Sequestering CO_2

Final Presentation

Group 8

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Overview

- Introduction to Sequestration
- Separation Methods
- Transportation Network
- Sequestration Methods
- Mathematical Model
- Results and Recommendations

What is sequestration?

- Storage to reduce atmospheric levels of CO_2
- Four Methods of Sequestration
  - **Geologic**
  - **Ocean**
  - Terrestrial
  - Mineral

Motivation

- Post-Industrial Revolution
  - CO_2 levels steady increase
- Global Warming/Greenhouse Effect
  - Greenhouse gases (i.e. CO_2)
- Kyoto Protocol
  - Possible ratification by U.S.
  - Requires 12% reduction in CO_2 emissions by 2010
- Climate Stewardship Act of 2003

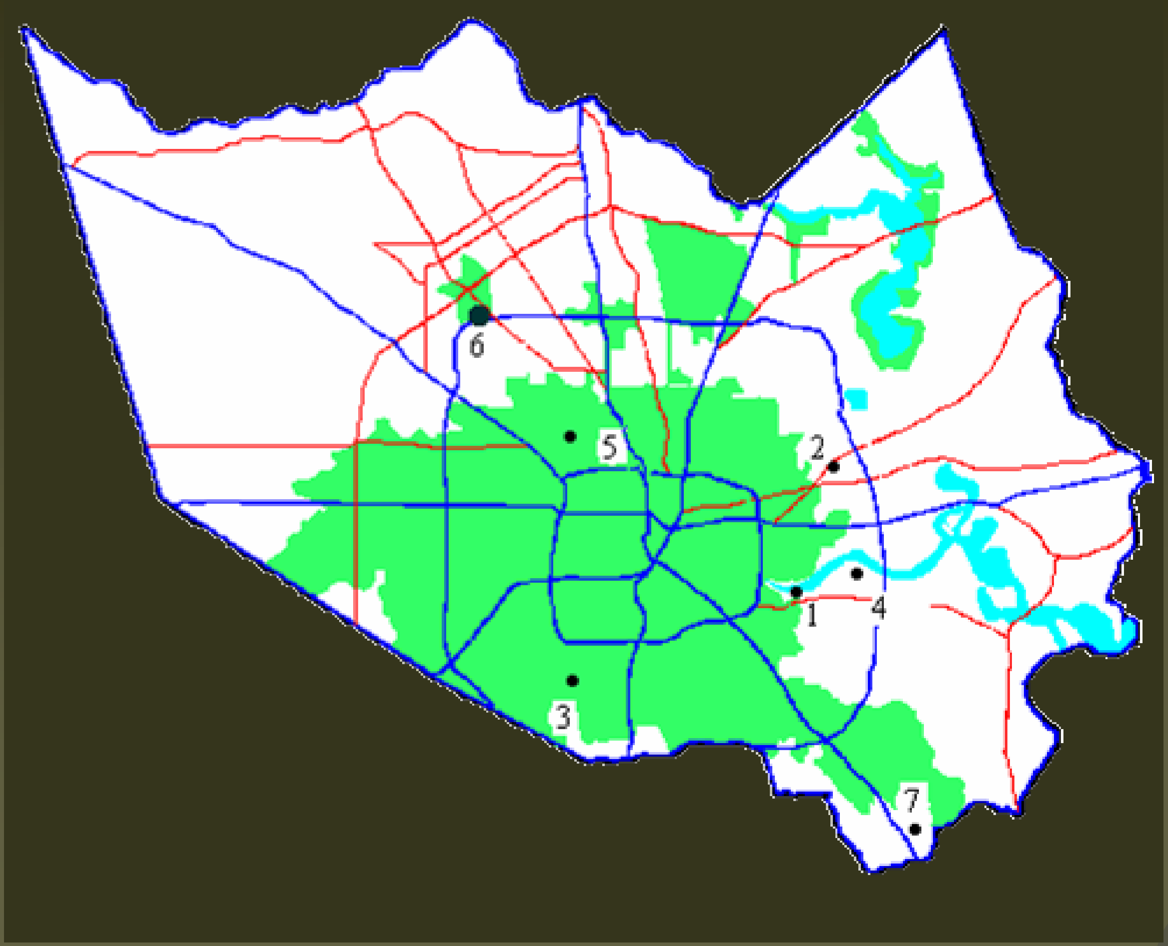
Power plant emissions

- Fossil fuel combustion
  - 97% of all CO_2 emissions
  - Power plants are major sites of fossil fuel combustion
- CO_2 emissions in U.S.
  - 2nd highest in Greenhouse Gas emissions per capita in 1998
  - Major cities are highest contributors
    - Houston, Texas

Reducing CO_2 in Harris County

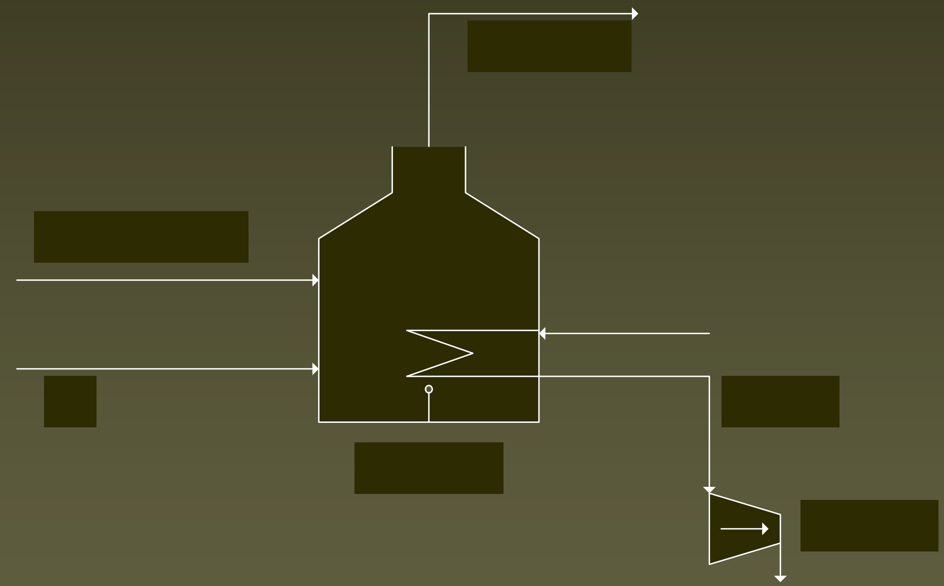
- Large power plants
- Proximity of depleted hydrocarbon reservoirs, brine aquifers, and the ocean
- Seven power plants in Harris County
  - emitted 5.3 million tons of CO_2 in 2000

Harris County Power Plants



Power Plant Schematic

- Burning of natural gas in air
- Heat generation to make steam
- Steam driven turbine for distribution of electrical power
- Reaction products emitted to atmosphere



Project Objectives

- Governmental Perspective
  - Recent legislation to decrease carbon dioxide emissions
- Determine reasonable emissions reduction requirements
  - Minimize electricity cost increase

Why Separate?

- Flue gas composition
  - ~ 4 wt% CO_2
- High flow rates
  - ~ 0.5-57 million tons/year
- Sequestration pressure
  - ~ 1000 psia

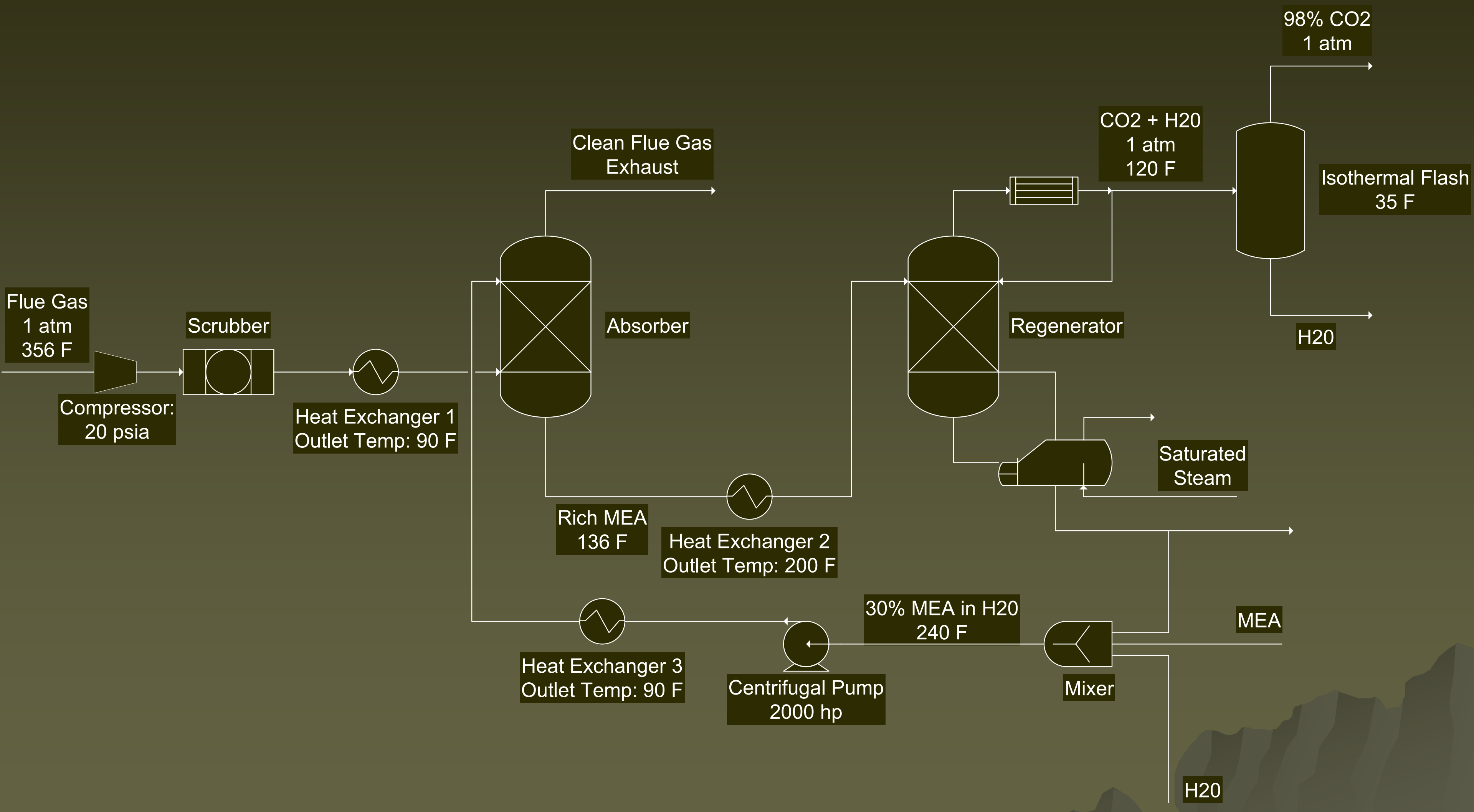
Methods of Separation

- **Absorption in a packed tower**
- Adsorption on solids
- Refrigeration
- **Oxygen-enriched fuel firing**
- Membrane Separation
- **Reaction with Calcium Hydroxide**

Absorption/Stripping

- Monoethanolamine solvent
  - High solubility of CO_2 in MEA
- Random packing (polyethylene rings)
  - Increased contact area between flue gas and solvent
- Separation with heat after absorption
  - 85% CO_2, 15% H_20

PFD



98% CO2
1 atm
CO2 + H20
1 atm
120 F
Clean Flue Gas
Exhaust
Isothermal Flash
35 F
Flue Gas
1 atm
356 F
Scrubber
Absorber
Regenerator
H20
Compressor:
20 psia
Heat Exchanger 1
Outlet Temp: 90 F
Saturated
Steam
Rich MEA
136 F
Heat Exchanger 2
Outlet Temp: 200 F
30% MEA in H20
240 F
MEA
Heat Exchanger 3
Outlet Temp: 90 F
Centrifugal Pump
2000 hp
Mixer
H20

Economics

- Commercially available units
  - Wittemann Carbon Dioxide Equipment
  - Includes all components
- Capital Cost
  - 250-15,000 kg/hr flue gas
  - $0.5-$50 million/unit
- Operating Cost
  - $0.17/kg flue gas

Calcium Hydroxide

- Carbonation

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \quad \Delta H_R = -179 \, {}^{kJ}\!/_{mol}$$

- Calcination

$$CaCO_3 \xrightarrow{580^\circ C} CaO + CO_2 \quad \Delta H_R = 4.19 \, {}^{kJ}\!/_{mol}$$

- Slaking

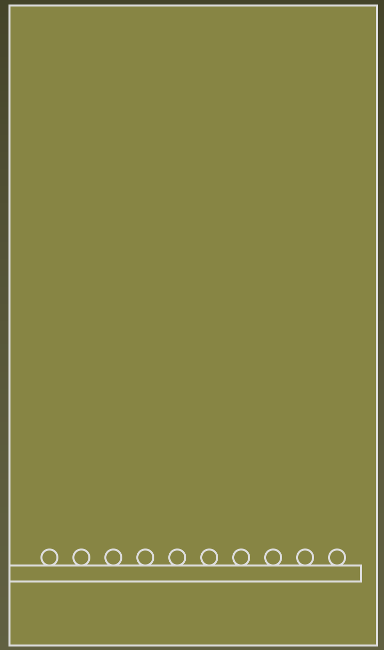
$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H_R = -63.9 \, {}^{kJ}\!/_{mol}$$

