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# A technical and economic assessment of ammonia-based post-combustion CO<sub>2</sub> capture at coal-fired power plants

Peter Versteeg\*, Edward S. Rubin

Department of Engineering and Public Policy, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA 15213, USA

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#### ABSTRACT

An ammonia-based post-combustion  $CO_2$  capture system processing flue gas from a supercritical coal-fired power plant was modeled, and its estimated performance and cost were compared to an amine-based capture system. For the ammonia system the absorber  $CO_2$  capture efficiency,  $NH_3$  slip, and solids precipitation were evaluated for changes in lean solution  $NH_3$  concentration,  $NH_3/CO_2$  ratio, and absorber temperature. Reductions in  $NH_3$  slip were also assessed for changes in absorber temperature and water wash flow rate. For 90%  $CO_2$  capture the levelized cost of electricity generation (annual revenue requirement) for the plant with ammonia-based capture was estimated at \$US 105/MWh, which is comparable to the levelized cost of electricity generation for the plant with an amine-based capture system. The cost of the ammonia-based system was found to depend strongly on the fraction of  $CO_2$  captured as well as on key process design parameters such as lean solution  $NH_3$  concentration. Uncertainties in system performance and cost also were estimated probabistically. Assumptions about plant financing and utilization, as well as uncertainties in cooling costs and reaction rates that affect absorber cost were found in particular to produce a wide range of cost estimates for ammonia-based  $CO_2$  capture systems, and as a result the importance of reducing these uncertainties is emphasized.

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## 1. Introduction

Ammonia-based post-combustion  $CO_2$  capture is being developed to lower  $CO_2$  emissions in the electric power and industrial sectors. This technology is being advanced by Alstom Power in the form of the Chilled Ammonia Process (CAP), where an ammonia-based solution is used to selectively capture  $CO_2$  from flue gas streams in a reduced temperature absorber (Hilton, 2009).

The proposed advantages of ammonia-based systems include the high CO<sub>2</sub> carrying capacity of ammoniated solutions when solids are allowed to precipitate in the process; the potential for low reboiler regeneration energy and reduced CO<sub>2</sub> compressor power because CO<sub>2</sub> can be regenerated above atmospheric pressure; and reduced solvent cost because ammonia is relatively inexpensive. Early investigations into the use of ammonia-based post-combustion CO<sub>2</sub> capture thus indicated significant improvements in performance over traditional amine technologies, with consequent benefits for lower cost (Bai and Yeh, 1997; Ciferno et al., 2005; Gal, 2006).

In contrast, further studies indicated that due to unwanted side reactions and problems of high ammonia levels entrained in the flue gas exiting the absorber (an effect called ammonia slip), many of the advantages of ammonia-based capture over amines would be offset by higher auxiliary loads and increased equipment costs elsewhere in the process (Mathias et al., 2009). Problems with slow rates of reaction within the absorber have further called into question the overall economic benefits of ammonia-based  $\rm CO_2$  capture due to the potential for large absorber sizes (Derks and Versteeg, 2009; Qin et al., 2010).

Absent from the literature, however, is a systematic analysis of the potential performance and costs of  $CO_2$  capture using ammonia from a systems perspective, as well as an assessment of how uncertainties in key performance and cost variables affect overall system costs. This paper attempts to fill that gap. The following section describes a process model developed in Aspen Plus® and used to estimate the performance of a  $CO_2$  capture system using an ammoniated solution applied to the flue gas stream of a coal-fired power plant. The next section then presents results of this model, including the effects of varying the lean solvent loading, absorber temperature and water wash conditions. A baseline case of system performance and cost is then established, and from this baseline an uncertainty analysis is performed to quantify the effects on system cost of uncertainty or variability in key system parameters.

<sup>\*</sup> Corresponding author. Tel.: +1 412 567 7785; fax: +1 412 268 3757. E-mail addresses: plv@andrew.cmu.edu, nscipete@gmail.com (P. Versteeg).

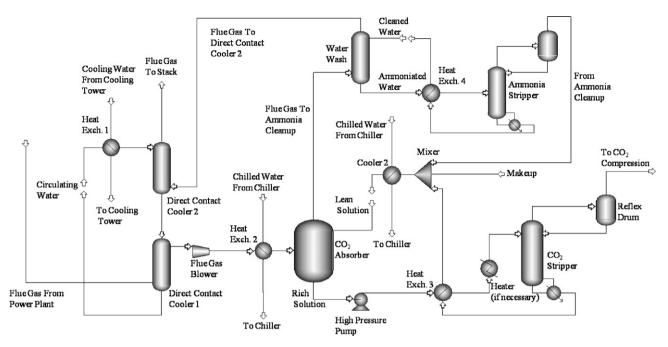


Fig. 1. The ammonia-based CO<sub>2</sub> capture system modeled in Aspen Plus<sup>®</sup> V7.2.

#### 2. Methodology

Ammonia-based CO<sub>2</sub> capture was simulated in the Aspen Plus® V7.2 framework using an electrolyte model intended for the study of CO<sub>2</sub> capture by ammonia under equilibrium conditions (Aspentech, 2010). To represent non-ideal behavior in the NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system the model uses the Redlich-Kwong equation of state for the vapor phase and the electrolyte non-random two liquid activity coefficient model for the liquid phase. In the liquid phase, CO<sub>2</sub> in solution exists as dissolved molecular CO<sub>2</sub> as well as bicarbonate (HCO<sub>3</sub><sup>-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>), and carbamate (H<sub>2</sub>NCOO<sup>-</sup>) ions while ammonia in solution exists as dissolved molecular NH<sub>3</sub> and ammonium (NH<sub>4</sub><sup>+</sup>) and carbamate (H<sub>2</sub>NCOO<sup>-</sup>) ions. The activity coefficient model represents the NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system as a series of ionic reactions describing the interaction between these species as shown in Eqs. (1)–(5), and the reaction describing the precipitation of ammonium bicarbonate as shown in Eq. (6). When precipitation of solids occurs, it can increase the CO<sub>2</sub> carrying capacity of the solution. These reactions occur and compete simultaneously, with the concentration of any species depending strongly on the concentrations of the other components as well as on state variables.

