NATIONAL PETROLEUM COUNCIL

Meeting the Dual Challenge

A Roadmap to At-Scale Deployment of Carbon Capture, Use, and Storage

Appendix E

Mature CO_2 Capture Technologies

December 12, 2019

This is a working document as approved by the National Petroleum Council on December 12, 2019. This document is subject to final editing and preparation of graphics for publication.

TABLE OF CONTENTS

I. INTRODUCTION

This appendix describes the absorption carbon dioxide (CO_2) capture technology known as amine scrubbing. Amine scrubbing is a mature absorption technology, one that has been practiced and refined at-scale for more than 40 years.

II. ABSORPTION: AMINE SCRUBBING

A. Introduction

This appendix reviews the technical results and opportunities for improving conventional aqueous amine scrubbing for CO_2 capture, based in large part on Rochelle.[1] The history of conventional amine scrubbing includes more than 30 applications on flue gas from gas combustion and six on flue gas from coal. Improvements in the process design and solvent selection have resulted in continuous reduction of energy use and capital cost. By analogy to the development of limestone slurry scrubbing for flue gas desulfurization, amine scrubbing has been and will continue to be the technology of choice for CO_2 capture.

Important process improvements have been developed for absorber intercooling and stripper configurations. New solvents have been selected and developed based on four energy properties: absorption rate, capacity, heat of absorption, and maximum temperature from thermal degradation. Other important solvent properties include resistance to oxidation, nitrosamine formation, amine aerosol formation, and amine volatility.

B. History

Improvements in energy consumption have been made over time. Figure E-1 shows the heat duty of select commercial units using capture on combustion gases from 1976 to the present. At Lubbock in 1983 the reboiler duty decreased with the substitution of 30% monoethanolamine (MEA) for 20% MEA. At the Mitsubishi Heavy Industries (MHI) plant in 1999, 30% MEA was replaced with KS-1. At a newer MHI plant in 2009, additional energy savings resulted from stripper process modifications.[2] The Cansolv plant at Boundary Dam (start-up in 2014) achieved energy savings with a new solvent and the use of lean vapor compression at the stripper.

---

[1] Rochelle, G.T. (2016). "A Review of Conventional Amine Scrubbing for CO_2 Capture," in *Absorption-Based Post-Combustion Capture of Carbon Dioxide*, Paul Feron, ed., Woodhead Publishing, Cambridge, MA. 2016.

[2] Iijima, M., Nagayasu, T., Kamijyo, T. and Nakatani, S. (2011). "MHI's Energy Efficient Flue Gas CO_2 Capture Technology and Large Scale CCS Demonstration Test at Coal-fired Power Plants in USA," MHI Technical Review, 48 (1).

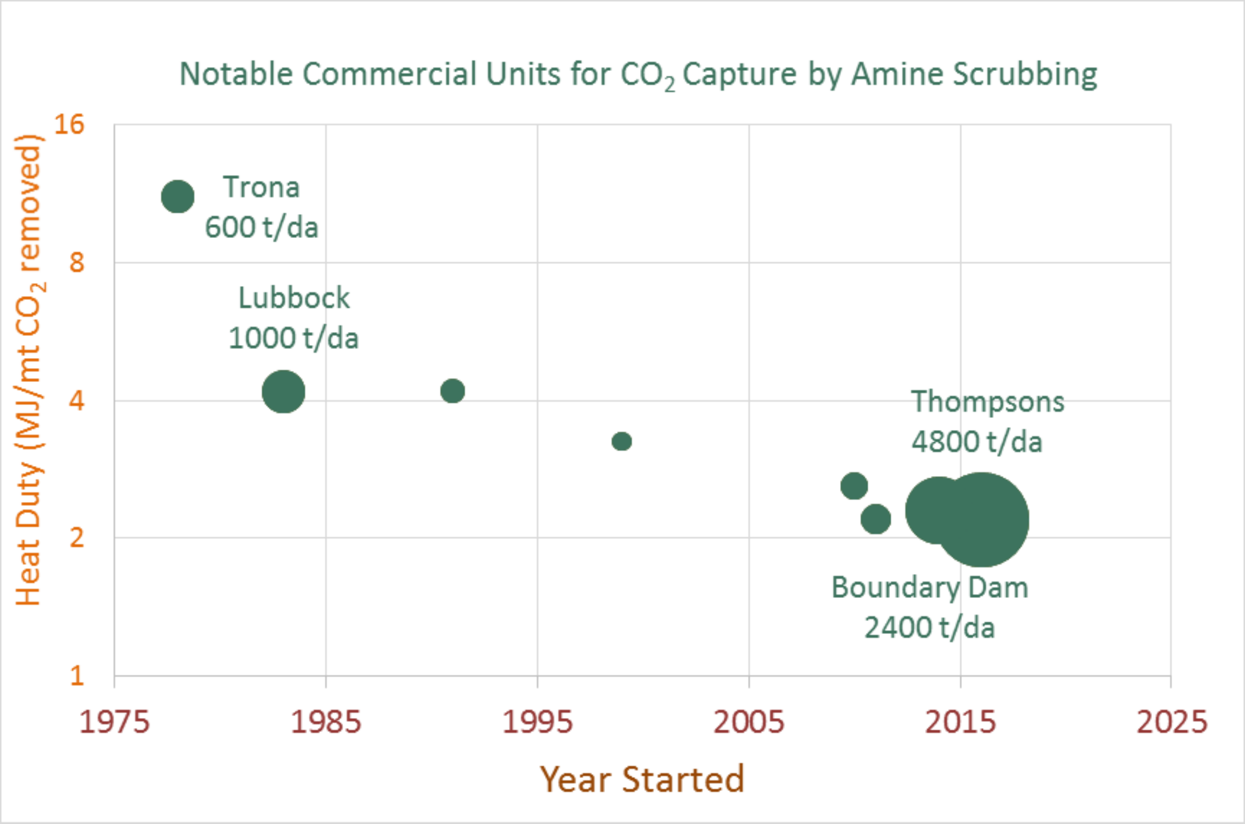


Figure E-1. Heat Duty of Notable Commercial Units

Source: Rochelle, G. T. (2014). "From Lubbock, TX to Thompsons, TX: A technical review of the progress in amine scrubbing," plenary presentation at Greenhouse Gas Control Technologies 12, Austin, Texas.

C. Analogy to Limestone Slurry Scrubbing

Table E-1 compares the development timeline of limestone slurry scrubbing for flue gas desulfurization to that of amine scrubbing for CO_2 capture. They were both identified as the initial technology of choice. However, because of technical difficulties and high cost projections, research and development (R&D) activities focused on advancing promising alternatives. Limestone slurry scrubbing is now the dominant technology for flue gas desulfurization. It is probable that amine scrubbing will be the primary technology for CO_2 capture from coal-fired power plants and possibly for other applications as it already has a higher technology readiness levels. However, it is possibly not the blanket solution for application in other sectors since chemical approaches are only necessary for low CO_2 concentrations (i.e., <15%) as mentioned in Chapter 5.

Table E-1. History Repeats in the Development of Limestone Slurry Scrubbing and Amine Scrubbing

$CaCO_3$	Event	Amine
1936	First commercial plant	1980
1958	"Almost Insurmountable difficulties."[3] "Although … technically feasible, it is an expensive method."[4]	1991
1960-75	Government funds research on advanced alternatives	1995-
1970-85	Government and Electric Power Research Institute fund test facilities	2010-
1968	60 to 250 megawatt (MW) prototypes	2014-
1977	500+ MW deployed per regulations	2025??
2019	First choice dominates	???

