EU), known as the Waste Incineration Directive (WID). Firing any amount of reclaimer waste in the boiler furnace triggers the WID; in other words, there is no minimum threshold. For hazardous waste containing greater than 1% halogenated organic substances, the requirement is 2 seconds retention time at a temperature of 1100°C; for all other wastes the WID stipulates that the boiler will have at least a two second residence time at 850°C. Emissions are continuously monitored for the following species: particulates, total organic carbon (TOC), hydrochloric acid, hydrofluoric acid, SO_2, NO_X and CO. Periodic monitoring is required for dioxins and trace metals and the WID stipulates emission limits for various pollutants. Similar to the case in the US, the regulatory requirement appears tenable to co-firing the waste in a furnace boiler.

7.4.3 Suitability of Reclaimer Sludge for Firing in Coal-Fired Furnace

The suitability of firing the reclaimer sludge in a SCPC furnace depends on the waste stream’s heating value, moisture content, and contaminant level. No minimum heating value requirement was identified per US or EU regulations. A comparison of the reclaimer waste heating values to typical values for EU and US coals is presented in Table 7-5. The undiluted sludge has a heating value equivalent to typical US and EU lignite coals, while the heating value of the diluted sludge is somewhat below the heating value for German lignite [22, 43].

Table 7-5 Typical Heating Values for US and EU Coals Compared to Reclaimer Sludge

Coal / Waste	Heating Value[a]	
	Btu/lb	kJ/kg
Undiluted reclaimer sludge	4,188 – 8,790	9716 – 20,393
Diluted reclaimer sludge	2,095 – 4,395	4860 – 10,196
Australia Bituminous (Base Case Coal)	11,150	25,870
USA Bituminous	12,788	29,668
USA Sub-bituminous	7,701	17,942
USA Lignite	4,000 – 8,300	9,280 – 19,256
German Lignite	4,882	11,374

[a] Heating values of coals from [43], with exception of USA lignite.

The amount of water in the sludge, and therefore the heating value, could presumably be adjusted slightly to ensure that the waste stream meets the individual operator's heating value requirements by adjusting operating parameters. At the projected flowrates of 406 – 1,902 kg/hr for the thermal reclaimer waste from a coal-fired unit, the addition of the reclaimer sludge on the overall combustion performance of the 900 MW_e base case SCPC plant should be negligible. The relative heat inputs are summarized in Table 7-6.

Table 7-6 Impact of Adding MDEA-PZ Thermal Reclaimer Waste to 900 MW_e SCPC Base Case Power Plant

Coal / Waste Stream	Flowrate, kg/hr	Heat Input, GJ/hr
Base Case Coal	293,300	7,815
Undiluted reclaimer waste	951	8.4

7.4.4 Suitability of Reclaimer Sludge for Firing in NGCC HRSG

The reclaimer waste is not suitable for primary combustion at a NGCC because of the significant differences in physical properties between natural gas and the liquid amine waste. The HRSG, part of the heat recovery system of a NGCC, may provide a viable disposition route for the waste stream. The amine waste would likely be introduced with the gas turbine exhaust which contains up to 15% O_2 and would provide the oxygen needed for combustion. Hunt et al [24] cites a gas turbine-powered US petrochemical plant that used supplementary firing in the HRSG to burn volatile organic compounds (VOCs); the VOCs were fed as gases to a supplementary burner and directed in the natural gas flames, oxidizing the combustible components of the stream. The HRSG appears to be a viable disposition method for some VOCs, but introducing a viscous or high water content sludge requires additional consideration.

The exhaust temperature of a gas turbine is 450-630°C and supplementary firing in the HRSG typically increases the temperature to ~800°C, which may be too low by some regulatory standards for destruction of the sludge's volatile components. For comparison, the Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste, requires incinerators to keep incineration gases at a temperature of at least 850°C for at least two seconds to guarantee complete waste combustion [44]. According to the US EPA-CICA Fact Sheet, most organic compounds are thermally destroyed between 590-650°C and typical hazardous waste incinerators operate around 980°C – 1200°C [23], thus the precise temperature regime necessary to destroy the waste shall be determined and compared to the temperature realistically achievable in a HSRG. Furthermore, the residence time in the HSRG upstream of the convective section is fairly short and would need to be evaluated to ensure enough time for destruction of the organic compounds.

The ion exchange and electrodialysis waste streams are largely water (95%), and as such are unlikely candidates for HRSG firing; the diluted reclaimer waste is 50% water and also seems unlikely. The undiluted reclaimer waste is mainly MEA, MDEA and/or PZ and associated degradation compounds and is therefore more suitable for co-firing. Only the undiluted reclaimer waste will be considered.

Typical NGCC exhaust gases are relatively clean so the HRSG is composed of closely spaced, finned heat exchange tubes because the gas stream is not corrosive. Fortunately, the reclaimer sludge resulting from NGCC units is free of chloride, one of the most widely recognized industrial corrosive constituents. The impact of other components, such as sulfates and nitrates, may adversely affect the closely packed fins making the HRSG more vulnerable to corrosion. Because gas combustion does not produce significant quantities of particulate matter, NGCC units are not typically equipped with particulate control. Considerations are therefore made for firing a sludge which may generate particulates, from both corrosion / abrasion and regulatory perspectives. Any increase in NO_X resulting from the combustion of the sludge could be treated in the NGCC's SCR. However, the sulfate content of the waste sludge may increase the plant's SO_2 emissions; NGCC power plants do not have SO_2 scrubbers as their SO_2 emissions are very low.

As an example, the MDEA/PZ reclaimer sludge for NGCC has a heating value of 9,690 Btu/lb (22,481 kJ/kg) and a flow rate of 419 kg/hr, resulting in a heat input of 9.4 GJ/hr. This compares to natural gas heat input of 4,906 GJ/hr for primary combustion of the base case NGCC unit. It is difficult to quantify the overall performance impact of the sludge because the level of required supplementary gas firing in the HRSG is difficult to estimate. Additional work is recommended to ascertain the amount of particulates generated from sludge combustion, the amount of supplementary gas necessary to combust the sludge, and the temperature necessary for waste destruction. A more viable option may be to fire the NGCC reclaimer sludge in a SCPC unit; only SCPC firing options will be further explored in the subsequent subsections.

7.4.5 Effect of Reclaimer Waste on Coal-Fired Power Plant Emissions

Further evaluation on the impact of Coal-fired power plant emission by using thermal reclaimer sludge cofiring in boiler MDEA/Pz was chosen at this stage to illustrate an example evaluation. If all of the MDEA/PZ in the thermal reclaimer sludge were fired in the coal-fired furnace, it would represent approximately 0.3% of the mass of coal fired in the furnace. While the amine sludge represents a small mass of material, some of the constituents are present in higher concentrations than are found in the coal (Table 7-7). The effect of the sludge on the flue gas and fly ash composition is described in the following subsections.

Table 7-7 Mass Contribution of Select Reclaimer Waste Constituents on SCPC Coal-Fired Furnace (MDEA/PZ thermal reclaimer case as example)

Parameter	Concentration of Constituent in Stream		Mass Flowrate, kg/hr for coal-fired, MDEA/PZ thermal reclaimer sludge		Ratio of Undiluted Sludge Flowrate to Coal Flowrate
	Coal	Undiluted Sludge	Coal	Undiluted Sludge	
Flowrate	-	-	293,300	951	0.32%
Moisture	9.5%	0%	27,864	0	0.0%
Sulfur	0.9%	2.6%	2,640	25	0.95%
Chloride	0.3%	1.1%	88	10.5	11.9%
Nitrogen (N)	1.4%	9.4%	4,106	89	2.2%
Mercury (Hg)	0.04 ppm	3.7 ppm	0.0123	0.0035	28.6%
Selenium (Se)	0.05 ppm	4.7 ppm	0.0147	0.0045	30.5%
Arsenic (As)	1.26 ppm	0.8 ppm	0.3696	0.0008	0.21%
Cadmium (Cd)	0.07 ppm	0.3 ppm	0.0197	0.0003	1.45%
Chromium (Cr)	0.47 ppm	9.2 ppm	4.6635	0.0087	0.19%
Lead (Pb)	6.8 ppm	0.9 ppm	1.9944	0.0009	0.04%
Ash	13.5%	1.2%	39,595	11.4	0.03%

7.4.5.1 *Moisture Content*

Higher moisture content means additional energy for the heat of vaporization, thus negatively impacting the boiler's efficiency. The undiluted thermal reclaimer waste stream has no water, while the ion exchange and electrodialysis wastes are 95% water. The diluted reclaimer waste is 50% water and would result in a 3.4% increase in the amount of moisture over the water content of the coal feedstock.

7.4.5.2 *Effect on Combustion*

Adding the dried sludge stream to the fuel would likely have little impact on combustion. Numerous examples of alternative fuels being added to coal fired boilers exist both to add heating value and to dispose of waste [20]. Based on the total mass of coal for the base case SCPC plant, the undiluted thermal MDEA/PZ reclaimer waste adds only 951 kg/hr, representing an increase of 0.32% by weight to the fuel.

7.4.5.3 *Metals*

The amine waste streams from coal-fired power plants contain metals such as mercury, lead, arsenic and chromium. According to Table 7-7, the metals of highest concern by percent increase are mercury and selenium followed by cadmium for the MDEA-PZ example. The base case assumed that a significant portion of these metals are absorbed and retained through the carbon capture and amine reclaiming process. If the reclaiming waste is fired in the coal-fired furnace, metals will achieve a higher steady state concentration upstream of the carbon capture unit as compared to the baseline plant modeled. Without considering cycling up due to firing of waste in the power plant, the model predicts Hg concentration in the MDEA/PZ coal-fired thermal reclaiming waste to be 3.7 ppm; whereas, the coal Hg concentration is only 0.04 ppm. Likewise, selenium concentrations in the waste were predicted to be ~100 times the coal concentration.

Control strategies shall be evaluated to determine the impact of this dynamic. As discussed previously, a coal-fired power plant could employ flue gas mercury control technologies to reduce the accumulation of mercury in the solvent. However, coal-fired power plants do not employ control technologies to specifically target vapor-phase selenium emissions. Some amount of selenium removal is realized through the fabric filter and wet flue gas desulfurization unit.

7.4.5.4 *Chloride*

The chloride content of the thermal reclaimer streams ranged from 0.5 to 2.5 weight percent, which compares to low-sulfur Australian coal and typical US coals (<20 to 2,000 ppm chloride). If all of the MDEA-PZ sludge is fired in the furnace, it would represent a 10-12% increase in the mass loading of chloride to the furnace; however, this value may be an overestimate as the model used a conservatively low value for HCl removal by the polishing SO_2 scrubber.

Hydrochloric acid is efficiently removed by FGD scrubbers; therefore, any increased chloride emissions from the FGD into the CO_2 capture process will be minimal. The increase in chloride concentration in the fuel could increase the potential for corrosion in the furnace and cold-end unit operations. Combustion of chlorides results in the formation of alkali chlorides that are aggressive corrosive materials which can deposit on boiler tubes and generate liquid phase corrosion [25]. Therefore, it is important that the amine sludge is well-distributed into the furnace to avoid localized areas of high chloride concentration.

7.4.5.5 *NO_X Emissions*

The firing of the amine sludge will increase fuel nitrogen concentration by 2-3% (from ~4100 kg N/hr to 4200 kg N/hr) for the MDEA-PZ case (Table 7-7). Some but not all of the added fuel nitrogen will convert to NO_X; however, the plant's existing downstream SCR should be able to accommodate this increase in NO_X. SCRs can accommodate flue gas streams with variable inlet NO_X concentrations. Increased ammonia feed rate to the SCR will be required to maintain NO_X emissions at near pre-sludge firing levels, assuming that the ammonia injection system possesses sufficient excess capacity. If the amine sludge introduces stratification to the NO_X profile (e.g., sludge is fed to only one corner of the boiler), then retuning of the ammonia injection grid may be necessary.

Alternatively, as discussed below in Section Use of Amine Sludge as an SNCR Reagent, it has been proposed to add the sludge as an SNCR reagent.

7.4.5.6 *SO_2 Emissions*

The sulfur content of the amine sludge represents a 1% increase when compared to the amount of sulfur in the coal being fed to the furnace (i.e., MDEA/PZ thermal reclaimer sludge introduces 25 kg/hr S, while the coal contributes 2640 kg/hr S). Coal sulfur concentrations can vary widely, and even though FGD scrubbers are typically designed to accommodate a relatively narrow range of inlet SO_2 concentrations, a 1% increase can be accommodated by most systems. Therefore, the unit's existing FGD unit should be capable of removing the added SO_2 without design modifications; however, additional FGD reagent would likely be needed to maintain SO_2 removal across the FGD. Maintaining a constant SO_2 emissions rate from the FGD scrubber would therefore only require a modest increase in reagent flowrate.

7.4.5.7 *Effect on Fly Ash Composition*

The fly ash may be impacted by higher metal levels in the reclaimer sludge being cycled back through the furnace boiler. Fly ash is largely silicon dioxide, calcium oxide, and small amounts of unburned carbon which gives the ash its characteristic color. Trace amounts of heavy metals present in the coal feedstock are typically present, and the metal concentrations could increase as a result of sludge co-firing. As mentioned previously and presented in Table 7-7, mercury and selenium represent the largest percent increase of the metals introduced with the waste sludge; these metals are the most volatile of the metals present in coal. Some of the mercury and selenium in the fired sludge will report to the fly ash, while most of the non-volatile metals will report to the fly ash. The possibility exists that the metal content of the fly ash may increase above specifications necessary for its beneficial reuse, negating a revenue stream for some utilities.

The combustion of the sludge itself is likely to result in a slight increase in particulate matter commensurate with the increase in material / fuel consumed. This increase is small (<0.05%) and can be considered negligible.

7.4.6 Use of Amine Sludge as an SNCR Reagent

The thermal reclaimer waste sludge can be fired in a boiler for disposal, but if it is introduced into the furnace at the proper conditions the waste sludge may yield the added benefit of serving as an SNCR or SCR reagent. Typical SNCR/SCR reagents are urea and ammonia. The high amine content of the reclaimer waste sludge (35-68%) makes it a potential candidate as a substitute reagent. The diluted amine content (0.5-3%) of the ion exchange and electrodialysis waste streams make them less suitable for this process.

The baseline plants in this study are a 900 MW_e SCPC fired furnace and an 800 MW_e NGCC unit. Each is equipped with an SCR which achieves a high level of NO_X removal. Three possible scenarios exist for using the waste reclaimer sludge for NO_X control:

1. Add the amine waste to the furnace in a temperature regime that is optimized for SNCR, thus allowing the units to operate with both SNCR and SCR for NO_X control.

2. Add the amine waste to the furnace in a temperature regime that favors formation of NH_3 for use in the SCR. The unit would exclusively rely on SCR for NO_X control.
3. Add the amine waste to another power generating unit for use as an SNCR reagent.

The technical considerations associated with each of these options will be discussed after an introduction to SNCR technology, which will help to illustrate the possibilities and challenges associated with these approaches.

SNCR reagents, typically ammonia or urea, are injected into the boiler furnace to react with existing NO_X to produce N_2. Theoretical conversions in excess of 90% are possible, but in practice typical removals for utility boilers are 10–25%. The SNCR process requires minor modifications to existing equipment (*e.g.*, ports and injection points into furnace boiler) and requires only minimal additional equipment (*e.g.*, reagent handling, vaporizer) when compared to more capitally intensive processes such as SCR. The capital cost of SNCR is approximately \$20/kW [26] compared to approximately \$300/kW for SCR [27]. The reagents are injected into the furnace and decompose into free ammonia radicals that react with NO_X; the overall reactions for NO are as follows:

Ammonia based SNCR: $2NO + 2NH_3 + \frac{1}{2} O_2 \rightarrow 2N_2 + 3H_2O$
Urea based SNCR: $2NO + CO(NH_2)_2 + \frac{1}{2} O_2 \rightarrow 2N_2 + CO_2 + 2H_2O$

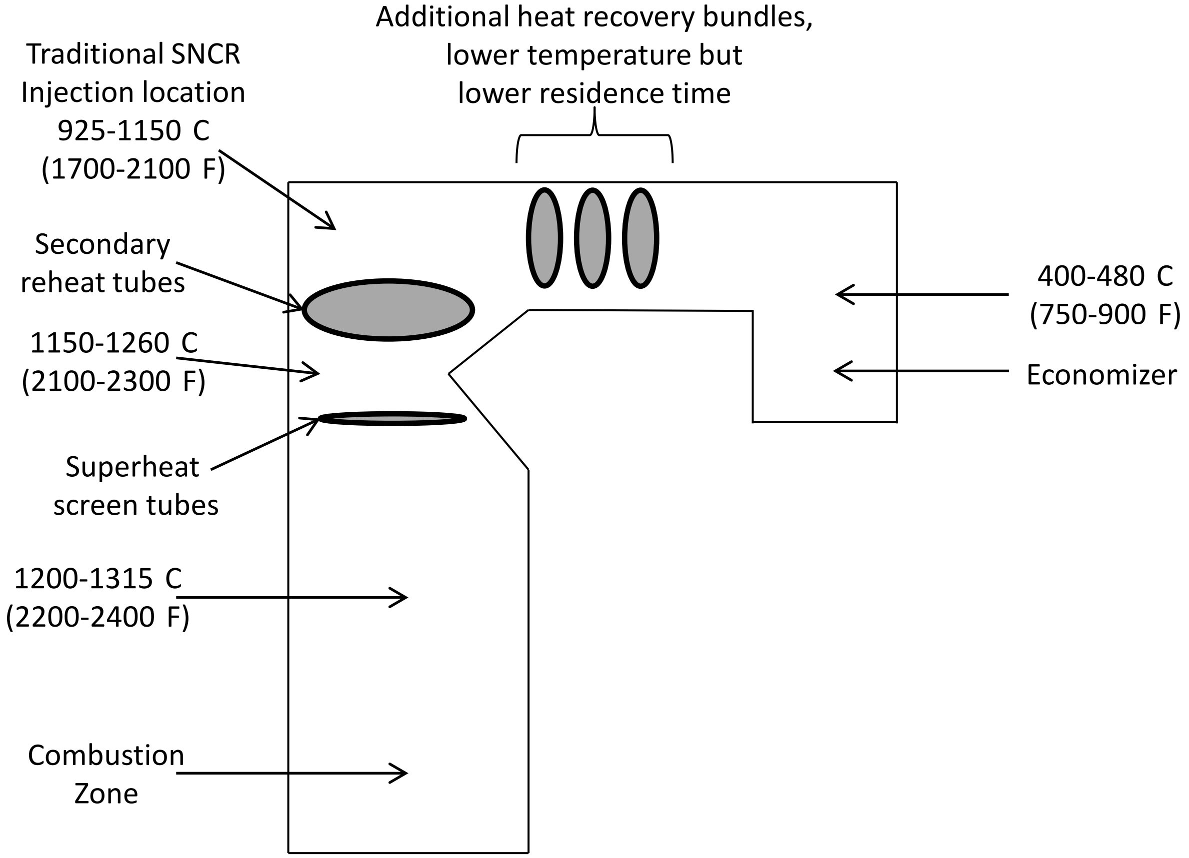
Several considerations are made when designing a SNCR process, including optimization of:

- Stoichiometry,
- Reagent distribution,
- Residence time, and
- Temperature [28].

Stoichiometry can be optimized by balancing the reagent concentration and flowrate with the anticipated NO_X concentration, desired conversion, and anticipated utilization. Reagent dispersal can be maximized by injecting the reagent into a turbulent zone to increase mixing, thereby minimizing mass transfer limitations. The location of the injection point is also optimized to allow adequate residence time (≥ 0.5 sec) for the reaction to proceed to completion, thereby lessening any kinetic limitations of the reduction reaction. Finally, the reaction thermodynamics can be optimized by injecting the reagent at a location where the reaction is within the desired temperature regime. Optimizing the SNCR process is specific to a given application and furnace configuration (among other factors) and several of the key parameters can be tuned by changes to the injection location.

If the temperature at the injection point is too low, the reagent will pass through the boiler unreacted, resulting in ammonia slip. If the temperature is too high, reaction with oxygen is more favorable which would generate additional NO_X. The general range for optimal SNCR operation using ammonia is 870-1090°C (1600-2000°F) and with urea is 900-1150°C (1650-2100°F) [28].

As the flue gas passes out of the combustion zone and begins to pass through superheat/reheat tubes, the flue gas is progressively cooled. Figure 7-3 shows a very simple schematic of the temperature regimes within a typical boiler furnace. Upstream of the convective section, the temperature is typically 1200-1315°C (2200-2400°F), too hot for NO_X reduction by traditional SNCR injection. The temperature grows cooler as the flue gas flows over additional tube banks until it reaches the economizer around 400-480°C (750-900°F). Unfortunately, as the flue gas temperature decreases, the space (and therefore time) available for reaction is also shortened. The optimal injection point strikes a balance between temperature and residence time, and multiple injection points are often needed in a single boiler to optimize these parameters while matching boiler load characteristics.



Source: Adapted from [28]

Figure 7-3 Simple Boiler Schematic Showing Temperature Regimes Relevant to SNCR Injection Points

In the US SCR units are typically located downstream of the economizer and before the air heater. The SCR catalyzes the oxidation of an ammonia or urea reagent to generate ammonia radicals which react with and reduce NO_X. The SCR reagent does not require the higher temperature regimes necessary for SNCR because the catalyst lowers the activation energy of radical formation; it does, however, require uniform distribution across the SCR catalyst bed for high NO_X conversion. To become adequately dispersed, the reagent is injected into the duct far enough upstream of the SCR to become evenly mixed with the flue gas.

All of these items are considered when evaluating the possibility of using the amine waste stream as a substitute for urea/ammonia for a NO_X reduction process. This concept was explored recently in laboratory-scale experiments which found 40% reduction in NO_X at 950°C (1742°F) and at a stoichiometric ratio of 1.6 [29]. The reduction was observed to increase to 96% with a stoichiometric ratio of 8.5, but reclaimer wastes were noted to have a lower NO_X reduction potential than ammonia. Furthermore, the authors found NO formation to increase at higher temperatures (>1000°C), possibly by oxidation of ammonia radicals, while NO is converted to NO_2 at lower temperatures (<800°C). The hydrocarbons present in the reclaimer waste further increase the complexity of the possible intermediates / reactions when compared to more traditional SNCR reagents such as NH_3. The potential to use reclaimer wastes was discussed with an industry expert [30] and the use of amines as an SNCR reagent was explored in the 1970s (45). Lower temperatures (1400-1500°F) are cited than those noted in the work by Botheju et al (2012), and the conversion of NO to NO_2 is cited as a predominant reaction pathway, corroborating some of the recent observations [29]. Taken together, this preliminary work and expert consultation indicates that while challenges exist the approach is worth exploring. The three options mentioned above for delivering the amine waste stream as a NO_X control agent are addressed below.

1. <u>Amine reclaimer waste sludge as SNCR Reagent with SCR</u>. The reclaimer waste can be added to an optimized temperature location within the furnace for SNCR operation. If the approach is successful, the NO_X burden of the SCR unit can be lowered, thereby lowering the SCR reagent needed. Considerations that are made for this option include:

    a. Less residence time for the NO_X reduction reaction to reach completion because the reagent is injected further downstream in a cooler portion of the furnace (see Figure 7-3). The design configuration of specific boilers shall be considered to ensure the residence time is sufficient.
    b. Less flexibility for units that have varying load and thus varying temperature profiles within the boiler as a function of time. The ability to inject a more traditional SNCR reagent at alternate locations may lessen this limitation.
    c. The superheat tubes may foul more quickly and localized corrosion impacts may be increased since the reagent will have less time to react prior to encountering downstream obstructions. Impurities in the reclaimer waste also heighten corrosion concerns.
    d. The consistency of the reclaimer waste amine content shall be considered. Significant variations could result in non-ideal reaction conditions; alternate SNCR reagents may be needed to ensure reliable SNCR operation when variations do arise. The injection locations for these alternate reagents may be different than the location for injecting the amine waste stream.
    e. The introduction of heavy metals and chlorides into the furnace could lead to some constituents cycling up in concentration. This was previously addressed in Section Effect of Reclaimer Waste on Coal-Fired Power Plant Emissions where adding the reclaimer sludge to the furnace for disposal was discussed.

    If a greenfield unit is engineered specifically to use the reclaimer waste as an SNCR reagent, it is possible that some SNCR benefit will be realized. The laboratory scale work of Botheju et al (2012) supports this premise [29]. However, based on other expert opinion [30], sole reliance on reclaimer waste for SNCR operation should not be considered best practice because the production of ammonia radicals is expected to be low.

2. Amine reclaimer waste sludge to form ammonia for SCR NO_X control. The reclaimer waste could be injected into the furnace to form ammonia which can supplement the ammonia (or, urea) injected to serve as an SCR reagent. Injection for the purposes of ammonia formation shall also be optimized for temperature and residence time. Injecting the waste stream further upstream in the gas path would be advantageous for allowing more time for mixing and uniform reagent distribution, reducing the likelihood that that the downstream SCR will be impacted by locally high ammonia/amine concentrations. However, one industry expert believes that appreciable ammonia formation is unlikely and the waste will more likely result in increased NO_X [30]. Work in the 1970's suggested this approach may be plausible, but per the primary author (30) the decrease of NO observed during much of the early work was actually conversion to NO_2 rather than reduction to N_2 (45). The increase in NO_X is not especially problematic because the added NO_X will be reduced at the SCR; additional ammonia reagent for the SCR will be required, however. This approach essentially results in the addition of the reclaimer waste to the furnace as a disposal method, which was addressed previously.

3. Amine reclaimer waste sludge as an SNCR reagent to a SCPC without SCR. The option of using the reclaimer waste exclusively as an SNCR reagent, replacing ammonia or urea, was recently investigated at the laboratory scale with some success [29]. Table 7-8 summarizes the viability of using reclaimer waste as an SNCR reagent for the base case 900MW_e SCPC power plant. Assumptions which were used to generate the data in Table 7-8 were:

- 900 MW_e SCPC plant, similar to the base case minus the SCR; 85% capacity factor;
- NO_X is between 0.10–0.15 lb/MMBtu (typical range for US coal-fired furnace with over-fire air), which translates to 740–1,111 lb NO_X/hr (336–504 kg NO_X/hr) or 16.1–24.2 lbmol/hr (7.3–11.0 kmolhr);
- 50% reduction in $NO_{X;}$
- Ammonia cost is €661/metric ton (or, $800/short ton); Urea cost is €259/metric ton (or, $313/short ton);
- Molar ratio of NO_X:Ammonia = 1; NO_X:Urea = 2; NO_X:Reclaimer sludge = Unknown (recent work suggests 1.6 may be adequate for some NO_X removal [29];
- Utilization is 1.5 for ammonia and urea; and
- Example thermal reclaimer waste from MDEA/PZ for coal-fired power plant.

Table 7-8 Comparison of Using Coal-Fired Thermal Reclaimer MDEA/PZ Waste as a SNCR Reagent Assuming a 900 MW_e SCPC

SNCR Reagent	Reagent Rate, kmol/hr	Reagent Rate, lg/hr	Cost, €1000/yr
Ammonia	5.5-8.2	93-140	459-688
Urea	2.7-4.1	164-247	317-475
Reclaimer Sludge	4.1 $kmol_{MDEA}$/hr and 0.2 $kmol_{PZ}$/hr		

The reclaimer sludge has the potential to displace at least half of the SNCR reagent needed. As shown in Table 7-6, this could result in a reagent cost savings of at least €160,000/year. There are some encouraging results obtained in recent lab experiments using MEA and reclaimer waste, which contains MEA as well as a host of amine degradation products, but previous work which investigated other amines (*e.g.*, monomethylamine, dimethylamine, and trimethylamine) indicates that this approach may be technically challenging [45]. Further investigation is warranted at both lab and full-scale before determining if it is viable to use the waste sludge as an SNCR reagent.

In conclusion, while laboratory results indicate that reclaimer waste can serve as a viable SNCR reagent [29], the reclaimer waste sludge is more likely to generate additional NO_X and only a small amount of ammonia or ammonia radicals. Introduction into the boiler for waste disposal serves to dispose the waste and any SNCR or SCR benefit can therefore serve as a supplement to the utility's overall NO_X control strategy.

7.4.7 Reclaimer Sludge Handling

A sludge handling system will be necessary to accept the produced reclaimer sludge and transport it to the furnace for firing. For this study, continuous production of the reclaimer sludge is assumed. The sludge will be removed from the reclaimer, diluted if necessary to facilitate pumping, and transferred to a dedicated storage tank. From this tank it would be piped to the coal milling area and introduced to the furnace. Two possible reclaimer sludge handling scenarios for introducing the sludge to the furnace are as follows:

1. The amine waste sludge is added via sludge lances, similar to the oil-fired guns used by the unit upon startup. It might be possible to tee into an existing oil delivery system, or a stand-alone system may be preferred. The sludge would need to be introduced at a burner level which is in operation during low load. For a wall-fired furnace, the sludge would likely be introduced along one row of burners; for a tangential-fired furnace, the sludge would be introduced at the four corners of one burner level.

2. The amine waste sludge is added just upstream of the coal mills (*i.e.*, injected as coal falls from the weigh belt into the pulverizer). This is a common approach when co-firing sewage sludge, which contains a similar amount of water compared to the amine waste sludge. [21]. The advantage of this firing configuration is good distribution of the sludge with the coal, which should minimize impacts on the furnace profile. Potential problems with this firing configuration include the possibility of corrosion in the pulverizer (due to chloride content of the sludge and other corrosive components) and the possibility of amine vapor being released upon heating in the pulverizer and thus affecting the local working environment. The reduction in mill temperature due to addition of the amine waste sludge would need to be evaluated to determine if the impact on overall operations is acceptable. The sludge would need to be added to multiple mills to ensure that it can be added when a given mill is out of service. Addition on multiple mills would also reduce the temperature decrease for mill outlets.

No additional protective equipment other than what is necessary for safe power plant operation would be needed to handle the reclaimer waste stream. The pH of the waste is 8-12; the alkaline nature of the thermal reclaimer material is a product of the chemistry of the carbon capture solvent and reclaiming process.

7.4.7.1 *Costs*

Co-firing the sludge will have costs associated with transport, storage, and introduction of the reclaimer waste to the furnace. A brief discussion regarding each of these areas is as follows. It is premature, however, to attach specific costs to these items because of the large uncertainties that exist.

The reclaimer waste sludge is a high viscosity liquid that may require dilution and heating to ensure the flow of the sludge. Costs associated with piping, water addition, and heated storage tanks may apply. The actual cost of these facilities will be site specific; however, they are estimated to be a small percentage of the overall cost of the carbon capture system. Even though the added facilities have a finite cost, the precise value cannot be accurately determined until a more detailed economic analysis of the proposed process is performed and can be considered negligible at this point.

A similar assessment can be made regarding the overall cost impact of the equipment needed to add the reclaimer waste to the boiler. Options exist for adding the waste through existing furnace ports (e.g., oil gun), dedicated new port / lance systems, or onto the pulverized coal; these options would require only minor modifications to existing equipment. Adding ports to a boiler furnace during the engineering design phase would have no real impact on equipment cost. Even if a new port is installed at an existing boiler furnace, the cost of a new port and lance system is minimal.

It would be necessary for plant operators to maintain additional furnace ports, piping, and tanks as well as to sample and monitor the reclaimer stream. This additional workload and maintenance schedule would not be anticipated to impact overall labor projections for a large coal-fired power plant. In summary, the incremental costs of co-firing the waste in the furnace boiler would be a small fraction of the capital cost of carbon capture system (<1%) and insignificant relative to the labor associated with operating a large power plant.

7.5 **Wastewater Treatment Plant (WWTP)**

The waste streams from the ion exchange and electrodialysis processes are suitable for treatment in a WWTP. The composition of these streams for the various solvent case studies for coal and NGCC power plants are summarized in Attachment 2 of this chapter.

The use of amine-based solutions for carbon capture at fossil-fuel power plants is not widely employed. Wastewater discharges from these systems are markedly different in composition from typical wastewater streams encountered at power plants. In the US, there are currently no regulatory limits for discharges of these carbon capture wastewater streams. The following discussion presents information on the types of wastewater streams and wastewater treatment systems typically encountered at power plants, a summary of existing and proposed US regulations related to power plant water wastewater discharges, and considerations for treatment of wastewater from ion exchange and electrodialysis solvent reclaimer processes in power plant applications associated with CO_2 capture.

7.5.1 Power Plant Wastewaters and WWTP Operations

All steam generating power plants, including both coal- and natural gas combined cycle plants, will have water discharges associated with the cooling water systems used in the steam condensation systems. These will either be once-through cooling water systems or cooling tower systems having a cooling tower blowdown discharge to purge salts from the cooling water. In addition, most steam electric units will have a boiler blowdown wastewater stream to purge salts from the water used in the steam water system.

In addition, coal-fired units will have wastewater streams associated with various flue gas air pollution control systems (particulate matter, SO_2, NO_x) that typically required treatment prior to discharge as discussed below. Natural gas-fired combined cycle units will not typically have any additional major wastewater streams associated with air pollution control devices since they generate lower emissions of particulate matter, sulfur dioxide, and nitrogen oxides.

Coal-Fired Units: As part of the US EPA's recently proposed revisions to the Steam Electric Effluent Limitation Guidelines (ELG), EPA conducted a detailed survey of the industry to determine the types of wastewater stream generated and the types of WWT operations currently in use at coal-, pet coke-, and oil-fired power plants for selected new waste stream types being considered in the revisions to the rule [33].

EPA determined that most plants (89 percent) are discharging at least some of their wastewater to surface waters or Publically Owned Treatment Works (POTWs), typically after some type of treatment process. Very few (10 of approximately 1100 coal- and pet-coke fired units) plants were found to discharge wastewaters to POTWs; these streams included FGD wastewater and/or fly ash or bottom ash transport water. Eleven percent of plants operated in a zero discharge mode resulting in no discharge of wastewater. EPA evaluated the technologies available to control and treat wastewaters. Any given plant may use one or more processes that generate wastewater, and they may treat these wastewaters separately or in various commingled combinations. WWT technologies for various power plant wastewater types are summarized in Table 7-9.

Table 7-9 Summary of Typical Power Plant Wastewaters and WWT Systems

Wastewater Type	WWT Technology	Description
FGD wastewater	Surface impoundments	Settling ponds are designed to remove particulates and suspended metals by gravity. Not designed to remove dissolved metals. Plants may add treatment chemicals to adjust pH prior to discharge to surface waters or POTWs. Some plants use surface impoundments to remove suspended solids prior to treatment in a more advanced process such chemical precipitation and/or biological treatment. FGD WW may be comingled with other plant wastewaters in the settling pond. Effective for treatment of metals associated with suspended solids particulate matter.
	Chemical precipitation (Physical/Chemical Treatment)	Treatment in a tank-based system in which chemicals are added to enhance the removal of suspended and dissolved solids, including certain dissolved metals. Dissolved metals are converted to insoluble metal ions and precipitated as insoluble metal hydroxides or sulfides. Typical reagents include lime, sodium hydroxide, and ferric chloride. Sulfide precipitation using organosulfides is also used at some plants to target removal of mercury. Not effective at removing selenium, nitrogen compounds, and certain elements that contribute to high TDS levels (e.g. bromides, boron, chlorides, sulfates, magnesium, etc.).
	Biological treatment	Typically fixed-film bioreactors used for removal of nitrate and selenium following chemical precipitation. Currently in use at a very limited number of power plants for treatment of FGD wastewater, but expected to become more widely used as a result of new ELG rules and discharge limits for FGD wastewater. Effective for removal of selenium, nitrate, as well as additional reductions of mercury, arsenic and other metals.
	Vapor-compression evaporation (VCE)	Uses thermal brine concentrator to produce a concentrated wastewater stream that can be further processed in crystallizer or spray dryer. Typically used in a zero-discharge plant configuration.
	Constructed wetlands	Engineered systems the use natural biological processes to reduce levels of metals, nutrients, and suspended solids. High levels of COD, nitrates, boron, sulfates, and chlorides can adversely affect constructed wetlands performance; therefore, FGD wastewater dilution is typically required prior to wetlands treatment.
Ash transport water (fly ash and bottom ash)	Surface impoundments	See above description. More advanced treatment systems such as chemical precipitation or biological treatment are not currently in use.

Wastewater Type	WWT Technology	Description
Combustion residual leachate from landfills or surface impoundments	Surface impoundments	See above description. Most commonly used technology. Leachate can be co-treated with FGD wastewater or treated independently. Most commonly used technology.
	Biological treatment	See above description. Limited use in current plants.
	Constructed wetlands	See above description. Limited use in current plants.
Metal cleaning wastes (chemical and non-chemical cleaning of metal process equipment)	Surface impoundments	See above description. Treatment systems used for this process stream vary widely depending on the type of metal cleaning being conducted. Treatment in surface impoundments is most common. Metal cleaning wastes may be associated with gas-fired units as well as coal-fired plants.
	Chemical precipitation	See above description. Also commonly used.
	Other	Constructed wetlands, filtration, reverse osmosis, clarification, and VCE also used. Metal cleaning wastes are also often shipped off-site for treatment or disposal.
Low Volume Waste (LVW) Sources [a]	Various	Typically comingled and treated with other waste streams. LVWs may be associated with gas-fired units as well as coal-fired plants.

a As defined in current proposed revisions to the ELG rule [1]: Wastewater from all sources including, but not limited to: ion exchange water treatment systems, water treatment evaporator blowdown, laboratory and sampling streams, boiler blowdown, floor drains, cooling tower basin cleaning wastes, and recirculating house service water systems. Sanitary and air conditioning wastes and carbon capture wastewater are not included.

7.5.2 US Regulatory Considerations – Effluent Limitation Guideline (ELG) Rules

The US EPA first issued effluent guidelines for the Steam Electric Power Generating Point Source Category (i.e., the Steam Electric effluent guidelines) in 1974 with subsequent revisions in 1977 and 1982. The current Steam Electric effluent guidelines are codified at 40 CFR Part 423 and include limitations for the following waste streams [34]:

1. Once-through cooling water;
2. Cooling tower blowdown;
3. Fly ash transport water;
4. Bottom ash transport water;
5. Metal cleaning wastes;
6. Coal pile runoff; and
7. Low-volume waste sources, including but not limited to wastewaters from wet scrubber air pollution control systems, ion exchange water treatment systems, water treatment evaporator blowdown, laboratory and sampling streams, boiler blowdown, floor drains, cooling tower basin cleaning wastes, and recirculating house service water systems (sanitary and air conditioning wastes are not included).

