ENGINEERING FEASIBILITY AND ECONOMICS OF CO_2 SEQUESTRATION/USE ON AN EXISTING COAL- FIRED POWER PLANT:
A LITERATURE REVIEW

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Task 1 Report

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Executive Summary

The overall objective of this study is to evaluate the technical feasibility and the economics of alternate CO_2 capture and sequestration/use technologies for retrofitting an existing pulverized coal-fired power plant. To accomplish this objective three alternative CO_2 capture and sequestration systems will be evaluated to identify their impact on an existing boiler, associated boiler auxiliary components, overall plant operation and performance and power plant cost, including the cost of electricity. The three retrofit technologies that will be evaluated are as follows:

- Coal combustion in air, followed by CO_2 separation from flue gas with Kerr-McGee/ABB Lummus Global's commercial MEA-based absorption/stripping process.
- Coal combustion in an O_2/CO_2 environment with CO_2 recycle
- Coal combustion in air with oxygen removal and CO_2 captured by tertiary amines

In support of this objective and execution of the evaluation of the three retrofit technologies a literature survey was conducted. It is presented in an "annotated" form, consistent with the following five sections:

- Coal Combustion in O_2/CO_2 Media
- Oxygen Separation Technologies
- Post Combustion CO_2 Separation Technologies
- Potential Utilization of CO_2
- CO_2 Sequestration

The objective of the literature search was to determine if the three retrofit technologies proposed for this project continue to be sound choices. Additionally, a review of the literature would afford the opportunity to determine if other researchers have made significant progress in developing similar process technologies and, in that context, to revisit the current state-of-the-art. Results from this literature survey are summarized in the following paragraphs.

Burning pulverized coal in an oxygen/recycled flue gas (largely CO_2) media continues to receive much attention in the literature as a practical way of addressing CO_2 capture for the purpose of mitigating the emission of greenhouse gases into the atmosphere. Comprehensive reports have been written by Argonne National Laboratory (sponsored by the DOE) that document results of pilot scale testing and field testing on a commercial, stoker-fired boiler firing coal in an oxygen/carbon dioxide (recycled flue gas) media. Though various researchers differ on some of the details, nearly all experimental and computational efforts to date conclude that burning pulverized coal in an O_2/CO_2 media represents a technically and economically sound choice for recovering CO_2, given the alternatives. The literature has indicated that appropriate mixtures of oxygen and recycled flue gas can be found to give boiler performance that is comparable to burning coal in air. There appear to be <u>no showstoppers</u> when considering issues like combustion efficiency, unburned carbon, NO_x, SO_2, ash deposition and heat transfer. One, very important, factor is the problem of in-leakage in a balanced draft unit. Any air in-leakage will directly, and adversely affect the recovered CO_2 purity target of $\geq$95%. While a pressurized unit would be ideally suited to this technology, it is possible to successfully address in-leakage issues. There will, undoubtedly, be some development required to optimize burner performance with oxy-fuel burners in commercial boilers. Having pure oxygen available is believed to enhance boiler operational flexibility; low load operation, for example, should be easier. The use of oxygen/recycled flue gas is said to require similar site area as a conventional plant. In comparisons with amine-based technologies for recovering CO_2 most evaluations show that burning coal in mixtures of oxygen and recycled flue gas to be more cost effective with higher net efficiencies.

Oxygen separation technologies, specifically their cost, directly affect the viability of the previously mentioned technology. Large-scale production of oxygen gas from the atmosphere is generally accomplished by: (1) cryogenic production systems, (2) absorption processes, and (3) ceramic membrane systems. Important factors in evaluating an oxygen plant are plant capacity range, oxygen purity range, power consumption, relative capital cost, relative oxygen cost and operating temperature. The best plants today require about 200 kWh/ton O_2, compared with the minimum theoretical energy requirement of 40 kWh/ton O_2. It has been calculated that about 16% of a power plant's output would be required by the oxygen plant. Though cryogenic plants probably produce the bulk of oxygen today, it is believed by some that ceramic membrane systems offer the most potential for lowering the cost of oxygen production.

Post-combustion CO_2 separation technologies can be categorized into one of the following:

- Chemical and physical absorption
- Chemical and physical adsorption
- Gas separation membranes
- Cryogenic separation

Chemical absorption for CO_2 separation currently represents the most "commercially ready" approach. To date all commercial CO_2 capture plants, such as those used to remove acid gases from natural gas streams, use processes based on chemical absorption with a monoethanolamine (MEA) type solvent. However, the use of such processes for recovering CO_2 from flue gases is complicated by: (1) low concentration of CO_2 in the flue gas, (2) low pressure of the flue gas, and (3) corrosion of absorption equipment having high solvent concentrations, especially in the presence of oxygen, and other trace constituents found in flue gas. If chemical absorbents are to be used in a boiler application, modifications (inhibitors) will have to be made to accommodate the conditions found in boiler flue gas. Solvent usage is adversely impacted by impurities in the flue gas, such as SO_2; for this reason it is important to locate CO_2 capture equipment downstream of the flue gas desulfurization equipment. Another significant factor in the use of MEA type solvents is the energy required for solvent regeneration (~3.3 MJ/kg CO_2).

Selective separation of CO_2 can be achieved by physical adsorption of the gas on high surface area solids, like zeolite. Desorption of the adsorbed gas is accomplished by operating the process in either a pressure swing adsorption (PSA) mode or a temperature swing adsorption (TSA) mode. PSA operation is less energy intensive than the TSA mode, but both processes are energy intensive relative to other post-combustion technologies.

The use of gas-separation membranes represents a new approach for the specific application of CO_2 recovery from flue gases. However, no commercial membranes have yet been developed for what is essentially a CO_2/N_2 separation. Efforts are still in developmental stages.

