Prediction and Validation of External Cooling Loop Cryogenic Carbon Capture (CCC-ECL) for Full- Scale Coal-Fired Power Plant Retrofit

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ABSTRACT

Bench-scale experiments and Aspen Plus™ simulations document full-scale, steady-state performance of the external cooling loop cryogenic carbon capture (CCC-ECL) process for a 550 MW_e coal-fired power plant. The baseline CCC-ECL process achieves 90 % CO₂ capture, and has the potential to capture 99+ % of CO₂, SO₂, PM, NO₂, Hg, and most other noxious species. The CCC-ECL process cools the power plant's flue gas to 175 K, at which point solid CO₂ particles desublimate as the flue gas further cools to 154 K. Desublimating flue gas cools in a staged column in direct contact with a cryogenic liquid and produces a CO₂-lean flue gas that warms against the incoming flue gas before venting. The CO₂/contacting liquid slurry separates through a filter to produce a CO₂ stream that warms to 233 K and partially flashes to provide a CO₂-rich product. The CO₂-rich product (99.2 %) liquefies under pressure to form a product for enhanced oil recovery (EOR) or sequestration. All contacting liquid streams cool and cycle back to the staged column. An internal CF₄ refrigeration cycle transfers heat from melting CO₂ to desublimating CO₂ by cooling contact liquid. An external cooling loop of natural gas or other refrigerant provides the additional heat duty to operate the cryogenic process. The nominal parasitic power loss of operating CCC-ECL is 82.6 MW_e or about 15 % of the coal-fired power plant's rated capacity. In different units, the energy penalty of CCC-ECL is 0.74 MJ_e/kg CO₂ captured and the resulting net power output is decreased to 467 MW_e. Lab- and skid-scale measurements validate the basic operation of the process along with the thermodynamics of CO₂ solids formation.

INTRODUCTION

Carbon dioxide (CO₂) affects the global climate in many ways. Within the USA, the Environmental Protection Agency proposed regulations limit CO₂ emissions from new electricity generation to 1,100 lbs. CO₂/MWh (500 kg CO₂/MWh)¹. Even new supercritical coal-fired power plants require significant CO₂ capture because their current CO₂ emissions range from 1,800 to 2,000 lbs. CO₂/MWh (820-910 kg CO₂/MWh)². Several technologies can achieve the necessary CO₂ standard. However, while the regulations are obtainable with current technologies, the associated energy penalty of CO₂ capture and resulting increased cost of electricity are substantial and pose significant changes to economies. A brief review of some competing technologies is presented as a reference. The main contribution of the present investigation is a description of external cooling loop cryogenic carbon capture (CCC-ECL), including skid-scale verification, and techno-economic simulations of a 90 % CO₂ capture CCC-ECL process at full-scale on a coal-fired power plant with the associated energy and economic comparisons to a similar plant with no capture.

Competing Technologies

CO₂ separation technologies target several industries, including energy production, cement production, aluminum and steel manufacturing, and natural gas production. Several reviews document the energy demands and costs for different technologies³⁻⁶. Technologies for coal-fired power plants generally fall into the categories of oxy-combustion, chemical looping, absorbents, adsorbents, membranes, and cryogenic processes. The minimum work to separate 90% of an initial 15% dry basis CO₂ stream into one stream of pure CO₂ and a second stream dominated by nitrogen is 0.15 MJ_e/kg CO₂. The minimum work of compression from 1 to 150 bar is about 0.22 MJ_e/kg CO₂, for a total of about 0.37 MJ_e/kg CO₂ captured when the heat rejection temperature and final CO₂ temperature are 298.15 K. Most of the alternative processes separate and produce CO₂ at 35-40 °C, in which case both the minimum separation and compression energies increase, with a total of about 0.38 to 0.42 MJ_e/kg depending on assumptions^{7, 8}. Literature estimates from third-party sources regarding energy demands of practical systems typically range from 1-1.5 GJ_e/tonne CO₂ captured⁸⁻¹¹, with the most recent US DOE estimates at the lower end of this range^{8, 12}. These energy penalties indicate the equivalent amount of work required, regardless of whether the energy is actually electricity, heat, or a combination of each. The energy analyses in this work follow the methods and use the computer codes and assumptions of the published, detailed US DOE results^{9, 11}.

Oxy-combustion. This method of CO₂ management uses a pre-combustion, cryogenic air separation unit that separates oxygen to combust with coal, resulting in nominally pure combustion products, CO₂ and H₂O. The resulting flue gas cools, condensing H₂O, and then nominally pure CO₂ is pressurized and sequestered or used for enhanced oil recovery. One full-scale power plant using this technology remains in consideration at White Rose (UK) while other major oxycombustion projects in the US and Europe lost support for a variety of reasons.

Hurdles for widespread adoption of oxy-combustion include its high energy penalty due to the extreme, low temperatures (~ 73 K) required for cryogenic distillation of O_2 from air¹³. The resulting energy penalty is in the range of 0.97-1.5 MJ_e/kg CO_2 captured^{9, 10, 14, 15}. There is little expectation for reducing the energy penalty due to the constraints in the air separation unit with similar molecular weights and vapor pressures of N_2 and O_2 .

Chemical Looping. Chemical looping poses a similar approach to CO_2 management, but oxygen is introduced as part of an oxidized metal, such as iron titanium oxide¹⁶, instead of as a gas. Oxygen, typically from air, binds to the solid metal carrier in a fluidized bed, and then the oxidized solid metal flows to a second fluidized in which it reacts with fuel to reduce the metal oxide and oxidize the fuel. The reduced solid metal returns to the first fluidized bed to be re-oxidized¹⁷. The combustion products undergo treatment similar to those of oxy-combustion. Some of the most significant concerns with the chemical looping include the effects of thermally cycling the oxidizing metal carrier. Deactivation with use and entropy losses due to heating and cooling of the solid particles significantly affect the energy penalty. While chemical looping systems exist at atmospheric conditions, energy penalties for these systems were not found in literature and have not been provided in this review. The energy penalty associated with carbon capture by pressurized chemical looping is less than if it were applied to the near atmospheric combustion of this study's base power plant. Disregarding the energy for compression, the energy penalty range is 0.2-0.5 MJ_e/kg CO_2 captured when applied to high-pressure combustion systems^{18, 19}. Current research and development includes work at the National Carbon Capture Center on a 150 kW_e equivalent system²⁰. NETL provides a summary of several other chemical looping projects²¹. Because chemical looping requires replacing most of an existing power plant, chemical looping usually competes better as an option for new installations rather than as a retrofit option.