Current US regulations specify numeric discharge limits for these stream types at existing and new plants as shown in Attachment 3. Numeric limits are specified for species such as pH, chlorine, oil/grease, total suspended solids, chromium, copper, iron, and zinc depending on the stream type. Zero discharge of all 126 priority pollutants is also specified for cooling tower blowdown, except chromium and zinc which have numeric limits.

The US EPA is currently considering revisions to these existing effluent limitation guidelines (ELG) for the steam electric power industry, which include limits for additional wastewater stream types [33]. On April 19, 2013, EPA announced proposed technology-based effluent limitation guidelines and presented preferred alternatives for four categories of plants:

1. Existing sources that discharge to surface waters;
2. Existing sources the discharge to POTWs;
3. New sources that discharge to surface waters; and
4. New sources the discharge to POTWs.

Numerous alternatives were presented in the proposed rule for the various wastewater streams listed above in Table 7-9. Presumably, when the final rule is promulgated, only a single alternative will be allowed. Although EPA revised the definition of LVW in the proposed rule to specifically exclude carbon capture wastewater, the current proposed rule does not contain specific limits for carbon capture wastewater. EPA cited the lack of data for this wastewater type due to the developmental nature of CO_2 control technologies, but EPA did not indicate in the proposed rule if or how they may revisit setting limits for this wastewater stream in the future. As such, the current most stringent proposed limits for other wastewater stream types can be used as an indicator of potential future limits for carbon capture technology wastewater. The most stringent of the proposed alternatives would establish numeric discharge limits for selected wastewater streams associated with the two categories of existing plants as shown below in Table 7-10. Wastewater streams would require treatment to these levels prior to discharge to surface waters or POTWs. If limits of “0.0” are shown, no discharge of these wastewater types are allowed under the most stringent proposed scenario. Note that discharge of ash transport waters and flue gas mercury control wastewaters is entirely prohibited. Similar limits are summarized for new plants in Table 7-11.

Table 7-10 Most Stringent Proposed ELG Limits for Existing Sources [33, 35]

	Proposed Limit for Units Discharging to Surface Waters		Proposed Limit for Units Discharging to POTWs (PSES)	
Pollutant or Property	**Daily Max**	**30 Day Avg.**	**Daily Max**	**30 Day Avg.**
Fly Ash and Bottom Ash Transport Water				
All pollutants	0.0	0.0	0.0	0.0
Metal Cleaning Wastes (chemical)				
Copper, total	-	-	-	-
Iron, total	-	-	-	-
Metal Cleaning Wastes (non-chemical)				
Copper, total	1.0 mg/l (ppm)	1.0 mg/l (ppm)	1.0 mg/l (ppm)	-
Iron, total	1.0 mg/l (ppm)	1.0 mg/l (ppm)	-	-
FGD Wastewater				
Arsenic, total	8 ug/l (ppb)	6 ug/l (ppb)	8 ug/l (ppb)	6 ug/l (ppb)
Mercury, total	242 ng/l (ppt)	119 ng/l (ppt)	242 ng/l (ppt)	119 ng/l (ppt)
Selenium, total	16 ug/l (ppb)	10 ug/l (ppb)	16 ug/l (ppb)	10 ug/l (ppb)
Nitrate/Nitrite as N	0.17 mg/l (ppm)	0.13 mg/l (ppm)	0.17 mg/l (ppm)	0.13 mg/l (ppm)
Flue Gas Mercury Control Wastewater				
All pollutants	0.0	0.0	0.0	0.0
Combustion Residual Leachate				
Total suspended solids	100 mg/l (ppm)	30 mg/l (ppm)	-	-
Oil and Grease	20 mg/l (ppm)	15 mg/l (ppm)	-	-
Gasification Wastewater (IGCC Power Systems)				
Arsenic, total	4 ug/l (ppb)	-	4 ug/l (ppb)	-
Mercury, total	1.76 ng/l (ppt)	1.29 ng/l (ppt)	1.76 ng/l (ppt)	1.29 ng/l (ppt)
Selenium, total	453 ug/l (ppb)	227 ug/l (ppb)	453 ug/l (ppb)	227 ug/l (ppb)
Total dissolved solids	38 mg/l (ppm)	22 mg/l (ppm)	38 mg/l (ppm)	22 mg/l (ppm)

Table 7-11 Most Stringent Proposed ELG Limits for New Sources [33, 35]

	Proposed Limit for Units Discharging to Surface Waters		Proposed Limit for Units Discharging to POTWs (PSNS)	
Pollutant or Property	**Daily Max**	**30 Day Avg.**	**Daily Max**	**30 Day Avg.**
Fly Ash Transport Water				
All pollutants	0.0	0.0	0.0	0.0
Bottom Ash Transport Water				
Total suspended solids	100 mg/l (ppm)	30 mg/l (ppm)	-	-
Oil and grease	20 mg/l (ppm)	15 mg/l (ppm)	-	-
All other wastewater pollutants	0.0	0.0	0.0	0.0
Metal Cleaning Wastes (chemical)				
Total suspended solids	100 mg/l (ppm)	30 mg/l (ppm)	-	-
Oil and grease	20 mg/l (ppm)	15 mg/l (ppm)	-	-
Copper, total	1.0 mg/l (ppm)	1.0 mg/l (ppm)	1.0 mg/l (ppm)	-
Iron, total	1.0 mg/l (ppm)	1.0 mg/l (ppm)	-	-
Metal Cleaning Wastes (non-chemical)				
Total suspended solids	100 mg/l (ppm)	30 mg/l (ppm)	-	-
Oil and grease	20 mg/l (ppm)	15 mg/l (ppm)	-	-
Copper, total	1.0 mg/l (ppm)	1.0 mg/l (ppm)	1.0 mg/l (ppm)	-
FGD Wastewater				
Arsenic, total	8 ug/l (ppb)	6 ug/l (ppb)	8 ug/l (ppb)	6 ug/l (ppb)
Mercury, total	242 ng/l (ppt)	119 ng/l (ppt)	242 ng/l (ppt)	119 ng/l (ppt)
Selenium, total	16 ug/l (ppb)	10 ug/l (ppb)	16 ug/l (ppb)	10 ug/l (ppb)
Nitrate/Nitrite as N	0.17 mg/l (ppm)	0.13 mg/l (ppm)	0.17 mg/l (ppm)	0.13 mg/l (ppm)
Flue Gas Mercury Control Wastewater				
All pollutants	0.0	0.0	0.0	0.0
Combustion Residual Leachate				
Arsenic, total	8 ug/l (ppb)	6 ug/l (ppb)	8 ug/l (ppb)	6 ug/l (ppb)
Mercury, total	242 ng/l (ppt)	119 ng/l (ppt)	242 ng/l (ppt)	119 ng/l (ppt)
Gasification Wastewater (IGCC Power Systems)				
Arsenic, total	4 ug/l (ppb)	-	4 ug/l (ppb)	-
Mercury, total	1.76 ng/l (ppt)	1.29 ng/l (ppt)	1.76 ng/l (ppt)	1.29 ng/l (ppt)
Selenium, total	453 ug/l (ppb)	227 ug/l (ppb)	453 ug/l (ppb)	227 ug/l (ppb)
Total dissolved solids	38 mg/l (ppm)	22 mg/l (ppm)	38 mg/l (ppm)	22 mg/l (ppm)

The proposed most stringent discharge limits for FGD wastewater, which are identical for both existing and new coal-fired units, can be used as an indicator of possible treatment levels that could be required for the reclaimer wastewater from the ion exchange the electrodialysis processes (refer to Attachment 2 for projected levels of various species in reclaimer wastewater streams for each case study coal and NGCC plant). Treatment to parts per billion levels of arsenic and selenium, and parts per trillion levels of mercury could be required in the treated reclaimer wastewater. Since the ion exchange and electrodialysis reclaimer processes are not designed to remove metals from the reclaimer waste, the projected metals composition for the various cases are shown as zero in Attachment 1; however, in reality, wastewaters from these two processes would likely contain some low level metals content that may need to be treated.

In the case of nitrate, the projected reclaimer wastewater composition is in the range of 0.4 to 1.3 wt% (4000 to 13,000 mg/l or ppm). This is well above the proposed discharge limit for FGD wastewaters of 0.13 mg/l [33].

Discharges to Publically or Federally Owned Treatment Works (POTW/FOTW) If an industrial user discharges wastewater to a POTW, then they will obtain an Indirect Discharger Permit from the POTW. There are categorical limits (based upon the steam electric industry characteristics) and local limits (based upon the capacity and permit limits of the individual POTW). Based upon the indirect discharger permit, the industrial user will typically need to "pretreat" their wastewater so that the POTW can complete treatment of the wastewater before final discharge.

Federal limitations on discharges of wastewaters to POTWs include general requirements as well as specific categorical discharge standards that apply to specific process wastewaters of particular industrial categories. (i.e. steam electric power generating point source category).

General Prohibitions - Regardless of whether the POTW is solely treating domestic wastewater and/or industrial wastewater, there are general prohibitions about what can be put down the drain as described below [34, 36].

Following is the information on the pollutant that are not allowed to be discharged to the wastewater treatment works:

- Pollutants that could cause pass through (a discharge which exits the POTW into waters in quantities or concentrations which, alone or in conjunction with one or more discharges from other sources, is a cause of a violation of any requirement of the POTW's National Pollutant Discharge Elimination System (NPDES) permit).
- Pollutants that could cause interference (a discharge which, alone or in conjunction with one or more discharges from other sources inhibits or disrupts the POTW and causes a violation of any requirement of the POTW's NPDES permit).
- Pollutants which create a fire or explosion hazard in the POTW/FOTW, including but not limited to waste streams with a closed cup flashpoint of less than 140°F (60°C).
- Pollutants that will cause corrosive structural damage to the POTW/ FOTW.
- Discharges with a pH below 5.0.
- Solid or viscous pollutants in amounts that will cause obstruction to the flow (i.e., fish cleaning stations, sand and sediment).

- No pollutants, including pollutants with oxygen demand, at a flow rate or concentration that will cause interference with the POTW/FOTW.
- Heat in amounts that would inhibit biological activity at the POTW/ FOTW resulting in interference is not discharged (i.e., scrubber water, boiler blow down).
- Petroleum, oil, nonbiodegradable cutting oil or products of mineral oil origin in amounts that would result in a pass through or interference (specifically check maintenance areas and oil/water separators).
- Pollutants which would result in the presence of toxic gases, vapors, or fumes within the POTW/FOTW in quantities that would cause acute worker health and safety problems no trucked or hauled pollutants except at discharge points designated by the POTW/FOTW.

As discussed previously, it is not common practice for power plants to discharge existing wastewaters to a POTW. It is likely that that the amine content of the reclaimer wastewater would prevent it from being amenable to discharge directly to a POTW (i.e., high strength BOD waste and high nitrogen levels.

Categorical Discharge Standards – The proposed steam electric power plant ELG rule proposes several alternatives for discharge to POTWs on a stream by stream basis. These are referred to as pretreatment standards for existing sources (PSES) and pretreatment standards for new sources (PSNS). The most stringent of these were summarized previously in Tables 7-8 and 7-9 for existing and new sources, respectively. These limits provide an indication of the treatment levels that may be required for listed power plant wastewaters before they can be discharged to a POTW, provided they also meet the general prohibition requirements listed above.

7.5.3 Technology Options and Feasibility

Depending on the outcome of the final ELG rule, it is possible that many existing and new coal-fired power plants in the US with wet FGD systems will adopt the use of chemical precipitation in combination with biological WWT system to meet FGD wastewater limits. For coal fired power plants that do not use wet FGD systems, chemical precipitation systems may be most common. If plants opt to become zero discharge facilities, additional treatment systems such as brine concentrators may be employed.

Treatment of the ion exchange and electrodialysis reclaimer wastewater in these types of existing WWT systems may be problematic. While the projected flow rates of these reclaimer wastewater streams (7 to 55 gpm) are on the lower end of typical power plant wastewater stream flow rates such as FGD wastewater (400 gpm on average according to EPA's proposed ELG rule for existing FGD systems), these treatment systems will not be effective for removal of amine solvents, and the nitrate levels in these reclaimer streams may far exceed the upper design limits for biological treatment processes used to reduce nitrate levels. Vendor information for one such biological treatment process (e.g., GE's ABMet® fixed-bed process) being tested and installed at coal-fired plants for treatment of FGD wastewater cited that the upper limit for nitrates in the WWT influent at 250 mg/l in order to meet discharge concentrations of less than 1 mg/l [37]. Infilco Degremont (IDI) also offers a continuous stirred tank biological treatment process designed for use for use in power plant applications [38].

Additional onsite WWT systems may be required in order to treat the solvent reclaimer wastewater which has organic compound loading characteristics more like wastewater encountered in refinery and/or chemical plant operations. In these other petrochemical industry applications, the wastewater is first treated to reduce the amine concentration by distillation, scrubbing, diffusion, or solid/liquid flotation [e.g. Induced Gas Flotation (IGF)] followed by biological treatment (anoxic and/or activated sludge system) to reduce nitrate levels. [39].

Advanced oxidation systems (Wet Air Oxidation, UV/Peroxide/Ozone) may also be potential technologies to degrade wastewaters containing MEA, MDEA and piperazine. The oxidation step converts these compounds to readily degradable organics and nitrate. In order to degrade these, a second step would likely be a bioreactor designed for dentrification (nitrate conversion to nitrogen gas). The denitrification step would require a carbon source to provide energy for the reaction. Although some organics would be expected to be present in the wastewater, it is likely that methanol or another carbon source would need to be supplemented to the bioreactor. Bioreactor technologies being developed for power plant applications, such as the ABMet technology, may work in this application; however, it might not be the ideal choice, as they are designed around metals removal with some denitrification capacity. Modifications of such systems might be required. A denitrification wastewater plant would be a more logical choice here, and could be designed to get to the levels needed. Moving-bed bioreactors (MBBR) have been used for this denitrification purpose, but it is not the only technology available. If the reclaimer wastewater contained trace levels of metals, the existing chemical precipitation and biological treatment systems could be applied in combination with advanced oxidation and denitrification.

Additional information on these technologies is provided below.

7.5.3.1 *Advanced Oxidation Systems*

Wet air oxidation (WAO) - WAO is the oxidation of soluble or suspended components in water using oxygen as the oxidizing agent. The wet oxidation process is typically used to pretreat difficult wastewater streams, making them amenable for discharge to a conventional biological treatment plant for polishing. WAO oxidizes and hydrolyzes organic contaminants in water at temperatures of 150 to 320°C and pressures of 150 to 3,200 psia. Materials of constructions are a significant consideration under these process conditions. Catalytic WAO systems are also available. Dissolved oxygen in water participates in the oxidation reaction for this process; therefore, either compressed air or high-pressure oxygen (or a combination of both) is used as a source of the oxygen. The WAO process converts organic compounds containing carbon, hydrogen, and oxygen into carbon dioxide (CO_2), water, and short-chain biodegradable compounds such as acetic acid and formaldehyde. VOCs such as aldehydes, ketones, and alcohols may be in the off-gas from a WAO system depending upon the composition of feed material. A thermal or catalytic oxidizer may be necessary to destroy these unwanted VOCs to meet environmental regulations. Wet oxidation treatment can be used to treat high strength waste streams in order to make them more suitable to conventional biological treatment.

Fenton’s Process and UV/Peroxide/Ozone - Numerous advanced oxidation processes exist that make use of Fenton’s reagent (Fe/peroxide) or various combinations of UV light, hydrogen peroxide, and ozone. All are based on the principal of highly reactive hydroxyl radical formation which is effective in destroying organic chemicals. These hydroxyl radicals attack organic molecules by either abstracting a hydrogen atom or adding hydrogen atom to the double bonds. This reaction process results in new oxidized intermediates with lower molecular weight, or carbon dioxide and water. These advanced oxidation technologies are particularly useful for treating biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in wastewater. They are used for the removal of recalcitrant organic constituents from industrial and municipal wastewater. Some of these compounds can pose severe problems in biological treatment systems due to their resistance to biodegradation or/and toxic effects on microbial processes. Thus they can be used as pretreatment methods to reduce the concentrations of toxic organic compounds from the reclaimer waste that may inhibit biological wastewater treatment processes.

7.5.3.2 *Denitrification Systems*

Biological removal of nitrogen can be carried out using various treatment configurations. It can be done using a single-unit process with various treatment zones or in separate stages. Suspended growth, fixed growth, or combined systems can be used. Whatever the treatment system used, they all require an aerobic zone for converting ammonia to nitrate and an anoxic zone for converting the nitrate to nitrogen gas. One such technology, moving bed bioreactors (MBBR), uses a reactor filled with specially designed plastic biofilm carriers which provide a large surface area for micro-organisms to grow on and perform specific biological treatment functions. Carriers are kept in suspension in the reactor either by the aeration system (aerobic zone) or mixers (anoxic zone). Bacteria from the wastewater attach themselves to the floating carriers. These systems offer the advantage of very compact configurations. The MBBR has a greater performance potential than other conventional fixed film type processes (e.g. trickling filters and rotating biological contactors).

7.5.4 Costs

Costs for various WWT systems will be highly dependent on the characteristics of the reclaimer wastewater influent and the required effluent composition, as well as the combination of technologies selected. Cost data for various WWT technologies that could be identified from the literature [40, 41 42] and other sources are provided below.

7.5.4.1 *Wet Air Oxidation*

Capital costs for wet air oxidation systems depend on the capacity of the system, oxygen demand reduction of the wastewater, severity of the oxidation conditions required to meet the treatment objectives, and the construction materials. WAO WWT systems have been evaluated for use in treatment of wastewater contaminated with weight percent levels of MEA-based chemical weapons agents [40]. Capital costs for WAO systems designed to treat 10 to 12 gpm of wastewater to destroy organic compounds were estimated in this 2003 study at $10,000,000 to $12,000,000, with annual operating costs of approximately $900,000 to $1,000,000. More recent cost data could not be located within constraints of this project; based on internal knowldege and expereience of URS the 2003 costs were used.

7.5.4.2 *UV/Peroxide/Ozone*

No cost information was identified.

7.5.4.3 *Moving Bed Bioreactor*

No cost information was identified for MBBR processes. As a general point of reference on costs for conventional biological aeration processes, EPA has estimated capital costs for package plants (pre-manufactured treatment facilities) used to treat wastewater in small communities or on individual properties [41]. According to manufacturers surveyed in the EPA study, package plants can be designed to treat flows as low as 0.002 MGD (1.4 gpm) or as high as 0.5 MGD (350 gpm), although they more commonly treat flows between 0.01 and 0.25 MGD. EPA estimated capital costs (year 2000 dollars) for conventional extended aeration systems at €1.39 to 2.18 per liter ($7 to $11 per gallon) treated for systems treating the range of solvent reclaimer flows expected to be encountered in the case study plants examined in this present study (7 to 55 gpm). This corresponds to a total capital cost of approximately $100,000 to $600,000, depending on the treatment capacity of the system required.

7.5.4.4 *Existing Power Plant WWT Technologies*

As a point of comparison, EPA prepared estimated costs for WWT systems that would be required to meet possible final ELG rule revisions for three case study power plant sizes as part of the ELG rulemaking process [42]. EPA's cost estimates for various combinations of chemical precipitation, biological treatment (focused on selenium), and thermal evaporation of FGD wastewater and landfill leachate are summarized in Table 7-12 for the largest plant size that EPA evaluated (500 to 600 MW). The annualized costs for these systems are on the same order of magnitude as the annualized costs for operating the reclaimer.

Table 7-12 US EPA Estimated Cost for WWT Technologies Applicable to Selected Power Plant Wastewater Streams

Treated Stream: WWT Technology	Model Plant 3 (approx 500-600 MW)		
	Capital Cost (2010 $)	Annual O&M Cost(2010 $)	Annualized Cost (2010 $)
FGD wastewater: CP + Bio	$23,610,000	$2,247,000	$4,476,000
FGD wastewater: CP + Evap	$50,527,000	$5,463,000	$10,232,000
Landfill leachate: CP	$8,244,000	$846,000	$1,625,000
Landfill leachate: CP + Bio	$14,216,000	$1,193,000	$2,535,000

Source: Adapted from [42].
1. EPA estimated leachate costs based on construction of a stand-alone treatment system for leachate flow. EPA stated actual costs may be lower if leachate is co-treated with FGD wastewater.
2. EPA's estimate of annualized costs based on the sum the operating and maintenance (O&M) costs and annualized capital costs, using a 7% interest rate and a 20-year service life for the equipment.
3. EPA did not specify the process stream design flow rates used to calculate these costs; however, flows might be expected to on the order of a few hundred gallons per minute.
CP: Chemical precipitation treatment.
CP + Bio: Chemical precipitation plus biological treatment.
CP + Evap: Chemical precipitation plus thermal evaporation.

7.6 Summary of Reclaimer Waste Disposition Options

Disposition options for the reclaimer waste streams generated by the various reclaiming technologies and 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 CO_2 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 presented here was based on the limited information provided from a mathematical model of the reclaimer waste stream. Waste from an operating process will need to be analyzed to definitively classify the waste and identify disposition options.

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 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 of an NGCC requires more investigation. A literature search identified at least one example in the US of using in-duct firing in the HRSG to dispose of gas-phase volatile organic waste [24]; further studies are needed to determine if the solid thermal reclaimer sludge would be sufficiently destroyed (for 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 a different set of regulatory obligations if they fire hazardous waste in their coal-fired boilers. Currently, most US electric generating power plants do not operate as hazardous waste incinerators.

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 reclaimer material's heating value 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 electrodialysis processes are best suited for disposal via wastewater treatment plants.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 existing 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 CO_2 control technologies.

The annualized costs for operating the reclaimer process presented in Chapter 5 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. These waste disposal costs are applicable to waste solvent profiles for the coal thermal reclaiming cases in Tables 5-24 through 5-26 in Section 5.6 using the initial assumption of a slipstream of 0.1 wt% of the total circulation rate. The annualized total revenue requirement (includes capital costs, operating and maintenance costs, and energy requirements) for these cases are €3.2MM/yr for MEA, €14.4MM/yr for PZ, and €11.9MM/yr for MDEA/PZ. In Section 5.7, analysis demonstrated that solvent losses via reclaiming were reduced when it was alternately assumed that the concentration of heat stable salts entering the reclaimer was 1.5 wt%; although the waste disposal costs were not explicitly calculated for this alternate assumption, it is expected that waste disposal costs would decrease if the mass flow rate of waste being disposed decreases. Therefore, selection of a reclaimer process should carefully consider the type of waste generated and associated costs of disposing of that waste.

REFERENCES

1. National Solid Wastes Management Association (NSWMA). MSW (Subtitle D) Landfills. http://www.environmentalistseveryday.org/publications-solid-waste-industry-research/information/faq/municipal-solid-waste-landfill.php
2. Environment, Health and Safety Online. Commercial Hazardous Waste Landfills. http://www.ehso.com/cssepa/tsdflandfills.php
3. Closure and Post-Closure Care Cost Estimating Software, Version 6.0, CostPro 6.0, United States Environmental Protection Agency; TetraTech EM, Inc, 2009.
4. "Cement Kiln Co-Processing (High Temperature Treatment)". International HCH and Pesticides Association (IHPA). June 2009. 06 June 2013. http://www.ihpa.info/docs/library/reports/Pops/June2009/DEFSBC_LogCEMENTKILN_180608_.pdf
5. US Code of Federal Regulations. 40 Code of Federal Regulations (CFR) 60, Subpart F
6. US Code of Federal Regulations. 40 CFR 63, Subpart LLL. Note: EPA has promulgated NESHAPs for various types of emitting sources, grouped by standard industrial classifications. The NESHAPs typically include maximum emission rates, called emission standards. These emission standards are generally based on the maximum achievable control technology (MACT). Therefore the rules are often referred to as MACT Standards.
7. US Code of Federal Regulations. 40 CFR 63, Subpart EEE
8. US Code of Federal Regulations. 40 CFR 60, Subparts CCCC and DDDD
9. US Code of Federal Regulations. 40 CFR Parts 239 to 282.
10. US Code of Federal Regulations. 40 CFR 261, Subpart B: Identification of Non-Hazardous Secondary materials that are Solid Wastes when they are Used as Fuels or Ingredients in Combustion Units. (§241.3 and §241.4)
11. US Code of Federal Regulations. 40 CFR 60, Subpart F: Standards of Performance for Portland Cement Kilns (§60.60 through §60.66). Limits presented are for the kiln alone, other limits are required for other processing equipment (clinker cooler) but these are not likely to be affected by introduction of amine sludge.
12. US Code of Federal Regulations. 40 CFR 63, Subpart LLL: National Emission Standards for Hazardous Air Pollutants for the Portland Cement Manufacturing Industry, (§63.1340 through §63.1358). Limits presented are for "existing "kilns, those that began construction before 5/6/09. Limits for new kilns are equal or lower.
13. US Code of Federal Regulations. 40 CFR 60, Subpart CCCC: Standards of Performance for Commercial and Industrial Solid Waste Incineration Units (New Units) (§60.§§60.2265) and Subpart DDDD: Emission Guidelines and Compliance timelines for Commercial and Industrial Solid Waste Incineration Units (Existing Units) (60.2500 through §60.2875). Limits presented are for "existing" kilns, those that began construction before 6/4/10 or modification before 8/7/13. Limits for new kilns are equal or lower.
14. US Code of Federal Regulations. 40 CFR 63, Subpart EEE, National Emission Standards for Hazardous Air Pollutants from Hazardous Waste Combustors (§63.1200 through §63.1221). Limits presented are for "existing" kilns, those that began construction or reconstruction before 4/20/04. Limits for new kilns are equal or lower.
15. http://www.epa.gov/osw/nonhaz/industrial/special/ckd/

16. US Code of Federal Regulations. 40 CFR 266.112. (This Rule is commonly referred to as the BIF Rule).
17. US Code of Federal Regulations. 40 CFR 266, Subpart H: Hazardous Wastes Burned in Boilers and Industrial Furnaces (§266.100 through §266.112)
18. US Code of Federal Regulations. Weitzman, Leo, *Cement Kilns as Hazardous Waste Incinerators*, Environmental Progress, Vol 2, No 1, page 11, February, 1983.
19. US Code of Federal Regulations. 40 CFR 63.1219: DRE=1 –(Win/Wout) with Win= the mass feed rate of a selected principal organic hazardous constituent fed to the unit and Wout= the mass emission rate of the same constituent.
20. Energy Justice Network. June 2013. http://www.energyjustice.net/biomass
21. Feasibility of CCS Sludge Cofiring in Power Plant. EON-UK. KCP-ENT-CAP-REP-0001. Revision 03.
22. Bowen, Brian H., and Marty W. Irwin. "Coal Characteristics – CCTR Basic Facts File #8". Indiana Center for Coal Technology Research. Purdue University. Presented October 2008. http://www.purdue.edu/discoverypark/energy/assets/pdfs/cctr/outreach/Basics8-CoalCharacteristics-Oct08.pdf.
23. US EPA. CICA Fact Sheet – Thermal Incinerator. Air Pollution Control Technology Fact Sheet. EPA-452/F-03-022 http://www.epa.gov/ttnchie1/mkb/documents/fthermal.pdf
24. Hunt, James. Heat recovery steam generators design options and benefits. Cogeneration and On-Site Power Production. Vol. 9, Issue 3. January 5, 2008. http://www.cospp.com/articles/print/volume-9/issue-3/features/heat-recovery-steam-generators-design-options-and-benefits.html
25. Dao, N. B. Duong, and David A. Tillman. (Foster Wheeler) "Chlorine issues with Biomass Cofiring in Pulverized Coal Boilers: Sources, Reactions, and Consequences – A Literature Review" pg 5. Presented at 34th International Technical Conference on Coal Utilization and Fuel Systems. May 31 2009. http://www.fwc.com/publications/tech_papers/files/TP_PC_09_01.pdfhttp://www.fwc.com/publications/tech_papers/files/TP_PC_09_01.pdfhttp://www.fwc.com/publications/tech_papers/files/TP_PC_09_01.pdf
26. Wojichowski, D. (2002). SNCR Systen - Design, Installation, and Operating Experience. *NETL*. Pittsburgh.
27. Cichanowicz, J. E. (2010). *Current Capital Cost and Cost-Effectiveness of Power Plant Emission Control Technologies*. Utility Air Regulatory Group (http://www.publicpower.org/files/PDFs/UARGSCR_FGDFinal.pdf).
28. Kitto, S., & Stultz, J. (1992). *Steam, Its Generation and Use (Babcock and Wilcox, 40th Edition).*
29. Botheju, D., Glarborg, P., & Tokheim, L. (2012). NOx reduction using amine reclaimer wastes (ARW) generateed in post combustion CO2 capture. *International Journal of Greenhouse Gas Control 10*, 33-45.
30. Muzio, L. (2013). Vice President, Ferco. (Dombrowski-URS, Interviewer)
31. "The Classification of Coal". The Engineering Tool Box. 06 June 2013. http://www.engineeringtoolbox.com/classification-coal-d_164.html
32. Hatt, Rodd. "Sticky When Wet – Moisture Impacts on Coal Handling and Heat Rate". World Coal. August 1997. http://www.coalcombustion.com/PDF%20Files/MOISTURE%2003.pdf

33. US EPA. Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category. EPA-HQ-OW-2009-0819. Pre-publication version released April 18, 2013.
34. US Code of Federal Regulations. 40 CFR 403
35. Client Alert. Latham & Hawkins Environmental, Land and Resources Department. No 1513. May 1, 2013.
36. Federal Facilities Environmental Stewardship and Compliance Assistance Center, FedCenter.gov. Discharges to a POTW/FOTW. June 2013. https://www.fedcenter.gov/assistance/facilitytour/wastewater/potw/
37. Harwood, Jay. Making the Change – Meeting EPA Effluent Limitation Guidelines. Presented by GE Water and Power at Power Engineering Webinar. May 23, 2013.
38. http://www.wateronline.com/doc/infilco-degremont-patented-biological-wastewater-treatment-process-0001
39. Personal email communication with Nalco, 6/12/13.
40. US Army Chemical Materials Agency (Provisional) Program Manager for Elimination of Chemical Weapons. FY03 Technology Evaluation for Chemical Demilitarization. Wet Air Oxidation Technology Assessment. Final Report. April 2003.
41. US EPA. Wastewater Technology Fact Sheet Package Plants. EPA Office of Water, Washington, D.C. EPA 832-F-00-016. September 2000
42. US EPA. Steam Electric Power Generating Effluent Guidelines Rulemaking Supplemental Information Package #2 for Federalism and Unfunded Mandates Reform Act (UMRA) Consultations. October 18, 2011.
43. SNC-Lavalin Inc. Impact of Impurities on CO_2 Capture, Transport and Storage. Report Prepared for IEA Greenhouse Gas R&D Programme, Report Number PH4/32. August 2004.
44. Summaries of EU Legislation, “Waste Incineration”. Last updated 27 October 2011. http://europa.eu/legislation_summaries/environment/waste_management/l28072_en.htm. Site accessed 29 June 2013.
45. Homogeneous Gas Phase Decomposition of Oxides of Nitrogen. EPRI, Palo Alto, CA and KVB, Inc: 1976. FP-253 Project 461-1.
46. Email from Andrew Botting of Scottish Environment Protection Agency to Jean Youngerman of URS, 04 July 2013.

Attachment 1: Composition of Amine Waste Sludge from Thermal Reclaiming Process

Amine waste sludge compositions were modeled for the following cases:

- Coal-fired plant, MDEA/PZ solvent
- Coal-fired plant, PZ solvent
- Coal-fired plant, MEA solvent
- NGCC plant, MDEA/PZ solvent
- NGCC plant, PZ solvent
- NGCC plant, MEA solvent

The following tables show the composition for each of these cases. In each table, there are two columns representing the same sludge; first column shows sludge on a water-free basis (this is intended to represent waste from the CHEM Group wiped film evaporator process, although in reality there is likely to be a finite amount of water in the sludge); second column shows sludge with 50% water content (water added to remove sludge from reclaimer for a kettle-type reboiler process; it also reduces amine volatility from the sludge).

Heat stable salts listed in the tables are assumed to be protonated with amine. Iron concentrations are based on pilot plant observations and analysis. The pH of these waste streams are expected to be ~10, based off of analysis of experimental samples.

<u>Acronyms</u>
MDEA = methyl diethanolamine
PZ = piperazine
MEA = monoethanolamine
DEA = diethanolamine
MAE = N-methyl-aminoethanol
MEA = monoethanolamine

Definitions:

Nonvolatile products: removed by reclaiming

HEIA	hydroxyethyl-imidazolidinone (cyclic urea of MEA dimer)
HEEDA	hydroxyethyl-ethylenediamine (dimer of MEA)
triHEIA	cyclic urea of MEA trimer
Trimer	MEA trimer
HEI	hydroxyethyl-imidazole
HEF	hydroxyethyl-formamide (formyl amide of MEA)

Volatile amines	amine degradation products at least as volatile as PZ; will not be removed by thermal reclaiming
EDA	ethylenediamine
2-imid	Imidazolidinone
2-PZOH	2-piperazinol (hemiaminal

NV PZ derivs	nonvolatile piperazine derivatives and polymers; removed by thermal reclaiming
AEP	1-(aminoethyl)-piperazine
HEP	1-(hydroxyethyl)-piperazine
1-EPZ	1-(ethyl)-piperazine

Volatile amines	amine degradation products at least as volatile as MDEA; will not be removed by thermal reclaiming
1-MPZ	1,4-dimethyl-piperazine
1,4-DMPZ	1-methyl-piperazine
2-PZOH	2-piperazinol (hemiaminal)
AEP	1-aminoethyl-piperazine

Nonvolatile amines	nonvolatile, removed by thermal reclaiming
DEA	diethanolamine
MAE	N-methyl-aminoethanol
MNPZ	1-nitrosopiperazine
Bicine	amino acid
HES	hydroxyethyl-sarcosine

Table 7-13 Thermal Reclaiming Waste, Coal-Fired, MDEA/PZ

Concentration	Units	Thermal Reclaiming, No Water Addition	Thermal Reclaiming, Water Addition
pH		8-12	8-12
Total Flow Rate	kg/hr	951	1902
Water	wt%	0	50
MDEA	wt%	51.1	25.5
PZ	wt%	10.5	5.3
NaOH	wt%	9.7	4.8
Formate	wt%	2.0	1.0
Other Heat Stable Salts	wt%	0.2	0.1
Sulfate	wt%	7.9	3.9
Nitrate	wt%	5.1	2.5
Chloride	wt%	1.1	0.5
Flouride	wt%	0.0	0.0
DEA + MAE + polymers	wt%	9.4	4.7
Bicine	wt%	1.1	0.5
MNPZ	wt%	0.6	0.3
Hg	ppm	3.7	1.8
Se	ppm	4.7	2.4
As	ppm	0.8	0.4
Cd	ppm	0.3	0.2
Cr	ppm	9.2	4.6
Pb	ppm	0.9	0.5
Fly ash	wt%	1.2	0.6
Fe + other SSM's	wt%	0.3	0.1
Heating Value	Btu/lb	8790	4395
Heating Value	kJ/kg	20446	10223

Table 7-14 Thermal Reclaiming Waste, Coal-Fired, PZ

Concentration	Units	Thermal Reclaiming, No Water Addition	Thermal Reclaiming, Water Addition
pH		8-12	8-12
Total Flow Rate	kg/hr	951	1902
Water	wt%	0	50
MDEA	wt%	51.1	25.5
PZ	wt%	10.5	5.3
NaOH	wt%	9.7	4.8
Formate	wt%	2.0	1.0
Other Heat Stable Salts	wt%	0.2	0.1
Sulfate	wt%	7.9	3.9
Nitrate	wt%	5.1	2.5
Chloride	wt%	1.1	0.5
Flouride	wt%	0.0	0.0
DEA + MAE + polymers	wt%	9.4	4.7
Bicine	wt%	1.1	0.5
MNPZ	wt%	0.6	0.3
Hg	ppm	3.7	1.8
Se	ppm	4.7	2.4
As	ppm	0.8	0.4
Cd	ppm	0.3	0.2
Cr	ppm	9.2	4.6
Pb	ppm	0.9	0.5
Fly ash	wt%	1.2	0.6
Fe + other SSM's	wt%	0.3	0.1
Heating Value	Btu/lb	8790	4395
Heating Value	kJ/kg	20446	10223

Table 7-15 Thermal Reclaiming Waste, Coal-Fired, MEA

Concentration	Units	Thermal Reclaiming, No Water Addition	Thermal Reclaiming, Water Addition
pH		8-12	8-12
Total Flow Rate	kg/hr	406	812
Water	wt%	0	50
MEA	wt%	34.6	17.3
NaOH	wt%	20.5	10.3
Formate	wt%	1.2	0.6
Other Heat Stable Salts	wt%	0.3	0.1
Sulfate	wt%	18.5	9.2
Nitrate	wt%	12.1	6.1
Nitrite	wt%	1.0	0.5
Chloride	wt%	2.5	1.3
Flouride	wt%	0.1	0.0
HEIA	wt%	2.9	1.4
triHEIA	wt%	1.0	0.5
HEEDA	wt%	0.5	0.2
Trimer	wt%	0.2	0.1
HEI	wt%	1.6	0.8
Hg	ppm	8.6	4.3
Se	ppm	11.0	5.5
As	ppm	1.8	0.9
Cd	ppm	0.8	0.4
Cr	ppm	21.6	10.8
Pb	ppm	2.2	1.1
Fly ash	wt%	2.9	1.4
Fe + other SSM's	wt%	0.2	0.1
Heating Value	Btu/lb	4188	2094
Heating Value	kJ/kg	9742	4871

Table 7-16 Thermal Reclaiming Waste, NGCC Plant, MDEA/PZ

Concentration	Units	Thermal Reclaiming, No Water Addition	Thermal Reclaiming, Water Addition
pH		8-12	8-12
Total Flow Rate	kg/hr	419	838
Water	wt%	0	50
MDEA	wt%	52.1	26.1
PZ	wt%	10.8	5.4
NaOH	wt%	6.9	3.5
Formate	wt%	3.0	1.5
Other Heat Stable Salts	wt%	0.3	0.1
Sulfate	wt%	2.3	1.2
Nitrate	wt%	5.0	2.5
Chloride	wt%	0.0	0.0
Flouride	wt%	0.0	0.0
DEA + MAE + polymers	wt%	16.2	8.1
Bicine	wt%	2.6	1.3
MNPZ	wt%	0.6	0.3
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.3	0.1
Heating Value	Btu/lb	9690	4844
Heating Value	kJ/kg	22540	11268