Cryogenic separation of gases takes advantage of the fact that under certain conditions of temperature and pressure, components of a gas mixture can exist in a different phase. Combinations of low temperatures and high pressures make cryogenic separation of CO_2 costly. Collecting CO_2 in the solid phase would be less costly, with the disadvantage that solid CO_2 is much more difficult to handle than liquid CO_2. Having CO_2 in solid or liquid form would not be appropriate for the intended end use of enhanced oil and/or gas recovery, or sequestration. To date a low temperature distillation process has not yet been found to separate CO_2 from N_2.

Though CO_2 recovery and utilization/sequestration options may be viewed/evaluated individually, in reality it makes sense to evaluate the integration of these technologies to take advantage of otherwise fugitive heat/power for the improvement of overall process efficiency.

Utilization of CO_2 from flue gas for useful industrial products is a potential alternative to other disposal methods. Most prevalent among the uses or potential uses for CO_2 are the following:

- Enhanced oil recovery (EOR) or enhanced gas recovery (EGR)
- Industrial uses
- Chemical conversion
- Biological methods

Of the above uses EOR is, by far, the largest current user of carbon dioxide, up to 80%. Enhanced gas recovery is another near-term use of carbon dioxide. Current work in this area involves use of CO_2 for enhanced recovery of natural gas and the use of CO_2 for enhancement of methane (natural gas) from coal deposits. Generation of methane from coal deposits that are currently too deep to economically mine may be of particular interest to the state of Ohio

The following are among the industrial uses that have been speculated for using CO_2:

- Waste water treatment
- Food packaging and freezing
- Additive for beverages and food
- Extraction (e.g. extraction of flavors from plants, of caffeine from coffee)
- Welding
- Refrigeration
- Fire extinguishers

Among the uses for CO_2 in chemical conversion processes are: (1) chemical conversion to fuels, and (2) conversion of carbon dioxide to other chemicals. For example, the conversion of CO_2 to methanol, which could be used as a transportation fuel, is popular in the Japanese literature. Examples of conversion to other chemicals includes production of agrochemicals, carboxylated products and polymers.

It seems reasonable to speculate that when CO_2 recovery becomes more commonplace two things will happen: (1) more uses will be found for what will become a highly available (free?) product, and (2) utilization will not be able to accommodate all the CO_2 that will become available, and, hence, sequestration will be necessary.

Based on a consensus of the work contained in the references reviewed, various researchers have examined the following potential options for large-scale carbon dioxide sequestration:

- Ocean sequestration of CO_2
- Land (geological) storage in depleted oil or gas reservoirs
- Land (geological) storage in coal formations
- Land (geological) storage in deep aquifers
- Land (geological) storage in salt domes or rock caverns
- Land storage of solid (frozen) CO_2 in thermally insulated repositories
- Sequestering CO_2 in mineral form

Ocean sequestration would be suitable for plants within a reasonable distance from the ocean. Review of available references indicated that the cost of excavating rock caverns was too high to be practical. Similarly, costs were prohibitive for storage of solid CO_2 (dry ice) in thermally insulated structures. Sequestration of CO_2 in mineral form is still in conceptual stages, leaving the depleted oil and gas reservoirs, depleted coal formations and deep aquifers as viable, land-based sequestration options. Particular attention was paid to CO_2 sequestration in the state of Ohio, for example the Mt. Simon Sandstone aquifer.

The literature survey has not uncovered any information that would necessitate a fundamental change in the effort as outlined in the Statement of Work in this project. However, information obtained during the literature survey has helped to identify certain issues that need to be addressed in concert with the existing work scope with three key examples, as follows:

- When burning coal in an oxygen/recycled flue gas media, furnace in-leakage will adversely impact the purity of CO_2 obtained. Based on in-leakage documented during trials with a commercial stoker-fired boiler resulted in flue gas with about 48% CO_2 versus their target of 95%. Though in-leakage has been accounted for in the subject proposal, the assumption of 5% leakage at the host site will be re-examined in light of what has been found in the literature.
- Tertiary amines are said to react with CO_2 only if the partial pressure of the CO_2 is well above atmospheric pressure, which makes them unattractive for CO_2 recovery from flue gases. The current Statement of Work currently calls for the evaluation of a system employing a tertiary amine; this will be carefully re-examined in view of the information gained from the literature survey.
- An oxygen/carbon dioxide medium was said to significantly decrease flame temperature compared with that achieved in air, under conditions of equivalent oxygen content. The claim is that to achieve the same adiabatic flame temperatures as in air the oxygen content would have to be 42% in the oxygen/carbon dioxide case. Calculations will be carried out in the subject project to verify (or refute) the literature on this issue.

In addition to the immediate purpose of serving as a reality check for evaluating the project work scope as currently written, the information obtained by the literature survey will be easily accessible for more detailed, specific use in the execution of follow-on tasks in this project.

Table of Contents

1.0 Introduction

This literature survey was conducted in fulfillment of Task 1 under the Statement of Work in OCDO contract CDO/D-98-8 and DOE contract DE-FC26-99FT40576. An open literature survey was carried out to provide information on the current state-of-the-art and to ensure use of the best information available during the execution of this contract.

The objective, as written under the Statement of Work, is to conduct a technical and economical assessment of retrofitting an existing pulverized coal-fired power plant with systems capable of significant reduction of greenhouse gases. To accomplish this objective three alternative CO_2 capture and sequestration options will be evaluated to identify their impact on an existing boiler, associated boiler auxiliary components, overall plant performance and power plant cost, including the cost of electricity. The three retrofit technologies that will be evaluated are:

- Coal combustion in air, followed by CO_2 separation from flue gas with Kerr-McGee/ABB Lummus Global's commercial MEA-based absorption/stripping process.
- Coal combustion in an O_2/CO_2 environment with CO_2 recycle
- Coal combustion in air with oxygen removal and CO_2 captured by tertiary amines

In support of this objective and to facilitate evaluation of the three retrofit technologies the literature survey was categorized into five sections:

- Coal Combustion in O_2/CO_2 Media (Section 2)
- Oxygen Separation Technologies (Section 3)
- Post Combustion CO_2 Separation Technologies (Section 4)
- Potential Utilization of CO_2 (Section 5)
- CO_2 Sequestration (Section 6)

A total of about 180 references were obtained. Technical papers comprise the majority of the referenced material, most of them being published in the last five years. Additionally, several comprehensive reports were obtained and relevant chapters from textbooks were reviewed.