Absorbents. Amine scrubbing processes are by far the most widely used form of CO_2 removal technology and have decades of industrial experience²². They are commercially available for multiple applications. Amine sorbents bind to the CO_2 , removing it from the process stream. The data from several literature sources show a large variation in energy penalties despite similar sorbent composition. They range from 0.97-4.20 MJ_e/kg CO_2 ²²⁻³¹ depending on the power plant and the design of the system. Generally, NETL reports an amine carbon capture system to have an associated energy penalty of 1.3 MJ_e/kg CO_2 captured¹⁰. Variations on compressors, pressures, percent sorbent, and the sorbent composition used are all major contributors to the energy penalties experienced by these processes²⁷. A major benefit of this system is that it is a very mature system, at least in its traditional uses in natural gas conditioning²². It is also commercially available for power plants, although many absorbents are not past the pilot scale. SaskPower's Boundary Dam integrated Carbon Capture and Sequestration project in Canada is the largest and first project of its type to demonstrate post-combustion capture on a commercial coal-fired power plant. The repowered 110-120 MW_e power plant will produce about one million tons of captured CO_2 per year, about 95% of its total output, much of which supplies enhanced oil recovery at the Weyburn oil field. It uses an amine-based solvent developed by Cansolv, a wholly owned subsidiary of Shell Oil Co. Additionally, a

Southern Company is constructing a Selexol process for the full-scale Kemper power plant (USA). Some drawbacks include the size of the process as well as the toxicity of the chemicals and the energy cost to the system. Other amine-type sorbents include Fluor's Econamine system, MHI's KS-1 solvent, and mixtures of primary, secondary, and tertiary amines. These sorbents, while differing from each other, have approximately similar energy penalties to more traditional MEA sorbents.

Other types of sorbents, such as Opticap by B & W, have many drawbacks similar to those mentioned for amines, but additionally have far less research supporting them and are not as commercially available. They are, however, sometimes more efficient as shown by a comparison conducted at NCCC, where Opticap proved significantly more efficient under similar circumstances as MEA²⁶.

Adsorbents. Due to the physical attraction between CO₂ and other species, adsorbents find some uses for CO₂ capture. Typical CO₂ adsorbents include zeolites, molecular sieves, and activated carbon. These preferentially adsorb CO₂ from air-fired combustion products. Once the adsorbent saturates with CO₂, it generally regenerates with a pressure and/or temperature swing. The energy penalty of adsorbents depends primarily on the energy required for the cyclical change in conditions and is in the range of 2.0-5.6 MJ_e/kg CO₂ captured^{22, 32}. More advanced adsorbents remain under development in several research programs.

Membranes. Membranes provide an alternative to chemicals. Membranes can either provide pre-combustion enrichment of O₂ or post-combustion CO₂ separation from a flue gas. CO₂ penetrates the membrane faster than other species, specifically N₂. The membranes are commonly made from polymers³³ and are sometimes made from other materials such as palladium³⁴. The membrane selectively separates components in the stream, specifically the CO₂ molecules. Testing of membranes remains at small scale compared to amine processes. The distinct advantage they have is the absence of toxic chemicals. Membrane separation requires replacement membranes³⁵ as well as significant pumping power³⁶, the latter resulting in energy penalties within the range of 0.95-1.9 MJ_e/kg CO₂ captured^{34, 37}. They also struggle to produce high purity CO₂.

Cryogenic Processes. Cryogenic technologies come in several forms, including the thermal swing process, inertial carbon extraction system, and the CCC-ECL. A thermal swing process freezes CO₂ as a solid directly on the surface of a heat exchanger. The heat transfer degrades with time as solid CO₂ fouls the surface. At some point, a second parallel heat exchanger begins processing the stream while the first warms and regenerates³⁸. In the case of 90 % CO₂ capture from a coal-fired power plant, Pan et al. report that the process energy penalty is 1.18 MJ_e/kg CO₂³⁹. Significant energy losses occur with the temperature swing of the heat exchanger. In addition, heat transfer rates reduce as CO₂ solids form on the heat exchanger surfaces. The continual handling of CO₂ solids is a major hurdle for adoption common among all of the cryogenic processes. Mechanical cleaning provides one means for handling the solids formation. While Alstom has generally been interested in this basic process, Shell has also

investigated similar processes and shown good agreement between predictions and experimentation⁴⁰. Alstom has slowed the development of the thermal swing process because of minor energy penalty improvements and major capital costs compared with conventional amine systems.

Inertial Carbon Extraction System, an expansion process, forms solid CO₂ without any of the surface fouling issues⁴¹. Flue gas is expanded through a nozzle, and solid CO₂ particles form with the heat transfer coming from expansion rather than a surface. A cyclone separates the gas/solid stream. The design, operation, and maturity of this process are significant obstacles to commercialization.

The CCC-ECL likewise operates with the formation of CO₂ solid particles at cryogenic temperatures. The CCC-ECL removes up to 99+% of the CO₂ from flue gas in a continuous process while maintaining a low energy penalty of 0.74 MJ_e/kg CO₂. The technology works by cooling the flue gas to low temperatures, removing water before reaching 273 K, and passing the gas through patented desublimating heat exchangers at temperatures near 150 K. This causes desublimation of the CO₂ to occur, leaving solid CO₂ in a slurry. The solid CO₂ separates from the contact liquid and melts under pressure as it warms back to room temperature. The advantages of this system include low energy penalty, grid-scale energy storage potential, process simplicity, low cost, multipollutant capture, and lack of toxic chemicals. CO₂ solids formation is the major technical problem with this technology. This has the potential to plug and foul heat exchangers and otherwise complicate the process. Sustainable Energy Solutions (SES) has patented three heat exchangers that operated at steady state with no compromise in performance when treating solids-forming fluids. With lab-, bench- and skid-scale validations completed at scales up to 1 ton of CO₂ per day, the technology is approaching pilot-scale in its development path. Process simulations using both Aspen Plus™ and an in-house SES code predict very similar results that compare favorably with alternative technologies. This paper presents simulation results with Aspen Plus™.