Ionic reactions

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$
 (1)

$$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$$
 (2)

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$$
 (3)

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{4}$$

$$NH_3 + HCO_3^- \leftrightarrow H_2NCOO^- + H_2O \tag{5}$$

Salt precipitation reaction

$$NH_4^+ + HCO_3^- \leftrightarrow NH_4HCO_3(s)$$
 (6)

In the literature the absorption of CO<sub>2</sub> is also represented by a series of molecular reactions as shown by Eqs. (7)–(11) (PCP, 2011; Qin et al., 2011), with ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>),

ammonium carbonate ((NH $_4$ ) $_2$ CO $_3$ ), and ammonium carbamate (NH $_2$ COONH $_4$ ) being formed.

Vapor-liquid reactions

$$NH_{3}(aq) + H_{2}O(1) + CO_{2}(g) \leftrightarrow NH_{4}HCO_{3}(aq),$$
  

$$\Delta H = -64.3 \text{ kJ/mol}$$
(7)

$$2NH_3(aq) + H_2O(l) + CO_2(g) \leftrightarrow (NH_4)_2CO_3(aq),$$
  

$$\Delta H = -101.2 \text{ kJ/mol}$$
(8)

$$(NH_4)_2CO_3(aq) + H_2O(l) + CO_2(g) \leftrightarrow 2NH_4HCO_3(aq),$$
  

$$\Delta H = -26.9 \text{ kJ/mol}$$
 (9)

$$2NH_3(g) + CO_2(g) \leftrightarrow NH_2COONH_4(aq),$$
  
 $\Delta H = -72.3 \text{ kJ/mol}$  (10)

Salt precipitation reaction

$$NH_4HCO_3(aq) \leftrightarrow NH_4HCO_3(s), \quad \Delta H = -26.3 \text{ kJ/mol}$$
 (11)

The ammonia-based  $CO_2$  capture process that was simulated is shown in Fig. 1. Ranges for process conditions such as lean solvent loading and absorber temperature were obtained from the patent describing the Chilled Ammonia Process (Gal, 2008). In Fig. 1, flue gas from a supercritical coal-fired power plant originally fitted with an amine-based  $CO_2$  capture process (Case 12, Woods et al., 2007) instead flows into the ammonia-based capture unit.

The capture of  $\mathrm{CO}_2$  is done at low temperatures (273–293 K) because this favours the reaction between aqueous ammonium carbonate and ammonium bicarbonate (Eq. (9)) and reduces the vapor pressure of ammonia above the absorber, effectively lowering the ammonia slip. Overall, low temperature absorption is accomplished by cooling and then chilling the flue gas, chilling the lean solution before it enters the absorber, and by removing the exothermic heat of reaction released within the absorber from the capture of  $\mathrm{CO}_2$  and the precipitation of ammonium bicarbonate.

In the baseline case for this analysis, the flue gas from the power plant at 330 K enters a direct contact cooler and its temperature is lowered with cooling water to 301 K. In this step, most of the water vapor in the gas condenses. The gas then passes through a blower to compensate for the pressure drop through the CO<sub>2</sub> capture system wherein compression increases the gas temperature to 323 K. The gas temperature is then again lowered to 279 K as it passes through a chilled water heat exchanger before entering the absorber. The lean solution from the CO<sub>2</sub> regenerator passes through a crossflow heat exchanger and then is further cooled to 281 K in another chilled water heat exchanger before it enters the absorber. Within the absorber the lean solution contacts the flue gas and selectively captures CO<sub>2</sub>. The resulting rich solution may contain significant quantities of precipitated solids. Heat released within the absorber is removed by chilling the absorber internally. That solution leaves at the bottom of the absorber while the decarbonized flue gas leaves

Streams chilled to temperatures below 283 K require electrical power of  $0.55 \, \text{kW/ton}$  refrigeration, while streams chilled to between 283 K and 302 K require  $0.47 \, \text{kW/ton}$  refrigeration (DOE, 2004; Platts, 2004). Water from the cooling tower at 294 K provides cooling for streams or components cooled to 302 K or above, such as the  $\text{CO}_2$  regenerator condenser.

The rich solution exiting the absorber passes through a high pressure pump which increases the solution pressure to 3.0 MPa. The solution then goes through a heat exchanger with a cold-inlet hot-outlet temperature approach of  $5.5\,^{\circ}$ C. If solids in the rich solution are not dissolved entirely in the heat exchanger, a separate heater is used to dissolve these solids before the rich solution enters the CO<sub>2</sub> stripper. In the high pressure (2.8 MPa) CO<sub>2</sub> stripper the lean solution is regenerated and returned to the absorber while the concentrated CO<sub>2</sub> stream goes to further compression.

As mentioned previously, a significant amount of ammonia may enter the vapor phase and exit the absorber with the flue gas. This ammonia slip is removed in a water wash system. Some ammonia also may be captured in the circulating water used by the direct contact coolers, but this analysis assumes that the water wash is the primary method for reducing ammonia slip. An ammonia stripper is used to clean the washing water, which is then recycled for contacting with the flue gas. The stripper distillate, including ammonia, carbon dioxide and water, is returned to the capture process.

Important process variables for the power plant and the ammonia-based  $CO_2$  capture system are shown in Table 1. Where specific values of process variables were unavailable in the open literature, values were selected within the ranges specified by the CAP patent or were estimated by the authors.

