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## Quantitative Evaluation of the Aqueous-Ammonia Process for CO<sub>2</sub> Capture Using Fundamental Data and Thermodynamic Analysis

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### Abstract

There is strong world-wide interest in developing new and improved processes for post-combustion capture of CO<sub>2</sub>, usually using chemical absorption. Developers of new processes make positive claims for their proposals in terms of low energy consumption, but these are usually difficult to validate. This paper demonstrates that rigorous application of thermodynamic analysis and process simulation provides a powerful way to quantitatively evaluate the energy requirements of CO<sub>2</sub>-capture processes by applying this methodology to the analysis of the chilled-ammonia process.

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## 1. Introduction

There is strong world-wide interest in developing new and improved processes for post-combustion capture of CO<sub>2</sub>, usually using chemical absorption [1,2]. Developers of new processes make positive claims for their proposals in terms of low energy consumption, but these are usually difficult to validate. This paper demonstrates that rigorous application of thermodynamic analysis and process simulation provides a powerful way to quantitatively discriminate among various CO<sub>2</sub>-capture processes, by applying this methodology to the analysis of an aqueous-ammonia process, specifically the chilled-ammonia process [3].

Chemical absorption is complicated and difficult to analyze because many complexes and ionic species may form and the calculated phase equilibrium and heats of absorption and stripping depend on proper representation of the speciation and the solution nonideality. But applied thermodynamicists and chemical engineers have many decades of experience in this area [4], and a variety of data (vapor-liquid and liquid-solid equilibrium, spectroscopic investigation of species distribution, calorimetric measurement of heats of solution, etc.) are usually available to develop and validate the thermodynamic models.

Process simulation of electrolyte systems is also an established tool in chemical engineering, and serves as an effective basis to rapidly and accurately analyze various process schemes [5]. Process simulation also provides the means to interpret laboratory experiments and identify the underlying phenomena.

This work demonstrates the power of thermodynamic analysis and process simulation by applying these tools to the analysis of the chilled-ammonia process.

## 2. Chemical Absorption for CO<sub>2</sub> Capture – Thermodynamic Analysis

A wide variety of processes for post-combustion capture of CO<sub>2</sub> are currently being researched, and these include absorption using solvents or solid sorbents, pressure- and temperature-swing adsorption, cryogenic distillation, and membranes [1,2]. The focus of the present analysis is on absorption using chemical solvents since this is the current state of the art [1,2]. In post-combustion CO<sub>2</sub>-capture processes by chemical absorption, the “lean” solvent preferentially absorbs CO<sub>2</sub> from the flue gas at the low absorption pressure (about 1 atm). The “rich” solvent is regenerated in a stripper at elevated temperatures to produce the CO<sub>2</sub> product and the lean solvent that is recycled back to the absorber. Chemical-absorption processes for post-combustion CO<sub>2</sub> capture are in successful operation today [6], and hence the competitiveness of a particular process is related to the associated process costs, most significantly the utility costs: heating (steam), cooling (cooling water) and chilling (refrigeration).

Thermodynamic analysis offers a powerful technique to perform reliable and accurate analysis of the utility costs of a chemical-absorption process [7]. An accurate thermodynamic model is needed for the complex, electrolytic system, but this can be accomplished today due to the availability of molecular-thermodynamic models and the underlying phase-equilibrium data, analytical data on speciation and calorimetric measurements of the heats of solution [4,7]. Once the thermodynamic model has been developed, commercial software (e.g., Aspen Plus® from Aspen Technology, Inc. and the OLI Engine® from OLI Systems, Inc) can routinely describe the entire integrated process, including absorbers, strippers and heat exchangers, as well as heat integration. Darde et al. [8] have presented thermodynamic analysis of the chilled-ammonia process.