The reference material was reviewed with the following questions in mind:

- What is the current state-of-the-art?
- Has there been progress beyond what the US Power Plant Laboratories had already reported?

- Has anyone else done the type of research that the US Power Plant Laboratories proposed?
- What are the techno-economic implications of the findings?
- Is there a better way to perform the work as outlined in the Statement of Work?

The wealth of material obtained (many of the reports were hundreds of pages in length) precluded a detailed review of each and every document. Answers to the above questions were necessarily based on opinions formed by a review of what was judged to be key content. Answers with respect to the current status, the progress, and the techno-economic implications appear in the text. At this point, we have not seen any other study, or reported work, which seems to cover the intended work of this project. We did not find a better way to perform the work that was outlined in the statement of work. However, recognizing that more detailed and useful information exists in the referenced material, several copies of literally every page have been generated and sorted into the five categories noted above for easy retrieval and more detailed use in later project tasks, as required.

A bibliography, sorted according to subject matter, appears at the end of the respective subject category section. Since some of the documents address more than one category they may appear more than once. General Bibliography (shown in the Table of Contents as Section 7) refer to those references that address a number of topics in a more general, or overview fashion.

2.0 Coal Combustion in O_2/CO_2 Media

2.1 Overview

One of the effective means of capturing CO_2 from a coal-fired boiler is to fire the boiler with a mixture of oxygen and recycled flue gas (comprised primarily of CO_2 and water vapor). Since the water vapor can be easily condensed and removed, the remaining gas would essentially be CO_2. The CO_2 could then be processed/compressed for beneficial uses such as enhanced oil recovery (EOR) or sequestered in a permanent storage location.

Approximately 15 references have been reviewed on the subject of burning pulverized coal in an O_2/CO_2 mixture, including three comprehensive reports by Argonne National Laboratory on work funded by the U.S. Department of Energy.

The objective of the literature survey for this section is to determine the effects of burning pulverized coal in a CO_2/O_2 mixture, as contrasted with combustion in air. In particular the literature has been reviewed with a focus on the effect of CO_2/O_2 on the following:

- Combustion efficiency
- Unburned carbon loss
- Heat transfer
- NOx
- SO_2
- CO
- Ash deposition

Additionally, attention will be given to optimum mixtures of CO_2/O_2 to produce the most favorable performance, the purity of CO_2 produced and whether or not it is advisable to remove moisture from the flue gas before recycling.

2.2 Findings by Weller, et al. (1985)

Very comprehensive tests were carried out by Argonne National Laboratory using one of Battelle's coal-firing facilities (about 400,000 Btu/h), a horizontally-oriented tunnel furnace that had been modified to burn coal in CO_2/O_2 mixtures. Three different CO_2/O_2 mixture ratios (by volume) were tested, namely 3.65, 2.42 and 2.23. The 2.42 mole ratio represents the case whereby the weight of nitrogen in air is replaced with the weight of carbon dioxide. The coal chosen for testing was from the Gage seam in Colorado; it was a high volatile, low ash, low sulfur coal with very high ash fusibility characteristics to preclude ash deposition problems while testing. Results of these tests were compared to those where coal was burned in air. It was noted that the recycled flue gas (mainly CO_2) was cooled sufficiently for all the moisture to be condensed. It was stated that the degree of simulation to a case where the flue gas is recycled hot, and contains significant quantities of water is not known.

Test results showed that a CO_2/O_2 ratio could be chosen that produces nearly the same heat transfer to the lower furnace and convective pass as was achieved by burning coal in air. For the particular experimental furnace used the optimum CO_2/O_2 ratio was slightly less than 2.42. Gas temperatures and temperature profiles were similar for all tests. Gaseous pollutant emissions (CO, NOx, SO_2 and hydrocarbons) were similar for all tests with the possible exception that the SO_2 emissions declined when the CO_2/O_2 ratio was reduced. Speculation on why this may have occurred is that more of the sulfur was captured in the ash and/or that more of the SO_2 was oxidized to SO_3. If the latter speculation turns out to be dominant, higher SO_3 concentrations would increase the dewpoint and possibly lead to increased cold-end corrosion. Particulate emissions, as measured at the stack, were similar for all tests except the highest CO_2/O_2 ratio, with particulate emissions being 25% higher for that test. The continuous radiation was lower for all flames with carbon dioxide/oxygen mixtures as compared to those with air. Attempts to derive gas or particle temperatures from the spectral measurements were not successful in that the temperatures obtained were significantly lower than those obtained by a high velocity, shielded thermocouple. Ash deposits, as measured in a simulated superheater section of the facility, were similar for tests with air and CO_2/O_2 mixtures with any small differences being explainable by small differences in gas temperatures.

The report concluded that results of measurements made in the combustion test facility indicate that the proposed process of firing coal in a large utility boiler in an atmosphere of recycled flue gas and added oxygen is technically feasible. The conclusion was based on the similarities between coal-air and coal-CO_2-O_2 flames concerning combustion characteristics, radiant heat transfer and emissions. It was stated that an engineering assessment would have to be made regarding many other factors, including fan capacity, controls and any problems associated with recycling $O_{2,}$ like condensation and boiler startup. On the plus side it was noted that a boiler operated with a mixture of recycled flue gas and oxygen provides a control variable not available when burning with air: namely the ratio of flue gas to oxygen. It is possible that this added variable could be used to increase operating flexibility in terms of useful turndown of fuel acceptability.