Table 7-17 Thermal Reclaiming Waste, NGCC Plant, PZ

Concentration	Units	Thermal Reclaiming, No Water Addition	Thermal Reclaiming, Water Addition
pH		8-12	8-12
Total Flow Rate	kg/hr	260	520
Water	wt%	0	50
PZ	wt%	68.3	34.2
NaOH	wt%	11.0	5.5
Formate	wt%	3.8	1.9
Other Heat Stable Salts	wt%	1.9	0.9
Sulfate	wt%	3.7	1.9
Nitrate	wt%	8.1	4.0
Chloride	wt%	0.0	0.0
Flouride	wt%	0.0	0.0
Non-Volatile PZ Polymers	wt%	2.5	1.3
MNPZ	wt%	0.4	0.2
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.4	0.2
Heating Value	Btu/lb	10410	5205
Heating Value	kJ/kg	24214	12107

Table 7-18 Thermal Reclaiming Waste, NGCC Plant, MEA

Concentration	Units	Thermal Reclaiming, No Water Addition	Thermal Reclaiming, Water Addition
pH		8-12	8-12
Total Flow Rate	kg/hr	150	300
Water	wt%	0	50
MEA	wt%	44.5	22.2
NaOH	wt%	17.3	8.6
Formate	wt%	3.8	1.9
Other Heat Stable Salts	wt%	0.8	0.4
Sulfate	wt%	6.5	3.2
Nitrate	wt%	14.5	7.2
Nitrite	wt%	1.7	0.9
Chloride	wt%	0.0	0.0
Flouride	wt%	0.0	0.0
HEIA	wt%	3.7	1.9
triHEIA	wt%	1.2	0.6
HEEDA	wt%	0.6	0.3
Trimer	wt%	0.2	0.1
HEI	wt%	4.8	2.4
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.3	0.2
Heating Value	Btu/lb	5382	2691
Heating Value	kJ/kg	12519	6259

Attachment 2: Summary of Estimated Stream Compositions for Ion Exchange and Electrodyalysis Solvent Reclaimer Wastewater

Amine waste sludge compositions were modeled for the following cases:

- Coal-fired plant, MDEA/PZ solvent
- Coal-fired plant, PZ solvent
- Coal-fired plant, MEA solvent
- NGCC plant, MDEA/PZ solvent
- NGCC plant, PZ solvent
- NGCC plant, MEA solvent

Definitions:

MEA	**monoethanolamine**
Nonvolatile products: removed by reclaiming	
HEIA	hydroxyethyl-imidazolidinone (cyclic urea of MEA dimer)
HEEDA	hydroxyethyl-ethylenediamine (dimer of MEA)
triHEIA	cyclic urea of MEA trimer
Trimer	MEA trimer
HEI	hydroxyethyl-imidazole
HEF	hydroxyethyl-formamide (formyl amide of MEA)

PZ	**Piperazine**
Volatile amines	amine degradation products at least as volatile as PZ; will not be removed by thermal reclaiming
EDA	ethylenediamine
2-imid	Imidazolidinone
2-PZOH	2-piperazinol (hemiaminal

NV PZ derivs	nonvolatile piperazine derivatives and polymers; removed by thermal reclaiming
AEP	1-(aminoethyl)-piperazine
HEP	1-(hydroxyethyl)-piperazine
1-EPZ	1-(ethyl)-piperazine

MDEA/PZ	**methyl diethanolamine / piperazine**
Volatile amines	amine degradation products at least as volatile as MDEA; will not be removed by thermal reclaiming
1-MPZ	1,4-dimethyl-piperazine
1,4-DMPZ	1-methyl-piperazine
2-PZOH	2-piperazinol (hemiaminal)
AEP	1-aminoethyl-piperazine

Nonvolatile amines	nonvolatile, removed by thermal reclaiming
DEA	diethanolamine
MAE	N-methyl-aminoethanol
MNPZ	1-nitrosopiperazine
Bicine	amino acid
HES	hydroxyethyl-sarcosine

Table 7-19 IE and ED Reclaiming Waste, Coal-Fired Plant, MEA

Concentration	Units	Ion Exchange	Electrodialysis
Total Flow Rate	kg/hr	5310	6405
Total Flow Rate	lbs/hr	11709	14123
Water	wt%	95	95
MEA	wt%	0.5	1.3
NaOH	wt%	1.7	1.4
Formate	wt%	0.1	0.1
Other Heat Stable Salts	wt%	0.0	0.0
Sulfate	wt%	1.4	1.2
Nitrate	wt%	0.9	0.8
Nitrite	wt%	0.1	0.1
Chloride	wt%	0.2	0.2
Flouride	wt%	0.0	0.0
HEIA	wt%	0.0	0.0
triHEIA	wt%	0.0	0.0
HEEDA	wt%	0.0	0.0
Trimer	wt%	0.0	0.0
HEI	wt%	0.0	0.0
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.0	0.0

Table 7-20 IE and ED Reclaiming Waste, NGCC Plant, MEA

Concentration	Units	Ion Exchange	Electrodialysis
Total Flow Rate	kg/hr	1661	2184
Total Flow Rate	lbs/hr	3663	4816
Water	wt%	95	95
MEA	wt%	0.8	1.8
NaOH	wt%	1.7	1.3
Formate	wt%	0.3	0.3
Other Heat Stable Salts	wt%	0.1	0.1
Sulfate	wt%	0.6	0.4
Nitrate	wt%	1.3	1.0
Nitrite	wt%	0.2	0.1
Chloride	wt%	0.0	0.0
Flouride	wt%	0.0	0.0
HEIA	wt%	0.0	0.0
triHEIA	wt%	0.0	0.0
HEEDA	wt%	0.0	0.0
Trimer	wt%	0.0	0.0
HEI	wt%	0.0	0.0
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.0	0.0

Table 7-21 IE and ED Reclaiming Waste, Coal-Fired Plant, PZ

Concentration	Units	Ion Exchange	Electrodialysis
Total Flow Rate	kg/hr	6700	9475
Total Flow Rate	lbs/hr	14774	20892
Water	wt%	95	95
PZ	wt%	1.0	2.2
NaOH	wt%	1.6	1.1
Formate	wt%	0.3	0.2
Other Heat Stable Salts	wt%	0.1	0.1
Sulfate	wt%	1.1	0.8
Nitrate	wt%	0.7	0.5
Chloride	wt%	0.2	0.1
Flouride	wt%	0.0	0.0
Non-Volatile PZ Polymers	wt%	0.0	0.0
MNPZ	wt%	0.0	0.0
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.0	0.0

Table 7-22 IE and ED Reclaiming Waste, NGCC Plant, PZ

Concentration	Units	Ion Exchange	Electrodialysis
Total Flow Rate	kg/hr	2249	3659
Total Flow Rate	lbs/hr	4959	8068
Water	wt%	95	95
PZ	wt%	1.6	2.9
NaOH	wt%	1.4	0.9
Formate	wt%	0.4	0.3
Other Heat Stable Salts	wt%	0.2	0.1
Sulfate	wt%	0.4	0.3
Nitrate	wt%	0.9	0.6
Chloride	wt%	0.0	0.0
Flouride	wt%	0.0	0.0
Non-Volatile PZ Polymers	wt%	0.0	0.0
MNPZ	wt%	0.0	0.0
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.0	0.0

Table 7-23 IE and ED Reclaiming Waste, Coal-Fired Plant, MDEA/PZ

Concentration	Units	Ion Exchange	Electrodialysis
Total Flow Rate	kg/hr	7376	12131
Total Flow Rate	lbs/hr	16264	26749
Water	wt%	95	95
MDEA	wt%	1.3	2.4
PZ	wt%	0.3	0.5
NaOH	wt%	1.4	0.8
Formate	wt%	0.3	0.2
Other Heat Stable Salts	wt%	0.0	0.0
Sulfate	wt%	1.0	0.6
Nitrate	wt%	0.6	0.4
Chloride	wt%	0.1	0.1
Flouride	wt%	0.0	0.0
DEA + MAE + polymers	wt%	0.0	0.0
Bicine	wt%	0.0	0.0
MNPZ	wt%	0.0	0.0
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.0	0.0

Table 7-24 IE and ED Reclaiming Waste, NGCC Plant, MDEA/PZ

Concentration	Units	Ion Exchange	Electrodialysis
Total Flow Rate	kg/hr	2586	4684
Total Flow Rate	lbs/hr	5702	10328
Water	wt%	95	95
MDEA	wt%	1.7	2.8
PZ	wt%	0.3	0.6
NaOH	wt%	1.3	0.7
Formate	wt%	0.5	0.3
Other Heat Stable Salts	wt%	0.0	0.0
Sulfate	wt%	0.4	0.2
Nitrate	wt%	0.8	0.4
Chloride	wt%	0.0	0.0
Flouride	wt%	0.0	0.0
DEA + MAE + polymers	wt%	0.0	0.0
Bicine	wt%	0.0	0.0
MNPZ	wt%	0.0	0.0
Hg	ppm	0.0	0.0
Se	ppm	0.0	0.0
As	ppm	0.0	0.0
Cd	ppm	0.0	0.0
Cr	ppm	0.0	0.0
Pb	ppm	0.0	0.0
Fly ash	wt%	0.0	0.0
Fe + other SSM's	wt%	0.0	0.0

Attachment 3: Summary of Current Existing Effluent Guidelines for the US Steam Electric Power Industry

Table 7-25 Summary of Current Existing Effluent Guidelines for the US Steam Electric Power Industry

Waste Stream	BPT (Best Practicable Control Technology Currently Available) [a]	BAT (Best Available Technology Economically Achievable) [a]	NSPS (New Source Performance Standards) [a]	PSES (Pretreatment Standards for Existing Sources) and PSNS (Pretreatment Standards for New Sources) [a]
All Waste Streams	pH: 6-9 S.U. [b] PCBs: Zero discharge	PCBs: Zero discharge	pH: 6-9 S.U. [b] PCBs: Zero discharge	PCBs: Zero discharge
Low-Volume Wastes	TSS: 100 mg/L; 30 mg/L Oil & Grease: 20 mg/L; 15 mg/L		TSS: 100 mg/L; 30 mg/L Oil & Grease: 20 mg/L; 15 mg/L	
Fly Ash Transport	TSS: 100 mg/L; 30 mg/L Oil & Grease: 20 mg/L; 15 mg/L		Zero discharge	Zero discharge (PSNS only) No limitation for PSES
Bottom Ash Transport	TSS: 100 mg/L; 30 mg/L Oil & Grease: 20 mg/L; 15 mg/L		TSS: 100 mg/L; 30 mg/L Oil & Grease: 20 mg/L; 15 mg/L	
Once-Through Cooling	Free Available Chlorine: 0.5 mg/L; 0.2 mg/L	Total Residual Chlorine: If > 25 MW: 0.20 mg/L instantaneous maximum; If < 25 MW, equal to BPT	Total Residual Chlorine: If > 25 MW: 0.20 mg/L instantaneous maximum; If < 25 MW, equal to BPT	
Cooling Tower Blowdown	Free Available Chlorine: 0.5 mg/L; 0.2 mg/L	Free Available Chlorine: 0.5 mg/L; 0.2 mg/L 126 Priority Pollutants: Zero discharge, except: Chromium: 0.2 mg/L; 0.2 mg/L Zinc: 1.0 mg/L; 1.0 mg/L	Free Available Chlorine: 0.5 mg/L; /0.2 mg/L 126 Priority Pollutants: Zero discharge, except: Chromium: 0.2 mg/L; 0.2 mg/L Zinc: 1.0 mg/L; 1.0 mg/L	126 Priority Pollutants: Zero discharge, except: Chromium: 0.2 mg/L; 0.2 mg/L Zinc: 1.0 mg/L; 1.0 mg/L
Coal Pile Runoff	TSS*: 50 mg/L instantaneous maximum	TSS*: 50 mg/L instantaneous maximum		

Waste Stream	BPT (Best Practicable Control Technology Currently Available) [a]	BAT (Best Available Technology Economically Achievable) [a]	NSPS (New Source Performance Standards) [a]	PSES (Pretreatment Standards for Existing Sources) and PSNS (Pretreatment Standards for New Sources) [a]
Metal Cleaning Wastes	TSS: 100 mg/L; 30 mg/L Oil & Grease: 20 mg/L; 15 mg/L Copper: 1.0 mg/L; 1.0 mg/L Iron: 1.0 mg/L; 1.0 mg/L	See *Chemical Metal Cleaning Wastes* below	See *Chemical Metal Cleaning Wastes* below	See *Chemical Metal Cleaning Wastes* below
Chemical	See *Metal Cleaning Wastes* above	Copper: 1.0 mg/L; 1.0 mg/L Iron: 1.0 mg/L; 1.0 mg/L	TSS: 100 mg/L; 30 mg/L Oil & Grease: 20 mg/L; 15 mg/L Copper: 1.0 mg/L; 1.0 mg/L Iron: 1.0 mg/L; 1.0 mg/L	Copper: 1.0 mg/L (daily maximum)
Non-chemical	See *Metal Cleaning Wastes* above	Reserved	Reserved	Reserved

Source: [U.S Code of Federal Regulations. 40 CFR Part 423].

a – The limitations for TSS, oil & grease, copper, iron, chromium, and zinc are presented as daily maximum (mg/L); 30-day average (mg/L). For all effluent guidelines, where two or more waste streams are combined, the total pollutant discharge quantity may not exceed the sum of allowable pollutant quantities for each individual waste stream. BPT, BAT, and NSPS allow either mass- or concentration-based limitations.

b – The pH limitation is not applicable to once-through cooling water.

Free Available Chlorine: 0.5 mg/L; 0.2 mg/L - 0.5 mg/L instantaneous maximum, 0.2 mg/L average during chlorine release period. Discharge is limited to 2 hrs/day/unit. Simultaneous discharge of chlorine from multiple units is prohibited. Limitations are applicable at the discharge from an individual unit prior to combination with the discharge from another unit.

Total Residual Chlorine: 0.20 mg/L instantaneous maximum. Total residual chlorine (TRC) = free available chlorine (FAC) + combined residual chlorine (CRC). TRC discharge is limited to 2 hrs/day/unit. TRC is applicable to plants ≥25 MW, and FAC is applicable to plants <25 MW. The TRC limitation is applicable at the discharge point to surface waters of the United States and may be subsequent to combination with the discharge from another unit.

126 Priority Pollutants: zero discharge - 126 priority pollutants from added maintenance chemicals (refer to App. A to 40 CFR 423). At the permitting authority's discretion, compliance with the zero-discharge limitations for the 126 priority pollutants may be determined by engineering calculations, which demonstrate that the regulated pollutants are not detectable in the final discharge by the analytical methods in 40 CFR part 136.

TSS*: 50 mg/L instantaneous maximum on coal pile runoff streams. No limitation on TSS for coal pile runoff flows ≥10-year, 24-hour rainfall event.

8 RECOMMENDATIONS

The primary purpose of solvent reclaiming from a CO_2 absorption post combustion capture process is to remove impurities and degradation products that have accumulated in the circulating solvent. The removal of these products improves energy performance and may ultimately reduce the amount of amine makeup. Impurities originate from components in the flue gas that are absorbed by the solvent and typically include transition metals, NO_2, and SO_2. Degradation products are formed from the oxidation and thermal degradation of the amine solvent and from the reaction of impurities with the amine to form products such as heat stable salts and high-molecular weight polyermic products (oligomers).

Although a substantial amount of information was documented within this report, several technical data gaps need to be addressed; the recommendations list below attempts to identify these technical gaps and provide guidance in collecting information to address these gaps. Data from pilot and demonstration plants will be important is reducing information gaps and achieving the recommendations below.

1. Test intermittent reclaiming by leased equipment from existing vendors in large pilot plants to manage solvent viscosity

Intermittent reclaiming will be cost effective in removing the bulk of solvent impurities. In acid gas treating experience, on-site reclaimers are frequently operated intermittently to reduce operator manpower and allow for removal of sludge and other maintenance. In acid gas treating it is also common to hire a vendor of reclaiming services to run an intermittent campaign with their own mobile equipment because the reclaiming vendor will offer on-site support when equipment is leased or rented.

Reclaimer development and demonstration of novel processes such as atmospheric and vacuum reclaiming are best tested using pilot-scale equipment; consideration should be given to determine the optimum thermal reclaiming design. Such equipment should be simple to design and fabricate. The most effective tests could be intermittent reclaiming with leased vendor equipment. Operation of the pilot reclaimer can provide demonstration and real world validation of non-volatiles atmospheric reclaiming.

Realistic testing of reclaiming will also require representative aged solvent. Because reclaiming will modify the steady-state composition of the aged solvent, valid testing will require long term (6-36 months) operation of the reclaimer at a pilot plant with real representative flue gas.

Non-volatile impurities such as heat stable salts and amine oligomers will increase the viscosity of the solvent. These can be removed by intermittent thermal reclaiming, ion exchange, or electrodialysis. Thermal reclaiming will be most effective in removing all of the non-volatile impurities. Ion exchange and electrodialysis will be most effective in specifically removing heat stable salts including formate, sulfate, and nitrate. Continuous ion exchange reclaiming for removal of ionic species used in conjunction with batch off-site thermal reclaiming should be evaluated as a potential option.

2. Consider the return of spent solvent to the amine supplier as a means to focus amine waste disposal.

If it is possible, the non-volatile reclaimer waste should be returned to the amine supplier to separate and recycle the useable amine. The chemical supplier should be better equipped than the power plant to handle the spent solvent. In the hands of the chemical supplier, the spent solvent might be regenerated into a valuable product, thus shedding the classification as a waste material. It will also minimize the quantity of waste that is ultimately produced. Of course, the amine supplier can expect a premium price for amine provided with this service. In the US, according to 40 CFR 261.3(c)(2)(i), materials that are reclaimed from solid wastes and that are used beneficially are not solid wastes and hence are not hazardous wastes unless the reclaimed material is burned for energy recovery or used in a manner constituting disposal.

3. Develop methods to selectively remove metals

Continuous reclaiming should be used to selectively remove dissolved metals. Fe^{+2} and Mn^{+2} should be removed continuously to minimize amine oxidation. Se, Hg, Cr and other dissolved metals should be removed continuously to minimize potential for environmental impact from solvent spills and to minimize safety risk for plant personnel.

Metals removal can be achieved by continuous thermal reclaiming. With the maximum corrosion rate experienced at Tarong pilot plant (Australia) in PZ testing, a continuous feed to the thermal reclaimer of 0.5 wt% of the total solvent circulation rate should achieve a steady-state Fe^{+2} concentration of 5 ppm.

Other methods should be considered and developed for metals removal. These could include selective ion exchange and metals precipitation/filtration induced by higher pH, sulfidation, or oxidation.

4. Develop methods to minimize and manage toxic impurities in spent solvent

Chromium, selenium, nitrosamines, and mercury appear to be the most important components in affecting hazardous properties of the waste solvent and resulting in classification of these wastes as hazardous in the US.

<u>Address corrosion to minimize chromium</u>

Pilot plant results suggest that dissolved chromium can accumulate in pilot plant solvent at 5 to 50 mg/L [1]. Presumably the chromium results from corrosion/leaching of stainless steel. It will be present in even greater concentration in bottoms product from a thermal reclaimer; a small amount of chromium could enter with the flue gas.

General research on understanding and minimizing corrosion will be important in addressing the disposal of reclaiming waste. Selection of construction metals that do not contain Cr or other hazardous metals should be considered.

Reclaiming processes should be developed that selectively remove and concentrate chromium and other hazardous metals to minimize the volume of hazardous waste.

Modify upstream treatment to minimize selenium

Selenium has been identified at hazardous concentration in reclaiming waste from at least two full-scale industrial amine scrubbing facilities. Apparently if selenium is present in the coal, enough of it gets through to be collected and accumulate in the solvent; subsequently, measurable concentrations of selenium are observed in the waste stream from thermal reclaiming. It is also possible that a small concentration of selenium may be present in ion exchange and electrodialysis discharge streams.

A research review of the experience with Se in flue gas desulfurization should be conducted to identify available remedies. It may be preferable to keep selenium in the solid (rather than liquor) phase in the FGD portion of the process. If the selenium is in the liquor phase, it is desired in the selenite ion (SeO_3^{2-}) form. Selenite is treatable with physical and chemical processes, while selenate ion (SeO_4^{2-}) requires biological processes for treatment. Anion exchange and electrodialysis should be investigated for its potential to concentrate selenium anions.

Continue research on the management of nitrosamine.

Nitrosamine has been determined in pilot plant samples at 0.1 to 7 mM. It is expected to be a carcinogen at low concentration. It is derived from NO_2 in the flue gas.

Research should be continued to develop methods of minimizing nitrosamine in the solvent and the reclaimer products. Ongoing research on nitrosamine management in systems using piperazine suggests that it can be minimized by increasing time and temperature to cause thermal decomposition in the stripper and thermal reclaimer bottoms.

Research should be initiated to remove NO_2 in the SO_2 polishing scrubber. Sulfite/thiosulfate should be effective. Alternatives to thermal destruction of nitrosamines include UV treatment and addition of inhibitors to reduce the rate of nitrosamine formation.

Investigate mercury removal by amine scrubbing

Elementalmercury (and a small amount of oxidized mercury) may accumulate in the solvent and thermal reclaimer product if it is present in the coal and is not removed by FGD or carbon injection. The analysis in this report assumed an exceptionally high removal for the residual mercury. Therefore it may not be a problem in actual systems.

Additional research should be performed to determine mercury removal by amine scrubbing.
Research should be performed on selective removal and concentration of mercury from the solvent. A thorough literature review of methods considered and developed for flue gas desulfurization should be helpful.

5. Develop improvements in thermal reclaiming to address corrosion and waste sludge handling.

Address corrosion by testing stainless steel and other alloys.
Corrosion may be minimized by cathodic protection. Specific equipment configurations should be developed to provide exceptional corrosion protection at the gas/liquid interface in the reclaiming reboiler.

Develop better methods of waste sludge handling
Since the sludge is solidified for hazardous waste disposal, this process step should be integrated into the reclaimer operation. The wiped film evaporator from CHEM Group appears to be effective equipment to address sludge handling and minimize thermal degradation in the reclaimer. Industry should consider sludge handling systems that will convert the sludge to solid at the reclaiming site; this would eliminate the need to transport the sludge off-site.

Develop continuous thermal reclaiming
Continuous processing should be easier to control, will require smaller equipment, and can conceptually be operated to provide consistent product.

Non-volatile degradation products include metals, amino acids, sulfate, nitrate, carboxylic acids, nitrosamines, amine oligomers, and amides. The traditional method of thermal reclaiming uses high temperature and pressure to volatilize the pure amine and leave behind the non-volatile degradation products, and it is typically operated in batch mode or as a semi-continuous bleed stream from the reclaimer bottoms. However, the higher operating temperature of thermal reclaiming can also result in additional thermal degradation of the amine, resulting in an even higher amine makeup rate.

For an amine such as piperazine, thermal reclaiming can be expected to operate at as much as 200°C. However, one inherent benefit of thermal reclaiming is that the higher temperature is expected to thermally decompose nitrosamines, such as mono-nitroso-piperazine (MNPZ). Also, alkali is typically added to reverse amides and neutralized acids, but the formation of carbonate salts may present a challenge for solvent handling and equipment maintenance.

6. Atmospheric Reclaiming of Non-Volatiles

A novel alternative to thermal reclaiming is to operate the reclaimer at atmospheric pressure or under vacuum, which would reduce or eliminate thermal degradation. With atmospheric reclaiming, the amount of alkali addition can be minimized with operation of the CO_2 capture system for over-stripping in the regenerator. For piperazine, the atmospheric reclaimer could be operated at 140-150 °C to minimize thermal degradation. However, due to the overhead vapor precipitation issues with piperazine, a direct contact condenser will need to be used, which will complicate the design and operation of the reclaimer (Figure 8-1). Unfortunately, nitrosamine decomposition may not occur with the lower operating temperatures, but could be addressed by operating the reclaimer at 150 °C with a longer residence time.

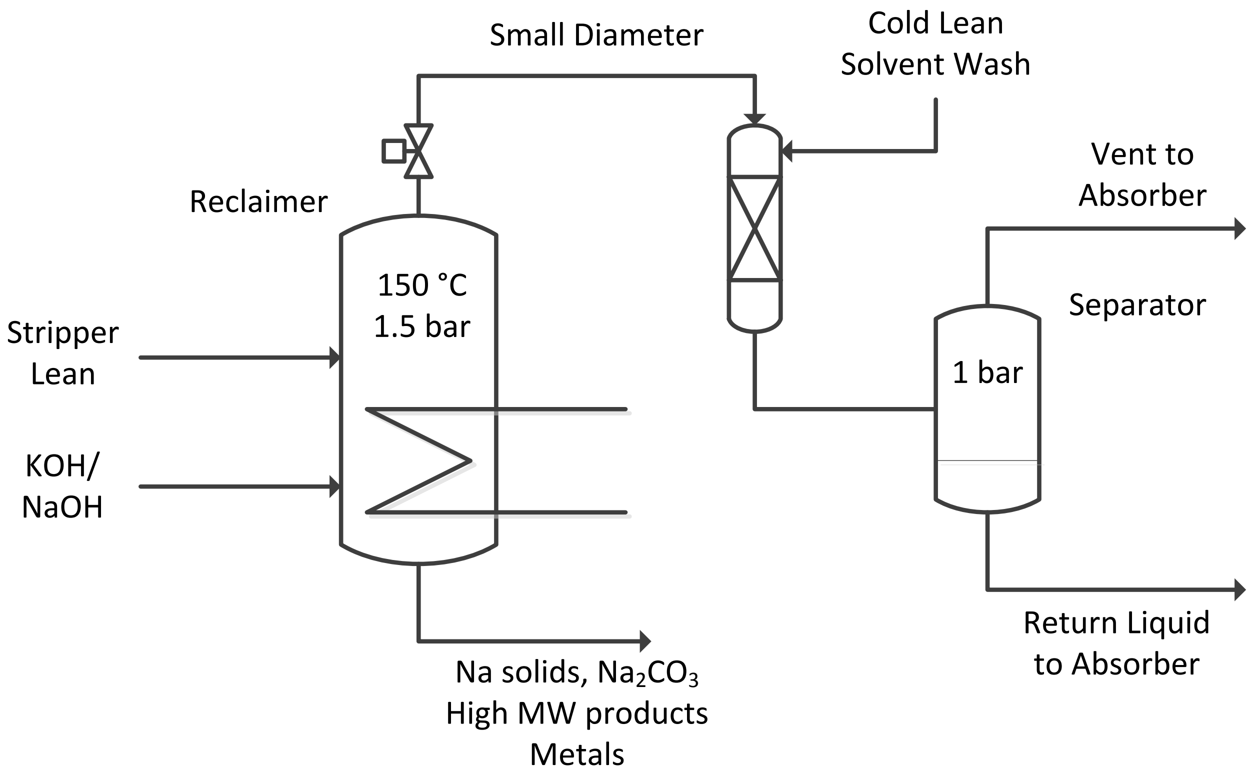


Figure 8-1 Atmospheric Reclaimer Design with Direct Contact Condenser for Piperazine Vapor

7. Address selectivity of ion exchange resins and electrodialysis membranes to remove transition metals along with heat stable salt anions

Wastewater treating
The quantity and quality of waste water produced from electrodialysis should be improved. Some impurities such as selenium anions may make the waste water unacceptable for discharge if there is any finite selenium removal from ion exchange or electrodialysis reclaiming systems.

Membrane and resin life
Membranes and ion exchange resin should be tested in the presence of representative transition metals, polyamine, and other real impurities that may bind irreversibly to the polymer. Non-steady state operations within the power and capture plants may result in the greatest stress on the reclaiming systems.

8. Minimize and quantify the frequency of process to define the true cost of reclaiming

The accumulation of impurities may be a strong function of upset operation. As pilot plants and commercial systems accumulate operating experience it will be important to carefully document upset frequency, intensity, and consequences. For example, the accumulation of sulfate will be strongly correlated with upsets of the FGD system and the SO_2 polishing system. Upset of the SCR will result in accumulation of nitrate, nitrosamine, and amine oxidation products resulting from NO_2 reactions.

Pre-scrubbing the flue gas to remove additional SO_X and NO_X would prove to be beneficial if the rate of incursion of HSS was controlled by flue gas contaminants versus oxidation/thermal degradation; an economic tradeoff of prescrubbing costs versus reclaimer savings would have to be performed.

Corrosion events will determine concentrations of the metals, Fe^{+2} and Mn^{+2} that catalyze oxidation. These could be caused by loss of control of temperature, CO_2 loading and other variables in the absorption/stripping system.

9. **Evaluate the following aspects of waste characterization and disposal**

- On and off site incineration and off site handling
- Characterize unknown or non-characterized compounds
- Characterize other potential CO_2 capture solvents listed in Tables 4-2 and 4-5
- Develop a procedure for characterization of a solvent as hazardous or not
- Developing a separate HSE program on how to handle toxicity evaluation of different solvents
- Develop a communication protocol with authorities on waste handling
- Address environmental standards and approval procedures with demonstration projects

REFERENCES

1. Chen et al. "Pilot plant results with piperazine.” Oral presentation, *GHGT-11*. Kyoto, Japan. November 19-23, 2012.

Nomenclature

CRF = capital recovery factor
G = flue gas flow rate, kmol/s
i= discount rate, %
k_d = thermal degradation rate constant, s^{-1}
L = solvent flow rate, kg/s
$MNPZ_i$ = initial value of nitrosamine in the solvent, mmol/kg
$MNPZ_{ss}$ = steady-state concentration of nitrosamine in the solvent, mmol/kg
$MNPZ(t)$ = current value for nitrosamine in the solvent, mmol/kg
MT = metric ton
MW = molecular weight (g/gmol)
n = plant life, yr
$Q_{reboiler}$ = reboiler duty, kJ/mol
t = time, s
TRR = total revenue requirement, $
T_{source} = process temperature, K
τ_{sump} = solvent residence time in stripper sump, s
V_{sump} = solvent holdup volume, L
V_{total} = total solvent inventory, L
W_{eq} = equivalent work, kJ/mol
W_{pump} = pump work, kJ/mol
$W_{compressor}$ = compressor work, kJ/mol
$y_{NO2, flue}$ = concentration of NO_2 in the entering flue gas, ppmv

Appendix A: Literature Review Summary

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
1	Bacon, T.; Bedell, S.; Niswander, R.; Tsai, S.; Wolcott, R.; *New Developments in Non-Thermal Reclaiming of Amine*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1988.	Electrodialysis	N/A	MDEA	N/A	550 lbs/day (no information on total process amine amount)	N/A	$130,000 capital costs to recover 2 lbmol/day of MDEA; Operating costs of $0.28/lb MDEA (utility, chemical costs)
1	Bacon, T.; Bedell, S.; Niswander, R.; Tsai, S.; Wolcott, R.; *New Developments in Non-Thermal Reclaiming of Amine*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1988.	Ion exchange	N/A	MDEA	N/A	40 lbs/day (no information on total process amine amount).	No added degradation	Operating costs of $0.20 to $0.28/lb MDEA (utility, chemical costs); capital costs of $175,000 to $200,000
1	Bacon, T.; Bedell, S.; Niswander, R.; Tsai, S.; Wolcott, R.; *New Developments in Non-Thermal Reclaiming of Amine*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1988.	Thermal	N/A	DEA / MDEA	Samples from DEA/MDEA blend plants saw THEED from 4.4 - 9.1 wt%, Bis-HEP wt% from 0.2-1.8 wt% and Bis-HEP/THEED ratio of 0.03-0.05. G	General example of 95% amine recovery.	N/A	Operating costs of $1.25/lb MDEA for 95% recovery ($2.10/lb off-site)
2	Holub, P.; Critchfield, J.; Su, W.; *Amine Degradation Chemistry in CO_2 Service*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1988.	N/A	N/A	DEA	Samples from DEA only plant saw THEED from 1.7 - 9.6 wt%, Bis-HEP wt% from trace - 2.3 wt% and Bis-HEP/THEED ratio of 0-0.02. Graphs of rate of heat stable salt formation.	States that some degradation products are not removed	N/A	N/A
2	Holub, P.; Critchfield, J.; Su, W.; *Amine Degradation Chemistry in CO_2 Service*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1988.	N/A	N/A	DEA / MDEA	Samples from DEA/MDEA blend plants saw THEED from 4.4 - 9.1 wt%, Bis-HEP wt% from 0.2-1.8 wt% and Bis-HEP/THEED ratio of 0.03-0.05. raphs of rate of heat stable salt formation.	N/A	N/A	N/A
3	Simmons, C.; *Reclaiming Used Amine and Glycol Solution*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1991.	Thermal	Distillation produced under reduced pressure so that boiling temperatures are kept below 450 °F, preferably less than 400 °F	N/A	N/A	N/A	N/A	Imperative that some solvent remains in still bottom residue to ensure sufficient amount for salts to remained dissolved & not crystallize; otherwise crystals cause operational problems.
4	Millard, M.; Beasley T.; Contamination Consequences and Purification of Gas Treating Chemicals Using Vacuum Distillation, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1993.	Thermal	Vacuum distillation, T < 400 °F	N/A	Can remove up to 99% of various contaminants.	Up to 95% recovery	Claims no additional thermal degradation is an achievable goal	N/A
4	Millard, M.; Beasley T.; *Contamination Consequences and Purification of Gas Treating Chemicals Using Vacuum Distillation*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1993.	Thermal	Vacuum distillation, T < 400 °F	MDEA	Sodium - 10,900 ppm reduced to 10 ppm; heat stable salts 1.2 wt% reduced to 0.01 wt%; formate 1700 ppm reduced to 50 ppm for 15,000 gallons batch application.	N/A	N/A	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
5	Nielsen, R.; Lewis, K.; *Controlling Corrosion in Amine Treating Plant*, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, 1995.	N/A	N/A	N/A	Recommends be considered when heat stable salt content is greater than 10% of the active amine concentration.	N/A	N/A	N/A
6	Burns, D.; Gregory, R.; *The UCARSEP Process for On-Line Removal of Non-Regenerable Salts from Amine Units*, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma 1995.	Electrodialysis	T < 110 °F	N/A	Maximum recommended anion level is ~3000 ppm.	Up to 98% overall recovery, although limited to ionic contaminants; 1-2 wt% amine loss	N/A	40 lb NaOH/lbmol salt removed; 207-251 gal waste generated per lbmol salt removed; $60/day power costs ($0.05/kWh) from 200 kW generator
6	Burns, D.; Gregory, R.; *The UCARSEP Process for On-Line Removal of Non-Regenerable Salts from Amine Units*, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma 1995.	Electrodialysis	T < 110 °F	N/A	Heat Stable Salt - 2.38 wt% reduced to 1.06 wt%; Formate 2.9 wt% reduced to 0.39 wt%; Thiocyanate - 0.088 wt% reduced to < 0.006 wt; Acetate 0.15 wt% reduced to 0.098 wt%; Ash - 3.56 wt% reduced to 0.72 wt%	96.6% recovery	N/A	N/A
6	Burns, D.; Gregory, R.; *The UCARSEP Process for On-Line Removal of Non-Regenerable Salts from Amine Units*, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma 1995.	Electrodialysis	T < 110 °F	N/A	Heat Stable Salt - 1.85 wt% reduced to 1.04 wt%; Formate 5.3 wt% reduced to 1.5 wt%; Thiocyanate - 1.5 wt% reduced to 0.13 wt%; Acetate- 0.50 wt% reduced to 0.21 wt%; Ash 8.69 wt% reduced to 2.78 wt%	96.1 % recovery	N/A	N/A
6	Burns, D.; Gregory, R.; *The UCARSEP Process for On-Line Removal of Non-Regenerable Salts from Amine Units*, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma 1995.	Electrodialysis	T < 110 °F	DEA	Heat Stable Salt - 3.95 wt% reduced to 1.23 wt%; Formate 0.54 wt% reduced to 0.25 wt%; Thiocyanate - 1.57 wt% reduced to 0.18 wt%; Acetate - 0.43 wt% reduced to 0.24 wt%; Ash - 3.08 wt% reduced to 2.4 wt%	96.0% recovery	N/A	N/A
6	Burns, D.; Gregory, R.; *The UCARSEP Process for On-Line Removal of Non-Regenerable Salts from Amine Units*, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma 1995.	Electrodialysis	T < 110 °F	DEA	Heat Stable Salt - 1.3 wt% reduced to 0.4 wt%; Formate - 0.45 wt% reduced to 0.33 wt%; Thiocyanate - 1.42 wt% reduced to 0.39 wt%; Acetate - 0.54 wt% reduced to 0.39 wt%; Ash - N/A	98.2% recovery	N/A	N/A
6	Burns, D.; Gregory, R.; *The UCARSEP Process for On-Line Removal of Non-Regenerable Salts from Amine Units*, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma 1995.	Ion Exchange	N/A	N/A	N/A	Up to 99% overall recovery, although limited to ionic contaminants	N/A	240-720 lb NaOH/lbmol salt removed; 25 lbmol removed per 80 gpm feed