CCC-ECL PHASE EQUILIBRIUM MODELS

The limited solid liquid vapor equilibrium (SLVE) calculated by the Peng-Robinson equation of state (PR-EOS) predicts the equilibrium achieved in a desublimation column. SLVE involves iteration and in these cases uses Raoult's Law for generating initial estimates. Equilibrium predictions assume that (1) no CO₂ liquid phase exists below its freezing point and (2) the solid phase is pure CO₂. CO₂ dissolution in other liquids is included.

Predictions depend heavily on solid-CO₂ vapor pressure. New parameters for solid-CO₂ vapor pressure correlations resulted from this investigation and based on least squares analyzes of several sources of CO₂ sublimation data. Table 1 summarizes the sources of solid-CO₂ vapor pressure data. Parameters comparisons for several empirical vapor pressure equations (Antoine, Riedel, Wagner, Span and Wagner⁴²) indicate that the Riedel and Wagner equations having the

smallest sum of squared errors. The 5-parameter Riedel equation with newly regressed parameters fit well with temperatures above 150 K, but has significant deviations at lower temperatures. The region of interest is from the triple point to processing temperatures around 150 K for 90 % carbon capture. A 6th parameter inside the exponential, $\frac{F}{T^2}$, improved the fit better than a variety of other options. The 6-parameter correlation is

$$P_{CO_2}^{sub} = \exp \left[57.52 + \frac{-3992.84}{T} - 4.9003 \cdot \ln(T) + 2.415 \cdot 10^{-15} \cdot T^6 + \frac{8125.6}{T^2} \right] \quad (1)$$

where T is the temperature in K and $P_{CO_2}^{sub}$ is the solid vapor pressure of CO₂ in Pa. Figure 1 compares the improvement in predicted residuals with DIPPR and NIST correlations of the Riedel forms in the temperature region of interest.

Table 1 Summary of published solid-CO₂ vapor pressure measurements

# of Data Points	Temperature [K]	Pressure [Pa]	Reference
62	69 - 103	7·10 ⁻⁸ - 0.05	Bryson et al. ⁴³
11	106 - 154	0.1 - 1,334	Tickner & Lossing ⁴⁴
7	138 - 195	133 - 100,000	Stull ⁴⁵
8	140 - 195	200 - 101,000	Kaye & Laby ⁴⁶
20	153 - 204	1,333 - 200,000	Thermodynamic Research Center ⁴⁷
6	154 - 196	1,509 - 111,000	Giauque & Egan ⁴⁸
131	154 - 217	1,490 - 527,000	Bilkadi et al. ⁴⁹
16	178 - 198	23,700 - 131,000	Ambrose ⁵⁰
19	192 - 195	86,000 - 102,000	Heuse & Otto ⁵¹
21	194 - 217	97,700 - 517,000	Fernandez-Fassnacht & Del Rio ⁵²
28	194 - 217	99,000 - 518,000	Meyers & Van Dusen ⁵³
1	195	101,325	Mullins et al. ⁵⁴
1	195	101,325	Marsh ⁵⁵
6	201 - 213	179,000 - 385,000	Baughman et al. ⁵⁶

Figure 1 Residuals of solid- CO_2 vapor pressure with correlations from DIPPR⁵⁷ & NIST⁵⁸

Raoult's law provides a starting point for estimating CO_2 phase equilibrium for vapor and solid phases. Raoult's law, applied to CO_2 sublimation, is

$$x_{\text{CO}_2} \cdot P_{\text{CO}_2}^{\text{sub}} = y_{\text{CO}_2} \cdot P \quad (2)$$

where x_{CO_2} and y_{CO_2} are the mole fractions of CO_2 in the condensed (solid) and vapor phases respectively, $P_{\text{CO}_2}^{\text{sub}}$ is the sublimation vapor pressure of CO_2 , and P is the total pressure. Donnelly and Katz reported that the melting point of the solid found in equilibrium with the vapor and liquid was the same as pure carbon dioxide, indicating that the CO_2 forms an essentially pure solid phase⁵⁹, so $x_{\text{CO}_2} = 1$. Therefore, Raoult's law predicts the mole fraction of CO_2 in the vapor phase as a function of temperature and total pressure (Eqn. 3) as

$$y_{\text{CO}_2} = \frac{P_{\text{CO}_2}^{\text{sub}}(T)}{P} \quad (3)$$

A Poynting correction factor and non-ideal fluid models improve SLVE equilibrium predictions for vapor-phase CO_2 , even while assuming a pure solid CO_2 phase and no CO_2 in a liquid phase. CO_2 does form in the liquid phase, but this does not appreciably affect the vapor concentration. Thus, solutions simultaneously predict SVE for CO_2 and VLE for all other components. These equilibria, are expressed, respectively, by

$$\phi_{CO_2}^{sub} \cdot P_{CO_2}^{sub} \cdot e^{\frac{V_{CO_2}^{solid} \cdot (P - P_{CO_2}^{sub})}{R \cdot T}} = y_{CO_2} \cdot \bar{\phi}_{CO_2}^{vap} \cdot P \quad (4)$$

$$\bar{\phi}_i^{liq} \cdot P_i^{vap} \cdot e^{\frac{V_i^{liquid} \cdot (P - P_i^{vap})}{R \cdot T}} = y_i \cdot \bar{\phi}_i^{vap} \cdot P \quad (5)$$

where i is the component, ϕ_i is the fugacity coefficient of i at the saturated solid/liquid pressure or total pressure for the vapor, the over bar on fugacity coefficients denotes a partial fugacity coefficient, V_i is the solid/liquid molar volume, and R is the universal gas constant. The liquid-phase CO_2 that forms due to solubility is not predicted because the liquid recirculates back into the desublimation column. While the CCC-ECL process does not operate at significant pressure, the Poynting correction factor term is included because the validation uses some high-pressure data. The Peng-Robinson equation of state (PR-EOS) estimates the fugacity coefficients, which approach unity at low pressure and high purity. Because the fugacity coefficients are functions of composition, the solutions are iterative.