The authors question the implications of the pilot scale test results on NO_x formation in commercial boilers. Nitrogen oxides were reported to be similar for all tests, i.e., those where coal was burned in air versus those where coal was burned in a mixture of carbon dioxide and oxygen. Peak flame temperatures during the pilot scale testing were reported to be slightly below 2600 F, considerably lower than what would be found in commercial pulverized coal-fired boiler. At these temperatures thermal NO_x would not be very significant and the main contribution to NO_x would be fuel nitrogen, hence the similarity of NO_x values among the tests. In a commercial application where peak gas temperatures routinely reach 3000 °F, or higher, thermal NO_x is a significant factor. Therefore, the authors believe that in a commercial application NOx would be lower for the CO_2/O_2 case, as compared with the case where coal is burned in air, because of the elimination of thermal NO_x from nitrogen in the air.

2.3 Findings by Kumar et al., 1987

Kumar, et al., reports on results of testing a 2.2 x 10^6 Btu/h stoker fired boiler when burning coal in a CO_2/O_2 mixture. The stoker-fired boiler was a commercial unit owned by Black Hills Power and Light Co. burning a Wyodak, low sulfur subbituminous coal having a heating value of about 8000 Btu/lb.

It was reported that the boiler could be successfully operated in a flue gas recycle mode with oxygen injection to produce increased levels of carbon dioxide in the flue gas. Operation in this mode was said to not have any noticeable effects on the boiler or the space-heating system, and it was noted that the operators only required minimal training.

The most significant issue pointed out in this report was the importance of preventing air in-leakage, in the case of a balanced draft unit, which was the case for this stoker. Stoker-fired boilers, like the one used in this test are designed for some in-leakage; indeed, air in-leakage serves to cool fixtures such as the furnace and ash pit doors. In-leakage also occurred in the coal feed system. Other points of air entry were said to be around the ID and FD fan shafts and damper drive motor linkages and ash removal augers and ducts. Firing coal with recycled flue gas and oxygen would be ideally suited to pressurized units where in-leakage would not be a problem. If balanced units are modified to fire with recycled flue gas and oxygen, attention must be given to sealing all significant sources of in-leakage. The authors note that this same attention would have to be given in the case of balanced draft pulverized coal-fired boilers, the coal-firing method to be evaluated in this project.

Because of the significant in-leakage the highest concentrations of CO_2 in any of the tests was 48.5%, which was well below the target of 95% or higher, as would be required for enhanced oil recovery purposes.

2.4 Findings by Abele, et al., 1987

The above referenced report covers results from testing carried out by Energy and Environmental Research under sub-contract to Argonne National Laboratory and funded by the DOE. Pilot scale testing was conducted in a tower-type test facility (10×10^6 Btu/h) modified for a recycled flue gas/oxygen mixture in place of air combustion. Tests were conducted in both a “wet-recycle” mode and a “dry-recycle” mode. In the wet mode no attempt was made to condense the moisture in the flue, whereas in the dry case most of the moisture was condensed and removed before recycling.

Performance criteria of particular interest included heat transfer (radiative and convective), flame stability, carbon burnout, and slagging and fouling tendencies. Results of the experimental program showed that satisfactory combustion of pulverized coal can be achieved in mixtures of recycled flue gas and pure oxygen. Optimum ratios of flue gas and oxygen were found for which performance changes were minimal when compared to performance in air. For the wet-recycle mode the optimum mole ratio (CO_2 + H_2O)/O_2 was found to be 3.25. At this point the overall heat transfer to both radiative and convective heat transfer surfaces was matched to that obtained with air. For the dry recycle case, where a substantial part of the moisture had been removed, the corresponding optimum recycle ratio was found to be 2.6. Performance parameters such as flame stability, carbon burnout and slagging and fouling tendencies were found to undergo minimal changes for optimum recycle conditions, as compared to firing in air. Flame stability was unchanged despite using recycle flue gas as the pulverized coal transport media instead of air. Deposits for all cases were found to be light, friable and easily removed and showed no difference relative to their effect on heat transfer. Nitrogen oxide emissions were found to be lower (80% and 70%, respectively) in wet- and dry-recycle cases, compared to air firing. The explanation given is that in the recycled cases flue gases containing NO_x undergo reburning as they pass through the main combustion zone which contain reducing hydrocarbon species.

Comparatively few operational problems were experienced. While there was some air in-leakage, it was minimial and flue gas concentrations of up to 94% CO_2 were obtained.

Safety was an important issue raised in this report. In one of their tests an explosion occurred. Investigation of conditions leading to the explosion revealed that a sudden interruption of coal flow occurred. This resulted in either a loss of flame or a very weak flame under conditions of high excess oxygen. As oxygen concentration increased the remaining unburned coal eventually caused an explosion. Such a situation could happen in a commercial boiler if a mill trip were to occur. This incident indicated the need for safety interlocks and appropriately positioned sensors.

2.5 Review of paper by Takano, et al., 1995

Takano begins by listing the advantages and disadvantages of O_2/CO_2 combustion, as follows:

Advantages:

- No need of a process to separate CO_2 from exhaust gas
- Combustion efficiency is enhanced by O_2 enriched combustion
- Boiler efficiency is enhanced (lower sensible heat loss)
- Flue gas treatment systems can be more compact (lower quantity of exhaust gas)
- NO_x emissions are reduced

Disadvantages:

- Large amount of energy required for oxygen production
- Recovered CO_2 contains impurities
- Recycling flue gas concentrates corrosive components in flue gas

He looks, in a paper study of a 1000MW pulverized coal boiler, at the following scenarios: (1) the base case, (2) O_2/CO_2 combustion with liquefaction of captured CO_2, (3) O_2/CO_2 combustion with gas compression of captured CO_2, and (4) conventional combustion with the amine absorption process. Though the gross thermal efficiency improves with O_2/CO_2 combustion over the base case, the net effiency drops from 39% for the base case to 30% for the O_2/CO_2 cases and to 27% for the case with amine absorption. In terms of cost, the O_2/CO_2 case with gaseous CO_2 compression was the least expensive option of the three carbon dioxide recovery cases evaluated.