Assumptions

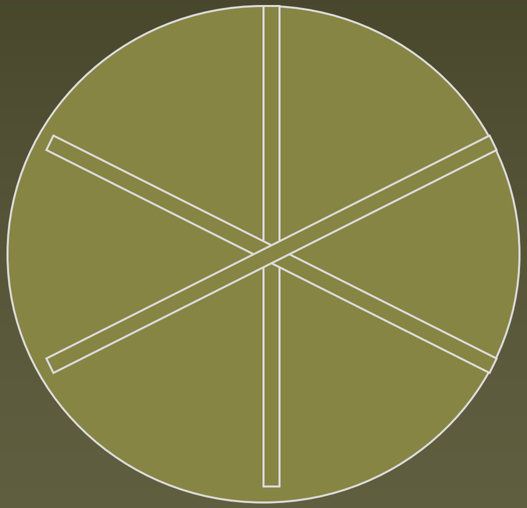
- High rate of reaction under alkaline conditions (pH>10)
  - Addition of NaOH
- Mass transfer limiting
  - Diffusion of CO_2 in $Ca(OH)_2$ solution

Modeling the system

- Flanking view



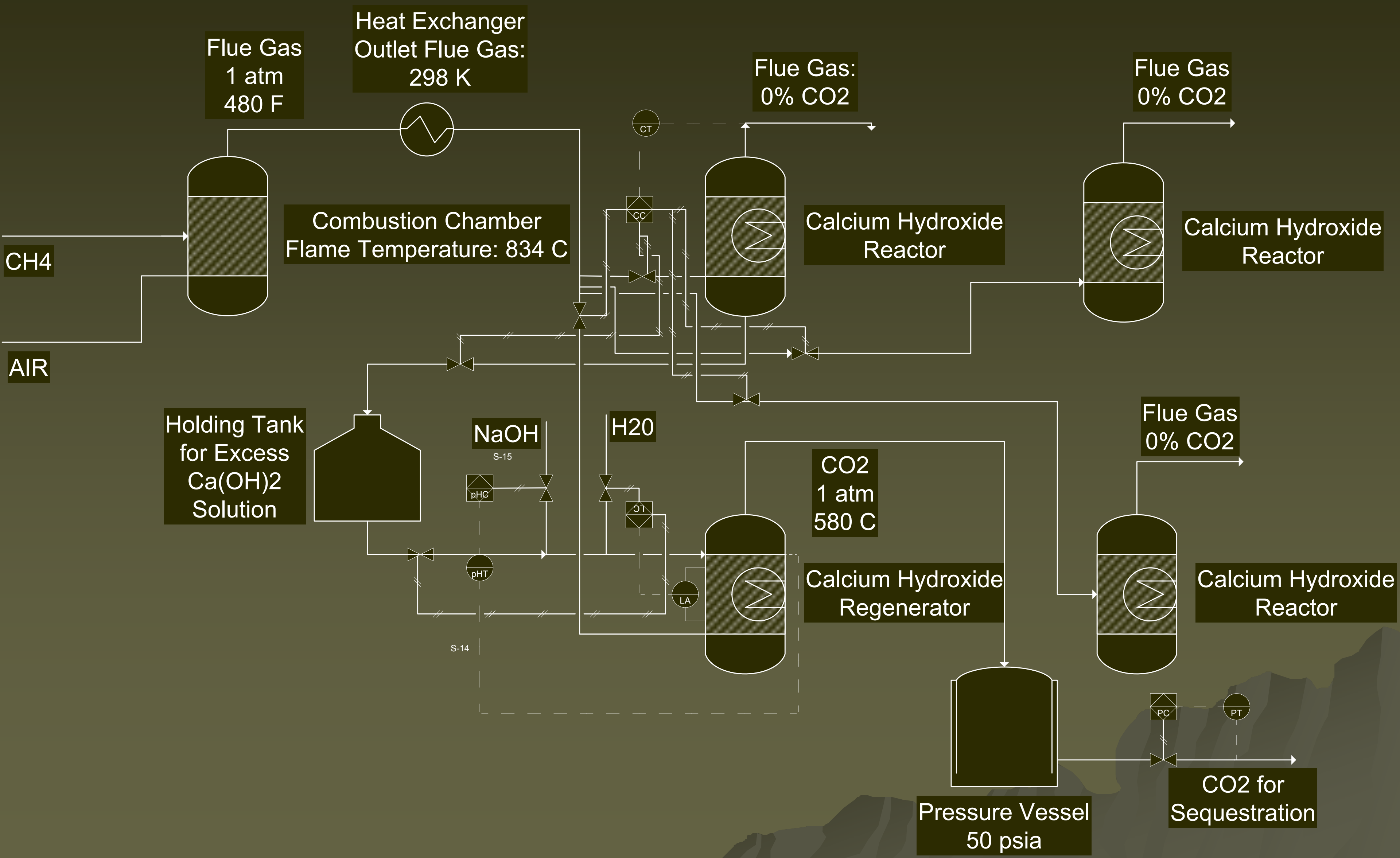
- Top view



Reactor Design

- Gas Sparger
  - Commercially available (Mott Corp)
  - Even distribution of bubbles
  - 2 mm diameter bubbles
- Cross-sectional area
  - Determined by throughput
  - Volumetric flow rate estimated by IGL
    - Compressibility factor=0.9989
- Height
  - Determined by rate of mass transfer

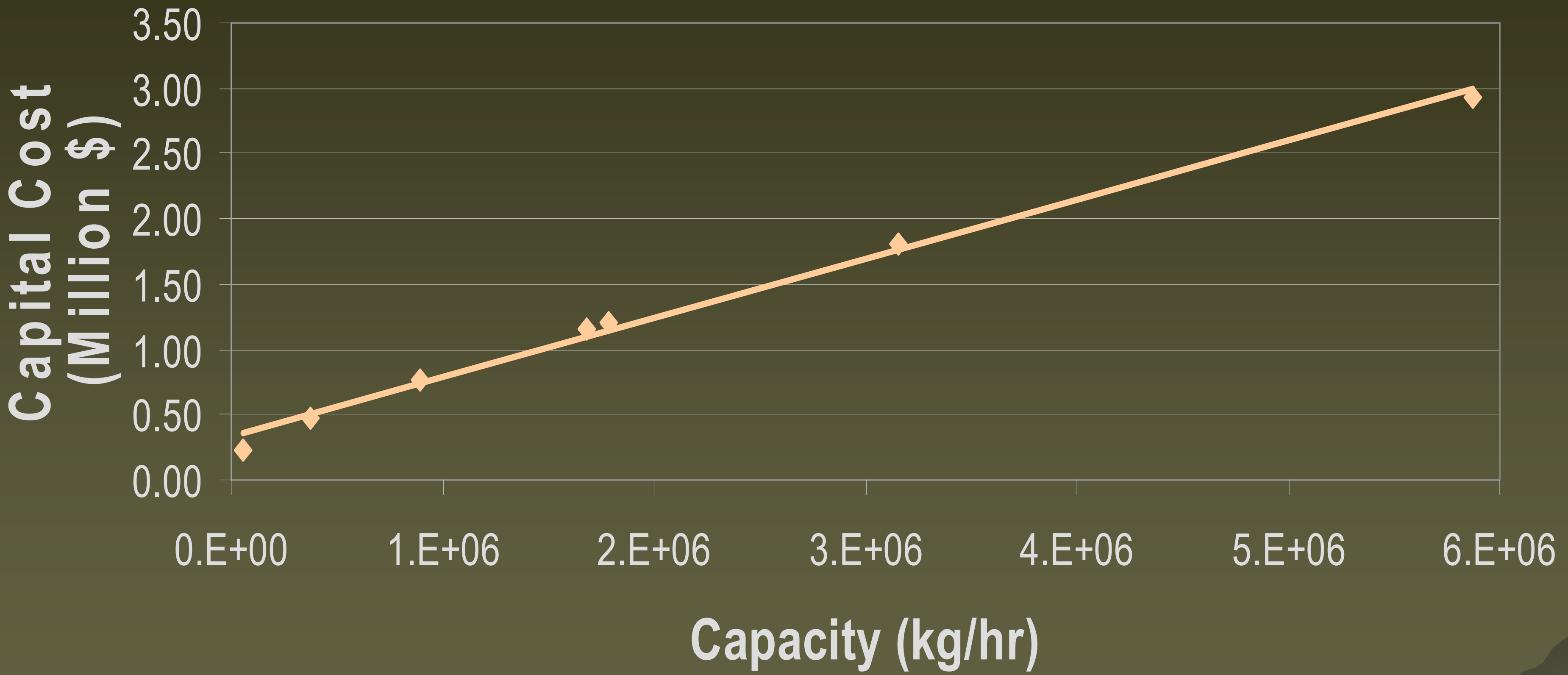
P&ID


Flue Gas
1 atm
480 F
Heat Exchanger
Outlet Flue Gas:
298 K
Flue Gas:
0% CO2
Flue Gas
0% CO2
CT
CC
Combustion Chamber
Flame Temperature: 834 C
Calcium Hydroxide
Reactor
Calcium Hydroxide
Reactor
CH4
AIR
Holding Tank
for Excess
Ca(OH)2
Solution
NaOH
S-15
H20
pHC
pHT
LA
S-14
CO2
1 atm
580 C
Calcium Hydroxide
Regenerator
Flue Gas
0% CO2
Calcium Hydroxide
Reactor
PC
PT
Pressure Vessel
50 psia
CO2 for
Sequestration

Economics

- Capital cost considerations
  - Heat Exchanger
  - Reactor
  - Calcium Hydroxide
  - Calciner
  - Gas Sparger
- Operating Cost
  - Hot/Cold Utilities

Capital Cost



Capital Cost ($)=
331,000+0.454*Capacity (kg/hr)

Operating Cost

- Energy Balance

$$Q \approx n\Delta H$$

- Final Operating Cost
  - $0.0047/kg flue gas

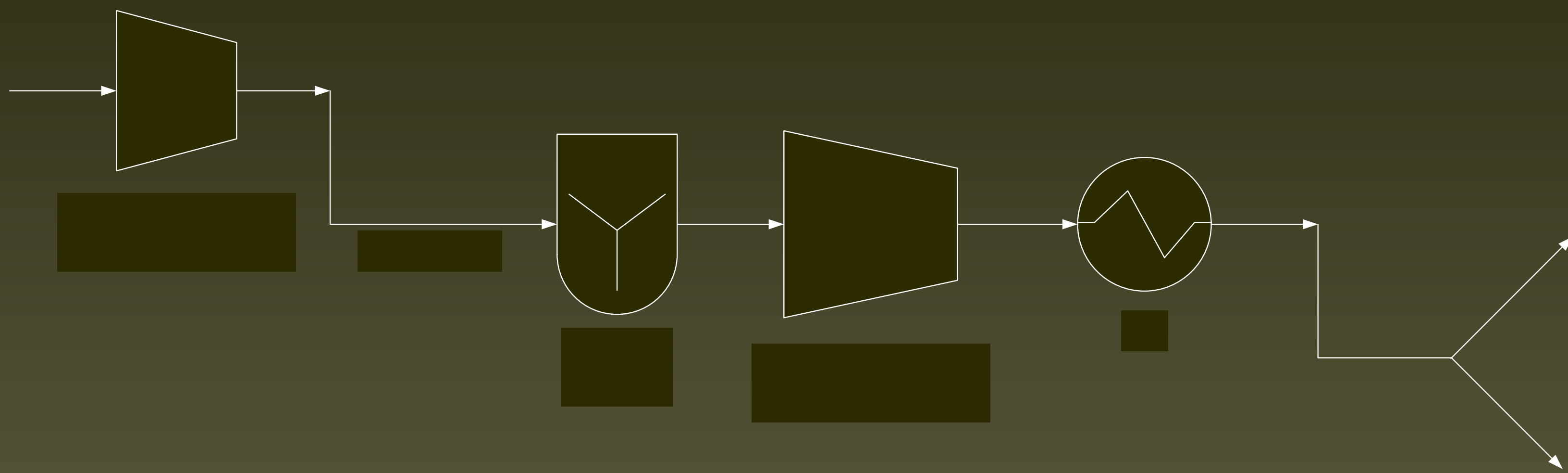
Oxygen-Enriched Fuel Firing

- Alternative to separation
- Air Separation
- Combustion in pure oxygen
- Drawbacks
  - High capital
  - High operating costs
  - Retrofit to existing equipment