The generalized form of the PR-EOS⁶⁰ is

$$P = \frac{R \cdot T}{V_m - b} - \frac{a(T)}{V_m (V_m + b) + b (V_m - b)} \quad (6)$$

$$a(T) = 0.45724 \frac{R^2 \cdot T_c^2}{P_c} \left[1 + \kappa \left[1 - \sqrt{\frac{T}{T_c}} \right] \right]^2 \quad (7)$$

$$b = 0.07780 \frac{R \cdot T_c}{P_c} \quad (8)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (9)$$

where V_m is the molar volume, T_c is the critical temperature, P_c is the critical pressure, and ω is the acentric factor.

For the PR-EOS, the fugacity coefficient (Eqn. 10) depends on the compressibility (Eqns. 11-13) with classic mixing/combining rules (Eqns. 14-15).

$$\ln(\bar{\phi}_i) = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln\left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right) \quad (10)$$

$$Z^3 - (1 - B)Z^2 + (A(T) - 3B^2 - 2B)Z - (A(T) \cdot B - B^2 - B^3) = 0 \quad (11)$$

$$A(T) = \frac{a(T) \cdot P}{R^2 \cdot T^2} \quad (12)$$

$$B = \frac{b \cdot P}{R \cdot T} \quad (13)$$

$$a(T) = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a(T)_i a(T)_j} (1 - k_{ij}) \quad (14)$$

$$b = \sum_{i=1}^N x_i b_i \quad (15)$$

where Z is the compressibility and k_{ij} is the binary interaction parameter.

Several data reviews estimate the thermodynamic parameters for the PR-EOS. This simulation uses the Aspen Plus' Pure APV80 database values along with the proposed solid vapor pressure correlation. Available thermodynamic data from NIST and DIPPR are widely accepted, but are generally limited to pure-component vapor/liquid data. Comparisons of the available data and predictions discussed below assure that PR-EOS parameters properly predict solid phase formation.

Validation of Prediction Methods

Literature data are not available for equilibrium conditions of flue gas and solid CO_2 . However, from the natural gas processing industry, CO_2 frost-point temperatures are extremely important and many groups report them. These measured frost-point temperatures provide a means validating with predictions to determine the applicability of the presented equilibrium methods. Table 2 summarizes the CO_2 frost-point temperature data. The goodness of fit or correlation is reported by the bias, average absolute deviation (AAD) and mean square error (MSE), defined as

$$\text{bias} = \frac{1}{n} \sum_{i=1}^n T_{\text{calc}} - T_{\text{exp}} \quad (16)$$

$$\text{AAD} = \frac{1}{n} \sum_{i=1}^n |T_{\text{calc}} - T_{\text{exp}}| \quad (17)$$

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^n (T_{\text{calc}} - T_{\text{exp}})^2 \quad (18)$$

where n is the number of data points in the data set, T_{calc} is the predicted frost-point temperature, and T_{exp} is the experimentally determined frost-point temperature. The new solid vapor pressure correlation makes a 0.2 K, 0.3 K, and 2.3 K² improvement in bias, AAD, and MSE, respectively, for predictions with the PR EOS compared to best published solid-vapor-pressure correlation of which we are aware, DIPPR.

Table 2 Summary of published CO_2 frost-point measurements with prediction goodness quantified by bias, AAD, and MSE for the PR EOS

Data	Temp [K]	Pressure [kPa]	Composition [% , balance CH_4]	Aspen Plus			DIPPR			New			Reference
				Bias	AAD	MSE	Bias	AAD	MSE	Bias	AAD	MSE	
				[K]	[K]	[K ²]	[K]	[K]	[K ²]	[K]	[K]	[K ²]	
<i>Frost-Point Measurements of Binary Systems</i>													
42	137-198	179-2785	0.1-10.7 CO_2	-1.4	2.0	5.5	-1.1	1.8	4.6	-0.8	1.6	3.8	Agrawal ⁶¹
75	132-210	156-4790	0.03-59 CO_2	-0.6	0.7	1.0	-0.2	0.4	0.5	-0.1	0.4	0.2	Pikaar ⁶²
17	191-210	293-4446	10.8-54.2 CO_2	-0.2	0.7	0.6	-0.1	0.7	0.6	-0.1	0.7	0.6	Zhang ⁶³
39	170-200	689-2413	2-16 CO_2	-1.4	1.4	2.4	-1.2	1.2	1.7	-1.2	1.2	1.6	GPSA ^{64 A}
47	168-185	962-2464	1-2.9 CO_2	0.4	2.3	6.9	0.8	2.4	14.7	1.0	2.5	8.4	Le ⁶⁵
11	130-201	5000	0.2-20.5 CO_2	-5.0	5.0	57.5	3.7	3.7	39.9	5.3	5.3	39.6	Kurata ^{66 A}

Frost-Point Measurements of Ternary Systems

19	154-172	172-2441	0.9 CO ₂ & 0.7-2.9 N ₂	-1.7	1.7	3.4	-1.3	1.4	2.4	-0.9	1.1	1.6	Agrawal ⁶¹
24	174-184	1243-2262	1.9 CO ₂ & 96-97 N ₂	-0.4	1.7	3.7	-0.3	1.6	15.2	-0.1	1.6	3.4	Le ⁶⁵

^Areported by ZareNezhad

Figure 2 compares the frost-point predictions using Raoult's law with measurements. Pikaar's data highlights the inadequacy of Raoult's law for high-pressure predictions. At low pressures, fugacity coefficients approach unity, but for the case of high-pressure measurements, the fugacity coefficient of the vapor phase deviates from unity. Figure 3 and Figure 4 show frost-point predictions with PR and SRK EOS, which account for the non-ideality at higher pressures and improve the agreement between predictions and measurements. Frost-point predictions generally fall within 3 K for both EOS, except for the measurements of Kurata, which are the highest pressure data at 5 MPa. The residuals of Le's measurements in binary systems trend with pressure and are thus suspicious. Otherwise, for both the PR and SRK EOS the predictions are generally within ± 3 K.