He also conducted bench scale tests to evaluate pulverized coal combustion in an O_2/CO_2 mixture. Conclusions from his bench-scale tests are that NO_x is greatly reduced in O_2/CO_2 combustion and there is the possibility of reducing SO_2 because of its capture by ash in the recycled flue gas.

2.6 Review of paper by Kimura, et al., 1995:

Test results were reported from a pilot scale facility, firing up to 150 kg/h (~330 lb/h) of pulverized coal (New Lands, Australia), that had been modified to allow flue gas/O_2 firing. Flue gas is used for coal transport and to dilute the oxygen to appropriate levels. A key point made in this paper concerns the use of pure oxygen injected directly down the center of the burner, and in some tests directly into the furnace. With the normal 30% O_2/70% flue gas mixture used in the windbox the flame was observed to be unstable and dark compared to that in the air-blown case. The explanation given for this is the higher specific heat of the CO_2 and water vapor versus that of air. It was calculated that, theoretically, 42% O_2 would be needed in the flue gas/oxygen mixture to give the same adiabatic flame temperature as the air-blown case. The authors will verify this calculation, since the O_2 appears quite high. In addition to injecting pure oxygen directly down the center of the burner to improve near-burner stability, pure oxygen was also injected directly into the furnace to achieve the same adiabatic flame temperature as would be obtained with air. The use of pure oxygen in the burner and furnace was shown to improve unburned carbon. Nitrogen oxides increased slightly with direct injection of oxygen, but not to the level produced with air-blown combustion. It was calculated that the optimum volume of directly injected oxygen corresponds to 15% of the total oxygen fed.

2.7 Review of paper by Croiset and Thambimuthu (1998):

Croiset and Thambimuthu conducted pilot scale testing in Canmet's vertically-oriented combustion test rig fired at 0.7 MM Btu/h, burning a North American Eastern bituminous coal. In addition to baseline testing in air, tests were conducted in CO_2/O_2 and in recycled flue gas/oxygen. Recycled flue gas was only done in the dry mode; i.e., the moisture was condensed and removed from the flue gas before recycling. For oxygen enriched cases flame temperature generally increased as oxygen concentrations increased. However, combustion in air (20.9% O_2) gave higher flame temperatures than oxygen enriched tests where O_2 was 28% (in the non-recycle case). The explanation for this is that the higher specific heat of CO_2, compared to air (mostly nitrogen) requires more heat to raise its temperature, thus impacting flame temperature. For 35% oxygen in both the recycle and non-recycle cases flame temperatures were close (slightly higher) than the air case. The air case showed the highest

NO_x. This was explained by the higher nitrogen concentrations in the air case and the higher thermal NO_x. Sulfur dioxides for the non-recycle oxygen cases were very similar to results from burning coal in air. However, for the dry recycle case SO_2 concentrations were lower than for the air case (about 260 ppm versus 310 ppm). This was explained by showing that some of the sulfur dioxide dissolved in the water, which was removed before recycling the flue gas. A concentration of 1000 ppmv of sulfate was found in the condensate water, verifying this claim.

2.8 Others

A number of other papers were reviewed to capture any additional information not covered in the preceding papers and reports. They include:

Nakayama (1992) reports on a feasibility study of burning pulverized coal in recycled flue gas and oxygen in a 1000MW power plant. He concludes that capturing CO_2 in this manner is less expensive than an amine-based process, has a higher net efficiency and requires no more site area than a conventional plant, whereas the amine-based plant would require 50% more area.

To determine ignition characteristics of pulverized coal in a CO_2 rich atmosphere, Kiga, et al., (1997) measured flame propagation speeds in a microgravity combustion chamber. Their results revealed that flame propagation speed was markedly lower in an O_2/CO_2 atmosphere compared with that in O_2/N_2 or O_2/Ar, and that it was improved by increasing the oxygen concentration. They also found lower SO_2 emissions with oxygen/flue gas mixtures compared to air-blown results, and NO_x values were equivalent to what would be attained in air-blown, staged combustion.

Meratla (1997) describes a process where coal is burned in CO_2/O_2, where all contaminents like NO_2, SO_2, are removed cryogenically along with capture of water, dust, partial CO_2 recovery and recovery of heat. Oxygen for combustion is produced by electrolysis at the site of a power plant with cheap power, like a hydroelectric plant in Canada. He points out that hydrogen from the electrolysis process can be sold at a profit to offset the costs of the oxygen production.

Okawa, et al., (1999) evaluated pulverized coal combustion in CO_2/O_2. They recommend an oxygen purity of 97.5%, produced cryogenically, as the optimum purity from a cost versus benefit standpoint. They also recommend an oxygen concentration of 30% in the oxygen/carbon dioxide mixture, the reason being comparable reactive heat transfer to that achieved in air combustion. They found the net efficiency of the oxygen/carbon dioxide fired plant to be 29.1% versus 39.6% for a conventional coal fired plant. Using the amine absorption method to recover carbon dioxide further reduced the net efficiency by 3% over the oxygen combustion method. Though burning coal in oxygen/carbon dioxide increased net thermal efficiency and saved costs due to elimination of the NO_x and SO_x processing equipment, when costs for oxygen production and CO_2 compression are added, operating and equipment annual costs were 3.8 billion yen (~38 million USD) higher than for the conventional plant. Use of the amine absorption plant would increase annual costs to 11.3 billion yen (~113 million USD) over a conventional plant.

For purposes of this section the paper by Kobayashi and Prasad(1999) is of primary interest from the standpoint of burner operation with enriched oxygen. They make the point that significant improvements have been made to oxy-fuel burners within the last several years, for industrial boiler applications. Initial operation of oxy-fuel burners produced high NO_x, but subsequent development has used flue gas recirculation to achieve low NO_x levels. They also make the point that radiative heat transfer is increased (over conventional combustion) due to higher concentrations of CO_2 and H_2O and the longer gas residence time because of reduced gas mass flow.

