

# **IPRO 302**

**CO<sub>2</sub> Mitigation: A Techno-Economic Assessment**

## **Final Report**

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**Illinois Institute of Technology**

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## 0.1 Introduction

IPRO 302 is an interdisciplinary team sponsored by Sargent & Lundy that is made up of students whose majors range from business to engineering and science. This semester, we have been investigating the possible solutions to collect and sequester the carbon dioxide that is generated from the combustion of coal in power plants. In addition to possible mitigation strategies, the current and future regulations regarding this issue have been studied.

## 0.2 Background

Since 1910, the Earth's temperature has been rising at a considerable rate. According to the World Meteorological Organization, the Earth's maximum temperature was attained in the 90's. Based on this and other pieces of evidence, there is a consensus between many scientists that global warming is a real problem. This increase is believed to come from carbon dioxide (CO<sub>2</sub>) emissions, as temperature has been rising since the invention of the auto-controlled steam engine. Coal, oil, and natural gas have powered our economies for years. Hydro-power and nuclear power are comparatively minor contributors to energy needs.

Whether or not CO<sub>2</sub> emissions are causing global warming is somewhat inconclusive, since the projected data from the models is not matching up with actual observations. In order to ascertain whether or not this is true, more conclusive research must be conducted. Despite this uncertainty, CO<sub>2</sub> emissions are believed by many to be a serious problem. Work is currently being done by both governmental bodies and private institutions to determine the best possible method to move forward with CO<sub>2</sub> mitigation. The U.S. Department of Energy has a target of 90% CO<sub>2</sub> sequestration at a cost increase of 30 percent or less of the cost of power plant electricity. By 2012, the cost increase should not be more than 10 %. Due to foreseen future governmental regulations of these emissions, the utility industry is also becoming interested in mitigating CO<sub>2</sub>. Sargent & Lundy, the sponsor for this IPRO, is currently working with the utility industry to formulate optimal CO<sub>2</sub> mitigation strategies. For more than 100 years, this company has provided comprehensive consulting, engineering, design, and analysis for electric power generation and power delivery projects worldwide.

The interest in mitigating CO<sub>2</sub> is fairly new, based on the potential environmental laws and problems. Over the past several years, there have been modifications to power plants, based on productivity and the price of upkeep. Currently, there are two integrated gasification combined cycle (IGCC) power plants in the United States, which are considered by many to represent an improved technology compared to the standard pulverized coal (PC) plants due to their higher efficiency. These IGCC plants also emit less carbon dioxide than a comparable PC plant.

There are two prominent issues regarding cost: the expense of modifying existing power plants and the problem of how to expand and adapt to the energy needs of this country in the next twenty to thirty years. Obviously, implementing a solution to reduce CO<sub>2</sub> emissions to every plant in America will be expensive. These additional costs may be passed on to consumers. The cost to implement such technology will have to be at the minimum point possible in order to have a robust energy industry.

The research that is conducted by IPRO 302 on such issues and mitigation strategies will be conveyed to Sargent & Lundy and will also be used to provide a basis for next semester's IPRO, which will design a power plant that includes CO<sub>2</sub> mitigation technology.

### 0.3 Purpose

The objective of this IPRO was to research and compile information on potential future CO<sub>2</sub> environmental regulations, current CO<sub>2</sub> mitigation technology, and CO<sub>2</sub> sequestration techniques. The results include an analysis of the items listed above as well as a high-level technical and economic comparison of the CO<sub>2</sub> mitigation technologies. This analysis was limited to coal-based power plants, either pulverized coal-fired or integrated gasification combined cycle. A future team will take the recommended mitigation technology for either the PC or IGCC plant and design a plant with this system.

### 0.4 Research Methodology

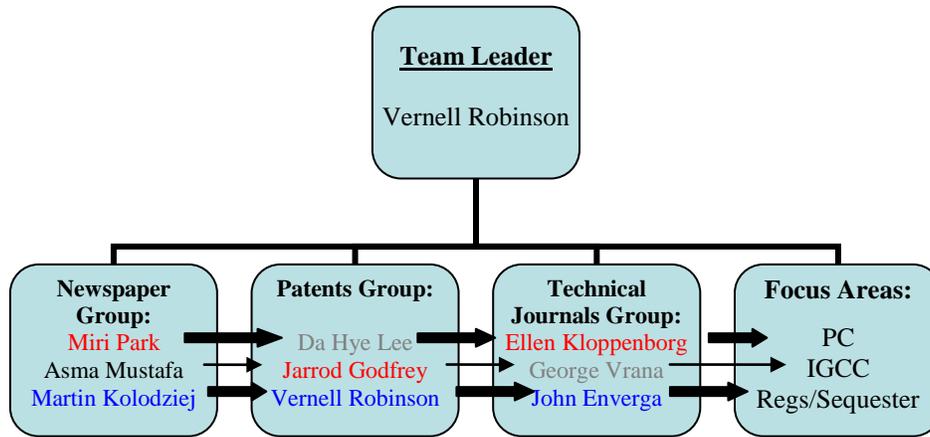
To accomplish the necessary research, the team broke up into three groups, each focused on a type of source: newspapers, patents, and technical journals. Within the source groups, each person focused on a particular topic, but did not limit their research to just that topic. Miri Park, Da Hye Lee, and Ellen Kloppenborg concentrated on the conventional pulverized coal-fired boiler approaches. Asma Mustafa, George Vrana, and Jarrod Godfrey looked at the integrated gasification combined cycle process. Martin Kolodziej, Vernell Robinson, and John Enverga studied the current and future regulations and sequestration techniques. Members reported on their topics to the group during full-class sessions. Additionally, students attended two smaller meetings to discuss the technology each week: one focused on their source type and the other on their focus area. Towards the end of the semester, the team also used the Department of Energy website for research on the different vendors for PC and IGCC mitigation technology.

### 0.5 Assignments

The IPRO group split into another set of sub teams in order to prepare the deliverables. The presentation team prepared the midterm and final presentations and the poster. The written report team wrote the project plan, midterm report, final report, and abstract. The ethics team attended the ethics workshop, presented this information to the whole group and led them in developing the code of ethics. These particular tasks were completed according to the schedule developed by the IPRO office.

Additionally, members volunteered for the additional tasks needed in order to successfully complete this project. Vernell Robinson was the team leader, created the meeting agendas, and made sure the meetings ran on schedule. Miri Park took meeting minutes, and Asma Mustafa compiled them. Jarrod Godfrey gathered all of the team members' schedules and arranged meetings using this information. Ellen Kloppenborg managed iGROUPS.

The team structure, Gantt chart, and a schedule of specific tasks, their duration, and the associated dates can be seen below.



Presentation team (Blue): John Enverga, Martin Kolodziej, Vernell Robinson  
 Written report team (Red): Jarrod Godfrey, Ellen Kloppenborg, Miri Park  
 Ethics team (Grey): Da Hye Lee, George Vrana

**Figure 1: Team Structure**

**Table 1: Task Schedule**

Task Name	Duration	Start	Finish
Read Ethics Book	41 days	Sat 9/1/07	Mon 10/1/07
Watch What's Up with the Weather Movie	10 days	Thu 9/6/07	Thu 9/13/07
Meeting Minutes	472 days	Tue 8/28/07	Wed 11/21/07
Project Plan	23 days	Mon 9/10/07	Fri 9/28/07
Code of Ethics	39 days	Mon 9/17/07	Wed 10/17/07
Midterm Written Report	19 days	Wed 10/3/07	Wed 10/17/07
Final Report	19 days	Fri 11/16/07	Fri 11/30/07
Abstract	19 days	Mon 11/12/07	Mon 11/26/07
Report for Sargent and Lundy	10 days	Fri 11/30/07	Fri 12/7/07
Midterm Oral Presentation	19 days	Mon 9/24/07	Mon 10/8/07
Preliminary Poster Review	10 days	Mon 10/8/07	Mon 10/15/07
Poster	19 days	Mon 11/12/07	Mon 11/26/07
Presentation	19 days	Thu 11/22/07	Mon 11/26/07
Ethics	1 day	Fri 9/14/07	Fri 9/14/07
Project Management	1 day	Sat 9/22/07	Sat 9/22/07
Project Plan	0 days	Fri 9/28/07	Fri 9/28/07
Code of Ethics	0 days	Wed 10/17/07	Wed 10/17/07
Midterm Written Report	0 days	Wed 10/17/07	Wed 10/17/07
Final Report	0 days	Fri 11/30/07	Fri 11/30/07
Abstract	0 days	Mon 11/26/07	Mon 11/26/07
Report for Sargent and Lundy	0 days	Fri 12/7/07	Fri 12/7/07
Midterm Oral Presentation	0 days	Mon 10/8/07	Mon 10/8/07
Poster	0 days	Mon 11/26/07	Mon 11/26/07
Presentation	0 days	Mon 11/26/07	Mon 11/26/07
Meeting Minutes	0 days	Fri 11/16/07	Fri 11/16/07
IPRO Day	0 days	Fri 11/30/07	Fri 11/30/07
iKnow Uploads	0 days	Fri 11/30/07	Fri 11/30/07

