# Sequestering $CO_2$ in Houston

By: *Lisa Cox, Meghan Forester, Jacob Hedden, Jennifer Scroggin, Thomas Smith*
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Since the Industrial Revolution, escalating carbon dioxide emissions have been the concern of many environmentalist groups. The issue of reducing atmospheric levels of carbon dioxide has become increasingly significant since carbon dioxide has been identified as a major contributor to the Greenhouse Effect and global warming. The major source of atmospheric carbon dioxide is fossil fuel combustion, power plants being a significant contributor. One possible solution to the problem is sequestration of carbon dioxide. Sequestration is the capturing and storing of carbon dioxide in order to prevent it from entering the atmosphere. This project evaluates options for separation of carbon dioxide from flue gas, transportation of the carbon dioxide to an intermediate collection point and ultimately to the sequestration site, selection of an appropriate sequestration site, and the economic implications of these types of changes on power plants and their consumers from the perspective of a governmental regulatory agency.

Harris County, Texas (Houston area) was chosen for this study due to its high concentration of power plants and the availability of multiple sequestration options. The lack of regulation on existing carbon dioxide emissions has given rise to taking a governmental perspective; the ratification of the Kyoto Protocol, a document that would require a 12% reduction in all carbon dioxide emissions, has generated diplomatic pressure on the U.S. to implement some form of regulating its contribution to the current levels of atmospheric carbon dioxide.

## Separation Methods

Separation of $CO_2$ from flue gas emissions is necessary to preserve the efficiency of the process of sequestration. Since flue gas contains only 4% carbon dioxide by weight, compression and sequestration of all components would be economically infeasible. Coupled with possible physical difficulties, this necessitates the use of some method of separation. Although there are several possible methods of separating $CO_2$ from flue gas, only three were considered for the purposes of this project. Other methods were eliminated on the basis of projected energy requirements.[1] Absorption in a packed tower, oxygen-enriched fuel firing, and reaction with calcium hydroxide were investigated for the power plants in Harris County.

- Absorption in a packed tower is a common method of separating mixtures of gases. A common solvent for $CO_2$ removal is monoethanolamine (MEA), which has a relatively high affinity for $CO_2$ at moderate temperatures (70 F). The absorption can easily be reversed by addition of heat to obtain a pure $CO_2/H_20$ stream. The equipment required for this process is commercially available as a single unit from Wittemann Carbon Dioxide Equipment[2], with prices ranging from \$0.5 - \$10 million for flow rates of 250 – 1,500 kilograms of flue gas per hour. The operating cost was projected using simulations in ProII for the duties of each piece of equipment. The operating cost for this method was estimated as \$0.17/kg flue gas.