Figure 2 Frost-point temperature predictions with Raoult's law vs. measurements for binary and ternary systems

Figure 3 Frost-point temperature predictions with PR EOS vs. measurements for binary and ternary systems

Figure 4 Frost-point temperature predictions with SRK EOS vs. measurements for binary and ternary systems

EXPERIMENTAL VALIDATION OF CCC-ECL SOLIDS FORMATION

Several experimental apparatuses demonstrate the basic functionality of CCC-ECL at lab- and bench-scales. Flue gas flowrates vary between 0.02-1.4 m³/min for the different scales. Figure 5 outlines the basic flow of the apparatuses. The first generation apparatus allowed visual verification of performance in the desublimating column⁶⁷ and had simpler materials for construction, making testing of multiple design iterations simpler. The optical access provides highly useful, but qualitative, information during its operation. The visual verification of the desublimating column performance was extremely important in the first attempted experimental runs to ensure proper operation and generating relevance between operation and measured process parameters. Later apparatuses performed better and operated longer at the expense of visual access.

Figure 5 Simplified diagram of testing apparatus

The visually accessible desublimating column exterior surface comprises two vacuum-separated concentric acrylic tubes. Internal stages of perforated Teflon sheeting create bubbles in a manner similar to sieve plates in conventional distillation. Stainless steel provides structural rigidity, a weir, and a downcomer. O-rings seal the stages against the exterior and the steel frame provides stage separation and support, see Figure 6. The acrylic construction and vacuum-sealed walls are for experimental convenience. Subsequent desublimation columns were designed similarly to the visually accessible desublimating column, but with stainless steel construction. The columns were generally insulated by at least 6 inches of expanded perlite. Future designs of contacting and non-contacting desublimation heat exchangers have been proposed and include a spray tower and fluidized bed⁶⁸.

Figure 6 Single stage of heat exchanger a) during operation with solid CO₂ particles suspended in contact liquid and b) post-operation, drained, with solid CO₂ remaining

Similarly for all apparatuses, heat exchangers are stainless steel brazed-plate styles (Duda Diesel, Pex Universe, & GEA-PHE). Pressure transducers (Transducers Direct) were calibrated with factory certification of 0.25 % accuracy. Thermocouples (Omega) have an uncertainty of ± 1 K. Mass flow controllers (Omega & Brooks) provide an arbitrary simulated flue gas composition, with the focus of this paper being a 85/15 mixture from cylinders (Airgas) containing 99.998 % pure N₂ and 99.5 % pure CO₂. Data was recorded by either a LabView compatible DAQ (National Instruments) or Simatics DCS (Siemens).

Three different gas analyzers measure CO₂ concentrations as experimentation progressed. A non-dispersive infrared (NDIR) M-700 emissions analyzer (Enerac) has a limited resolution of 0.1 %. A 5975C quadrupole mass spectrometer (Agilent Technologies) provides additional gas analysis, specifically (1) verifying the adequacy of CO₂ measurements of NDIR analyzers and (2) quantifying the trace elements (i.e. contacting liquid). For portable skids, an industrial ABB EL3040 analyzer provides continuous results with an increased resolution compared to the M-700 (0.006 %). The EL3040 also uses NDIR techniques and is limited to the CO₂ concentration range of 0-3 %. Analyzers are calibrated with NIST-traceable Mesa Specialty gases and with in-house calibration gases. In-house calibration gases are volumetrically made in a 1 L syringe (SGE).

Solid separation occurs in a semi-continuous batch strainer, hydrocyclone, and continuous filter press. The batch strainers are simple in design and operation, but are constrained to semi-continuous batch operation. While the molecular sieve used to dry the flue gas has similar batch-wise operation, it does not undergo large cryogenic temperature swings to

expel the water. Considering the cost of refrigeration, a temperature-swing strainer has a significant, detrimental effect on the energy penalty. To provide for continuous operation, a hydrocyclone and a continuous filter press operate in series. The hydrocyclone is of typical design and operation. The continuous filter press is auger driven, with special considerations given to the properties of the solid CO₂ particles. The resulting separation achieved in bench-scale experiments is 2.6 % of the contact liquid remaining in the solid CO₂. To achieve the separation necessary for 99.94 % recovery of contact liquid, a standard flash drum is used after the solid CO₂ stream melts and warms. With the addition of the flash drum, less than 0.1 % of the contact liquid remains in the stream, and the CO₂ meets specifications for EOR and sequestration.

The most significant energy consumption in the CCC-ECL process involves refrigeration. Previously, the equilibrium predictions by PR-EOS were presented with validation of CO₂ frost-point temperatures in binary and ternary mixtures composed primarily of CH₄. The operability and thermodynamic predictions of solid CO₂ formation were validated by experiments ranging in scale from synthetic flue gas flow rates of 0.02-1.4 m³/min (i.e., up to a 20 kW_e equivalent retrofit plant). Figure 7 shows the experimental measurements of an hour-long run at 1.4 m³/min. The prediction uses the PR-EOS with uncertainties from temperature and pressure measurements. The EL3040 recorded CO₂ concentration and the target 0.2 % CO₂ in the exit gas represents 98.7 % CO₂ capture. The prediction adequately describes the highly varied CO₂ capture performance for the entire 85 minutes. Changes in operating conditions caused the other peaks before 85 minutes. Steady operation with the same equipment meets target capture of 90+ % continuously but does not test the model accuracy over a range of flow conditions. The experimental results from this and many other runs validate the ability of the PR-EOS to describe the conditions necessary for full-scale demonstration of solid CO₂ formation in the CCC-ECL process.