# IPRO 302 – CO<sub>2</sub> Mitigation: A Techno-Economic Assessment - Fall 2007

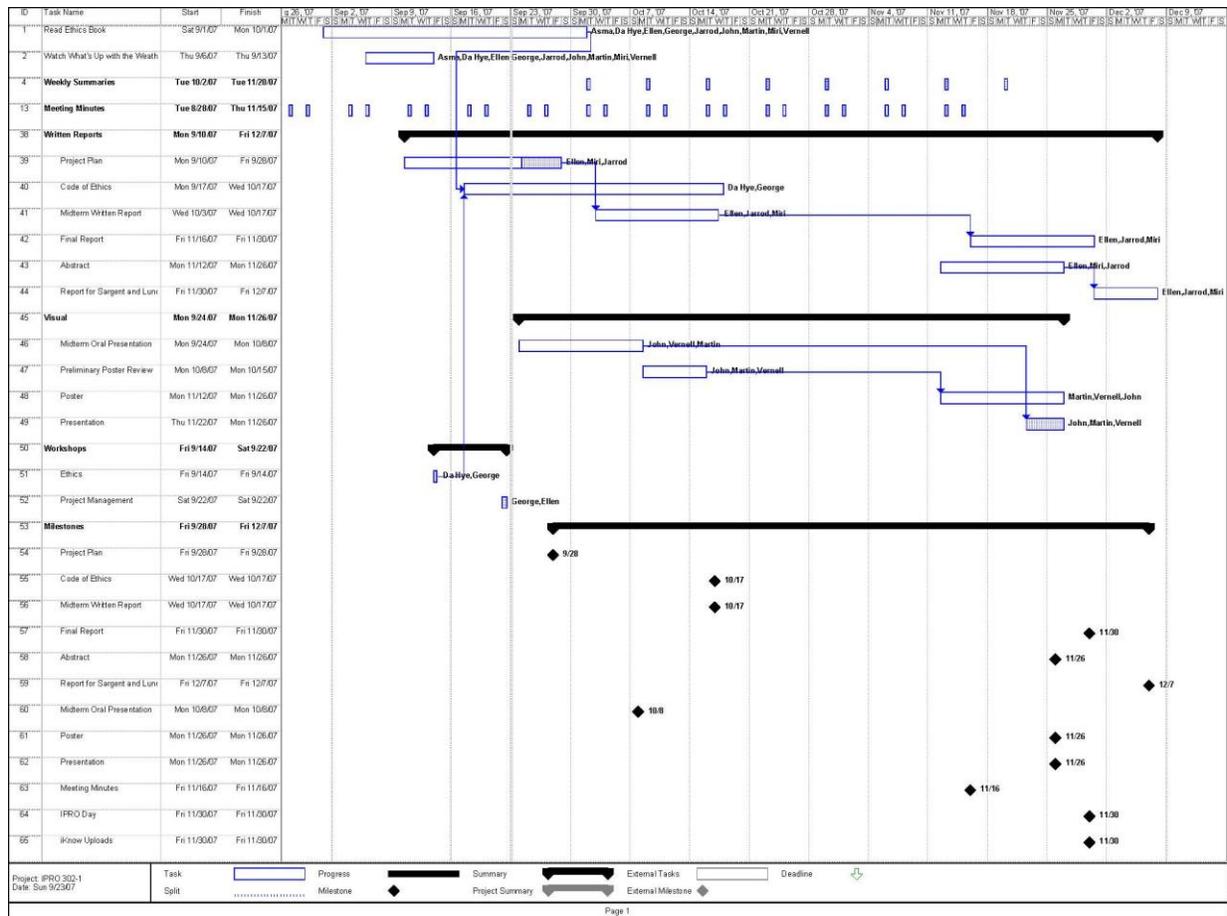


Figure 2: Gantt Chart

## 0.6 Learning Objectives

### Teamwork

IPRO 302 worked well as a team this semester. Often when tasks arose that were not previously foreseen, team members readily volunteered their aid in these assignments. The peer evaluation process helped members to appreciate each other skills. These evaluations were completed by all team members and included comments to specific members concerning individual growth potential. IPRO 302 members were encouraged to leave constructive feedback during this process and to recognize diligent efforts in team organization, communication, and task completion.

Very few problems regarding teamwork occurred throughout the project. In some cases, perhaps due to miscommunication or misunderstanding, individual subgroup meetings were not well attended. Fortunately, this potential problem had been foreseen and a master list of all team members' contact information had been formulated early in the initial project stage. Consequently, these cases were not significant as missing team-members could in most cases be reached by phone or email within the same day.

Having a three dimensional team structure enabled more overlap between team subgroups, encouraged further communication among team members, and encouraged the resolution of objections in a timely manner.

### **Communications**

In addition to the two regularly scheduled IPRO meeting sessions per week that all team members were asked to attend, team members also met with two of their subgroups weekly. Thus, much of the communications between team-members could be done in person. The three dimensional matrix team structure encouraged team members to communicate with other team members from different disciplines as well. Furthermore, effective use of email was used by all team members to direct appropriate research information to the respective research subgroup individuals. Members were continuously encouraged to not simply ignore other information during their research process that may be related to other segments of the project, or under the responsibility of another subgroup, but rather to forward it to the appropriate research parties or subgroup.

In most cases, communication problems, such as misunderstandings about regularly scheduled meeting times, were resolved promptly through direct communication with the involved parties. In order to avoid isolating specific individuals' misbehavior, general statements regarding the initial miscommunication were clarified to all team members during the follow-up team meetings.

### **Ethical Behavior**

Though the nature of the project was interesting, none of the team-members expressed an interest in obtaining employment from the sponsoring company. Due to this fact, there was no feeling of competition among team members trying to achieve superior appearances to the sponsor. Through the code of ethics preparation, this had been foreseen as a potential risk affecting the team. Fortunately, this was non-existent and team members were in fact very cooperative with each other. Team members were encouraged at all times to be honest and respectful towards other team members, regardless of their ethnic, cultural, religious and class differences. Because no ethical issues thus arose, there was no need for discussion of ethical issue resolution.

## 0.7 Obstacles

The magnitude of information available on the different technologies was difficult to sort through and organize. Team members had to learn to determine which information was current and relevant to the ultimate goal and objectives of the project. In order to break down the information and make it easier to understand we split the team into smaller sub teams comprised of three people. Sub teams met weekly to discuss findings, help each other discover which data is important, and aid one another in the information gathering process. By having each team-member span several sub-teams, communication and situational awareness were further enhanced among all team members. Representatives from Sargent & Lundy also helped alleviate some of this problem, by further defining the problem for us.

Additionally, members of the team came from different disciplines, which made it difficult to work as a combined effort because of different approaches to solving problems within the

project. This project introduced several key concepts that deal with mechanical and chemical engineering that were foreign to several team members because of their different backgrounds; understanding and comprehending these key concepts were barriers for members, but additional time spent studying has helped to lessen them.

Unexpected personal issues presented additional obstacles in this project and could not have been avoided. Team members filled in for others while they were dealing with such difficulties.

## 0.8 Results

### **Regulations**

Due to the concern about CO<sub>2</sub> emissions, regulatory requirements are being designed to limit the amount of this gas that can be released into the atmosphere. This is a major issue for the power industry, since coal-fired power plants emit much CO<sub>2</sub> and would require major changes in order to lessen this amount. The current regulations, as well as predicted future ones, were studied in order to determine the limits on the amount of CO<sub>2</sub> which could be emitted. This amount affects how much of a change in power plants would be needed.

### **Current Regulations**

Concerns regarding carbon dioxide mitigation laws are becoming the subject of many more political discussions than ever before. The subject is strongly making its way into the main stream and is capturing the attention of lawmakers and politicians, as well as investors and power generation companies. The political stage is still divided, however, and currently there are no federal laws effecting CO<sub>2</sub> containment. Many states are taking CO<sub>2</sub> mitigation issues into their own hands, while the presidential administration is still uncertain and opposes these mandatory changes. Because of this hesitation, the United States is falling farther behind other countries which have demonstrated leadership positions for the global cause of lessening the adverse effects of CO<sub>2</sub> increase in our atmosphere.

In the United States, New York and California, two of the most active states, have actually made future greenhouse gas cuts legally binding. So far 29 states have at least made plans to take aim in some way on CO<sub>2</sub> reduction due to burning fossil fuels. Starting in 2009, New York plans to auction credits that allow plants to emit limited amount of CO<sub>2</sub> each year. In 2015 the program would cut emissions by 10% by reducing amount of such credits available. This program would affect coal power plants the most, as they account for double the CO<sub>2</sub> emissions of natural gas. In addition the governor of New York announced a plan this year to cut electrical consumption by 2015 through increased efficiency standards. Three states including California, New Jersey and Hawaii went even further and put targeted statewide CO<sub>2</sub> reduction into laws that future administrations will have to meet. New Jersey's law mandates a cut to 1990 levels by 2020 and a cut by 2050 of 80% of the current 2007 levels. California and Hawaii's laws require cuts to 1990 levels by 2020. Additionally, California's law requires that a plan to reach this goal be in place by 2011. However, a state-by-state approach cannot take the place of federal laws, which are unlikely during this presidency.

The current and future regulations will gain more sophistication as additional research and testing is completed. As more possible ways to approach and solve this problem are found,

further strict regulations will follow. Current regulations are thought to forecast a good image of future laws regarding CO<sub>2</sub> mitigation.

### **Federal Legislation**

There are many reasons as to why there is not enough incentive to pass federal laws regarding CO<sub>2</sub> regulation. They can roughly be split into a few categories: preservation of self-interests, beliefs about global warming and its effects, and the risks, uncertainty, and other side-effects involved with reducing CO<sub>2</sub> emissions.

The self-interests being considered are those of the energy companies, the main source of carbon emissions. These companies are very large, important and influential, so they are able to have a voice in the federal government through members of Congress who support their agenda. Thus, bills about CO<sub>2</sub> regulations have something going against them in the form of congressmen who may vote based on the desires of their major constituents.

Opponents of CO<sub>2</sub> regulation try to sell the fact that there is no human-caused global warming, or if there is, then the results of the phenomenon are beneficial to humanity. Some of these people may refer to various scientists' theories, which say that global warming is a natural process independent of human activity and could be part of a warming/cooling cycle that has been present on Earth since the planet's formation. Therefore, they conclude that reducing CO<sub>2</sub> emissions would have no effect on the temperature change that the Earth is having.

Other regulation opponents may say that there is no warming whatsoever, and that the temperature change is very gradual, if not non-existent. Some even make appeals to emotion and point out that global warming is good, since most people enjoy warmer weather anyway!

In addition to the agendas of energy companies, the public in general does not seem convinced that global warming exists. Because the climate and environmental change on Earth due to global warming is a gradual process, some feel that the effects are non-existent, despite evidence pointing to the contrary (melting ice caps and possible flooding of low-elevation coastal cities). These skeptics say the same hot summers and cold winters occur year after year with very little change. Overall, the general apathy towards global warming has made it very hard for CO<sub>2</sub> regulations to be approved by both Capitol Hill and the White House.

Even for people who do (mildly) believe in global warming, opposition to CO<sub>2</sub> regulation comes in the form of the risks and uncertainty in regulating CO<sub>2</sub> emission. Most CO<sub>2</sub> mitigation technologies have yet to be tested on a wide, national-level scale. The U.S. is still too reliant on current energy technologies, and it is natural to expect that some would be resistant to change.

All CO<sub>2</sub> mitigation technologies have another side-effect that the public may not like: taxes. Many of these technologies are very costly to construct and maintain, and they will inevitably rely on governmental funding. This means that taxes may be increased in order to provide for this funding. Naturally, this idea does not go over well with people.

## **Coal-Fired Power Plants**

Pulverized coal-fired (PC) power plants provide much energy in the United States, but also generate much carbon dioxide. Based on these potential future regulations, work is being done in two major ways to reduce emissions: building efficient plant designs, such as supercritical, ultrasupercritical, and integrated gasification/combined cycle (IGCC) power plants and developing technology that can be added on to the existing plant design in order to separate and collect the CO<sub>2</sub> that is produced.