Transportation Network

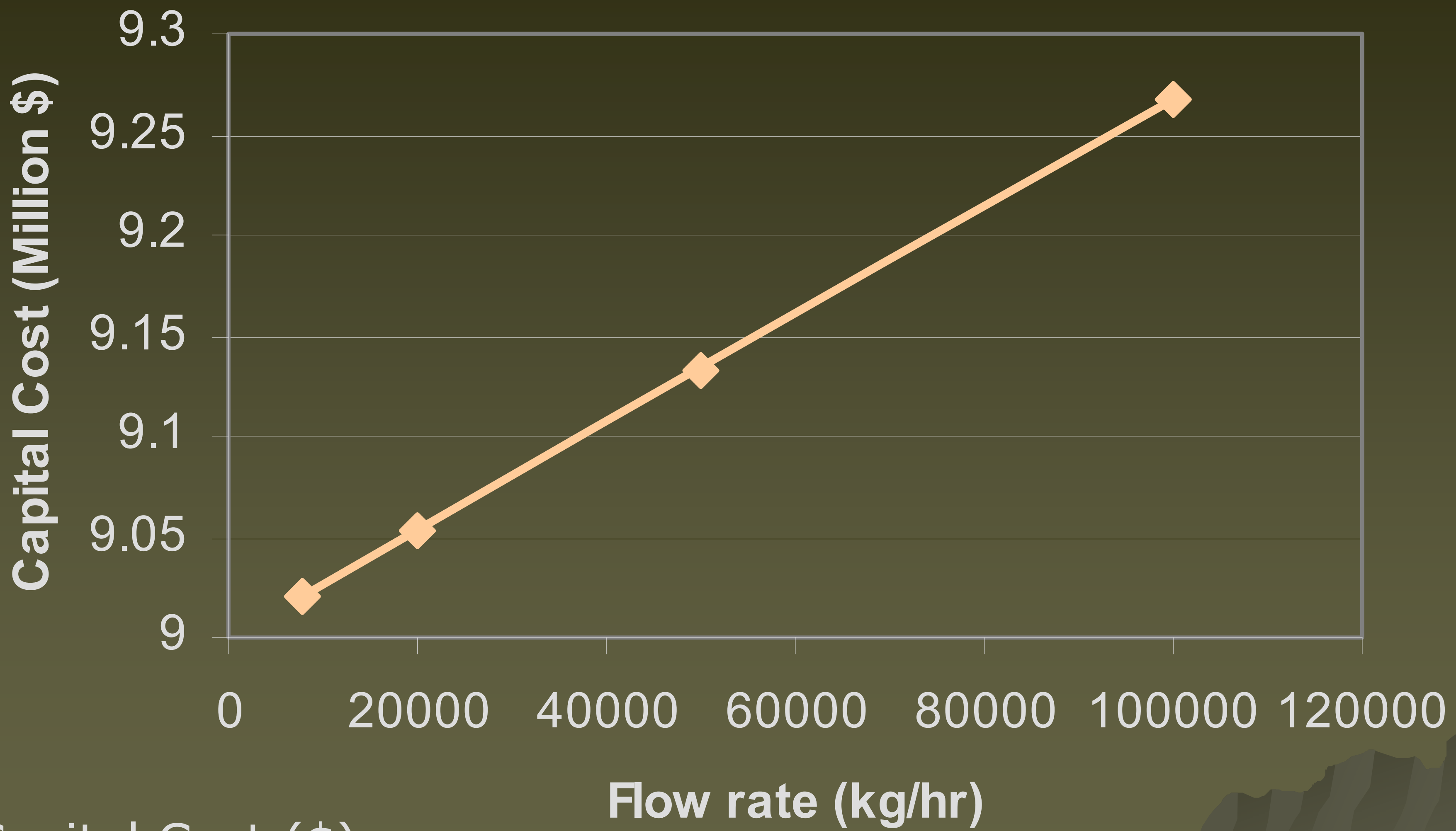
- Required for delivery of CO_2 to collection point
  - "Sam Bertron" power plant
- Compressed at site of separation
- Combined and liquefied at collection point
  - Compressed for sequestration (1300 psia)
  - Liquefied with cooling

Transportation Schematic



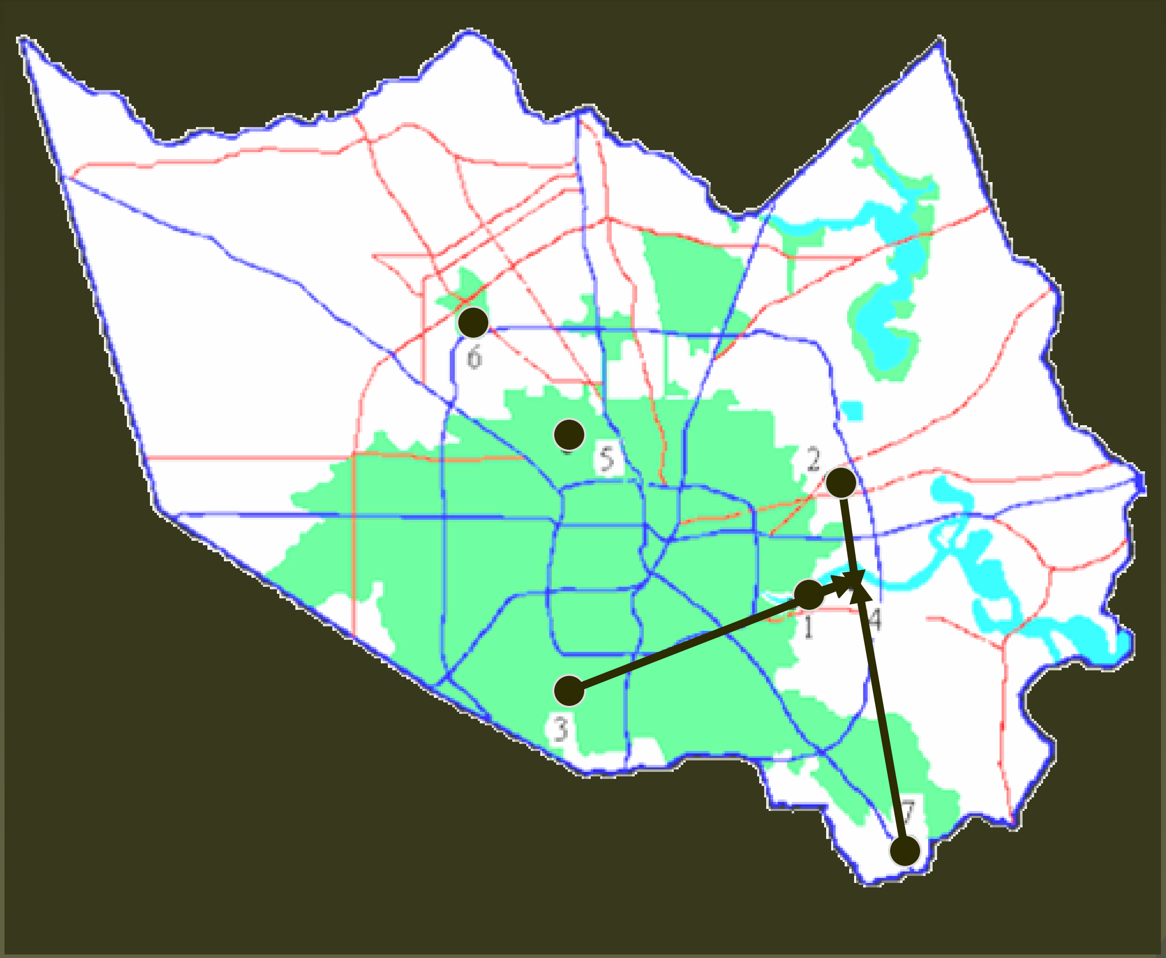
- Capital Cost
  - $9.02-$9.35 million
  - 8,400-131,000 kg/hr
- Operating Cost
  - $.83/ton CO_2

Transportation Capital Cost



Capital Cost ($)=
9,000,000+2.67*Capacity (kg/hr)

Final Piping Network



Ocean Sequestration

- Ocean capacity
  - Largest capacity sequestration method
  - Est. 1.4×10^{12} to 2×10^{16} metric tons
- Injection
  - Various depths
  - Liquid CO_2

Overview

- Formation of clathrate hydrates
  - Densities change with injection depth
  - Effects long-term storage potential

Injection Depth	Clathrate Hydrate	Implications
Shallow (< 2700 m)	Low density	CO_2 resurfacing
Deep (≥ 2700 m)	High density	Ocean floor pooling

Complications

- Rapid injection decreases pH
  - Considerable effect on ocean environment
- Legal restrictions
  - CO_2 considered an industrial waste
- Transportation costs
  - Economically prohibitive
  - LPG tankers
    - $650 million
  - Rigid Pipeline
    - $16 million/km

Transportation Costs

Fraction Sequestered	Power Requirements	Required # Tankers (1Tanker /325MW)	Minimum # Tankers	Cost (Million $)
0.1	398.5	1.23	2	100
0.2	797	2.45	3	150
0.3	1195.5	3.68	4	200
0.4	1594	4.90	5	250
0.5	1992.5	6.13	7	350
0.6	2391	7.36	8	400
0.7	2789.5	8.58	9	450
0.8	3188	9.81	10	500
0.9	3586.5	11.04	12	600
1	3985	12.26	13	650

Conclusions

- Economics unfavorable
- Safety issues for ocean ecosystem
- Legal constraints on waste disposal in ocean
- Other sequestration options exist

Geologic Sequestration
Brine Aquifers

- Largest estimated geologic CO_2 sequestration capacity (est. 500 billion tons CO_2 globally)

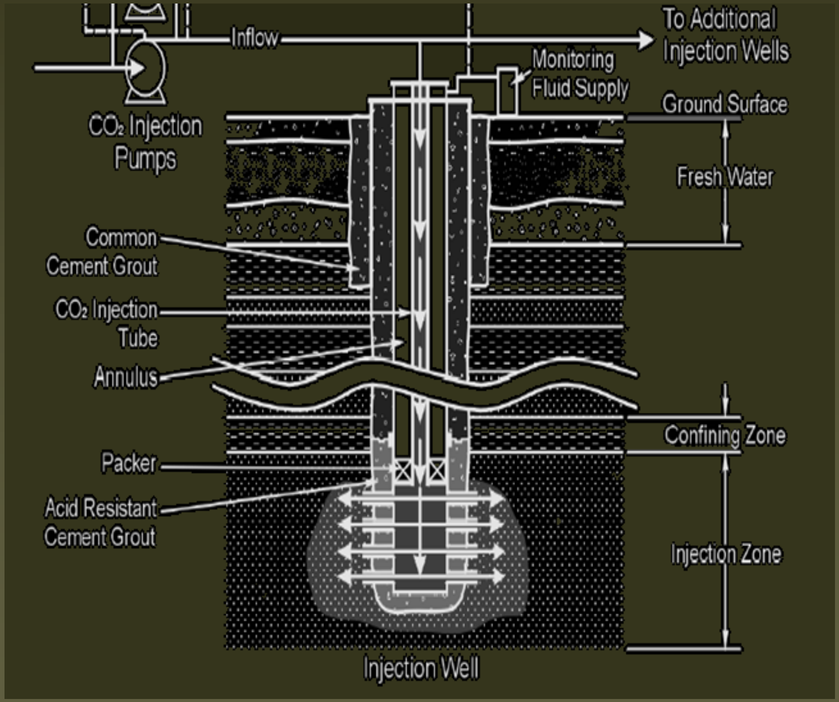
- Most aquifers are easily accessible from CO_2 generation sources and many are already utilized for waste disposal

- Current studies are investigating “sealing” layer rock properties and the possibility of brine displacement which could contaminate potable water

Brine Aquifers – Process Overview

Considerations:

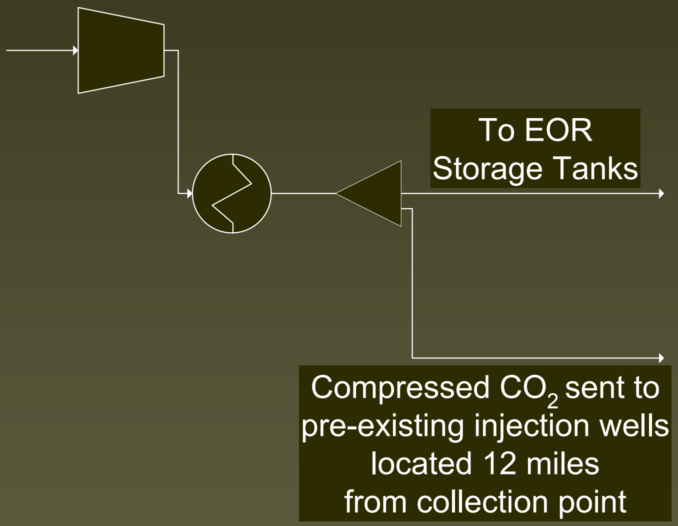
- Non-hydrocarbon producing injection interval
- Supercritical CO_2 desired for injection
- "Sealing" boundary layers



