

CO₂ Capture for PC Boilers using Flue-Gas Recirculation: Evaluation of CO₂ Recovery, Transport, and Utilization

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CO₂ Capture for PC Boilers using Flue-Gas Recirculation: Evaluation of CO₂ Recovery, Transport, and Utilization

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INTRODUCTION

The U.S. Department of Energy (DOE) is investigating retrofitting boilers with flue gas recirculation as a strategy for CO₂ recovery from conventional pulverized coal (PC) plants because of the current motivation to reduce greenhouse gas emissions. However, this technology was conceived nearly twenty years ago at Argonne National Laboratory as a low-cost CO₂ source for enhanced oil recovery (EOR). The fundamental concept is to replace combustion air with oxygen diluted by recirculated CO₂ from the flue gas. This eliminates N₂-CO₂ separation, permitting more economical CO₂ recovery than competing amine systems. A molar ratio of CO₂/O₂ of ~3 is necessary to preserve the heat transfer performance and gas path temperatures, allowing this system to be applied as a retrofit. (Figure 1 shows the process.)

Cost Studies—Summary. Argonne currently employs the latest version of the ASPEN process design software to reconcile and build upon two earlier process design studies conducted for TransAlta (Calgary, Alberta). Initially, Fluor-Daniel (Greenville, SC) performed a design study for an monoethanolamine (MEA) scrubber to remove CO₂ from flue gas for a PC-fired boiler using low sulfur sub-bituminous coal. Subsequently, ABB Power Plant Laboratories (Windsor, CN, now Alstom Power) performed a site-specific CO₂/O₂ recycle retrofit design study for the TransAlta Sundance Unit 1 boiler using the same coal. For the latter project, Argonne represented the U.S. DOE interests and participated in the planning, development, and review of the report along with CANMET, the Alberta Research Council, and SFA Pacifica. Significantly, the ABB study found that no major modification of the boiler was required for the retrofit. These results confirm technical viability of the recirculation strategy and are consistent with the earlier work performed for Argonne. The ABB study also concludes that advances in technology to reduce the high cost of air separation are needed to produce cost-competitive CO₂ for EOR in today's market. With 100% CO₂ capture and dry CO₂ compressed to pipeline conditions (2,000 psi) the cost of power generation rises from a base cost of 18.3 mills/kWh for the fully amortized existing plant to 58.6 mills/kWh, equivalent to \$42 per ton of CO₂ captured. This cost compares favorably to the case with 90% CO₂ capture by an MEA scrubber, which raises costs to 60.9 mills/kWh, equivalent to \$50/ton CO₂. If a \$50/ton CO₂ carbon tax is imposed, the costs for MEA increase to 65.7 mills/kWh because of residual CO₂ emissions. The recycle option is unaffected by the CO₂ tax because all CO₂ is captured. For both systems, pipeline costs and CO₂ field charges may add an additional 36.6 mills/kWh (see Table 1 and the three appended economics tables).

Sulfur Impacts on CO₂ Recycle—Summary. In addition to reconciling and extending these studies across the full energy cycle, our interest is to extend this analysis to U.S. plants that might be retrofit candidates. A key difference is that the Sundance plant uses extremely low sulfur coal (0.2% S), and a retrofit at a U.S. plant will require sulfur cleanup. Therefore, we have focused on sulfur's fate in the gas path and the performance of sulfur removal equipment. We have also extended previous analyses by considering upstream and downstream processes, with the ultimate goal of completing a life-cycle assessment. Bench-scale flue-gas desulfurization (FGD) work supported by this project is the first published work to show that efficient FGD performance can be maintained in a high-CO₂ and high-SO₂ environment (see Fig. 2).