For PC plants, the technologies necessary for CO<sub>2</sub> capture and sequestration are mature and have been in operation for more than 30 years. CO<sub>2</sub> removal using amines has been around for more than 65 years, with commercial plants first built in the early 1980's. These plants were able to remove 1,200 tons/day of carbon dioxide, and since mid 1990's plants have been able to remove 3,000 tons/day. Increasing this amount to 10,000 tons/day, the amount produced by a 500 MW PC plant, should be achievable.

There are also several new technologies being developed for pulverized coal-fired power plants in order to remove the carbon dioxide before it reaches the stack. One big advantage to using one of these systems is that existing power plants can be retrofitted with them. The four main types of CO<sub>2</sub> removal technologies are absorption, adsorption, membrane separation, and cryogenic processes. Right now, chemical absorption is the most economically viable. However, the addition of these systems does add about 85% to the capital cost of the plant.

IGCC power plants differ from standard PC plants, providing much cleaner energy with reduced emissions. Within the gasification stage of the plant, synthetic gas is produced by breaking down coal with the aid of heat, pressure, pure oxygen and water. Since most of the particulate can be captured in this phase, it produces clean gas which in turn lowers CO<sub>2</sub> emissions. The synthetic gas is then used to power the turbine-generator set. Excess heat is also captured throughout the plant creating steam to power a second generator. Additionally, part of the slipstream can be used in a Fischer-Tropsch process to produce additional chemicals, the sale of which provides added profit.

Although there are only two operational IGCC power plants in use in the United States today, there are future plans to invest in this technology. The U.S Department of Energy is investing one billion dollars in order to run a future generation program that aims to build and test IGCC plant technologies for the next 10 years. A near-term goal for IGCC is the construction of a 275MW demonstration and validation plant by 2008. The capital cost is \$1000/KW and zero HHV emission is targeted. A long term goal is the design of a commercial plant by 2015 for fuel cell gas turbine hybrid. This plant would have a capital cost of 850/KW, run at 65% efficiency, produce zero emissions, and contain a sequestration option.

Adding CO<sub>2</sub> mitigation technology to IGCC plants is not cheap. Capital costs increase by approximately a third with this technology.

There are many ways being studied to enhance the performance of IGCC. One project plans to enhance the performance of the IGCC by developing the F-class gas turbine to run on synthetic (syn) gas. Another aims to produce syn gas composed of H<sub>2</sub> and CO. A reaction of the syn gas

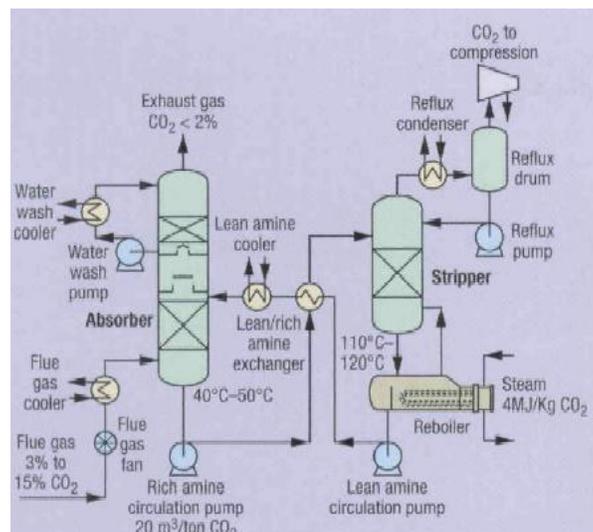
and steam will produce additional amounts of H<sub>2</sub> and CO<sub>2</sub> for capture and storage. The initial target is to capture 90% with the goal of raising the target to 100%.

## CO<sub>2</sub> Removal Solvents

Within both PC and IGCC power plants, solvents are the means of removing the CO<sub>2</sub> from the flue gas stream. Amines, a form of chemical solvent, are most commonly used for PC plants, and Selexol, a physical solvent, is most commonly used for IGCC plants. Rectisol is also used in power plants.

### Amines

In an amine process, the flue gas is compressed to around 1.3 bar (sometimes 5 bar) and cooled to about 50 °C in order to increase the CO<sub>2</sub> capture rate. It enters the packed column absorber at the bottom and then contacts the amine in countercurrent flow. Amines are bases and react with the carbon dioxide, an acid, to form a water soluble salt. The exhaust gas from this process usually leaves the absorber with less than two percent CO<sub>2</sub> content. A water wash system is used at the top of the absorber to minimize the amount of amine that is carried out with the exhaust flue gas. The amine containing CO<sub>2</sub> is pumped from the bottom of the absorber through a lean/rich heat exchanger to a packed column stripper. Heat is then applied, separating the CO<sub>2</sub> and the sorbent. The evaporated sorbent, water vapor, oxygen and carbon dioxide leave the top of the stripper, where the water and sorbent are condensed and accumulated in a reflux drum. From there, they will be sent back to the top of the stripper column. The CO<sub>2</sub> leaves the top of the reflux drum at a pressure of about 4.25 psig. This is much less than what is needed for storage and use, so compression is needed.



**Figure 3: Diagram of an amine removal system**

There are various amines being used for this process, which can have primary, secondary, or tertiary structures. Primary and secondary amines are faster than tertiary amines at removing carbon dioxide, but are more corrosive and have the capacity to absorb CO<sub>2</sub> at the ratio of a half mole of CO<sub>2</sub> per mole of amine. Tertiary amines are capable of absorbing up to one mole of CO<sub>2</sub> per mole of amine and require less energy to regenerate after the reaction. This amount of

energy is very important, since up to seventy percent of the total operating costs in a carbon dioxide capture plant can come from the energy needed to regenerate the amine.

Monoethanolamine (MEA) and diethanolamine (DEA) are the most commonly used primary and secondary amines, and methanol diethanolamine (MDEA) is the tertiary amine that is found most frequently. MEA is the cheapest alkanolamine at around \$1 per ton of CO<sub>2</sub>. It is usually used in an aqueous solution that has a concentration between 15 and 30 percent.

Testing has been done on other amines, including ethyl ethanolamine (EEA), ethylene diamine (EDA), and diethyl monoethanolamine (DMEA), as well as combinations of primary/secondary amines and tertiary amines to see if they would be better at CO<sub>2</sub> removal than the currently used reactants. One study found EDA to be very promising, since it was faster and could absorb more CO<sub>2</sub> than MEA. EEA and DMEA also may work well for this process. The combination of MEA and MDEA lowered the amount of CO<sub>2</sub> that was absorbed, and the same amount of energy was found to be needed for regeneration of the amine. This result is believed to be due to the harsh environmental conditions in a coal-fired power plant. The conditions in the power plant, particularly the sulfur compounds that form, can also cause the amines to degrade. MEA was found to degrade at 0.5 mole percent per day. Degradation rates were even higher in the combined MEA and MDEA reaction. Sterically hindered amines, which are chemically modified, are also being tested. They slow down the reaction rate with the amine, produce an unstable intermediate carbonate solution, increase the CO<sub>2</sub> loading, and decrease the amount of energy needed for regeneration.

Very high energy requirements, solvent losses due to flooding, deactivation of amines, and the production of CO<sub>2</sub> during the solvent regeneration process are problems with the technology utilizing a chemical absorption in a liquid solvent. The steam regeneration done in the stripper requires between four and six MJ/kg of recovered carbon dioxide, and the production of that steam produces additional CO<sub>2</sub> if it is obtained through a fossil fuel combustion process.

### Rectisol

Rectisol is an acid gas removal process that was developed by Linde and Lurgi. Methanol is used as the solvent in this process that removes acid gases, which include hydrogen sulfide and carbon dioxide, from the feed gas. The Rectisol process is useful at removing trace contaminants, like ammonia from the gases. Advantages to it include a relatively low utility consumption, flexibility in configuration, and a cheap, readily available solvent. Below, a basic diagram of this process can be seen.

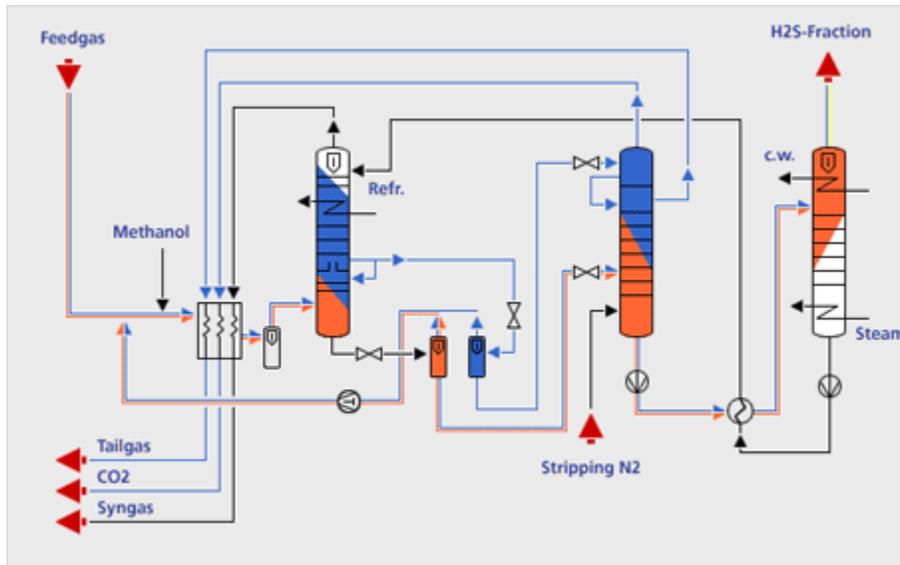


Figure 4: Diagram of a Rectisol System

### Selexol

Selexol is an acid gas removal solvent that is licensed by UOP. The physical solvent used is made of a dimethyl ether of polyethylene glycol and is capable of removing hydrogen sulfide and carbon dioxide from the feed gas stream, as well as mercaptans, ammonia, HCN, COS, and metal carbonyls. Feed conditions for the Selexol process range from 300 to 2000 psia, and the partial pressures of the acid gases drive the process. Selexol is used in more than fifty units, and the process has been employed for over thirty years.