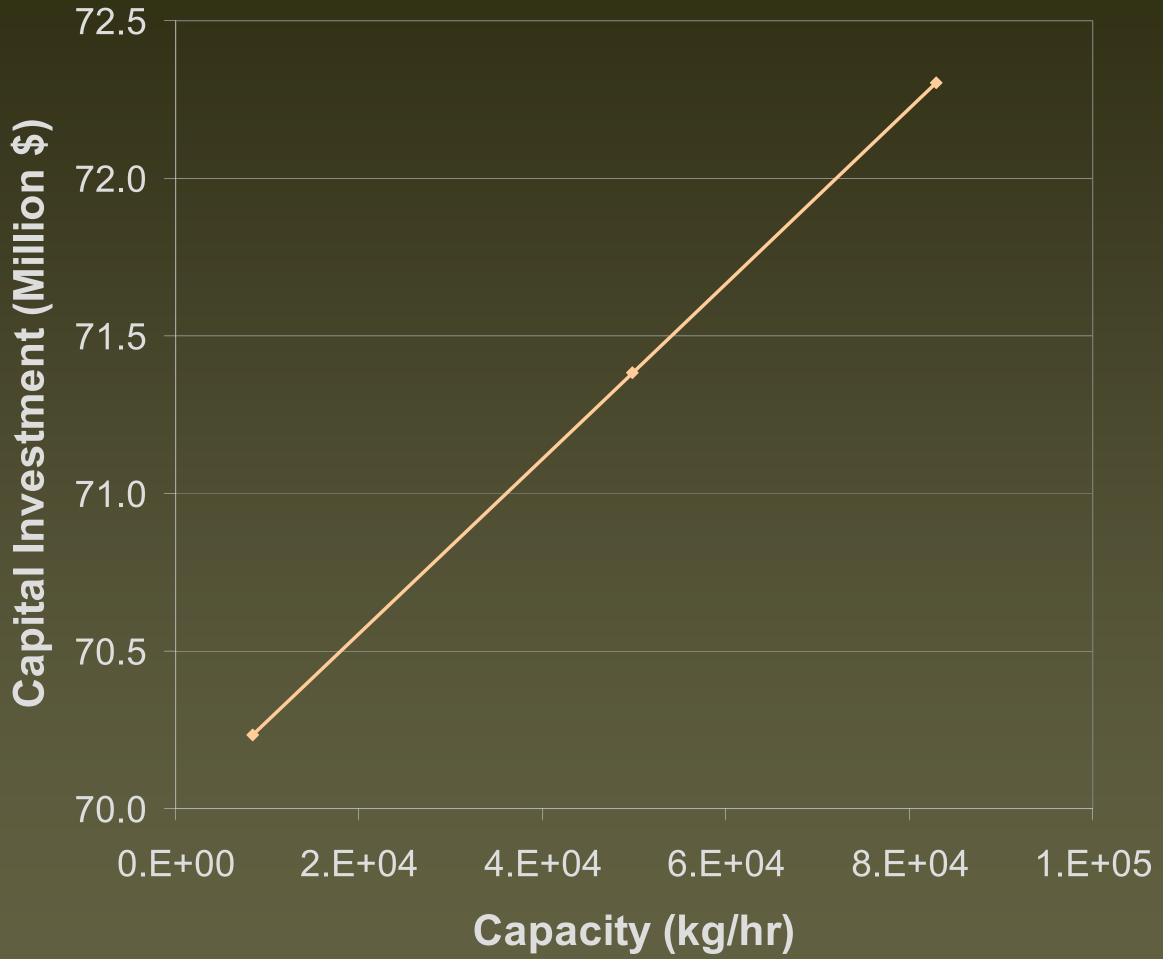
Source: *Engineering & Economic Assessment of Carbon Dioxide Sequestration in Saline Formations*

Brine Aquifers – Harris County

- Frio Formation is brine-bearing sandstone – shale sequence
- 28–35% porosity
- Anahuac Formation provides thick clay wedge seal
- Est. capacity of 230-390 Billion tons CO_2



Capital Investment for Brine Aquifers



Capital Cost ($) =

70,000,000 + 27.75*Capacity (kg/hr)

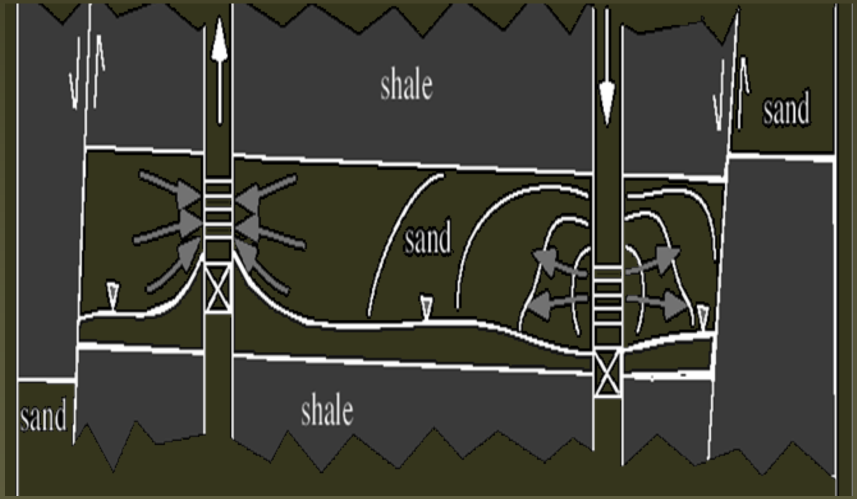
Geologic Sequestration
EOR

- 32 Million tons CO_2 utilized annually in US
- Injection technology well developed
- Current research projects monitoring injected CO_2 flow patterns to better assess true sequestration capability
- Profit potential from CO_2 sales could help offset separation and transportation costs

EOR – Process Overview

- CO_2 injected into depleted oil reservoirs
- Reservoir pressure increases
- Crude oil viscosity decreases
- As a result, recovery factors increase by ~10%

Crude Oil CO_2



Source: *http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/2a4.pdf*

EOR Option for Harris County

Capacity Assessment

- 51 oil wells
- Average well conditions:

  40 acres surface area

  37 feet pay height

  3,100 feet depth

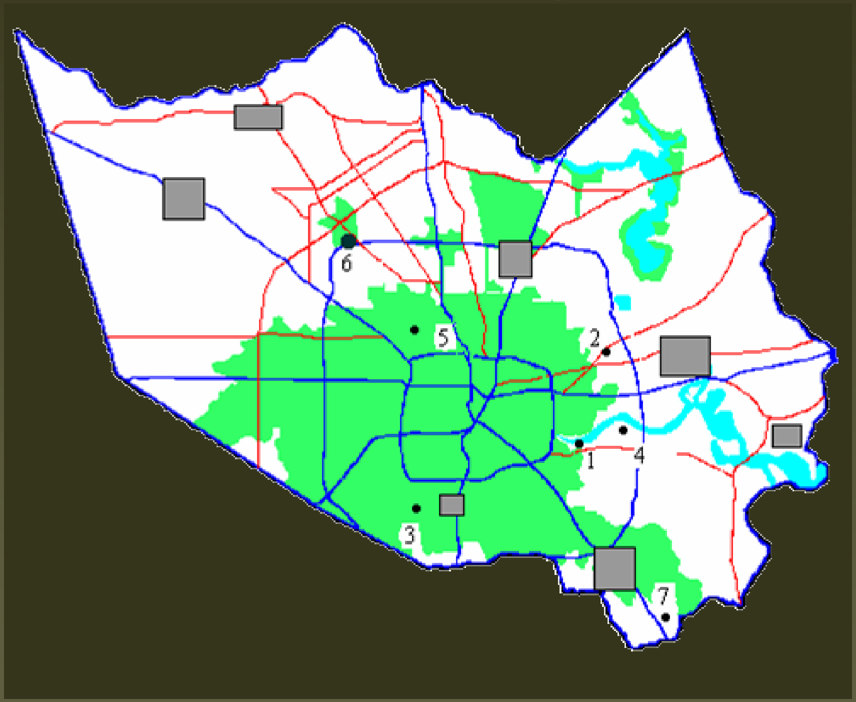
  115 °F & 1364 psi

  API gravity 29°
- Assumptions:

  15% porosity

  45% water saturation

Concentration of Oil Wells in Harris County



EOR Option for Harris County

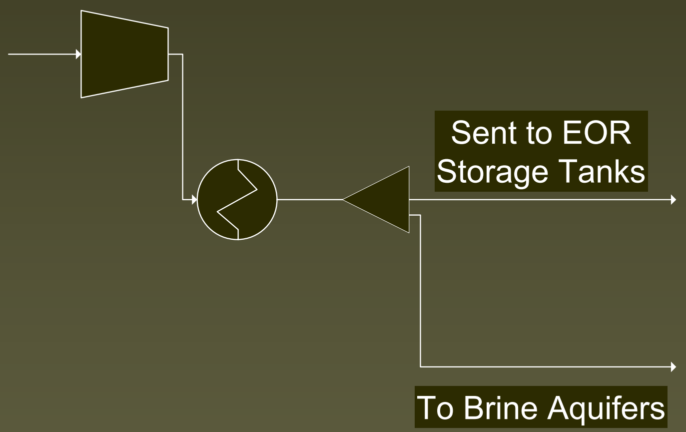
- Estimated Oil in Place:
  48 Million bbls originally
  34 Million bbls currently remaining
  29 Million bbls ultimately unrecoverable

- CO_2 solubility at reservoir conditions:
  780 scf/bbl in crude oil
  160 scf/bbl in water

- Sequestration Capacity:
  1.7 Million tons CO_2 soluble in unrecoverable crude oil & formation water

EOR
Specifications & Parameters

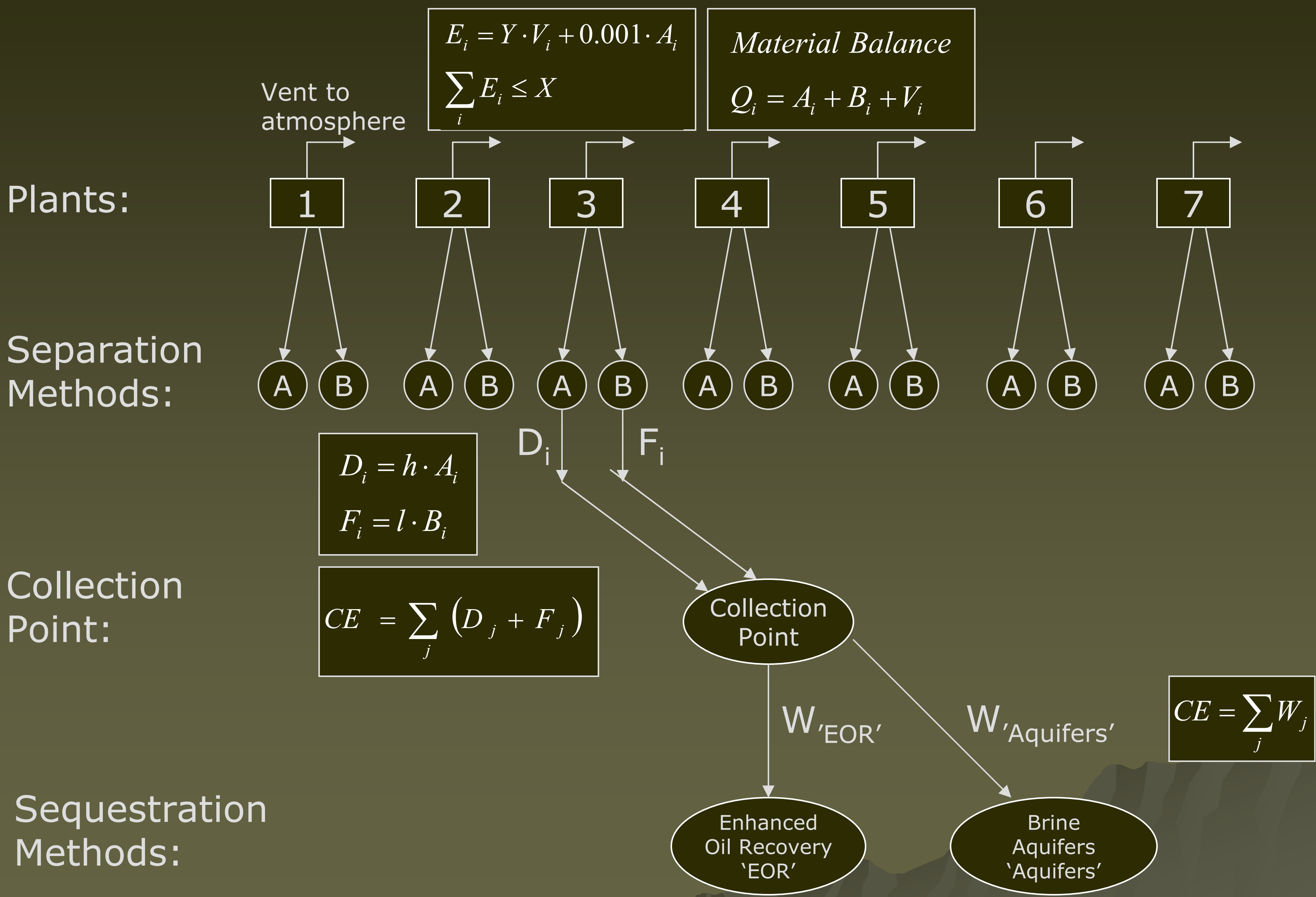
- Additional Fixed Capital Investment of $300,000
- Selling Price of CO_2 $35/ton



Planning Model

- Linear Model
- General Algebraic Modeling System (GAMS) Interface
- Uses CPLEX to solve linear model
  - Material Balances
  - Cost Equations
  - Emissions Trading
  - Enhanced Oil Recovery

Flow Sheet for Model



Cost Equations

- Equipment Costs
- Operating Costs
- Transportation Costs
- Total Capital Investment
- Profit from selling CO_2
- Profit from emissions trading
- Total Annualized Cost

Equipment Costs

- Each separation and sequestration method has a binary variable
  - 1 if used
  - 0 if not used
- Equipment costs are assumed to be linear with capacity

$$\begin{bmatrix}\text{Equipment}\\ \text{Cost}\end{bmatrix}=\begin{bmatrix}\text{Binary}\\ \text{Variable}\end{bmatrix}\times\begin{bmatrix}\text{Fixed}\\ \text{Cost}\end{bmatrix}+\left[\text{Capacity}\right]\times\left[\text{Variable Cost}\right]$$

Operating Costs

- Includes
  - Utility cost
  - Raw materials

$$\begin{bmatrix} \text{Operating} \\ \text{Cost} \end{bmatrix} = \begin{bmatrix} \text{Flow} \\ \text{Rate} \end{bmatrix} \times \begin{bmatrix} \text{Operating} \\ \text{Slope} \end{bmatrix}$$

- Units of operating cost slope are $/(kg/hr)

Transportation Costs

- Similar to operating cost
- Depends on the distance to transport

$$\begin{bmatrix}\text{Transportation}\\ \text{Cost}\end{bmatrix} = \begin{bmatrix}CO_2\\ \text{Flow Rate}\end{bmatrix} \times \begin{bmatrix}\text{Site}\\ \text{Distance}\end{bmatrix} \times \begin{bmatrix}\text{Transportation}\\ \text{Slope}\end{bmatrix}$$