Pipeline and Reservoir Integration—Summary. Product transport introduces a new set of important technical and economic challenges. CO₂ transportation for enhanced oil recovery (EOR) represents a mature technology with operating experience dating from mid-1980s. Using ASPEN, we have compared the various equations of state (EOS) that predict the physical properties of CO₂ in mixtures with acid gas (SO₂, H₂S) and inerts such as N₂. This analysis included verification of computer software for simulating the behavior of these gases in transportation pipelines over 100 km in length by comparison with published data that include the transition into a supercritical fluid. The pressures are expected to range up to 16 MPa. The multi-parameter equation-of-state sets that proved to be most accurate (Fig. 3) were the Peng-Robinson with Boston Mathias enhancement (PRBM) and the Swartzentrube-Renon Polar EOS (SR Polar). However, while the SR Polar EOS predicted fluid density accurately (with under 2% error), it did not show the supercritical transition as pipeline temperature rose above 65°C. Using the validated PRBM equations, we find that trace levels of SO₂ will seriously derate supercritical-CO₂ pipeline capacities. As a result, in this project we have adopted a low SO₂ product specification.

PROJECT TEAM

The principal investigator is Richard Doctor, P.E., a chemical engineer with industrial experience at ARCO Oil prior to joining Argonne. He led the DOE environmental monitoring work with the \$2.2-billion Great Plains coal-gasification plant, including extensive interaction with regulatory agencies, which resulted in installation of more than \$80 million in capital improvements. The current project is one of a series he has led that address both process design and life-cycle issues for power cycles with low CO₂ emissions.

Dr. John C. Molburg is developing the process design in cooperation with Dr. Norman F. Brockmeier, who has special expertise with the ASPEN code. Prior to joining Argonne, Dr. Molburg was a system planner and was responsible for technology transfer and research coordination at Centerior Energy and at the Cleveland Electric Company. He has provided process modeling in Argonne's evaluations of low-CO₂ coal gasification processes, and has worked extensively on power system modeling for environmental and economic analysis.

Dr. Marshall Mendelsohn conducted bench-scale FGD studies at high CO₂ partial pressures in support of this project. Dr. Mendelsohn currently is funded by NETL to study mercury removal in wet and dry flue-gas treatment systems. Extension of the current project may involve collaborative efforts of Dr. Jong Kim of Argonne and Dr. Stefan Finsterle of Lawrence Berkeley National Laboratory to investigate improving the efficiency of TOUGH2 and iTOUGH2 geological reservoir models.

PROCESS DESCRIPTION

Our analysis extends earlier work by adding processes upstream and downstream of the PC plant. We assume technical feasibility for flue gas recycle conversion, and we use the results of earlier studies to calibrate and optimize a process model of the PC-recycle plant. The overall system under study is shown below.

Coal arrives with a topsize of 5 in. and is crushed to a topsize of no more than 1.5 in. before being fed to the pulverizer. Part of the total recycle gas is used as the coal transport medium, which is essential for pulverizer operation. This steam is subsequently mixed with oxygen and used as primary "air." The remaining recycle gas is mixed with oxygen and serves as secondary "air." With

the correct mix of CO₂-rich flue gas and oxygen (mole ratio CO₂/O₂ ~3) the heat exchange will meet the original design duty.

CO₂ Capture for PC Boilers Using Flue-Gas Recirculation

Raw Materials Supply	Coal Mining	Deep-mined, high-sulfur Illinois bituminous coal
		Surface-mined, low-sulfur western coal
	Coal Cleaning	Jig plant cleaning for Illinois coal
		No cleaning of surface-mined coal
	Coal Transport	Rail transport
	Air Separation	Cryogenic process, 99% purity
Alternative systems with lower purity		
Water	Local availability assumed	
Power Plant	Coal Crushing and Pulverizing	Recycled flue gas used as drying medium and for coal transport
	Combustion	Conventional furnace retrofit to use mix of O ₂ and recycled flue gas as oxidant
	Power Generation	Rankine cycle with high-, intermediate-, and low-pressure turbines
	Gas Separation and Cleanup	Particulate removal via ESP or fabric filter
		Sulfur removal via limestone scrubber
	CO ₂ Product Preparation	Drying
Removal of noncondensable gases		
Compression		
Product and Waste Distribution	Power Transmission	Transmission lines and losses are not included in the system
	CO ₂ Transport	Supercritical pipeline delivers CO ₂ to oil field
		Injection into field
		Transport through field
	Solids Disposal	Ponding of scrubber sludge; ash and slag recovered for sale
	Emissions	Conventional air emissions from combustion are avoided

After the boiler, the flue gas passes through the air heater, which is now used to preheat the recirculated flue gas. The flue gas is cooled in retrofit gas coolers to reduce its moisture content before being recycled to the boiler (not shown in Fig. 1). Flue gas sensible heat is also used to preheat oxygen in a retrofitted O₂ heater. Particulates are then removed using the existing electrostatic precipitator (ESP), and SO₂ is removed by a new FGD system.