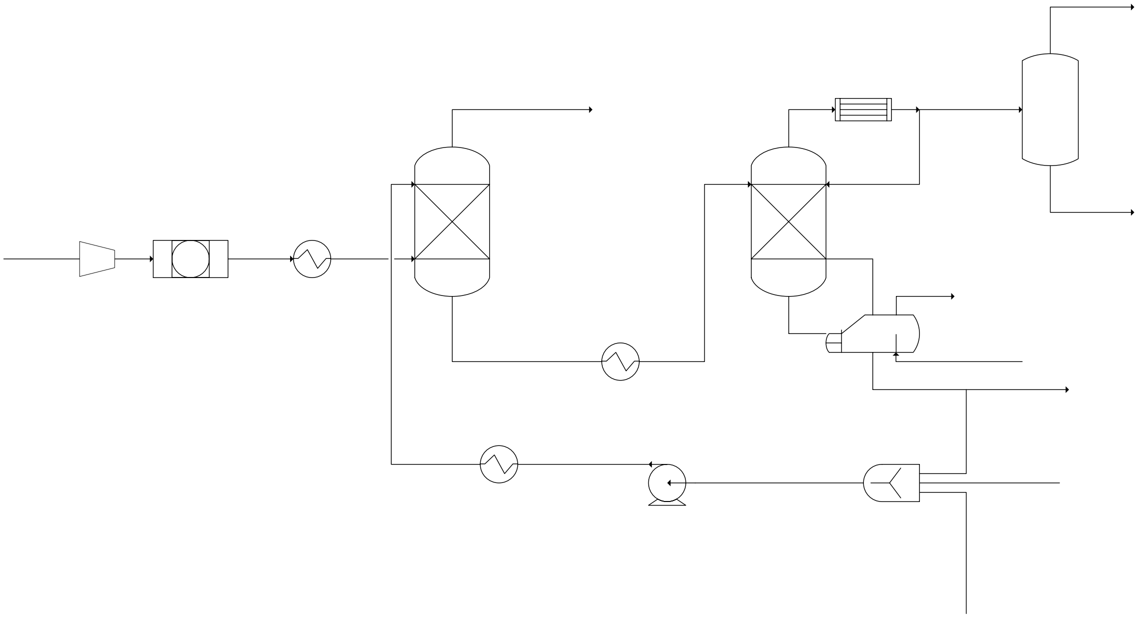

***Figure 1.*** *PFD of MEA absorption/stripping method*

- Oxygen enriched fuel firing was another method considered for separation. This approach involved the separation of air in order to facilitate combustion in pure oxygen. Separation after combustion to isolate $CO_2$ is necessary because of dilution due to impurities, such as nitrogen, in the air. If fossil fuels were combusted in pure oxygen, the flue gas would theoretically contain only $CO_2$. Other potential benefits of this method, aside from a nearly pure $CO_2$ flue gas, would be the reduction of $NO_x$ emissions as well as decreased capital costs for power plants (since the volume of reactants would be significantly reduced upon eliminating the unnecessary components of air). The capital costs involved with this method, however, presented an economic strain that was lacking in the other methods considered. Air separation units alone ranged from \$38-\$56 million for production of 2000-3000 tons of oxygen per day. This does not include necessary modifications to the existing equipment to ensure that air ingress is prevented. The operating cost for this method was calculated as \$0.114/kg flue gas. Coupled with the significant capital cost involved with this method, its removal from consideration was justified on an economical basis.
- Reaction with calcium hydroxide, although still in its developmental stages, was considered as a viable option for performing the necessary separation. In this method, flue gas is bubbled through a solution of calcium hydroxide, which reacts with the carbon dioxide component of flue gas to form calcium carbonate, an inert solid compound that precipitates out of solution. Once capacity is reached, the excess solution is removed and the remaining solid is heated to 580 C, at which point carbon dioxide is released from calcium carbonate, resulting in the formation of calcium oxide. Subsequent addition of water regenerates the calcium hydroxide for reuse. The reactor design for this method was developed based on two-film theory of mass transfer to approximate the rate of diffusion of carbon dioxide into water. This was based on the assumption that the system is mass transfer limiting, which is valid since documented experiments have conclusively shown high rates of reaction under alkaline conditions (pH>10). The capital cost was obtained by sizing the reactor, pricing the required amount of calcium hydroxide, sizing a gas sparger, and approximating the cost of necessary heat exchangers. For

flow rates ranging from 50,000-200,000 kilograms of flue gas per hour, the calculated capital costs for this method were \$85,000-\$250,000. The operating cost, based on heats of reaction, was calculated as \$0.0235/kg flue gas. Considering the relative capital and operating costs of each method indicated that calcium hydroxide is the most economically favorable and was therefore selected as the method of separation for this project.