D. Basic Chemistry and Rates

Four classes of aqueous solvents can be considered for CO_2 absorption/stripping (Table E-2): carbonates, tertiary amines, hindered amines, and secondary or primary amines.

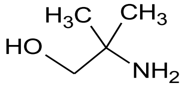
These four differ in heat of CO_2 absorption, kinetics of CO_2 absorption, and intrinsic CO_2 stoichiometry. Hot potassium carbonate is offered in a process by Honeywell UOP. It operates isothermally near 100°C with pressure swing regeneration; its low heat of absorption is unfavorable for thermal swing regeneration. Tertiary amines such as methyldiethanolamine (MDEA) are used in blends with rate promoters such as piperazine (PZ). Hindered amines such as aminomethylpropanol (AMP) can be used alone or in combination with rate promoters. Secondary or primary amines such as MEA and PZ can be used alone or as rate promoters with tertiary amines, hindered amines, or potassium carbonate.

---

[3] Bienstock, D., Brunn, L.W., Murphy, E.M., and Benson, H.E. (1958). "Sulfur Dioxide—Its Chemistry and Removal from Industrial Waste Gases," Bureau of Mines Information Circular 7836, U.S. Department of the Interior.

[4] Booras, G.S. and Smelzer, S.C. (1991). "An Engineering and economic evaluation of CO_2 removal from fossil-fuel-fired power plants," Energy, 16, 1295-1305.

Table E-2. Alternative Aqueous Amine Chemistry

Class	**Typical reaction**	**-ΔHabs (kJ/mol)**	**Kinetics**
Carbonate	CO_3 = + CO_2 + H_2O ↔ 2 HCO-3	40	Very slow
Tertiary Amine	R3N + CO_2 ↔ R3NH+ + HCO-3	60	Slow
Hindered Amine	 + CO_2 ↔ AMPH+ + HCO-3	60–70	Moderate
Secondary or Primary Amines	2R2NH + CO_2 ↔ R2NHCOO-+ $R2NH_2$+	70–80	Fast

Water is an essential component of these amine solvents. In the absence of other constraints such as solid precipitation, the water concentration is optimized to trade off viscosity and the intrinsic CO_2 capacity. Lower viscosity enhances the heat and mass transfer performance. Water also provides stripping steam in the regeneration, which permits operation at greater pressure. In the simple stripper, water in the stripper overhead reduces energy performance. However, regeneration configurations, such as the advanced flash stripper, eliminate this disadvantage. Furthermore, polar solvents will always contain water from the flue gas. Therefore, it is not reasonable to suggest that solvents with little or no water will necessarily be better than conventional aqueous solvents.[5]

E. Simple Flowsheet

The amine scrubbing process relies upon thermal swing regeneration which works best with lower absorber temperature and greater stripper temperature. In the conventional process the inlet flue gas and lean solvent would be cooled to 30°C to 40°C with cooling water or ambient air. The stripper temperature (and pressure) would be limited by the thermal degradation of the solvent or by the conveniently available temperatures of the condensing steam or other heat source.

The energy use of the amine scrubbing process can be as much as 50% of the annualized process cost. In a power plant, as much as 40% of the steam may be extracted from the power cycle at 3 to 6 bar for use in the reboiler. Electricity will be used to compress the CO_2 to a final pressure of 100 to 150 bar. The total loss of electricity production may be approximated as equivalent work (W_{EQ}) by the relationship:

$$\mathbf{W_{EQ} = W_{pump} + W_{comp} + 90\% \frac{T_{reb} + \Delta T - 313K}{T_{reb} + \Delta T} Q_{reb}}$$

The effect of reboiler duty on the electricity burden is represented by a Carnot efficiency that increases with the condensing temperature of the steam, including a ΔT for the reboiler (5°C to 10°C) and 90% efficiency for the turbine.

---

[5] Yuan, Y., and Rochelle, G.T. (2019). "Water-lean solvents for CO_2 capture will not use less energy than second generation aqueous amine processes," presented at IJGCC.

Figure E-2 shows that the selected lean loading can be used to minimize equivalent work. At higher lean loading, the working capacity is reduced and the sensible heat requirement increases. At lower lean loading more steam is required to strip the solvent. Lower lean loading also enhances the rate behavior of the absorber.

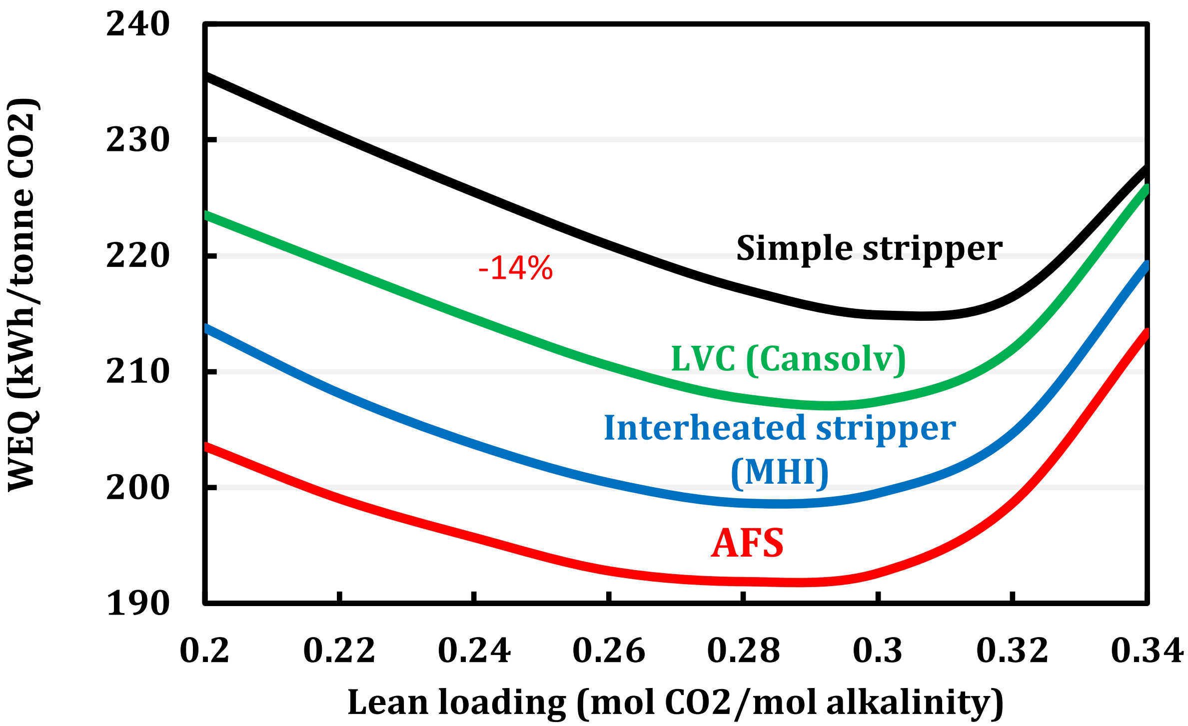


Figure E-2. Electricity Burden with Alternative Stripper Configurations. 8 m PZ, 150°C, 150 bar CO_2, Wmin = 113 kilowatt-hour per tonne CO_2
Source: Rochelle, G. T. (2014). "From Lubbock, TX to Thompsons, TX: A technical review of the progress in amine scrubbing," plenary presentation at Greenhouse Gas Control Technologies 12, Austin, Texas.