Typically, the recycle is extracted after FGD. We have also investigated extraction of some of the recycle prior to FGD. If it were feasible, using “dirty” recycle could reduce the size and cost of retrofit FGD by nearly 80%, because the volume of gas sent for treatment may be as small as 20% of the volume from conventional PC combustion. The product CO₂ comes from the FGD and is dried and compressed to a supercritical state at 2,000 psig.

Sulfur Dioxide in CO₂ Product. Sulfur dioxide is of great importance to CO₂ recovery from PC boilers. Because SO₂ is destructive to solvents used for either chemical or physical absorption of CO₂, it must be removed. It was this concern that originally led Argonne researchers to consider separating nitrogen from CO₂ before combustion. The problem then becomes separating SO₂ from CO₂ rather than separating CO₂ from N₂ in the presence of the damaging SO₂. A second consideration is the performance and fate of SO₂ during EOR operation. Under some circumstances, SO₂ (and even NO_x) does not have to be removed. In general, the presence of SO₂ and NO_x will not hamper and may even improve EOR operations. In addition, for some formations, these gases are not always passed through to the extraction wells but are absorbed by the mineral formations

through which the oil passes. However, two considerations dictate the need for SO₂ removal in CO₂ recycle. (1) Acid gases in the presence of moisture will accelerate corrosion of the pipeline and other equipment, although this is partly mitigated through dehydration. (2) The pipeline is derated by even trace levels of SO₂.

Scrubber Performance. Concerns related to the high sulfur concentration in U.S. coals in contrast to the very low sulfur content of the coal used at the TransAlta Sundance Unit 1 are part of the motivation for this study. One of these concerns is that alkali scrubber SO₂ removal systems might experience performance degradation as a result of the high partial pressure of CO₂ in the recycle gas (compared to that in conventional flue gas). The formation of carbonates might reduce reagent utilization and reduce collection efficiency. We have resolved this concern with a series of laboratory-scale scrubber tests. Baseline performance for the laboratory scrubber was established by using a gas mix comparable with that used in conventional plant flue gas (14% O₂, 17.5% CO₂, 3,600 ppmv SO₂, and about 200 ppmv NO, with the balance N₂). Flue gas from a CO₂ recycle plant was simulated with premixed gas of 12.2% N₂, 3% O₂, 3,300 ppmv SO₂, 170 ppmv NO, and the balance CO₂. These gas streams were passed through the scrubber until the SO₂ removal efficiency declined because the recirculating scrubber reagent became saturated. The principal test result is that the high CO₂ concentration does not impede SO₂ removal. It was also observed that good reagent performance is maintained longer in cases of high CO₂ concentration.

Another significant result is that scrubber sludge oxidation due to sulfate is very limited in the high CO₂ cases. This result is due to the low oxygen content of the test gas rather than the high CO₂ concentration. The observation, however, is relevant to a CO₂ recycle plant, since oxygen content must be strictly limited in the CO₂ product gas. Therefore, excess O₂ and air in-leakage will be tightly controlled, resulting in low oxygen content in the flue gas. Forced oxidation of the scrubber sludge will probably be required, but this step must be performed in a separate vessel to avoid introducing O₂ into the flue gas stream. Current scrubber practice relies on forced oxidation in the scrubber sump.

High-Sulfur Recycle. Another sulfur-related issue is that the flue gas recycle system could greatly reduce the volume of gas that must be treated by the SO₂ abatement system. Because the recycle system has eliminated nitrogen as a diluent, the net amount of flue gas produced is only about 20% of that produced in a conventional plant. Substitution of recycled flue gas is merely an expedient to preserve boiler temperature profiles. It does not affect the net gas generation. If the recycle is extracted prior to gas cleanup, the remaining gas volume going to treatment is small. This change could result in considerable savings in the construction and operation of gas cleanup equipment. Of course, such an approach will result in the buildup of SO₂ and other impurities in the boiler. The recycle might even be extracted prior to particulate removal, resulting in ash recycling. This approach is not generally expected to be appropriate in a retrofit situation, and existing plants have already made the investment in highly efficient particulate removal systems. Most likely, a dirty recycle stream will be extracted after particulate removal. We have incorporated a split recycle in our model: some of the full recycle is extracted before sulfur removal and some after. In this way, the buildup of SO₂ can be controlled as required for a particular boiler. This is a fundamental design issue for the CO₂ recycle retrofit.