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
6	Burns, D.; Gregory, R.; *The UCARSEP Process for On-Line Removal of Non-Regenerable Salts from Amine Units*, Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma 1995.	Thermal	Vacuum distillation	N/A	N/A	85 - 95% recovery	N/A	40 lb NaOH/lbmol salt removed; 5-15% waste (of total inventory)
7	Meisen, A.; Abedinzadegan, M.; Abry, R.; Millard, M.; *Degraded Amine Solutions: Nature, Problems, and Distillative Reclamation,* Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma 1996.	Thermal	Vacuum	Sulfinol D	Chloride - 14500 ppmw reduced to 1000 ppmw	N/A	N/A	Process requires gas-fired heater, cross exchanger, inlet separator, vapor scrubber, overhead accumulator, vacuum pump, reflux condenser, cooler and carbon filter
7	Meisen, A.; Abedinzadegan, M.; Abry, R.; Millard, M.; *Degraded Amine Solutions: Nature, Problems, and Distillative Reclamation,* Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma 1996.	Thermal	Vacuum	MDEA	Heat stable salts - 7.6 wt% reduced to 0.2 wt%; Ash - 4.2 wt% to 0.4 wt%	N/A	N/A	N/A
7	Meisen, A.; Abedinzadegan, M.; Abry, R.; Millard, M.; *Degraded Amine Solutions: Nature, Problems, and Distillative Reclamation,* Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma 1996.	Thermal	Vacuum	DEA	Heat stable salts - 3.25 wt% reduced to 0.6 wt%	N/A	N/A	N/A
7	Meisen, A.; Abedinzadegan, M.; Abry, R.; Millard, M.; *Degraded Amine Solutions: Nature, Problems, and Distillative Reclamation,* Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma 1996.	Thermal	Vacuum	DIPA	HPM-OX 4 wt% reduced to 1 wt%	N/A	N/A	N/A
8	Smith, W.; *Good Operating Practices for Amine Treating Systems*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1996.	N/A	N/A	MEA. DEA, DGA	N/A	N/A	N/A	0.03 lb NaOH per 12 gallons
9	Grinsven, P.; Heeringen, E.; Dillon, M.; *DIPA as the Preferred Solvent for Amine Treatment in Refinery Applications*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma 1999.	Thermal	N/A	Sulfinol-M	N/A	Up to 95% recovery	N/A	N/A
10	Barnes, D.; *Reduction of Heat Stable Salt Formation in a Monoethanolamine (MEA)* CO_2 *Removal System*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1999.	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
11	Drake, M.; *New Unit Provides Latest Technology for Amine Reclaiming with Vacuum Distillation,* Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma 2000.	Thermal	N/A	DEA	Heat stable salts - 3.5 wt% reduced to 0.04 wt%; DEA-F 4.2 wt% reduced to 0.33 wt%; Dimer/Polymers - 8.6 wt%, reduced to .24 wt%	95% recovery	N/A	Utilities - CW, Hot Oil; Unit Operations - Vacuum Reclaimer, Distillation Column, Solvent Polishing Unit, Vapor Recovery Vessel, Waste Vessel
12	Jouravleva, D.; Peter, D.; Sheedy, M.; *Impact of Continuous Removal of Heat Stable Salts on Amine Plant Operation* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2000.	Thermal	N/A	MEA	Heat stable salt - 3.5 wt% to 0.4 wt% as MDEA	N/A	N/A	Skid-mounted AmiPur unit (60"x60"x86") can reclaim 100-150 lb/day HSS
13	Barker, R.; Kehl, T.; *Overcoming Operating Challenges at AEC Oil & Gas Sexsmith with Sulfinol D* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2001.	Thermal	N/A	MDEA	Inlet solvent degradation level 17wt%, "significant amount" of solvent degradation components remained after reclaiming. Subsequent reclaiming effort a few years later achieved a 1.5 wt% ending residual content. No explanation for difference.	"Large" solvent loss during first reclaiming. During the next reclaiming a few years later, the waste tank was rerun to minimize solvent losses.	N/A	N/A
14	Corsi, C.; Santa Fe, P.; *Considerations for Design - Operation of a Reclaimer* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2002.	Thermal	338 - 356°F, 27.5 psia	DGA	1600 ppm chloride, reduced to 10 ppm in the amine system	Lab experiment testing amount of amine recovered vs. reclaimer temperature. Showed importance of operating at highest possible temperature below the point of degradation.	N/A	Horizontal kettle type heat exchanger; 9 to 30 gpm amine treated; max 5.15 MMBtu/hr heat input (180 C reclaiming, treat 17 gpm amine)
15	Smit, C.; Heeringen, G.; Grinsven, P.; *Degradation of Amine Solvents and the Relation with Operational Problems* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2002.	Thermal	N/A	MDEA	5-6 wt% degradation products reduced to 0.5 - 1.1 wt%.	N/A	N/A	N/A
16	Alvis, S.; Jenkins, J.; *Contaminant Reporting in Amine Gas Treating Service* , Proceedings of Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2004.	Thermal	N/A	MEA	Strong acid anions - 6.28 wt%, strong cations - 0.01 wt%, bound amine - 7.36 wt%, formamides - 4.95 wt%, HEEU 8.19 wt%, non-ionic - 20.37%	N/A	N/A	N/A
16	Alvis, S.; Jenkins, J.; *Contaminant Reporting in Amine Gas Treating Service* , Proceedings of Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2004.	Thermal	N/A	MDEA	Bicine - 2700 ppm reduced to 48 ppm	N/A	N/A	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
16	Alvis, S.; Jenkins, J.; *Contaminant Reporting in Amine Gas Treating Service* , Proceedings of Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2004.	Thermal	N/A	DEA	THEED - 1.9 wt% reduced to "nd"	N/A	N/A	N/A
17	Wagner, R.; Judd, B.; *Fundamentals - Gas Sweetening* , Proceedings of Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2006.	Electrodialysis	N/A	N/A	Works best in systems with a high level of HSS contamination	Brine effluent stream typically contains some amine	N/A	N/A
18	Daughton, D.; Veroba, B.; Diglycolamine Solvent Quality Improvement with Thermal Reclaiming, Proceedings of Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2007.	Thermal	T = 355-360°F	DGA	Degradation product - 10-22 wt% with merchant reclaiming, reduced to 3 wt% with continuous reclaimer. Solids - up to 200 mg/l with merchant reclaiming, average of 50 mg/l. No operating problems with BHEEU levels of 25 wt%. HSS removal of 50% typical with merchant reclaiming.	N/A	N/A	Merchant reclaiming 2 times/yr, costing $1.8 - 2.5 million DCN per year (2000), lasting 30-40 days. Costs include mobilization of units, natural gas for fired heater, caustic, tanks for waste material, caustic, hoarding & heating equipment, contractor labor, electrical utilities, permitting costs, supervision, etc. Switched to continuous unit: capital costs C$8 million, operating costs $450,000 to 550,000 CDN per year with amine design flow rate at initial installation 50 gpm. Supplemental water requirement ranges from 40-62 gpm; amine flow of 15-25 gpm once target BHEEU levels achieved. Design 400°F steam flowrate of 50,000 lb/hr or 41 MMBtu/hr, normaloperation averaged 10,000 lb/hr. of steam. Recommend reclaimer vessel L/D of 2 to minimize liquid carry over.
19	Hakim, N.; Benmoulay, A.; Oehlschlaeger, F.; *Qatargas DIPA Losses Minimization Approach* , Proceedings of Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2007.	Thermal	225°C, 180°C recommended	DIPA	Principle degradation product oxazolidone - 6-7 wt% in case study. Recommends degradation compounds kept below 10 wt%.	N/A	States that at 180°C a certain thermal degradation cannot be avoided and has to be accepted	Steam rate: 900-1,200 kg/hr (25 bar, 225 C) - can use to calculate energy requirement
20	Cummings, A.; Smith, G.; *Advances in Amine Reclaiming - Why There's No Excuse to Operate a Dirty System* , Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2007.	Electrolysis	N/A	N/A	Some positive results in removing bicine, but amino acid removal is still being developed. Removes formate, which pushes equilibrium to form amine + formate. Not effect with oxazolidones or diamines and ureas.	N/A	N/A	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
20	Cummings, A.; Smith, G.; *Advances in Amine Reclaiming - Why There's No Excuse to Operate a Dirty System* , Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2007.	Ion exchange	N/A	N/A	MPR's HSSH ion exchange process has had success for bicine removal, especially at low level bicine impurities. Other ion exchange providers have had difficulty in removing bicine. Selective can remove formate and no formamide (which can be converted back to amine). Not effect with oxazolidones, or diamines and ureas.	Amine levels in waste increase the lower the target HSS concentration - trade-off between anion removal and amine loss	N/A	1 mol NaOH consumption per mol HSS; Water demand 20% of the demand 15 yrs ago
20	Cummings, A.; Smith, G.; *Advances in Amine Reclaiming - Why There's No Excuse to Operate a Dirty System* , Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2007.	N/A	N/A	N/A	Bicine - recommended to be kept as low as 250 ppm. 1000 to 4000 ppm seen. In collection of 1739 amine samples from 273 plants, 825 had more than 100 ppm bicine. Heat stable salts - recommend kept to 5000 ppm or less. Amides - Formamides present from less than 1 wt% to 15wt% and higher. Formammide to formate ratio highest in DIPA (2:1), around 1:1 in DEA. Oxazolidones - most common in DIPA and Sulfinol-D systems, not as problematic in DEA and MEA. Diamines and ureas are also present (does not give concentration.)	N/A	N/A	N/A
20	Cummings, A.; Smith, G.; *Advances in Amine Reclaiming - Why There's No Excuse to Operate a Dirty System* , Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2007.	Thermal	N/A	MEA, DGA	Has been suggested that distillation can remove amino acids, but no identifiable instances in the literature supporting this. Amides can increase which traps good amine in the reclaimer bottoms. Should be able to recover amine from amides, but takes operating skill. Can separate oxazolidones, but wastes the amine molecule contained. Can successfully remove diamines and ureas.	Thermal reclaiming sends the most amine to waste compared to ion exchange; examples give range of 3.4 - 5.6 mol amine loss/mol HSS, due to amines left in the bottoms & degradation.	States that the accumulation of heat stable salts in DGA leads to higher reclaiming temperatures and therefore more degrading of theamine. To bring the reclaimer back to correct operation, the contaminants must be purged which increases solvent waste. Suggests ion exchange for treatment of HSS.	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
21	Sargent, A.; Economic Evaluation Techniques Applied to Heat Stable Salt Management, Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2008.	N/A	N/A	N/A	Reclaiming necessary when HSS in 2-5 wt% range. Examples of HSS buildup - 0.6 wt%/mo, 1.3 wt%/mo (coker off gas treatment), 0.06 wt%/mo (refinery hydrogen recycle stream), 0.25 wt%/mo (refinery)	N/A	N/A	Used NPV analysis without actually providing detailed cost information
22	Richards, R.; Sweatt, G,; Ralph, W.; White, L.; *New Design for High Pressure Reclamation of DGA Agent Solutions* , Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 2010.	Thermal	350-360°F, stripper pressure (traditional DGA reclaiming); 360°F, 130 psig (proposed high pressure application)	DGA	Recommends urea/BHEEU concentration < 5 wt%, some plants operate with concentration as high as 20 wt%. Examples of accumulation rates of 0.01 wt%/d to 0.042 wt%/d. Example of 20 wt% BHEEU dropped to & maintained at 1.7wt% with installation of new reclaimer.	Calculates a 97.4% minimum BHEUU conversion in a conventional reclaimer	N/A	Traditional unit operates below boiling point of DGA; product carried overhead by stripping with water vapor. Typically semi-batch - once reclaimer is full of heavy materials a boil-out procedure is used to maximize recovery. Residence time is 1 hour or more. Heat requirement is about 250 kW per gpm of feed. Typical refinery cycle time is 3-9 months. Example of merchant reclaiming costs of $100,000/yr (1994 1998, 3 times total). On site reclamation took about a month. Describes higher pressure design which is continuous and requires around 20 kW per gpm of heat.
23	Street, D.; *Alkanolamines: Operational Issues and Design Consideration* , Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 1995.	Electrodialysis	N/A	N/A	N/A	Works best with high level of HSS contamination. Brine effluent stream typically contains some amine.	N/A	N/A
23	Street, D.; *Alkanolamines: Operational Issues and Design Consideration* , Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 1995.	N/A	N/A	N/A	HSS should e limited to 1-2 wt%(as wt% amine)	N/A	N/A	N/A
23	Street, D.; *Alkanolamines: Operational Issues and Design Consideration*, Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 1995.	Thermal	355 - 360°F	DGA	Major degradation products are BHEEU and BHEETU, which should be maintained at less than 3- 5 wt%.	N/A	N/A	N/A
24	Stern, L.; *Amine Reclaiming*, Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 1996.	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
25	Davy, P.; Jouravleva, D.; *Amipur - Heat Stable Salts Removal System* , Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 1999.	Ion exchange	N/A	MDEA	HSS reduced from 2.4 to 1.5 wt% over the course of 4 months. Anions include formate, thiocyanate, acetate, thiosulfate, and sulfate.	Processes 0.4 gpm of amine	N/A	N/A
26	Jenkins, J.; Daniels, C.; *Use of Reclamation for Amine Hygiene Management*, Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 2010.	Thermal	Vacuum	N/A	Contaminants include HSS, DEAF, THEED, and oxidative degradation products. Residue decreased by about 60% for 2 cases.	N/A	N/A	N/A
27	Scott, B.; *Brimstone Sulfur Recovery Symposium*, Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 1997.	N/A	N/A	N/A	Rule of thumb maximum of 10 wt% HSS as amine	N/A	N/A	DEA: $0.70/gallon reclaimed; MEA: $0.50/gal, MDEA: $2.75/gal (distillation reclaiming)
28	Haws, R.; Jenkins, J.; *Contaminants in Amine Gas Treating Service* , Brimstone Engineering Sulfur Recovery Symposium, Vail, Colorado, 2000.	N/A	N/A	N/A	N/A	N/A	N/A	N/A
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	Electrodialysis	N/A	N/A	Does not remove nonionic species. Best for moderate to high salt concentrations.	98% recovery, limited to ionizable degradation products. Typically a 5 - 15 gpm slipstream. Claimed that a mobile unit can remove over 3000 lb/day of HSS.	N/A	Stream must be cool, lean, and hydrocarbon and particulate free. Heat stable salts must be neutralized.
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	Ion exchange	N/A	N/A	Does not remove nonionic species. Best for low salt concentrations.	99% recovery, limited to ionizable degradation products	N/A	Stream must be cool, lean, and hydrocarbon and particulate free.
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	Thermal	10-20 psig	MEA	N/A	85-95% recovery. Recommends slip stream of 0.5 - 2% of main flow.	High still temperatures lead to amine degradation.	N/A
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	Thermal	5 psig, kettle temperature of 360-380°F	DGA	BHEEU major degradation product - should be kept to less than 5% of total solution	85-95% recovery. Recommends slip stream of 1 - 2% of main flow.	High still temperatures lead to amine degradation.	300 psig steam typical
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	Thermal	vacuum, recommend T < 400°F. Typical 50 - 100 mmHg abs @ 350°F	DEA	N/A	85-95% recovery	High still temperatures lead to amine degradation.	N/A
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	Thermal	vacuum, recommend T < 400°F. Typical 50 - 100 mmHg abs @ 350°F	DIPA	N/A	85-95% recovery	High still temperatures lead to amine degradation.	N/A
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	Thermal	vacuum, recommend T < 400°F. Typical 50 - 100 mmHg abs @ 350°F	MDEA	N/A	85-95% recovery	High still temperatures lead to amine degradation.	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	Thermal	N/A	N/A	Removal of all solids and nonvolatile species	85-95% recovery. Amine remaining in discharged bottoms is unavoidable.	N/A	Energy intensive; need fuel gas or high temp heat source. Heat stable salts must be neutralized.
29	Kohl, A.; Nielsen, R. *Gas Purification,* 5th ed.; Gulf Publishing Co.: Houston, 1997.	N/A	N/A	N/A	Recommends amine decomposition products not be allowed to exceed 10%.	N/A	N/A	N/A
30	Maddox, R.; Morgan, D. *Gas Conditioning and Processing* Vol. 4, 4th ed; Campbell Petroleum Series: Norman, 1998.	Thermal	N/A	N/A	N/A	Slipstream typically 3% or less of circulation rate	N/A	Typical cycle is 28 days. There should be sufficient space under the tubes in the kettle. Packed column needed on the top of the reclaimer.
31	Bacon,T.; *Amine Solution Quality Control Through Design, Operation, and Correction* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1987	N/A	N/A	N/A	Maintain HSS concentration below 10% of amine concentration. Chlorides - 10-15 ppm can accelerate corrosion, but up to 1000 ppm can be acceptable.	N/A	N/A	N/A
32	Ballard, D.; *Techniques to Cut Energy/Corrosion/Chemical/ Costs in Amine Units* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1986	N/A	N/A	N/A	N/A	N/A	N/A	N/A
33	Pauley, C.; *CO_2 Recovery from Flue Gas; A Case Study* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1984.	Thermal	260-300°F	MEA	Heat stable salts range from 0.01% solvent to 0.08% solvent (solvent design 18-20% MEA)	N/A	N/A	N/A
34	Kosseim, A.; Cullough, J.; Coarsey, C.; *Amine Guard ST A New Energy-Efficient System* , Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1984.	N/A	N/A	N/A	N/A	N/A	N/A	N/A
35	Arnold, D.; Barrett, D; Isom, R.; *CO_2 Production from Coal Fired Boiler Flue Gas by MEA Process* ; Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, *1982.*	Thermal	N/A	MEA	Analysis for reclaimer sample 1: pH - 11; potassium - 0.001%; sodium - 0.7%; chloride - 0.04%; sulfate - 4.8%; sulfite - 80 ppm; CO_2 - 1.7%; NH_3 - 1700 ppm; nitrate - 5300 ppm; nitrite - <1 ppm; MEA - 46%; Insols - 0.02%. Analysis for reclaimer sample 2: pH - 10; potassium - 0.009%; sodium - 2.0%; chloride - 0.2%; sulfate - 4.8%; sulfite - 140 ppm; CO2 - 1.0%; NH3 - 1100 ppm; nitrate - 7000 ppm; nitrite - <1 ppm; MEA - 33%; Insols - 0.08%.	N/A	N/A	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
36	Huval, M.; Van de Venne, H.; Gas Sweetening in Saudi Arabia in Large DGA Plants, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1981.	Thermal	360 - 380°F. Issues when top temperature ~ 310°F.	DGA	BHEEU content kept to 2%.	0.5 to 2% amine slipstream. Before dumping kettle, DGA is first vaporized to minimize reclaimer losses. Minimum amount lost in dumping is 10%.	N/A	375 psig steam used in reclaimer. Includes schematic of reclaimer kettle.
37	Hall, W.; Barron, J; *Solving Gas Treating Problems - A Different Approach* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1981.	Ion Exchange	DEA	N/A	N/A	N/A	N/A	N/A
38	Butwell, K.; Kubek, D.; Sigmund, P.; Primary *Versus Secondary Amines - Characteristics in Gas Conditioning* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1979.	Thermal	370-380°F	DGA	N/A	Up to 90% BHEEU conversion	N/A	N/A
38	Butwell, K.; Kubek, D.; Sigmund, P.; *Primary Versus Secondary Amines - Characteristics in Gas Conditioning, Proceedings of the Laurance Reid Gas Conditioning Conference*, Oklahoma City, Oklahoma, 1979.	Thermal	Vacuum	DIPA	Oxazolidone concentration up to 20%; levels may be 5-10% even with reclaiming	Losses of 1-2 lbs amine/MMSCF typical for natural gas & synthesis gas industries	N/A	N/A
38	Butwell, K.; Kubek, D.; Sigmund, P.; *Primary Versus Secondary Amines - Characteristics in Gas Conditioning, Proceedings of the Laurance Reid Gas Conditioning Conference*, Oklahoma City, Oklahoma, 1979.	Thermal	290-300°F	MEA	N/A	0.5 - 2.0% slip stream. Losses of 1-2 lbs amine/MMSCF typical for natural gas & synthesis gas industries	N/A	150 psig steam typical; small quantities of base added
38	Butwell, K.; Kubek, D.; Sigmund, P.; *Primary Versus Secondary Amines - Characteristics in Gas Conditioning, Proceedings of the Laurance Reid Gas Conditioning Conference*, Oklahoma City, Oklahoma, 1979.	Thermal	370-380°F with steam sparge	DGA	N/A	Losses of 1-2 lbs amine/MMSCF typical for natural gas & synthesis gas industries	N/A	375 psig steam typical; small quantities of base added
38	Butwell, K.; Kubek, D.; Sigmund, P.; *Primary Versus Secondary Amines - Characteristics in Gas Conditioning, Proceedings of the Laurance Reid Gas Conditioning Conference*, Oklahoma City, Oklahoma, 1979.	Thermal	50 -100 mmHg, 350°F	DEA	N/A	N/A	N/A	14-trayed distillation column
39	Jones, V.; *Fundamentals of Gas Treating Manual for Design of Gas Treaters* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1978.	N/A	N/A	DEA	N/A	N/A	N/A	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
40	Heisler, L.; Weiss, H.; *Operating Experience at Aderklaa with Alkanolamine Gas Treating Plants for Sour Natural Gas Sweetening* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1975.	Thermal	N/A	DEA	N/A	2% slipstream	N/A	N/A
41	Butwell, K.; Perry, C.; *Performance of Gas Purification Systems Utilizing DEA Solutions* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1975.	N/A	N/A	DEA	N/A	N/A	N/A	N/A
42	Scheirnam, W.; Pritchard, J.; *Diethanolamine Solution Filtering and Reclaiming in Gas Treating Plants* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1973.	N/A	N/A	DEA	N/A	N/A	N/A	Add 50% more sodium carbonate than the theoretical requirement; add when HSS exceed 0.5 wt%. Discusses use of precoat and carbon filters
43	Newton, P.; *Operating Experience with the Sulfinol Process* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1971.	Thermal	0-5 psig	Sulfinol -D	Maintain 2-4% degradation products. Slipstream is 30-50 gph for ~100 MMCF (@915 psig) unit.	N/A	N/A	Kettle type reboiler with packed column & condenser. Uses 150 psigsteam.
44	Perry, C.; *Basic Design and Cost Data on MEA Treating Units* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1967.	Thermal	285-300°F	MEA	3% slipstream recommended.	N/A	N/A	Kettle type reboiler with mist extractor. Recommend adding make-up water to the reclaimer reboiler, and soda ash to increase salt removal. $3950 equipment & delivery cost for reclaimer for 40 gpm amine unite (1967).
45	Dingman, J.; Allen, D.; Moore, T.; *Minimize Corrosion in MEA Sweetening Units* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1966.	Thermal	N/A	MEA	1-2% slipstream recommended.	N/A	N/A	Recommend the addition of a stoichiometric amount of alkali. Reboilers should use wide tube spacing, also leaving space at the bottom of the kettle. Steam sparger typical built into kettle. Stainless steel tubes often used, although carbon steel can be used if acids are neutralized properly.
46	Blake, R.; Rothert, K.; *Reclaiming Monoethanolamine Solutions* , Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma, City, Oklahoma, 1966.	Thermal	0 psig or regeneration column pressure. T < 300°F.	MEA	1-3% slipstream or turn over all solution is 3-7 days. "Typical" analysis: MEA - 14 wt% increased to 15 wt%; degradation products - 8 wt% reduced to 0.1 wt%; Heat stable salts - 0.2 wt% reduced to 0.1 wt%; inorganic residue (ash) - 3.0 wt% reduced to nil.	N/A	N/A	Equipment includes: kettle type reboiler, vapor line, liquid knockout drum, high pressure steam, soda ash, steam spargers. Shell usually CS, tubes SS. Need sufficient level under the tubes in reboiler. Gives procedure for analytical analysis to determine amount of soda ash - no harm in adding too much, but it will raise the boiling temperature and increase viscosity.

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
47	Beck, J.; *Operational Problems in CO2 Removal at the Mitchell Plant*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1960.	Thermal	N/A	MEA	N/A	N/A	N/A	Initially added 1 lb of soda ash per day to each 40 gpm of amine. This was adjusted to maintain 0.15 wt% soda ash. This resulted in soda ash accumulating in reclaimers; dropped concentration to 0.03 wt% which was sufficient. Discuss importance of sufficient space under tube bundles.
48	Wonder, D.; Blake, R.; Fager, J.; Tierney, J.; *An Approach to Monoethanolamine Solution Control: Chemical Analysis and Its Interpretatio*, Proceedings of the Laurance Reid Gas Conditioning Conference, Oklahoma City, Oklahoma, 1959.	Thermal	256-300°F, 5 psig	MEA	1 - 3% slipstream	N/A	N/A	Cycle length dependent on contamination level; cycles become longer as contamination levels decrease. Suggests use of liquid knockout drum.
49	Dumee, L.; Scholes, C.; Stevens, G.; Kentish, S. Purification of aqueous amine solvents used in post combustion CO_2 capture: A review. *International Journal of Greenhouse Gas Control, 10,* 443-455, 2012.	Thermal	N/A	N/A	Max Compositions (ppm): Oxalate-250, Sulfate-500, Formate-500, Sulfite-500, Chloride-500, Glycolate-500, Malonate-500, HEEDA-500, Acetate-1000, Succinate-100, Formamide-3000, Thiosulfate-10000, Thiocyanate-10000	>85%	4-31 kg waste generated/ton CO2 (5 to 15% of initial inventory)	Cost and energy intensive process, but generates concentrated waste stream
50	Dumee, L.; Scholes, C.; Stevens, G.; Kentish, S. Purification of aqueous amine solvents used in post combustion CO_2 capture: A review. *International Journal of Greenhouse Gas Control, 10,* 443-455, 2012.	Ion Exchange	<45°C	N/A	Max Compositions (ppm): Oxalate-250, Sulfate-500, Formate-500, Sulfite-500, Chloride-500, Glycolate-500, Malonate-500, HEEDA-500, Acetate-1000, Succinate-100, Formamide-3000, Thiosulfate-10000, Thiocyanate-10000	99%	Ion exchange resins susceptible to fouling from iron, high temperatures; 40-50% of inventory leaves as waste	1500 kg of acid and 500 kg of NaOH per cubic meter of resin (using 15 wt% acid, 10 wt% NaOH); 1 mol NaOH per mol of HSS; Cannot remove non-ionic contaminants, and generate large quantities of waste (ideal only if HSS concentration is low)
51	Dumee, L.; Scholes, C.; Stevens, G.; Kentish, S. Purification of aqueous amine solvents used in post combustion CO_2 capture: A review. *International Journal of Greenhouse Gas Control, 10,* 443-455, 2012.	Electrodialysis	40°C	N/A	Max Compositions (ppm): Oxalate-250, Sulfate-500, Formate-500, Sulfite-500, Chloride-500, Glycolate-500, Malonate-500, HEEDA-500, Acetate-1000, Succinate-100, Formamide-3000, Thiosulfate-10000, Thiocyanate-10000	98%	Membranes have lifetime of 10-15 years in pH range of 2-9; lifetime decreases at higher pH	Has higher power consumption than ion exchange and generates more waste than distillation, but has lower chemical/water usage than ion exchange; Membranes are potential cost barrier
52	Dumee, L.; Scholes, C.; Stevens, G.; Kentish, S. Purification of aqueous amine solvents used in post combustion CO_2 capture: A review. *International Journal of Greenhouse Gas Control, 10,* 443-455, 2012.	Neutralization	N/A	N/A	Max Compositions (ppm): Oxalate-250, Sulfate-500, Formate-500, Sulfite-500, Chloride-500, Glycolate-500, Malonate-500, HEEDA-500, Acetate-1000, Succinate-100, Formamide-3000, Thiosulfate-10000, Thiocyanate-10000	N/A	N/A	0.03-0.13 kg NaOH/ton CO2 required for neutralization; 0.03-0.06 kg activated carbon/ton CO2 required for filtration

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
53	Smith, G.D.; Tooley, N.; Cummings, A.L. Making Amine Systems Sing, GPA Europe Sour Gas Processing Symposium, Barcelona, Spain, May 13-15, 2009.	Distillation	N/A	N/A	Max 5000 ppm of HSS, 250 ppm bicine; formamide observed in concentrations from 1 wt% to 15 wt%	85-95%	Amide formation can actually increase during thermal reclaiming, but thermal reclaiming is most successful for diamines and ureas	Total annual benefit for four refineries ranged from $1 to $30 million dollars.
54	Smith, G.D.; Tooley, N.; Cummings, A.L. Making Amine Systems Sing, GPA Europe Sour Gas Processing Symposium, Barcelona, Spain, May 13-15, 2009.	Electrodialysis	N/A	N/A	Max 5000 ppm of HSS, 250 ppm bicine; formamide observed in concentrations from 1 wt% to 15 wt%	98%	Membrane fouling is a major cause of downtime and membrane expense	One micron pre-filter recommended for solids removal
55	Smith, G.D.; Tooley, N.; Cummings, A.L. Making Amine Systems Sing, GPA Europe Sour Gas Processing Symposium, Barcelona, Spain, May 13-15, 2009.	Ion Exchange	N/A	N/A	Max 5000 ppm of HSS, 250 ppm bicine; formamide observed in concentrations from 1 wt% to 15 wt%	>99%	N/A	Best for low salt concentrations
56	Abdi, M.A.; Golkar, M.M. Improve Contaminant Control in Amine Systems. *Hydrocarbon rocessing, 80(10)* , 102, 2001.	Thermal	N/A	DEA	THEED - 4.2 wt%, BHEP - 2.9 wt%, HSS - 2.2 wt%, Other Contaminants - 3.3 wt%	80-90%	N/A	Single-stage distillation
57	Price, J.; Burns, D. Clean amine solvents economical and online. *Hydrocarbon Processing, 74(8)* 140-141, 1995.	Electrodialysis	105°F amine feed	MDEA	HSS - 2.4 wt% reduced to 1.1 wt%	N/A	Yields waste stream that is 5 wt% salt solution (generated 8.7 gallons of brine per gallon of reclaimed amine)	N/A
58	Thomason, J. Reclaim gas treating solvent. *Hydrocarbon Processing, 64(4),* 75-78, 1985.	Thermal	280°F	DEA	N/A	40-75%	N/A	Used 65 psig steam for distillation, passed CO2 over liquid level in shell and tube HX to absorb water/solvent into the CO2
59	Verma, N.; Verma, A. Amine system problems arising from heat stable salts and solutions to improve system performance. *Fuel Processing Technology, 90(4),* 483-489, 2009.	Thermal	150°C	MDEA	HSS - reduced from 5 wt% to 2 wt%	N/A	N/A	N/A
60	Verma, N.; Verma, A. Amine system problems arising from heat stable salts and solutions to improve system performance. *Fuel Processing Technology, 90(4),* 483-489, 2009.	Ion Exchange	N/A	MDEA	Reduced HSS to 0.5 wt%	N/A	N/A	N/A
61	Chapel, D.G.; Mariz, C.L. Recovery of CO_2 Flue Gases: Commercial Trends, Canadian Society of Chemical Engineers Annual Meeting, Saskatoon, Canada, October 4-6, 1999.	Thermal	N/A	Econamine	N/A	N/A	Water is added to the reclaimer to reduce operating temperature; Reclaimer Waste: 0.8 gallons per ton CO2	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
62	Strazisar, B.R.; Anderson, R.R.; White, C.M. Degradation Pathways for Monoethanolamine in a CO2 Capture Facility. Energy and Fuels, 17(4), 1034-1039, 2003.	Thermal	N/A	MEA	Identified 19 degradation products qualitatively; Quantifies 16 different ion concentrations; Notes that Hg was found at concentration of 1.0 ppb, and nitrosamines were not detectible in reclaimer	N/A	N/A	N/A
63	Rooney, P.C.; Bacon, T.R.; DuPart, M.S. Effect of heat stable salts on MDEA solution corrosivity, *Hydrocarbon Processing, 75,* 95-103, 1996.	Neutralization	N/A	MDEA	Max Concentrations (ppm): Oxalate-250, Sulfate-500, Formate-500, Acetate-1000, Thiosulfate-10000, HSS-0.5 wt%	N/A	N/A	Maximum injection of 6 gpm caustic per 100 gpm of amine to avoid corrosion issues
64	de Groot, M.T.; Bos, A.A.C.M.; Lazaro, A.P.; de Rooij, R.M.; Bargeman, G. Electrodialysis for the concentration of ethanolamine salts, *Journal of Membrane Science, 371(1),* 75-83, 2011.	Electrodialysis	N/A	MEA	N/A	N/A	N/A	Power Consumption for applying direct current: 0.35 kWh/kg MEA; Adding pumping efficiency doubles this number
65	Dandekar, S.; Shao, J. Continuous removal of contaminants from amine solutions. *Petroleum Technology Quarterly, 16(5),* 81-87, 2011.	Ion Exchange	N/A	MDEA	Reduced HSS concentration from 8.5 wt% to below 4 wt%	N/A	N/A	Designed for 21.8 gpm amine; Equipment includes resin bed, cartridge filters, caustic reservoir (Eco-Tec AmiPur unit)
66	Shao, J.; Vaz, L. Effectiveness of Continuous Removal of Heat Stable Salts from Contaminated Amine Scrubbing Solutions. *Chemical Industry Digest, 20(11),* 53, 2007.	Ion Exchange	N/A	MDEA	Reduced HSS concentration from 3.5 wt% to less than 0.5 wt% (refinery application #1); Reduced HSS from 3.8 wt% to 1.0 wt% (refinery application #2)	N/A	N/A	Each regeneration cycle lasts approximately 15 minutes; dilute caustic soda used to regenerate resin column
67	Kentish, S.E.; Stevens, G.W. Innovations in separations technology for the recycling and re-use of liquid waste streams. Chemical Engineering Journal, 84(2), 149-159, 2001.	Ion exchange	N/A	N/A	N/A	N/A	N/A	N/A
68	Abdi, M.A.; Meisen, A. A Novel Process for Diethanolamine Recovery from Partially Degraded Solutions. 1. Process Description and Phase Equilibrium of the DEA-BHEP-THEED-Hexadecane System. Industrial and Engineering Chemistry Research, 38(8), 3096-3104, 1999.	Thermal	N/A	DEA	N/A	N/A	N/A	N/A
69	Abdi, M.A.; Meisen, A. A Novel Process for Diethanolamine Recovery from Partially Degraded Solutions. 2. Process Analysis. Industrial and Engineering Chemistry Research, 38(8), 3105-3114, 1999.	Thermal	151 to 185°C, 1.1 to 6.7 kPa	DEA	N/A	N/A	N/A	Tested concept in 50-mm ID column, with packed height of 250-mm.
70	Mezher, T.; Fath, H.; Abbas, Z.; Khaled, A. Techno-economic assessment and environmental impacts of desalination technologies. Desalination, 266(1), 263-273, 2011.	Electrodialysis	N/A	N/A	N/A	N/A	Waste concentrate concentration: 140-600 mg/L of total dissolved solids.	Quotes 17 kWh/m3 for desalination electrodialysis of seawater, and 3-7 kWh/m3 for brackish water ($0.60/m3).

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
71	Vitse, F.; Baburao, B.; Dugas, R.; Czarnecki, L.; Schubert, C. Technology and Pilot Plant Results of the Advanced Amine Process. Energy Procedia, 4, 5527-5533, 2011.	N/A	N/A	UCARSOL	online reclaiming system kept HSS below 0.5 wt% during pilot plant testing	N/A	N/A	N/A
72	Schulte, D.; Graham, C.; Nielsen, D.; Almuhairi, A.H.; Kassamali, N. The Shah Gas Development (SGD) Project - A New Benchmark. 89th Annual Gas Processors Association Annual Convention, Austin, Texas, March 21-24, 2010.	Thermal	2% slipstream fed to thermal reclaimer, 182°C, Regenerator Pressure	DGA	Designed to keep BHEEU concentration below 5 wt%	N/A	N/A	N/A
73	Manning, W.; Misiong, G.; Norton, D. Troubleshooting Amine Plants. 85th Annual Gas Processors Association Annual Convention, Grapevine, Texas, March 5-8, 2006.	N/A	N/A	N/A	Chloride - keep below 250 ppm, Fe - 15 ppm limit, Hydrocarbons - 1000 ppm; Suggests caustic neutralization between 2-5 wt% HSS, and reclaiming before 10 wt% HSS	N/A	N/A	N/A
74	Parisi, P.; Bosen, S. Electrodialysis - Effective Amine Reclamation with Minimal Operational Impact. 85th Annual Gas Processors Association Annual Convention, Grapevine, Texas, March 5-8, 2006.	Electrodialysis	N/A	N/A	>90% reduction in heat stable salt concentrations	99.5%	N/A	N/A
75	Haws, R. Contaminants in Amine Gas Treating. 83rd Annual Gas Processors Association Annual Convention, San Antonio, Texas, March 14-17, 2004.	Thermal	N/A	N/A	Comprehensive tables provide comprehensive practical limits for contaminant concentrations for MEA, DGA, DEA and MDEA. MEA: HSS - 2.5 wt%, Formamide - 3.0 wt%, HEED - 0.5 wt%, HEEU - 1.0 wt%; DGA: HSS - 2.5 wt%, Formamides - 3.0 wt%, BHEEU - 6.0 wt%; DEA: HSS - 2.5 wt%, Formamides - 3.0 wt%, THEED - 1.5 wt%; MDEA: HSS - 2.5 wt%, Bicine - 0.4 wt%, Other - 2.5 wt%	N/A	N/A	N/A
76	Wang, M.; Lawal, A.; Stephenson, P.; Sidders, J.; Ramshaw, C.; Yeung, H. Post-combustion CO2 Capture with Chemical Absorption: A State of the Art Review. Chemical Engineering Research and Design, 89(9), 1609-1624, 2011.	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
77	Kameche, M.; Xu, F.; Innocent, C.; Pourcelly, G.; Derriche, Z. Characterisation of Nafion 117 membrane modified chemically with a conducting polymer: An application to the demineralisation of sodium iodide organic solutions. Separation and Purification Technology, 52(3), 497-503, 2007.	Electrodialysis	N/A	N/A	N/A	N/A	N/A	N/A
78	Xu, F.; Innocent, C.; Pourcelly, G. Electrodialysis with ion exchange membranes in organic media. Separation and Purification Technology, 43(1), 17-24, 2005.	Electrodialysis	N/A	N/A	N/A	N/A	N/A	N/A
79	American Water Works Association. Electrodialysis and Electrodialysis Reversal. 1995.	Electrodialysis	Requires 10 micron cartridge filtration pre-treatment; aeration (oxidation) and filtration required for Fe, H_2S, Cl.	N/A	N/A	N/A	N/A	Unit with 1 hp pumps for feed and concentrate can process up to 11,000 gpm wastewater per day (5 ft by 2.5 ft by 7 ft). Pumping pressure ranges from 50 to 75 psi to overcome DP losses. Energy consumption ranges from 3 to 18 kWh/1,000 gal depending upon feedwater quality.
80	Byszewski, C.H. "Process for the removal of heat stable salts." U.S. Patent 6,517,700, February 11, 2003.	Electrodialysis	Uses base neutralization upstream of electrodialysis unit.	N/A	N/A	80-99%	N/A	Electrodialysis unit will contain 10 to 500 repeat units (40 to 200 preferably). Holdup tanks required for feed process and base streams
81	Rooney, P.C. "Amine heat stable salt neutralization having reduced solids." U.S. Patent 5,912,387, June 15, 1999.	Thermal	Add neutralizing solution to free 75-80% of amine present in HSS.	N/A	N/A	N/A	N/A	N/A
82	Gregory, R.A.; Cohen, M.F. "Aqueous Alkanolamines using an Electrodialysis Cell with an Ion Exchange Membrane." U.S. Patent 5,910,611, June 8, 1999.	Electrodialysis	N/A	N/A	Reduce 10,000 gallon inventory from 10-15 wt% salt concentration by 60-90%.	N/A	N/A	Claims much lower energy requirements than traditional thermal distillation. Tank required for waste solution. Membrane selectivity ranges from 72-82%.
83	Coberly, S.H.; Laven, T.H.; Cummings, A.L. "Amine Heat Stable Salt Removal from Type II Anion Exchange Resin." U.S. Patent 5,788,864, August 4, 1998.	Ion Exchange	70-120°F	N/A	N/A	N/A	N/A	Beds are regenerated using water and then alkali metal hydroxide (5-12 wt%); 12 to 35 lb of NaOH equivalent per cubic foot of resin
84	Audeh, C.A.; Yan, T.Y. "Clean up of Ethanolamine Solution by Treating with Weak Ion Exchange Resins." U.S. Patent 5,292,493, March 8, 1994.	Ion Exchange	Treat 4-20% slipstream. Ammonium solution used to regenerate resin beds.	N/A	N/A	N/A	N/A	N/A
84	Cummings, A.L.; Veatch, F.C.; Keller, A.E.; Thompsen, J.C.; Severson, R.A. "Process for Monitoring and Controlling an Alkanolamine Reaction Process." U.S. Patent 5,162,084, November 10, 1992.	Ion Exchange	90-105°F using pre-cooler	N/A	N/A	N/A	85-100 lb of acid per cubic foot of resin required for regeneration.; 10-15 lb NaOH required for regeneration	N/A

Citation #	Citation	Reclaimer Type	Reclaimer Conditions	Solvent System	Reclaimer Inlet/Outlet Composition	Amine Recovery	Reclaimer Degradation	Equipment/Operating Information
84	Yan, T.Y. "Clean up of Ethanolamine to Improve Performance and Control Corrosion of Ethanolamine Units." U.S. Patent 4,795,565, January 3, 1989.	Ion Exchange	N/A	N/A	N/A	N/A	N/A	N/A
84	Pottiez, F.; Verbeest, R. "Process for the Regeneration of Alkanolamines by Distillation, Alkali Hydroxide Treatment, Heat, Phase Separation and Distillation." U.S. Patent 3,664,930, May 23, 1972.	Thermal	Residence time of 15 minutes at boiling temperature of system.	N/A	N/A	N/A	N/A	Use 15-25 wt% NaOH, depending upon oxazolidone concentration.
84	Taylor, F.C. "Refining Petroleum with an Alkanolamine Absorbent and Reactivation of the Spent Alkanol Amine." U.S. Patent 2,797,188, June 25, 1957.	Thermal	N/A	N/A	N/A	N/A	N/A	N/A
84	Butwell, K.F.; Kubek, D.J.; Sigmund, P.W. Alkanolamine Treating. Hydrocarbon Processing, 61(3), 1982.	Thermal	290-300°F, Atmospheric Pressure, 0.5 to 2.0% slipstream	MEA	N/A	N/A	N/A	Use 150 psig steam with single-stage, horizontal, kettle-type HX
84	Butwell, K.F.; Kubek, D.J.; Sigmund, P.W. Alkanolamine Treating. Hydrocarbon Processing, 61(3), 1982.	Thermal	370-380°F	DGA	N/A	N/A	N/A	Use 375 psig steam
84	Butwell, K.F.; Kubek, D.J.; Sigmund, P.W. Alkanolamine Treating. Hydrocarbon Processing, 61(3), 1982.	Thermal	50 mm Hg absolute at 350°F	DIPA	N/A	N/A	N/A	14-tray distillation column
84	Butwell, K.F.; Kubek, D.J.; Sigmund, P.W. Alkanolamine Treating. Hydrocarbon Processing, 61(3), 1982.	N/A	5-10% slipstream through carbon beds	DEA	N/A	N/A	N/A	2.5 gpm/ft2, bed height of 8-12 feet

Note: The comprehensive literature review in Appendix A is meant to provide a complete list of all literature that was reviewed in an attempt to gain more understanding on amine reclaiming processes (not all of this litertaure is cited in the main body of the report).