F. Advanced Absorption

Figure E-3 shows the tradeoff between the total packing area (capital cost) and the solvent rate (rich loading, energy performance). At a given lean loading and infinite packing area, there is a minimum solvent rate or liquid-to-gas ratio (L/G).[6] As in the common distillation process, the economic optimum packing area probably occurs at the solvent rate between 1.1 and 1.3 times the minimum rate.

---

[6] L/G is one of the most important parameters in wet scrubbing systems. It is usually defined as the flow of liquid over the gas flow rate that is being treated and is usually expressed in units of gallons per 1000 cubic feet or liters per cubic meter (L/m^3)

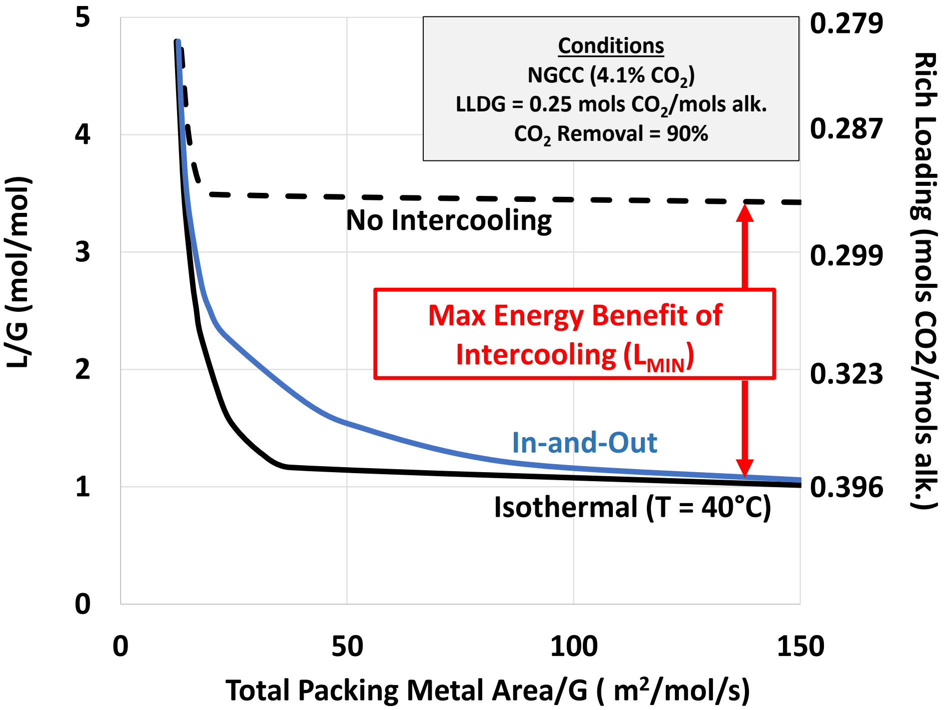


Figure E-3. Effect of Intercooling on Packing Area, 8 m PZ
Source: Sachde, D. J. and Rochelle, G. T. (2014). "Absorber Intercooling Configurations using Aqueous Piperazine for Capture from Sources with 4 to 27% CO_2," Energy Proc, 63, 1637-1656.

CO_2 absorption is an exothermic reaction which results in a temperature bulge (temperature increase) in the absorber. In many cases, intercooling may be used to reduce the absorber packing cost and increase the rich loading. Figure E-3 shows that the effect of intercooling on required packing area is significant even at lower lean loading. More complex intercooling configurations such as pump around the bottom section of packing may be useful at lean loading greater that a critical value.[7]

The contractor design for the absorber for CO_2 capture has improved from that used for acid gas treating. The larger demonstrations of CO_2 capture use modern structured packing with larger a corrugation angle to minimize pressure drop while maintaining equivalent wetted area for mass transfer.[8] The earliest absorbers in capture systems were round, carbon steel vessels. Boundary Dam uses a rectangular concrete absorber. The MHI design at Thompsons uses a rectangular metal absorber to treat 240 MW of coal-fired flue gas. Full-scale commercial designs will probably use a single rectangular absorber to treat all of the flue gas from one boiler.

---

[7] Sachde, D. J. and Rochelle, G. T. (2014). "Absorber Intercooling Configurations using Aqueous Piperazine for Capture from Sources with 4 to 27% CO2," Energy Proc, 63, 1637-1656.

[8] Tsai, R. E. (2010). "Mass Transfer Area of Structured Packing," Ph.D. Dissertation. University of Texas at Austin.

G. Advanced Regeneration Systems

The simple stripper loses efficiency because of water vapor that passes overhead and is condensed with no heat recovery. Numerous process configurations have been proposed and tested to address this weakness. Figure E-2 compares the energy performance of the three most significant stripper enhancements to that of simple stripping. Large scale commercial applications of amine scrubbing will probably utilize these or similar configurations to enhance energy performance. The interheated stripper is an important part of the Energy Saving Process (ESP) used by MHI in several smaller commercial units and was likely adopted for the 240 MW plant at Thompsons. Lean vapor compression (LVC) is included with the Boundary Dam project. It has been tested in several pilot plants including the Fluor process at Wilhelmshaven.

Figure E-4 gives an energy analysis with the advanced flash stripper using piperazine. This configuration has been successfully tested in pilot plants at the University of Texas and the National Carbon Capture Center.[9,10] Rich solvent with a loading of 0.4 mol/equivalent PZ is fed to two cross exchangers in series with a convective steam heater to the sump of the stripper. The hot lean solution is returned through the exchangers. Cold rich solvent is bypassed through an exchanger to recover latent and sensible heat from the CO_2 product. Warm rich solvent is extracted between the exchangers near its bubble point temperature at the pressure of the stripper, then combined with the heated cold rich bypass and fed to the top of the stripper to recover the latent heat of water from the primary flash.

---

[9] Chen, E. (2015) "Pilot plant results for 5 m piperazine with the advanced flash stripper," presented at TCCS-8, Trondheim, Norway, June 18, 2015.

[10] Rochelle, G.T. et al. (2019). "Pilot plant demonstration of piperazine with the advanced flash stripper," presented at Greenhouse Gas Control Technologies 14, submitted to IJGCC.