Figure 7 Experimental results of CO₂ concentration in exiting flue gas while operating near atmospheric pressure and 133-153 K with inlet composition of 15 % CO₂, balance N₂

FULL-SCALE CCC-ECL PROCESS SIMULATION

This embodiment of the CCC process provides a retrofit option to remove 90+ % of the CO₂ from the flue gas of a coal-fired power plant. The following calculations assume a 550 MW_e net output prior to addition of CO₂ capture. The cryogenic carbon capture cools the treated power plant's flue gas to 175 K. The CO₂ in the flue gas forms solid particles as the flue gas further cools to 154 K in a staged column with direct cryogenic liquid contact. The clean flue gas warms against the incoming flue gas and vents to the atmosphere. The CO₂/contacting liquid slurry undergoes filtration and subsequently the nearly pure solid warms to 233 K and provides a CO₂ rich product. The CO₂ liquefies and leaves the process prepared for enhanced oil recovery (EOR) or sequestration. All contacting liquid streams cool and recycle back to the staged column. An internal refrigeration cycle with CF₄ transfers heat from melting CO₂ to desublimating CO₂. An

external cooling loop of natural gas provides the additional heat duty to operate the cryogenic process. The streams and equipment discussions appear separately below. Figure 8 shows a simplified process flow schematic.

Figure 8 Simplified schematic of CCC-ECL process flow

Flue Gas. Due to the potential formation of sulfuric acid and solid sulfur products, the CCC process uses gas after the power plant's flue gas desulfurization unit (FGD). The CCC process has demonstrated potential as a SO_x , NO_x , Hg, PM_{xx} , and HC removal device as well as a CO_2 mitigation system, and this has been demonstrated many times to be very efficient, but the focus here is on CO_2 . The flue gas from the FGD includes 2.4 % O_2 , 68.08 % N_2 , 13.53 % CO_2 , 15.17 % H_2O , and 0.82 % Ar at 330.15 K and 102.042 kPa. Cooling the gas to 290 K condenses approximately 90 % of the water. To overcome subsequent pressure drops, a blower pressurizes the flue gas to 127.6 kPa. The flue gas cools to near 273 K and regenerating mol sieve beds remove the residual water to ensure no ice formation as the flue gas cools in a multi-stream heat exchanger to 175 K. The cooled flue gas enters the bottom of a 10-stage desublimating column and bubbles up through the tower while being cooled to 154 K by direct contact with a counter-current contacting liquid. The cleaned flue gas leaves the top of the heat exchanger with less than 10 % of the incoming CO_2 . It is possible to capture 99+ % CO_2 with colder temperatures (144

K), and experiments and theory demonstrate this. However, this simulation uses the DOE benchmark of 90 % CO₂ capture. The separated gas recuperatively warms against incoming flue gas. Before the light gas stream returns to the stack, it augments an evaporative cooler to cool process water to near freezing temperatures.

Contact Liquid. The contact liquid is in a closed loop with minor losses into the CO₂ byproduct and the light flue gas. In general, contacting liquids should have low vapor pressures to decrease losses through evaporation and otherwise be environmentally and physically benign. The contact liquid prevents CO₂ solids from forming on surfaces and greatly simplifies solid CO₂ transport as a slurry, thus preventing process freeze up. At its coldest temperature of 154 K, the contact liquid enters the top stage of a desublimating column and cools the flue gas through direct contact, leaving the bottom stage as a slurry with solid CO₂ entrained in the flow. A pump pressurizes the slurry prior to entering a solid-liquid separator. The separator consists of an auger-driven continuous filter press. The bulk contact liquid, now free of solids, re-cools against a closed-loop refrigeration system in preparation to reenter the desublimating column. Contact liquid recovered from the CO₂-rich stream returns to the process. To counter the minor losses, a makeup stream of pressurized contacting liquid cools from ambient temperature.

Vapor pressure data for contacting liquids are commonly not available at these operating conditions. Experimental vapor pressure measurements ensure compliance with hydrocarbon emission standards.

CF₄ Refrigeration. The CF₄ refrigeration loop moves the cooling duty of melting CO₂ melting to the colder temperature of desublimating CO₂. After condensing against the melting CO₂, and some sub cooling, it splits into five streams, each expanded by a valve to a different pressure defined by the stage of the CF₄ compressor to which it will return. This produces a stepping effect in the heat exchanger that overcomes entropy losses against contact liquid and other streams undergoing sensible heating/cooling.

CO₂-Rich Product. The CO₂ separates from the slurry at the bottom of the desublimation column in a hydrocyclone followed by a continuous press filter. After filtration, the CO₂-rich product is 93.3 % CO₂ and warms and melts against condensing CF₄. After warming against the flue gas to 233 K, the CO₂-rich stream enters a contact liquid removal process for final separation (99.2 % CO₂ purity). As part of the contact liquid removal, the CO₂-rich stream warms and flashes to remove the remaining contact liquid. The CO₂ vapor warms and recompresses before liquefying against the vaporizing CO₂-rich stream. After liquefaction, a liquid pump pressurizes it to 100 bar with cooling duty once again recovered before leaving the process for EOR or sequestration. Some studies suggest that a higher discharge pressure may be necessary⁶⁹⁻⁷¹, which case is investigated in the sensitivity analysis.

External Cooling. Even with significant heat integration, the CCC-ECL process requires additional refrigeration. Natural gas acts as a refrigerant due to its reasonable

pressure/temperature refrigeration capability, high maturity and availability of compression, and its potential to enable energy storage. It is nominally composed of 95 % CH₄, 3 % C₂H₆, and 2 % C₃H₈. The natural gas liquefies and cools to 179 K before expanding in a turbine to 1,145 kPa resulting in a temperature of 153 K. The expansion vaporizes a significant fraction, 25.4 %, with the remaining natural gas vaporizing to cool contact liquid in the CCC-ECL process for subsequent CO₂ desublimation. This expanded natural gas is the coldest temperature achieved in the CCC-ECL process. The natural gas recuperatively warms against incoming natural gas before being compressed to initial conditions. A mixed refrigerant loop supports the natural gas liquefaction and comprises nominally 4.2 % CH₄, 84.5 % C₂H₆, 2.8 % C₄H₁₀, and 8.5 % iso-C₅H₁₂. Because of the heavier hydrocarbons in the mixed refrigerant, the compressor intercoolers must have a phase separator, and a pump removes and pressurizes the liquid. Alternatively, the recirculating natural gas stream could be conditioned such that no liquids condense to simplify the compressor operation.