2.9 Bibliography

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3.0 Oxygen Separation Technologies

3.1 Overview

As reviewed in the previous section, the input of an oxygen stream to the combustor is an important part of a carbon dioxide sequestration process that is based on an existing coal-fired plant where combustion occurs in an oxygen/recycled flue gas media. Thus, in this section, the technical literature on the state-of-the-art of oxygen separation technologies will be reviewed. Here, references that contained information on the energy requirements, capital and operating costs, and how the purity of the output stream affected the energy and economics were sought. This initial literature review, however, did not produce as many references on this subject as were expected. Specifically, less than 10 technical publications were found that specifically addressed this subject, and they form the basis of this initial summary.

For the large-scale production of oxygen gas from atmospheric air, the following choices exist:

- Cryogenic production systems
- Absorption
- Ceramic membrane systems

In addition, researchers from Argonne National Laboratories (Jody, Daniels, and Wolsky, 1997) have recently reviewed the possibility of using chemical cycles for the separation of oxygen from air. This study concluded, however, that the lack of current technical data does not permit an evaluation of the economic competitiveness of such systems.

A general overview of these three technologies, and their application to industrial combustion systems is given in the technical paper of researchers from Praxair (Kobayashi and Prasad, 1999). Along with a summary of the current state-of-the-art of these technologies, a comparison of these three technologies is presented in this paper that considers the following parameters:

- Plant capacity range

- Oxygen purity range
- Power consumption
- Relative capital cost
- Relative oxygen cost
- Operating temperature
- Age of the technology

These authors point out that the energy consumption of an oxygen production plant can represent a major energy penalty. Specifically, in one example for oxygen converted coal-fired power generation plant, using conventional technology (200 kWh/ton O_2), they calculated that about 16% of the power output of the plant would be required for oxygen production. Furthermore, they point out that the minimum theoretical energy requirement (see Royal Society of Chemistry, 1990) is 40 kWh/ton O_2, which is only 20% of the power requirement of today's best technology. This led them to conclude that large-scale oxygen production technologies are far from mature and that there is room for substantial improvements in their state-of-the-art.

In the following sections, the technical literature on the three possible oxygen production technologies will be summarized.

3.2 Cryogenic Production Systems

Cryogenic systems that produce commercial quantities of gas and liquid products represent the majority of industrial gas supplies (Kobayashi and Prasad, 1999). The fundamentals of operation and system designs for cryogenic oxygen production systems are discussed in a number of books on the subject of gas separation or oxygen-enhanced combustion. They include:

- Royal Society of Chemistry (1990). This reference text on the separation of gases includes a chapter on cryogenic air separation as well as a separate chapter on gas separation fundamentals.
- Isalski (1989). This text includes a section on cryogenic separation systems in a chapter on air separation processes. In addition, it contains a chapter on separation plant hardware.
- Baukal (1998). A separate chapter on oxygen production, featuring cryogenic oxygen production, is given in this reference text on oxygen enhanced combustion.

Also, the use of cryogenic air separation (Air Products and Chemicals) is discussed in a paper dealing with air separation unit integration for alternative fuel projects (Smith, Klosak, and Sorensen, 1998).

3.3 Adsorption Systems

Adsorption processes for oxygen production have been commercially available for over 30 years (Kobayashi and Prasad, 1999). The basic technology of this type of process is discussed in the reference book of the Royal Society of Chemistry (1990) and the text of Isalski (1989).

Synthetic zeolites are used for oxygen production via selective adsorption of nitrogen from air. This separation is driven by a cyclic pressure fluctuation resulting in a varied adsorption loading capacity for nitrogen. Depending on the range of pressure used, adsorption processes are called:

- Vacuum Pressure Swing Adsorption (VPSA)
- Pressure Swing Adsorption (PSA)
- Vacuum Swing Adsorption (VSA)

Kobayashi and Prasad (1999) note that the development of advanced adsorbents, improved process cycles and equipment, has resulting in increased capacity for the adsorption separation process as well as a reduction in power consumption (to below 200 kWh/ton O_2). Furthermore, they expect further improvements in technology as more advanced adsorbents are developed.

3.4 Ceramic Membrane Systems

Ceramic membrane based oxygen separation systems, either electrically or pressure driven, have appeared under a number of names. These include:

- Oxygen Transport Membrane (OTM)
- Ion Transport Membrane (ITM)
- Mixed Ionic- Electronic Conductor (MIEC)
- Solid Electrolyte Conductor (SELIC)

A brief overview of this technology is given in the review paper of Kobayashi and Prasad (1999) from Praxair. They state that the use of ceramic membrane systems, either electrically or pressure driven, offers a method for substantially reducing the cost of oxygen production in the future. Furthermore, they expect that ceramic membrane technology will offer the lowest power cost, lowest capitol cost, and overall the lowest oxygen cost of the competing technologies in the future. These conclusions are also implied by researchers from Air Products, who reviewed advanced integration concepts for oxygen plants and gas turbines in IGCC applications (Richards and Russek, 1998).

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4.0 Post Combustion CO_2 Separation Technologies

4.1 Overview

Given the objective of the proposed work, namely to evaluate three alternative CO_2 capture and sequestration/use systems for an existing, pulverized coal-fired boiler, the review of post-combustion carbon dioxide separation technologies was necessarily focused on those approaches that were suitable for this application.   A new coal-fired plant, for example, would offer many new, relatively less expensive opportunities for CO_2 capture such as an integrated gasification-combined cycle (IGCC) power plant (Herzog, et al, 1997).

Post combustion CO_2 separation technologies currently represent the most viable approach to recovering carbon dioxide from existing coal-fired boilers. However, even though post-process CO_2 capture has been practiced in other industries for many years, the idea of using these same separation technologies in the power industry must recognize significant changes in scale of equipment and process conditions.