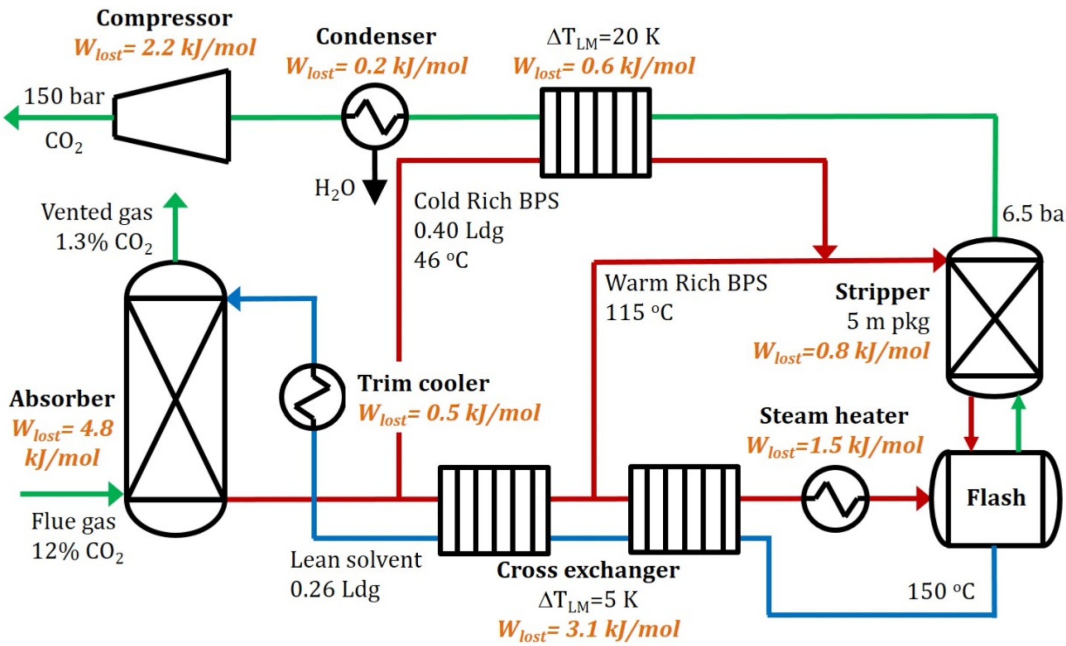


Figure E-4. Lost Work with the Advanced Flash Stripper (8 m PZ), Weq = 31.1 kJ/mol, Wmin = 18 kJ/mol, Wlost = 13.7 kJ/mol

Source: Rochelle, G. T. (2014). "From Lubbock, TX to Thompsons, TX: A technical review of the progress in amine scrubbing," plenary presentation at Greenhouse Gas Control Technologies 12, Austin, Texas.

Because the advanced flash stripper is optimized by adjusting the rates of cold and warm bypass, it is able to recover practically all of the heat in the stripper overhead. Therefore, most of the exergy is lost in tradeoffs of capital cost with work loss. Exergy is lost in the absorber (4.8 kJ/mol) with the driving force for absorption; this is ultimately a tradeoff of packing capital cost and energy lost. Approximately 3.1 kJ/mol is lost in the cross-exchanger with the heat transfer ΔT, a tradeoff of exchanger area capital cost and energy. Roughly 2.2 kJ/mol is lost in the intercooled, adiabatic compressor, perhaps to be minimized by operating the stripper at greater T/P. Around 1.5 kJ/mol is lost with the ΔT in the steam heater, mostly a tradeoff of heater capital with work loss.

Figure E-5 shows that the electricity burden with advanced amine scrubbing is approaching the minimum work (113 kWh/tonne CO_2 removed) required to separate and compress the CO_2 to a pressure of 150 bar. The advanced flash stripper is expected to reduce this burden by another 4%, but these process innovations are producing diminishing returns. It is possible to expect ultimate requirement of 200 kWh/tonne, with a thermodynamic efficiency of 56%, but there is little room left for reduction of the electricity burden.

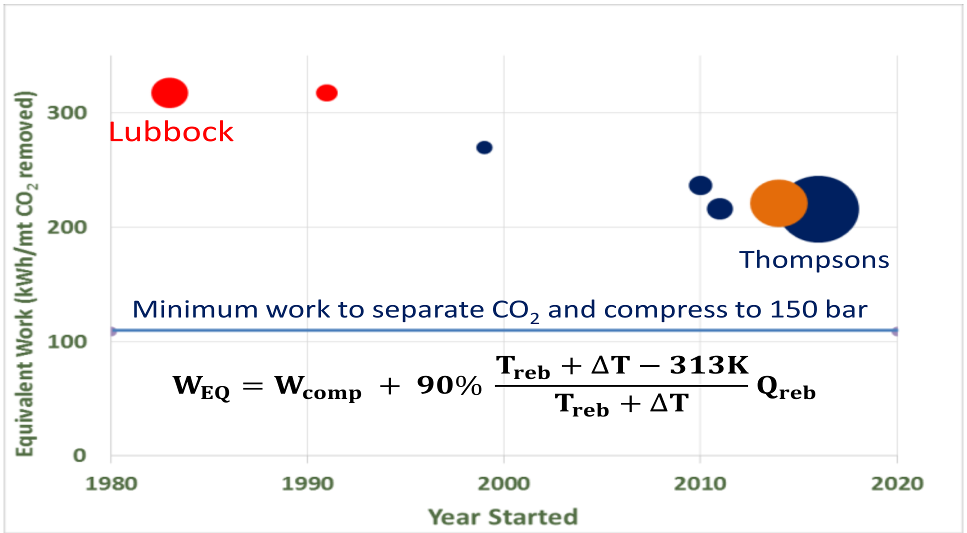


Figure E-5. Electricity Burden of Commercial Units
Source: Rochelle, G. T. (2014). "From Lubbock, TX to Thompsons, TX: A technical review of the progress in amine scrubbing," plenary presentation at Greenhouse Gas Control Technologies 12, Austin, Texas.

H. Energy Criteria for Solvent Selection

Four solvent properties dominate the selection of solvents based on energy performance—working capacity of the solvent, its CO_2 absorption rate, heat of CO_2 absorption, and thermal degradation. With an advanced process configuration each of these solvent properties is tied to an important capital cost/energy use tradeoff.

Solvent capacity for CO_2 determines the capital cost and energy loss of the cross exchanger. The rate of CO_2 absorption determines the absorber packing requirement and loss of work as driving force. The heat of CO_2 absorption and maximum operating temperature determine the compressor, reboiler, and stripper capital cost and lost work.

1. Capacity

The capital and energy cost of the cross exchanger depend on the working capacity of the solvent through a trade-off of the exchanger size and approach temperature. The effect of solvent capacity would be eliminated with an infinitely large exchanger, but that would result in a prohibitive capital cost.

At the optimum conditions of a plate-and-frame exchanger, the energy cost and the capital cost depend on the working capacity of the solvent and its important heat transfer properties as given by the normalized working capacity of the solvent, ΔC_{norm} (mol CO_2/kg solvent):[11]

$$\Delta C_{norm} = \Delta C_{solv}\left(\frac{k}{k_{5\ m\ PZ}}\right)^{0.325}\left(\frac{C_p}{C_{p,5mPZ}}\right)^{-0.825}\left(\frac{\mu}{\mu_{5\ m\ PZ}}\right)^{-0.175}$$

The working capacity of the solvent (ΔC_{solv}, mol CO_2/kg solvent) must be estimated with adjustment for the performance of the absorber. A consistent rich loading for all solvents can be estimated as the loading that gives an equilibrium partial pressure of 5 kPa at 40°C. This gives a reasonable driving force at the bottom of an absorber with an inlet at 40°C and 12% CO_2 (coal flue gas). The lean loading can be estimated as that which gives an equilibrium partial pressure of 0.5 kPa at 40°C. With 90% CO_2 this condition gives the same relative driving force, is achievable using intercooling with most solvents, and frequently minimizes the energy requirement of the stripper.