## 3. Chilled-Ammonia Process

Aqueous-ammonia processes [9] have been proposed as energy-efficient alternatives to traditional alkanolamine absorption-stripping processes [6,10] for post-combustion capture of CO<sub>2</sub>. This work focuses on the chilled-ammonia process, which has been patented by Gal [3]. The process description presented here is concise, and the reader is referred to Gal's patent [3] for further details. Figure 1 presents the flow diagram of the process modeled in this work. Flue gas that has been desulfurized (not shown) has its pressure raised slightly using a blower, is cooled to 100°F using cooling water, is chilled to 41°F via refrigeration, and then enters the absorber (represented as a spray tower with chilled-liquid recirculation). The other process streams entering the absorber are make-up ammonia and lean solvent from the stripper. The lean solvent is chilled to 47°F and its CO<sub>2</sub> loading is at the point where solid ammonium bicarbonate (ABC) will precipitate. The absorber removes CO<sub>2</sub> from the flue gas mainly by the precipitation of ABC and has a recirculation loop with refrigeration that maintains it at a target temperature in

the range 30-50°F. The refrigeration load comes from three demands (flue-gas-chiller, recycle solvent chiller and absorber chiller). The solvent flow rate is set to absorb 90% of the CO<sub>2</sub> in the flue gas.

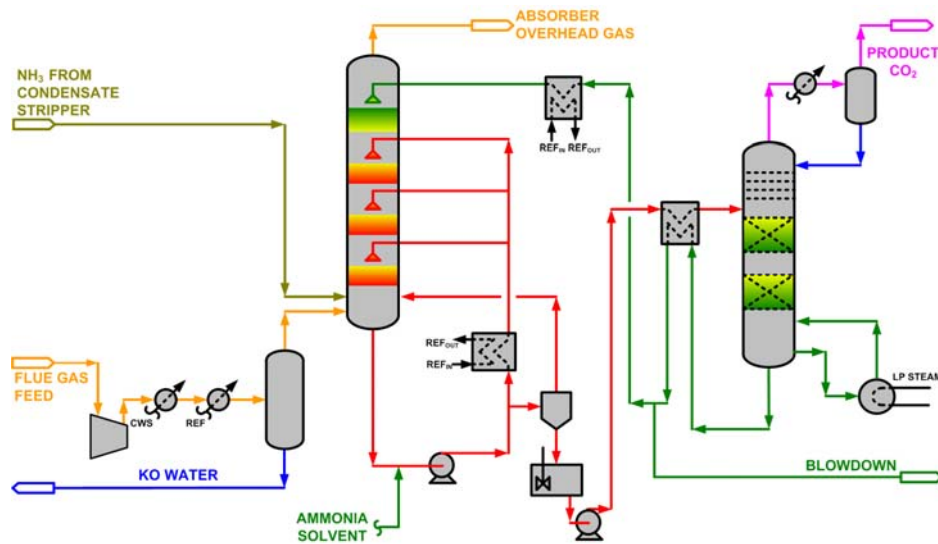


Figure 1 – Flow diagram of the chilled-ammonia process

The rich solvent is pumped to a higher pressure, heated in a cross exchanger (minimum approach temperature set to 10°F) with the hot lean solvent and enters a stripper that operates at 450 psia and produces the CO<sub>2</sub> product as distillate and the lean solvent as the bottoms. The stripper reboiler duty is set to achieve the CO<sub>2</sub> concentration in the lean solvent.

The specified variables in the flow diagram shown in Figure 1 are the flow and composition of the flue gas, the absorber temperature (30-50°F) and the NH<sub>3</sub> concentration of the solvent on a CO<sub>2</sub>-free basis. The key calculated results are the heat load (stripper reboiler duty), the refrigeration load (sum of three chiller duties) and the ammonia slip in the absorber.