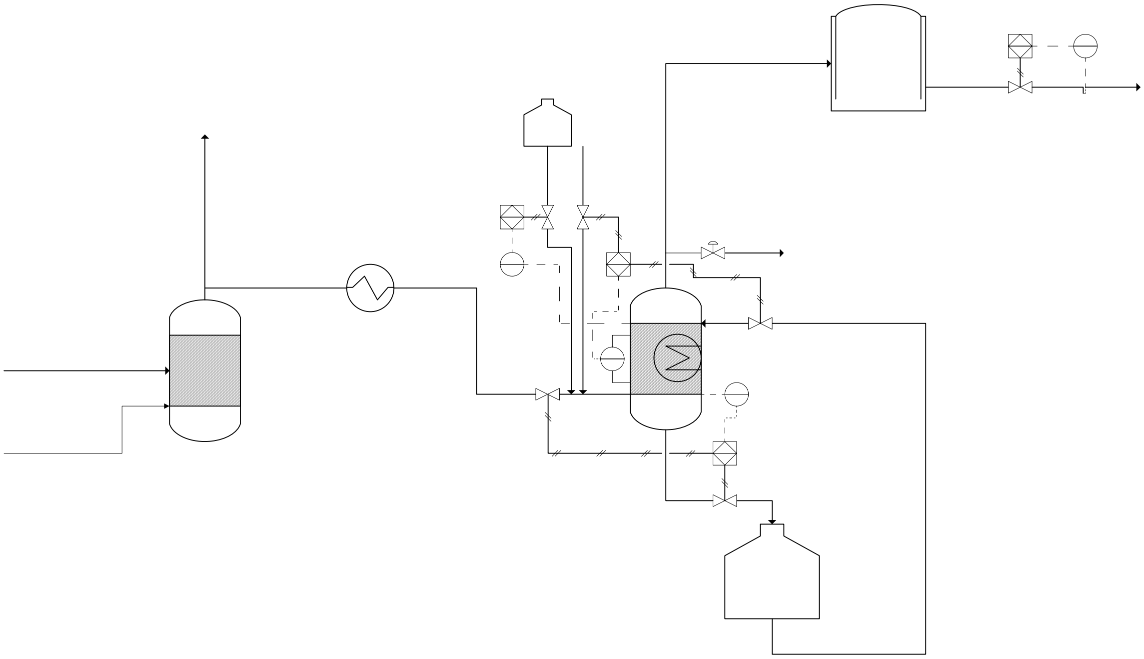

*Figure 2.* *P&ID for calcium hydroxide*

**Transportation Network Design**

After separation from flue gas, purified carbon dioxide must be transported to some site of sequestration. Because of the considerable distance of each plant from these sites, it would be economically infeasible to construct a piping network from each plant to the desired location for sequestration; in order to facilitate higher efficiency in transporting the carbon dioxide from each plant, a collection point was chosen (Sam Bertron) according to its close proximity to the chosen site.

Modeling an adequate piping network for the transport of $CO_2$ from each power plant to the Sam Bertron collection point entailed the use of Pro/II simulation software. Linearization of the economics provided by Pro/II was accomplished using two simulations, which approximated the compressor duties and pipe diameters for 10% and 15% overall reductions in $CO_2$ emissions. Compressors at each power plant location initially compress the CO2 to 20 psia and piped to the designated collection point. The incoming streams from all power plants are subsequently combined using a mixer and compressed to 1020 psia. A heat exchanger then cools the process stream from 740 F to 84 F, liquefying the carbon dioxide for sequestration either in brine aquifers or for use in enhance oil recovery applications.

The final design of the transportation network featured six small compressors for each power plant (save the one designated as the collection point) and one larger compressor to compress the carbon dioxide to an adequate sequestration pressure. For a 15% reduction in CO2 emissions, the total annualized capital was determined to be \$9.66 million per year. The corresponding operating cost was \$5.90 million per year. For a 10% reduction, the annualized capital was \$9.59 million per year and the operating cost was \$3.75 million per year.

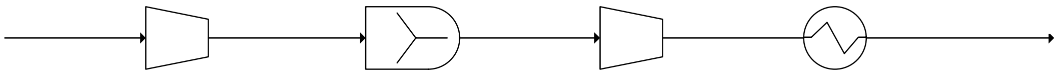

***Figure 3.*** *PFD for transportation network*

### *Ocean Sequestration*

The ocean represents the largest potential carbon dioxide sequestration option, with the capability of containing 85% of all the Carbon Dioxide produced globally. The ocean naturally sequesters carbon in a process termed the 'biological pump'. This process refers to the consumption of surface carbon dioxide by phytoplankton, ultimately processing carbon through the food chain. Direct injection of carbon dioxide into the ocean presents the opportunity to increase the speed at which the ocean consumes carbon. However, limited research is available which focuses on ocean sequestration since the technological concepts are relatively new. Important factors to consider in studying ocean sequestration include research of the reactions in ocean-liquid $CO_2$ systems and the environmental impact, injection methods, and potential transportation costs.

Study of the kinetic behavior of ocean water and carbon dioxide is necessary in order to assess the environmental impact of ocean sequestration. Available research indicates that injection of $CO_2$ into ocean water results in the formation of clathrate hydrates, ice-like formations of water and $CO_2$. The depth of injection is important in determining the density of the clathrate hydrate complex that forms. The injection depths are shallow (200-400m), mid-water (400-2700m), and deep water (>2700m). Clathrate hydrates formed at each of these injection depths display different characteristics. Experiments indicate that shallow water injection of $CO_2$ results in a less dense hydrate formation that will rise to the surface of the ocean and lead to a potential re-release of $CO_2$ into the atmosphere. This is less likely to be a problem at mid-water injection depths, while deep-water injection results in the formation of a hydrate complex denser than water, which will eventually form a pool of hydrate-covered liquid at the ocean floor. Deep-water injection is the focus of most current research.