## 3. Results for baseline design

#### 3.1. Lean solvent NH<sub>3</sub> concentration and NH<sub>3</sub>/CO<sub>2</sub> sensitivity

To reduce energy demand, the process attempts to take advantage of Eq. (9), the low energy reaction between ammonium carbonate and ammonium bicarbonate. Ideally if Eq. (9) were the only reaction pathway, the lean solution would consist primarily of ammonium carbonate and water, with an  $NH_3/CO_2$  ratio near 2.0. However several researchers have noted that other reactions occur leading to the formation of unwanted species (Mathias et al., 2009), and under many circumstances where the  $NH_3/CO_2$  ratio is 2.0, ammonium carbonate may not be even the primary constituent in the lean solution (Qin et al., 2011). This leads to questions regarding the best lean solvent  $NH_3/CO_2$  ratio for the process. The patent cited above for the CAP recommends using a range between 1.0 and 4.0. In this section, the impact of variations in lean solution  $NH_3/CO_2$ 

**Table 1**Key variables for the power plant and ammonia-based CO<sub>2</sub> capture system.

Parameter	Units	Value
Base power plant <sup>a</sup>		
Coal flow rate, Illinois No. 6	kg/h	266,089
Coal higher heating value (as	k]/kg	27,113
received)	31 0	,
Coal cost	\$2007/tonne	45.32
Supercritical steam cycle	MPa/°C/°C	24.1/593/593
Gross plant power output with	MWe	663.4
amine-based CO <sub>2</sub> capture		
SCR NO <sub>x</sub> removal efficiency	%	86
Wet FGD system SO <sub>2</sub> removal efficiency	%	98
Flue gas flow rate into CO <sub>2</sub> capture system	kg/h	3,099,560
Flue gas CO <sub>2</sub> mole fraction into CO <sub>2</sub> capture system	%	13.3
Flue gas temperature into CO <sub>2</sub>	K	330.4
capture system		
Flue gas pressure into CO <sub>2</sub> capture system	kPa	104.8
Flue gas SO <sub>2</sub> into CO <sub>2</sub> capture system <sup>b</sup>	ppm	38
Flue gas NO <sub>x</sub> into CO <sub>2</sub> capture	nnm	42
system <sup>b</sup>	ppm	42
Ammonia-based CO <sub>2</sub> capture system		
Water flow rate into direct contact cooler 2	kg/s	1452
Heat exchanger 1 cooling water flow rate	kg/s @ 299.8 K	5000
Heat exchanger 2 chilling water flow rate	kg/s @ 275.9 K	1000
Heat exchanger 3 temperature	°C	5.5
approach Lean solvent flow rate	lea/c	1000
	kg/s K	283.1
Absorber temperature Lean solvent NH3 wt%	K %	283.1 0–30
Lean solvent NH <sub>3</sub> Wt% Lean solvent NH <sub>3</sub> /CO <sub>2</sub> ratio	• •	1.5-4.0
Allowable ammonia slip after water	mol/mol	1.5-4.0
wash	ppm	10

<sup>&</sup>lt;sup>a</sup> The power plant parameters are based on Case 12 in Woods et al. (2007).

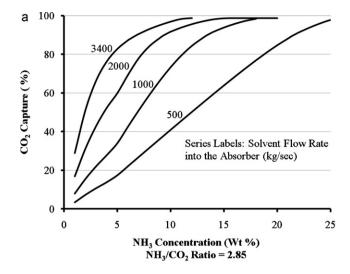
ratio and NH<sub>3</sub> concentration on absorber CO<sub>2</sub> capture, NH<sub>3</sub> slip, and solids formation is investigated over this range.

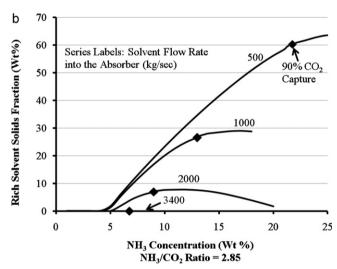
Previous work by the authors found that while lean solutions with high ammonia concentrations and relatively low solvent flow rates had the potential for a high CO<sub>2</sub> capture efficiency, one consequence was high solids precipitation in the rich solvent, as shown in Fig. 2 (Versteeg and Rubin, 2011). At the We Energies pilot plant Alstom found that solids formation for chilled ammonia posed an operational challenge due to blockages in process equipment (Bollinger et al., 2010). Due to this concern over operating with high solids in the rich solution, the present analysis employs a baseline lean solvent flow rate of 1000 kg/s to reduce solids formation in the rich solution to approximately 30-40 wt% in the baseline design (vs. 60 wt% at the lower sorbent flow of 500 kg/s rate in our previous study). This is similar to wet limestone flue gas desulfurization systems which can operate with an absorber slurry density of 15-20 wt% suspended solids and 35-45 wt% suspended solids after the first dewatering stage (Kohl and Nielsen, 1997; Stultz and Kitto, 2005).

The absorber temperature was held constant at  $283.1 \, \text{K}$  and the NH $_3$  concentration and NH $_3$ /CO $_2$  ratio of the lean solution were varied parametrically to explore system behavior under these conditions. The resulting CO $_2$  capture efficiency, NH $_3$  slip and solids precipitation are shown in Fig. 3a–c.

These results indicate that both the ammonia concentration and the NH<sub>3</sub>/CO<sub>2</sub> ratio significantly affect CO<sub>2</sub> capture, ammonia slip,

<sup>&</sup>lt;sup>b</sup> This analysis assumes that the  $SO_2$  and  $NO_x$  entering the  $CO_2$  capture system is removed by Direct Contact Cooler 1 and therefore has a negligible impact on the  $CO_2$  capture process.



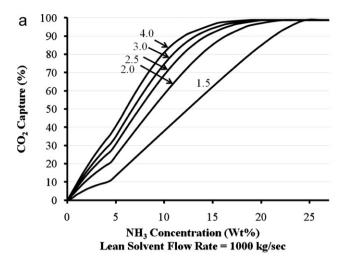


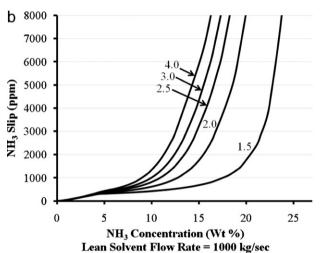
**Fig. 2.** (a) Lean solvent  $NH_3$  concentration vs.  $CO_2$  capture and (b) lean solvent  $NH_3$  concentration vs. rich solvent solids concentration for several solvent flow rates. Diamonds represent 90%  $CO_2$  capture.