Appendix B: Reclaimer Material Balances

Table B-1. MEA Coal - Thermal Reclaiming Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate								
Ammonia	17.03	kg/hr	23.92	23.90	0.02	0.00	0.02	23.92
Formate	45.00	kg/hr	5,011.26	5,006.25	5.01	5.01	0.00	5,006.25
Other HSS's	88.00	kg/hr	1,122.23	1,121.11	1.12	1.12	0.00	1,121.11
Sulfate	96.00	kg/hr	75,019.91	74,944.89	75.02	75.02	0.00	74,944.89
Nitrate	62.00	kg/hr	49,140.80	49,091.66	49.14	49.14	0.00	49,091.66
Nitrite	46.00	kg/hr	4,003.20	3,999.20	4.00	4.00	0.00	3,999.20
Chloride	35.45	kg/hr	10,249.99	10,239.74	10.25	10.25	0.00	10,239.74
Flouride	19.00	kg/hr	222.72	222.49	0.22	0.22	0.00	222.49
HEIA	130.00	kg/hr	11,682.64	11,670.95	11.68	11.68	0.00	11,670.95
triHEIA	173.00	kg/hr	3,886.72	3,882.84	3.89	3.89	0.00	3,882.84
HEEDA	104.00	kg/hr	1,978.91	1,976.93	1.98	1.98	0.00	1,976.93
triHEIA	147.00	kg/hr	699.28	698.58	0.70	0.70	0.00	698.58
HEI	112.00	kg/hr	6,437.40	6,430.96	6.44	6.44	0.00	6,430.96
Hg	200.59	kg/hr	3.50	3.50	0.0035	0.0035	0.00	3.50
Se	78.96	kg/hr	4.47	4.47	0.0045	0.0045	0.00	4.47
As	75.00	kg/hr	0.74	0.74	0.0007	0.0007	0.00	0.74
Cd	112.00	kg/hr	0.33	0.33	0.0003	0.0003	0.00	0.33
Cr	52.00	kg/hr	8.75	8.74	0.0088	0.0088	0.00	8.74
Pb	207.20	kg/hr	0.88	0.87	0.0009	0.0009	0.00	0.87
Fly ash	60.00	kg/hr	11,671.00	11,659.33	11.67	11.67	0.00	11,659.33
Fe + other SSM's	56.00	kg/hr	962.80	961.84	0.96	0.96	0.00	961.84
Monoethanolamine	61.08	kg/hr	2,810,701.30	2,807,890.59	2,810.70	140.54	2,670.17	2,810,560.76
Carbon Dioxide	44.00	kg/hr	242,968.28	242,725.32	242.97	0.00	242.97	242,968.28
Water	18.02	kg/hr	6,574,343.14	6,567,768.79	6,574.34	0.00	6,574.34	6,574,343.14
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	83.44	0.00	0.00
Total		kg/hr	9,810,144.18	9,800,334.03	9,810.14	406.08	9,487.50	9,809,821.53

Table B-2. MEA Coal – Ion Exchange Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	23.92	23.90	0.02	0.00	0.00	0.02	23.92
Formate	45.00	kg/hr	5,568.07	5,562.50	5.57	0.00	5.01	0.56	5,563.05
Other HSS's	88.00	kg/hr	1,246.93	1,245.68	1.25	0.00	1.12	0.12	1,245.81
Sulfate	96.00	kg/hr	83,355.46	83,272.10	83.36	0.00	75.02	8.34	83,280.44
Nitrate	62.00	kg/hr	54,600.89	54,546.29	54.60	0.00	49.14	5.46	54,551.75
Nitrite	46.00	kg/hr	4,448.00	4,443.56	4.45	0.00	4.00	0.44	4,444.00
Chloride	35.45	kg/hr	11,388.87	11,377.48	11.39	0.00	10.25	1.14	11,378.62
Flouride	19.00	kg/hr	247.46	247.21	0.25	0.00	0.22	0.02	247.24
HEIA	130.00	kg/hr	12,980.71	12,967.73	12.98	0.00	0.00	12.98	12,980.71
triHEIA	173.00	kg/hr	4,318.58	4,314.26	4.32	0.00	0.00	4.32	4,318.58
HEEDA	104.00	kg/hr	2,198.79	2,196.59	2.20	0.00	0.00	2.20	2,198.79
triHEIA	147.00	kg/hr	776.98	776.20	0.78	0.00	0.00	0.78	776.98
HEI	112.00	kg/hr	7,152.67	7,145.52	7.15	0.00	0.00	7.15	7,152.67
Hg	200.59	kg/hr	3.89	3.89	0.0039	0.00	0.00	0.00	3.89
Se	78.96	kg/hr	4.97	4.97	0.0050	0.00	0.00	0.00	4.97
As	75.00	kg/hr	0.82	0.82	0.0008	0.00	0.00	0.00	0.82
Cd	112.00	kg/hr	0.37	0.37	0.0004	0.00	0.00	0.00	0.37
Cr	52.00	kg/hr	9.73	9.72	0.0097	0.00	0.00	0.01	9.73
Pb	207.20	kg/hr	0.97	0.97	0.0010	0.00	0.00	0.00	0.97
Fly ash	60.00	kg/hr	12,967.78	12,954.81	12.97	0.00	0.00	12.97	12,967.78
Fe + other SSM's	56.00	kg/hr	1,069.78	1,068.71	1.07	0.00	0.00	1.07	1,069.78
Monoethanolamine	61.08	kg/hr	2,810,701.30	2,807,890.59	2,810.70	0.00	28.11	2,782.59	2,810,673.19
Carbon Dioxide	44.00	kg/hr	242,968.28	242,725.32	242.97	0.00	0.00	242.97	242,968.28
Water	18.02	kg/hr	6,574,343.14	6,567,768.79	6,574.34	5,046.22	5,046.22	6,574.34	6,574,343.14
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	92.71	0.00	0.00
Total		kg/hr	9,830,378.35	9,820,547.97	9,830.38	5,046.22	5,311.81	9,657.50	9,830,205.47

Table B-3. MEA Coal – Electrodialysis Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	23.92	23.90	0.02	0.00	0.00	0.02	23.92
Formate	45.00	kg/hr	5,476.79	5,471.31	5.48	0.00	5.01	0.47	5,471.77
Other HSS's	88.00	kg/hr	1,226.49	1,225.26	1.23	0.00	1.12	0.10	1,225.36
Sulfate	96.00	kg/hr	81,988.97	81,906.98	81.99	0.00	75.02	6.97	81,913.95
Nitrate	62.00	kg/hr	53,705.79	53,652.09	53.71	0.00	49.14	4.56	53,656.65
Nitrite	46.00	kg/hr	4,375.09	4,370.71	4.38	0.00	4.00	0.37	4,371.08
Chloride	35.45	kg/hr	11,202.17	11,190.97	11.20	0.00	10.25	0.95	11,191.92
Flouride	19.00	kg/hr	243.40	243.16	0.24	0.00	0.22	0.02	243.18
HEIA	130.00	kg/hr	12,767.91	12,755.14	12.77	0.00	0.00	12.77	12,767.91
triHEIA	173.00	kg/hr	4,247.78	4,243.54	4.25	0.00	0.00	4.25	4,247.78
HEEDA	104.00	kg/hr	2,162.74	2,160.58	2.16	0.00	0.00	2.16	2,162.74
triHEIA	147.00	kg/hr	764.24	763.47	0.76	0.00	0.00	0.76	764.24
HEI	112.00	kg/hr	7,035.41	7,028.38	7.04	0.00	0.00	7.04	7,035.41
Hg	200.59	kg/hr	3.83	3.82	0.00	0.00	0.00	0.00	3.83
Se	78.96	kg/hr	4.89	4.88	0.00	0.00	0.00	0.00	4.89
As	75.00	kg/hr	0.81	0.81	0.00	0.00	0.00	0.00	0.81
Cd	112.00	kg/hr	0.36	0.36	0.00	0.00	0.00	0.00	0.36
Cr	52.00	kg/hr	9.57	9.56	0.01	0.00	0.00	0.01	9.57
Pb	207.20	kg/hr	0.96	0.96	0.00	0.00	0.00	0.00	0.96
Fly ash	60.00	kg/hr	12,755.20	12,742.44	12.76	0.00	0.00	12.76	12,755.20
Fe + other SSM's	56.00	kg/hr	1,052.24	1,051.19	1.05	0.00	0.00	1.05	1,052.24
Monoethanolamine	61.08	kg/hr	2,810,701.30	2,807,890.59	2,810.70	0.00	84.32	2,726.38	2,810,616.97
Carbon Dioxide	44.00	kg/hr	242,968.28	242,725.32	242.97	0.00	0.00	242.97	242,968.28
Water	18.02	kg/hr	6,574,343.14	6,567,768.79	6,574.34	6,085.41	6,085.41	6,574.34	6,574,343.14
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	91.19	0.00	0.00
Total		kg/hr	9,827,061.27	9,817,234.21	9,827.06	6,085.41	6,405.69	9,597.97	9,826,832.18

Table B-4. MEA NGCC – Thermal Reclaiming Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate								
Ammonia	17.03	kg/hr	9.15	9.14	0.01	0.00	0.01	9.15
Formate	45.00	kg/hr	5,642.61	5,636.97	5.64	5.64	0.00	5,636.97
Other HSS's	88.00	kg/hr	1,263.62	1,262.36	1.26	1.26	0.00	1,262.36
Sulfate	96.00	kg/hr	9,720.96	9,711.24	9.72	9.72	0.00	9,711.24
Nitrate	62.00	kg/hr	21,704.49	21,682.79	21.70	21.70	0.00	21,682.79
Nitrite	46.00	kg/hr	2,597.99	2,595.39	2.60	2.60	0.00	2,595.39
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
HEIA	130.00	kg/hr	5,544.57	5,539.02	5.54	5.54	0.00	5,539.02
triHEIA	173.00	kg/hr	1,844.64	1,842.79	1.84	1.84	0.00	1,842.79
HEEDA	104.00	kg/hr	939.19	938.25	0.94	0.94	0.00	938.25
triHEIA	147.00	kg/hr	331.88	331.54	0.33	0.33	0.00	331.54
HEI	112.00	kg/hr	7,248.43	7,241.18	7.25	7.25	0.00	7,241.18
Hg	200.59	kg/hr	0.00	0.00	0.0000	0.0000	0.00	0.00
Se	78.96	kg/hr	0.00	0.00	0.0000	0.0000	0.00	0.00
As	75.00	kg/hr	0.00	0.00	0.0000	0.0000	0.00	0.00
Cd	112.00	kg/hr	0.00	0.00	0.0000	0.0000	0.00	0.00
Cr	52.00	kg/hr	0.00	0.00	0.0000	0.0000	0.00	0.00
Pb	207.20	kg/hr	0.00	0.00	0.0000	0.0000	0.00	0.00
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	456.57	456.12	0.46	0.46	0.00	456.12
Monoethanolamine	61.08	kg/hr	1,332,871.31	1,331,538.43	1,332.87	66.64	1,266.23	1,332,804.66
Carbon Dioxide	44.00	kg/hr	115,218.74	115,103.52	115.22	0.00	115.22	115,218.74
Water	18.02	kg/hr	3,117,639.48	3,114,521.84	3,117.64	0.00	3,117.64	3,117,639.48
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	25.90	0.00	0.00
Total		kg/hr	4,623,033.62	4,618,410.58	4,623.03	149.84	4,499.10	4,622,909.68

Table B-5. MEA NGCC – Ion Exchange Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	9.15	9.14	0.01	0.00	0.00	0.01	9.15
Formate	45.00	kg/hr	6,269.57	6,263.30	6.27	0.00	5.64	0.63	6,263.93
Other HSS's	88.00	kg/hr	1,404.02	1,402.62	1.40	0.00	1.26	0.14	1,402.76
Sulfate	96.00	kg/hr	10,801.07	10,790.27	10.80	0.00	9.72	1.08	10,791.35
Nitrate	62.00	kg/hr	24,116.10	24,091.99	24.12	0.00	21.70	2.41	24,094.40
Nitrite	46.00	kg/hr	2,886.65	2,883.77	2.89	0.00	2.60	0.29	2,884.06
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HEIA	130.00	kg/hr	6,160.63	6,154.47	6.16	0.00	0.00	6.16	6,160.63
triHEIA	173.00	kg/hr	2,049.59	2,047.55	2.05	0.00	0.00	2.05	2,049.59
HEEDA	104.00	kg/hr	1,043.54	1,042.50	1.04	0.00	0.00	1.04	1,043.54
triHEIA	147.00	kg/hr	368.75	368.38	0.37	0.00	0.00	0.37	368.75
HEI	112.00	kg/hr	8,053.81	8,045.76	8.05	0.00	0.00	8.05	8,053.81
Hg	200.59	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.00	0.00
Se	78.96	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.00	0.00
As	75.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.00	0.00
Cd	112.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.00	0.00
Cr	52.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.00	0.00
Pb	207.20	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.00	0.00
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	507.30	506.80	0.51	0.00	0.00	0.51	507.30
Monoethanolamine	61.08	kg/hr	1,332,871.31	1,331,538.43	1,332.87	0.00	13.33	1,319.54	1,332,857.98
Carbon Dioxide	44.00	kg/hr	115,218.74	115,103.52	115.22	0.00	0.00	115.22	115,218.74
Water	18.02	kg/hr	3,117,639.48	3,114,521.84	3,117.64	1,577.74	1,577.74	3,117.64	3,117,639.48
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	28.78	0.00	0.00
Total		kg/hr	4,629,399.72	4,624,770.32	4,629.40	1,577.74	1,660.78	4,575.14	4,629,345.46

Table B-6. MEA NGCC – Electrodialysis Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	9.15	9.14	0.01	0.00	0.00	0.01	9.15
Formate	45.00	kg/hr	6,166.79	6,160.62	6.17	0.00	5.64	0.52	6,161.15
Other HSS's	88.00	kg/hr	1,381.01	1,379.63	1.38	0.00	1.26	0.12	1,379.74
Sulfate	96.00	kg/hr	10,624.00	10,613.38	10.62	0.00	9.72	0.90	10,614.28
Nitrate	62.00	kg/hr	23,720.76	23,697.04	23.72	0.00	21.70	2.02	23,699.05
Nitrite	46.00	kg/hr	2,839.33	2,836.49	2.84	0.00	2.60	0.24	2,836.73
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HEIA	130.00	kg/hr	6,059.64	6,053.58	6.06	0.00	0.00	6.06	6,059.64
triHEIA	173.00	kg/hr	2,015.99	2,013.98	2.02	0.00	0.00	2.02	2,015.99
HEEDA	104.00	kg/hr	1,026.44	1,025.41	1.03	0.00	0.00	1.03	1,026.44
triHEIA	147.00	kg/hr	362.71	362.34	0.36	0.00	0.00	0.36	362.71
HEI	112.00	kg/hr	7,921.78	7,913.86	7.92	0.00	0.00	7.92	7,921.78
Hg	200.59	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Se	78.96	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As	75.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	112.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	52.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	207.20	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	498.99	498.49	0.50	0.00	0.00	0.50	498.99
Monoethanolamine	61.08	kg/hr	1,332,871.31	1,331,538.43	1,332.87	0.00	39.99	1,292.89	1,332,831.32
Carbon Dioxide	44.00	kg/hr	115,218.74	115,103.52	115.22	0.00	0.00	115.22	115,218.74
Water	18.02	kg/hr	3,117,639.48	3,114,521.84	3,117.64	2,075.27	2,075.27	3,117.64	3,117,639.48
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	28.31	0.00	0.00
Total		kg/hr	4,628,356.10	4,623,727.74	4,628.36	2,075.27	2,184.49	4,547.44	4,628,275.18

Table B-7. PZ Coal – Thermal Reclaiming Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate								
Ammonia	17.03	kg/hr	67.37	67.30	0.07	0.00	0.07	67.37
Volatile Amines	86.14	kg/hr	8.97	8.97	0.01	0.00	0.01	8.97
Formate	45.00	kg/hr	17651.39	17,633.74	17.65	17.65	0.00	17,633.74
Other HSS's	88.00	kg/hr	8589.80	8,581.21	8.59	8.59	0.00	8,581.21
Sulfate	96.00	kg/hr	75019.91	74,944.89	75.02	75.02	0.00	74,944.89
Nitrate	62.00	kg/hr	48450.36	48,401.91	48.45	48.45	0.00	48,401.91
Chloride	35.45	kg/hr	10249.99	10,239.74	10.25	10.25	0.00	10,239.74
Flouride	19.00	kg/hr	222.72	222.49	0.22	0.22	0.00	222.49
Non volatile PZ derivs/polymers	172.00	kg/hr	12913.41	12,900.50	12.91	12.91	0.00	12,900.50
MNPZ	115.00	kg/hr	2226.40	2,224.17	2.23	2.23	0.00	2,224.17
Hg	200.59	kg/hr	3.50	3.50	0.00	0.00	0.00	3.50
Se	78.96	kg/hr	4.47	4.47	0.00	0.00	0.00	4.47
As	75.00	kg/hr	0.74	0.74	0.00	0.00	0.00	0.74
Cd	112.00	kg/hr	0.33	0.33	0.00	0.00	0.00	0.33
Cr	52.00	kg/hr	8.75	8.74	0.01	0.01	0.00	8.74
Pb	207.20	kg/hr	0.88	0.87	0.00	0.00	0.00	0.87
Fly ash	60.00	kg/hr	11671.00	11,659.33	11.67	11.67	0.00	11,659.33
Fe + other SSM's	56.00	kg/hr	1943.76	1,941.81	1.94	1.94	0.00	1,941.81
PZ Amine	86.14	kg/hr	7022401.45	7,015,379.05	7,022.40	351.12	6,671.28	7,022,050.33
Carbon Dioxide	44.00	kg/hr	2223950.68	2,221,726.73	2,223.95	0.00	2,223.95	2,223,950.68
Water	18.02	kg/hr	10191205.08	10,181,013.88	10,191.21	0.00	10,191.21	10,191,205.08
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	94.15	0.00	0.00
Total		kg/hr	19,626,590.96	19,606,964.37	19,626.59	634.22	19,086.51	19,626,050.89

Table B-8. PZ Coal – Ion Exchange Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	67.37	67.30	0.07	0.00	0.00	0.07	67.37
Volatile Amines	86.14	kg/hr	8.97	8.97	0.009	0.00	0.00	0.009	8.97
Formate	45.00	kg/hr	19,612.65	19,593.04	19.61	0.00	17.65	1.96	19,595.00
Other HSS's	88.00	kg/hr	9,544.22	9,534.67	9.54	0.00	8.59	0.95	9,535.63
Sulfate	96.00	kg/hr	83,355.46	83,272.10	83.36	0.00	75.02	8.34	83,280.44
Nitrate	62.00	kg/hr	53,833.73	53,779.90	53.83	0.00	48.45	5.38	53,785.28
Chloride	35.45	kg/hr	11,388.87	11,377.48	11.39	0.00	10.25	1.14	11,378.62
Flouride	19.00	kg/hr	247.46	247.21	0.25	0.00	0.22	0.02	247.24
Non volatile PZ derivs/polymers	172.00	kg/hr	14,348.24	14,333.89	14.35	0.00	0.00	14.35	14,348.24
MNPZ	115.00	kg/hr	2,226.40	2,224.17	2.23	0.00	0.00	2.23	2,226.40
Hg	200.59	kg/hr	3.89	3.89	0.0039	0.00	0.00	0.0039	3.89
Se	78.96	kg/hr	4.97	4.97	0.0050	0.00	0.00	0.0050	4.97
As	75.00	kg/hr	0.82	0.82	0.0008	0.00	0.00	0.0008	0.82
Cd	112.00	kg/hr	0.37	0.37	0.0004	0.00	0.00	0.0004	0.37
Cr	52.00	kg/hr	9.73	9.72	0.0097	0.00	0.00	0.0097	9.73
Pb	207.20	kg/hr	0.97	0.97	0.0010	0.00	0.00	0.0010	0.97
Fly ash	60.00	kg/hr	12,967.78	12,954.81	12.97	0.00	0.00	12.97	12,967.78
Fe + other SSM's	56.00	kg/hr	2,159.73	2,157.57	2.16	0.00	0.00	2.16	2,159.73
PZ Amine	86.14	kg/hr	7,022,401.45	7,015,379.05	7022.40	0.00	70.22	6952.18	7,022,331.23
Carbon Dioxide	44.00	kg/hr	2,223,950.68	2,221,726.73	2223.95	0.00	0.00	2223.95	2,223,950.68
Water	18.02	kg/hr	10,191,205.08	10,181,013.88	10191.21	6,365.27	6,365.27	10191.21	10,191,205.08
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	104.61	0.00	0.00
Total		kg/hr	19,647,338.85	19,627,691.51	19,647.34	6,365.27	6,700.29	19,416.93	19,647,108.44

Table B-9. PZ Coal – Electrodialysis Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	67.37	67.30	0.07	0.00	0.00	0.07	67.37
Volatile Amines	86.14	kg/hr	8.97	8.97	0.009	0.00	0.00	0.01	8.97
Formate	45.00	kg/hr	19,291.13	19,271.84	19.29	0.00	17.65	1.64	19,273.48
Other HSS's	88.00	kg/hr	9,387.75	9,378.37	9.39	0.00	8.59	0.80	9,379.16
Sulfate	96.00	kg/hr	81,988.97	81,906.98	81.99	0.00	75.02	6.97	81,913.95
Nitrate	62.00	kg/hr	52,951.21	52,898.26	52.95	0.00	48.45	4.50	52,902.76
Chloride	35.45	kg/hr	11,202.17	11,190.97	11.20	0.00	10.25	0.95	11,191.92
Flouride	19.00	kg/hr	243.40	243.16	0.24	0.00	0.22	0.02	243.18
Non volatile PZ derivs/polymers	172.00	kg/hr	14,113.02	14,098.91	14.11	0.00	0.00	14.11	14,113.02
MNPZ	115.00	kg/hr	2,226.40	2,224.17	2.23	0.00	0.00	2.23	2,226.40
Hg	200.59	kg/hr	3.83	3.82	0.0038	0.00	0.00	0.0038	3.83
Se	78.96	kg/hr	4.89	4.88	0.0049	0.00	0.00	0.0049	4.89
As	75.00	kg/hr	0.81	0.81	0.0008	0.00	0.00	0.0008	0.81
Cd	112.00	kg/hr	0.36	0.36	0.0004	0.00	0.00	0.0004	0.36
Cr	52.00	kg/hr	9.57	9.56	0.0096	0.00	0.00	0.0096	9.57
Pb	207.20	kg/hr	0.96	0.96	0.0010	0.00	0.00	0.0010	0.96
Fly ash	60.00	kg/hr	12,755.20	12,742.44	12.76	0.00	0.00	12.76	12,755.20
Fe + other SSM's	56.00	kg/hr	2,124.32	2,122.20	2.12	0.00	0.00	2.12	2,124.32
PZ Amine	86.14	kg/hr	7,022,401.45	7,015,379.05	7,022.40	0.00	210.67	6,811.73	7,022,190.78
Carbon Dioxide	44.00	kg/hr	2,223,950.68	2,221,726.73	2,223.95	0.00	0.00	2,223.95	2,223,950.68
Water	18.02	kg/hr	10,191,205.08	10,181,013.88	10,191.21	9,001.20	9,001.20	10,191.21	10,191,205.08
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	102.89	0.00	0.00
Total		kg/hr	19,643,937.56	19,624,293.62	19,643.94	9,001.20	9,474.95	19,273.08	19,643,566.70

Table B-10. PZ NGCC – Thermal Reclaiming Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate								
Ammonia	17.03	kg/hr	21.69	21.67	0.02	0.00	0.02	21.69
Volatile Amines	86.14	kg/hr	9.52	9.51	0.01	0.00	0.01	9.52
Formate	45.00	kg/hr	9823.13	9,813.30	9.82	9.82	0.00	9,813.30
Other HSS's	88.00	kg/hr	4858.55	4,853.69	4.86	4.86	0.00	4,853.69
Sulfate	96.00	kg/hr	9720.96	9,711.24	9.72	9.72	0.00	9,711.24
Nitrate	62.00	kg/hr	20927.07	20,906.14	20.93	20.93	0.00	20,906.14
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Non volatile PZ derivs/polymers	172.00	kg/hr	6531.95	6,525.41	6.53	6.53	0.00	6,525.41
MNPZ	115.00	kg/hr	961.65	960.68	0.96	0.96	0.00	960.68
Hg	200.59	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Se	78.96	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
As	75.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Cd	112.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Cr	52.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Pb	207.20	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	971.65	970.68	0.97	0.97	0.00	970.68
PZ Amine	86.14	kg/hr	3549680.80	3,546,131.12	3,549.68	177.48	3,372.20	3,549,503.32
Carbon Dioxide	44.00	kg/hr	1015371.89	1,014,356.52	1,015.37		1,015.37	1,015,371.89
Water	18.02	kg/hr	5151446.45	5,146,295.00	5,151.45	0.00	5,151.45	5,151,446.45
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	28.49	0.00	0.00
Total		kg/hr	9,770,325.30	9,760,554.97	9,770.33	259.77	9,539.05	9,770,094.02

Table B-11. PZ NGCC – Ion Exchange Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	21.69	21.67	0.02	0.00	0.00	0.02	21.69
Volatile Amines	86.14	kg/hr	9.52	9.51	0.010	0.00	0.00	0.01	9.52
Formate	45.00	kg/hr	10,914.59	10,903.67	10.91	0.00	9.82	1.09	10,904.76
Other HSS's	88.00	kg/hr	5,398.38	5,392.99	5.40	0.00	4.86	0.54	5,393.53
Sulfate	96.00	kg/hr	10,801.07	10,790.27	10.80	0.00	9.72	1.08	10,791.35
Nitrate	62.00	kg/hr	23,252.30	23,229.04	23.25	0.00	20.93	2.33	23,231.37
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Non volatile PZ derivs/polymers	172.00	kg/hr	7,257.72	7,250.46	7.26	0.00	0.00	7.26	7,257.72
MNPZ	115.00	kg/hr	961.65	960.68	0.96	0.00	0.00	0.96	961.65
Hg	200.59	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Se	78.96	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
As	75.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Cd	112.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Cr	52.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Pb	207.20	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	1,079.61	1,078.53	1.08	0.00	0.00	1.08	1,079.61
PZ Amine	86.14	kg/hr	3,549,680.80	3,546,131.12	3,549.68	0.00	35.50	3,514.18	3,549,645.31
Carbon Dioxide	44.00	kg/hr	1,015,371.89	1,014,356.52	1,015.37	0.00	0.00	1,015.37	1,015,371.89
Water	18.02	kg/hr	5,151,446.45	5,146,295.00	5,151.45	2,137.20	2,137.20	5,151.45	5,151,446.45
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	31.66	0.00	0.00
Total		kg/hr	9,776,195.66	9,766,419.47	9,776.20	2,137.20	2,249.68	9,695.37	9,776,114.84

Table B-12. PZ NGCC – Electrodialysis Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	21.69	21.67	0.02	0.00	0.00	0.02	21.69
Volatile Amines	86.14	kg/hr	9.52	9.51	0.010	0.00	0.00	0.01	9.52
Formate	45.00	kg/hr	10,735.66	10,724.92	10.74	0.00	9.82	0.91	10,725.84
Other HSS's	88.00	kg/hr	5,309.89	5,304.58	5.31	0.00	4.86	0.45	5,305.03
Sulfate	96.00	kg/hr	10,624.00	10,613.38	10.62	0.00	9.72	0.90	10,614.28
Nitrate	62.00	kg/hr	22,871.11	22,848.24	22.87	0.00	20.93	1.94	22,850.18
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Non volatile PZ derivs/polymers	172.00	kg/hr	7,138.74	7,131.60	7.14	0.00	0.00	7.14	7,138.74
MNPZ	115.00	kg/hr	961.65	960.68	0.96	0.00	0.00	0.96	961.65
Hg	200.59	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Se	78.96	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
As	75.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Cd	112.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Cr	52.00	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Pb	207.20	kg/hr	0.00	0.00	0.0000	0.00	0.00	0.0000	0.00
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	1,061.91	1,060.85	1.06	0.00	0.00	1.06	1,061.91
PZ Amine	86.14	kg/hr	3,549,680.80	3,546,131.12	3,549.68	0.00	106.49	3,443.19	3,549,574.31
Carbon Dioxide	44.00	kg/hr	1,015,371.89	1,014,356.52	1,015.37	0.00	0.00	1,015.37	1,015,371.89
Water	18.02	kg/hr	5,151,446.45	5,146,295.00	5,151.45	3,476.22	3,476.22	5,151.45	5,151,446.45
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	31.14	0.00	0.00
Total		kg/hr	9,775,233.31	9,765,458.07	9,775.23	3,476.22	3,659.17	9,623.41	9,775,081.49

Table B-13. MDEA/PZ Coal – Thermal Reclaiming Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate								
Ammonia	17.03	kg/hr	54.33	54.28	0.05	0.00	0.05	54.33
1-MPZ + 1,4-DMPZ	107.18	kg/hr	52.03	51.98	0.05	0.00	0.05	52.03
AEP	129.20	kg/hr	0.81	0.81	0.00	0.00	0.00	0.81
Formate	45.00	kg/hr	18,726.63	18,707.90	18.73	18.73	0.00	18,707.90
Other HSS's	88.00	kg/hr	1,731.58	1,729.85	1.73	1.73	0.00	1,729.85
Sulfate	96.00	kg/hr	75,019.91	74,944.89	75.02	75.02	0.00	74,944.89
Nitrate	62.00	kg/hr	48,450.36	48,401.91	48.45	48.45	0.00	48,401.91
Chloride	35.45	kg/hr	10,249.99	10,239.74	10.25	10.25	0.00	10,239.74
Flouride	19.00	kg/hr	222.72	222.49	0.22	0.22	0.00	222.49
DEA + MAE + polymers	90.00	kg/hr	89,090.60	89,001.51	89.09	89.09	0.00	89,001.51
Bicine	163.00	kg/hr	10,210.00	10,199.79	10.21	10.21	0.00	10,199.79
MNPZ	115.00	kg/hr	5,363.40	5,358.04	5.36	5.36	0.00	5,358.04
Hg	200.59	kg/hr	3.50	3.4978	0.0035	0.0035	0.0000	3.4978
Se	78.96	kg/hr	4.47	4.4694	0.0045	0.0045	0.0000	4.4694
As	75.00	kg/hr	0.74	0.7384	0.0007	0.0007	0.0000	0.7384
Cd	112.00	kg/hr	0.33	0.3303	0.0003	0.0003	0.0000	0.3303
Cr	52.00	kg/hr	8.75	8.7445	0.0088	0.0088	0.0000	8.7445
Pb	207.20	kg/hr	0.88	0.8744	0.0009	0.0009	0.0000	0.8744
Fly ash	60.00	kg/hr	11,671.00	11,659.33	11.67	11.67	0.00	11,659.33
Fe + other SSM's	56.00	kg/hr	2,398.80	2,396.40	2.40	2.40	0.00	2,396.40
MDEA-PZ Amine	111.82	kg/hr	11,720,564.26	11,708,843.70	11,720.56	586.03	11,134.54	11,719,978.23
Carbon Dioxide	44	kg/hr	620,046.94	619,426.89	620.05	0.00	620.05	620,046.94
Water	18.02	kg/hr	11,647,425.74	11,635,778.31	11,647.43	0.00	11,647.43	11,647,425.74
Sodium Hydroxide	40	kg/hr	0.00	0.00	0.00	91.98	0.00	0.00
Total		kg/hr	24,261,297.77	24,237,036.47	24,261.30	951.17	23,402.12	24,260,438.59

Table B-14. MDEA/PZ Coal – Ion Exchange Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	54.33	54.28	0.05	0.00	0.00	0.05	54.33
1-MPZ + 1,4-DMPZ	107.18	kg/hr	52.03	51.98	0.05	0.00	0.00	0.05	52.03
AEP	129.20	kg/hr	0.81	0.81	0.00	0.00	0.00	0.00	0.81
Formate	45.00	kg/hr	20,807.36	20,786.55	20.81	0.00	18.73	2.08	20,788.64
Other HSS's	88.00	kg/hr	1,923.97	1,922.05	1.92	0.00	1.73	0.19	1,922.24
Sulfate	96.00	kg/hr	83,355.46	83,272.10	83.36	0.00	75.02	8.34	83,280.44
Nitrate	62.00	kg/hr	53,833.73	53,779.90	53.83	0.00	48.45	5.38	53,785.28
Chloride	35.45	kg/hr	11,388.87	11,377.48	11.39	0.00	10.25	1.14	11,378.62
Flouride	19.00	kg/hr	247.46	247.21	0.25	0.00	0.22	0.02	247.24
DEA + MAE + polymers	90.00	kg/hr	98,989.55	98,890.56	98.99	0.00	0.00	98.99	98,989.55
Bicine	163.00	kg/hr	11,344.44	11,333.10	11.34	0.00	0.00	11.34	11,344.44
MNPZ	115.00	kg/hr	5,363.40	5,358.04	5.36	0.00	0.00	5.36	5,363.40
Hg	200.59	kg/hr	3.8903	3.8864	0.0039	0.0000	0.0000	0.0039	3.8903
Se	78.96	kg/hr	4.9710	4.9660	0.0050	0.0000	0.0000	0.0050	4.9710
As	75.00	kg/hr	0.8213	0.8205	0.0008	0.0000	0.0000	0.0008	0.8213
Cd	112.00	kg/hr	0.3674	0.3671	0.0004	0.0000	0.0000	0.0004	0.3674
Cr	52.00	kg/hr	9.7258	9.7161	0.0097	0.0000	0.0000	0.0097	9.7258
Pb	207.20	kg/hr	0.9726	0.9716	0.0010	0.0000	0.0000	0.0010	0.9726
Fly ash	60.00	kg/hr	12,967.78	12,954.81	12.97	0.00	0.00	12.97	12,967.78
Fe + other SSM's	56.00	kg/hr	2,665.34	2,662.67	2.67	0.00	0.00	2.67	2,665.34
MDEA-PZ Amine	111.82	kg/hr	11,720,564.26	11,708,843.70	11,720.56	0.00	117.21	11,603.36	11,720,447.05
Carbon Dioxide	44.00	kg/hr	620,046.94	619,426.89	620.05	0.00	0.00	620.05	620,046.94
Water	18.02	kg/hr	11,647,425.74	11,635,778.31	11,647.43	7,102.41	7,102.41	11,647.43	11,647,425.74
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	102.20	0.00	0.00
Total		kg/hr	24,291,052.24	24,266,761.19	24,291.05	7,102.41	7,476.23	24,019.45	24,290,780.64