Approximately 50 references dealing with CO_2 separation have been reviewed. The reference material are comprised of technical papers, relevant chapters from several books and topical reports by universities and research organizations. All but one of the references were published after 1990, with the bulk of the material being published within the last three to four years.

Upon reviewing the reference material on the subject of post combustion CO_2 separation, the technologies can generally be categorized into one of the following areas:

- Chemical and Physical Absorption
- Chemical and Physical Adsorption
- Gas Separation Membranes
- Cryogenic Separation

To date, all commercial CO_2 capture plants use processes based on chemical absorption with a monoethanolamine (MEA) type solvent (Herzog, et al.,1997). Some companies have formulated chemical sorbents wherein improvements have been made to the basic MEA technology (Kaplan, DOW Chemical, 1982; Mariz, et al., Fluor Daniel, 1999; Mimura, et al., MHI, 1999). Still others have combined the virtues of an amine-based sorbent with the high surface area afforded by a polymeric adsorbent support structure (Satyapal, et al.,1999). Also, building on the foundation of MEA-based sorbents, Petroscience Research has formulated “designer solvents” which specifically address the conditions found in effluent combustion gas streams (Chakma, 1999). The Kerr-McGee/ABB Lummus Global CO_2 recovery technology is based on absorption and stripping principle with mono-ethanolamine (MEA) solvent. This technology is commercially proven in three coal-fired plants and a fourth plant is under construction (Gupta, J.C., ABB Lummus Global, Houston, Texas, private communication, 1999).

Combustion conditions in an existing coal-fired boiler could be changed to facilitate the post combustion capture of CO_2. For example, burning coal in a mixture of O_2 and recycled CO_2 will result in much higher concentrations of CO_2. Higher concentrations of CO_2 will greatly facilitate its capture by one of the chemical absorption techniques (IEA, 1999; Herzog, et al., 1997). Detailed coverage on the effects of burning coal in a CO_2/O_2 mixture has been covered in Section 2.

Selective separation of CO_2 can be achieved by physical adsorption of the gas on high surface area solids created by steam activation or as naturally occurring substances like zeolite (Reichle, 1999). Physical adsorption can be operated in either a pressure swing adsorption (PSA) mode or a thermal swing adsorption mode (TSA). These processes are energy intensive and not particularly well-suited to recovery of CO_2 from coal-fired boilers (IEA, 1993; Reichle, 1999).

The use of gas-separation membrane technologies represents a new approach for the specific application of CO_2 recovery from combustion gases. The recovery of carbon dioxide from flue gases is essentially a CO_2/N_2 separation scheme; no commercial membrane systems have yet been developed for this separation, but research is ongoing (Hendriks, 1994; Feron, et al., 1999).

Low temperature distillation (cryogenics) represents yet another approach to recovering specific gases, notably the commercial recovery of oxygen. Schemes have been proposed for both the liquefaction and the solidification of CO_2 as a means of recovering this gas (Hendricks, 1994).

Other technologies which might fall into the realm of new or novel approaches include development of inorganic membranes by the sol-gel method (Osada, 1999), the use of a carbon fiber composite molecular sieve (Burchell, et al., 1997), physical adsorption techniques (Ishibashi, 1999; Ito, 1999) and single step removal of CO_2 and nitrogen from the gas phase in an electrical discharge system (Morvova, et al., 1999).

In addition to the primary task of CO_2 capture, attention has been given during the literature review to the impact of a particular technology on equipment constructability/availability, efficiency (steam consumption), plant integration, implication to overall plant cycle efficiency and cost.

4.2 Recovery by Chemical and Physical Absorption Processes

Physical absorption processes are governed by Henry's law, i.e., they are temperature- and pressure-dependent with absorption occurring at high pressures and low temperatures (Reichle, 1999). Reichle (1999) goes on to say that physical absorption processes are economical when partial pressures of CO_2 are high (greater than 525kPa), as they are in natural gas refining plants, where CO_2 concentrations of 0.1 to 6 % can be effectively removed with amines. Since compressing atmospheric pressure flue gas from a coal-fired plant to the required pressures (for physical absorption to be effective) is not economically viable, physical absorption is not viewed as a near-term technology.

Chemical absorption is preferred for low to moderate CO_2 partial pressures, as would be found in a coal-fired boiler flue gas. The most common among solvents in commercial use for neutralizing CO_2 are the family of alkanolamines (Reichle, 1999). Hendriks (1994) divided the alkanolamines into three classes, according to their reactivity to CO_2: primary, secondary and tertiary amines. Primary amines, monoethanolamine (MEA) and diglycolamine (DGA) are the most reactive. Examples of secondary amines are diethanolamine (DEA) and diisopropanolamine (DIPA), and are less reactive than the primary amines. Examples of tertiary amines are triethanolamine (TEA) and methyldiethanolamine (MDEA). Tertiary amines only react with CO_2 if the partial pressure of CO_2 is well above atmospheric, and are therefore unattractive for recovery of CO_2 from flue gases (Hendricks, 1994). Other chemical solvents in use are ammonia and hot potassium carbonate (Reichle, 1999).

In addition to chemical and physical sorbents, the IEA (1993) refers to hybrid solvents that combine the best characteristics of both chemical and physical solvents and are usually composed of a number of complementary solvents. Hybrid solvents often out-perform conventional solvents and the tendency has been to develop tailor-made solvents where proportions are varied to suit the particular application. Typical hybrid solvents mentioned by IEA (1993) are A-MDEA, Purisol, Sulfinol, and UCARSOL.