2. CO_2 Absorption Rate

CO_2 is usually absorbed into aqueous amine by the mechanism of mass transfer with fast reaction in the liquid boundary layer. The liquid film resistance for mass transfer in MEA can be expressed in terms of the CO_2 partial pressure driving force by:[12]

$$\frac{1}{k_g^{'}} = \frac{\gamma_{CO2}^{0.5} H_{CO2,H2O}}{\sqrt{k\gamma_{MEA}^2 [MEA]_i^2 D_{CO2}}} + \frac{1}{k_{l,prod}^{o}}\left(\frac{\Delta P_{CO2}^{*}}{\Delta [CO_2]_T}\right)$$

At normal absorption conditions the absorption rate does not depend on $k^o_{l,prod}$ (a function of packing properties and fluid mechanics) but it does depend on the square root of the kinetics (a property of the solvent). The important property of the packing is the wetted area.

As shown in Figure E-6, k_g' decreases with increasing equilibrium CO_2 partial pressure over the solution, which is a surrogate for the CO_2 loading.

---

[11] Yuan, Y., and Rochelle, G.T. (2019). "Water-lean solvents for CO_2 capture will not use less energy than second generation aqueous amine processes," presented at IJGCC.

[12] Dugas, R. E. (2009). "Carbon Dioxide Absorption, Desorption, and Diffusion in Aqueous Piperazine and Monoethanolamine," Ph.D. Dissertation. University of Texas at Austin.

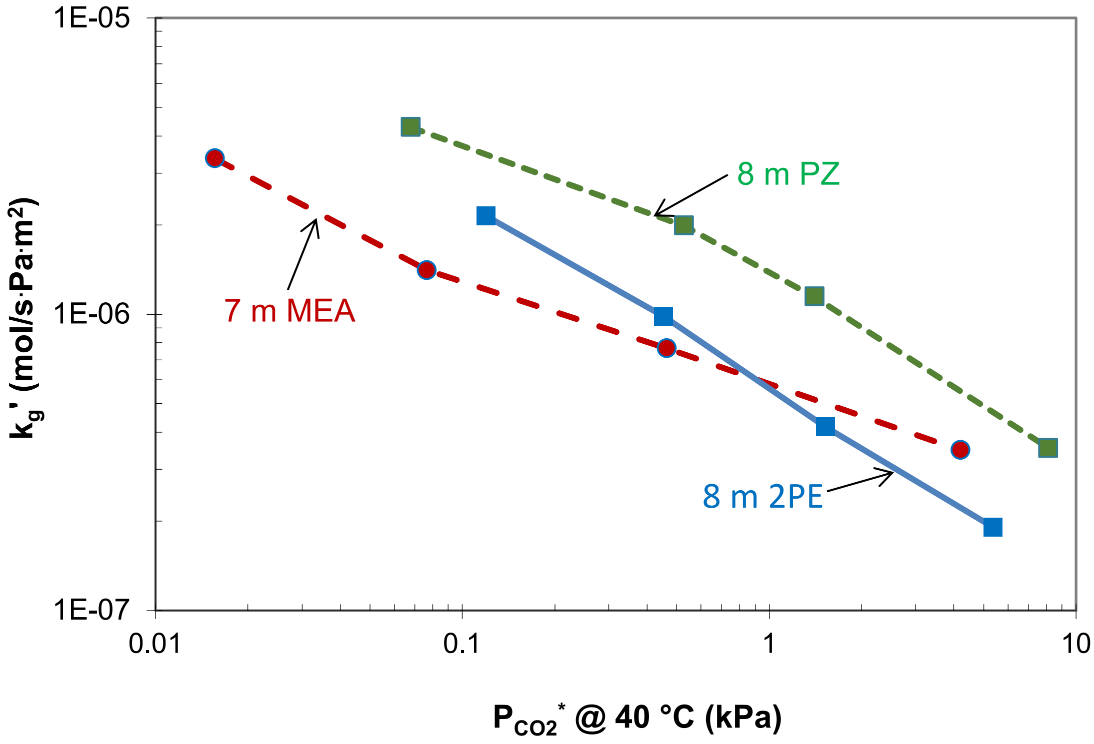


Figure E-6. Normalized CO_2 Absorption Rate at 40°C Measured by Wetted Wall Column
Source: Chen, X. (2011) "Carbon Dioxide Thermodynamics, Kinetics, and Mass Transfer in Aqueous Piperazine Derivatives and Other Amines," Ph.D. Dissertation, University of Texas at Austin.

The kinetics of CO_2 reaction with primary and secondary amines can be given by the base-catalyzed mechanism:[13]

$$r_{CO2} = -\sum k_B [B] Amine [CO_2]$$

The base, B, can be water, the parent amine, or another amine species.

The CO_2 reaction rate with tertiary amines is much slower. This reversible fast reaction must occur in the boundary layer or bulk solution to provide a route to the equilibrium concentration of bicarbonate. Usually tertiary amines for CO_2 capture are used with a rate promoter such as a primary or secondary amine.

---

[13] Crooks, J. E. and Donnellan, J. P. (1989). "Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution," J Chemical Soc, Perkin Transactions 2, 2(4), 331.

3. Heat of CO_2 Absorption

Greater heat of CO_2 absorption (ΔH) will improve the energy performance of amine scrubbing with thermal swing regeneration because the vapor pressure of CO_2 (P^*_{CO2}) increases with temperature (T) and the heat of absorption, as explained by the Clausius-Clapeyron relationship:

$$\frac{d\ln\,(P^*_{CO2})}{d\frac{1}{T}} = -\frac{\Delta H}{R}$$

Greater stripper temperature (and pressure) will also be beneficial in many cases.

Two components of the reboiler heat duty go in opposite directions with the heat of absorption. The heat duty in mol steam/mol CO_2 removed (S_{rxn}) will be directly proportional to the heat of CO_2 absorption ($\Delta HCO2$):

$$S_{rxn} = {}^{\Delta H_{CO_2}}\!\big/_{\Delta H_{H_2O}}$$

The heat duty associated with the stripping steam (S H_2O) will decrease with increasing heat of CO_2 absorption:

$$S_{H_2O} = \left[\frac{H_2O}{CO_2}\right]_A EXP\left[\frac{-(\Delta H_{CO2} - \Delta H_{H2O})}{R}\left(\frac{1}{T_A} - \frac{1}{T_S}\right)\right]$$

The pressure of the stripper (P CO_2) will also increase with the heat of CO_2 absorption:

$$P_{CO2} = P_{CO2,lean\ abs}\ \exp\left(\frac{\Delta H_{CO2}}{R}\left[\frac{1}{313} - \frac{1}{T_{mox}}\right]\right)$$

$$P_{total} = P_{CO2} + P_{H2O}\ (T_{max})$$

The maximum temperature of the stripper (T_{max}) will usually be determined by the thermal degradation of the solvent. Compression work will be reduced at greater P_{total}/greater T_{max}. Greater stripper temperature will require greater steam temperature and increase the work equivalent of the steam heat per the relationship for W_{eq}.

4. Thermal Degradation

Thermal degradation of the solvent sets the maximum stripper T/P. If the stripper is operated at the maximum temperature compatible with the conveniently available steam pressure, the stripper and compressor capital cost will be minimized and the overall performance will be improved. Therefore, it can be expected that an optimized design will operate the stripper 5°C to 10°C colder than the available condensing steam temperature or at T_{max}, whichever is lower. In a new plant it will usually be ideal to select a condensing steam temperature that is 5°C to 10°C hotter than T_{max}.