Table B-15. MDEA/PZ Coal – Electrodialysis Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	54.33	54.28	0.05	0.00	0.00	0.05	54.33
1-MPZ + 1,4-DMPZ	107.18	kg/hr	52.03	51.98	0.05	0.00	0.00	0.05	52.03
AEP	129.20	kg/hr	0.81	0.81	0.00	0.00	0.00	0.00	0.81
Formate	45.00	kg/hr	20,466.26	20,445.79	20.47	0.00	18.73	1.74	20,447.53
Other HSS's	88.00	kg/hr	1,892.43	1,890.54	1.89	0.00	1.73	0.16	1,890.70
Sulfate	96.00	kg/hr	81,988.97	81,906.98	81.99	0.00	75.02	6.97	81,913.95
Nitrate	62.00	kg/hr	52,951.21	52,898.26	52.95	0.00	48.45	4.50	52,902.76
Chloride	35.45	kg/hr	11,202.17	11,190.97	11.20	0.00	10.25	0.95	11,191.92
Flouride	19.00	kg/hr	243.40	243.16	0.24	0.00	0.22	0.02	243.18
DEA + MAE + polymers	90.00	kg/hr	97,366.77	97,269.41	97.37	0.00	0.00	97.37	97,366.77
Bicine	163.00	kg/hr	11,158.47	11,147.31	11.16	0.00	0.00	11.16	11,158.47
MNPZ	115.00	kg/hr	5,363.40	5,358.04	5.36	0.00	0.00	5.36	5,363.40
Hg	200.59	kg/hr	3.83	3.82	0.00	0.00	0.00	0.00	3.83
Se	78.96	kg/hr	4.89	4.88	0.00	0.00	0.00	0.00	4.89
As	75.00	kg/hr	0.81	0.81	0.00	0.00	0.00	0.00	0.81
Cd	112.00	kg/hr	0.36	0.36	0.00	0.00	0.00	0.00	0.36
Cr	52.00	kg/hr	9.57	9.56	0.01	0.00	0.00	0.01	9.57
Pb	207.20	kg/hr	0.96	0.96	0.00	0.00	0.00	0.00	0.96
Fly ash	60.00	kg/hr	12,755.20	12,742.44	12.76	0.00	0.00	12.76	12,755.20
Fe + other SSM's	56.00	kg/hr	2,621.64	2,619.02	2.62	0.00	0.00	2.62	2,621.64
MDEA-PZ Amine	111.82	kg/hr	11,720,564.26	11,708,843.70	11,720.56	0.00	351.62	11,368.95	11,720,212.64
Carbon Dioxide	44.00	kg/hr	620,046.94	619,426.89	620.05	0.00	0.00	620.05	620,046.94
Water	18.02	kg/hr	11,647,425.74	11,635,778.31	11,647.43	11,524.39	11,524.39	11,647.43	11,647,425.74
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	100.53	0.00	0.00
Total		kg/hr	24,286,174.46	24,261,888.29	24,286.17	11,524.39	12,130.94	23,780.16	24,285,668.44

Table B-16. MDEA/PZ NGCC – Thermal Reclaiming Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate								
Ammonia	17.03	kg/hr	13.42	13.41	0.01	0.00	0.01	13.42
1-MPZ + 1,4-DMPZ	107.18	kg/hr	46.50	46.45	0.05	0.00	0.05	46.50
AEP	129.20	kg/hr	0.37	0.37	0.00	0.00	0.00	0.37
Formate	45.00	kg/hr	12,414.17	12,401.76	12.41	12.41	0.00	12,401.76
Other HSS's	88.00	kg/hr	1,153.05	1,151.90	1.15	1.15	0.00	1,151.90
Sulfate	96.00	kg/hr	9,720.96	9,711.24	9.72	9.72	0.00	9,711.24
Nitrate	62.00	kg/hr	20,927.07	20,906.14	20.93	20.93	0.00	20,906.14
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
DEA + MAE + polymers	90.00	kg/hr	67,926.42	67,858.49	67.93	67.93	0.00	67,858.49
Bicine	163.00	kg/hr	10,949.33	10,938.38	10.95	10.95	0.00	10,938.38
MNPZ	115.00	kg/hr	2,316.60	2,314.29	2.32	2.32	0.00	2,314.29
Hg	200.59	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Se	78.96	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
As	75.00	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Cd	112.00	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Cr	52.00	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Pb	207.20	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	1,079.21	1,078.13	1.08	1.08	0.00	1,078.13
MDEA-PZ Amine	111.82	kg/hr	5,273,016.88	5,267,743.87	5,273.02	263.65	5,009.37	5,272,753.23
Carbon Dioxide	44	kg/hr	278,955.68	278,676.73	278.96	0.00	278.96	278,955.68
Water	18.02	kg/hr	5,240,112.27	5,234,872.16	5,240.11	0.00	5,240.11	5,240,112.27
Sodium Hydroxide	40	kg/hr	0.00	0.00	0.00	29.11	0.00	0.00
Total		kg/hr	10,918,631.93	10,907,713.30	10,918.63	419.25	10,528.49	10,918,241.79

Table B-17. MDEA/PZ NGCC – Ion Exchange Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	13.42	13.41	0.01	0.00	0.00	0.01	13.42
1-MPZ + 1,4-DMPZ	107.18	kg/hr	46.50	46.45	0.05	0.00	0.00	0.05	46.50
AEP	129.20	kg/hr	0.37	0.37	0.00	0.00	0.00	0.00	0.37
Formate	45.00	kg/hr	13,793.53	13,779.73	13.79	0.00	12.41	1.38	13,781.11
Other HSS's	88.00	kg/hr	1,281.17	1,279.89	1.28	0.00	1.15	0.13	1,280.01
Sulfate	96.00	kg/hr	10,801.07	10,790.27	10.80	0.00	9.72	1.08	10,791.35
Nitrate	62.00	kg/hr	23,252.30	23,229.04	23.25	0.00	20.93	2.33	23,231.37
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DEA + MAE + polymers	90.00	kg/hr	75,473.80	75,398.32	75.47	0.00	0.00	75.47	75,473.80
Bicine	163.00	kg/hr	12,165.92	12,153.76	12.17	0.00	0.00	12.17	12,165.92
MNPZ	115.00	kg/hr	2,316.60	2,314.29	2.32	0.00	0.00	2.32	2,316.60
Hg	200.59	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Se	78.96	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
As	75.00	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Cd	112.00	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Cr	52.00	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Pb	207.20	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	1,199.12	1,197.92	1.20	0.00	0.00	1.20	1,199.12
MDEA-PZ Amine	111.82	kg/hr	5,273,016.88	5,267,743.87	5,273.02	0.00	52.73	5,220.29	5,272,964.15
Carbon Dioxide	44.00	kg/hr	278,955.68	278,676.73	278.96	0.00	0.00	278.96	278,955.68
Water	18.02	kg/hr	5,240,112.27	5,234,872.16	5,240.11	2,456.52	2,456.52	5,240.11	5,240,112.27
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	32.35	0.00	0.00
Total		kg/hr	10,932,428.62	10,921,496.19	10,932.43	2,456.52	2,585.81	10,835.48	10,932,331.67

Table B-18. MDEA/PZ NGCC – Electrodialysis Material Balance

Component	MW	Units	Stream 1 - Lean Solvent from Regenerator	Solvent 2 - Lean Solvent Not Sent to Reclaimer	Stream 3 - Reclaimer Feed	Stream 4 - Water Addition for Reclaiming	Stream 5 - Amine Waste	Stream 6 - Reclaimed Amine	Stream 7 - Lean Solvent with Reclaimed Amine
Flow Rate									
Ammonia	17.03	kg/hr	13.42	13.41	0.01	0.00	0.00	0.01	13.42
1-MPZ + 1,4-DMPZ	107.18	kg/hr	46.50	46.45	0.05	0.00	0.00	0.05	46.50
AEP	129.20	kg/hr	0.37	0.37	0.00	0.00	0.00	0.00	0.37
Formate	45.00	kg/hr	13,567.40	13,553.84	13.57	0.00	12.41	1.15	13,554.99
Other HSS's	88.00	kg/hr	1,260.16	1,258.90	1.26	0.00	1.15	0.11	1,259.01
Sulfate	96.00	kg/hr	10,624.00	10,613.38	10.62	0.00	9.72	0.90	10,614.28
Nitrate	62.00	kg/hr	22,871.11	22,848.24	22.87	0.00	20.93	1.94	22,850.18
Chloride	35.45	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flouride	19.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DEA + MAE + polymers	90.00	kg/hr	74,236.52	74,162.28	74.24	0.00	0.00	74.24	74,236.52
Bicine	163.00	kg/hr	11,966.48	11,954.51	11.97	0.00	0.00	11.97	11,966.48
MNPZ	115.00	kg/hr	2,316.60	2,314.29	2.32	0.00	0.00	2.32	2,316.60
Hg	200.59	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Se	78.96	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As	75.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	112.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	52.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	207.20	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fly ash	60.00	kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe + other SSM's	56.00	kg/hr	1,179.46	1,178.28	1.18	0.00	0.00	1.18	1,179.46
MDEA-PZ Amine	111.82	kg/hr	5,273,016.88	5,267,743.87	5,273.02	0.00	158.19	5,114.83	5,272,858.69
Carbon Dioxide	44.00	kg/hr	278,955.68	278,676.73	278.96	0.00	0.00	278.96	278,955.68
Water	18.02	kg/hr	5,240,112.27	5,234,872.16	5,240.11	4,450.19	4,450.19	5,240.11	5,240,112.27
Sodium Hydroxide	40.00	kg/hr	0.00	0.00	0.00	0.00	31.81	0.00	0.00
Total		kg/hr	10,930,166.87	10,919,236.70	10,930.17	4,450.19	4,684.41	10,727.76	10,929,964.46

Appendix C: Power Plant Reference Cases

3.0 Reference Plant Design Basis

To provide a frame of reference for discussion of the scale-up issues associated with the post-combustion CO_2 capture, full scale conceptual designs were developed. This section provides the design basis for the conceptual designs. Reference plant designs were selected on the basis of recent trends in the power generation industry. Power plant designs chosen for this study are typical of modern day large-scale commercial power plants.

3.1 POWER PLANT DESIGNS

Power plant designs for a large SCPC and a large NGCC were selected to represent modern day power plants typical of those currently being constructed around the world. Two reference cases were developed for each design. The first reference case is representative of a power plant built without CO_2 capture. The second reference case is representative of a power plant constructed with integral post-combustion CO_2 capture and compression facilities. A summary of the four cases is presented in Table 3-1. The basis for the post-combustion CO_2 capture technology is discussed in Section 3.2.

A CO_2 capture efficiency of 90 percent was selected for the CO_2 capture reference cases. This percentage was selected because industry experience suggests that attempting to achieve capture rates much higher than this would result in diminishing returns. Therefore, 90 percent is generally considered an optimum level of CO_2 capture.

The power plant reference cases were evaluated at a barometric pressure of 101.325 kilopascals-absolute (kPa), temperature of 15 degrees Celsius (°C), and relative humidity of 60 percent. The two SCPC cases were developed assuming the use of low sulfur Australian coal. Representative coal properties are presented in Table 3-2. The two NGCC cases were developed assuming natural gas with the properties presented in Table 3-3.

Table 3-1 Power Plant Design Cases

	DESIGN CASE 1 SCPC WITHOUT CAPTURE	DESIGN CASE 2 SCPC WITH CO_2 CAPTURE	DESIGN CASE 3 NGCC WITHOUT CAPTURE	DESIGN CASE 4 NGCC WITH CO_2 CAPTURE
CO_2 Capture, % of Gross	N/A	90	N/A	90
Technology Description	Supercritical pulverized coal Rankine cycle with 1 two-pass tangential or wall-fired boiler and 1 reheat condensing steam turbine.		Natural gas combined cycle with 2x G-Class gas turbines, 2x three-pressure heat recovery steam generators, and 1x reheat steam turbine.	
Nominal Gross Output, MW	900	TBD(1)	810	TBD(1)
Unit Output Frequency, Hz	60	60	60	60
Fuel	Australian Low-Sulfur	Same as Case 1	Natural Gas	Same as Case 3
Fuel Quantity	Note 1	Same as Case 1	Note 1	Same as Case 3
Throttle Conditions (MS temperature, HRH temperature, MS pressure) ° C / ° C / bar(a) (° F / ° F / psia)	582 / 582 / 254.4 (1,080 / 1,080 / 3,690)		565.6 / 565.6 / 124.1 (1,050 / 1,050 / 1,800)	
Supplemental Firing	N/A	N/A	No	No
Heat Rejection	Wet mechanical draft cooling tower			
Auxiliary Boiler During Normal Operations	No	No	No	No
Air Quality Control Systems	Selective Catalytic Reduction, PAC Injection, Fabric Filter, Wet Flue Gas Desulfurization		Dry Low NO_x Combustion, Selective Catalytic Reduction, Oxidation Catalyst	
CO_2 Export Pressure, bar(a) (psia)	N/A	110 (1,600)	N/A	110 (1,600)

Notes:

(1) Fuel quantity to be determined as part of the study. As a basis of the design, CO_2 capture case will use the same amount of fuel as the non-capture case. Calculated values are presented in Section 4.0.

Table 3-2 Study Design Coal: Low Sulfur Australian

As-Received Proximate Analysis, wt%			**Ash Analysis, wt%**		
Gross Calorific Value	6,270	kcal/kg	Silica	46.8	%
Hardgrove Grindability Index	50		Aluminum	26	%
Moisture	9	%	Iron	11	%
Ash	13.5	%	Calcium	5.6	%
Volatiles	25.2	%	Magnesium	1.5	%
Fixed Carbon	52.3	%	Sodium	0.4	%
			Potassium	0.7	%
As-Received Ultimate Analysis, wt%			Sulfur Trioxide (SO_3)	4.1	%
Carbon	65.3	%	Phosphorus	1.1	%
Hydrogen	3.9	%	Titanium	1	%
Oxygen	6.3	%	Manganese	0.3	%
Nitrogen	1.3	%	Other	1.5	%
Sulfur	0.7	%			
Ash	13.5	%	**Other Properties**		
Moisture	9	%	Initial Deformation	1,200	° C
Chlorine	0.07	%	Hemi	1,240	° C
			Flow	1,300	° C
Notes: wt% - Weight percentage kcal/kg – Kilocalories per kilogram					

Table 3-3 Study Design Natural Gas

Methane (CH_4), vol%	92
Ethane (C_2H_6), vol%	6
Propane (C_3H_8), vol%	1
CO_2, vol%	0.5
Nitrogen (N_2), vol%	0.5
Total Sulfur	8 ppmw
Hydrogen Sulfide (H_2S)	3 ppmw
Notes: vol% – Volumetric percentage ppmw – Parts per million by weight	

4.0 Reference Power Plant Designs

4.1 COAL FUELED PLANTS

4.1.1 Main Power Block Description

SCPC power plants utilize proven technology with high reliability and are relatively easy to operate and maintain. Various designs and configurations exist that offer flexibility to match electrical system demands and type(s) of fuel available.

The function of the steam generator of an SCPC power plant is to provide the controlled release of heat in the fuel and the efficient transfer of heat to the feedwater and steam. The transfer of heat produces main steam (MS) at the pressure and temperature required by the high-pressure (HP) turbine. Heat is also transferred through the reheater to increase the temperature of the HP turbine exhaust, or cold reheat (CRH) steam, to the conditions required by the intermediate-pressure (IP) turbine as hot reheat (HRH) steam. Exhaust from the IP turbine is admitted to the LP turbine. The MS and HRH steam drive a steam turbine generator (STG) to produce rotational mechanical energy. The rotational mechanical energy is converted to electrical energy by a statically excited electric generator coupled to the turbine.

Waste heat from the condensing of LP steam in the condenser is typically rejected to either an open or closed cycle cooling water system. Selection of the cooling water system is location-specific and dependent on several factors, including the availability of raw water and suitable discharge location. This study assumes the use of a closed circulating cooling water system utilizing a wet mechanical-draft cooling tower for heat rejection from the condenser and other plant cooling needs. A high-level block flow diagram for an SCPC power plant is illustrated on Figure 4-1.

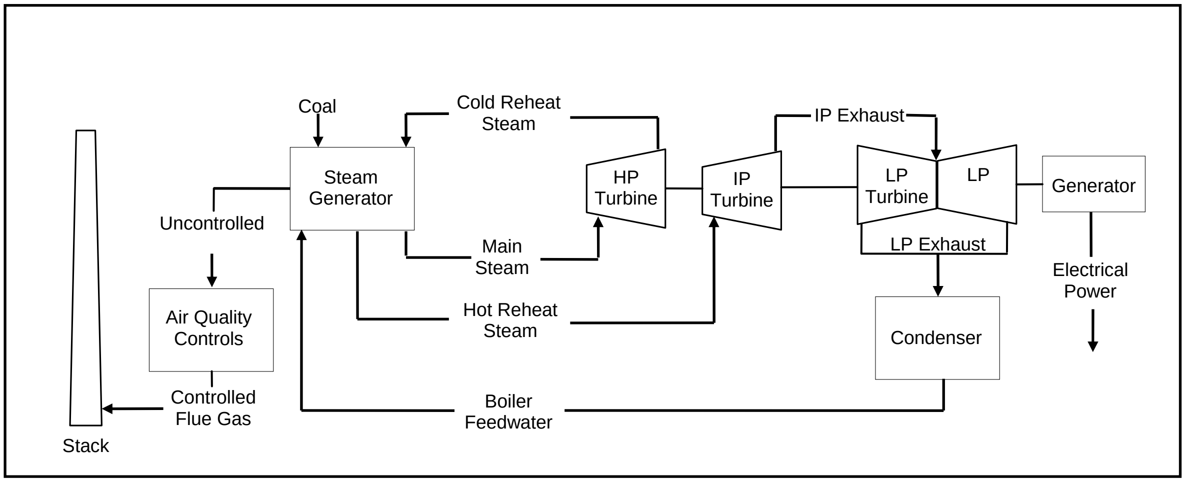


Figure 4-1 Typical SCPC Power Plant

After being heated by the LP and HP feedwater heaters, boiler feedwater is fed through the steam generator's economizer, where initial heat transfer from the flue gas to the working fluid takes place. Feedwater is supplied to the bottom header of the economizer, flows upward and absorbs heat within the economizer, then enters the economizer outlet header. Feedwater exits the economizer and is supplied to headers at the bottom of the furnace walls. Feedwater in the headers flows upwards by forced circulation through the furnace waterwall tubes in a once-through operation (i.e., no boiler drum). Because the pressure of the feedwater is above the critical point of water, the feedwater does not boil. However, it increases in specific volume as its enthalpy increases. A "fluid" above the critical point of water, often referred to as supercritical steam, is produced in the waterwalls of an SCPC steam generator, which is supplied to the primary superheater in the convective pass of the boiler.

With SCPC technology, coal is pulverized then suspended in a primary air stream and conveyed to coal burners. At the burners, this mixture of primary air and coal is further mixed with secondary air and, with the presence of sufficient heat for ignition, the coal combusts in suspension. The furnace enclosure is constructed of membrane waterwalls that absorb the radiant heat of combustion produced by the high combustion temperatures at the burners and produce steam. Current pulverized fuel combustion technology also includes features to minimize unintended products of combustion. For the reference SCPC plant, low nitrogen oxide (NO_x) burners (LNBs) and overfire air (OFA, staged combustion) are used to reduce NO_x formation. Carbon monoxide (CO) emissions are minimized by carefully controlling air-fuel ratios.

Once the products of coal combustion (ash and flue gas) have been cooled sufficiently by the waterwall surfaces so that the ash is no longer molten but in solid form, convective heat transfer surfaces absorb most of the remaining heat of combustion. These convective heat transfer surfaces include the superheaters, reheaters, and economizers located within the steam generator enclosure downstream of the furnace. The final section of boiler heat recovery is in the air preheater, where the flue gas leaving the economizer surface is further cooled by regenerative or recuperative heat transfer to the incoming combustion air.

With SCPC combustion technology, the majority of the solid ash components in the coal will be carried in the flue gas stream all the way through the furnace and convective heat transfer components to enable collection with particulate removal equipment downstream of the air pre-heaters. Typically, no less than 80 percent of the total ash will be carried out of the steam generator for collection downstream. Approximately 15 percent of the total fuel ash is collected wet from the furnace as bottom ash, and 5 percent is collected dry in hoppers located below the steam generator economizer and regenerative air heaters.

For the reference plant, a balanced draft configuration was assumed, as is typical for most modern SCPC units. In this configuration, the boiler operates under slightly negative pressure, and all draft pressure conveying the flue gas is supplied by ID fans that are located downstream of the air preheater. For the CO_2 capture case, the ID fan must be large enough to push the flue gas through the absorber and out the absorber stack.

4.1.2 Post-Combustion Emissions Control Description (Excluding CO_2 Capture)

The following AQC equipment and systems are included in the reference SCPC power plant: selective catalytic reduction (SCR), powdered activated carbon (PAC), pulse jet fabric filter (PJFF), and WFGD. A caustic polishing scrubber is also included for the CO_2 capture case. These systems are discussed later in this section.

Note that the post-combustion AQC equipment and systems assumed for the reference SCPC power plant are representative of a modern power plant design with a comprehensive suite of air emissions control equipment. However, because of the generic nature of the study and nonspecific location of the power plant, no specific power plant stack emissions targets were selected. The reference SCPC plant flue gas configuration is presented on Figure 4-2.

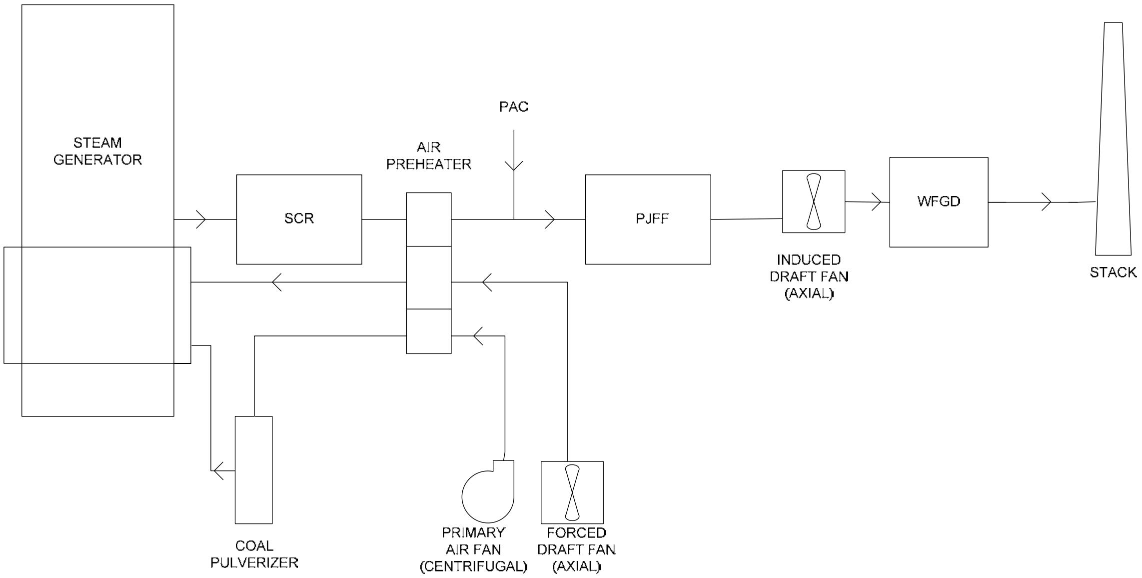


Figure 4-2 Reference SCPC Plant Flue Gas Configuration (polishing scrubber not shown)

4.1.2.1 NO_x Reduction

An SCR system was selected for the reference SCPC power plant. Electric utilities frequently use SCR systems for the reduction of NO_x. A selective noncatalytic reduction (SNCR) system could have been chosen as well, but SCR systems are more efficient at NO_x reduction and can generally achieve lower outlet NO_x concentrations, which is beneficial to the CO_2 capture process.

SCR systems utilize ammonia as a reagent and a catalyst (typically vanadium-based) for NO_x removal. Ammonia is injected into the SCR where it reacts with NO_x to create nitrogen and water. The SCR for the SCPC reference plant is located between the economizer outlet and the air preheater inlet because the ammonia needs to be injected at temperatures between about 315 and 425° C (600 and 800° F). It is possible to locate the SCR downstream of all post-combustion emissions control equipment, but the gas-to-gas reheat needed to obtain the necessary temperature is expensive.

4.1.2.2 Mercury Reduction

A PAC injection system was selected for the reference SCPC power plant. This system injects powdered activated carbon, often lignite based, into ductwork upstream of a particulate removal device. Elemental and oxidized forms of mercury (Hg) are adsorbed onto the carbon surfaces.

4.1.2.3 Particulate Matter Reduction

A PJFF was selected for the reference SCPC power plant. PJFFs are common particulate removal devices for meeting particulate matter emissions requirements. Fabric filters essentially act as industrial-scale vacuum cleaners, with the particulate-laden flue gas passing through fabric bags. As the flue gas passes through the bags, the particulate collects on the bag surface as a filter cake, and the clean air passes through.

An electrostatic precipitator (ESP) was not selected for this study for two primary reasons. First, a PJFF can aid Hg removal by allowing more contact opportunities between the PAC and Hg on the bags' filter cakes. Second, PJFFs are able to meet low particulate emissions for a wide range of fuels and operations.

4.1.2.4 Sulfur Dioxide Reduction

Selection of the SO_2 reduction system for the reference plant is important because SO_2 is a contaminant for amine-based CO_2 capture systems, causing the formation of heat stable salts and degradation of the amine solvent. A WFGD system was selected for the reference SCPC power plant. WFGD is recommended because of its superior SO_2 removal capabilities compared to a dry or semi-dry FGD. Circulating dry scrubbers (CDS) are able to achieve similar SO_2 removal rates, but they use lime as their reagent, which is much more expensive than limestone.

Several types of WFGDs exist, but this study assumes a limestone forced oxidation (LSFO) type. There are several different types of absorbers that might achieve similar performance. In all cases, a limestone slurry is contacted with the flue gas by sprays, gas contact devices such as dual flow trays, or bubbling the gas through a tank of the slurry. Oxidation air is introduced into the processed slurry pool at the bottom of the tower. The oxidation air converts all of the calcium sulfite into sulfate form, which is commonly known as gypsum. Depending on the technology/equipment vendor, various methods are used to increase the liquid-to-gas contact, such as contact trays, absorber rings, etc. The gypsum byproduct is potentially marketable.

4.1.2.5 SO_2 Polishing (SCPC Power Plant with CO_2 Capture Only)

Amine-based CO_2 capture systems require low levels of SO_2 in the inlet flue gas because SO_2 reacts with the amine solvent to produce heat stable salts that degrade the amine solvent. Different technology vendors will require different levels of SO_2 in the inlet flue gas, so a typical value of 10 parts per million (ppm) SO_2 was assumed for this study. While WFGD systems have recently demonstrated SO_2 outlet concentrations as low as 10 ppm with low-sulfur fuels similar to the study design low-sulfur Australian coal, WFGD vendors generally do not guarantee this degree of sulfur removal. Therefore, a polishing scrubber downstream of the WFGD was selected for the SCPC power plant reference design case with post-combustion CO_2 capture. As WFGD and other SO_2 reduction technologies are operated more aggressively, consistently achieving higher sulfur removal rates, vendors might eventually guarantee a maximum SO_2 outlet concentration of 10 ppm.

The polishing scrubber uses a sodium hydroxide (NaOH) caustic reagent. As an alkali metal, sodium is much more reactive with acidic compounds, such as SO_2, than calcium, so caustic scrubbers are capable of achieving very low SO_2 emissions rates. However, caustic solutions are more expensive than calcium-based reagents, so maximum SO_2 removal should be achieved in the WFGD and the caustic scrubber only used for “polishing” the flue gas.

4.1.3 Post-Combustion CO_2 Capture Description

Black & Veatch modeled a generic process for CO_2 capture from the SCPC power plant. The CO_2 capture process was modeled using Bryan Research and Engineering, Inc. ProMax 3.2 software and a solvent with the properties of monoethanolamine (MEA). The property package used for the simulations was “Amine Sweetening – PR,” which uses the Peng-Robinson equation of state for the vapor properties and the Electrolytic ELR package for the liquid properties. The column type was TSWEET Kinetics, with a VLE flash, and the convergence was based on the Composition Dependent Enthalpy Model and Boston-Sullivan Non-Ideal Inner Loop Model.

The data from the simulation were adjusted to reflect published information for various enhanced amines to provide a more accurate picture of the performance of state-of-the-art CO_2 capture technologies. The main adjustment to the simulation was the solvent regeneration duty, which was assumed to be the same on a CO_2-mass specific basis for both SCPC and NGCC cases. The rich and lean stream flow rates in the simulation were 8.2 million kilogram per hour (kg/h) and 7.5 million kg/h, respectively. Additional data from the simulation, including temperature and stream information, are provided in Appendix B. While additional optimizations may be performed that would improve the design and performance of the system and potentially reduce its cost, the design envisioned serves as a good basis for discussion of the technology requirements that will be necessary for scaling up CO_2 capture systems for large coal fired power plants. Optimization of the CO_2 capture process was not a primary goal of this study.

The CO_2 capture process flow schematic is presented in the simplified process flow diagram (PFD) in Appendix C of this report. The CO_2 recovery plant consists of three main sections: CO_2 absorption, solvent stripping, and CO_2 compression. The major pieces of equipment include an absorption column, stripper column, and CO_2 compressor.

The flue gas is directed from the polishing scrubber to the CO_2 absorber column which has a footprint of approximately 18 m by 18 m. The CO_2 absorber is a rectangular concrete column with stainless steel internals that divide the column into six parallel sections. Each parallel section of the CO_2 absorber has a cross section of approximately 7 m by 7 m and three main vertical segments: the CO_2 absorption segment, the overhead cooling segment, and the water wash segment. The absorber would likely have to be lined either with a thin corrosion-resistant steel alloy material or a polymer. The exact nature of the lining would be dictated by the amine selected.

The flue gas is introduced into the bottom of the absorber and moves upward through the lower CO_2 absorption segment of the column. As the flue gas ascends through the column packing, it comes into contact with amine solvent that is introduced at the top of the CO_2 absorption segment of the column and descends countercurrent to the flue gas flow. As the lean solvent comes into contact with the flue gas, it absorbs the CO_2 in the flue gas and reacts to form amine salts. The absorption process is driven by the difference in the partial pressures of the CO_2 in the flue gas and the solution, and the reaction of the CO_2 in the amine solution reduces its partial pressure in the solution. The reaction of amine with CO_2 is shown in Equation 4-1.

$$RNH_2 + CO_2 \leftrightarrow RNHCOO^- + H^+ \qquad \text{Equation 4-1}$$

Lower temperatures enhance the amine/CO_2 reaction, so it is important that the solvent be kept at a low temperature (usually between 32° and 55° C). However, the reaction of amine with CO_2 is exothermic, and it raises the temperature of the solution. A side draw is often necessary in the CO_2 absorption segment to remove some of the solvent, cool it, and return it to the absorption segment. For the purposes of this study, Black & Veatch has assumed that the entire solvent stream is withdrawn and cooled.

The flue gas leaving the CO_2 absorption segment has had 90 percent of the CO_2 removed and is almost totally free of sulfur oxide (SO_x) and NO_2. However, a significant amount of amine solvent and moisture is carried in the flue gas from the CO_2 absorption segment. Therefore, as the flue gas leaves the absorption segment, it moves upward into the cooling segment in the middle part of the absorption column, where the treated flue gas is cooled and washed by water flowing countercurrent to the flue gas stream. Because amine is more readily dissolved in cool water, the water that is used to wash the amine from the flue gas is cooled in a plate-and-frame heat exchanger before it is recycled to the top of the segment. To prevent the wash water from becoming too concentrated with amine, excess wash water is mixed with lean amine and sent to the top of the CO_2 absorption segment.

Although cooling the treated flue gas will condense some water, amine-free water from elsewhere in the capture process is added to maintain a water balance in the amine absorber. This water is introduced into the overhead segment of the column, where the fresh water reduces the amine in the flue gas down to a few parts per million. A demister is used at the exit of the overhead segment of the column to remove water droplets that may have been entrained with the flue gas. The clean flue gas leaving the demister in the overhead segment of each parallel section is combined into one stream and vented to the atmosphere through a stack at the top of the absorption column.

The rich solvent from the bottom of the CO_2 absorber is sent to two parallel stripper columns by a rich solution pump through three plate-and-frame rich/lean solvent heat exchangers. The strippers are cylindrical, packed columns where the rich solvent is heated to liberate the CO_2. After leaving the rich/lean heat exchanger, the pre-heated rich solvent is introduced into the upper sections of the strippers, where it contacts stripping steam. The steam in the strippers is produced by eight reboilers (four per stripper column) at the bottom of each stripper which use LP steam from the power plant to boil the solvent. As the amine solution is heated, the reaction between amine and CO_2 is reversed, causing a higher CO_2 partial pressure in the solution, which results in CO_2 desorption into the vapor phase.

Water/CO_2 vapor exits the top of each stripper and is cooled by five shell and tube heat exchangers to condense the water. The water is separated from the CO_2 stream in two dedicated knockout drums and returned to each stripper column. The CO_2 is relatively free of water vapor and is at a pressure of about 1.7 bar(a) (25 psia). Before being sent to the pipeline, the CO_2 needs to be compressed to 110 bar(a) (1,600 psia), which puts it in a supercritical phase and facilitates transportation by pipeline. The CO_2 from each knockout drum is combined into one stream for compression. Compression from 1.7 bar(a) to 110 bar(a) is accomplished with three stages of compression. The first and second intercooler stages have five and two shell and tube heat exchangers, respectively. After the first stage of compression and cooling, water is condensed from the CO_2 stream and removed in a knockout drum. Although not considered in this study, a pump could be used in the last stage of compression to optimize compression power. At high pressures, the water in the CO_2 stream dissolves more CO_2 and becomes acidic. To avoid corrosion, two adsorbent beds are used to dehydrate the CO_2 stream after the second stage of compression. Only one adsorbent bed is dehydrating at any given time, while the other is being regenerated. The final CO_2 stream has a purity of greater than 99.5 percent.

The lean solvent from each stripper reboiler is cooled in the rich/lean heat exchangers and then further cooled to a temperature suitable for absorption by five lean solution plate and frame coolers prior to being introduced back into the CO_2 absorber through a lean solution pump.

Oxygen, SO_2, and NO_2 react with primary amine solvents in the CO_2 absorber, and these reactions form heat stable salts. Primary amines can also degrade to secondary amines, which would then react with other NO_x compounds. The accumulation of heat stable salts can cause corrosion and solution foaming. Reclamation (not discussed in this study) will be necessary to remove the heat stable salts accumulated in the solvent. Each technology vendor will have its own method of reclaiming solvent, but will typically use a distillation or ion exchange process.

4.1.4 Electricity Generation Performance Summaries

A summary of power plant performance for Cases 1 and 2 is presented in Table 4-1. Integration of 90 percent CO_2 capture and compression processes is expected to reduce the net electrical export capability of an SCPC power plant by about 30 percent. CO_2 emissions to atmosphere, on an absolute metric tonnes per hour (t/h) basis, were reduced from 702 t/h to 73 t/h, a reduction of about 90 percent. CO_2 emissions to the atmosphere, on a net megawatt-hour (MWh-net) basis, were reduced from 834 kg/MWh-net to 124 kg/MWh-net, a net reduction of about 85 percent. A side-by-side comparison of the SCPC power plant reference cases to the NGCC power plant reference cases is presented in Appendix D.

4.1.5 Mass and Energy Balances

Table 4-2 shows the main stream information for the Case 2 CO_2 capture process. The steam use in the stripper reboilers is about 1,740 gigajoule per hour (GJ/h) or 821 t/h of 4.5 bar(a) saturated steam. A simplified PFD of the overall reference SCPC power plant with integral CO_2 capture and compression processes is presented in Appendix C.

Table 4-1 Electricity Generation Performance Summary – Cases 1 and 2

	UNIT	CASE 1	CASE 2
Reference Case Description		Supercritical Pulverized Coal Rankine Cycle	
Fuel Type		Coal	Coal
CO_2 Capture	%	None	90
ELECTRICAL OUTPUT			
Total Gross Output	MW	900.1	756.6
Auxiliary Electric Load			
Power Block	MW	35.5	35.1
Flue Gas Fans	MW	17.2	44.0
Air Quality Systems	MW	5.8	8.5
CO_2 Capture	MW	N/A	5.2
CO_2 Compression	MW	N/A	75.0
Total Auxiliary Electric Load	MW	58.5	167.8
Net Plant Output	MW	841.6	588.8
Energy Penalty (Net output)	%	N/A	-30.0
Energy Penalty (Net output reduction per tonne-CO_2 to pipeline)	MW/(t-CO_2 captured)	N/A	0.40
ELECTRICAL PRODUCTION EFFICIENCY			
Fuel Input (NCV)	GJ/h	7,500	7,500
Fuel Input (GCV)	GJ/h	7,815	7,815
Net Plant Heat Rate (NCV)	kJ/kWh	8,912	12,738
Net Plant Heat Rate (GCV)	kJ/kWh	9,285	13,272
Net Plant Thermal Efficiency (NCV)	%	40.4	28.3
Net Plant Thermal Efficiency (GCV)	%	38.8	27.1
CO_2 EMISSIONS			
CO_2 for Transport	t/h	N/A	629
CO_2 to Atmosphere	t/h	702	73
CO_2 to Atmosphere	kg/MWh-net	834	124

Table 4-2 Case 2 CO_2 Capture Process Major Stream Information

MEDIUM:		FLUE GAS	FLUE GAS	CO_2	CO_2
FROM:		POLISHING SCRUBBER	ABSORBER	STRIPPER	COMPRESSION
TO:		ABSORBER	ATMOSPHERE	COMPRESSION	STORAGE
Mole-flow	kmol/h	135,350	117,802	15,021	14,297
Mass-flow	kg/s	1,083	891	178	175
Mass-flow	t/h	3,898	3,209	642	630
Vol.-flow, gas	Nm^3/min	50,562	44,007	5,611	5,341
Pressure	kPa	115.51	108.61	186.16	11,032
Temperature	°C	54	51	48	38
COMPOSITION					
N_2	%mole	70.22	80.68	0.01	0.02
CO_2	%mole	11.78	1.35	95.18	99.98
O_2	%mole	5.03	5.78	0.00	0.00
H_2O	%mole	12.97	12.19	4.80	0.00
NO_2	%mole	0.00	0.00	0.00	0.00
CO	%mole	0.00	0.00	0.00	0.00
SO_2+SO_3	%mole	0.00	0.00	0.00	0.000
Total	%mole	100.00	100.00	100.00	100.00
MOLAR FLOW					
N_2	kmol/h	95,041.37	95,039.12	2.21	2.21
CO_2	kmol/h	15,943.99	1,591.21	14,297.47	14,294.39
O_2	kmol/h	6,808.00	6,809.98	0.30	0.30
H_2O	kmol/h	17,554.64	14,361.01	720.82	0.00
NO_2	kmol/h	0.00	0.00	0.00	0.00
CO	kmol/h	0.00	0.00	0.00	0.00
SO_2+SO_3	kmol/h	2.17	0.00	0.00	0.00
Total	kmol/h	135,350.17	117,801.32	15,020.80	14,296.90
MASS FLOW					
N_2	kg/s	739.74	739.72	0.02	0.02
CO_2	kg/s	194.92	19.45	174.79	174.75
O_2	kg/s	60.52	60.53	0.00	0.00
H_2O	kg/s	87.85	71.87	3.61	0.00
NO_2	kg/s	0.00	0.00	0.00	0.00
CO	kg/s	0.00	0.00	0.00	0.00
SO_2+SO_3	kg/s	0.04	0.00	0.00	0.00
Total	kg/s	1,083.06	891.58	178.41	174.77

kg/s - Kilograms per second.
kmol/h - Kilomoles per hour.
Nm^3/min - Normal cubic meter per minute.