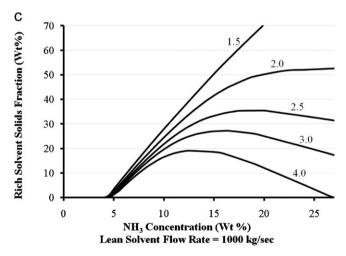
and solids precipitation in the absorber. Increases in either the NH $_3$  concentration or the NH $_3$ /CO $_2$  ratio increase the percent CO $_2$  captured as well as the NH $_3$  slip, while increases in NH $_3$  concentration and decreases in NH $_3$ /CO $_2$  ratio increase the wt% solids. Fig. 3a further indicates that a decrease in the NH $_3$ /CO $_2$  ratio below 2.0 results in a significant reduction in the fraction of CO $_2$  that can be captured as well as a large increase in the amount of solids precipitated. NH $_3$ /CO $_2$  ratios above 3.0 result in lower levels of solids precipitation but high levels of ammonia slip and only marginal improvements in CO $_2$  capture efficiency. Based on these results, an NH $_3$ /CO $_2$  ratio of 2.5 was chosen for use in the remainder of this analysis as this provided a balance between reduced solids handling requirements—to aid in absorber and process design at higher levels of CO $_2$  capture—and reduced ammonia slip.

#### 3.2. Effects of absorber temperature

Lowering the temperature of the absorption process can help control ammonia slip, but the trade-off is that lower temperatures increase the chilling energy requirements of the process and are expected to have a negative effect on the reaction kinetics, increasing the absorber size. In this section, the lean solvent flow rate and  $NH_3/CO_2$  ratio were held constant at  $1000 \, kg/s$  and 2.5, respectively,

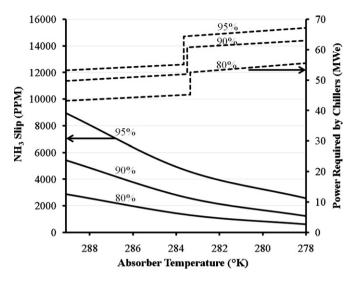






**Fig. 3.** (a)  $CO_2$  capture (%), (b)  $NH_3$  slip (ppm), and (c) wt% solids in rich sorbent exiting the absorber as a function of lean sorbent  $NH_3$  concentration and  $NH_3/CO_2$  ratio. The labels in the figures represent the lean solvent  $NH_3/CO_2$  ratio.

while the temperature of the absorber was varied between 277.6 and 288.8 K ( $40-60\,^{\circ}$ F). The resulting ammonia slip and absorber cooling power requirements are shown in Fig. 4 for several different levels of  $CO_2$  capture, which is adjusted by changing the NH<sub>3</sub> concentration in the lean solvent. The temperature of the flue gas and the lean solvent entering the absorber were held constant by Heat Exchanger 2 and Cooler 2, respectively, shown in Fig. 1. The power



**Fig. 4.** Ammonia slip and absorber cooling requirements as a function of absorber temperature for three levels of  $CO_2$  capture (80, 90 and 95%). The labels represent the %  $CO_2$  captured. Reducing the temperature below 283 K results in a step change in the unit energy required for cooling.

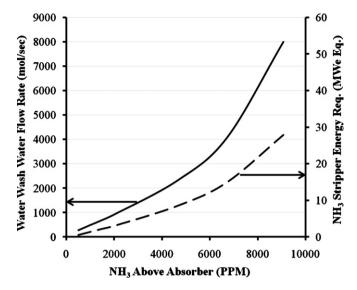
required by the chillers to cool the absorber assumes 0.55 kW/ton of refrigeration for chilling below 283 K, and 0.47 kW/ton refrigeration for chilling above 283 K (DOE, 2004; Platts, 2004). The chiller power requirement increases with increasing percentage of CO<sub>2</sub> captured (as more exothermic heat of reaction is removed) and also with reductions in the absorber temperature. Ammonia slip also increases for higher fractions of CO<sub>2</sub> capture, but decreases at lower absorber temperatures. Most of the absorber cooling energy is for removal of the exothermic heat released by the capture of CO<sub>2</sub> and the precipitation of solids.

## 3.3. Water wash requirements for ammonia removal

The water wash above the absorber removes ammonia from the flue gas by contacting the gas stream with water in a column. The cleaned flue gas exits the top of the column with a low ammonia concentration while the resulting sour water is sent through a heat exchanger to a sour water stripper. Vapor from the sour water stripper containing NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O is returned to the CO<sub>2</sub> capture process. Fig. 5 shows the water required to reduce the NH<sub>3</sub> concentration in the flue gas stream to 10 parts per million (ppm). The corresponding steam energy requirement also is shown as electrical energy equivalent, assuming the steam enthalpy is 3276 kJ/kg, the condensate enthalpy is 749 kJ/kg, and the heat-to-electricity conversion efficiency used to penalize the power plant for the loss of low-pressure steam use is 0.22 (IECM, 2011). In this analysis the lean solvent flow rate, the NH<sub>3</sub>/CO<sub>2</sub> ratio, and the absorber temperature were held constant at 1000 kg/s, 2.5, and 283.1 K, respectively, and the ammonia slip exiting the absorber was varied by adjusting the lean solvent wt% NH<sub>3</sub>. As shown in Fig. 5, both the wash water requirement and the NH<sub>3</sub> stripper energy requirement increase as the ammonia level entrained in the flue gas stream increases.

### 3.4. System performance and cost

Estimates of the performance and cost of the coal-fired power plant with ammonia-based CO<sub>2</sub> capture are shown in Tables 2 and 3. These results are based on performance data from the Aspen Plus® model of the ammonia capture system and associated cost data from Aspen Icarus®, together with scaled data from the literature and from the Integrated Environmental Control Model power plant simulator (IECM, 2011).



**Fig. 5.** Wash water flow rate and associated NH<sub>3</sub> stripper energy required to reduce the ammonia slip in the flue gas stream to 10 ppm, for various levels of ammonia slip exiting the absorber.