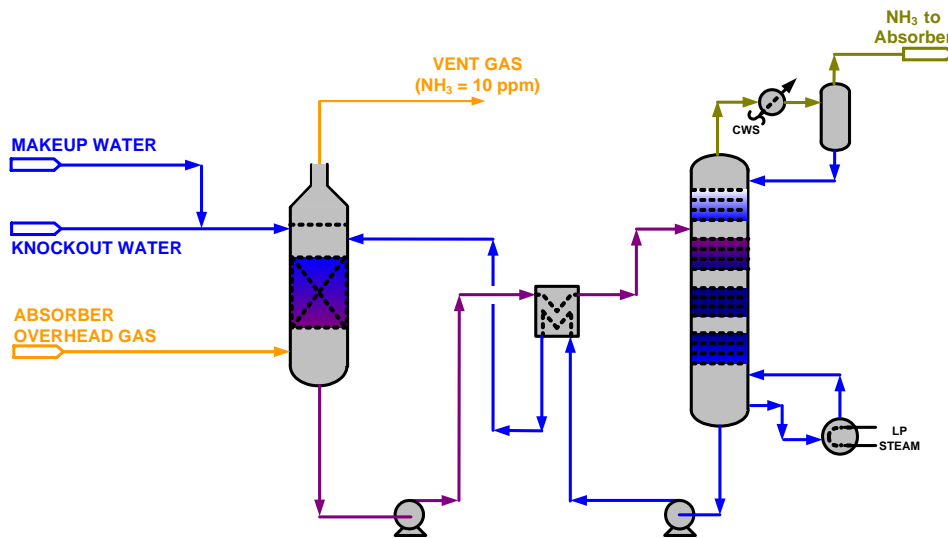


Figure 2 – Absorber-stripper system for NH<sub>3</sub> abatement from the CO<sub>2</sub> absorber overhead

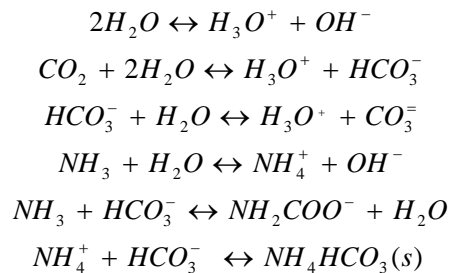
The  $\text{NH}_3$  slip in the absorber overhead is too high (240-2,200 ppmv, as shown in Section 5) for direct discharge into the environment, and thus needs additional treatment ( $\text{NH}_3$  abatement). Figure 2 presents the  $\text{NH}_3$ -abatement scheme analyzed in this work. The minimum approach temperature in the  $\text{NH}_3$ -abatement cross exchanger has been set to  $10^\circ\text{F}$ , and the recycle solvent flow rate and the stripper reboiler duty have been set to achieve 10 ppmv  $\text{NH}_3$  in the vent gas and water flow rate from the stripper overhead to balance water losses from the flow diagram of Figure 1. In other words, the purpose of the  $\text{NH}_3$ -abatement system is to control  $\text{NH}_3$  discharge into the environment and to maintain a water balance in the plant.

#### 4. Thermodynamic Model

The thermodynamic model used here was presented previously at the 7<sup>th</sup> Annual Conference on Carbon Capture & Sequestration [11]. Thermodynamic models for electrolyte systems require a chemistry model, which is a theoretically correct and practical representation of the ionization reactions that occur in the system, and a nonideality model [4].

The chemistry model for the  $\text{NH}_3$ - $\text{CO}_2$ - $\text{H}_2\text{O}$  system, which is presented in Table 1, identifies the acid-base effects through which  $\text{NH}_3$  as a weak base causes the chemical absorption of the weak acid  $\text{CO}_2$ . Absorbed  $\text{CO}_2$  exists as molecular  $\text{CO}_2$  (very small), and bicarbonate, carbonate and carbamate anions, while  $\text{NH}_3$  in solution exists as molecular  $\text{NH}_3$ , ammonium cation and carbamate anion. The final model should not only represent the total  $\text{CO}_2$  and  $\text{NH}_3$  in solution, but also quantitatively describe the concentrations of the various species since effects like heats of solution depend on correct speciation [4,7]. The chemistry model in Table 1 also includes the formation of  $\text{NH}_4\text{HCO}_3(\text{s})$  or ABC since this solid precipitates in the absorber.