4.1.6 Equipment

Preliminary major equipment lists and site arrangement drawings were developed for each of the reference power plant cases. Both the major equipment lists and site arrangement drawings illustrate the differences between a conventional large-scale modern power plant and a similar power plant constructed with integrated 90 percent CO_2 capture and compression processes. Key information on the SCPC plant with capture is provided in Table 4-3.

Table 4-3 Key Equipment Information for SCPC Plant with Capture

FEATURE	VALUE
Number of Absorbers	1
Absorber Cross-Sectional Area, m^2	317
Absorber Height, m	28
Number of Strippers	2
Stripper Diameter, m	7.2
Stripper Height, m	23
Number of Stripper Reboilers	8
Number of Rich/Lean Exchangers	3
Number of Stripper Overhead Coolers	5
Number of Lean Amine Coolers	5
Number of CO_2 Compressor Trains	2

The preliminary major equipment lists (Appendix E) provide the description, type, quantity installed, key design parameters, and other information for each piece of equipment listed.

The preliminary site arrangement drawings (Appendix F) for the reference cases serve as a good comparison tool to show the relative scale of the CO_2 capture and compression equipment and structures compared to the remainder of the power plant.

The layout of the SCPC plant with CO_2 capture took into account the following objectives:

- Minimize the distance between the polishing scrubber and absorber in order to minimize flue gas duct length/cost.
- Minimize the distance between the power plant's Rankine steam cycle and stripper reboilers in order to minimize the steam and return condensate piping length/cost.
- Minimize the distance between the stripper reboilers and stripper columns.
- Minimize the distance between the stripper columns and CO_2 compression in order to minimize LP CO_2 piping length/cost.
- Minimize the distance between CO_2 compression and high-voltage electrical systems.
- Maintain access to AQC equipment, flue gas fans, stripper reboilers, process pumps, and other process heat exchangers.

The balance of the process equipment, composed primarily of heat exchangers and pumps, was placed on a multi-tiered steel structure situated between the absorber and stripper columns. The location of the balance of the process equipment is considered less critical than the location of the absorber, strippers, reboilers, and CO_2 compression.

4.1.7 Utility Requirements

A summary of utility consumption and waste production for Reference Cases 1 and 2 is presented in Table 4-4. In accordance with the reference case design basis, the fuel requirements for both cases are the same. Because of this, makeup requirements for most of the AQC systems chemicals and waste streams for bottom ash, fly ash, and FGD gypsum byproduct remain unchanged. Case 2 does have additional chemical requirements in the form of sodium hydroxide for the polishing scrubber, advanced amine solvent, and adsorbent for CO_2 dehydration. Case 2 will also have an additional waste stream composed in part of spent amine solvent. Water requirements for Case 2 are markedly greater, with a total makeup water requirement of about 12,600 m^3/h compared to the Case 1 total makeup flow of 9,900 m^3/h. Most of the difference is in the cooling tower makeup requirements. It is expected that about 80 percent of the FGD makeup water requirement can be met by the cooling tower blowdown stream. The 58 m^3/h of water condensed from the CO_2 capture process can also be used as cooling tower makeup.

Table 4-4 Utility Requirements and Waste Summary – Cases 1 and 2

	UNIT	CASE 1	CASE 2
Reference Case Description		Supercritical Pulverized Coal Rankine Cycle	
Fuel Type		Coal	Coal
CO_2 Capture	%	None	90
PLANT UTILITY CONSUMPTION			
Fuel	kg/h	293,300	293,300
Makeup Water			
FGD(s)	m^3/h	295	59
Cooling Tower	m^3/h	9,600	12,500
Cycle Makeup	m^3/h	25.9	26.1
29% Aqueous Ammonia	kg/h	960	960
Powdered Activated Carbon	kg/h	350	350
Limestone	kg/h	7,600	7,600
Sodium Hydroxide Granules (NaOH)	kg/h	N/A	32
Advanced Amine Solvent$^{(1)}$	kg/h	N/A	283
CO_2 Dehydration Adsorbent$^{(2)}$	kg/h	N/A	16
PLANT WASTE PRODUCTION			
Wastewater			
Cooling Tower Blowdown	m^3/h	1,900	2,300
FGD Bleed Streams	m^3/h	100	100.5
CO_2 Capture Wastewater	m^3/h	N/A	(Note 3)
Bottom Ash	kg/h	4,000	4,000
Fly Ash/PJFF Solids	kg/h	36,700	36,700
Gypsum (10% moisture)	kg/h	13,100	13,100
Amine Waste	kg/h	N/A	146

Notes:

1. Amine degradation includes degradation from oxygen and sulfur, but excludes NO_2.
2. Bed replacement every 3 to 5 years.
3. The CO_2 capture plant is expected to have minimal wastewater discharge. The water condensed from flue gas and CO_2 streams is used for cooling tower makeup.

4.2 NATURAL GAS PLANTS

4.2.1 Main Power Block Description

NGCC power plants are mature designs that have been used to produce electricity from natural gas since the 1960s. NGCC power plants are considered to be highly reliable and efficient. Various designs and configurations of this technology exist that offer flexibility to match electrical system demands and type(s) of fuel available.

The selected NGCC reference configuration is designed around two Mitsubishi Heavy Industries (MHI) 501GAC combustion turbine generators (CTGs). The 501GAC has just recently been made available commercially. The 501GAC is a large advanced class, heavy frame, single-shaft, single casing machine with a 17 stage axial flow compressor, a four stage turbine, and 16 can-annular-type combustors. The compressor operates at a 20:1 compression ratio. The baseload turbine inlet temperature is approximately 1,500° C (2,732° F). The generator is driven at the compressor end to allow for axial exhaust to the HRSG. Modulating inlet guide vanes are used to maintain high exhaust temperatures for combined cycle operation at part-load conditions. The MHI 501GAC is fully air cooled in lieu of steam cooling as found on the MHI 501G1 (60 Hz) and 701G2 (50 Hz).

The CTG produces electricity and high temperature exhaust by compressing large volumes of air, adding heat to the compressed air through combustion of natural gas, and expanding the hot air to drive a turbine coupled to a generator to produce electricity. Approximately two-thirds of the electricity generated by a heavy frame CTG-based combined cycle is produced by the CTGs (excluding supplemental firing in the HRSGs, if used).

Additional electricity is produced using two triple pressure reheat HRSGs, which utilize the thermal energy from the hot CTG exhaust gases to generate steam. The HRSGs supply HP, IP, and LP steam to a single reheat STG. A schematic of a combined cycle power plant is shown on Figure 4-3. The HRSG configuration depicted on Figure 4-3 is a horizontal flue gas flow design. A vertical flue gas flue design is also commonly used. A number of power augmentation options are available for combined cycle power plants, such as CTG inlet air cooling and HRSG supplemental duct firing. These options have not been included in this study.

Waste heat from the condensing of LP steam in the condenser is typically rejected to an open cooling water system, a closed cycle cooling water system, or an air cooled condenser is used. Selection of the cooling water system is location-specific and dependent on several factors, including the availability of raw water and suitable discharge location. This study assumes the use of a closed circulating cooling water system utilizing a wet mechanical-draft cooling tower for heat rejection from the condenser and other plant cooling needs.

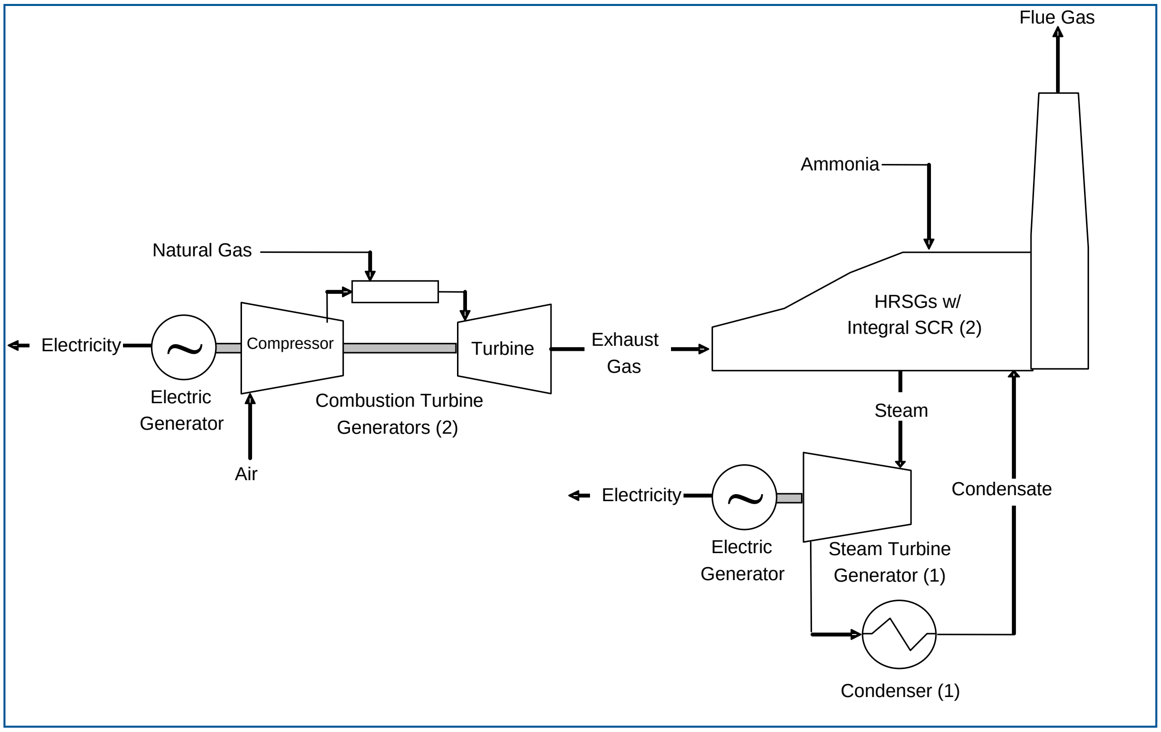


Figure 4-3 **Typical NGCC Plant**

4.2.2 Post-Combustion Emissions Control Description (Excluding CO_2 Capture)

An oxidation catalyst and SCR system were selected for the NGCC reference plant design cases.

4.2.2.1 Carbon Monoxide Reduction

An oxidation catalyst was selected for the reference NGCC power plant. An oxidation catalyst, often referred to as a CO catalyst, oxidizes CO and unburned hydrocarbons in the exhaust gases to form CO_2. The use of an oxidation catalyst is a proven post-combustion control technology widely used to abate CO emissions. No reagent injection is necessary. The oxidation catalyst reactor housing is situated in the exhaust gas path and is integral to the HRSG, located upstream of the SCR system.

4.2.2.2 NO_x Reduction

The gas turbines selected for the reference NGCC power plant minimize NO_x emissions using dry low NO_x (DLN) combustion systems. In addition, an SCR system was selected to further reduce NO_x emissions. The SCR reactor housing and ammonia injection grid are situated in the exhaust gas path and are integral to the HRSG, located downstream of the oxidation catalyst in an area of the HRSG where temperatures are between about 315 and 425° C (600 and 800° F). Ammonia is injected into the SCR, where it reacts with NO_x to create nitrogen and water. Ammonium bisulfate and ammonium sulfite could form and foul surfaces downstream of the ammonia injection grid for higher sulfur fuels. However, for natural gas with a sulfur concentration of 8 ppm, ammonium bisulfate and ammonium sulfite formation is not a concern.

4.2.3 Post-Combustion CO_2 Capture Description

Black & Veatch modeled a generic process for CO_2 capture from the combined cycle power plant. The CO_2 capture process was modeled using Bryan Research and Engineering, Inc. ProMax 3.2 software and properties of a generic MEA and using the same thermodynamic property package as settings as described in Section 4.1.3. The data from the simulation were adjusted to reflect published information for various enhanced amines to provide a more representative picture of the performance of state-of-the-art CO_2 capture technologies. The main adjustment to the simulation was the solvent regeneration duty, which was assumed to be the same on a CO_2-mass specific basis for both SCPC and NGCC cases. The rich and lean stream flow rates in the simulation were 3.3 million kg/h and 3.2 million kg/h, respectively. Additional data from the simulation, including temperature and stream information, is provided in Appendix B. While additional optimizations may be performed that would improve the design and performance of the system and potentially reduce its cost, the design envisioned serves as a good basis for discussion of the technology requirements that will be necessary for scaling up CO_2 capture systems for large combined cycle power plants.

The CO_2 capture process flow schematic is presented in the simplified PFD in Appendix C of this report. The CO_2 recovery plant consists of three main sections: CO_2 absorption, solvent stripping, and CO_2 compression. The major pieces of equipment are an absorption column, stripper column, and CO_2 compressor.

The flue gas is directed from each HRSG outlet to the CO_2 absorber column by a flue gas fan. The CO_2 absorber is a rectangular concrete column with stainless steel internals that divide the column into six parallel sections. Each parallel section of the CO_2 absorber has a cross section of approximately 7 m x 7 m and has four main vertical segments: the quench cooler segment, the CO_2 absorption segment, the overhead cooling segment, and the water wash segment.

The absorption process is driven by the difference in the partial pressures of the CO_2 in the flue gas and the solution, and the reaction of the CO_2 in the amine solution reduces its partial pressure in the solution. Lower temperatures enhance the amine/CO_2 reaction (refer to Equation 4-1), so it is important that the solvent be kept at a low temperature (usually between 32 and 55° C). In the combined cycle application, it is particularly important that the low temperature be maintained because of the lower partial pressure of CO_2 in the flue gas. For the purposes of this study, Black & Veatch has assumed that the entire solvent stream is withdrawn and cooled at a suitable point in the absorber column. Additionally, the pressure drop through the absorber and out of the absorber vent is expected to be about 13.8 kilopascals gauge (kPa[g]) (2 pounds per square inch gauge [psig]). The flue gas exiting the HRSG is at a temperature of approximately 100° C and at a pressure near atmospheric. This means that the flue gas must be cooled and slightly pressurized before entering the CO_2 absorption segment of the absorber. The flue gas pressure is increased by two parallel fans located upstream of the absorber. Because of the large volume of the flue gas, the fans consume a significant amount of power.

The hot, pressurized flue gas is introduced into the bottom of the absorber and moves upward through the quench cooler segment of each parallel section. Cold water descends through packing to enhance contact between the flue gas and the cold water. The water is heated as it descends through the cooler, and part of it evaporates into the flue gas stream. This evaporation is more than offset by the water in the flue gas that condenses as it cools. The hot water exits the bottom of the absorber and is cooled in three plate-and-frame quench water coolers before it is recycled back to the top of the quench cooler segment of the absorber. The cool flue gas (approximately 32° C) then enters the lower CO_2 absorption segment of the column. As the flue gas ascends through the column packing, it comes into contact with amine solvent that is introduced at the top of the CO_2 absorption segment and descends countercurrent to the flue gas flow. As the lean solvent comes into contact with the flue gas, it absorbs the CO_2 in the flue gas and reacts to form amine salts. However, the reaction of amine with CO_2 is exothermic, so it raises the temperature of the solution. This means that a side draw is necessary at some point in the CO_2 absorption segment to remove some of the solvent, cool it down, and return it to the absorption segment.

The flue gas leaving the CO_2 absorption segment has had 90 percent of the CO_2 removed and is almost totally free of NO_2. However, a significant amount of amine solvent and moisture is carried in the flue gas from the CO_2 absorption segment. Therefore, as the flue gas leaves the absorption segment, it moves upward into the cooling segment in the absorption column, where the treated flue gas is cooled and washed by water flowing countercurrent to the flue gas stream. Because amine is more readily dissolved in cool water, the water used to wash the amine from the flue gas is cooled in a plate-and-frame heat exchanger before it is recycled to the top of the segment. To prevent the wash water from becoming too concentrated with amine, excess wash water is mixed with lean amine and sent to the top of the CO_2 absorption segment.

Although cooling the treated flue gas will condense some water, amine-free water from elsewhere in the capture process is added to maintain a water balance in the amine absorber. This water is introduced into the overhead segment of the column, where the fresh water reduces the amine in the flue gas to a few parts per million. A demister is used at the exit of the overhead segment of the column to remove water droplets that may have been entrained with the flue gas. The clean flue gas leaving the demister in each parallel section is combined into one stream and vented to the atmosphere through a stack at the top of the absorption column.

The rich solvent from the bottom of the CO_2 absorber is sent to a single stripper column by a rich solution pump through two plate-and-frame rich/lean solvent heat exchangers. The stripper is a cylindrical, packed column, where the rich solvent is heated to liberate the CO_2. After leaving the rich/lean heat exchangers, the pre-heated rich solvent is introduced into the upper sections of the stripper, where it contacts stripping steam. The steam in the stripper is produced by four reboilers at the bottom of the stripper, which use LP steam from the power plant to boil the lean solvent. As the rich amine solution is heated, the reaction of amine and CO_2 moves to the left, causing a higher CO_2 partial pressure in the solution, which results in CO_2 desorption into the vapor phase.

Water/CO_2 vapor exits the top of each stripper and is cooled by two shell-and-tube heat exchangers to condense the water. The water is separated from the CO_2 stream in a knockout drum and returned to the stripper column. The CO_2 is relatively free of water vapor and is at a pressure of about 1.7 bar(a). Before being sent to the pipeline, the CO_2 needs to be compressed to about 110 bar(a), which puts it in a supercritical phase and facilitates transportation by pipeline. Compression from 1.7 bar(a) to 110 bar(a) is accomplished with three stages of compression. After the first stage of compression and cooling, water is condensed from the CO_2 stream and removed in a knockout drum. At high pressures, the water in the CO_2 stream dissolves more CO_2 and becomes acidic. To avoid corrosion, adsorbent beds are used to dehydrate the CO_2 stream after the second stage of compression and intercooling. Only one bed is dehydrating at any given time, while the other is being regenerated. The final CO_2 stream has a purity of greater than 99.5 percent.

The lean solvent from each stripper reboiler is cooled in the rich/lean heat exchanger and then further cooled to a temperature suitable for absorption by one lean solution plate-and-frame cooler prior to being introduced back into the CO_2 absorber through a lean solution pump.

Oxygen and NO_2 react with primary amine solvents in the CO_2 absorber, and these reactions form heat stable salts. Primary amines can also degrade to secondary amines, which would then react with other NOx compounds. The accumulation of heat stable salts can cause corrosion and solution foaming. Reclamation (not discussed in this study) will be necessary to remove the heat stable salts accumulated in the solvent. Each technology vendor will have its own method of reclaiming solvent, but will typically use distillation or ion exchange processes.

4.2.4 Electricity Generation Performance Summaries

A summary of power plant performance for Cases 3 and 4 is presented in Table 4-5. Integration of 90 percent CO_2 capture and compression processes is expected to reduce the net electrical output capability of an NGCC power plant by about 14.5 percent. CO_2 emissions to atmosphere, on a t/h basis, were reduced from 276 t/h to 28 t/h, a reduction of about 90 percent. CO_2 emissions to atmosphere, on a MWh-net basis, were reduced from 349 kg/MWh-net to 41 kg/MWh-net, a net reduction of about 88 percent. A side-by-side comparison of the SCPC power plant reference cases to the NGCC power plant reference cases is presented in Appendix D.

4.2.5 Mass and Energy Balances

Table 4-6 shows the main stream information for the CO_2 capture process. The steam use in stripper reboilers is about 700 GJ/h or 330 t/h of 4.5 bar(a) saturated steam.

Table 4-5 Electricity Generation Performance Summary – Cases 3 and 4

	UNIT	CASE 3	CASE 4
Reference Case Description		2-on-1 G-Class Gas Turbine Combined Cycle	
Fuel Type		Natural Gas	Natural Gas
CO_2 Capture	%	None	90
ELECTRICAL OUTPUT			
Gross Output			
STG	MW	280.4	223.7
Gas Turbine Generators (total)	MW	529.5	529.5
Total Gross Output	MW	809.9	753.2
Auxiliary Electric Load			
Power Block	MW	19.6	22.1
Flue Gas Fans	MW	N/A	26.1
CO_2 Capture	MW	N/A	3.6
CO_2 Compression	MW	N/A	25.5
Total Auxiliary Electric Load	MW	19.6	77.3
Net Plant Output	MW	790.3	675.9
Energy Penalty (Net output)	%	N/A	-14.5
Energy Penalty (Net output reduction per tonne-CO_2 to pipeline)	MW/(t-CO_2 captured)	N/A	0.46
ELECTRICAL PRODUCTION EFFICIENCY			
Fuel Input (NCV)	GJ/h	4,906	4,906
Fuel Input (GCV)	GJ/h	5,433	5,433
Net Plant Heat Rate (NCV)	kJ/kWh	6,208	7,259
Net Plant Heat Rate (GCV)	kJ/kWh	6,874	8,038
Net Plant Thermal Efficiency (NCV)	%	58.0	49.6
Net Plant Thermal Efficiency (GCV)	%	52.4	44.8
CO_2 EMISSIONS			
CO_2 for Transport	t/h	N/A	250
CO_2 to Atmosphere	t/h	276	28
	kg/MWh-net	349	41

Table 4-6 Case 4 CO_2 Capture Process Major Stream Information

MEDIUM:		FLUE GAS	FLUE GAS	CO_2	CO_2
FROM:		FLUE GAS FANS	ABSORBER	STRIPPER	COMPRESSION
TO:		ABSORBER	ATMOSPHERE	COMPRESSION	STORAGE
Mole-flow	kmol/h	154,287	147,909	5,975	5,687
Mass-flow	kg/s	1,212	1,139	71	70
Mass-flow	t/h	4,362	4,098	255	250
Vol.-flow, gas	Nm^3/min	60,353	55,254	2,232	2,125
Pressure	kPa	117.21	108.61	186.16	11,032
Temperature	°C	109	51	43	38
COMPOSITION					
N_2	%mole	75.16	78.40	0.02	0.02
CO_2	%mole	4.09	0.42	95.18	99.97
O_2	%mole	11.99	12.51	0.01	0.01
H_2O	%mole	8.76	8.68	4.80	0.00
NO_2	%mole	0.00	0.00	0.00	0.00
CO	%mole	0.00	0.00	0.00	0.00
SO_2+SO_3	%mole	0.00	0.00	0.00	0.000
Total	%mole	100.00	100.00	100.00	100.00
MOLAR FLOW					
N_2	kmol/h	115,961.49	115,960.51	1.10	1.10
CO_2	kmol/h	6,312.99	614.00	5,687.00	5,685.77
O_2	kmol/h	18,502.25	18,503.42	0.34	0.34
H_2O	kmol/h	13,510.22	12,832.60	286.74	0.00
NO_2	kmol/h	0.00	0.00	0.00	0.00
CO	kmol/h	0.00	0.00	0.00	0.00
SO_2+SO_3	kmol/h	0.00	0.00	0.00	0.00
Total	kmol/h	154,286.95	147,910.53	5,975.18	5,687.21
MASS FLOW					
N_2	kg/s	902.57	902.56	0.01	0.01
CO_2	kg/s	77.18	7.51	69.52	69.51
O_2	kg/s	164.46	164.47	0.00	0.00
H_2O	kg/s	67.61	64.22	1.43	0.00
NO_2	kg/s	0.00	0.00	0.00	0.00
CO	kg/s	0.00	0.00	0.00	0.00
SO_2+SO_3	kg/s	0.00	0.00	0.00	0.00
Total	kg/s	1,211.82	1,138.76	70.97	69.52

4.2.6 Equipment

Preliminary major equipment lists and site arrangement drawings were developed for each of the reference power plant cases. Both the major equipment lists and site arrangement drawings illustrate the differences between a conventional large-scale modern power plant and a similar power plant constructed with integrated 90 percent CO_2 capture and compression processes.

The preliminary major equipment lists (Appendix E) provide the description, type, quantity installed, key design parameters, and other information for each piece of equipment listed. Key information on the NGCC plant with capture is provided in Table 4-7.

Table 4-7 Key Equipment Information for NGCC Plant with Capture

FEATURE	VALUE
Number of absorbers	1
Absorber Cross-Sectional Area, m^2	317
Absorber Height, m	28
Number of Strippers	1
Stripper Diameter, m	7
Stripper Height, m	23
Number of Stripper Reboilers	4
Number of Rich/Lean Exchangers	2
Number of Stripper Overhead Coolers	2
Number of Lean Amine Coolers	1
Number of CO_2 Compressor Trains	2

The preliminary site arrangement drawings (Appendix F) for the reference cases serve as a good comparison tool to show the relative scale of the CO_2 capture and compression equipment and structures compared to the remainder of the power plant.

The layout of the NGCC plant with CO_2 capture took into account the following objectives:

- Minimize the distance between the HRSGs and absorber in order to minimize flue gas duct length/cost.
- Minimize the distance between the power plant's Rankine steam cycle and stripper reboilers in order to minimize the steam and return condensate piping length/cost.
- Minimize the distance between the stripper reboilers and stripper column.
- Minimize the distance between the stripper column and CO_2 compression in order to minimize low pressure CO_2 piping length/cost.
- Minimize the distance between CO_2 compression and high voltage electrical systems.
- Maintain access to combustion turbines, HRSGs, steam turbine, flue gas fans, stripper reboilers, process pumps, and other process heat exchangers.

The balance of the process equipment, composed primarily of heat exchangers and pumps, was placed on a multi-tiered steel structure situated between the absorber and stripper columns. The location of the balance of the process equipment is considered less critical than the location of the absorber, stripper, reboilers, and CO_2 compression.

4.2.7 Utility Requirements

A summary of utility consumption and waste production for Reference Cases 3 and 4 is presented in Table 4-8. In accordance with the reference case design basis, the fuel requirements for both cases are the same. Because of this, makeup requirements for aqueous ammonia are unchanged. Case 4 does have additional chemical requirements in the form of advanced amine solvent and adsorbent for CO_2 dehydration. Case 4 will also have an additional waste stream composed in part of spent amine solvent. Water requirements for Case 4 are markedly greater, with a total makeup water requirement of about 6,400 m^3/h compared to the Case 3 total makeup flow of 4,400 m^3/h. Approximately 64 m^3/h of condensate from the flue gas quench segment of the absorber and CO_2 compression intercoolers is also used for cooling tower makeup.

Table 4-8 Utility Requirements and Waste Summary – Cases 3 and 4

	UNIT	CASE 3	CASE 4
Reference Case Description		2-on-1 G-Class Gas Turbine Combined Cycle	
Fuel Type		Natural Gas	Natural Gas
CO_2 Capture	%	None	90
PLANT UTILITY CONSUMPTION			
Fuel	kg/h	50,400	50,400
Fuel	NM^3/h	68,600	68,600
Makeup Water			
Cooling Tower	m^3/h	4,400	6,400
Cycle Makeup	m^3/h	7.7	8.1
29% Aqueous Ammonia	kg/h	200	200
Advanced Amine Solvent(1)	kg/h	N/A	210
CO_2 Dehydration Adsorbent(2)	kg/h	N/A	7
PLANT WASTE PRODUCTION			
Wastewater			
Cooling Tower Blowdown	m^3/h	880	1,300
CO_2 Capture Wastewater	m^3/h	N/A	(Note 3)
Amine Waste	kg/h	N/A	108

Notes:

1. Amine degradation includes degradation from oxygen and sulfur, but excludes NO_2.
2. Bed replacement every 3 to 5 years.
3. The CO_2 capture plant is expected to have minimal wastewater discharge. The water condensed from flue gas and CO_2 streams is used for cooling tower makeup.

Appendix D: Amine Reclaimer Spreadsheet Model

Disclaimer: This amine reclaimer spreadsheet is confidential information and has been transmitted to IEAGHG for example purposes only.
Trimeric, The University of Texas and URS assume no responsibility for these calculations if the inputs are manipulated from their original values.

Manual Inputs
Adjusts automatically with solvent choice

Input Parameters

General specifications			Notes/Reference
Flue Gas	**Coal**		Specify "Coal" or "NGCC"; see "Base Case Parameters" tab for parameters dependent on selection
Solvent	**8 m PZ**		Specify "7 m MEA", "8 m PZ", or "7/2 m MDEA/PZ"; see "Base Case Parameters" tab for parameters influenced by selection
Reclaimer type	**Ion Exchange**		Specify "Thermal," "Ion Exchange," or "Electrodialysis"; see "Base Case Parameters" tab for parameters influenced by selection
CO_2 Removal	%	90	90 % capture of CO_2 is assumed to be typical for post-combustion capture
Absorber operating temperature	°C	40	Assumption per Aspen model from University of Texas
Stripper operating temperature	°C	150	Thermal degradation rate of $3x10^{-6}$ s^{-1} (120 °C for MEA) deemed tolerable in previous study (Davis, 2009)
Cross exchanger hot side approach temperature	°C	5	Assumption per Aspen model from University of Texas
Total liquid holdup	minutes	30	Determines total solvent inventory. In conversations with pilot plant operators, 30 minutes holdup is typical for an amine scrubbing plant.
Residence time in sump & reboiler	minutes	5	Assumption per Aspen model from University of Texas
Residence time in packing	minutes	5	Assumption per Aspen model from University of Texas
Residence time in cross exchanger (hot rich solvent)	minutes	0.5	Majority of oxidation assumed to occur in rich solvent during and after heating in the cross exchanger and before entering the stripper where any remaining dissolved oxygen will be flashed off. Holdup estimated to be 30 seconds (Closmann, 2011)
Dissolved stainless steel metal concentration	0: low; 1: high	1	No consistent rate of corrosion could be determined from literature review, value specifies whether dissolved metal concentration is high enough to catalyze oxidation.
Amine vapor concentration leaving water wash	ppmv	1	1 ppmv assumed to be an acceptable emission rate
Reclaimer drawoff ratio [feed/L]	kg/kg	0.001	Mass flow rate of reclaimer feed relative to solvent circulation rate

Results

Lean solvent composition (with reclaiming)

Total contamination	wt%	1.24
Total heat stable salts accumulation	wt%	0.92
Ammonia	wt%	0.00
EDA + 2-imid	wt%	0.10
1-MPZ + 1,4-DMPZ	wt%	0.00
AEP (MDEA/PZ)	wt%	0.00
Formate	wt%	0.11
Oxalate, acetate, glycolate	wt%	0.05
Sulfate	wt%	0.42
Nitrate	wt%	0.28
Nitrite	wt%	0.00
Chloride	wt%	0.06
Fluoride	wt%	0.00
HEIA	wt%	0.00
triHEIA	wt%	0.00
HEEDA	wt%	0.00
MEA trimer	wt%	0.00
HEI	wt%	0.00
Nonvolatile PZ derivatives	wt%	0.15
DEA + Polymers	wt%	0.00
HeGly	wt%	0.00
Bicine	wt%	0.01
MNPZ	ppm (wt)	123.40
Nitroso-HeGly	ppm (wt)	0.00
Hg	ppm (wt)	0.20
Se	ppm (wt)	0.25
As	ppm (wt)	0.04
Cd	ppm (wt)	0.02
Cr	ppm (wt)	0.49
Pb	ppm (wt)	0.05
Fly ash	wt%	0.07
Fe + other SSM's	ppm (wt)	109.71

Reclaimer waste composition

Reclaimer feed rate	kg/hr	16,211
Waste stream (dry)	kg/hr	284
Waste stream (total)	kg/hr	5,674
Waste stream (total)	kg/MT CO_2	8.40
Amine	wt%	1.0
NaOH	wt%	1.6
Formate	wt%	0.3
Oxalate, acetate, glycolate	wt%	0.1
Sulfate	wt%	1.1
Nitrate	wt%	0.7
Nitrite	wt%	0.0
Chloride	wt%	0.2
Fluoride	wt%	0.0
HEIA	wt%	0.0
triHEIA	wt%	0.0
HEEDA	wt%	0.0
MEA trimer	wt%	0.0
HEI	wt%	0.0
Nonvolatile PZ derivatives	wt%	0.0
DEA + Polymers	wt%	0.0
HeGly	wt%	0.0
Bicine	wt%	0.0
MNPZ	wt%	0.0
Nitroso-HeGly	ppm	0.0
Hg	ppm	0.0
Se	ppm	0.0
As	ppm	0.0
Cd	ppm	0.0
Cr	ppm	0.0
Pb	ppm	0.0
Fly ash	wt%	0.0
Fe + other SSM's	wt%	0.0

Amine Loss Rates

Thermal degradation rate	mmol/kg/hr	0.020
Oxidation rate	mmol/kg/hr	0.054
Nitrosation rate	mmol/kg/hr	0.027
Volatile amine loss rate	mmol/kg/hr	0.016
Additional loss in reclaimer waste	mmol/kg/hr	0.084
Total amine makeup rate	mmol/kg/hr	0.200
Total amine makeup rate	kg/MT CO_2	0.21

Contaminant accumulation rates

Ammonia generation	mmol/kg/hr	0.086
Ammonia emission rate	ppmv	5.40
Formate	mmol/kg/hr	0.041
Oxalate, acetate, glycolate	mmol/kg/hr	0.010
HEIA	mmol/kg/hr	0.000
triHEIA	mmol/kg/hr	0.000
HEI	mmol/kg/hr	0.000

Nonvolatile PZ derivatives	mmol/kg/hr	0.008
DEA + Polymers	mmol/kg/hr	0.000
HeGly	mmol/kg/hr	0.000
Bicine	mmol/kg/hr	0.000
Sulfate	mmol/kg/hr	0.080
Nitrate	mmol/kg/hr	0.081
Nitrite	mmol/kg/hr	0.000
Chloride	mmol/kg/hr	0.030
Fluoride	mmol/kg/hr	0.001
Hg	µg/kg/hr	0.360
Se	µg/kg/hr	0.460
As	µg/kg/hr	0.076
Cd	µg/kg/hr	0.034
Cr	µg/kg/hr	0.901
Pb	µg/kg/hr	0.090
Fly ash	mg/kg/hr	1.201

Disclaimer: This amine reclaimer spreadsheet is confidential information and has been transmitted to IEAGHG for example purposes only.
Trimeric, The University of Texas and URS assume no responsibility for these calculations if the inputs are manipulated from their original values.