- Transportation cost slope
  - $/((Kg/hr) mile)

Profit from Selling CO_2

- Sell for EOR
- Profit = Flow rate to EOR (Price of CO_2)
- Can only sell a certain amount for this purpose

$$W_{'EOR',t} \leq 17{,}400 \text{ kg/hr}$$

Emissions Trading

- 2 Categories of Emissions Trading (ET)
  - Internal : Among 7 power plants in Harris County
  - External : If Harris County plants exceed required emissions reductions, excess units of reduction can be sold for profit

Emissions Trading

- Incentive to capture and sequester more CO_2
- Helps to offset costs to electricity consumers
- Terminology
  - Emissions Reduction Credit (ERC)
  - 1 ERC is 1 ton of CO_2 sequestered beyond required reduction

Emissions Trading

- No official government CO_2 ET program
- Pricing Estimates
  - Wharton Econometric Forecasting Associates
  - $54/ERC
  - Will vary over time with same trend as electricity prices

Emissions Trading

- Voluntary Programs
  - Chicago Climate Exchange
- Equation for model
  - ET within network in Harris county generates no profit
  - Externally, profit can be generated
  - Profit = Price per ERC (Number of ERCs)

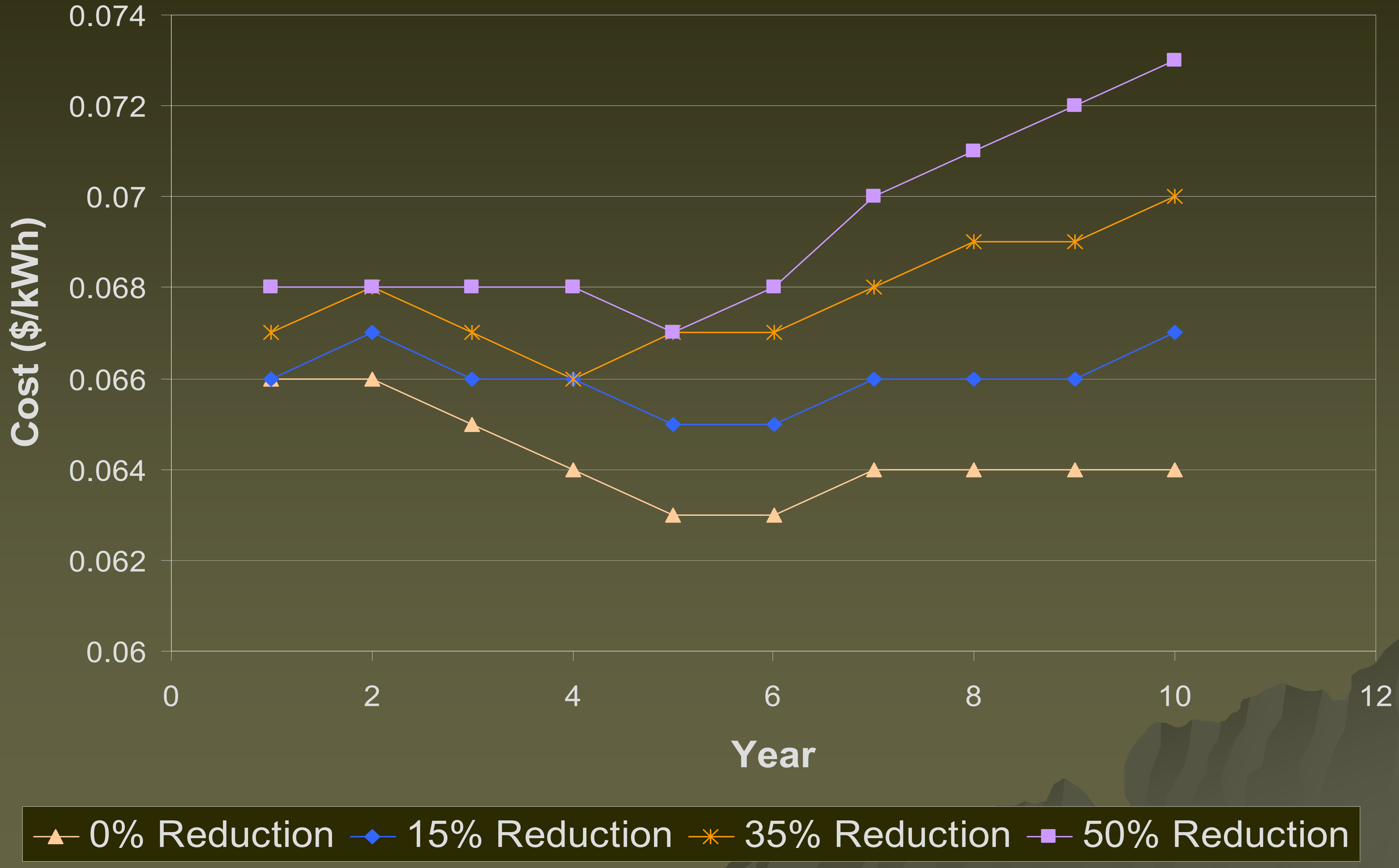
Total Annualized Cost

- Translation to electricity price increase
  - Divide by the total capacity of all of the plants in the network
  - Result: $/kWh needed for the sequestration to pay for itself
- Objective of mathematical model: minimize cost increase to electricity consumers

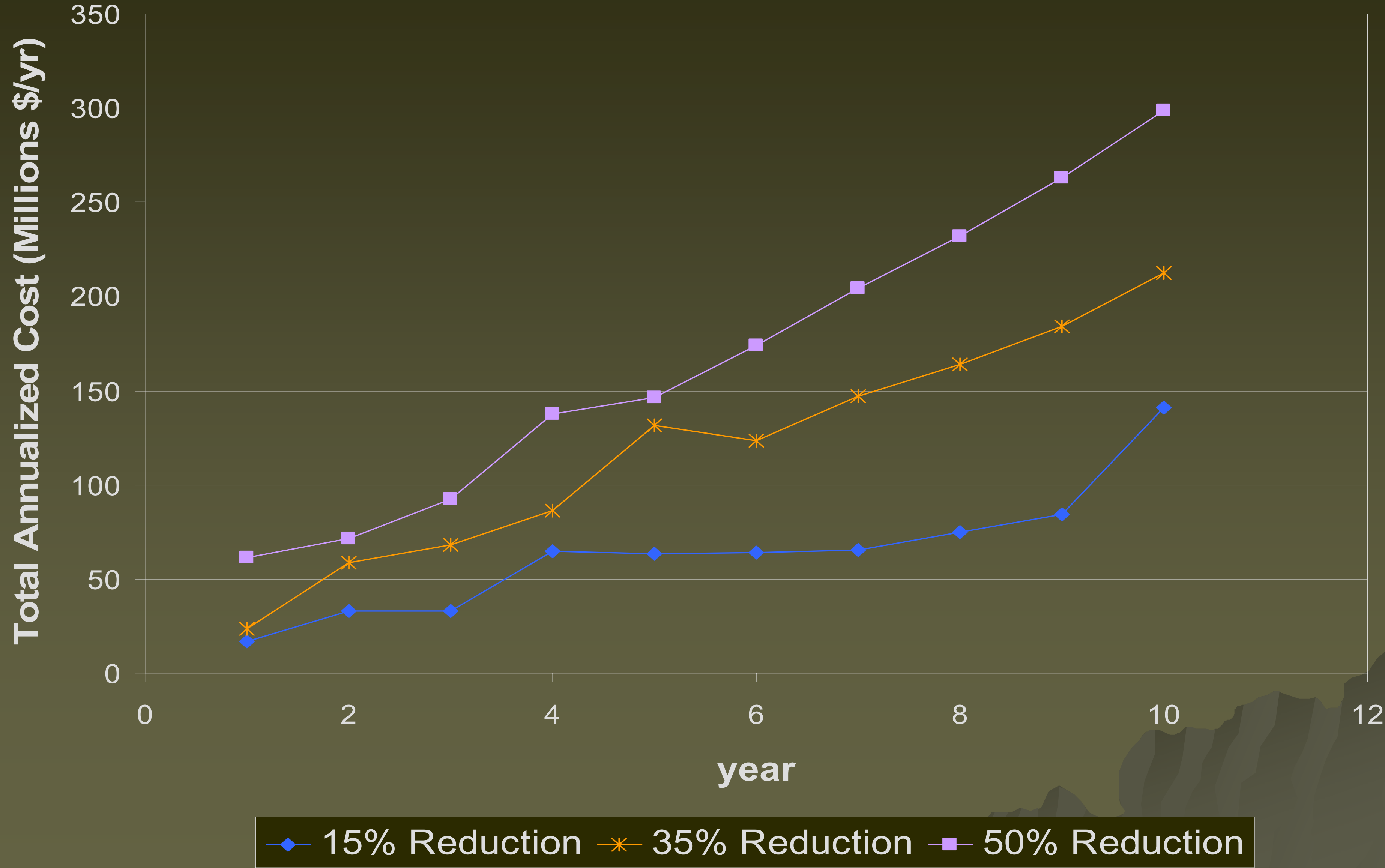
Model Results - Summary

- 15% Reduction over 10 years (1.5% per year)
- Calcium Hydroxide separation in all cases
- Depending % emissions reduction, different plants will separate and sequester CO_2
- Use Brine Aquifers to sequester

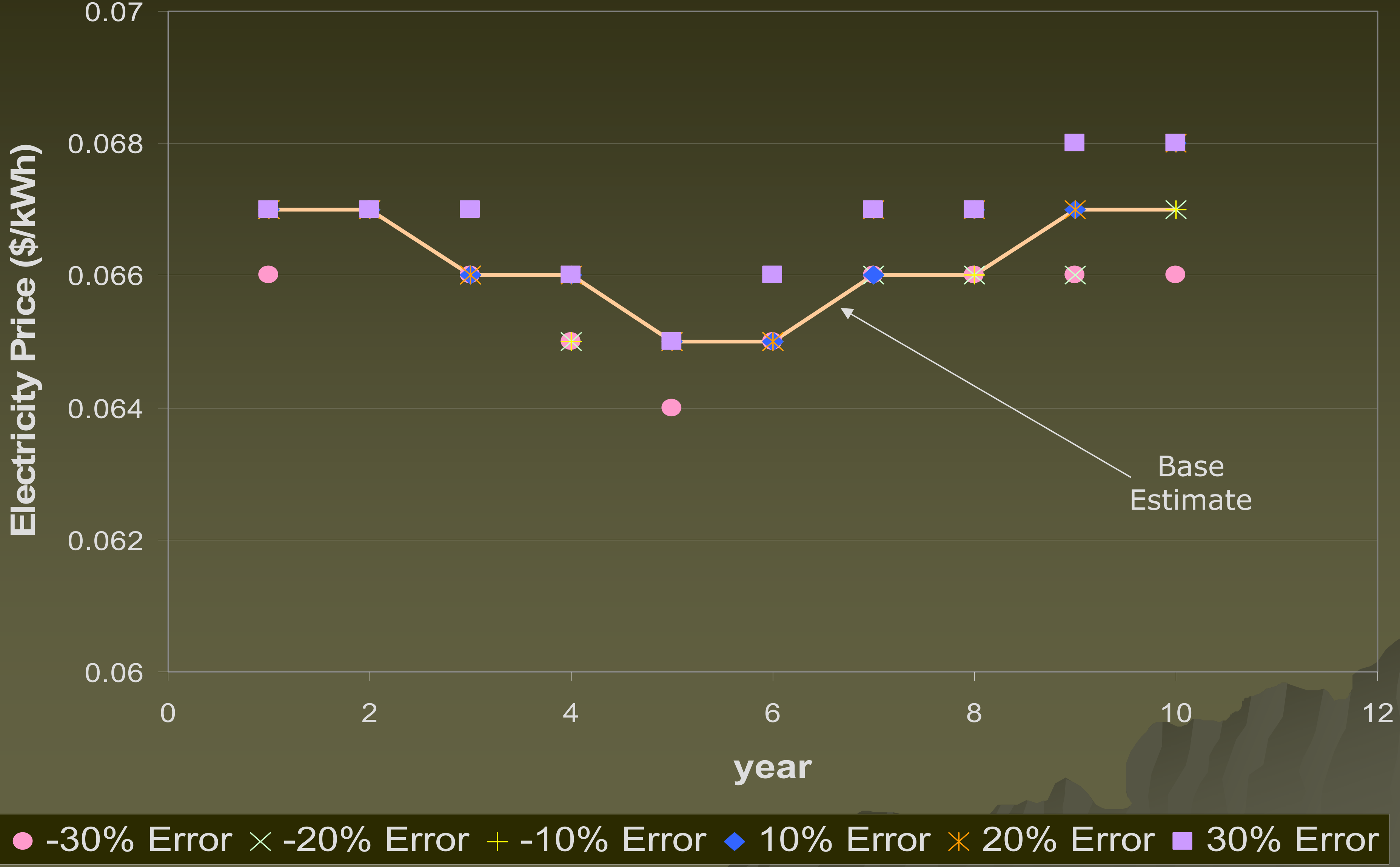
Model Results – Electricity Cost Scenarios