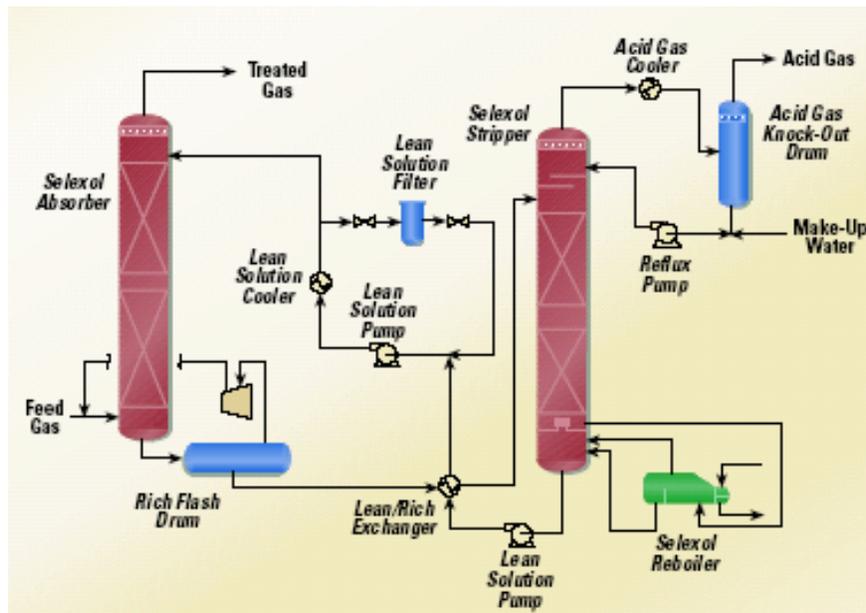


Figure 5: Diagram of the Selexol Process

## **Membrane Separation Technology**

Solvents are the main way of separating CO<sub>2</sub> from the flue gas, but work is being done to determine other methods to accomplish this. A new technology that is still in its early stages of applicability to IGCC is membrane separation. Membrane separation has advantages over liquid-gas absorption technologies: clean operation, smaller size, simplicity in operation and maintenance, and compatibility with different plant designs. Other studies have suggested that efficiency can be increased and costs reduced to physical absorption by using the membrane technology. However, these studies are based on a technology that is still in its preliminary stages.

Polymer-based membranes have properties that can reduce CO<sub>2</sub> to fifty-percent purity; however, the efficiency notably decreases when CO<sub>2</sub> purity requirements rise. Polymeric membrane technology also has several other limitations including limited selectivity, poor flux in comparison to other membrane materials. The stability of polymers is affected by high temperature, making it not feasible for plants with high temperature gas limitations. Although ceramic membranes could be used in high temperatures, this would require higher initial capital costs.

Since CO<sub>2</sub> purity is lower in a single stage of separation, examination of multiple stages were conducted. Studies of low temperature separation with polymeric membranes in combination with high temperature separation with ceramic membranes proved that the technology was feasible, but the result was an energy change between eight and fourteen percent depending on the staging and pressure.

Other studies have been performed to show efficiency of metallic based membranes. Studies showed that these membranes are 1.7 percent more efficient than industry standard absorption plants such as Selexol or Pressure Swing Absorption (PSA); other economic aspects were not considered in these studies. Metallic membrane technology does have its disadvantages, such as the high cost due to the metallic film and reduced H<sub>2</sub> permeation and selectivity due to deactivation of the metal by H<sub>2</sub>S. An exciting notion of this technology is reducing the overall stage from two stages involving carbon separation and the water-gas shift and absorption-stripping into one smaller stage of membrane reactor (MR) technology. Since plants can save costs by removing a large absorption unit, the higher material costs involved in MR technology will be offset. It should be noted that metallic membrane technology also requires additional heat exchanges to provide a sweep-gas stream of precise temperature that produces an optimal reaction.

As the diagram shows, a thin tubular membrane of Pd-Ag alloy filled with a packed catalyst is enclosed in another steel tubular frame. The entry and exit ports located on the tubular frame let in sweep gas and let out permeate gas. Steam and CO are primarily in the sweep gas phase, and mostly hydrogen and CO<sub>2</sub> are in the permeating gas phase.

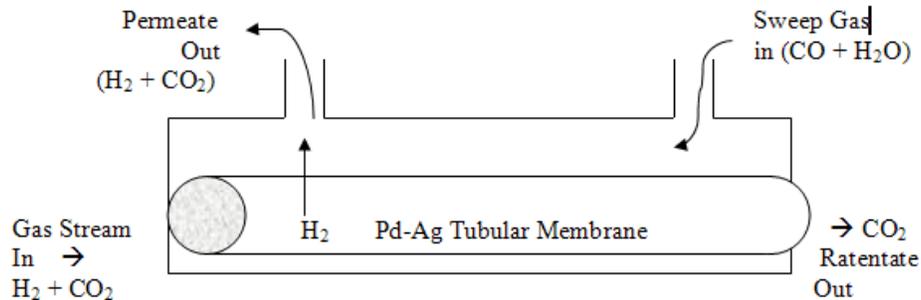


Figure 6: Diagram of Counter-flow Membrane Reactor

The water-gas shift reaction and CO<sub>2</sub> separation are obtained through the palladium-based reactor. Hot steam and carbon monoxide, which make up sweep gas, are compressed to 11.5 bar, and then fed into the outer steel tube where the water-gas shift (WGS) reaction is applied. Once the WGS process has been applied, hydrogen, carbon dioxide and steam remain. The water content is then removed through a condensation stage, and heat energy is transformed into more incoming sweep gas through an exchange stage. Cooler dry gas is fed into the inner Pd-Ag tubular membrane where H<sub>2</sub> gas diffuses through the membrane in turn, leaving CO<sub>2</sub>. CO<sub>2</sub> is further filtered through the tubular membrane with a packed catalyst. The hydrogen can be permeated across the membrane by increasing the sweep gas and further enhanced by optimizing the partial pressure profiles in the reactor. Disadvantages still exist within the design, including the greater reduction of net power from 9.4 percent to 12.5 percent, which occurs because thermal power is need to produce steam from the cycle in order to use sweep gas, which lowers steam efficiency. Yet another disadvantage is the need for higher compression in order to liquefy CO<sub>2</sub> from the membrane reactor. After calculating everything that is needed to run a proficient palladium membrane system, it would cost around \$61.20/MWh versus \$54-\$79/MWh for basic IGCC systems.

An International Panel on Climate Change report has considered gas permeation membranes inappropriate. Reasons why membranes are often rejected include: their high energy requirement, limited resistance of polymers to high temperatures, sensitivity to clogging, inadequacy for high feed flow rates, and too low selectivity. It has been noted that the temperature issue can be ignored, since flue gas is usually cooled to 40 – 60 °C in order to increase absorption efficiency. Recently, membranes have been used with flow rates of about 1,000 metric tons/day in natural gas applications.

The energy needed for membranes is larger at a 10 % concentration of CO<sub>2</sub>, and can start to compete at 20 %. The membrane selectivity needed for the 20 % concentration is about 60, and some membranes have achieved this level. If vacuum pumping is done instead of compression with a 20 % concentration, the energy required drops drastically to 0.75 MJ/kg of recovered CO<sub>2</sub>. This amount is close to the best absorption situations. Vacuum operation is not generally used in industry, however, because it takes up much more space than pumps and is less efficient.

### **Turbine Technology for Coal-Fired Power Plants**

Another key portion of the power plant, particularly in IGCC systems is the turbine. General Electric and Siemens are the two main vendors for this technology.

### GE H-Turbine Systems

GE has developed innovative solutions to address most of the problems associated with synthesis fuel combustion in their gas turbines. To deal with the increased operating temperatures associated with using hydrogen as fuel, GE demonstrates that the steam reheat process of the plant can be combined with the gas turbine bucket and nozzle cooling on the gas turbine itself. This allows the generator to operate at a much higher firing temperature, thereby increasing the fuel-efficiency up to two percentage points, to a total of 60%. In addition, the GE *H-System*<sup>TM</sup> design process follows the strict guidelines of “Design for Sigma Six” methodology, ensuring that all components meet the highest standards of quality, excellence, and customer satisfaction. General Electric has also determined that NO<sub>x</sub> emissions can be minimized by lowering the combustion temperature as much as possible and by raising the firing temperature to the safest possible limit. In most gas turbine designs predating the *H-System*, the stage 1 nozzle is cooled with compressor discharge air. In the *H-System* design however, the stage 1 nozzle is cooled with closed-loop steam cooling. This process reduces the temperature drop across the stage 1 nozzle to less than 80°F, allowing firing temperatures as high as 2600°F, a full 200° F higher than in previous designs. The *H-System* also combines advanced materials technologies, such as thermal-barrier coatings and single-crystal super-alloy stage 1 nozzle and bucket. With a higher turbine compression ratio of 23:1, the GE *H-System* also incorporates advanced control systems that continuously monitor turbine diagnostics, and facilitate user operation. To ensure that hydrogen-rich syngas is properly mixed with airflow, the turbines use advanced fuel injectors which use swirled vanes to impart rotation to the admitted airflow. This also minimizes flashback and flameholding. Lower emissions over the entire load range are also achieved through the use of staged combustion modes: diffusion, piloted premix, and full-premix modes.

Under development since 1992 with the support of the U.S. Department of Energy, the *H-System* actually combines three processes that were previously independently engineered: the gas turbine itself, a three-pressure-level Heat Recovery Steam Generator (HRSG), and a reheat steam turbine. GE believes that by engineering the components together, they can more accurately maximize efficiency while reducing the footprint or size of the production unit. It also allows them to more accurately model and design in order to manage undesirable conditions such as transient ones which occur during startup and shutdown.

### Siemens F-class turbines

The Siemens Hydrogen Turbine Development program is working closely with the Department of Energy FutureGen program to develop a gas turbine capable of operating reliably with hydrogen and syngas. Siemens is modifying the proven SGT6-5000F design to endure added stresses of syngas and hydrogen fuels. A major challenge to designers is that in combustion, the hydrogen flame speed is significantly higher than that of natural gas. As such, an advanced hydrogen gas turbine will need to be able to withstand increased firing temperatures, higher pressure ratios, steam as well as increased mass flow rates.

In order to avoid expected performance loss and leakage due to the higher pressures involved in a hydrogen gas turbine, designers need to develop advanced technologies to withstand increased moisture content, and increased thermal load on airfoils. This requires developing advanced materials that offer superior cooling, alloy strength and bond-coat performance such as Ceramic Matrix Composites (CMCs), low conductivity thermal barrier coatings (TBCs) and advanced alloy castings. The hydrogen turbine blades and vanes themselves will have highly effective turbine airfoil cooling schemes such as dimples, fins, impingement jets, cylindrical film holes, and trailing edge ejection holes.

Siemens has also developed advanced control mechanisms to ensure superior mechanical integrity. These include a plenitude of advanced sensors for fast response fuel monitoring to improve combustion stability. Many temperature sensors will continuously monitor factors such as turbine inlet temperature, gas path temperature, and infrared temperature measurements of thermal barrier coating integrity on rotating blades. Furthermore, an impressive array of engine health monitoring devices are employed for robust, reliable control such as embedded sensors to measure strain, temperature, acoustics, debris detection, and vibration.