For this baseline estimate, the CO<sub>2</sub> capture efficiency was 90%, the NH<sub>3</sub> concentration was 14.4 wt% at a lean solvent flow rate of 1000 kg/s, the NH<sub>3</sub>/CO<sub>2</sub> ratio was 2.5, the absorber temperature was 283.1 K, ammonia slip after the water wash was limited to 10 ppm, and the solids content in the rich solution was 33 wt%. Note that a more stringent emissions limit for NH<sub>3</sub> slip (e.g. 2 ppm, as found in some SCR facilities) would further increase the cost of the ammonia-based system. Where not available directly from the models, equipment power consumption was scaled linearly from reference loads and process flow conditions, and equipment capital costs were scaled from reference costs and process flows and conditions. This scaling methodology for specific equipment has been described previously (Rao, 2002). All costs are reported in constant 2007 dollars, and were scaled using the Marshall and Swift Equipment Cost Index (Marshall and Swift, 2009). The levelized cost of electricity (LCOE) also is calculated in real terms excluding the effects of inflation, and including transport, storage, and maintenance costs of \$3.75/tonne CO<sub>2</sub> (Woods et al., 2007).

As shown in Tables 2 and 3, the levelized cost of electricity for the baseline ammonia-based  $CO_2$  capture system is \$105/MWh, which is comparable to the LCOE for the plant with an amine-based capture system. The ammonia-based  $CO_2$  system benefits from lower steam loads and reduced compressor power requirements, but the chilling loads and associated costs offset these benefits.

By varying the lean solvent  $NH_3$  concentration for the same process conditions and cost estimating methodology, the LCOE and  $CO_2$  avoidance cost were calculated as a function of the  $CO_2$  capture efficiency. The results are shown in Fig. 6. At capture efficiencies above approximately 90% the LCOE rises at an increasing rate due to the increasing steam demands for  $CO_2$  regeneration and  $NH_3$  cleanup, and the increased chilling requirements of the  $CO_2$  capture system. There is a minimum in the  $CO_2$  avoidance cost between approximately 90% and 94% capture. Lower levels of  $CO_2$  capture lead to higher avoidance costs due to the high capital requirements of the process, while avoidance costs rise above 95%  $CO_2$  capture due to the rapidly increasing costs of  $NH_3$  cleanup.

#### 3.5. Effect of carbon price

The economics and level of  $CO_2$  capture depend critically on the restrictions or requirements imposed by policy and regulations limiting emissions of  $CO_2$ . Most commonly, this is expressed in terms of

**Table 2**Power plant performance estimates, All values are in MWe equivalent.

Parameter	No CO <sub>2</sub> capture <sup>a</sup>	Amine capture system <sup>a</sup>	Ammonia capture system	Notes and primary data sources for ammonia syster
Potential power available	580.2	827.6	827.6	Based on coal flow rate
Auxiliary steam loadb				
Heater			5.1	Aspen Plus®
CO <sub>2</sub> stripper		164.2	103.4	Aspen Plus®
NH <sub>3</sub> stripper			3.5	Aspen Plus®
Steam turbine power	580.2	663.4	715.6	Based on aux. steam load
Auxiliary electrical load				
Flue gas blower			18.9	$\Delta P$ = 3 psi, scaled IECM data
Heat exchanger 1 pumps			2.2	Aspen Plus®, scaled IECM data
Heat exchanger 2 pumps			0.4	Aspen Plus®, scaled IECM data
Gas cooling water pumps			0.6	Aspen Plus®, scaled IECM data
Chiller for heat exch. 2			5.7	Aspen Plus®, RDC 2003, Platts (2004)
Chiller for absorber cooling			48.2	Aspen Plus®, RDC 2003, Platts (2004)
Chiller for solvent cooling			6.0	Aspen Plus®, RDC 2003, Platts (2004)
Absorber cooling pumps			5.1	Aspen Plus®, scaled IECM data
Solvent circulation pumps			3.5	Aspen Plus®, scaled IECM data
Econamine FG plus system		23.2		-
CO <sub>2</sub> compression		46.9	16.9	Aspen Plus®, scaled IECM data, Woods et al. (2007)
Balance of plant	30.1	49.2	49.0	Scaled IECM data
Plant net power	550.1	546.0	558.7	
Plant efficiency (% HHV)	39.1%	27.2%	27.9%	
Plant derating of CO <sub>2</sub> capture (%)		30.4%	28.6%	

<sup>&</sup>lt;sup>a</sup> The power plant parameters are based on Case 12 in Woods et al. (2007).

a "carbon price" (or tax) that an emission source must pay for each tonne of CO<sub>2</sub> emitted. For a power plant emitting CO<sub>2</sub> this additional cost increases the cost of electricity in proportion to the level of CO<sub>2</sub> emissions. Fig. 7 shows the effect of CO<sub>2</sub> price on the LCOE for three cases: (1) the baseline power plant with an ammonia-based CCS system capturing 90% CO<sub>2</sub>, (2) the same plant capturing 80% CO<sub>2</sub>, and (3) the uncontrolled power plant with no CCS system. For a CO<sub>2</sub> price of up to \$73/tonne CO<sub>2</sub>, the PC plant without CCS is the lowest cost option. At higher prices the plant with an ammoniabased system capturing 90% CO<sub>2</sub> is the least costly. In this analysis the plant with only 80% capture is more expensive than the other two options at all carbon prices. This is consistent with the results in Fig. 6 showing a higher cost of CO<sub>2</sub> avoided as the capture efficiency decreases. The carbon price of \$73/tonne CO<sub>2</sub> is also similar to values found for amine-based capture systems at similar PC power plants.

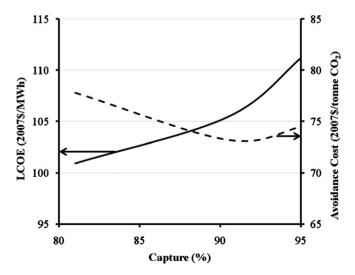
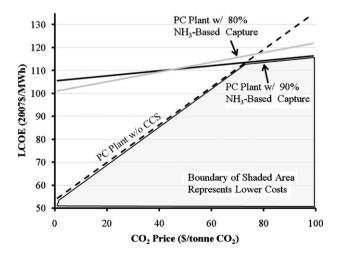


Fig. 6. Levelized cost of electricity and  $CO_2$  avoidance cost as a function of  $CO_2$  capture efficiency for the baseline PC power plant. All costs in constant 2007 US dollars.