Table 1 - Chemistry Model for the  $\text{NH}_3$ - $\text{CO}_2$ - $\text{H}_2\text{O}$  system



The nonideality model used here is the ElectrolyteNRTL [12] model available in Aspen Plus®, and the model parameters were adjusted to provide a good fit of the available vapor-liquid equilibrium [13,14], solid-liquid equilibrium [15], calorimetric [16] and speciation [17] data.

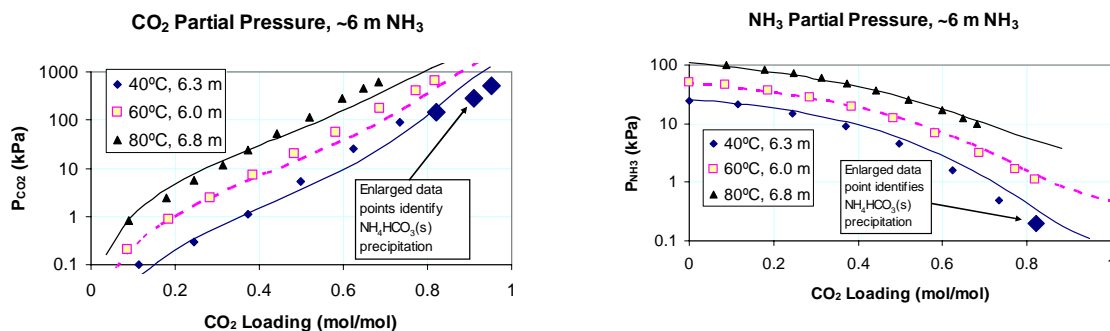


Figure 3 – Comparison between model calculations and data [14] for the partial pressures of  $\text{CO}_2$  and  $\text{NH}_3$  in 6m  $\text{NH}_3$  solutions.

Figure 3 demonstrates that the model provides good agreement with the vapor-liquid equilibrium data of Kurz et al. [14], and Figure 4 indicates that the speciation predictions of the model agree with the Raman spectra

measurements of Wen and Broker [17]. Mathias et al. [11] have further shown that the model provides an accurate representation of solid-liquid equilibrium [15] and calorimetric [16] data.

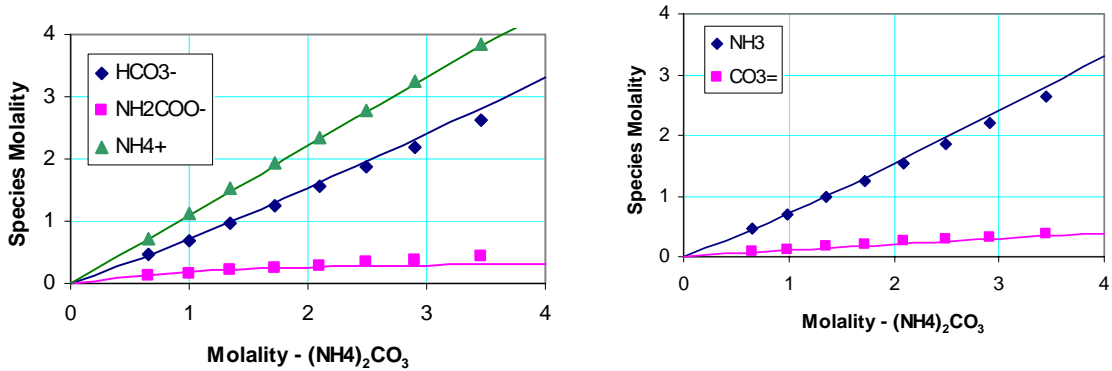


Figure 4 – Speciation in the (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> system at 295 K. Comparison between model calculations and the data of Wen and Broker [17].