Current Siemens gas turbines including the popular W501G, already use such advanced technologies such as TBCs, single crystal turbine blades, advanced brush seals, closed-loop steam cooling, and advanced firing patterns for reduced emissions.

## Vendors

The major vendors who have implemented these technologies into systems for PC plants are: Alstom, Fluor, MHI, and Powerspan. IGCC systems have been developed by ConocoPhillips, General Electric, MHI, Shell, and Siemens.

## Pulverized Coal-Fired Plants

### Alstom

Alstom’s supercritical system uses a MEA solution as its solvent. With a 90% capture rate, it is 24.5 % efficient. For a power plant producing a net power output of 303 MW, the total investment cost for the system would be about \$400 million, or \$1,319/kW. Regeneration for this system requires approximately 3.6 MJ/metric ton of CO<sub>2</sub>. Operation and maintenance costs are therefore estimated at approximately \$20 million per year. The amount of CO<sub>2</sub> captured is around 680,000 pounds per hour, and the mitigation cost has been calculated to be \$81/ton. Alstom has designed a 5 MW, 90% capture pilot plant in Wisconsin to test its chilled-ammonia system. This pilot plant was scheduled to open in 2007.

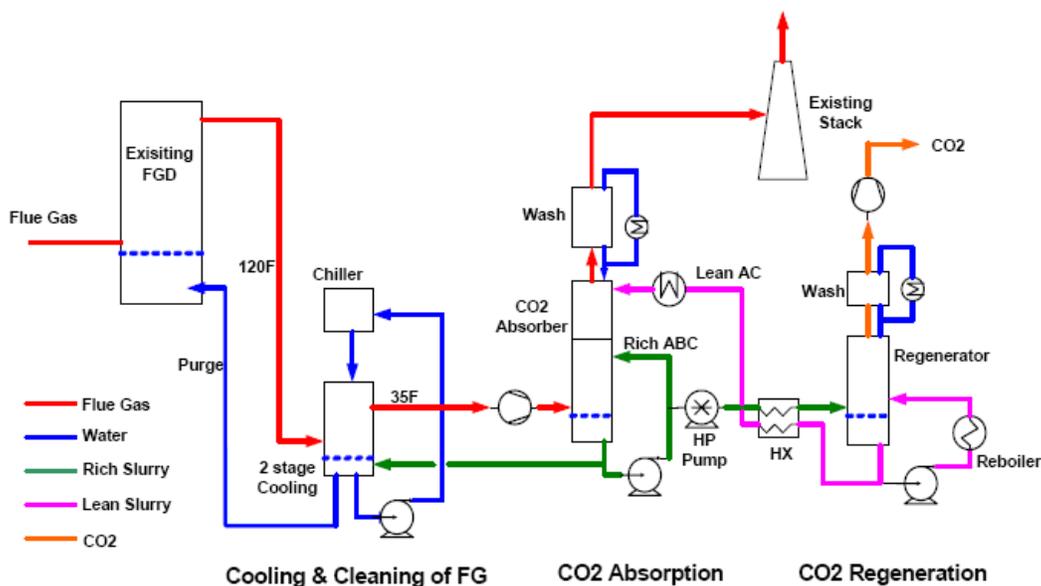


Figure 7: Alstom’s CO<sub>2</sub> removal system

### Fluor

Fluor has designed the Ecoamine FG Plus Technology to remove CO<sub>2</sub> from PC plant flue gas streams. A 30 wt% inhibited MEA solution is used for the Ecoamine process.

This system is thought to be advantageous over a standard systems using MEA because reaction rates are increased, more CO<sub>2</sub> can be absorbed by the amine, and less steam is needed for stripping, due to a split flow configuration, and integrated steam generation.

An economic evaluation of Ecoamine FG Plus Technology has been conducted by the National Energy Technology Laboratory. A system with this technology is compared to one without CO<sub>2</sub> capture, which contains a double-reheat supercritical steam turbine (3,500 psig/1050°F/1050°F) and a selective catalytic reduction unit. Staged combustion for low NO<sub>x</sub> formation is used in the coal-fired boiler, and SO<sub>2</sub> emissions are limited by use of a wet limestone forced oxidation flue gas desulfurizer. The base system has a gross power output of 425 MW of electricity and is 41 percent efficient. Evaluation is done assuming 400 MW of net power generation, an 80% capacity factor and Illinois #6 bituminous coal. A Ecoamine FG Plus system that captures 90 % of CO<sub>2</sub>, compresses it to 2,200 psia, transports it ten miles and stores it in a saline aquifer was estimated to increase the cost of electricity 48% over the base cost and cost \$31/metric ton of CO<sub>2</sub> avoided. A plant with such a system is 30 percent efficient and would require a 44.7 percent increase in capital costs.

A study, done in 2007 dollars, compares supercritical and ultrasupercritical PC plants with carbon capture. Turbines were 3500psig/1110°F/1150°F and 4000psig/1350°F/1400°F. The economic life of the plant is taken to be twenty years, the capacity factor is 85%, and the carbon dioxide is transported fifty miles and stored in a saline formation. The gross power for the supercritical case is 667 MW, and ends up as a net 549 KW. For the ultrasupercritical case, gross power is 650 MW and net power is 545 MW. The efficiency for the supercritical case is 27.2 % and 32.1 % for the ultrasupercritical case. An energy penalty, which is the percentage decreased in net power plant efficiency due to the capture of carbon dioxide compared to the plant without carbon capture, was found to be 12.2 % for supercritical and 7.4 % for ultrasupercritical. The total plant cost of energy, including capital, production, transportation, storage, and monitoring would be 11.44 cents/KWh for the supercritical plant and 10.98 cents/KWh for the ultrasupercritical plant. These are a cost of 5.15 and 4.69 cents/KWh greater than the plants without carbon capture. The supercritical plant costs \$68 per ton of CO<sub>2</sub> avoided, and the ultrasupercritical one costs \$75 per ton of CO<sub>2</sub> avoided. Total plant cost will be approximately \$2,900/kW.

An additional 2007 study compared a subcritical case (2,400 psig/1050°F/1050°F) and a supercritical case (3500 psig/1100°F/1100°F). Without carbon capture, the efficiency is about 37 percent for the subcritical and 39 percent for the supercritical and the gross rating is 580MW. A gross output of about 670 MW is needed by the plants with carbon capture to achieve approximately the same net output. Subcritical plants with carbon capture were approximately 25 percent efficient and supercritical ones were approximately 27 % efficient. CO<sub>2</sub> capture was compressed to 15.3 MPa and transported fifty miles to a saline aquifer. Calculated costs include transportation, storage, and monitoring. Plant costs increased by approximately 85 percent for both subcritical and supercritical conditions, and capital costs were approximately \$2,900/kW for both. For a levelized cost over 20 years, the cost of CO<sub>2</sub> avoided was about \$68/ton. With 90% CO<sub>2</sub> capture, 5,125,716 tons per year will be collected using the supercritical plant and 4,646,790 tons will be collected from the ultrasupercritical plant.

This process was originally designed by Dow Chemical and called GAS/SPEC FT-1, before it was bought by Fluor Daniel in 1989. It was used with natural gas and fuel-oil derived flue gas for commercial plants sizes of between 6 and 1000 metric tons per day mainly in the 1980's, collecting the CO<sub>2</sub> for enhanced oil recovery. When crude oil prices collapsed, many of the plants were shut down. Over the past three decades, twenty-one commercial plants have been built, ten of which have had capacities over 60 metric tons per day. Eight of these ten are still operating, and seven of them operate on flue gas from natural gas. Pilot plant scale testing has been done for coal-based flue gas.

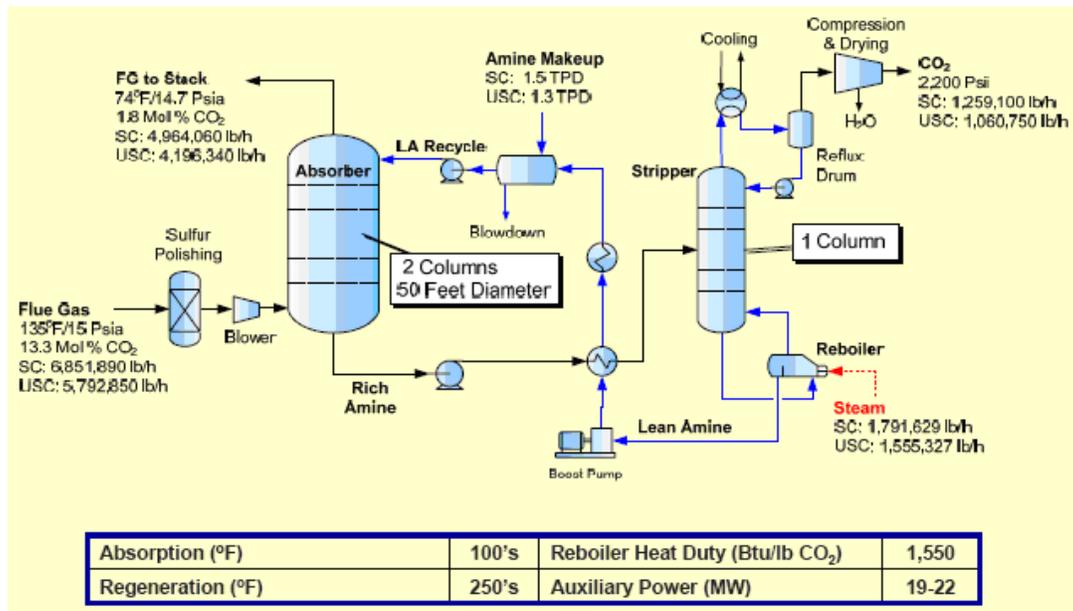


Figure 8: Fluor's Ecoamine CO<sub>2</sub> Removal Process

### Mitsubishi

Together with Kansai Electric Power Co., MHI has developed technology for recovering CO<sub>2</sub> using the solvent KS-1. In comparison with conventional monoethanolamine (MEA) solvent used by other companies, KS-1 realizes a great deal of energy saving and is very small in deterioration and corrosion. The first plant using the KS-1 solvent and recovery technology was established in Kedah, Malaysia October 1999. This plant used a flue gas volume of 47,000Nm<sup>3</sup>/H and had a recovery CO<sub>2</sub> quantity of 160 tons/day at a 99.9% purity volume. The plant had an operating capacity of 250 MMSCFD.