The thermal degradation property of a solvent can be specified as its T_{max}—the temperature at which the thermal degradation rate constant of the loaded solvent is 2%/week or $2.9e^{-8}$ s^{-1}. The T_{max} of MEA is about 120°C. Namjoshi tabulated available T_{max} for a number of solvents. Rochelle describes four important degradation mechanisms:[14,15]

- "Diamine structures where two secondary or primary Ns are separated by two or three carbons readily degrade at T_{max} of 104 to 118°C in the presence of CO_2 to produce cyclic ureas (imidazolidinone)."[16]
- "Primary and secondary alkanolamines with two or three carbons between the N and oxygen degrade by reversibly forming a cyclic oxazolidinone from the carbamate, which then reacts with another amine to form a dimer of the starting amine."[17] T_{max} varies from 102 to 127°C.
- In blends of tertiary amines with secondary or primary amines the reactive amine will react with alpha carbons on the protonated tertiary amine, especially with methyl groups. Tertiary blends with piperazine have T_{max} from 120 to 140°C.
- "Piperazines, morpholine, piperidines, and long chain diamines degrade by ring closing or opening with T_{max} from 140 to 170°C."

I. Solvent Management Criteria

Other important solvent properties determine the loss of solvent and the resulting secondary environmental impact. Oxidative degradation of the solvent is a problem unique to flue gas treating. The formation and decomposition of nitrosamine represents an important side reaction with flue gas impurities that can result in toxic products. Amine volatility and its loss as an amine aerosol may be the most significant secondary environmental impact.

1. Oxidative Degradation

Amine oxidation is a unique problem in the application of amine scrubbing to CO_2 capture from oxygen-containing flue gas. Even with numerous detailed investigations over the last 15 years, there is not yet a clear understanding of the mechanisms by which it takes place.

---

[14] Namjoshi, O. A. (2015). "Thermal Degradation of PZ-Promoted Tertiary Amines for CO_2 Capture," Ph.D. Dissertation, University of Texas at Austin.

[15] Rochelle, G. T. (2012). "Thermal Degradation of Amines for CO_2 Capture," Curr Opin Chem. Eng, 1(2), 183-190.

[16] Ibid.

[17] Ibid.

Chi,[18] Goff,[19] and Voice[20] showed that Fe++, Mn++ (from corrosion or leaching of fly ash) and Cu++ (added as a corrosion inhibitor) are potent catalysts of MEA oxidation.

Sexton,[21] Freeman (2011), and Voice[22] identified a number of amines including PZ and MDEA that are resistant to oxidation at absorber conditions. Goff and Voice identified a number of oxidation inhibitors including Inhibitor A that are effective at absorber T, but these seem to fail at stripper T in a cyclic system.[23,24] In a simple world, the resistant amines or other amines with oxidation inhibitors would react at elevated exchanger and stripper temperature with the saturated level of dissolved oxygen left in the rich solution from the absorber. This lower level of oxidation could be further minimized by stripping out the dissolved oxygen before the rich solution is heated.

In bench-scale experiments with cycling to stripper temperature, Closmann[25] and Voice[26] showed that the elevated temperature of the stripper results in levels of oxidation that can only be explained by a shuttle mechanism. Higher concentrations of dissolved metal (such as Fe++) may oxidize in the absorber (to Fe+++) and then serve as oxidizing agents at the stripper temperature. Dissolved metals appear to be critical to this mechanism, so oxidation would be minimized by reducing corrosion, utilizing thermal reclaiming, and otherwise minimizing the accumulation of dissolved metals. The amount of oxidation would also be minimized by reducing the time and temperature at stripper conditions.

Amine selection also impacts the oxidation rate with the shuttle mechanism. With the cycling apparatus, Voice showed that the oxidation of selected amines can vary by a factor of 20 (Figure E-7).[27] PZ and tertiary amines such as MDEA are resistant to oxidation. Hindered amines such as AMP are especially resistant.

---

[18] Chi, S. (2000). "Oxidative Degradation of Monoethanolamine," M.S. Thesis. University of Texas at Austin.

[19] Goff, G. (2005). "Oxidative Degradation of Aqueous Monoethanolamine in CO_2 Capture Processes: Iron and Copper Catalysis, Inhibition, and O_2 Mass Transfer," Ph.D. Dissertation. University of Texas at Austin.

[20] Voice, A. K. (2013), "Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing," Ph.D. Dissertation. University of Texas at Austin.

[21] Sexton, A. J. (2008). "Amine Oxidation in CO_2 Capture Processes," Ph.D. Dissertation. University of Texas at Austin.

[22] Voice, A. K. (2013), "Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing," Ph.D. Dissertation. University of Texas at Austin.

[23] Goff, G. (2005). "Oxidative Degradation of Aqueous Monoethanolamine in CO_2 Capture Processes: Iron and Copper Catalysis, Inhibition, and O_2 Mass Transfer," Ph.D. Dissertation. University of Texas at Austin.

[24] Voice, A. K. (2013), "Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing," Ph.D. Dissertation. University of Texas at Austin.

[25] Closmann, F. (2011) "Solvent Management of MDEA/PZ," Ph.D. Dissertation. University of Texas at Austin.

[26] Voice, A. K. (2013), "Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing," Ph.D. Dissertation. University of Texas at Austin.

[27] Ibid.

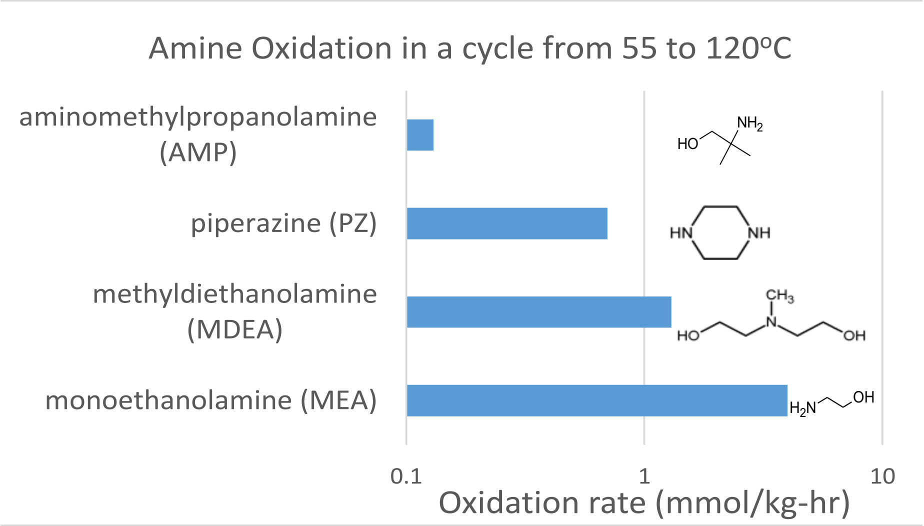


Figure E-7. Oxidation Rate of Common Amines with Cycling from 55°C to 120°C
Source: Voice, A. K. (2013), "Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing," Ph.D. Dissertation. University of Texas at Austin.

Sexton quantified a number of the oxidation products of MEA.[28] Formate and ammonia appear as oxidation products that are common to practically all amines. At stripper conditions, the formate equilibrates with the respective amide of a parent primary or secondary amine. Aldehydes and their respective imines and hemiaminals are also common in many systems. Many of the aldehyde species are in reversible equilibria, but there can be stable species such as hydroxyethylimidizole (HEI) formed in MEA systems from ammonia, MEA, glyoxal, and formaldehyde. PZ oxidizes to 2-hydroxy-piperazine, a stable hemiaminal.