### CO<sub>2</sub> Heat of Solution in 8 Wt% NH<sub>3</sub> @ 100°F

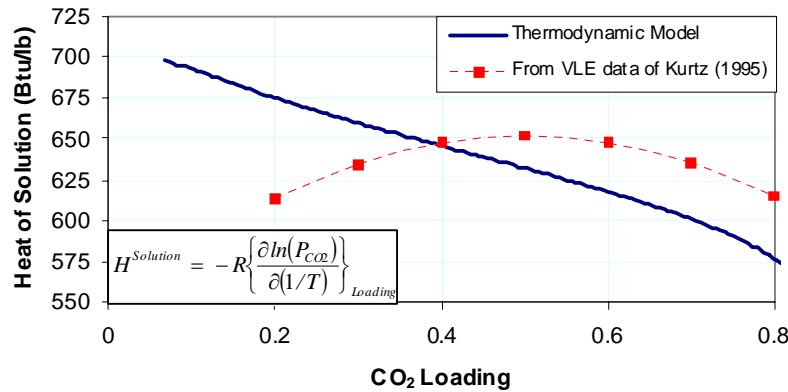


Figure 5 – Heat of solution of CO<sub>2</sub> in 8 wt% NH<sub>3</sub> at 100°F. Comparison between model predictions and thermodynamic analysis of the data of Kurtz et al. [14]

Figure 5 presents two independent calculations for the differential heat of solution of CO<sub>2</sub> in aqueous NH<sub>3</sub>. The thermodynamic analysis directly used the measured partial pressures of CO<sub>2</sub> to estimate its heat of solution.

$$H^{Solution} = -R \left\{ \frac{\partial \ln(P_{CO_2})}{\partial (1/T)} \right\} \quad (1)$$

The agreement between the two results, as well as agreement with the calorimetric data of Rumpf et al. [16] (previously presented by Mathias et al. [11]) clearly support the model validity and accuracy. The CO<sub>2</sub> heat of solution in aqueous NH<sub>3</sub> is less than that in aqueous MEA (which is about 800 Btu/lb CO<sub>2</sub> [18]), but is much higher than the 262 Btu/lb presumed by many researchers in the field [9]. As discussed by Mathias et al. [11], the incorrect estimation of the heat of solution (262 Btu/lb) results from fixed speciation rather than allowing the species

distribution to follow chemical equilibrium consistent with the chemistry model (Table 1) and measured data (e.g., Raman spectra [17]).

## 5. Process Analysis

The thermodynamic model for the  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$  system has been used to study a particular case of post-combustion  $\text{CO}_2$  capture by the chilled-ammonia process. The flue gas stream has a flow rate of 149,991 lbmol/hr with mole percents of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{O}_2$  as 11.04, 13.73, 71.75 and 3.48, respectively.