The method of injection is also of concern when injecting liquid $CO_2$ at mid to deep ocean depths. The density of liquid $CO_2$ is greater than that of ocean water at depths greater than 2600 m. It is thus required that the injection rate of liquid $CO_2$ be slow in order to yield a homogeneous formation that will dissolve slowly, and have less hydrate formation than rapidly injected liquid $CO_2$.

In addition to the lack of research regarding this technology, associated transportation costs are expected to significantly exceed those related to other sequestration methods. Options for transporting liquid $CO_2$ include rigid pipelines, flexible pipelines, and LPG tankers (similar to Liquid Petroleum transport vessels). Cost estimates for rigid pipelines are dependent on the distance into the ocean required for sequestration. In research experiments this distance has ranged from 14,000 ft to as far as 311 miles. The resulting transportation networks range in cost from approximately \$9 billion to \$47 million, respectively. An even more expensive option for transporting liquefied $CO_2$ is LPG tankers. These tankers can be as much as \$50 million per tanker; 13 tankers would be required to transport all the CO2 emitted each day of power generation in Harris County. This is a total cost of \$650 million, without consideration of injection equipment or an injection platform.

Although ocean sequestration offers enormous potential for long-term storage of $CO_2$, there is little scientific data to support the environmental safety of implementing a large-scale sequestration operation. Much more research is necessary in order to provide appropriate guidelines for using the ocean as a means of sequestration, and to ensure that there will be a minimized effect on the ocean. Therefore, the focus of this project will be to utilize geological methods of storing carbon dioxide.

### ***Geologic Sequestration***

The two options that are considered viable for geologic sequestration of carbon dioxide in Harris County are sequestration in depleted hydrocarbon reservoirs as well as sequestration by injection into brine aquifers.

#### *Enhanced Oil Recovery*

Carbon dioxide is currently injected into depleted hydrocarbon reservoirs as a part of enhanced oil recovery operations. This injection process is utilized to increase reservoir pressure, decrease oil viscosity, and thus increase production (Figure 4). An additional benefit to this process is the potential for sequestration of dissolved carbon dioxide in unrecoverable crude oil and formation water. Sequestration in hydrocarbon reservoirs through enhanced oil recovery is an economically attractive option due to the fact that profit generated through the sale of the carbon dioxide helps to offset some of the separation and transportation costs. However, the capacity of this method is limited by the amount of unrecoverable oil and the compatibility of the existing wells with the technology.