Plant Environmental Permits. While the best option for CO₂ recycle is likely to be coal-specific and plant-specific, the retrofit concept should continue to attract interest. In addition to CO₂ recycle's straightforward economic advantage, another advantage is that the operator would have fewer operating permits to monitor. Both MEA and CO₂ recycle will require FGD. However, in MEA sodium scrubbing is required to lower sulfur levels, necessitating disposal permits for high-leachability waste. MEA wastes and spent chemicals will require special permitting, and the new

MEA-related cooling towers will require modified air permits and blow-down water permits. In contrast, an air-separation package looks very attractive.

ACKNOWLEDGMENT

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Table 1. Comparative Electric Power Generation Costs (mills/kWh)

	Cost - Base	Cost - CO ₂	CO ₂ Tax[1]	Transport	Reservoir	TOTAL
Natural Gas with co-gen [2]	41.5	59.5	2.0	2.6	11.4	73.5
Hydroelectric	82.0	0.0	0.0	0.0	0.0	82.0
PC Coal with CO ₂ recycle [retrofit]	18.3	58.6	0.0	6.8	29.8	95.2
IGCC Coal	52.4	65.7	4.5	5.7	25.1	96.5
PC Coal with MEA [retrofit]	18.3	60.9	4.8	6.1	26.8	98.7
Nuclear	125.5	0.0	0.0	0.0	0.0	125.5