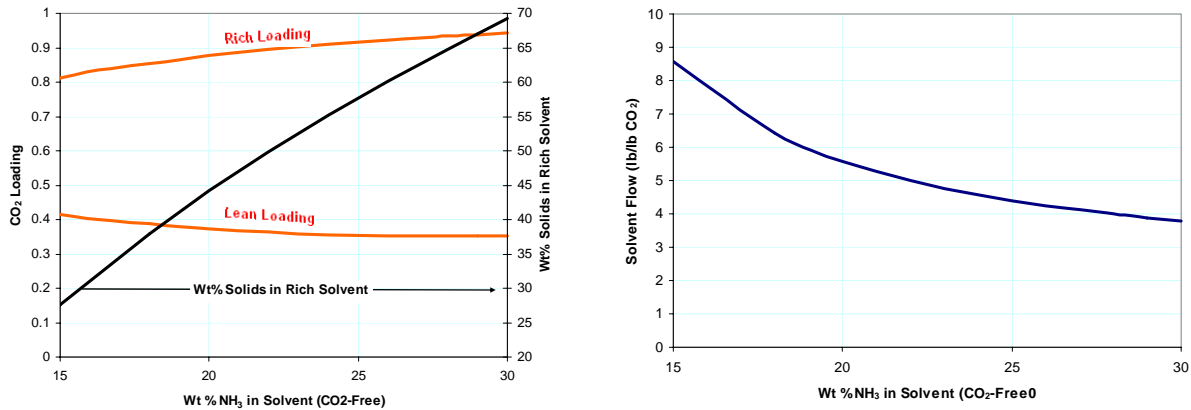


Figure 6 – Effect of  $\text{NH}_3$  concentration in the solvent on weight fraction solids in the rich solvent, lean and rich  $\text{CO}_2$  loadings and solvent flow rate. The absorber temperature is  $50^\circ\text{F}$ .

The first part of the study kept the absorber temperature fixed at  $50^\circ\text{F}$  and varied the  $\text{NH}_3$  composition in the solvent. Figure 6 indicates that increasing the  $\text{NH}_3$  concentration in the solvent decreases the solvent circulation rate since the solids content of the rich solvent increases and the difference between the rich and lean  $\text{CO}_2$  loadings also increase. The  $\text{NH}_3$  slip from the absorber is only weakly dependent on the  $\text{NH}_3$  concentration and depends mainly on temperature; at  $50^\circ\text{F}$ , the  $\text{NH}_3$  slip is 2,230 ppmv. This study focused on the 26 wt%  $\text{NH}_3$  ( $\text{CO}_2$ -free basis) solvent where the solids content of the rich solvent is 60.2%. For 26 wt%  $\text{NH}_3$ , the stripper duty is 985 Btu/lb  $\text{CO}_2$ , while the  $\text{NH}_3$  abatement regenerator duty is 1,022 Btu/lb  $\text{CO}_2$ , which gives a total LP steam requirement of 2,007 Btu/lb  $\text{CO}_2$ . This LP steam requirement is very high compared to typical LP steam requirements for alkanolamine-based processes, which are typically in the 1,200 to 1,500 Btu/lb  $\text{CO}_2$  range [9].

The  $\text{NH}_3$ -abatement regenerator steam requirement is high because the  $\text{NH}_3$  slip is high at the absorber temperature of  $50^\circ\text{F}$ . Figure 7 presents the reduction in  $\text{NH}_3$  slip achieved as the absorber temperature is reduced. If the absorber can be run at  $30^\circ\text{F}$ , the  $\text{NH}_3$  slip can be reduced to 242 ppmv, but  $\text{NH}_3$  abatement will still be needed to reduce the  $\text{NH}_3$  concentration in the flue gas discharged to the stack at the target level of 10 ppmv. Figure 8 shows how the absorber stripper duty and  $\text{NH}_3$  abatement regenerator duty vary as the absorber temperature is decreased. The total steam requirement is approximately constant below about  $35^\circ\text{F}$ , and in fact has a weak minimum of about 1,291 Btu/lb  $\text{CO}_2$  at  $35^\circ\text{F}$ . Hence, the steam requirements will be equivalent to alkanolamine-based  $\text{CO}_2$  capture processes if the absorber can be run at  $35^\circ\text{F}$ . But the chilled-ammonia process also incurs a refrigeration load of about -1,180 Btu/lb  $\text{CO}_2$  (Figure 8), which will require significant use of compressor power.

The results presented here provide good insight into the energy costs of the chilled-ammonia process, but further analysis is needed for quantitative comparison between this process and competing processes. The stripper reboiler operates at a relatively high temperature ( $302^\circ\text{F}$ ), while the reboiler of the  $\text{NH}_3$ -abatement regenerator operates at a fairly low temperature ( $228^\circ\text{F}$ ), thus their steam requirements should be considered differently. A coefficient of performance should be applied to the chilling duty and initial analysis indicates that one unit of compressor duty will obtain approximately five units of chilling energy. Finally, alkanolamine processes produce  $\text{CO}_2$  at a low pressure, while the chilled-ammonia process produces  $\text{CO}_2$  at a relatively high pressure (450 psia). Detailed analysis of all these effects is in progress and will be presented in the future.