## 4. Uncertainty analysis for key system parameters

In this section we explore the effects of uncertainty using two methods of analysis. Fig. 8 first shows the impact on the levelized cost of electricity of a uniform  $\pm 10\%$  change from the baseline value of several key variables for the plant with ammonia-based capture. The tornado diagram shows that plant utilization and financing assumptions dominate the levelized cost calculation for equal changes in all variables. However, significant cost changes are also driven by the  $\text{CO}_2$  stripper energy requirements, chilling requirements and absorber capital cost.

In practice, of course, some parameters are more uncertain or variable than others. Thus, a probabilistic analysis was undertaken to more realistically characterize the impact on total plant cost of uncertainties or variability in key system parameters relative to the baseline plant design with ammonia capture. The parameter distribution functions for this analysis are shown in Table 4.



**Fig. 7.** Effect of a  $CO_2$  price on the levelized cost of electricity for (a) the baseline power plant with an ammonia-based system that captures 90%  $CO_2$ , (b) the same plant with an ammonia-based system that captures 80%  $CO_2$ , and (c) the baseline plant without a CCS system.

<sup>&</sup>lt;sup>b</sup> The auxiliary steam load is shown as electrical energy equivalent, assuming the steam has an enthalpy of 3276 kJ/kg and a pressure of 902 kPa, the water condensate has an enthalpy of 749 kJ/kg, and the heat-to-electricity conversion efficiency used to penalize the power plant for the loss of low-pressure steam use is 0.22 (IECM, 2011).

**Table 3** Power plant cost estimates. All values are in 2007 \$millions.

Parameter	No CO <sub>2</sub> capture <sup>a</sup>	Amine capture system <sup>b</sup>	Ammonia capture system	Notes and primary data sources
CO <sub>2</sub> capture process area costs				
DCC #1			30.9	Aspen Plus®, scaled IECM data, Rao (2002
DCC #2			23.3	Aspen Plus®, scaled IECM data, Rao (2002
Flue gas blower			6.3	Aspen Plus®, scaled IECM data, Rao (2002
Heat exch. 1			6.7	Aspen Icarus®
Heat exch. 2			2.9	Aspen Icarus®
Heat exch. 1 pumps			1.4	Aspen Plus®, scaled IECM data, Rao (2002
Heat exch. 2 pumps			0.5	Aspen Plus®, scaled IECM data, Rao (2003
Cooling water circ pumps			0.7	Aspen Plus®, scaled IECM data, Rao (200
Chiller system			54.6	Aspen Plus®, DOE, 2004; Platts (2004)
Absorber			105.1	Aspen Plus®, scaled IECM datad
Absorber pumps			2.4	Aspen Plus®, scaled IECM data, Rao (2002)
Heat exch. 3			41.6	Scaled Aspen Icarus® data
Solvent circulation pumps			7.9	Aspen Plus®, scaled IECM data, Rao (2002
Solvent heater			2.2	Aspen Icarus®
Solvent cooler			2.2	Aspen Icarus®
CO <sub>2</sub> stripper			35.1	Aspen Plus®, scaled IECM data, Rao (200
CO <sub>2</sub> stripper reboiler			13.4	Aspen Plus®, scaled IECM data, Rao (200)
Water wash			2.2	Aspen Icarus®
Heat exch. 4			0.1	Aspen Icarus®
NH <sub>3</sub> stripper			1.5	Aspen Icarus®
NH <sub>3</sub> cleanup pumps			0.8	Aspen Plus®, scaled IECM data, Rao (2002)
Steam extractor			3.3	Scaled IECM data
Sorbent reclaimer			1.1	Scaled IECM data
Sorbent processing			1.1	Scaled IECM data
Drying and compress unit			18.6	Aspen Plus®, scaled IECM data
CO <sub>2</sub> system (PFC)			365.9	rispent rus (seureu izem untu
General facilities capital			5.7	1.57% PFC from Woods et al. (2007)
Eng. and home office fees			34.3	9.37% PFC from Woods et al. (2007)
Project contingency cost			59.9	16.38% PFC from Woods et al. (2007)
Process contingency cost			17.1	4.67% PFC from Woods et al. (2007)
CO <sub>2</sub> system (TCR)		393.9	483.0	Based on area costs
Base plant (TCR) <sup>c</sup>	670.8	881.3	884.1	Scaled IECM data
Cooling tower (TCR)	35.8	62.7	62.7	Scaled IECM data
$NO_x$ control (TCR)	25.0	33.7	33.7	Scaled IECM data
TSP control (TCR)	37.4	49.8	49.8	Scaled IECM data
SO <sub>2</sub> control (TCR)	112.1	138.7	138.7	Scaled IECM data
CO <sub>2</sub> system and TS&M O&M/year <sup>e</sup>		24.1	22.3	Scaled IECM data
Balance of plant O&M/year	103.1	128.9	128.9	Scaled IECM data
Plant total capital requirement	881.1	1560.0	1652.0	Based on TCR costs
Total O&M costs/year	103.1	153.0	151.3	Total O&M
Capital required (\$/kW-net)	1601.0	2857.0	2956.8	Based on performance
Revenue required (\$/MWh)	53.5	104.8	105.4	Ī
CO <sub>2</sub> avoidance cost (\$/tonne avoided)		72.2	73.2	

<sup>&</sup>lt;sup>a</sup> The power plant parameters are based on Case 12 in Woods et al. (2007).

Uncertainty distributions were complied following the methodology outlined in Frey and Rubin (1991), with distributions inferred either from the literature or estimated by the authors. Uncertain variables were grouped into three categorizes: capture system performance parameters, capture system cost parameters, and plant financing and utilization parameters.

One important source of uncertainty is the reaction rate for  $\rm CO_2$  capture in the absorber, which is dependent on species concentration and temperature. Details of these reaction rates are not yet well understood and for this reason the Aspen model used here assumes (for simplicity and transparency) the bounding case of equilibrium conditions. Experimental work, however, suggests that rates for ammonia based- $\rm CO_2$  capture could be 3–10 times slower

than for MEA (Darde et al., 2011; Qin et al., 2010). Under these conditions, absorber sizing estimates indicate that the absorber for an ammonia-based process would be 2–3 times larger, and thus more costly, than for an amine-based process (Chang, 2009; Zhuang, 2011). This cost uncertainty stemming from uncertain reaction rates is reflected in the distribution of the CO<sub>2</sub> absorber cost in Table 4. The skewed distribution reflects a likelihood of much higher cost relative to the baseline case of an equilibrium reactor.