### Powerspan

Powerspan's ECO<sub>2</sub> process uses an ammonia bicarbonate solution instead of an amine to remove CO<sub>2</sub> from a pulverized coal plant. This is advantageous, because ammonia can absorb more carbon dioxide than MEA, requires less energy for regeneration, costs less, and has lower equipment corrosion rates. After the absorption of CO<sub>2</sub> by the ammonia bicarbonate, the solution is regenerated and ammonia and carbon dioxide are released. The ammonia is recycled and the CO<sub>2</sub> is further prepared for storage. This reaction has been tested at 130 °F with a gas residence time of four to five seconds. With these conditions, carbon dioxide removal has been 90%.

ECO<sub>2</sub> testing is now moving from the lab scale to pilot plants. Evaluation will be started in 2008 at FirstEnergy's R.E. Burger Plant. This pilot operation will process a 1 MW slipstream from

the 50 MW commercial unit. If it is successful, a 100MW system is planned for a commercial demonstration unit. This unit would start operations in 2011, and full-scale systems could be expected to begin in 2015. Additionally, Powerspan recently announced plans for a large-scale demonstration of its ECO<sub>2</sub> technology at NRG Energy's WA Parish Plant in Fort Bend County, Texas. This unit would process flue gas from a 125 MW plant and is expected to start operating in 2012.

Powerspan has been partnering with the National Energy Technology Laboratory for much of this testing and agreed in August to partner with BP Alternative Energy on the demonstration and commercialization of ECO<sub>2</sub>.

Capital costs for a 500 MW plant would be in the range of \$150 to 250 million, provided a pollution control unit (ECO) is already installed. The US Department of Energy has estimated that an ECO<sub>2</sub> system will cost \$14/ton of CO<sub>2</sub> removed and 5.5 cents/kWh.

### **Integrated Gasification Combined Cycles (IGCC)**

#### **ConocoPhillips**

ConocoPhillips has developed the E-Gas technology. This system uses a fire-tube boiler and a two-stage, slurry-fed, oxygen-blown, entrained-flow design. It is designed to be compact, in order to reduce capital and operating costs. This compactness is obtained using the two-stage gasifier and a continuous slag removal system. The E-Gas system is good for a wide variety of coals, from pet coke to PRB to bituminous and blends. In addition to removing CO<sub>2</sub> from the flue gas stream, sulfur and other particulate are also withdrawn.

With CO<sub>2</sub> capture, a gross 681 MW plant produces 515 MW of net power at a HHV efficiency of 31.30 %, a plant cost of \$1,861/kW, and a cost of electricity of 6.94 cents per kWh. These calculations are done assuming January 2006 dollars, an 85% capacity factor, a 13.8% annual capital charge factor, and a coal cost of \$1.34 per MMBtu. A study done in January 2007 dollars found the total plant cost to be \$2431/kW. The efficiency of the process does become lessened by high moisture and high ash coals. The amount of oxygen needed also increases for these cases. Currently, ConocoPhillips gasification technology is being used at the 265 MW Wabash River IGCC plant near West Terre Haute, IN. CO<sub>2</sub> mitigation is not being done at this plant, however. Six additional plants are in the planning stages.

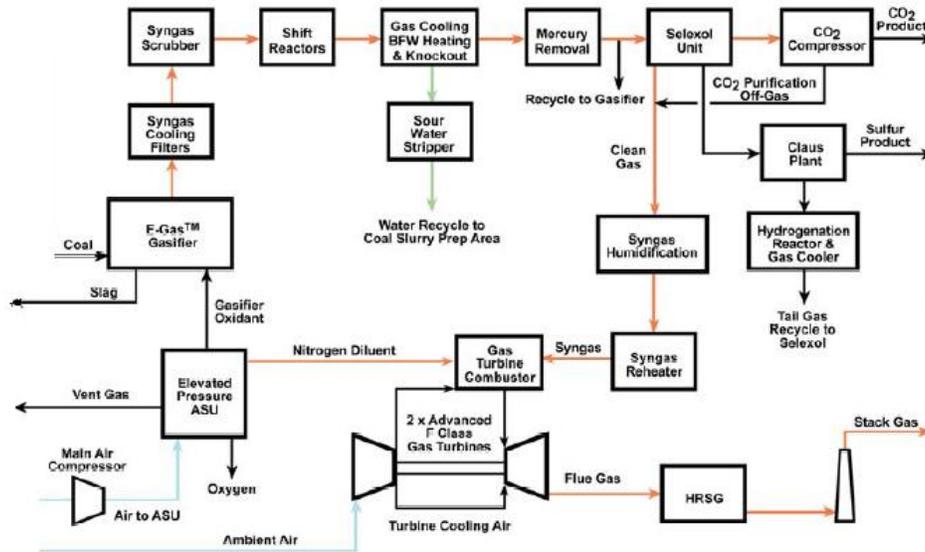


Figure 9: Diagram of ConocoPhillips E-Gas Process

### General Electric

General Electric has been working with IGCC technology for more than 30 years. One hundred and twenty operating gasifiers are using this technology, more than any of the other vendors. GE technology can provide output ranging from 10 MW to 1.5 GW. Their slurry-fed, entrained flow design is oxygen blown and uses Selexol as a solvent. GE’s process is good for bituminous coal, pet coke, or blends of pet coke/low-rank coals. With this technology, there is the option of adjusting the capacity of the plant, depending on the demand and off-peak hours operation. One or both gasifiers can be turned down as needed.

An extra approximately \$400/kW is required for a plant with CO<sub>2</sub> capture. A plant with gross power of 741 MW produces net power of 563 MW and has a HHV efficiency of 32.60 %. This plant would cost \$1,950/kW and have a cost of electricity of 6.74 cents per kWh. The CO<sub>2</sub> mitigation cost comes out to \$35/metric ton of CO<sub>2</sub> avoided. This is in January 2006 dollars for an 85 % capacity factor, 13.8 % annual capital charge factor, and \$1.34 per MMBtu coal cost. Another study, done in January 2007 dollars, found the total plant cost for this technology to be \$2390/kW. GE gasifiers with full or partial water quench provide best CO<sub>2</sub> capture economics for bituminous coals.

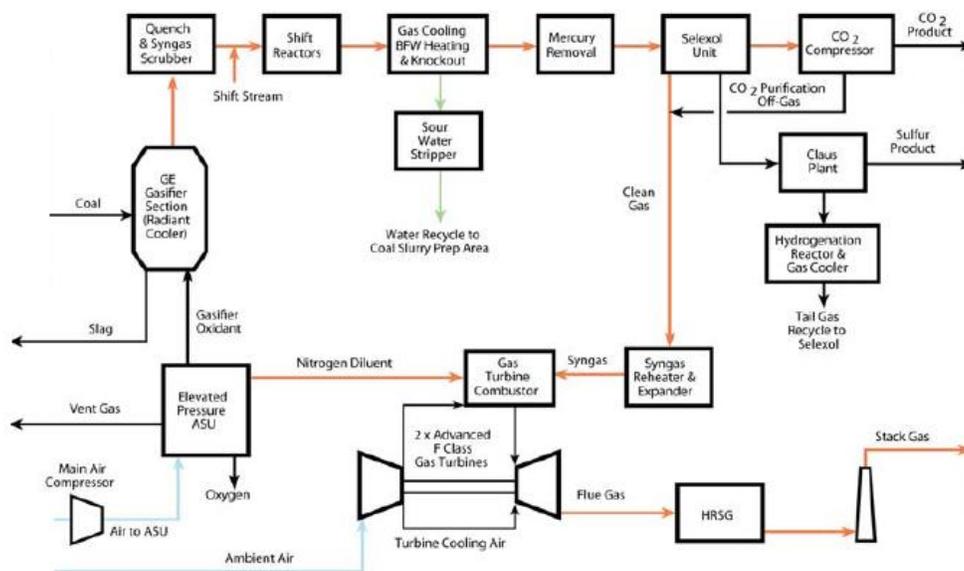


Figure 10: Diagram of GE's IGCC Design

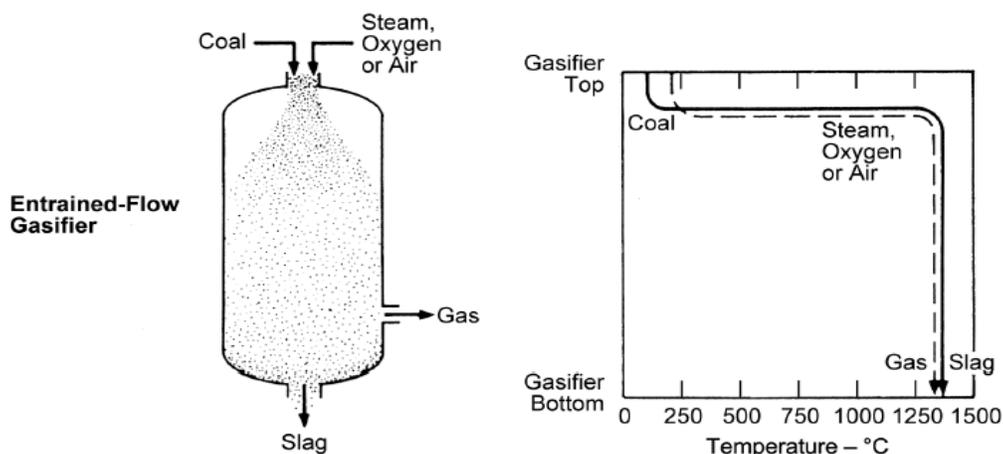


Figure 11: Entrained-Flow Gasifier (GE, ConocoPhillips, Shell, Siemens, MHI)

### Mitsubishi Heavy Industry

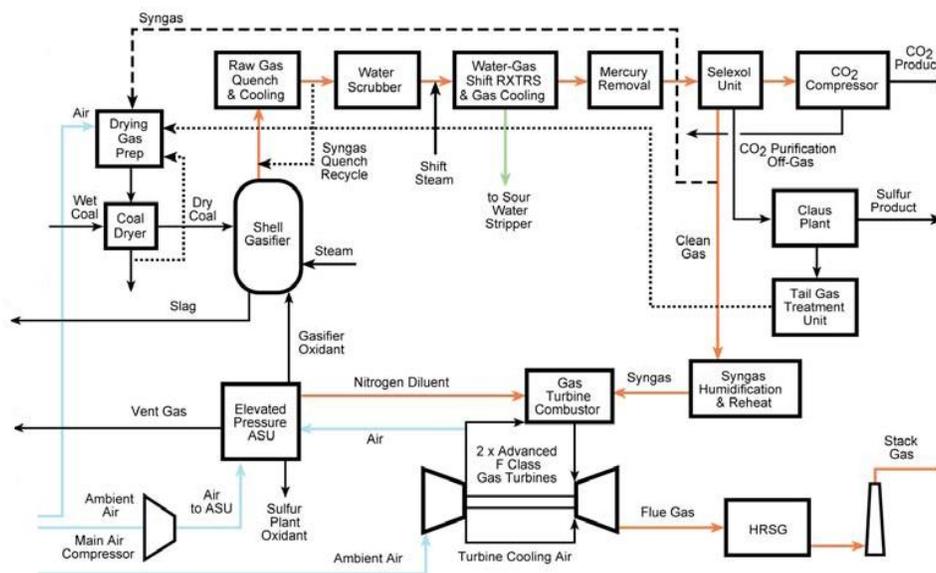
MHI has been working with IGCC technology since the late 80's and early 90's. In its attempts to achieve higher thermal efficiency and better environmental performance, MHI has been working on a demonstration plant project with a 250MW of gross power output and is currently in the final phase before commercialization. In this power plant, MHI uses a pressurized, air-blown, two-stage, entrained-bed coal gasifier and a dry coal feed. This air blown IGCC system is expected to raise the average thermal efficiency of Japanese coal-fired power plants by 6%. The commercial plant will likely bring more credibility and reliability for the future IGCC technology. The plant is expected to begin a test run this year.