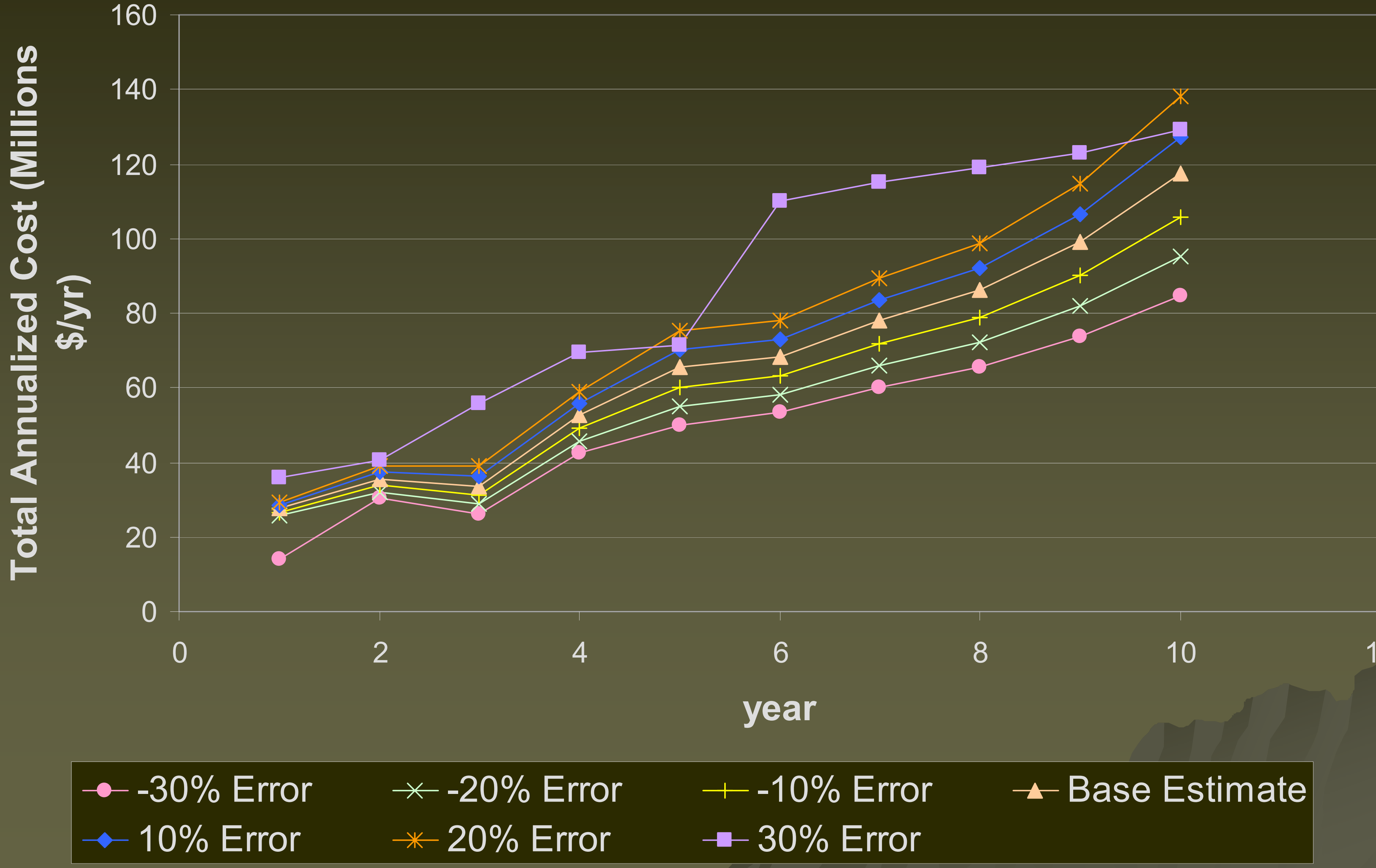
Model Results – Emissions Reductions (Total Annualized Cost)



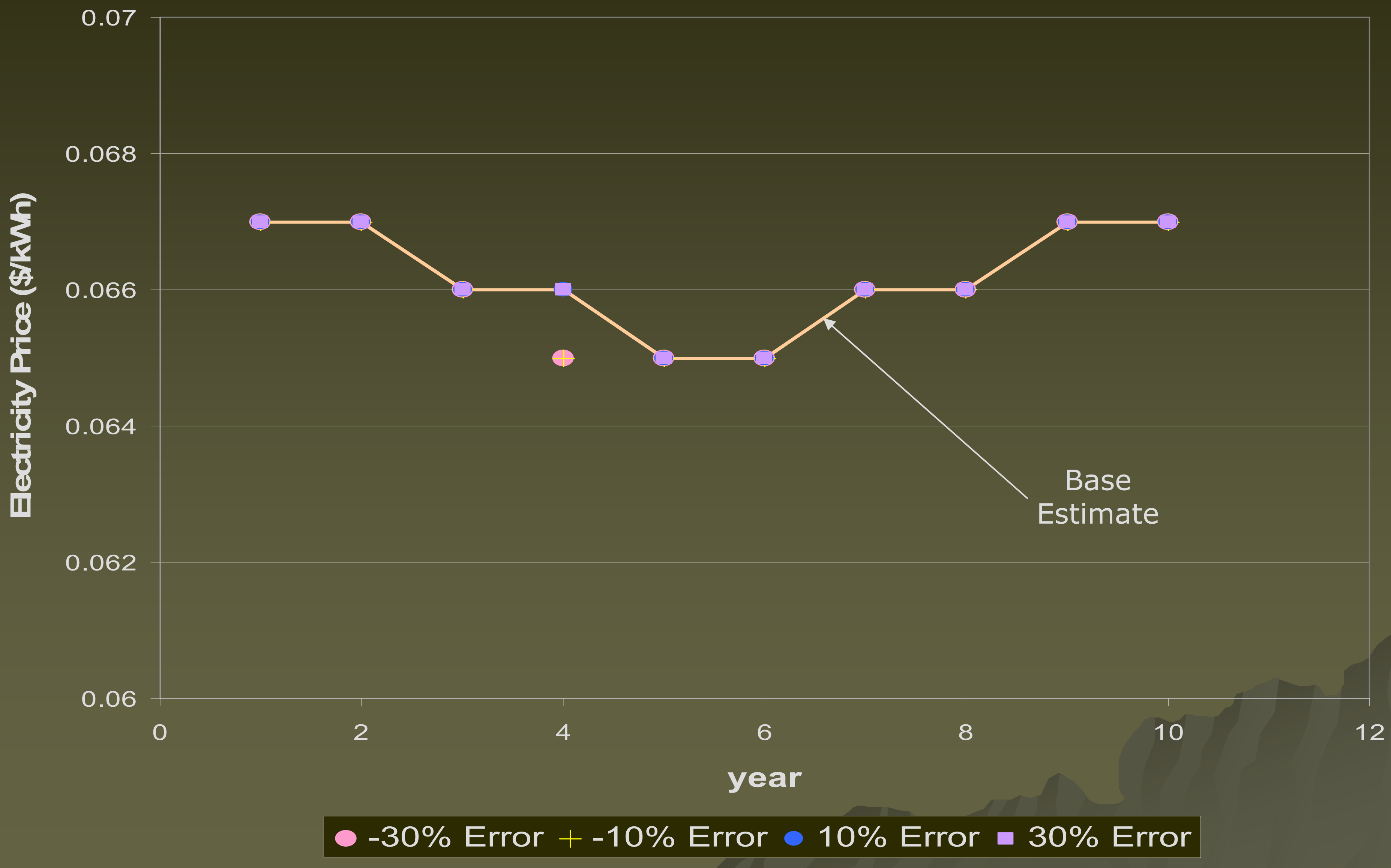
Model Results – Electricity Price due to changing $Ca(OH)_2$ Cost



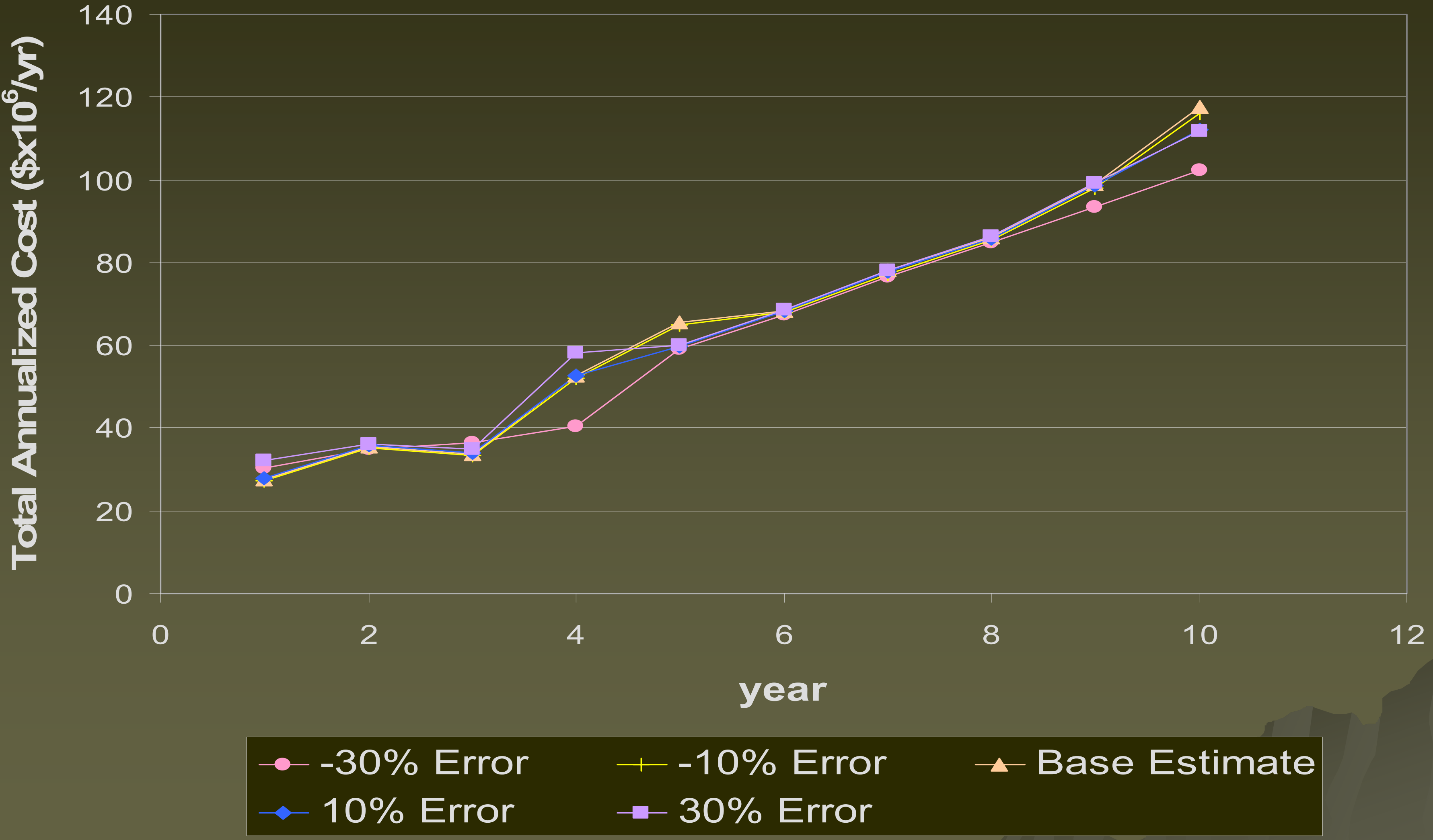
Model Results – Total Annualized Cost for changing $Ca(OH)_2$ Cost



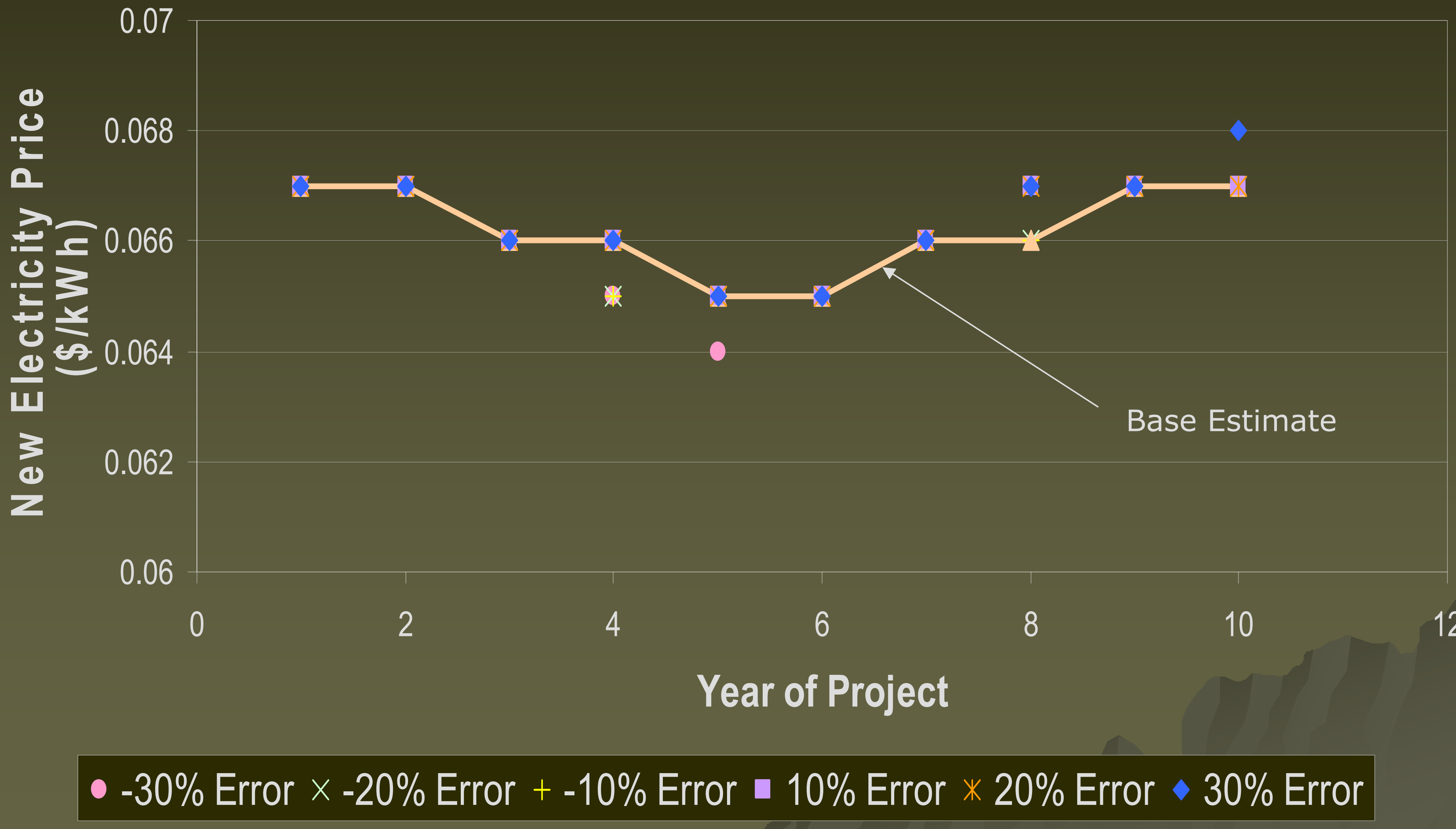
Model Results – Electricity Price for Transportation Cost Variation