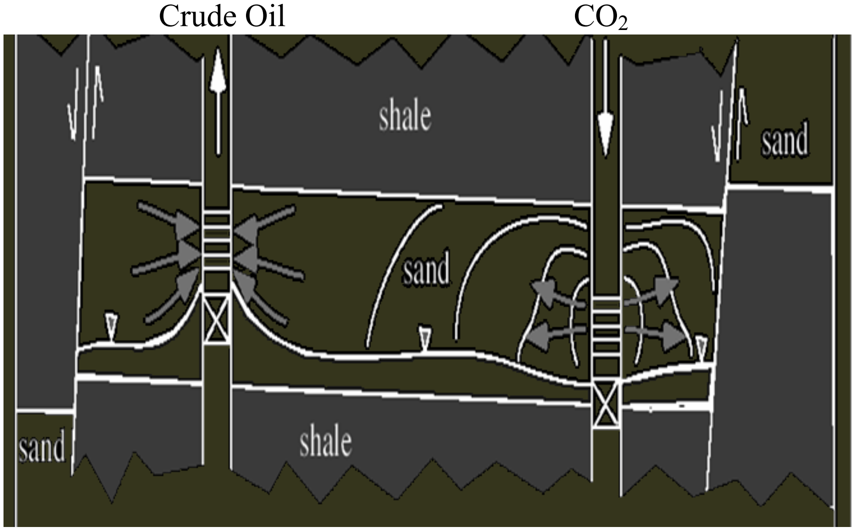

***Figure 4.*** *Process overview for enhanced oil recovery*

In evaluating the potential application of this technology to Harris County, sequestration capacity and the required fixed capital investment were considered. Based on the solubility of carbon dioxide in crude oil and formation water at average reservoir conditions, the estimated capacity for sequestration in hydrocarbon reservoirs in Harris County is 1.7 million tons of carbon dioxide. In order to estimate the required capital investment, the perspective was taken that the purified liquid carbon dioxide product would be stored on site and sold to companies which would be responsible for marketing, transporting, and injecting the carbon dioxide into various fields. The estimated fixed capital investment for this process is $300,000, which includes costs for holding tanks and pipelines. The estimated selling price of carbon dioxide is $35/ton. This price was chosen based on the actual processing costs incurred by other carbon dioxide processing plants. This price would not completely offset the processing costs incurred in this type of application due to the inherent inefficiencies of such a process. However, this price would insure that the carbon dioxide was priced competitively.

### *Brine Aquifer Injection*

Brine aquifer sequestration is an attractive option due to the high sequestration capacity of the formations. Additionally, there are many potential injection points near carbon dioxide generation sites. Currently, researchers are proposing a field study which would assess the sequestration potential of the Frio Sand. The Frio Sand is a sandstone-shale sequence that underlies much of the Texas Gulf Coast, including Harris County. This formation is non-hydrocarbon producing and is “sealed” from the other zones by the layers of non-porous shale (Figure 5). Other studies have estimated the potential sequestration capacity of this formation at 230 – 390 billion tons of carbon dioxide; thus this method could be utilized for sequestration of the entire carbon dioxide stream for Harris County. Based on piping the carbon dioxide from the closest collection point to pre-existing Frio injection wells (a distance of 12 miles), the linearized capital investment – flow rate function was estimated as $70,000,000 + 27.75×[flow rate (kg/hr)] for use in the mathematical model.

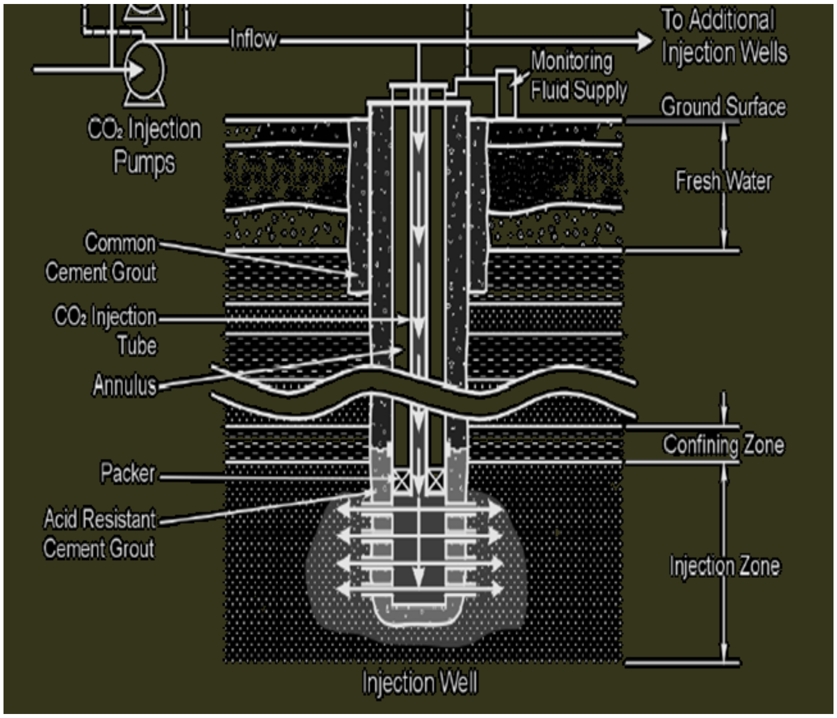

***Figure 5.*** *Process overview for brine aquifer injection*

## Planning Model

There are numerous choices to be made in this process:

- Which plants should capture and sequester $CO_2$
- Which method should be used to separate the $CO_2$
- Where to sequester the $CO_2$ so it is not released into the atmosphere
- Possibility of profit to offset costs from emissions trading

In order to simplify this decision-making process, a mathematical model was programmed into the General Algebraic Modeling System (GAMS). GAMS is an interface in which a mathematical model can be entered, and then the CPLEX solver was applied to find the optimal solution. The objective of the mathematical model was to determine the process configuration that has the lowest overall price increase of electricity.