MHI's new IGCC plant produces net power of 220 MW, has a LHV efficiency of 42% on 135 Btu/scf syngas fuel, and is expected to have 48% gross efficiency.

## Shell

Shell's IGCC technology has been licensed to more than 15 customers. The process has an oxygen-blown, entrained flow design and utilizes a dry-feed gasifier. The technology involves a two-stage Selexol process and the operation of the turbine on a high hydrogen content syngas, both of which have limited or no commercial operating experience. The water treatment needed by this system is greatly reduced as compared to other oxygen-blown, entrained-flow gasifiers by the use of a recycle gas stream instead of quenching the hot raw gas with a water spray.

A gross 667 MW power plant nets 501 MW at 30.60 % efficiency, a cost of \$2,250/kW, and a cost of electricity of 7.38 cents/kWh. . Adding carbon dioxide capture to an IGCC plant was shown to increase capital costs by more than \$650/kW. This is using the same assumptions of January 2006 dollars, an 85 % capacity factor, a 13.8% annual capital charge factor, and a coal cost of \$1.34 per MMBtu. A study in January 2007 dollars found that Shell's IGCC with carbon capture would cost \$2668/kW.



**Figure 12: Shell's IGCC design**

## Siemens

Siemens' SFG Gasifier, formerly Gas Schwarze Pumpe, has a reliable cooling screen design and can operate with pressures up to 40 bar. Its dry feed system is oxygen-blown, and it has an entrained flow system with high carbon conversion. It accepts a wide variety of feedstocks, including bituminous coals, sub-bituminous coals, lignite, biomass, and liquid wastes. Fuel can be fed pneumatically or as slurry. Such gasifiers have been in operation since the mid 1970's, and thus have more than twenty years of proven operational history. One disadvantage to this technology is that using ash-free fuels like oil and natural gas requires that the gasifier be fitted with a cooling wall with refractory linings. According to Siemens, these linings need to be replaced every 10 years. There are four plants in operation with this technology.

## **CO<sub>2</sub> Compression and Transportation**

The carbon dioxide stream from both PC and IGCC systems must be extremely pure in order to minimize the storage volume of carbon dioxide and allow for compression to a supercritical state. This compression can occur because CO<sub>2</sub> in a supercritical state has a density near that of a liquid. In order for efficient sequestration, CO<sub>2</sub> must be compressed to 1,160 – 1450 psig for unmineable coal seams, 2175 – 2320 psig for enhanced oil recovery, 2175 – 2610 psig for abandoned oil and gas fields, or 4,495 psig for deep-sea storage at a depth of two miles. In the past CO<sub>2</sub> has been compressed to 5,075 psig, but most of the compression that has been done is only up to about 3,900 psig.

An integrally-gear, 9-state, motor driven compressor, which would be able to compress CO<sub>2</sub> from 2.18 psig to 2610 psig would cost about \$6 million. Similar compressors are in use today. One in Saskatchewan, Canada compresses 1.35 million tons per year of CO<sub>2</sub> from 2.18 psig to 2712 psig for enhanced oil recovery. Another is used offshore Norway to compress one million tons per year of CO<sub>2</sub> for storage in a saline reservoir.

Transportation of pressurized CO<sub>2</sub> is a relatively inexpensive process. Costs, including installation, operation, and maintenance for 25 years of a 50 km long, six inch pipeline, come out to be less than \$0.50 per ton.

## **Sequestration**

The process of managing this collected CO<sub>2</sub> is known as sequestration. There are three main types of sequestration: terrestrial, geologic, and oceanic. In terrestrial sequestration, biological materials such as crops, trees, and grasses absorb CO<sub>2</sub> from the air and eventually transfer it to the soil. In geologic sequestration, carbon dioxide is injected into permanent storage, often in depleted oil or natural gas fields, unmineable coal seams, or saline aquifers. In ocean sequestration, CO<sub>2</sub> absorption into the ocean water is enhanced by feeding phytoplankton nutrients in order to stimulate their growth. Another form of ocean sequestration is by direct injection into the ocean floor, where high pressures can cause the CO<sub>2</sub> to condense into a liquid. There also exist other forms of sequestration that mainly involve chemical conversion of CO<sub>2</sub>, “farmed” biological systems that could absorb the gas, enhancing the CO<sub>2</sub> absorption rate for plants by genetic engineering, among other things.

In Illinois (and other Midwestern states), the main focus of research is the geologic and terrestrial forms of sequestration.

### **Geologic Sequestration**

The storage reservoirs that hold CO<sub>2</sub> are usually more than 2,500 feet deep and made up of sandstone or other porous rocks. Layers of nonporous rock act as a seal to prevent leakage of carbon dioxide. Pressures in these reservoirs are normally above 1,100 psi, which helps the CO<sub>2</sub> be more easily contained for long periods of time, due to the supercritical nature of the fluid. Depleted oil and gas fields are very attractive for this use because their geology is well understood, they have succeeded at containing oil and gas for long periods of time, and the amount of material that has been retrieved from these areas is a known value. Deep saline aquifers can hold 1,000 to 10,000 giga tons of carbon dioxide or more. Empty natural gas and oil fields, as well as enhanced oil recovery applications, can sustain 1,000 giga tons.

CO<sub>2</sub> can also be pumped into oil and gas field that are still in use. The net effect is that the gas can be used to push out the oil and gas that is still lying within. This process is a form of enhanced oil and gas recovery. Highly pressurized CO<sub>2</sub> (pressures equal to about 1800 psi or 124 times the regular atmospheric pressure) is pumped into the oil field. This gas expands and then displaces the gas and oil in the reservoir, pushing it out. According to the U.S. Department of Energy, gas injection accounts for 50 percent of the oil retrieved by enhanced oil recovery (EOR) techniques. EOR is quite profitable and was first tested in Texas in 1972. When performing this technique, care must be taken so that the pressure of the injected gas does not exceed the original pressure.

The pressurized CO<sub>2</sub> from the power plant flows into the pores of the rocks in the reservoir. Scientists believe that over time the CO<sub>2</sub> may react with minerals to form a stable solid, dissolve into salt water, or pool below the rocks capping the reservoir.

### **Effects of Geological Sequestration**

There are many concerns regarding geological sequestration. Safety is a big issue. The fluid is acidic and health effects are observed for CO<sub>2</sub> concentrations of 15,000 ppm or greater. Loss of consciousness or death may occur at 50,000 to 100,000 ppm. Sequestration sites need to be kept far away from the drinking water supply, geological faults, and places where seismic activity may be possible. There are also questions about the ownership and liability for storage reservoirs.

Several leaks from sequestration reservoirs have occurred in the past. In 1982, the Sheep Mountain CO<sub>2</sub> dome in Southern Colorado experienced failure in one of its production wells. Seven years after initial production, a well blew out and was uncontrollable for seventeen days. The flow rate was estimated between 7000 to 11,000 tons of CO<sub>2</sub> per day. No one killed in the accident, despite the massive amount of CO<sub>2</sub> leakage. The environment surrounding the area helped mitigate some of the effects the CO<sub>2</sub> may have had (the sloped terrain and local weather conditions enabled the CO<sub>2</sub> to mix rapidly with the atmosphere). The failure was immediately recognized as dry ice accumulation on the casing, which “blew off the well in chunks.” The case appears to provide an upper limit of CO<sub>2</sub> leakage from a single well. The well was finally able to be controlled and closed, with no documented subsequent leakage. From this case, it can be concluded that proper placement of wells, monitoring, and operations can prevent substantial harm from CO<sub>2</sub> emission rates of this magnitude.

Studies have been done that show the effect that CO<sub>2</sub> sequestration can have on groundwater. In 2004, a Department of Energy pilot field experiment injected more than 1800 tons of CO<sub>2</sub> into the Frio saline formation in Texas. This experiment was designed to validate simulations of CO<sub>2</sub> transport and fate in one of the largest saline formations in the U.S. A monitoring well located about 100 feet from the injection well collected direct fluid samples using a U-tube apparatus. This tool, among others, detected the arrival of a CO<sub>2</sub> plume in the monitoring well 7 days after injection. A substantial amount of dissolved metal was recovered in the U-tube. The workers initially thought that the well casing was reacting to carbonic acid in the reservoir. However, laboratory studies and geochemical analyses confirmed that a substantial fraction of the metals were the product of mineral dissolution, specifically the oxide and hydroxide coatings of mineral grains that represent less than two percent of the surrounding rock. The rapidity of mobilization and the high concentrations suggested strongly that carbonic acid formed from dissolved CO<sub>2</sub> brines might quickly and dramatically alter groundwater chemistry.

The effects of CO<sub>2</sub> sequestration vary based on the kind of aquifer, in particular carbonate systems or siliclastic systems. This classification is based on the composition of the reservoir rock. The composition of the rock greatly affects the response to any carbon acid that forms. Silicate materials react slowly with CO<sub>2</sub>, which means that there is little change in porosity and permeability over the duration of the injection; however, the brines with the dissolved CO<sub>2</sub> will remain acidic. In contrast, carbonate rocks react quickly with CO<sub>2</sub> and could change permeability and porosity quickly. However, the rapid kinetics will result in rapid increase of brine pH and buffering of the brine-CO<sub>2</sub> system, reducing reactivity over time. From these “competing effects,” it is not clear which fundamental rock composition is more prone to leakage or to mobilization of metals, and little work has focused on direct comparison of these two primary aquifer compositions.