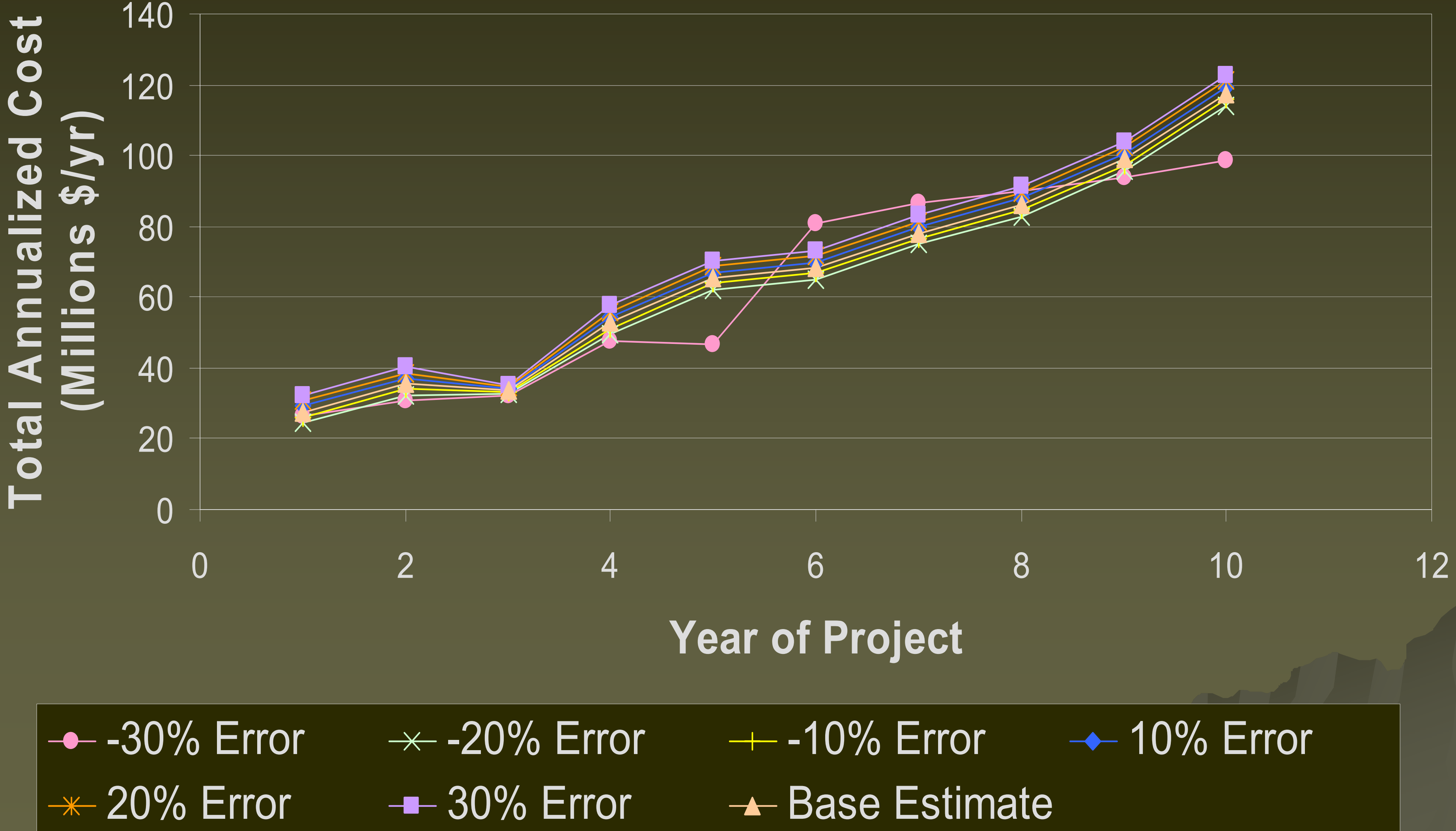
Model Results – Total Annualized Cost for Transportation Variation



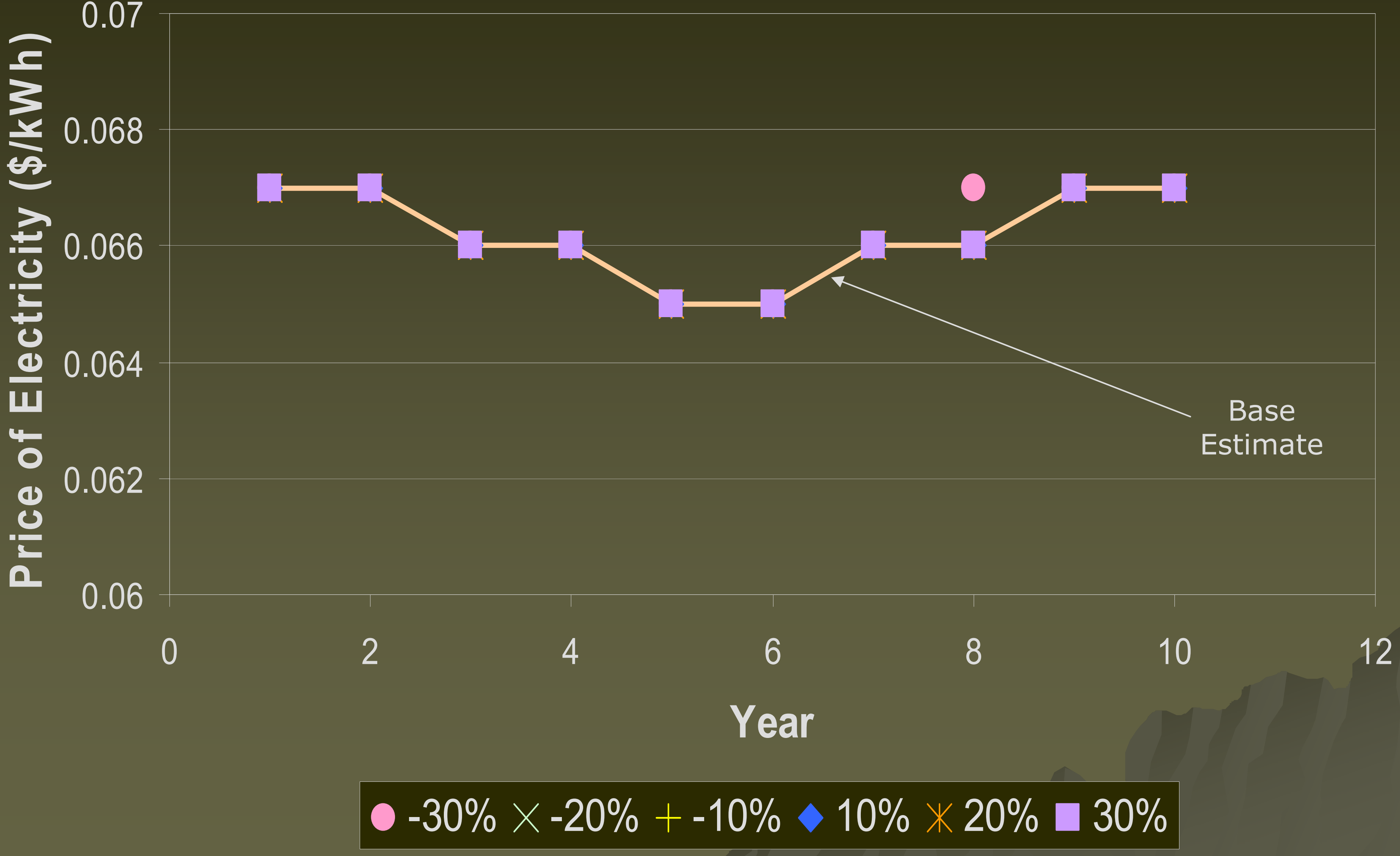
Model Results – Aquifers Electricity Price Sensitivity



Model Results – Aquifers Total Annualized Cost Sensitivity



Model Results – Price Sensitivity for ERC



Model Results – Price Sensitivity for ERC

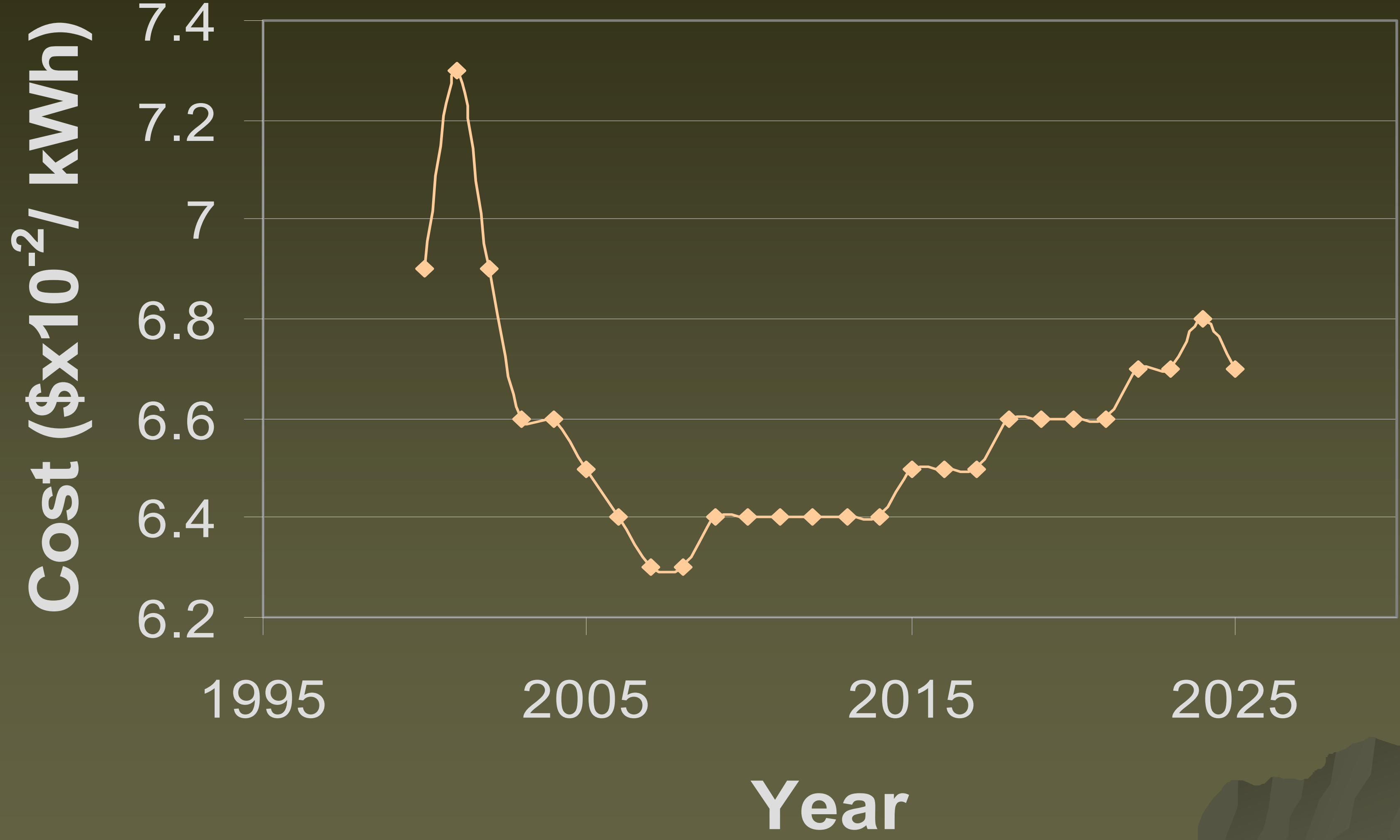
Model Results

- Price Sensitivity of CO_2
  - In order to use EOR some capital investment is required
  - Current price of CO_2 \$35/ton (\$0.039/kg)
  - EOR is not a viable option in the 30% deviation range for the price of CO_2
  - In order for EOR to be used, the price of CO_2 would have to be \$370/ton (\$0.41/kg)
    - This is extremely unlikely
    - Demonstrated by Stochastic Model