Pressurization. The flue gas blower is a single-stage compressor in Aspen Plus. The CF₄, natural gas, and mixed refrigerant compressors are 8-stage compressors with intercoolers after each stage of compression. The CO₂ vapor compressor is a single-stage compressor with no after-cooler. Compressor intercoolers have a 5 kPa pressure drop per pass, greatly affecting the efficiency of the lowest-pressure stages. Compressors operate with 90 % polytropic efficiency, typical of commercial guarantees for such equipment at this scale. Compressor energy consumption is the primary energy demand in the CCC-ECL process, and thus under great scrutiny.

Heat Exchange. Brazed-plate heat exchangers are the primary heat exchange in the CCC-ECL system. They operate with a 1 K minimum internal temperature approach. The melting CO₂ heat exchanger is similar in design to a jacketed, stirred tank with the CF₄ condensing in the jacketing tubes while the solid melts and is stirred on the inside of the tank. A conservative approach simulates this as a co-current heat exchanger with 1 K approach temperature on the exiting streams. A full-scale counter-current implementation of the melting heat exchanger would have higher efficiency.

Other, more traditional heat exchangers provide compression inter-stage cooling and water cooling. Basic compressor inter-stage coolers are shell and tube heat exchangers with a minimum internal approach temperature of 5 K, though brazed-plate systems would increase efficiency decrease cost. The evaporative cooler is a 10-stage cooling column. All heat exchangers have at least a 5 kPa pressure drop per pass. Designs from Chart Energy and Chemicals suggest pressure drops ranging from 2 kPa to 19 kPa and these are included in the sensitivity analysis.

A 10-stage desublimation column uses a series of Gibbs reactors in the simulation, allowing solids formation at each stage. The desublimation column has 5 cm of liquid height per

stage, resulting in a 0.37 kPa pressure drop per stage. As an alternative to a desublimation column, experimental results on a desublimation spray tower have improved efficiencies for heat and mass transfer. Up to 96 % CO₂ capture has been demonstrated and predictions of performance are within 2.3 %⁷². Pending future research and development, the desublimation spray tower may provide opportunities for lowering the total energy penalty of the CCC-ECL process.

Solid Separation. The CO₂ solids separator is a combination of a hydrocyclone, to concentrate the solid CO₂ particles, followed by a continuous press filter, removing contact liquid down to 6.7 %. The press filter captures 100 % of the solid CO₂. This does not take solubility into account, which may increase the concentration of CO₂ in the recycled contact liquid, but this will simply recirculate and should not affect energy or cost. It may help reduce viscosity.

Turbines. The two expansion turbines handle vapor-liquid phases. Turbines have 92 % isentropic efficiency. The turbines operate at temperatures ranging from 154-195 K and expand the hydrocarbon liquids with a portion of the stream vaporizing. LNG operations employ cryogenic hydraulic turbines that operate at nearly the same conditions and on the same scale⁷³ as those in this model. Valves could replace the turbines to reduce capital expenditures with only a 2.4% increase in energy demand.

RESULTS SUMMARY & DISCUSSION

CCC-ECL is capable of 90 % CO₂ capture with a simulated energy penalty of 0.74 MJ_e/kg CO₂. Table 4 summarizes the energy consumption. Three compressors drive the refrigeration and account for 80.9 % of the total energy penalty. The majority of the remaining energy penalty is due to the flue gas blower. The flue gas blower overcomes pressure drop and accounts for 16.7 % of the total energy penalty. The energy consumption of the blower may decrease by creating lower discharge pressures. Lower discharge pressures occur with improved cooling towers. The remaining power consumption is 2.4 % of the total energy penalty and thus less significant potential for improvement from an energy penalty perspective.

Table 3 Energy requirement by unit

Unit	Energy Required [MW _e]
Blower	13.76
CF ₄ Compressor	27.93
CO ₂ Compressor	0.70
Natural Gas Compressor	18.55
Mixed Refrigerant Compressor	20.37
Contact Liquid and Slurry Pumps	2.21

Liquid CO ₂ Pump	0.98
Mixed Refrigerant Liquid Pumps	0.11
Natural Gas Turbine	-1.38
Mixed Refrigerant Turbine	-0.63
Total	82.59

Table 4 details the total energy balance, including the previously discussed 82.6 MW_e of power consumed by process equipment. Process losses match the heat in/out of the plant and are less than 0.27 % of total heat as benchmarked by NETL⁷⁴.

Table 4 Energy balance

	Sensible + Latent	Power	Total
Heat In	[MW]	[MW]	[MW]
Flue Gas	-1860.4		-1860.4
Makeup Contact Liquid	-3.8		-3.8
Cooling Water	-13426.4		-13426.4
Process Units		82.6	82.6
Totals	-15290.6	82.6	-15208.0
Heat Out			
Cooling Water	-14252.9		-14252.9
N ₂ -Rich Gas	-178.7		-178.7
CO ₂ -Rich Liquid	-1037.1		-1037.1
Water Condensate 991	157.0		157.0
E416A	-28.2		-28.2
E416B	29.2		29.2
E416C	-0.9		-0.9
C306 Cooling Water	32.7		32.7
C570 Cooling Water	21.4		21.4
C700 Cooling Water	44.2		44.2
Process Losses*	5.4		5.4
Totals	-15208.0	0.0	-15208.0
Difference			0.0

Table 5 summarizes the mass balance based on the full-scale simulation. The total mass balance closes within 0.01 %.