[1] \$50/ton CO₂

[2] Natural Gas pricing = \$1.50/1000 scf

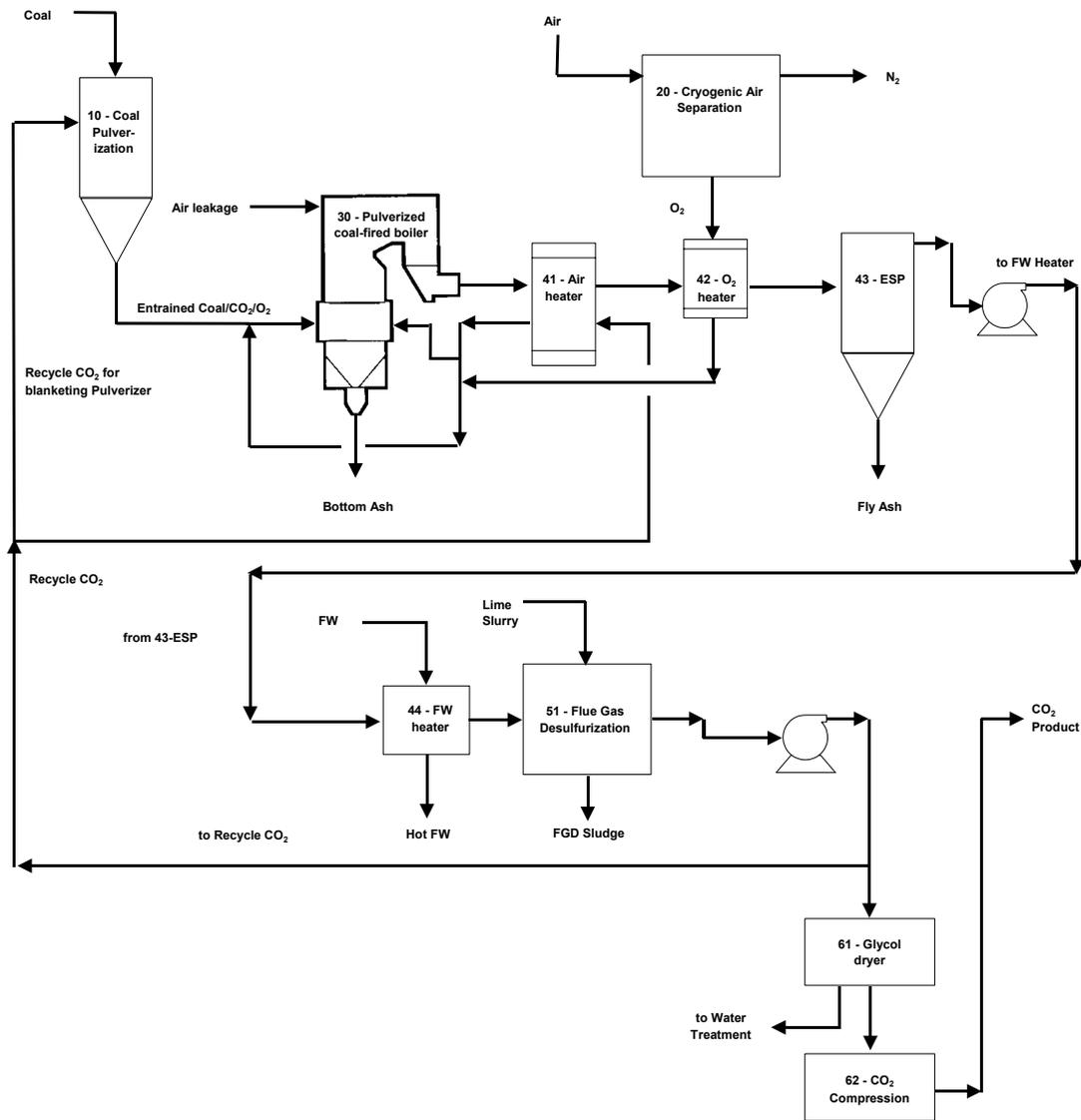


Fig. 1 Pulverized coal-fired boiler with CO₂ recycle provides CO₂ at 2,000 psig

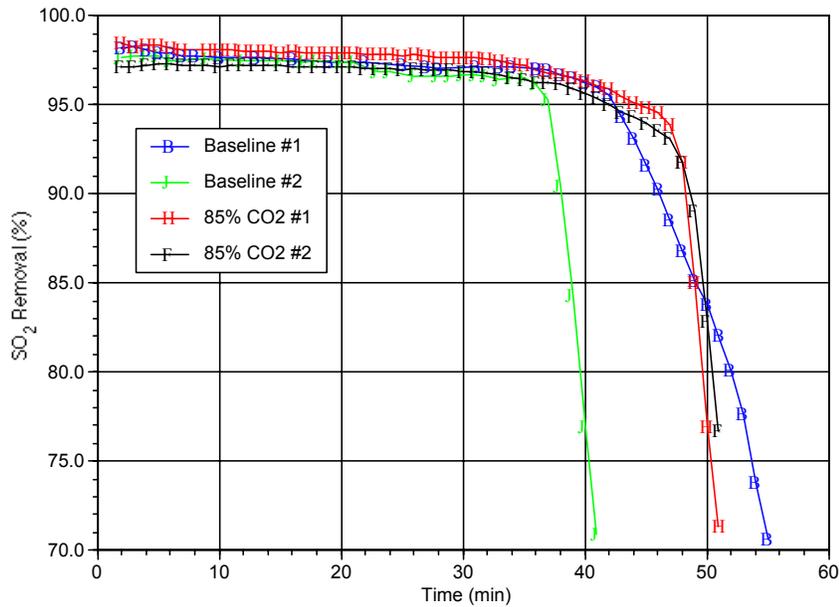


Fig. 2. In high CO₂/high SO₂ flue-gas desulfurization, reagent performance is maintained