Figure 6 shows a flow diagram of the program logic for the mathematical model. The boxes labeled 1-7 represent the seven plants that are being considered in the sequestration network. Each plant has the option to either vent their flue gas to the atmosphere or send it to separation methods A or B. Separation A is the packed tower absorption method and B is separation with $Ca(OH)_2$. The program has been written such that each plant can either use one method exclusively or a combination of the two methods. Once the $CO_2$ has been separated, it must be transported to a collection point. After the $CO_2$ has been collected, it is either sent on to its final sequestration location in a brine aquifer, or the $CO_2$ is sold for EOR.

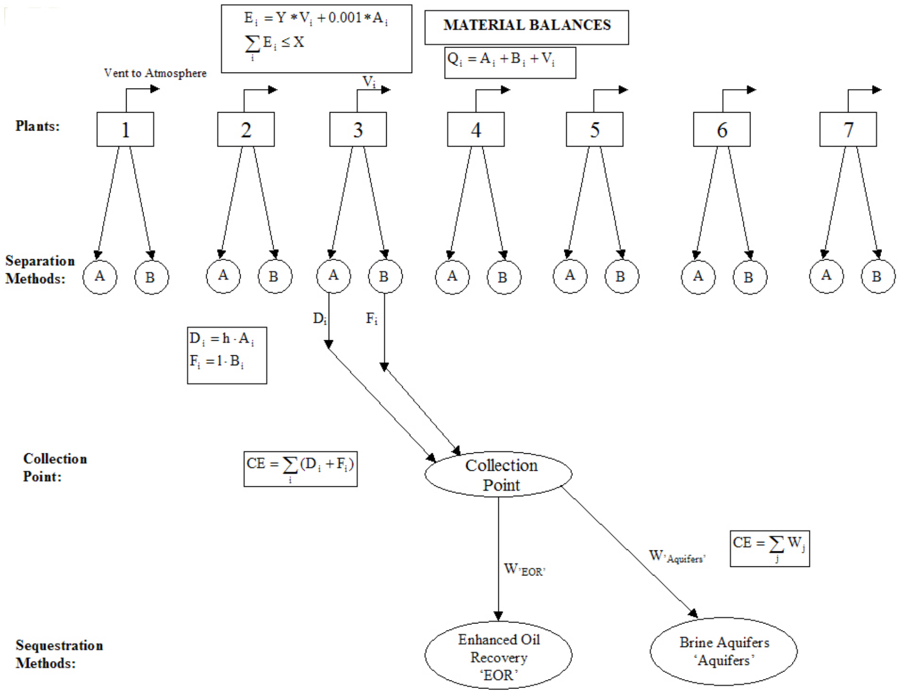

***Figure 6.*** *Flow Diagram for Mathematical Model*

If EOR is chosen, there is profit to the seven power plants in the sequestration network. The current price for $CO_2$ is \$35/ton. However, not all of the $CO_2$ that is separated can be sequestered in this method because the service companies that will use the $CO_2$ will not need all of it. For this reason, limits have been placed on $W'_{EOR}$' so that the supply of $CO_2$ will never exceed the demand for $CO_2$. The remaining $CO_2$ that is not sold will be sequestered in a brine aquifer.

## Emissions Trading

In the event that the seven power plants in the sequestration network exceed the government's required emissions reductions, they will be rewarded by the ability to sell their excess emissions. When the government reduces the amount of emissions allowed, each plant is given a certain number of Emission Reduction Credits (ERCs). Since currently there is not a program that provides for ERCs specifically for $CO_2$, the emissions trading for this project will be based on the assumption that the ERCs will be similar to programs that are currently in use to limit $NO_x$ emissions. According to the EPA, 1 ERC is the equivalent to the right to emit 1 metric ton of $NO_x$ emissions[3]. Therefore, for this project 1 ERC will be taken as the right to emit 1 metric ton of $CO_2$.

The main benefit of an emissions trading policy is that the power plants are encouraged to exceed the minimum required emissions reduction, therefore making the environment cleaner. The net result of the program is that for every 1 metric ton of extra $CO_2$ reduction that the power plants have, they sell 1 ERC, which offsets the cost of setting up the sequestration program.