The results of the uncertainty analysis are shown in Fig. 9. Using only the performance parameter uncertainty distributions, the analysis indicates that the probability that the levelized cost of electricity will be equal to or lower than the deterministic case is about 30%. However, when the uncertainties in cost parameters

b The plants without CO<sub>2</sub> capture and with amine-based CO<sub>2</sub> capture are based on Case 11 and on Case 12 in Woods et al., respectively. These plants were modeled in the IECM with a 75% capacity factor and a fixed charge factor of 0.143 for the plant with CCS (higher risk) and 0.113 for the plant without CCS (lower risk) as in Rubin and Zhai (2011). A risk premium for CCS also is assumed by DOE/NETL in recent cost studies.

<sup>&</sup>lt;sup>c</sup> The base plant cost for the ammonia-based CO<sub>2</sub> capture system design is higher than for the amine system because a larger steam turbine is required.

<sup>&</sup>lt;sup>d</sup> The reference IECM cost was a wet FGD scrubber.

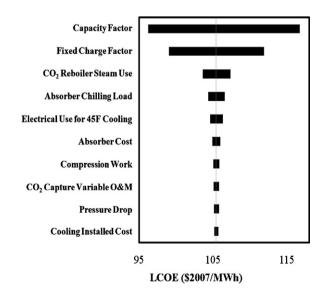
 $<sup>^{\</sup>rm e}$  O&M costs for the plants with CCS include (1) CO<sub>2</sub> transport, storage, and maintenance costs of \$3.75/tonne CO<sub>2</sub>, (2) fixed costs of \$8.0 M/year, and (3) variable costs related to solvent losses. Variable losses for the amine system include caustic (\$0.6 million/year), activated carbon (\$0.6 million/year), and MEA makeup of 0.1 kg/tonne CO<sub>2</sub> at a unit cost of \$2361/tonne MEA (Woods et al., 2007) which equals \$0.9 M/year. In the ammonia system, flue gas contaminants act as nucleation sites for the condensation of water in DCC1 and are mostly removed (Gal, 2008) resulting in few operational problems (Hilton, 2009). Absorber slip losses at 10 ppm are approximately 0.02 kg/tonne CO<sub>2</sub> at a unit cost of \$135/tonne 28% aqueous NH<sub>3</sub> (\$483/tonne NH<sub>3</sub>) (Woods et al., 2007), which equals to \$0.01/tonne CO<sub>2</sub> or \$0.04 M/year. If all the SO<sub>2</sub> entering the capture system formed heat stable salts and an activated carbon bed (\$0.6 M/year) was required, NH<sub>3</sub> losses would be approximately 0.13 kg/tonne CO<sub>2</sub> or \$0.3 M/year, raising the LCOE only slightly to \$105.7/MWh.

**Table 4**Nominal values and uncertainty parameters assessed in the ammonia-based CO<sub>2</sub> capture system.

Parameter	Units	Nominal (x)	Values (or $\sigma$ as % of $x$ )	References
Capture system performance				
Chilling loads required at <283 K	Tons refrigeration	103,000	Normal (x, 10%)	Author estimate
Chilling loads required at 283-302 K	Tons refrigeration	21,333	Normal (x, 10%)	Author estimate
Chiller electrical use, 276 K water product	kW/tonne refrigeration	0.55	Triangular (0.47, 0.55, 0.60)	Platts (2004)
Chiller electrical use, 280 K water product	kW/tonne refrigeration	0.47	Triangular (0.47, 0.47, 0.55)	Platts (2004)
CO <sub>2</sub> regeneration heat requirement	kJ/kg CO <sub>2</sub>	2293	Normal (x, 10%)	Author estimate
Pumping head	kPa	207	Triangular (150, 207, 250)	Rao (2002)
Pump efficiency	%	75	Uniform (70, 75)	Rao (2002)
$\Delta P$ across $CO_2$ capture system	kPa	20.7	Triangular (14, 26, 30)	Rao (2002)
Blower efficiency	%	75	Uniform (70, 75)	Rao (2002)
CO <sub>2</sub> compression, 27.5-152.7 bar	kWh/kg CO <sub>2</sub>	0.03	Triangular (0.028, 0.03, 0.032)	
Capture system cost				
Reference chilling equipment costs (PFC)	\$2007/tonne refrigeration	441	Uniform $(0.7x-1.3x)$	Author estimate
Reference IECM costs (PFC)	\$2007	251.9	Uniform $(0.7x-1.3x)$	Author estimate
Reference Aspen Icarus® costs (PFC)	\$2007	59.4	Uniform $(0.7x-1.4x)$	Author estimate
CO <sub>2</sub> absorber costs (PFC)	\$2007	105.1	Uniform $(0.7x-2.5x)$	Zhuang (2011)
General facilities capital	% of PFC	1.57 <sup>a</sup>	Normal (x, 10%)	Berkenpas et al. (1999)
Eng. and home office fees	% of PFC	9.37 <sup>a</sup>	Triangular (0.7x, 1x, 1.5x)	Berkenpas et al. (1999)
Project contingency cost	% of PFC	16.38 <sup>a</sup>	Normal (x, 20%)	Berkenpas et al. (1999)
Process contingency cost	% of PFC	4.67 <sup>a</sup>	Normal (x, 30%)	Berkenpas et al. (1999)
CO <sub>2</sub> system fixed O&M/year	\$2007 million/year	8.0	Uniform $(0.7x-1.3x)$	Author estimate
CO2 system variable O&M/year + TS&M	\$2007 million/year	14.0	Uniform $(0.7x-1.3x)$	Author estimate
Plant financing and utilization				
Power plant fixed charge factor	Fraction	0.143	Uniform (0.130, 0.180)	Rubin and Zhai (2011)
Power plant levelized capacity factor	=	0.75	Uniform (0.65, 0.85)	Rubin and Zhai (2011)