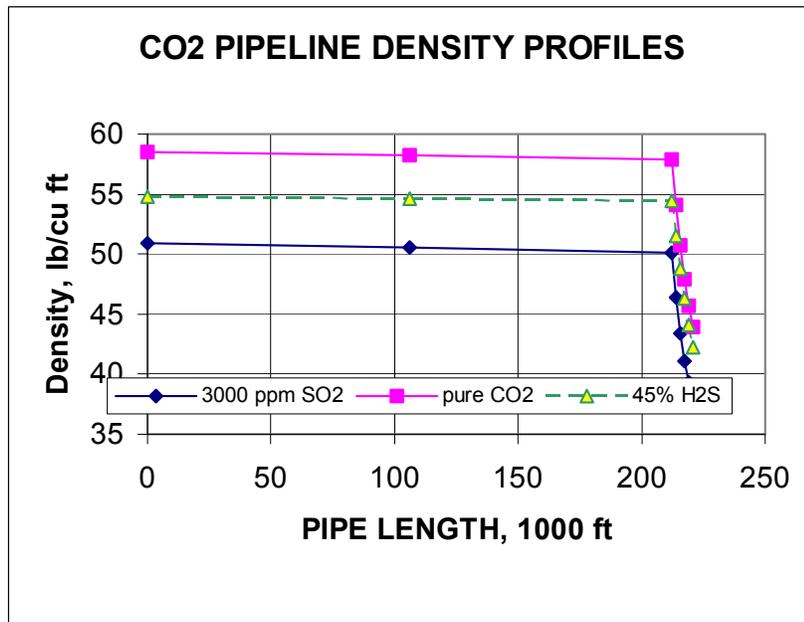


Fig. 3. Validated Peng-Robinson Boston-Mathias EOS shows that trace levels of SO₂ will seriously derate supercritical CO₂ pipelines leading to the project adopting a low SO₂ product.

Capital Costs for CO₂ Recirculation vs. MEA CO₂ Capture

(Assumptions for each case provided on following pages)

Gross Power (MW)	300.0	300.0
Internal Power (MW)	94.0	94.1
Net Power (MW)	206.0	205.9

System	Retrofit CO ₂ Recycle 100% CO ₂ Capture		MEA CO ₂ Recovery 90% CO ₂ Capture	
	cont.*	Capital Cost, \$K	cont.*	Capital Cost, \$K
Direct Costs				
Air-Separation Plant/Compr.	0.0%	\$101,000	0.0%	
Amine Scrubber	0.0%		0.0%	\$67,992
Ducts/Dampers/Air heaters/Controls	0.0%	\$2,571	0.0%	\$1,697
Feedwater Heater	0.0%	\$395	0.0%	
O ₂ Heater	0.0%	\$193	0.0%	
Seal Boiler for 1% in-leakage	0.0%	\$22	0.0%	
Cooling Towers/Cooling Pumps	0.0%		0.0%	\$35,790
Flue Gas Desulfurization/Caustic	0.0%	\$6,317	0.0%	\$8,423
Chemical Treatment	0.0%		0.0%	\$8,949
CO ₂ Conditioning and Compression	0.0%	\$36,828	0.0%	\$33,145
Direct Costs Sub-total		\$147,326		\$155,995
Indirect Costs				
General Facilities	10.5%	\$15,469	10.5%	\$16,379
Engineering Fees	8.0%	\$11,786	8.0%	\$12,480
Process Contingency	2.0%	\$2,947	2.0%	\$3,120
Project Contingency	20.0%	\$35,506	20.0%	\$37,595
Sub-total		\$65,707		\$69,574
Total Plant Cost-TPC		\$213,033		\$225,568
Cost (\$/kW Gross Power)		\$710		\$752
Interest & Inflation	20.0%	\$42,607	20.0%	\$45,114
Total Plant Investment-TPI		\$255,640		\$270,682
Royalties	0.6%	\$884	0.6%	\$936
Initial Inventory	2.0%	\$2,947	3.3%	\$5,148
Start-up Costs	4.6%	\$6,777	4.6%	\$7,176
Spare Parts	2.2%	\$3,241	2.2%	\$3,432
Working Capital	3.3%	\$4,862	3.3%	\$5,148
TOTAL		\$274,350		\$292,521

Retrofit CO₂ Recycle
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Net Power (MW) = 300.00
Capacity factor = 85%
Annual Net Power Production (MW) = 2,233,800
CO₂ Emissions (T/D) = 0