The total annualized cost is then calculated by adding the capital cost with the transportation and operating costs and then subtracting the profit from the emissions trading program and the enhanced oil recovery. This total annualized cost is divided by the total capacity of all of the power plants to determine the amount by which the price of electricity will increase if this sequestration process is put into affect. The objective of the mathematical model is to minimize the price increase of electricity.

The mathematical model is used to consider several different levels of emissions reductions to be implemented steadily over the ten year life of the project. Figure 7 shows how the price of electricity is affected by the percentage of emissions reduction. The result is that 15% emissions reduction will be implemented over ten years.

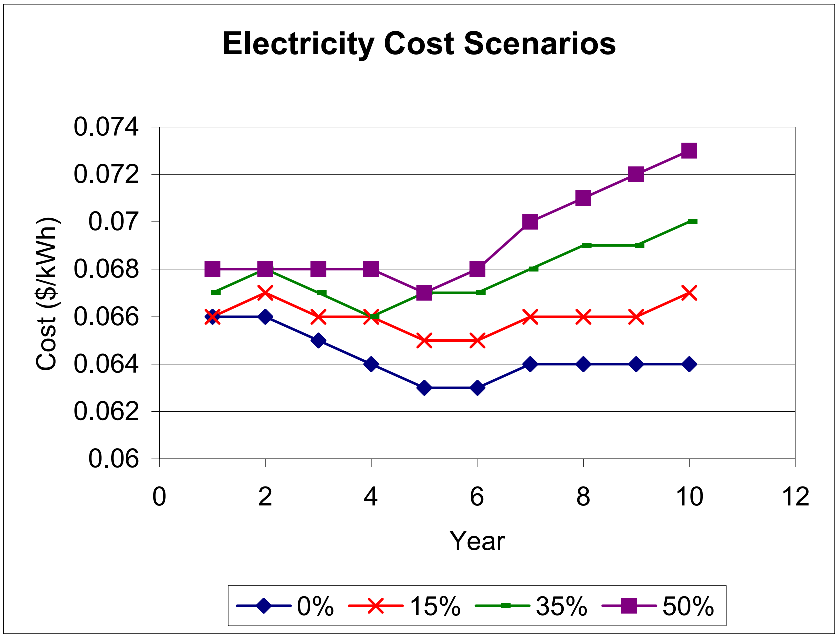

***Figure 7.*** *Emissions Reductions Scenarios*

The mathematical model is a powerful tool for evaluating the price estimates used for this project. A price sensitivity analysis was conducted for each of the major components of the project and it was found that the estimate that has the most impact on the result that the model gives is the calcium hydroxide separation process. Figure 8 shows how the total annualized cost for the entire project is affected by error in the price estimates for calcium hydroxide.

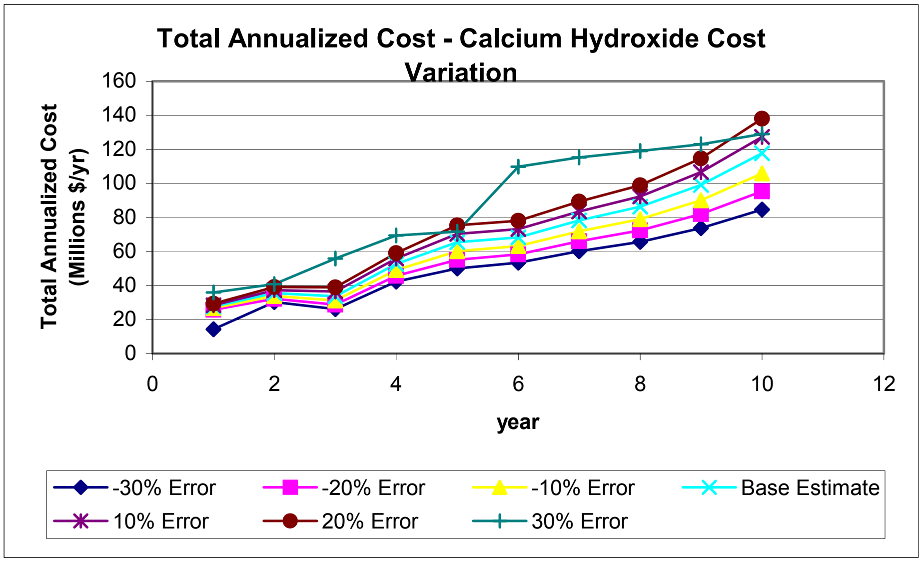

***Figure 8.*** *Price Sensitivity Analysis for* $Ca(OH)_2$

## Risk

In order to incorporate risk into the mathematical model, the variables with the greatest amount of risk are examined more closely. These variables are the price of electricity, the cost of an emissions reduction credit, and the cost of carbon dioxide. These values are forecasted by basing them all on the trend of electricity prices that is determined from forecasts provided by the energy information administration[4]. From these graphs, the average values and standard deviations are calculated. Then, assuming a normal distribution, several scenarios are generated within the mathematical model to simulate all of the possible market conditions that could result.