<sup>&</sup>lt;sup>a</sup> From Woods et al. (2007).

are also included, the cumulative distribution function shifts predominately to the right (i.e., higher costs), primarily due to the effects of higher CO<sub>2</sub> absorber cost related to uncertain reaction rates, as discussed earlier. This distribution function shows only a 10% chance that the LCOE will be equal to or less than the deterministic case. This result highlights the importance of the absorber cost and suggests that further research into how reaction rates affects absorber size for specific absorber designs is needed. Finally, when uncertainties in plant financing and utilization parameters are also included, the probability that the LCOE will be less than or equal to the deterministic value rises to 20%. The cumulative probability distribution also widens significantly. Costs now range from \$80/MWh to \$160/MWh, with the 95% confidence interval ranging from \$95/MWh to \$143/MWh. This broad range indicates the importance of financial and plant utilization assumptions on the overall cost of the plant, as seen earlier in Fig. 8. With all uncertainties included the ammonia-based system has a median (50%

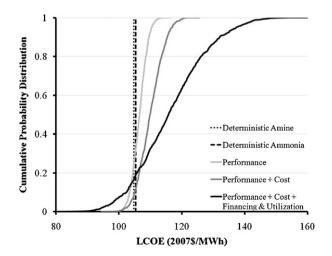


**Fig. 8.** A tornado graph indicating the change in the levelized cost of electricity for a  $\pm 10\%$  change in the input of ten important variables.

probability) cost of electricity of \$115.8/MWh. The average LCOE is only slightly higher at \$116.5/MWh, reflecting the asymmetric distributions for several parameters. These values are approximately 10% higher than the deterministic LCOE reported earlier.

The uncertainty distributions in Fig. 9 also affect the  $CO_2$  avoidance cost. In contrast to the deterministic estimate of \$73/tonne  $CO_2$  for the ammonia-based system with 90% removal, the median LCOE in Fig. 9 corresponds to an avoidance cost of \$88/tonne  $CO_2$  while the 95% confidence interval for LCOE corresponds to avoidance costs of \$60 to \$127/tonne  $CO_2$  avoided. This represents the likely range of carbon price or tax required in a market-based regime to make ammonia-based CCS more economical than a similar PC plant with no CCS.

Finally, for comparison, the deterministic cost estimate of the baseline plant with an amine-based capture system also is shown in Fig. 9. While we have not conducted a probabilistic estimate for the amine-based plant, the similarity in LCOE to the baseline ammonia-based system suggests that there is no clear "winner" between these two processes based on current information.



**Fig. 9.** Cumulative probability distribution of the levelized cost of electricity of the baseline PC plant with ammonia-based CO<sub>2</sub> capture.

#### 5. Discussion

The uncertainty analysis presented above explores possible departures from the baseline performance and cost assumptions and produces a broader range of potential cost estimates for the ammonia-based CO2 capture system assessed here. Those costs are generally higher than the deterministic estimate for the baseline system. However, since ammonia-based CO<sub>2</sub> capture is far less mature than amine-based CO<sub>2</sub> capture there may be considerable room for improvement in the technology (Chung, 2009). For example, though slow reaction rates in the absorber have the potential to significantly increase system costs, additives are currently being investigated to speed up reaction rates (Chang, 2009; Lee et al., 2008). And although the analysis presented in this paper limited the NH<sub>3</sub> concentration and lean solvent flow rate to avoid aggressive solids formation, a lower solvent flow rate coupled with higher NH<sub>3</sub> concentration could lead to reduced energy requirements and lower cost if the high solids formation can be managed in a way that does not compromise system reliability. There is some precedent for this as large-scale solids handling has been successfully accomplished in wet limestone-based flue gas desulfurization systems applied to coal-fired power plants (Stultz and Kitto, 2005). Future process improvements may also take advantage of the potential for heat integration of the CO<sub>2</sub> regeneration and NH<sub>3</sub> cleanup systems where significant amounts of heat are rejected by the CO2 compressors and chillers—an option not investigated in this analysis.

Ultimately the viability of ammonia-based  $\mathrm{CO}_2$  capture also may be location dependent. For example, a plant located in a characteristically cold climate, or with direct access to a large cooling sink such as a deep water lake, would have lower parasitic energy demands for the process chillers. This could significantly improve the performance and cost outlook of ammonia-based  $\mathrm{CO}_2$  capture in specific applications. Future refinements of the present analysis await the availability of additional data from pilot plants and other ongoing studies of ammonia-based  $\mathrm{CO}_2$  capture.

#### 6. Conclusion

This paper has estimated the performance and costs of ammonia-based  $CO_2$  capture systems operating on the flue gas from a coal-fired power plant. The modeling effort described how changes in sorbent flow rate,  $NH_3/CO_2$  ratio and  $NH_3$  concentration can affect  $CO_2$  capture,  $NH_3$  slip, and solids precipitation. An analysis of the absorber cooling requirements and the ammonia cleanup system described tradeoffs in the energy required to reduce ammonia slip. This process step adds significant energy loads and costs to an ammonia-based  $CO_2$  capture process.

An economic analysis showed that the cost of a new supercritical PC power plant with an ammonia-based CO<sub>2</sub> capture system is comparable to that of a power plant with an amine-based CCS system. The analysis also quantified the sensitivity of the levelized cost of electricity and the CO2 avoidance cost to changes in the CO<sub>2</sub> capture efficiency. For the baseline plant design, the minimum avoidance cost occurred at removal efficiencies of about 90-94%. For carbon prices above \$73/tonne CO<sub>2</sub> a 90% capture system was found to be more economical than a plant with no CCS or one capturing only 80% CO<sub>2</sub>. A more comprehensive probabilistic analysis also showed how uncertainty or variability in key CO<sub>2</sub> capture system variables, as well as plant financing and utilization parameters, affect the overall costs of electricity for the plant. This revealed a much broader range of cost estimates, consistent with the precommercial state of current ammonia-based capture technology. The potential for improved process performance and lower system costs also was discussed.

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