OPERATING COSTS	Basis	Units	Unit Cost	Annual Cost
Fuel - 0.2% S sub-bituminous		3,497 T/D	\$25.00 \$/T	27,123,595
Consumables				
BFW Chemicals				50,000
CW Chemicals				225,000
Ash and FGD sludge Disposal		446 T/D	\$2.00 \$/T	276,735
Limestone		23 T/D	\$25.00 \$/T	209,639
Chemical and Dessicant				42,293
Plant Labor				
Oper Labor (w benefits)		3.5 men/shift	\$25.50 \$/h	781,748
Supervision/support		25% of above		195,437
Utilities				
Maintenance - Base Plant		3.85% Power	\$65.00 \$/MWh	5,590,085
Air Separation/ CO2 Compressor		94.0 MW	\$65.00 \$/MWh	45,495,060
Natural Gas and other utilities		636,484 Mscf	\$1.50 \$/Mscf	954,726
Flue Gas Desulfurization		5.00% Power	\$65.00 \$/MWh	7,259,850
Maintenance - CO ₂ Capture		2.7% of Direct		3,977,799
Insurance & Local Taxes		0.9% of Direct + Base		2,992,600
Other - % of Oper Labor		12.5% of above		122,148
CO ₂ Emissions Trade Purchase			\$0.00 \$/T	0
Net Operating Cost				72,621,383

COSTS OF ELECTRICITY

Levelizing Factors	Constant (\$)	Basis (K\$)	
Capital Charge	0.111	\$274,350	
Fuel	1.025	\$27,124	
Operating & Maintenance	1.000	\$72,621	
Cost of Electricity - Levelized	mills/kWh		
Capital Charge	13.63		
Fuel	12.45		
Operating & Maintenance	32.51		
Total Cost of Electricity	58.59 mills/kWh	Basis 300.0 MW	
CO ₂ Capture	42.23 \$/T CO ₂	6,877 T/D	100%

MEA CO₂ Recovery

Net Power (MW) = 300.00

Capacity factor = 85%

Annual Net Power Production (MW) = 2,233,800

CO₂ Emissions (T/D) = 688

OPERATING COSTS	Basis	Units	Unit Cost	Annual Cost
Fuel - 0.2% S sub-bituminous		3,497 T/D	\$25.00 \$/T	\$27,123,595
Consumables				
BFW Chemicals				\$50,000
CW Chemicals				\$225,000
Ash/Sorbent Disposal	446 T/D		\$2.00 \$/T	\$276,735
Limestone	23 T/D		\$25.00 \$/T	\$209,639
Caustic (20% Solution)	11 T/D		\$80.00 \$/T	\$273,020
Chemical and Dessicant				\$38,064
MEA Chemical Make-up	11.6 T/D		\$855.00 \$/T	\$3,077,060
Corrosion Inhibitor	20% MEA			\$615,412
MEA CW Chemicals	7% MEA			\$215,394
Plant Labor				
Oper Labor (w/benefits)	4.0 men/shift		\$25.50 \$/h	\$893,426
Supervision/support	25% of above			\$223,356
Utilities				
	3.85% Power		\$65.00 \$/MWh	\$5,590,085
Maintenance - Base Plant				\$5,000,000
MEA System/CW/CO Compr.	94.0 MW		\$65.00 \$/MWh	\$45,495,060
Flue Gas Desulfurization	5.00% Power		\$65.00 \$/MWh	\$7,259,850
Maintenance - CO ₂ Capture	2.7% of Direct			\$4,211,854
Insurance & Local Taxes	0.9% of Direct + Base			\$3,070,618
Other - % of Oper Labor	12.5% of above			\$139,598
CO ₂ Emissions Trade Purchase	687.7 T/D		\$0.00 \$/T	\$0
Net Operating Cost				\$75,829,776

COSTS OF ELECTRICITY

Levelizing Factors	Constant (\$)	Basis (K\$)
Capital Charge	0.111	\$292,521
Fuel	1.025	\$27,124
Operating & Maintenance	1.000	\$75,830

Cost of Electricity - Levelized	mills/kWh
Capital Charge	14.54
Fuel	12.45
Operating & Maintenance	33.95

Total Cost of Electricity	60.93 mills/kWh	Basis	300.0 MW
CO ₂ Capture	49.64 \$/T CO ₂	6,189 T/D	90%