The result of the risk analysis is shown in Figure 9. From the graph it is seen that there is a slightly more than 25% probability that the total price increase of electricity over the ten year life of the project will be $0.014/kWh.

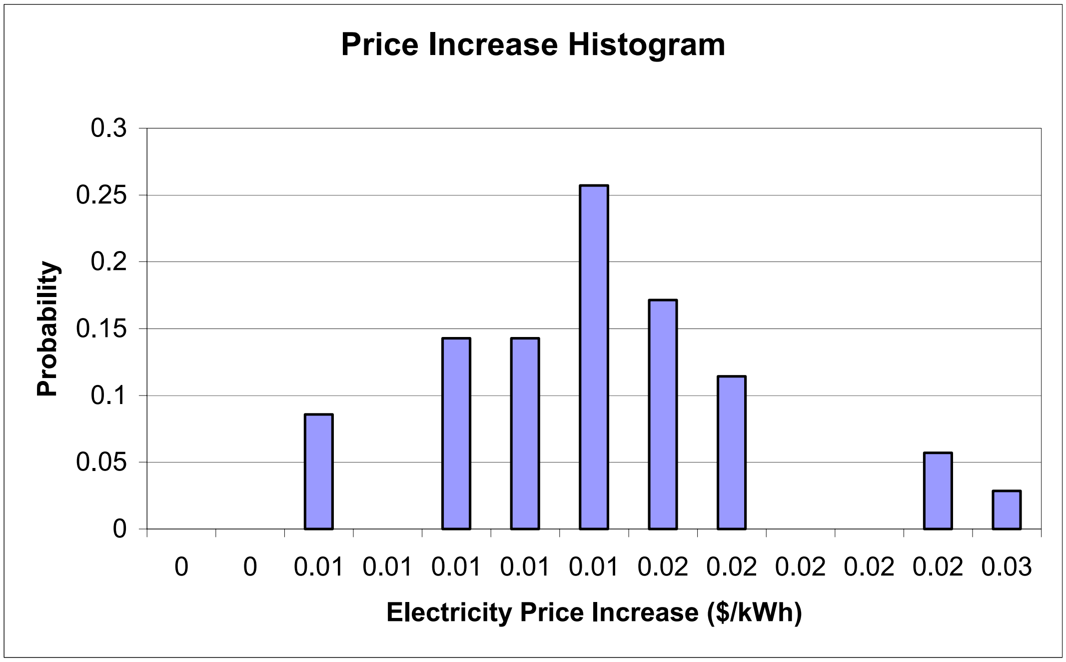

***Figure 9.*** *Results of Risk Analysis*

## Recommendations

The result of the risk model suggests the best possible actions to take given all of the possible market scenarios that could occur. The model suggests that a 15% reduction in emissions should be enforced over a period of ten years. The recommended separation method is Calcium hydroxide. Over the course of the project lifetime the amount of sequestered $CO_2$ from each power plant will vary each year with the goal of minimizing electricity cost increases. The recommended sequestration method is brine aquifers due to its large capacity. This project will improve the quality of the environment in Harris County with minimal impact to the consumers of electricity.

It should be noted that the process implemented to sequester $CO_{2.}$ Thus, it is necessary to determine the ratio of $CO_2$ generated to the $CO_2$ sequestered. The calculation is for a 15% reduction in emissions, since it is the highest level reached over the ten year life of the project. The calculations show that the fraction of $CO_2$ emitted to $CO_2$ sequestered is 0.21. This means that for every unit of $CO_2$ that is sequestered, a unit that is 21% of that is actually generated by the process. This can be translated into an “actual” $CO_2$ reduction that takes this generation into account. The result is that when the mathematical model says a 15% reduction has been achieved, in reality the total emissions have only been reduced by 12%.

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