### Illinois Locations for Geological Sequestration

The Illinois Basin is a large coal bed (containing 38 billion tons of recoverable coal) that has been considered for the sequestration of CO<sub>2</sub>. It covers most of Illinois, as well as some parts of Indiana and Kentucky. The deepest coal beds lie around southeastern Illinois and are indicated by the darker areas on the map below.

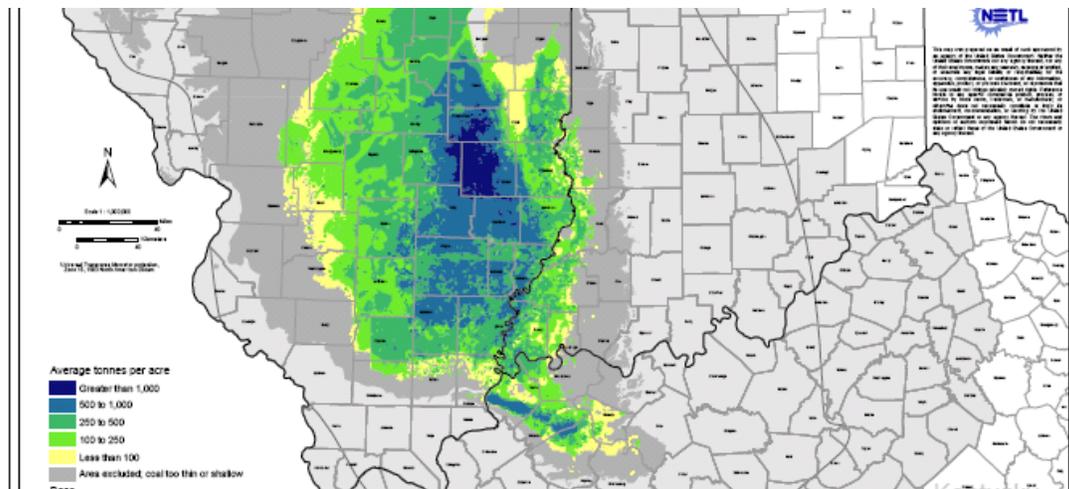


Figure 13: Map of the Illinois basin provided by the National Energy Technology Laboratory (NETL.)

The towns considered for the FutureGen initiative, a \$1 billion project backed by the U.S. Department of Energy and a non-profit consortium of coal producers and energy generators, lie around this area. Mattoon and Tuscola, Illinois are considered not only for their proximity to the deep basin but also for their equidistance between the major cities of Chicago, St. Louis, and Indianapolis. The overall goal of FutureGen is to build a power plant with virtually zero emissions. The cost to build this plant would be \$1.45 billion and is expected to generate 275 megawatts of power, enough to service 150,000 homes. It turns coal into gas for use in hydrogen fuel cells and sequesters carbon dioxide underground.

### Terrestrial Sequestration

Besides injecting CO<sub>2</sub> in the ground, another way to sequester this gas involves the use of plant life as well as soils, since CO<sub>2</sub> is involved in the photosynthesis process that plants undergo to create food. Forests and other forms of vegetation are among the largest carbon sinks on the

planet, absorbing two billion tons of CO<sub>2</sub> annually (one-third of all human-produced emissions so far.) In 2001, the net amount of CO<sub>2</sub> sequestered by vegetation and soils in the U.S. was around 840 million tons, which offsets about 15 percent of total CO<sub>2</sub> emissions produced by energy generation, transportation, and other human activity. However, it has been noted by the Environmental Protection Agency (EPA) that the amount of sequestration has declined ever since this time.

As of now, terrestrial sequestration occurs naturally with the forests, croplands, and other forms of vegetation and soils absorbing CO<sub>2</sub>. It is simply a matter of maintaining this plant life so that they can continue to synthesize this carbon compound. In addition, terrestrial sequestration can be enhanced by adding more plant life. Planting trees, as well as reforestation of degraded lands is one such form of enhancement, as well as changing the tillage methods used on agricultural lands. On top of this, there is research done on the replacement of fossil fuels with biomass fuels, fuels created from plant life that absorbed CO<sub>2</sub>.

If terrestrial sequestration is maintained and/or enhanced, it will be able to offset ten to twenty percent of the world's CO<sub>2</sub> emissions, sequestering about 100 billion tons of CO<sub>2</sub> over 50 years. In addition, terrestrial sequestration promotes the health of the environment in other ways besides averting global warming. Trees and other plants are important for wildlife, and they also reduce soil erosion.

One drawback of terrestrial sequestration is that it may not promote biodiversity; for example, forestry may encourage the growth of tree-dwelling life but may hinder the development of grassland-dwelling life. In addition, there is a limit to how much plants and soils can sequester CO<sub>2</sub>, but steps can be taken to ensure that any stored CO<sub>2</sub> does not go back into the atmosphere.

### **CO<sub>2</sub> Use in the Food and Beverage Industry**

Carbon dioxide does have some current uses, particularly in the food and beverage industry. CO<sub>2</sub> can be dissolved in water-based liquids to produce carbonic acid. This reaction is used for the carbonation of soda and mineral water. The CO<sub>2</sub> must be in a very pure form to be able to be used in this type of application. Carbon dioxide can also be used as a cryogenic fluid for chilling or quick freezing processes. In the dry ice or carbon dioxide snow form, CO<sub>2</sub> can be used to keep food and beverages cool during transportation.

### **“Novel” Forms of Sequestration**

There exist other forms of sequestration which have been considered, but little research has been done to test their effectiveness, thus they are called by some people “novel” forms of sequestration. Many of these techniques are chemical processes that convert the CO<sub>2</sub> into other, perhaps more useful substances. The chemical processes could occur in two ways, abiotically and biologically. An example of an abiotic process would be an advanced catalyst that could convert the CO<sub>2</sub>, or mineral uptake. A biotic process would involve harnessing the CO<sub>2</sub> conversion abilities of biological systems such as plants and microbes. In other words, someone interested in sequestering CO<sub>2</sub> could enhance and/or cultivate a biological system designed to convert the gas. This process would be similar to terrestrial sequestration, but would involve processes such as genetic engineering of plants to enhance CO<sub>2</sub> absorption rate, the use of microbes (possibly water dwelling) for CO<sub>2</sub> fixation, and engineering photosynthesis systems.

According to the U.S. Department of Energy, biological systems do not require pure CO<sub>2</sub>, and so no costs would be needed to capture, compress, and separate the CO<sub>2</sub> from other gases.

### **Sequestration Projects**

The U.S. Department of Energy has advanced to a second stage of its plan to develop carbon sequestration technologies. One-hundred million dollars was given to seven projects created in 2002 to support the U.S. sequestration network. These projects were used to determine the most suitable technologies, regulations, and infrastructure requirements for CO<sub>2</sub> sequestration. Teams used computer modeling and geographic, as well as economic, analysis to identify sites with the potential to store over 600 billion metric tons of CO<sub>2</sub>, equivalent to 200 years of US energy source emissions. Stage two of this project involves the same group of seven organizations doing a four year (2005-2009) study concentrated on field testing and validation of sequestration technologies. They will also identify the most promising regional repositories for CO<sub>2</sub>, look into permitting requirements, and identify best management practices. The seven projects are listed below.

- 1.) Big Sky Regional CSP will demonstrate geologic storage in mafic/basalt rock formations.
- 2.) Midwest Geological Sequestration Consortium will determine the ability, safety, and capacity of geological reservoirs to store CO<sub>2</sub> in deep coal seams, mature oil fields, and saline reservoirs.
- 3.) Midwest Regional CSP will test injections into deep geologic reservoirs to demonstrate safety and effectiveness.
- 4.) Southeast Regional CSP will examine three field sequestration validation tests on enhanced oil recovery, stacked reservoirs, coal seams, and saline reservoirs.
- 5.) Southwest Regional CSP will conduct five field tests on carbon sink targets and deep saline sequestration.
- 6.) Plains CO<sub>2</sub> Reduction Partnership will complete four field trials of storage, monitoring, and mitigation in oil/gas reservoirs and unmineable coal seams.
- 7.) West Coast Regional CSP will conduct two storage tests in gas and saline reservoirs.

Recently, the United States Department of Energy committed \$197 million over the next ten years to fund three new carbon sequestration projects. An additional \$250 million in governmental funding is also expected to be granted. That money will fund four more projects, including one in Illinois.

### **Regulations Involving Sequestration**

There are many areas of sequestration, each with its own set of items that could be regulated. For surface leakage, topics include: human health, ecosystem health, and the effectiveness of climate change mitigation. The category of groundwater quality encompasses the safety and aesthetics of drinking water as well as irrigation water quality. Underground Injection Control (UIC) regulations set by the U.S. EPA with an objective of protecting public sources of drinking water will likely form the framework for these laws. Handling the risk of induced seismic activity is a regional impact that will likely be managed in the future. Permanence, or how long the CO<sub>2</sub> can be stored away, is another issue. Laws will probably be created covering the minimum time required for sequestration, maximum allowable leakage rates, and monitoring requirements for completed geological sequestration projects. Development of monitoring and

verification (M & V) protocols will need to be developed, as well as geological sequestration siting guidelines.

## 0.9 Recommendations

For PC plants, Fluor was selected to be the most cost-effective, efficient and mature technology. The recommendation was made based on their comparatively long history of working with CO<sub>2</sub> removal systems and the pilot plant testing of the Ecoamine system that has already been done, which places them ahead of Alstom and Powerspan. Fluor's efficiencies for subcritical, supercritical, and ultrasupercritical plants are all higher than Alstom's chilled ammonia system. Additionally the cost of CO<sub>2</sub> mitigation is cheaper for Fluor's system, \$68/ton for sub and supercritical systems and \$75/ton for ultrasupercritical plants as opposed to Alstom's \$81/ton. The only drawback to this system is the comparatively high capital cost.

For the IGCC plant General Electric was selected to be the most cost-effective, efficient and mature technology. Their large number of currently operating plants as compared to Shell, ConocoPhillips and the other vendors places them at a much higher maturity level. Their efficiency is slightly higher than Shell and ConocoPhillips, and the total plant and operating costs are low. The flexibility in the capacity of the plant is also a large advantage. One disadvantage is that the GE system uses more water than the ConocoPhillips system (4579 gallons per minute as compared to 4135 gallons per minute).

These two systems are recommended to Sargent & Lundy and next semester's I PRO team for further study. It should be noted that much of the testing on this technology is still in progress. Future completion of some of the pilot plant and commercial testing may change the recommendations of this team.

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