Manual Inputs

Flue Gas Options	**Unit**	**Coal**	**NGCC**	**Active Value**	**Source/Basis for Assumption**
Gross Power	MW$_e$	900.1	809.9	900.1	IEAGHG Post Combustion Capture Scale Up Study, 2013/05, February, Table 1-2
CO_2/MWhr	tonne/MWhr	0.834	0.349	0.834	IEAGHG Post Combustion Capture Scale Up Study, 2013/05, February, Table 1-2
CO_2	vol%	11.78	4.09	11.78	IEAGHG Post Combustion Capture Scale Up Study, 2013/05, February, Tables 4-2 and 4-6
O_2	vol%	5.03	11.99	5.03	IEAGHG Post Combustion Capture Scale Up Study, 2013/05, February, Tables 4-2 and 4-6
H_2O	vol%	12.97	8.76	12.97	IEAGHG Post Combustion Capture Scale Up Study, 2013/05, February, Tables 4-2 and 4-6
SO_2	ppmv	5	0.5	5	Assumption decided by project team based upon coal plants with FGD for SO2 removal and natural gas plants
NO_x	ppmv	45	15	45	Communication with a NOx combustion expert for coal-fired units equipped with SCR
NO_2	ppmv	1.5	0.5	1.5	Communication with a NOx combustion expert for coal-fired units equipped with SCR
HCl	ppmv	1.85	0	1.85	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
HF	ppmv	0.075	0	0.075	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
Hg	µg/Nm^3	1.8	0	1.8	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
Se	µg/Nm^3	2.3	0	2.3	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
As	µg/Nm^3	0.38	0	0.38	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
Cd	µg/Nm^3	0.17	0	0.17	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
Cr	µg/Nm^3	4.5	0	4.5	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
Pb	µg/Nm^3	0.45	0	0.45	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
Fly ash	µg/Nm^3	6	0	6	United States Mercury and Air Toxics (MATS) Rule; 2010 Information Collection Request (ICR) from US EPA
SO_2 removal	%	90	90	90	Assumption decided by project team based upon pilot plant experience (Nielsen, 2013)
NOx removal (as nitrate)	%	10	10	10	Assumption decided by project team based upon pilot plant experience (Nielsen, 2013)
NO_2 removal (as nitrite)	%	0	0	0	Based on solvent selection: MEA = 65 %, PZ & MDEA/PZ = 100 %
HCl/HF removal	%	90	90	90	Assumption decided by project team
Hg removal	%	50	50	50	Assumption decided by project team
Se removal	%	50	50	50	Assumption decided by project team
As removal	%	50	50	50	Assumption decided by project team
Cd removal	%	50	50	50	Assumption decided by project team
Cr removal	%	50	50	50	Assumption decided by project team
Pb removal	%	50	50	50	Assumption decided by project team
Fly ash removal	%	50	50	50	Assumption decided by project team
Lean Loading	mol CO_2/mol alkalinity	0.31	0.28	0.31	Assumption per Aspen model from University of Texas
Rich Loading	mol CO_2/mol alkalinity	0.41	0.37	0.41	Assumption per Aspen model from University of Texas

Reclaiming Options	**Unit**	**Thermal**	**Ion Exchange**	**Electrodialysis**	**Active Value**	**Source/Basis for Assumption**
Amine Recovery (%)	%	95	99	97	99	Refer to Table 5-3 of "Evaluation of Reclaimer Sludge Disposal from Post-Combustion CO2 Capture"
Heat Stable Salt Removal (%)	%	100	90	91.5	90	Refer to Table 5-3 of "Evaluation of Reclaimer Sludge Disposal from Post-Combustion CO2 Capture"
Nonvolatiles Removal (%)	%	100	0	0	0	Generic Assumption Based Upon Literature Review
Metals Removal (%)	%	100	0	0	0	Generic Assumption Based Upon Literature Review
NaOH added to reclaimer feed	mol/mol heat stable salt	1	1	1	1	Generic Assumption Based Upon Literature Review
Water added to reclaimer waste	kg water/kg waste	0	19	19	19	Generic Assumption Based Upon Literature Review. Using wiped film evaporator to remove thermal sludge without dilution

Solvent Options	**Unit**	**7 m MEA**	**8 m PZ**	**7/2 m MDEA/PZ**	**Active Value**	**Source/Basis for Assumption**
Default stripper temperature	°C	120	150	135	150	
Concentration (amine 1)	m	7	8	7	8	
Concentration (amine 2)	m			2	0	

Concentration (total)	m	7	8	9	8	
Molecular Weight (amine 1)	g/mol	61.08	86.14	119.16	86.14	
Molecular Weight (amine 2)	g/mol			86.14	0	
Molecular Weight (average)	g/mol	61.08	86.14	111.82	86.14	
Lean Loading (Coal)	mol CO_2/mol alkalinity	0.12	0.31	0.11	0.31	Assumption per Aspen model from University of Texas
Rich Loading (Coal)	mol CO_2/mol alkalinity	0.51	0.41	0.25	0.41	Assumption per Aspen model from University of Texas
Lean Loading (NGCC)	mol CO_2/mol alkalinity	0.12	0.28	0.11	0.28	Assumption per Aspen model from University of Texas
Rich Loading (NGCC)	mol CO_2/mol alkalinity	0.49	0.37	0.25	0.37	Assumption per Aspen model from University of Texas
Alkalinity per mole amine 1	mol alkalinity/mol amine	1	2	1	2	
Alkalinity per mole amine 2	mol alkalinity/mol amine	0	0	2	0	
Alkalinity per mole amine (avg)	mol alkalinity/mol amine	1	2	1.22	2.00	
k_0 of thermal degradation	s^{-1}	2.91E-08	2.91E-08	2.91E-08	2.91E-08	First-order reaction rate constant of thermal degradation(Freeman, 2011)
T_0 of thermal degradation	°C	121	163	138	163	(Freeman, 2011)
E_a of thermal degradation	kJ/mol	157	184	184	184	(Freeman, 2011)
k_0 of oxidation	$s^{-1}kPa^{-1}$	1.94E-07	5.15E-08	6.43E-08	5.15E-08	From experimental data in cyclic degradation rig (Voice, 2013)
T_0 of oxidation	°C	127	160	125	160	(Voice, 2013: NH_3 generation activation energy in HTCS)
E_a of oxidation	kJ/mol	46	32	55	32	(Voice, 2013: NH_3 generation activation energy in HTCS)
Thermal degradation stoichiometry		**MEA**	**PZ**	**MDEA/PZ**	PZ	Data: MEA: Davis, 2009; PZ: Freeman, 2011; MDEA/PZ: Closmann, 2011
NH_3	mol/mol amine degraded	0	0.29	0	0.29	See Chapter 4.2.1 of report for complete description of solvent degradation
EDA/2-imid	mol/mol amine degraded	0	0.09	0.00	0.09	
1-MPZ/1,4-DMPZ	mol/mol amine degraded	0	0	0.18	0.00	
AEP (MDEA/PZ only)	mol/mol amine degraded	0	0	0.008	0.00	In MDEA/PZ, AEP is more volatile than MDEA and will not be removed by thermal reclaiming
HEIA	mol/mol amine degraded	0.2	0	0	0	
triHEIA	mol/mol amine degraded	0.05	0	0	0	
Total formate	mol/mol amine degraded	0	0.39	0.007	0.39	Formate and formamide
Total acetate/oxalate/glycolate	mol/mol amine degraded	0	0.02	0.000	0.02	
Nonvolatile PZ derivatives	mol/mol amine degraded	0	0.40	0	0.40	Includes AEP, HEP, PZ polymers
DEA + Polymers	mol/mol amine degraded	0	0	0.64	0.00	DEA and polymers formed from secondary thermal degradation of DEA
Oxidation stoichiometry		**MEA**	**PZ**	**MDEA/PZ**	PZ	Data: MEA: (Voice, 2013) and (da Silva, 2013); PZ: (Voice, 2013) and (Freeman, 2011); MDEA/PZ: (Voice, 2013) and (Closmann, 2011)
NH_3	mol/mol amine degraded	0.67	1	0.22	1.000	See Chapter 4.3.1 of report for complete description of solvent oxidation
EDA/2-imid	mol/mol amine degraded	0	0.17	0.00	0.166	
1-MPZ/1,4-DMPZ	mol/mol amine degraded	0	0	0.27	0.000	
Total formate	mol/mol amine degraded	0.12	0.11	0.12	0.113	
Total acetate/oxalate/glycolate	mol/mol amine degraded	0.01	0.033	0.006	0.033	
Nitrate	mol/mol amine degraded	0.01	0.01	0.01	0.0124	
Nitrite	mol/mol amine degraded	0.002	0.005	0.001	0.005	
HEI	mol/mol amine degraded	0.06	0	0	0	
HeGly	mol/mol amine degraded	0.22	0	0	0	
Bicine	mol/mol amine degraded	0	0	0.05	0	
DEA + Polymers	mol/mol amine degraded	0	0	0.39	0	DEA and polymers formed from secondary thermal degradation of DEA
MNPZ	mol/mol amine degraded	0	0.005	0.001	0.005	
Nitrosamine formation and decomposition		**MEA**	**PZ**	**MDEA/PZ**	PZ	
NO_2 absorption as nitrite	%	65	100	100	100	
Conversion of nitrite to MNPZ	%	0	100	100	100	
NH_3	mol/mol NNO degraded	1	1	1	1	
Total formate	mol/mol NNO degraded	1	1	1	1	

Disclaimer: This amine reclaimer spreadsheet is confidential information and has been transmitted to IEAGHG for example purposes only.
Trimeric, The University of Texas and URS assume no responsibility for these calculations if the inputs are manipulated from their original values.

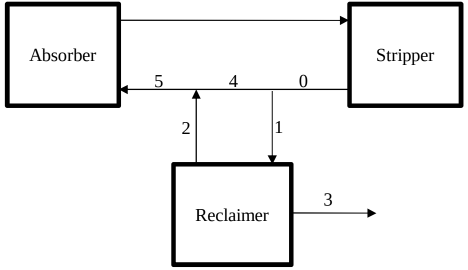
Hours to Reach Steady -State (Nth Hour) 1111

	Lean Solvent Composition (Stream 0)			Feed Stream (Stream 1)					Reclaimed Amine (Stream 2)			Reclaimer Waste Stream (Stream 3)				Lean Solvent (Stream 4)	Lean Solvent Post-Reclaiming (Stream 5)		
	Parameter	**Value**	**MW**	**mg/hr**	**mmol/hr**	**kg/hr**	**wt %**	**ppmw**	**kg/hr**	**wt %**	**ppmw**	**mmol/hr**	**kg/hr**	**wt %**	**ppmw**	**kg/hr**	**kg/hr**	**wt %**	**ppmw**
Reclaimer feed rate	kg/hr	16211																	
Volatile amines/ammonia																			
Ammonia	mmol/kg	0.20	17.00		3,310	0.056	0.000		0.056							56.2	56.3	0.000	
EDA + 2-imidazolidone	mmol/kg	11.91	86.09		193,098	16.624	0.101		16.624							16,607.2	16,623.8	0.101	
1-MPZ + 1,4-DMPZ	mmol/kg	0.00	107.18		0	0.000	0.000		0.000							0.0	0.0	0.000	
AEP (MDEA/PZ)	mmol/kg	0.00	129.20		0	0.000	0.000		0.000							0.0	0.0	0.000	
Heat stable salts																			
Formate	mmol/kg	25.1	45.00		406,553	18.29	0.111		1.829				16.47	0.29		18,277	18,278	0.111	
Oxalate, acetate, glycolate	mmol/kg	5.62	88.00		91,161	8.02	0.049		0.802				7.22	0.127		8,014	8,015	0.049	
Sulfate	mmol/kg	44.7	96.00		724,151	69.5	0.423		6.952				62.6	1.1		69,449	69,456	0.423	
Nitrate	mmol/kg	45.0	62.00		730,127	45.3	0.276		4.527				40.7	0.7		45,223	45,227	0.275	
Nitrite	mmol/kg	0.1	46.00		2,410	0.11	0.001		0.011				0.10	0.00		111	111	0.001	
Chloride	mmol/kg	16.5	35.45		267,936	9.5	0.058		0.950				8.5	0.15		9,489	9,490	0.058	
Fluoride	mmol/kg	0.67	19.00		10,862	0.206	0.001		0.021				0.186	0.003		206	206	0.001	
Nonvolatile amines																			
HEIA	mmol/kg	0.00	130.00		0	0.0	0.000		0.000				0.0	0.00		0	0	0.000	
triHEIA	mmol/kg	0.00	173.00		0	0.00	0.000		0.000				0.00	0.000		0	0	0.000	
HEEDA	mmol/kg	0.00	104.00		0	0.00	0.000		0.000				0.00	0.000		0	0	0.000	
MEA trimer	mmol/kg	0.00	147.00		0	0.000	0.000		0.000				0.00	0.000		0	0	0.000	
HEI	mmol/kg	0.00	112.00		0	0.00	0.000		0.000				0.00	0.00		0	0	0.000	
Nonvolatile PZ derivatives	mmol/kg	8.59	172.00		139,238	23.95	0.146		23.949				0.00	0.00		23,925	23,949	0.146	
DEA + Polymers	mmol/kg	0.00	90.00		0	0.00	0.000		0.000				0.00	0.00		0	0	0.000	
Amino acids																			
HeGly	mmol/kg	0.0	119.00		0	0.0	0.000		0.000				0.0	0.00		0	0	0.000	
Bicine	mmol/kg	0.4	163.00		6,489	1.1	0.006		1.058				0.0	0.00		1,057	1,058	0.006	
Nitrosamines																			
MNPZ	mmol/kg	1.087	115.00		17,617	2.026	0.012		2.026				0.0	0.00	0	2,024	2,026	0.012	
Nitroso-HeGly	mmol/kg	0.000	148.00		0	0.000	0.000		0.000				0.0	0.00	0	0	0	0.000	
Metals/contaminants																			
Hg	ppm (wt)	0.400	200.59	3,245	16.2	0.003		0.198	0.003				0.000		0.00	3.24	3.24		0.198
Se	ppm (wt)	0.511	78.96	4,146	52.5	0.004		0.253	0.004				0.000		0.0	4.14	4.15		0.253
As	ppm (wt)	0.085	75.00	685	9.1	0.001		0.042	0.001				0.000		0.00	0.684	0.685		0.042
Cd	ppm (wt)	0.038	112.00	306	2.74	0.000		0.019	0.000				0.000		0.000	0.306	0.306		0.019
Cr	ppm (wt)	1.001	52.00	8,111	156	0.008		0.494	0.008				0.000		0.0	8.10	8.11		0.494
Pb	ppm (wt)	0.100	207.20	811	3.91	0.001		0.049	0.001				0.000		0.00	0.810	0.811		0.049
Fly ash	ppm (wt)	1,334	60.00	10,815,130	180,252	10.8	0.066		10.815				0.0	0.00		10,804	10,815		
Fe + other SSM's	ppm (wt)	100	56.00	1,801,214	32,165	1.801	0.011		1.801				0.00	0.000		1,799	1,801		
Amine			86.14		67,990,281	5,857	35.67		5,798	35.7			59	1.0		5,850,826	5,856,624	35.7	
Carbon Dioxide			44.00		21,076,987	927	5.65		927	5.72						926,460	927,387	5.65	
Water			18.02			9,427	57.4		9,427	58.1			5,390.713	95.000		9,417,426	9,426,852	57.4	
Sodium Hydroxide			40.00									2,233,198	89.3	1.6		0.000	0.000		
Total						16,418			16,224				284			16,401,770	16,417,994		

Notes
Assumes reclaiming is controlled by required rate of HSS (heat-stable salt) removal
Solvent composition at Nth hour calculated by steady state balance (function of slipstream ratio and rate of HSS removal for technology)
Feed Stream (Stream 1) = (Solvent circulation rate)*(Reclaimer drawoff ratio in "Summary" tab)
Feed stream composition = lean solvent composition
Reclaimed Amine (Stream 2) = (Amine in reclaimer feed)*(% amine recovered) + SUM[(contaminant)*(100 - % removal by reclaiming of contaminant type)]
Reclaimer Waste Stream (Stream 3) = Feed Stream - Reclaimed Amine
Lean Solvent (Stream 4) = Stream bypassing reclaimer

Lean Solvent Post-Reclaiming (Stream 5) = Reclaimed Amine (Stream 2) + Lean Solvent (Stream 4)

Simplified process flow diagram (liquid flows only):



Disclaimer: This amine reclaimer spreadsheet is confidential information and has been transmitted to IEAGHG for example purposes only.
Trimeric, The University of Texas and URS assume no responsibility for these calculations if the inputs are manipulated from their original values.

Manual Inputs

Parameter	Value	Units	Equation/Notes/Reference
General process specifications			
Gas feed (G)	144,830	kmol/hr	G = (MW_e)*(Tonne CO_2/MWh)*(1/0.044 kmol CO_2/tonne CO_2)*(kmol gas/kmol CO_2)
CO_2 removed	15,355	kmol/hr	CO_2 Removed = (% Removal)*(MW_e)*(Tonne CO_2/MWh)*(1/0.044 kmol CO_2/tonne CO_2)
CO_2 removed	676	MT/hr	MT/hr = (kmol/hr)*(44 kg/kmol)/(1000 kg/MT)
Gas leaving absorber	129,475	kmol/hr	Mass balance of gas in and out of absorber (neglects trace absorption of flue gas contaminants and stripping of amines and contaminants into gas phase)
Amine concentration	8	m	Input from "Base Case Parameters" tab
Amine molecular weight (MW amine)	86.14	g/mol	Input from "Base Case Parameters" tab
Amine concentration	40.8	wt% (CO_2 free)	(wt % amine) = (m amine)*(MW amine)/((m amine)*(MW amine)+1000 g)
Amine concentration	4.74	mol/kg (CO_2 free)	(mol/kg amine) = (m amine)/((m amine)*(MW amine)+1000 g)
Lean loading (alpha lean)	0.31	mol CO_2/mol alk	Input from "Base Case Parameters" tab
Rich loading (alpha rich)	0.41	mol CO_2/mol alk	Input from "Base Case Parameters" tab
Alkalinity/amine	2.00	mol alk/mol amine	Alkaline nitrogen equivalent/mole of amine
Lean amine concentration (C_amine)	4.19	mol/kg solvent	C_amine = (m amine)/((m amine)*(MW amine) + 1000 g H_2O + (alpha)*(m amine)*(44 g/mol CO_2))
Rich amine concentration	4.04	mol/kg solvent	C_amine = (m amine)/((m amine)*(MW amine) + 1000 g H_2O + (alpha)*(m amine)*(44 g/mol CO_2))
Capacity ($CapCO_2$)	0.95	mol CO_2/kg solvent	$CapCO_2$ = (alpha rich - alpha lean)/(mol alk/mol amine)/(MW amine)*(wt % amine)
Solvent circulation rate (L)	16,210,923	kg/hr	L = (CO_2 removed)/($CapCO_2$)
L/G	3.89	wt/wt	L/G = L/(G*(MW gas))
Total solvent inventory	8,105,461	kg	Inventory = (total solvent holdup)/L
Thermal degradation			
Stripper sump & reboiler thermal degradation			
k_0	2.91E-08	1/s	First-order reaction rate constant of thermal degradation(Freeman, 2011)
T_0	163	°C	(Freeman, 2011)
Activation energy (E_a)	184	kJ/mol	(Freeman, 2011)
Temperature of sump/reboiler (T)	150	°C	Input from "Summary" tab
Residence time of stripper sump+reboiler (τ)	5	min	Input from "Summary" tab
First-order rate constant (k)	6.11E-09	1/s	k = k_0*exp(-E_a/R*(1/T-1/T_0))
Amine thermal degradation rate [R]	0.185	mol amine/MT CO_2	R = k*C_amine*tau/(Cap_CO_2)
Amine thermal degradation rate	15.9	g amine/MT CO_2	g/MT CO_2 = (mol/MT CO_2)*(MW amine)
Amine thermal degradation rate	0.015	mmol/kg/hr	mmol/kg/hr = 1000*(mol/MT CO_2)*(MT CO_2/hr)/(kg solvent inventory)
Stripper packing thermal degradation			
residence time	5	min	Input from "Summary" tab
inlet flash ΔT	5	°C	Assumption per Aspen model from University of Texas: drop in temperature due to flashing upon entering stripper (Davis, 2009)
inlet T after flash	140	°C	T after flash = stripper sump T - cross exchanger hot side approachΔT - flash ΔT
Temperature profile	0		0 = constant at inlet conditions; 1 = linear change between inlet and sump (based off previous study (Davis, 2009), constant at inlet conditions is considered to be a better rep

Stripper packing divided into 10 equal segments:

Segment	T	k (s^-1)	R (mol/MT CO_2)
1	140	1.72E-09	0.005
2	140	1.72E-09	0.005
3	140	1.72E-09	0.005
4	140	1.72E-09	0.005
5	140	1.72E-09	0.005
6	140	1.72E-09	0.005
7	140	1.72E-09	0.005
8	140	1.72E-09	0.005
9	140	1.72E-09	0.005
10	140	1.72E-09	0.005

Thermal degradation rate in packing	4.32	g/MT CO_2	sum of segments
% of total thermal degradation	21.4	%	% of total thermal degradation which occurs in the stripper packing

Summary of thermal degradation

Total thermal degradation rate	20.2	g/MT CO_2	sum of packing, sump and reboiler rates
Total thermal degradation rate	0.020	mmol/kg/hr	1000*(g/MT CO_2)*(MT CO_2/hr)/((MW amine)*(solvent inventory))

Cyclic Oxidation

O_2	5.03	kPa	Input from "Base Case Parameters" tab
metals	1	(binary)	Are there metals present to catalyze oxidation rate? 1 = yes, 0 = no
Maximum temperature of oxidation	145	°C	Assumes majority of oxidation takes place in hot rich side of cross exchanger before remaining dissolved oxygen is flashed off upon entering the stripper
Residence time at max ox. temperature	30	seconds	Input from "Summary" tab
k_0	5.15E-08	(s-kPa)^-1	From experimental data in cyclic degradation rig (Voice, 2013)
T_0	160	°C	(Voice, 2013: NH_3 generation activation energy in HTCS)
E_a	32	kJ/mol	(Voice, 2013: NH_3 generation activation energy in HTCS)
metals catalysis factor	1.667		(Voice, 2013) ratio of catalyzed to uncatalyzed oxidation rate
k_ox	1.88E-07	s^-1	k_ox = (catalysis factor)*k_0*exp(-Ea/R*(1/T-1/T_0))
Amine oxidation rate	434	mol/hr	R = k_ox*tau_ox*C_amine*L
Amine oxidation rate	55.3	g/MT CO_2	g/MT CO_2 = (mol/hr)*(MW amine)/(MT CO_2/hr)
Amine oxidation rate	0.054	mmol/kg/hr	mmol/kg/hr = (mol/hr)/1000/(kg solvent inventory)

Flue gas contaminants

O_2	0.050	vol/vol	Input from "Base Case Parameters" tab
H_2O	0.130	vol/vol	Input from "Base Case Parameters" tab
CO_2	0.118	vol/vol	Input from "Base Case Parameters" tab
N_2	0.702	vol/vol	Input from "Base Case Parameters" tab
MW_gas	28.79	g/mol	MW of gas (ignoring trace contaminants, average of O_2, H_2O, CO_2, and N_2)
G	3,244,539	Nm^3/hr	Assumes ideal gas (STP = 1 atm, 0 degC, R = 8.206*10^-5 m^3-atm/mol-K)
Sulfate rate	651,735	mmol/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Nitrate rate	651,735	mmol/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Nitrite rate	0	mmol/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Cl rate	241,142	mmol/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
F rate	9,776	mmol/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Hg rate	2,920	mg/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Se rate	3,731	mg/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
As rate	616	mg/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Cd rate	276	mg/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Cr rate	7,300	mg/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Pb rate	730	mg/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)
Fly ash rate	9,733,617	mg/hr	Rate of x = (Concentration of x in gas phase)*(% removal of x from gas)*(G)

Degradation product accumulation rates

thermal degradation rate	0.020	mmol/kg/hr	Thermal degradation stoichiometry: Davis, 2009
oxidation rate	0.054	mmol/kg/hr	Oxidative degradation stoichiometry: Voice, 2013 (unless otherwise noted)
NH_3 thermal stoichiometry	0.287	mol/mol amine degraded	Rate of accumulation of x = (Rate of degradation of amine)*(stoichiometry of x)
NH_3 oxidative stoichiometry	1.000	mol/mol amine	2/3 mol NH_3 produced per mole of MEA oxidized (Voice 2013)
NH_3 rate	0.059	mmol/kg/hr	Total rate = (thermal rate)*(thermal stoichiometry) + (oxidative rate)*(oxidative stoichiometry)
EDA thermal stoichiometry	0.094	mol/mol amine degraded	
EDA oxidative stoichiometry	0.166	mol/mol amine degraded	
EDA rate	0.011	mmol/kg/hr	
1-MPZ + 1,4-DMPZ thermal stoichiometry	0.000	mol/mol amine degraded	
1-MPZ + 1,4-DMPZ oxidative stoichiometry	0.000	mol/mol amine degraded	
1-MPZ + 1,4-DMPZ rate	0.000	mmol/kg/hr	
AEP thermal stoichiometry (MDEA/PZ only)	0.000	mol/mol amine	

AEP rate	0.000	mmol/kg/hr	
Formate thermal stoichiometry	0.385	mol/mol amine	
Formate oxidative stoichiometry	0.113	mol/mol amine	62 mmol/kg total formate accumulated after degradation of 500 mmol/kg of MEA in cyclic oxidation apparatus (Voice, 2013)
Formate thermal rate	0.008	mmol/kg/hr	
Formate oxidative rate	0.006	mmol/kg/hr	
Formate rate	0.014	mmol/kg/hr	
Other HSS thermal stoichiometry	0.021	mol/mol amine	
Other HSS oxidative stoichiometry	0.033	mol/mol amine	7.1 mmol/kg total acetate and oxalate accumulated after degradation of 500 mmol/kg of MEA in cyclic oxidation apparatus (Voice, 2013)
Other HSS rate	0.002	mmol/kg/hr	
Nitrate oxidative stoichiometry	0.012	mol/mol amine	6.2 mmol/kg nitrate accumulated after degradation of 500 mmol/kg of MEA in cyclic oxidation apparatus (Voice, 2013)
Nitrate rate	0.001	mmol/kg/hr	
Nitrite oxidative stoichiometry	0.005	mol/mol amine	1.1 mmol/kg nitrite accumulated after degradation of 500 mmol/kg of MEA in cyclic oxidation apparatus (Voice, 2013)
Nitrite rate	0.000	mmol/kg/hr	
HEIA thermal stoichiometry	0.000	mol/mol amine	0.2 moles HEIA produced per mole of amine thermally degraded (Davis, 2009)
HEIA rate	0.000	mmol/kg/hr	
triHEIA thermal stoichiometry	0.000	mol/mol amine	0.05 moles triHEIA produced per mole of amine thermally degraded (Davis, 2009)
triHEIA rate	0.000	mmol/kg/hr	
HEEDA Equilibrium constant	39.4	(alpha)^-1	HEEDA and MEA trimer are in equilibrium w/ the steady state concentration of HEIA and triHEIA, as a function of loading (Davis, 2009)
Nonvolatile PZ derivatives thermal stoichiometry	0.40	mol/mol amine	
Nonvolatile PZ derivatives rate	0.008	mmol/kg/hr	
HEI ox stoic	0.000	mol/mol amine	32 mmol/kg HEI accumulated after degradation of 500 mmol/kg of MEA in cyclic oxidation apparatus (Voice, 2013)
HEI rate	0.000	mmol/kg/hr	
DEA + Polymers thermal stoichiometry	0.000	mol/mol amine	
DEA + Polymers oxidative stoichiometry	0.000	mol/mol amine	
DEA + Polymers rate	0.000	mmol/kg/hr	
HeGly oxidation stoichiometry	0.000	mol/mol amine	~1.8 moles HeGly per mole total formate observed in Esbjerg pilot plant (da Silva, 2012)
HeGly rate	0.000	mmol/kg/hr	
Bicine oxidation stoichiometry	0.000	mol/mol amine	
Bicine rate	0.000	mmol/kg/hr	
Ammonia VLE			Determines rate of ammonia emissions in flue gas and concentration in solvent
k_H$_0$	27	mol/kg*bar	Henry's Law: p = k_H*c; k_H = k_H$_0$*exp(K*(1/T - 1/298.15)); (Assumes solubility in water ~ solubility in aqueous amine) (Dean, 1992)
K	2100		(Dean, 1992)
T	40	°C	Absorber operating temperature
k_H	37.8	mol/kg*bar	Henry's constant: k_H = k_H$_0$*exp(-K*(1/T-1/T$_0$))
Concentration in solvent	0.204	mmol/kg	R-(c/k_H)*G = 0: at steady state rate of NH$_3$ generation equals rate of emission: therefore concentration in solvent c = R*k_h/G
Concentration in absorber gas out	5.40	ppmv	Concentration in gas = k_H/c
Nitrosation of PZ			(Fine, 2013)
y_NO$_2$	1.5	ppmv	Concentration of NO$_2$ in gas entering absorber
% of NO$_2$ absorbed as nitrite (beta)	100	%	% of NO$_2$ entering absorber that is absorbed into the solvent as nitrite
% of nitrite forming MNPZ (delta)	100	%	All nitrite will react to MNPZ in a PZ-containing solvent
G/L	0.0089	kmol/kg	Gas volumetric flow rate relative to solvent mass flow rate
Nitrosation rate	0.027	mmol/kg/hr	Rate = (delta)*[(beta)*(y_NO$_2$)*G/(inventory)+rate of nitrite from oxidation]
k_decomp_sump	2.73E-05	s^-1	Thermal decomposition rate of nitrosamine (k = k$_0$*exp(-Ea/R*(1/T-1/T$_0$))
k_decomp_packing	1.43E-05	s^-1	Thermal decomposition rate of nitrosamine (k = k$_0$*exp(-Ea/R*(1/T-1/T$_0$))
MNPZ steady state concentration	1.09	mmol/kg	C_steady state = (delta)*[(beta)*(y_NO$_2$)*(G/L)+(nitrite from ox)*(inventory/L)]/(k_decomp*tau_heated+(Reclaimer drawoff ratio)*(% nonvolatile amine reclaimed))
Decomposition rate	0.03	mmol/kg/hr	R = (C_NNO)*(L)/(V)*(k_decomp)*(tau_heated)
NH$_3$ stoichiometry	1	mol/mol NNO degraded	Assumption for moles of ammonia produced per mole of nitrosamine degraded
Formate stoichiometry	1	mol/mol NNO degraded	Assumption for moles of formate produced per mole of nitrosamine degraded
NH$_3$ rate	0.03	mmol/kg/hr	R(NH$_3$) = x(NH$_3$/NNO)*R(NNO decomposition)
Formate rate	0.03	mmol/kg/hr	R(HCO$_2$) = x(HCO$_2$/NNO)*R(NNO decomposition)
Acetate/Oxalate/Glycolate rate	0.01	mmol/kg/hr	Assumes other HSS's accumulate at same ratio to formate as in oxidative degradation
Nitrosation of HeGly	Disclaimer: This estimate is based off results from an unpublished ongoing study being conducted by UT Austin and is subject to change; see Fine, 2013 for comparable published result w/ PZ		

HeGly concentration	0.0	mmol/kg	Steady state HeGly concentration (with reclaiming) OR accumulated HeGly (without reclaiming)
y_NO$_2$	1.5	ppmv	Concentration of NO_2 in gas entering absorber
% of NO_2 absorbed as nitrite (beta)	0	%	% of NO_2 entering absorber that is absorbed into the solvent as nitrite
% of nitrite forming NHeGly (delta)	0.00	%	% conversion of nitrite to nitrosamine is a linear function HeGly concentration: delta = 0.07*C_HeGly
G/L	0.0089	kmol/kg	Gas volumetric flow rate relative to solvent mass flow rate
k_decomp_sump	2.73E-05	s^-1	Thermal decomposition rate of nitrosamine (k = k_0*exp(-Ea/R*(1/T-1/T_0))
k_decomp_packing	1.43E-05	s^-1	Thermal decomposition rate of nitrosamine (k = k_0*exp(-Ea/R*(1/T-1/T_0))
NHeGly steady state concentration	0.000	mmol/kg	C_steady state = (delta)*[(beta)*(y_NO$_2$)*(G/L)+(nitrite from ox)*(inventory/L)]/(k_decomp*tau_heated+(Reclaimer drawoff ratio)*(% nonvolatile amine reclaimed))
Decomposition rate	0.00E+00	mmol/kg/hr	R = (C_NNO)*(L)/(V)*(k_decomp)*(tau_heated)
NH_3 stoichiometry	1	mol/mol NNO degraded	Assumption for moles of ammonia produced per mole of nitrosamine degraded
Formate stoichiometry	1	mol/mol NNO degraded	Assumption for moles of formate produced per mole of nitrosamine degraded
NH_3 rate	0.00E+00	mmol/kg/hr	$R(NH_3) = x(NH_3/NNO)*R(NNO decomposition)$
Formate rate	0.00E+00	mmol/kg/hr	$R(HCO_2) = x(HCO_2/NNO)*R(NNO decomposition)$
Acetate/Oxalate/Glycolate rate	0.00E+00	mmol/kg/hr	Assumes other HSS's accumulate at same ratio to formate as in oxidative degradation

Summary

Product accumulation rates

Ammonia	0.086	mmol/kg/hr	
Ammonia emission rate	5.40	ppmv	
EDA + 2-imid	0.011	mmol/kg/hr	
1-MPZ + 1,4-DMPZ	0.000	mmol/kg/hr	
AEP (MDEA/PZ only)	0.000	mmol/kg/hr	
Formate	0.041	mmol/kg/hr	
Oxalate, acetate, glycolate	0.010	mmol/kg/hr	
HEIA	0.000	mmol/kg/hr	
triHEIA	0.000	mmol/kg/hr	
HEI	0.000	mmol/kg/hr	
Nonvolatile PZ derivatives	0.008	mmol/kg/hr	
DEA + Polymers	0.000	mmol/kg/hr	
HeGly	0.000	mmol/kg/hr	
Bicine	0.000	mmol/kg/hr	
Sulfate	0.080	mmol/kg/hr	
Nitrate	0.081	mmol/kg/hr	sum of accumulation from flue gas and oxidation
Nitrite	0.000	mmol/kg/hr	sum of accumulation from flue gas and oxidation
Chloride	0.030	mmol/kg/hr	
Fluoride	0.001	mmol/kg/hr	
Hg	0.360	µg/kg/hr	
Se	0.460	µg/kg/hr	
As	0.076	µg/kg/hr	
Cd	0.034	µg/kg/hr	
Cr	0.901	µg/kg/hr	
Pb	0.090	µg/kg/hr	
Fly ash	1.201	mg/kg/hr	

Lean solvent composition (without reclaiming)

Operating time	1111	hrs
Ammonia	0.204	mmol/kg
EDA + 2-imid	11.91	mmol/kg
1-MPZ + 1,4-DMPZ	0.00	mmol/kg
AEP (MDEA/PZ)	0.00	mmol/kg
Formate	45.14	mmol/kg
Oxalate, acetate, glycolate	2.417	mmol/kg
Sulfate	89	mmol/kg
Nitrate	90	mmol/kg
Nitrite	0.3	mmol/kg

Chloride	33.1	mmol/kg	
Fluoride	1.34	mmol/kg	
HEIA	0.0	mmol/kg	
triHEIA	0.00	mmol/kg	
HEEDA	0.00	mmol/kg	[HEEDA] = [HEIA]/(39.36*(alpha lean)) at steady state
MEA trimer	0.000	mmol/kg	[MEA trimer] = [triHEIA]/(39.36*(alpha lean)) at steady state
HEI	0.0	mmol/kg	
Nonvolatile PZ derivatives	8.6	mmol/kg	
DEA + Polymers	0.0	mmol/kg	
HeGly	0.0	mmol/kg	
Bicine	0.0	mmol/kg	
MNPZ	1.09	mmol/kg	
Nitroso-HeGly	0.000	mmol/kg	
Hg	0.400	ppm (wt)	
Se	0.511	ppm (wt)	
As	0.085	ppm (wt)	
Cd	0.038	ppm (wt)	
Cr	1.00	ppm (wt)	
Pb	0.100	ppm (wt)	
Fly ash	1,334	ppm (wt)	
Fe + other SSM's	100	ppm (wt)	Assumed to be ~ 100 ppm for "high metals" case, 1 ppm for "low metals" case

Disclaimer: This amine reclaimer spreadsheet is confidential information and has been transmitted to IEAGHG for example purposes only
Trimeric, The University of Texas and URS assume no responsibility for these calculations if the inputs are manipulated from their original values

Acronym/Phrase	**Full Name/Note**
Conc	concentration
deg	degradation
Ea	activation energy (kJ/mol)
G	flue gas flow rate
heated oxidation	section where oxidation rate is greatest (hot rich solvent flow before entering stripper)
HSS	heat stable salts
k	1st order rate constant (s^-1)
L	solvent circulation rate
MT CO_2	metric tonne of CO_2
MW	molecular weight (g/mol)
NGCC	natural gas combined cycle
ox	oxidation
packing	stripper packing
R	rate (of degradation or accumulation)
sump	stripper sump
T	temperature
Total liquid holdup	total residence time, determines solvent inventory
y_NO_2	Concentration of NO_2 in gas phase entering the absorber (ppmv)
τ or tau	residence time
Solvents	
MDEA	N-methyl-N,N-diethanolamine
MEA	N-ethanolamine
PZ	Piperazine
Contaminants	
AEP	N-aminoethyl-piperazine
As	Arsenic
DEA + polymers	1,1-diethanolamine and polymers formed from the thermal degradation of DEA
Cd	Cadmium
Cl	Chloride
Cr	Chromium
1,4-DMPZ	1,4-dimethyl-piperazine
EDA	Ethylenediamine
EPZ	N-ethyl-piperazine
F	Fluoride
Fe	Ferrous iron

HCl	Hydrogen chloride (gas phase)
HEEDA	Hydroxyethyl-ethylenediamine (dimer of MEA)
HEF	Hydroxyethyl-formamide (formyl amide of MEA)
HeGly	N-hydroxyethyl-glycene
HEI	Hydroxyethyl-imidazole
HEIA	Hydroxyethyl-imidazolidinone (cyclic urea of MEA dimer)
HEP	N-hydroxyethyl-piperazine
HF	Hydrogen fluoride (gas phase)
Hg	Mercury
2-imid	2-imidazolidone
1-MPZ	N-methyl-piperazine
MNPZ	N-nitroso-piperazine
NH_3	Ammonia
NHeGly	N-nitroso-(N-hydroxyethyl-glyciene)
NO_2	Nitrogen dioxide
NO_3	Nitrate
NO_X	Nitrogen oxides in gas phase (generally NO, not including NO_2)
Nonvolatile PZ derivs	Thermal decomposition products of PZ that are less volatile than PZ (AEP, HEP, EPZ, etc)
Pb	Lead
Se	Selenium
SO_2	Sulfur dioxide
SO_4	Sulfate
SSM	Stainless steel metal ions (iron, nickel, chromium, and manganese
triHEIA	cyclic urea of MEA trimer
Trimer	MEA trimer

References

(Closmann, 2011)	Closmann FB. *Oxidation and Thermal Degradation of Methyldiethanolamine/Piperazine in CO2 Capture* . The University of Texas at Austin. Ph.D. Dissertation. 2011.
(Da Silva, 2012)	da Silva EF, Lepaumier H, Grimstvedt A, Vevelstad SJ, Einbu A, Vernstad K, Svendsen HF, Zahlsen K. “Understanding 2-Ethanolamine Degradation in Postcombustion CO_2 Capture.” *Industrial & Engineering Chemistry Research* . 2012; 51:13329-13338.
(Davis, 2013)	Davis JD. *Thermal Degradation of Aqueous Amines Used for Carbon Dioxide Capture* . The University of Texas at Austin. Ph.D. Dissertation. 2009.
(Dean, 1992)	Dean, J.A., *Lange's Handbook of Chemistry* , McGraw-Hill, Inc., 1992.
(Fine, 2013)	Fine NA, Goldman MJ, Nielsen PT, Rochelle GT. "Managing n-nitrosopiperazine and dinitrosopiperazine." *Energy Procedia* . 2013; 37:273-284
(Freeman, 2011)	Freeman SA. *Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture* . The University of Texas at Austin. Ph.D. Dissertation. 2011.
(Nielsen, 2013)	Nielsen PT, Li L, Rochelle GT. "Piperazine degradation in pilot plants." *Energy Procedia* . 2013; 37:1912-1923
(Voice, 2013)	Voice AK. *Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing.* The University of Texas at Austin. Ph.D. Dissertation. 2013.

All other assumptions are explained in detail in the report submitted to IEAGHG