Unfortunately, primary and tertiary amines oxidize to form some secondary amines, so these systems are not immune to nitrosamine formation. MEA oxidizes to make some hydroxyethylglycine. MDEA oxidizes to make large quantities of diethanolamine.

2. Nitrosamine

All amines are oxidized by NO_2 from the flue gas. Secondary amines react with nitrite at stripper conditions to make carcinogenic nitrosamines that may create significant secondary environmental impacts. Fine has completed a comprehensive model of the nitrosamine cycle.[29]

---

[28] Sexton, A. J. (2008). "Amine Oxidation in CO_2 Capture Processes," Ph.D. Dissertation. University of Texas at Austin.

[29] Fine, N. A. (2015). "Nitrosamine Management in Aqueous Amines for Post-Combustion Carbon Capture," Ph.D. Dissertation, University of Texas at Austin.

NO_2 contained in the flue gas as 2% to 5% of the total NOx is partially removed in a typical SO_2 polishing scrubber. With the addition of thiosulfate to inhibit sulfite oxidation, 70% to 95% of the NO_2 can be removed in the polishing scrubber.[30]

Residual NO_2 will be removed in the amine absorber by reaction with the amine in the liquid to produce oxidized amine and nitrite. Secondary and tertiary amines will remove 90% to 99% of the NO_2. Primary amines react more slowly and may remove as little as 50%.

NO_2 may also catalyze amine oxidation in the absorber by acting as a free radical initiator. In pilot plant testing, the oxidation of piperazine is always significantly greater in the presence of >1 ppm NO_2.[31]

At the temperature and residence time of the stripper, practically all of the nitrite reacts with the amine. Reaction with secondary amine produces stoichiometric nitrosamine. Reaction with primary and tertiary amine is slower and produces oxidation products and N_2. Since solvents comprising tertiary and/or primary amines will have secondary amines that are products of degradation, nitrosamines will still be produced at the stripper condition.

At the temperature of the stripper the nitrosamine thermally degrades to oxidation products and probably N_2O. The nitrosamine will accumulate to a steady-state concentration where the rate of production from NO_2 incursion into the absorber is equal to the rate of thermal decomposition. Estimated values of steady-state nitrosamine with 120^oC stripping that vary from 0.9 millimolar (mM) in MEA to 20.5 mM in MDEA/PZ.[32]

Nitrosamine accumulation can be managed by solvent selection, high temperature stripping, NO_2 removal in the polishing scrubber, and upstream NOx controls.

3. Amine Volatility

Although moderate levels of amine volatility (10 to 100 ppm) are managed by the water wash at the absorber gas outlet, excessive amine volatility will require a more costly water wash system. Amines with low or no volatility cannot be reclaimed easily by evaporation. Therefore, we are looking for amine solvent with a moderate or possibly low volatility.

---

[30] Selinger, J. L. (2018), "Pilot plant modeling of advanced flash stripper with piperazine," MS Thesis, University of Texas at Austin.

[31] Rochelle, G. T. et al. (2019). "Pilot plant demonstration of piperazine with the advanced flash stripper," presented at Greenhouse Gas Control Technologies 14, submitted to IJGCC.

[32] Fine, N. A. (2015). "Nitrosamine Management in Aqueous Amines for Post-Combustion Carbon Capture," Ph.D. Dissertation, University of Texas at Austin.

Nguyen[33] and Du[34] measured amine volatility in water for 44 solvents. Du correlated the Henry's constant, H_{amine} (Pa), of amine in water with 14 structure parameters:[35]

$$ln\, H_{amine,313.15K}\ (Pa) = 17.5 + \sum k_j\, n_j$$

where k_j is the parameter value for functional group j, and n_j is the number of occurrences of group j in an amine structure.

Amines with acceptable volatility all have at least two hydrophilic groups (N, O, OH, etc.). Amines with more than three hydrophilic groups are essentially nonvolatile. Alkyl groups on tertiary amines substantially increase volatility. Adding molecular weight as alkyl groups always increases the amine volatility.

The effect of CO_2 loading on amine volatility varies with the solvent. In MDEA or AMP the volatility of the amine slightly increases with CO_2 loading because the bicarbonate salts out the somewhat hydrophobic amine. In PZ and other polyamines, CO_2 loading significantly reduces the volatility of the amine by speciating it out as a carbamate or protonated amine ion.

4. Amine Aerosol Emissions

Flue gas that contains significant aerosol nuclei (>106 particles/cm^3) as H_2SO_4 (1 to 10 parts per million by volume (ppmv)), fine fly ash, etc., may result in economically and environmentally unacceptable amine emissions as liquid aerosol (<2.5 µm drops). A number of pilot plants with coal-fired flue gas and other dirty gas sources have observed total carryover exceeding 10 ppm amine with a water wash that should have reduced the emissions of vapor amine to <2 ppm.

One explanation is that the aqueous nuclei have an amine solvent concentration that is rich in CO_2. The bulk amine solvent has a lower CO_2 loading. With most amines, the amine vapor pressure over the bulk solvent is greater than that of the aerosol, so amine transfers to the aerosol, taking with it CO_2 and water. If the nuclei only grow a little (to <2.5 µm), they are not captured in the water wash. If there is growth to greater than 2.5 µm, these drops may be captured in the water wash. With this complicated mechanism, results should be expected to vary with the solvent, process, and flue gas source.

Nevertheless, MHI, Aker, and BASF have all reported successful testing of countermeasures to minimize amine aerosol emissions. Aker has patented and demonstrated use of greater temperature

---

[33] Nguyen, B-T. N. (2013). "Amine Volatility in CO_2 Capture," Ph.D. Dissertation, University of Texas at Austin.

[34] Du, Y. (2016). "Amine solvent development for carbon dioxide capture," Ph.D. Disseration, University of Texas at Austin.

[35] Ibid.

in the top of the absorber.[36,37] BASF discusses use of a dry bed of packing between the absorber and water wash.[38] MHI reports work identifying the problem as SO_3 in the flue gas and resolving the problem with countermeasures. Mertens et al. showed that the appropriate use of a gas/gas heat exchanger before the flue gas desulfurization system would minimize H_2SO_4 nuclei before the amine scrubber and therefore reduce amine aerosol emissions. TNO demonstrated the use of a Brownian Diffusion Filter to remove the aerosol after the water wash.[39] Despite these measures this is an open problem area, the mechanisms and countermeasures of which are not completely understood.

Aerosol emissions have not been observed in pilot plants or commercial units with coal-fired flue gas that has passed through a bag filter, usually with injection of activated carbon or hydrated lime that removes any SO_3.

5. Amine Cost and Availability

Amine molecules are expensive and are likely to remain so. Even if oxidation and thermal degradation can be minimized there will be steady-state and episodal impurities in the flue gas, especially from coal, that will result in amine losses and prohibitive makeup costs. MEA losses equivalent to \$1 to \$2/tonne CO_2 are acceptable with an amine price of \$2/kg. With five times less loss, an amine cost of \$10/kg might be acceptable.