Risk Analysis

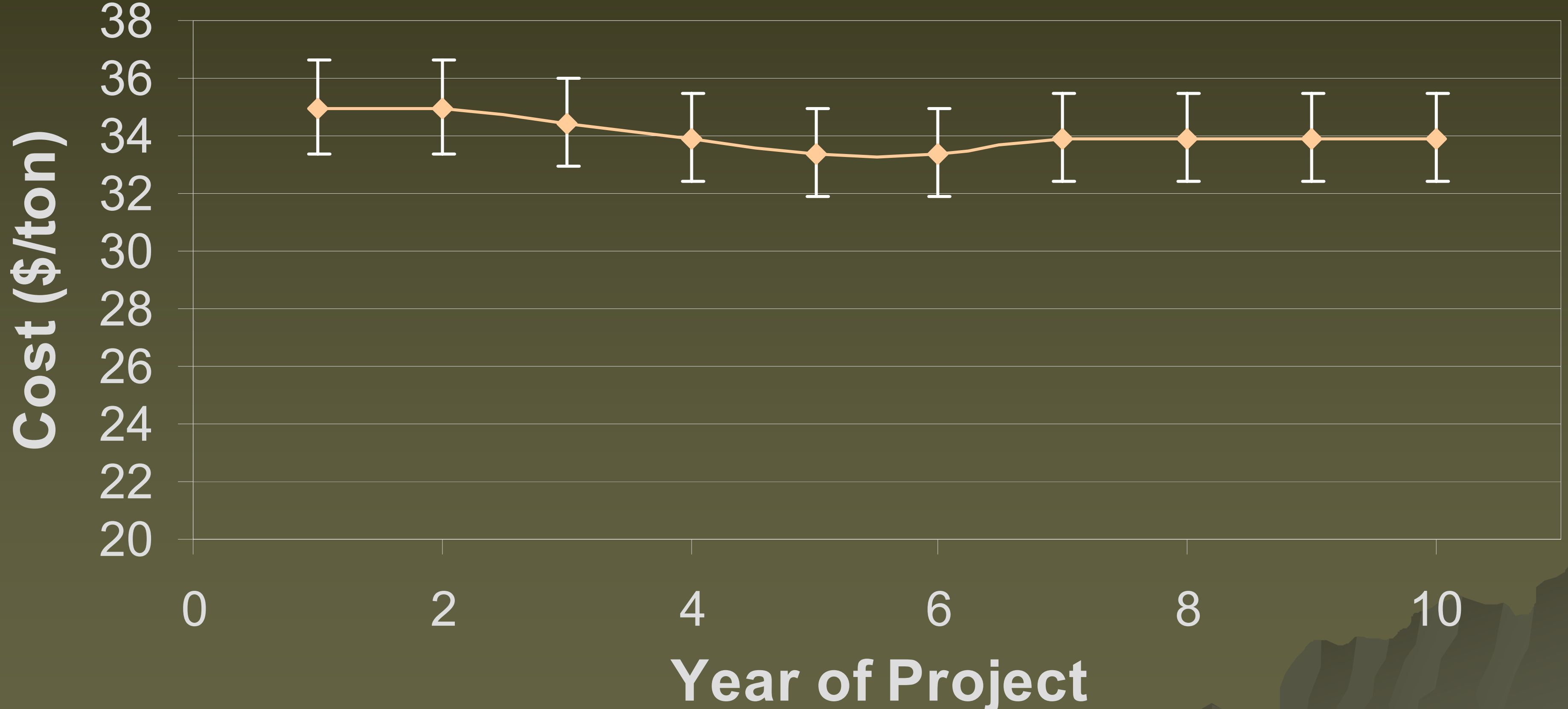
- Incorporate risk into mathematical model
- Variables with the greatest amount of risk
  - Price of Electricity
    - Forecasting by Energy Information Administration
  - Price of CO_2
  - Price of ERC
  - Price of CO_2 and ERC will vary with same trend as electricity cost

Forecasting of Electricity Prices



Source: Energy Information Administration
http://www.eia.doe.gov/oiaf/aeo/aeotab_1.htm

Forecasting of CO_2 Prices



Forecasting of ERC Prices

Conversion to Stochastic Model

- Obtain average values for each year for risky variables
- Obtain standard deviation for each year
- Add scenarios to the model
  - Assume normal distribution with 30 scenarios
  - Generate values for variables within model

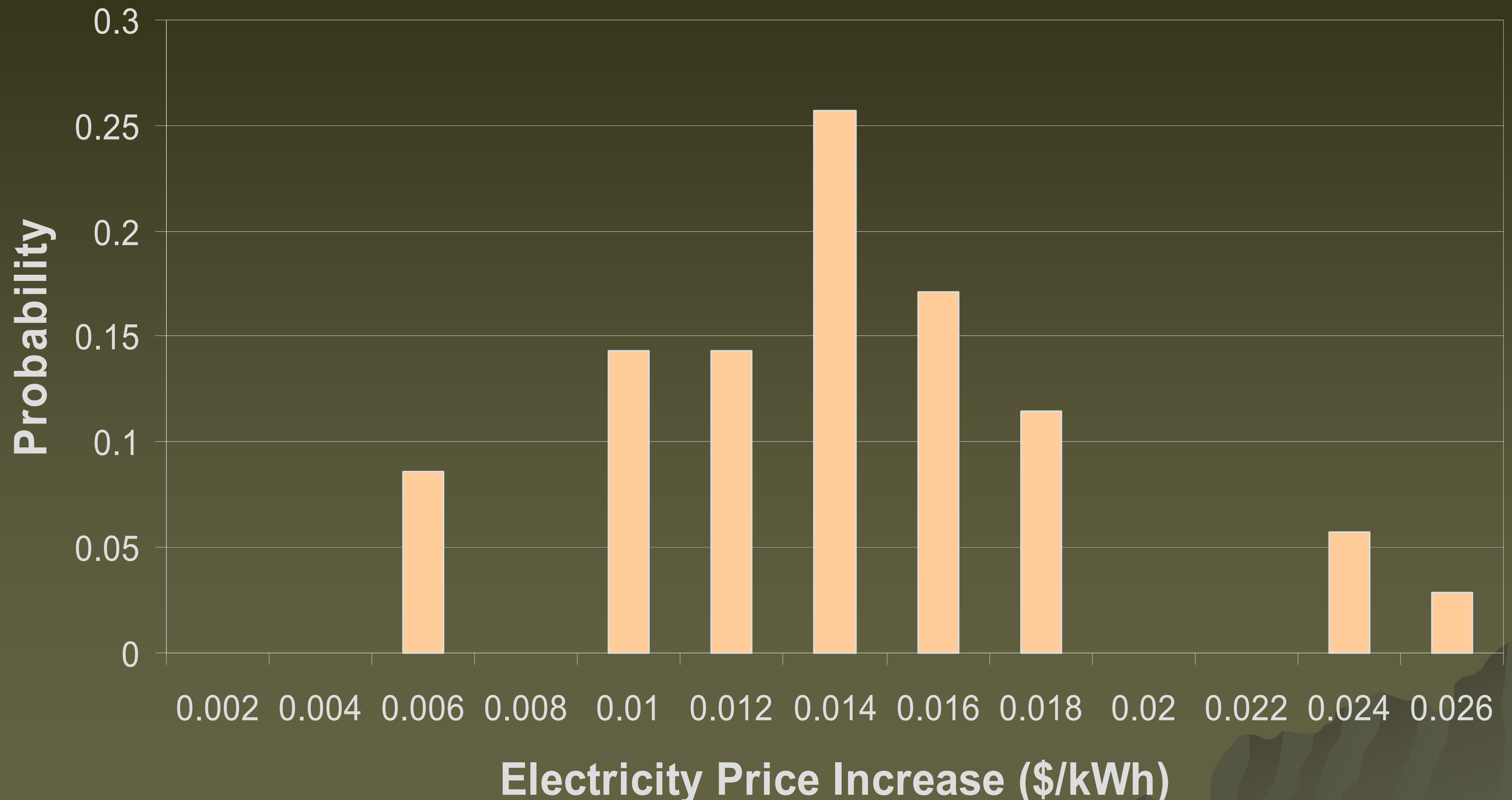
Conversion to Stochastic Model

- Change objective function
  - Minimize expected cost increase of electricity
  - Expected Value:

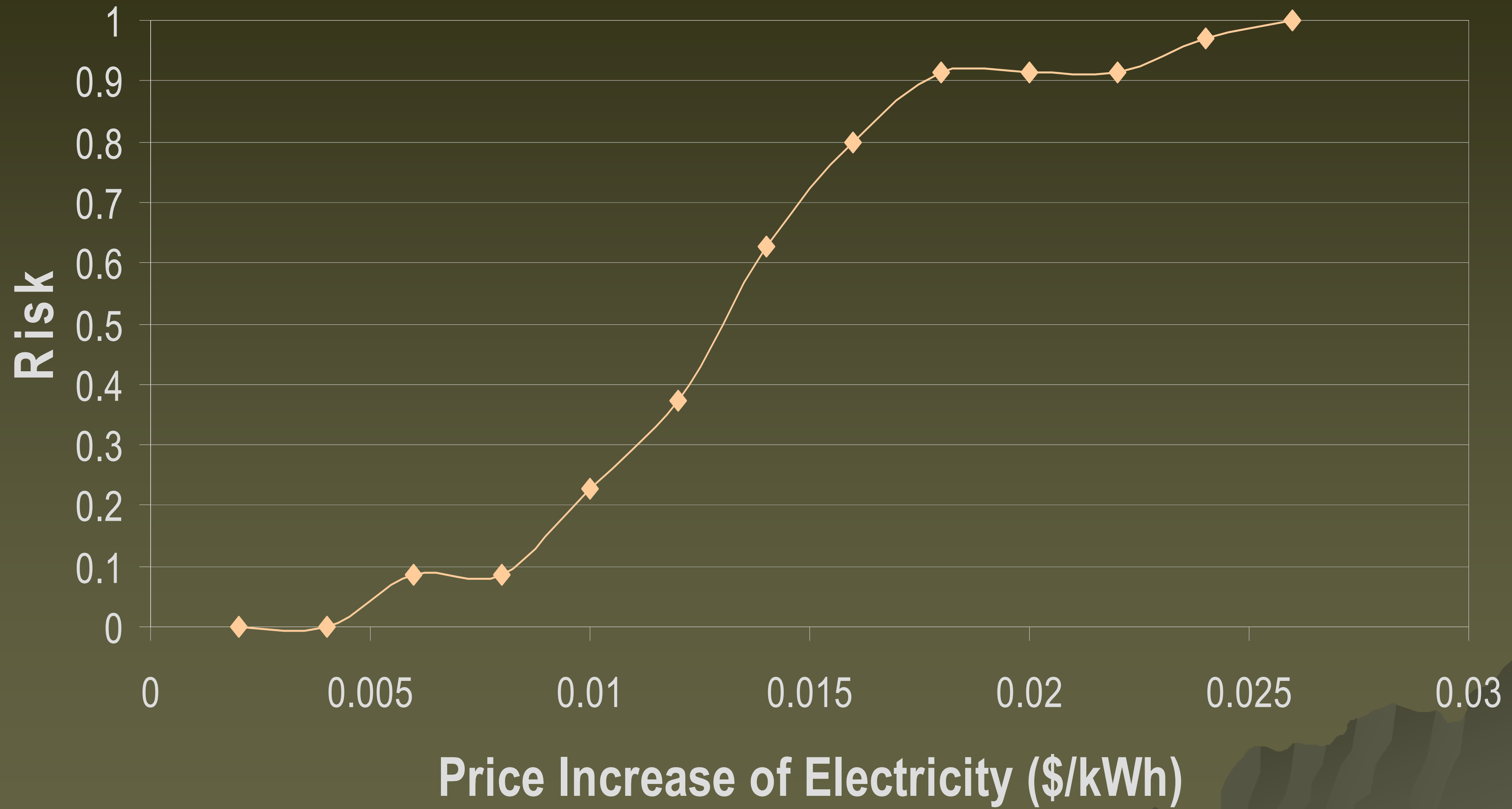
$$E(x) = \Pr\{x\} \cdot x$$

- The stochastic model will tell us "Here and Now" decisions
  - What should we install now to have the best result for all of the possible scenarios

Results of Stochastic Model – Price Histogram



Risk Curve



1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Risk
0
0.005
0.01
0.015
0.02
0.025
0.03
Price Increase of Electricity ($/kWh)

Recommendations

- Stochastic model doesn't warrant any major changes over deterministic model
  - 15% Reduction over 10 years
  - Calcium Hydroxide separation in all cases
  - Depending % emissions reduction, different plants will separate and sequester CO_2
  - Use Brine Aquifers to sequester

Recommendations

- Stochastic model recommends different capacities than deterministic model

Year	Plant where $Ca(OH)_2$ System Installed	
	Deterministic Model	Stochastic Model
1	Sam Bertron	Sam Bertron and Deepwater
2	Webster	Greens Bayou, Hiram Clarke, and Webster
3	Increase Capacity of Sam Bertron and add Hiram Clarke	Increase Capacity of Greens Bayou
4	Increase Capacity of Sam Bertron	Increase Capacity of Greens Bayou
5	TH Wharton	No additions necessary
6	No additions necessary	Increase Capacity of Greens Bayou
7	No additions necessary	No additions necessary
8	Greens Bayou	No additions necessary
9	Deepwater	Increase Capacity of Sam Bertron
10	No additions necessary	Increase Capacity of Sam Bertron