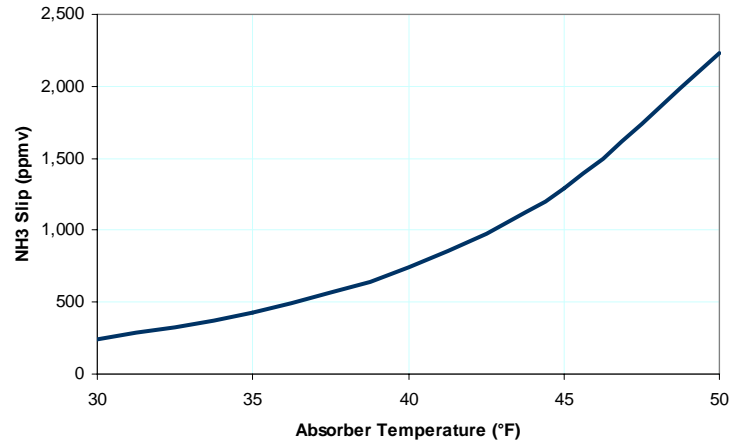


Figure 7 – NH<sub>3</sub> slip in absorber as a function of absorber temperature.

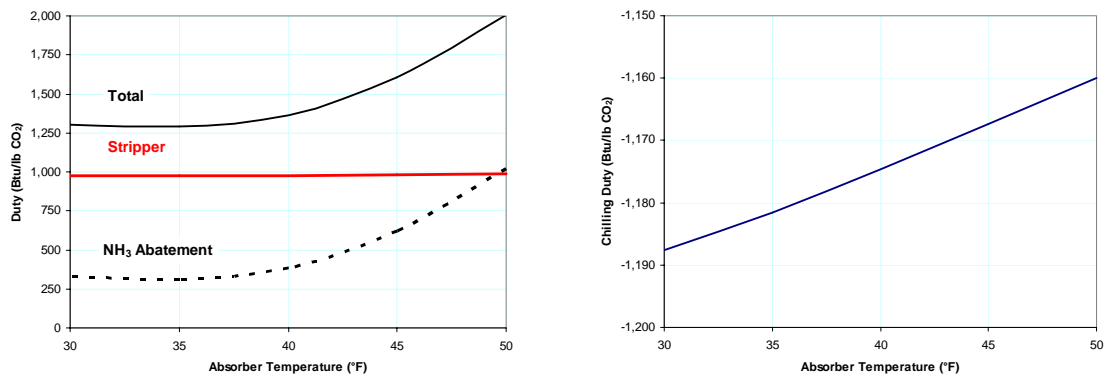


Figure 8 – Utility loads for NH<sub>3</sub> concentration of 26 wt% (CO<sub>2</sub>-free) as a function of temperature.

## 6. Conclusions

This work has demonstrated that the combination of an accurate and reliable thermodynamic model and process simulation provides a powerful tool to analyze and evaluate proposed processes for post-combustion CO<sub>2</sub> capture, even complex processes like chilled-ammonia that feature electrolytes and solids formation. The modeling tool reveals how the process performance changes with operating conditions and identifies the optimum conditions to operate the process, which is an NH<sub>3</sub> solvent concentration of about 26 wt% and an absorber temperature of about 35°F. Finally, the modeling tool estimates the utility needs of the process. The chilled-ammonia process is judged to be equivalent to alkanolamine-based absorption processes for LP steam consumption, but may be rendered noncompetitive because of the large refrigeration loads that are not needed in alkanolamine-based processes. It should be noted that the analysis presented here does not address operational challenges to successfully achieve the operating conditions of the chilled-ammonia process.

## 7. References

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