Table 5 Mass balance (flow rates in kg/hr)

In	O₂	N₂	CO₂	H₂O	Contacting liquid	Ar	Total
Flue Gas	57726	1433810	447670	205464	0	24608	2169278

Makeup							
Contacting liquid	0	0	0	0	5483	0	5483
Water	0	28	44	3020154	0	0	3020226
Totals	57726	1433838	447714	3225618	5483	24608	5194987

Out	O₂	N₂	CO₂	H₂O	Contacting liquid	Ar	Total
N ₂ -Rich Gas	57726	1433782	43834	17439	72	24608	1577461
CO ₂ -Rich Liquid	0	0	403836	0	5339	0	409175
Water	0	56	88	3208179	0	0	3208323
Totals	57726	1433838	447758	3225618	5411	24608	5194959
Rel. Difference	0.000	0.000	0.000	0.000	0.003	0.000	0.000

Some contacting liquid in the system is lost during direct contact with the flue gas and during CO₂ separation in a flash drum. The concerns are primarily the environmental and economic impact of the combined losses. As simulated, the contacting liquid present in the exhausted N₂-rich gas is acceptable by EPA source guidelines for hydrocarbon emissions. Contacting liquid in the CO₂-rich stream is of lesser environmental concern since similar hydrocarbons exists in the ground where the CO₂ will be used for EOR. The economic impact of the contacting liquid losses at full-scale implementation of CCC-ECL will likely change the economics of its supply and demand. However, hydrocarbons suitable as contacting liquid generally come from oil and gas fractionation, with potential supplies greatly outweighing any potential need. Experimental tests completed with many hydrocarbons generally indicate that losses will be minor.

A sensitivity analysis shows the effects of variations from the current base model. These variation reflect an industry review of common challenges, available technologies, and expected technological improvements. Table 6 shows the results of the sensitivity analysis. The 4 % CO₂ inlet variation corresponds to a natural gas combined cycle power plant that has less CO₂ emissions per unit power produced. Excluding the natural gas case, the energy penalty ranges from 0.71-0.92 MJ_e/kg CO₂, which compares very favorably with other technologies.

If high-pressure is required for EOR or sequestration as suggested by some studies^{69, 71}, the energy penalty would increase by 0.004 MJ_e/kg CO₂. Without the turbines on the liquid natural gas and mixed refrigerant streams, the process loses 2.1 MW_e and the energy penalty would increase by 0.016 MJ_e/kg CO₂.

An economic analysis used the same scenarios as the energy sensitivity analysis. All equipment prices came from Aspen Plus' built-in economic analysis, excluding multi-stream heat exchangers. A price quote from Chart Energy and Chemicals provided the basis for the multi-stream heat exchangers in the model. Deviations from the base scenario have a price difference equal to 86 \$/m² multiplied by the change in heat transfer area. The change in heat transfer area assumed that U and ΔT were constant in the equation

539

$$Q = UA\Delta T$$

(19)

540 where U is the heat transfer coefficient, A is the heat transfer area, ΔT is a correlation for the
 541 temperature difference inside a plate and frame heat exchanger, and Q is the heat duty. $UA\Delta T$ is
 542 the quotient of the heat duty calculated by Aspen Plus for the base case and the area for the heat
 543 exchanger as determined by Chart. This value determined the new area with heat duties
 544 calculated by Aspen Plus for each scenario. Table 6 shows the capital expenditure (CAPEX)
 545 attributed to carbon capture, energy penalty, and cost of electricity (COE). The 4 % CO₂ inlet
 546 case refers to a natural gas power plant and is the cheapest scenario in the analysis.

547

Table 6 Economic analysis of process variations and resulting cost of electricity (COE)

Case / Variable	Base Case	Variation	CAPEX [\$x10 ⁶]	Energy Penalty [MJ _e /kg CO ₂]	COE [cents/kWh]
No CO₂ Capture			-	-	5.89
Amine CO₂ Capture			469	1.379	10.65
Base CCC-ECL Case			361	0.738	8.96
CO ₂ Inlet	16 %	4 %	217	1.669	6.67
		12 %	345	0.920	8.74
		14 %	357	0.819	8.89
CO ₂ Capture	90 %	89 %	359	0.711	8.93
		91 %	365	0.740	9.03
		99 %	391	0.846	9.45
Cooling Water Temp	289 K	281 K	362	0.717	8.97
		303 K	367	0.772	9.06
Efficient Turbines ^A	92 %	89 %	364	0.738	9.00
		94 %	366	0.737	9.07
HX Temp Approach	1 K	2 K	318	0.772	8.88
		4 K	299	0.863	8.95
Pressure Drop	5 kPa	Mfg Quote	369	0.832	9.16
Compressor Efficiency ^B	90 %	85 % CF ₄	363	0.752	9.02
		92 % CF ₄	362	0.732	8.99
		85 % NG	363	0.747	9.01
		92 % NG	362	0.734	8.99
		85 % MR	363	0.748	9.01
		92 % MR	362	0.733	8.99
Blower Efficiency ^B	90 %	85 %	363	0.745	9.01
		92 %	362	0.734	8.99

548

^ATurbine efficiencies are isentropic. ^BCompressor and Blower efficiencies are polytropic.

549

550 CONCLUSIONS

551 CCC-ECL experiments at several scales up to 1 tonne per day demonstrate the process
552 feasibility and robustness. These experiments also provide data with which to compare CCC-
553 ECL simulations over a broad range of operating conditions and in both steady and transient
554 modes. CCC-ECL simulations reliably track observed behaviors in all but the most extreme
555 startup and shutdown scenarios and in all reasonably steady scenarios. Equilibrium predictions of
556 solid CO₂ formation agree with both lab- and skid-scale data. Basic operation on small-scale
557 systems demonstrate 90 % CO₂ capture on flue gas streams as high as 1.4 m³/min. The CO₂
558 stream produced by the CCC-ECL process has a relatively high purity of 99.2 % CO₂. The
559 emissions of volatile hydrocarbons from CCC-ECL meets current EPA source emission
560 guidelines and total contact liquid losses should not be economically constraining.

561 CCC-ECL simulations for retrofit of a 550 MW_e coal-fired power plant indicate an
562 energy penalty for 90 % CO₂ capture of 0.74 MJ_e/kg CO₂ captured. Reasonable best- and worst-
563 case scenarios are between 0.71-0.92 MJ_e/kg CO₂ captured. The estimated energy penalty is 1.67
564 MJ_e/kg CO₂ in the case of CCC-ECL implementation for a natural gas combined cycle power
565 plant (4 % CO₂ inlet concentration). The estimated cost of the CCC-ECL retrofit for this plant is
566 \$361 MM Capex. The financial result is an increased cost of electricity in the range of 2.85-3.56
567 cents/kWh. The energy and cost numbers compare favorably with alternative systems.

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