The amine price will be related to the number of reaction steps to get from common raw material to the amine. MEA requires three steps:

Ethane → Ethylene → ethylene oxide → MEA

Piperazine can be synthesized from MEA with one more step or produced as a co-product of ethylenediamine with three steps:

Ethane → Ethylene → Ethane dichloride → PZ

---

[36] Bade, O. M., Knudsen, J. N., Gorset, O., and Askestad, I. (2014). "Controlling amine mist formation in CO_2 capture from Residual Catalytic Cracker (RCC) flue gas," Energy Proc, 63, 884–892.doi: 10.1016/j.egypro.2014.11.098.

[37] Bade, O. M., Woodhouse, S., Gorset, O., and Andersson, V, (2014). "Method for Mist Control, US Patent Application," 2014/0116251 A1. 2014-May-01.

[38] Moser P., Schmidt S., Stahl K., Vorberg G., Lozano G. A., Stoffregen T., and Rösler F. (2014). "Demonstrating Emission Reduction – Results from the Post-combustion Capture Pilot Plant at Niederaussem," Energy Proc, 63, 902–910.doi: 10.1016/j.egypro.2014.11.100.

[39] Mertens, J., Bruns, R., Schallert, B., Faniel, N., Khakharia, P., Albrecht, W., Goetheer, E., Blondeau, J., and Schaber, K. (2015). "Effect of a Gas-Gas-Heater on H_2SO_4 aerosol formation: implications for mist formation in amine-based carbon capture," Int J Greenhouse Gas Cont, 39, 470–477.doi: 10.1016/j.ijggc.2015.06.013.

HMPD (4-hydroxy-1-methyl-piperidine) requires 7 steps and will probably be too expensive unless another route can be found with fewer steps:

Propane → propylene → ethyl-methacrylate → Michael addition → Dieckmann condensation → Decarboxylation → hydrogenation → HMPD

6. Molecular Weight

Large molecules are not attractive. The equivalent weight (molecular weight/number of active amine groups) is an indicator of the cost of amine inventory and makeup in the event of degradation; more kilograms of amine are required to get the same performance.

Even if the equivalent weight is acceptable, large molecules result in greater solvent viscosity. Greater viscosity reduces the heat transfer coefficient and the diffusion coefficient of CO_2 and amine. Large molecules also have intrinsically reduced diffusion coefficients of their own.

7. Corrosion

Most amine solvents are not compatible with carbon steel at all conditions. Structured packing and the plates for plate-and-frame exchangers are thin and require stainless steel regardless.

Corrosion measurements with MEA solvents suggest that stainless steel should be used at practically all conditions. However, several solvents including MDEA and PZ are not corrosive to carbon steel at lower temperature or form a protective film of FeCO3 that may protect carbon steel at stripper temperature.

Corrosion measurements with PZ bench-scale and pilot-scale experiments; have shown that carbon steel is resistant to corrosion at absorber temperature but fails at stripper temperature when there is a larger concentration of degradation products.[40,41] SS 316L can also fail at 150°C in the stripper.

Materials selection will play a critical role in commercial plant reliability and capital cost. Corrosion measurements and understanding represent an important need to minimize risk and cost.

J. Summary of Important Representative Solvents

The experimental properties of amine solvents tested at the University of Texas at Austin are summarized by Li.[42] Coal-fired flue gas was used as the basis for estimating the parameters. The

---

[40] Rochelle, G.T. et al. (2019) 'Pilot plant demonstration of piperazine with the advanced flash stripper' presented at Greenhouse Gas Control Technologies 14, submitted to IJGCC.

[41] Liu, C-T., Fischer, K., Rochelle, G.T. (2019). "Corrosion of carbon steel by aqueous piperazine protected by FeCO3," presented at Greenhouse Gas Control Technologies 14, submitted to the *International Journal of Greenhouse Gas Control*.

[42] Li, L. (2015). "Carbon dioxide solubility and mass transfer in aqueous amines for carbon capture," Ph.D. Dissertation. University of Texas at Austin.

capacity was evaluated at loading that gives an equilibrium CO_2 partial pressure at 40°C of 5 kPa at rich conditions and 0.5 kPa at lean conditions.

1. Monoethanolamine

MEA is an important candidate for CO_2 capture by amine scrubbing because it is the least expensive of the important solvents. It is produced in large quantities from the reaction of ammonia and ethylene oxide, a primary raw material for antifreeze polyester. It is a primary amine near the optimum pKa so it has an average rate of CO_2 absorption and above average normalized capacity with excellent viscosity. Its heat of CO_2 absorption is high, so it performs well with thermal swing regeneration.

Unfortunately, MEA is prone to oxidative degradation and its T_{max} for thermal degradation is 120°C. Oxidation inhibitors, nitrogen sparging to remove dissolved oxygen, or other methods will be required to manage oxidation.

2. Piperazine

PZ is an excellent solvent alternative. More work has been published on this second generation solvent than on others. With the highest rate of CO_2 absorption, 5 m (30 wt %) PZ is 2.6 times faster than MEA. Its normalized capacity is 22% greater than 7 m MEA. Its heat of absorption is low (64 kJ/mol), but with excellent thermal stability, Pmax is 14 bar, so that can make up for the lower ΔHabs. Piperazine interacts with NO_2/nitrite to produce nitrosamine. However, the nitrosamine is easily degraded at 150°C, which is achievable with the thermally stable PZ.

3. PZ Blends

Most tertiary and hindered amines react too slowly with CO_2 to provide an acceptable rate of CO_2 absorption. However, they usually provide excellent capacity; the greatest normalized capacity (1.14) is achieved with 4.8 m AMP or 8 m 2-PE, both hindered amines. Therefore, a blend of PZ or another fast amine with a tertiary or hindered amine usually provides good rate and good capacity. Unfortunately, PZ usually accelerates the thermal degradation of the other amine, so few of these blends have high T_{max} or P_{max}. Furthermore, mononitrosopiperazine will accumulate in most of these solvents that regenerate at 120°C, so the nitrosamine must be managed by NO_2 prescrubbing or other means.

Although 7 m MDEA/2 m PZ duplicates many of the good properties of PZ, it does not have its issues of solid solubility. MDEA/PZ has been used for many years as a gas treating solvent. It is not as resistant as PZ to oxidation but is more stable than MEA. Thermal degradation limits regeneration to 120°C.

Although 2 m PZ with 4 m 2-amino-2-methyl-1-propanol (AMP) also has properties comparable to 5 m PZ, it has no issues of solid solubility. It should be just as stable or more stable to oxidation but is limited by thermal degradation to 128°C. AMP has a greater volatility than MEA in lean solution, so water wash will be more critical.

Although practically equivalent to 5 m PZ in rate, capacity, and thermal stability, 2 m PZ with 3 m 4-hydroxy-1-methyl-piperidine (HMPD) does not have any issue with solid solubility. The HMPD component is comparable in volatility to MEA. However, the production of HMPD requires four reaction steps from ethylmethacrylate, so the cost of the amine will be high.

K. Conclusions

Conventional amine scrubbing was first used decades ago and has continued to be a dominant technology for post-combustion capture. There are no insurmountable technical problems in its deployment.

Second generation amine scrubbing will provide an energy performance better than 50% thermodynamic efficiency, with an electricity burden approaching 200 kWh/tonne CO_2 in the coal-fired application.

Amine aerosol emissions and amine oxidation are not yet completely understood and managed. These loss mechanisms will need to be addressed in any significant commercial application of amine scrubbing.

Corrosion/materials selection is not well understood and must be addressed for each new solvent development.