Monoethanolamines (MEA) represent the most commonly used sorbent for CO_2 removal. MEA was developed 60 years ago as a general, non-selective solvent to remove acid gases, such as CO_2 and H_2S, from natural gas streams (Herzog, et al., 1997). The process was modified to incorporate inhibitors to resist solvent degradation and equipment corrosion when applied to CO_2 capture from flue gases (Herzog, et al., 1997). Even with the inhibitors, the solvent strength had to be kept low to avoid corrosion; this resulted in large equipment sizes and high regeneration energy requirements (Herzog, et al.,1997). The use of alkanolamines must be balanced against the high energy penalty of regenerating them using steam stripping (Reinchle, 1999). According to Kaplan (1982) recovery of CO_2 from fossil fuel flue gas is complicated by three factors: (1) low concentration of CO_2 in the gas, (2) low pressure of the gas, and (3) corrosion of absorption equipment having high solvent concentrations, especially in the presence of oxygen. Older CO_2 recovery plants used amine concentrations of about 12%, whereas concentrations as high as 30% can be used if inhibitors are present to reduce the severe corrosion properties of the solvent.

Impurities in coal-fired boiler flue gases such as particulates, SO_2, NO_x, and oxygen are deleterious to most amine-based solvents (Hendriks, 1997). Hendriks (1997) cites other literature with regard to the critical levels of SO_2; some researchers have claimed critical levels as low as 10 ppm (Mariz,1999) if solvent losses are to be kept to an acceptable level, while other researchers say optimum SO_2 levels are between 50 and 100 ppm. IEA (1993) reports that SO_2 is about 100 times more soluble in Selexol than CO_2 and is not easily recovered other than by thermal means; they recommend SO_2 concentrations no higher than 10 ppm. The adverse impact of SO_2, as detailed above, demonstrates why it's advantageous to locate the CO_2 capture equipment downstream of the flue gas desulfurization unit. Additives can be employed to offset oxidation of the solvent by oxygen. According to Hendricks (1994), currently used additives allow MEA concentrations up to 30% without major corrosion problems.

A performance comparison between MEA and DEA was carried out by Hendricks (1994) using the flow sheet simulation program ASPEN PLUS. In terms of operational power requirements DEA required less energy (3.3 MJ/kg CO_2 recovered) than the MEA (4.0 MJ/kg CO_2 recovered) for comparable (90%) CO_2 recovery (Hendricks, 1994). However, because of the expected increase in investment costs (for the DEA system), it is not certain whether a recovery system using DEA will lead to lower costs, despite its lower energy consumption. Significantly, Herzog (1997) estimates that the costs of separation and capture, including compression to the required pressure for the sequestration option used, are generally about three-fourths of the total costs of ocean or geologic sequestration. Reichle (1999) reported that when using a base case pulverized coal plant with flue gas desulfurization for comparison, the cost of eliminating CO_2 emissions from advanced power generation plants ranged from \$35 to \$264 per ton of CO_2, and power cost increases ranged from 25 to 215 mills/kWh. Thambimuthu (1998) gives \$35/t CO_2 as a cost of avoided emissions on a pulverized coal-fired system with flue gas desulfurization and MEA capture.

Three papers were reviewed which discussed commercially available chemical absorbent systems, as follows:

- Mariz, et al. (1998): In this paper two commercially available processes by Fluor Daniel (Econamine FG^{SM} Process) and MHI/KEPCO (KS-1/KP-1 Process) are compared. The Fluor Daniel process is similar to conventional amine technology with the exception that flue gas cooling is required and SO_2 must be less than 10 ppm. The KS-1 (solvent) is three times more expensive than MEA but its consumption is half, and it needs no inhibitor. KP-1 refers to the packing structure which results in a lower solvent circulation rate, lower pressure drop and lower steam consumption in the regenerator. Mariz finds capital costs lower with the Econamine process and slightly lower operating costs. CO_2 removal costs, amortized over a 25 year period were found to be $26/ton for the Econamine and $28/ton for the KS-1/KP-1 processes, respectively.

- Mimura, et al. (1998): This paper discusses improvements to MHI/KEPCO's KS-1/KP-1 process, specifically the solvent. Two new solvents have been developed, referred to as KS-2 and KS-3. KS-3 was said to have lower regeneration energy requirements than KS-1 and KS-2, both of which are much lower than MEA. It is claimed that with KS-3 SO_x (50 ppm) and dust had no effect on CO_2 absorption.
- Kaplan (1982): This article in Chemical Engineering discusses Dow Chemical Company's proprietary alkanolamine-based solvent referred to as Gas/Spec FS-1L with an energy-conserving system design developed by Procon. Both companies are marketing this technology under separate licenses.

Additionally, in the realm of commercially-ready systems Kerr-McGee/ABB Lummus Global's process involves combustion of coal in air, followed by CO_2 separation from flue gas with a MEA-based absorption/stripping process. This technology is commercially proven at several installations at Trona, California, Soda Ash; at AES Shady Point, Poteau, Oklahoma, Cogeneration; and at Sua Pan, Botswana, Soda Ash, where it has been successfully operational for a number of years for the purpose of providing CO_2 gas for chemical production and food processing (Gupta, J.C., ABB Lummus Global, Houston, Texas, 1999, private communication).

A major challenge in installing very large-scale CO_2 plants (e.g., 5000 short tons/day or larger as required for a large coal-fired power plant) is limitations on equipment from a constructability and availability point of view. According to Gupta, ABB Lummus Global, in concert with leading vendors of compressors, towers, tower internals, blowers, re-boilers, etc., has developed multiple train concepts with common equipment to minimize costs and yet retain operational flexibility and reliability. Gupta has also indicated that ABB Lummus Global has developed a scheme that permits the use of low level heat available from various sources, e.g., boiler flue gas, hot condensate, inter-stage cooling during CO_2 compression as means for reducing the amount of regenearation steam consumption.

According to Hendricks (1994) the CO_2 recovery unit (employing an alkanolamine) can be added to a power plant without major changes to the power plant. Heat for the recovery process is extracted from the low-pressure turbine resulting in less steam for power production. Additional power losses occur due to pumping the solvent, some compression of the flue gas to overcome pressure drop through the process and compression of the recovered CO_2.

4.3 Recovery by Chemical and Physical Adsorption Processes

Reviewing the article by Reichle (1999) shows the following: Selective separation of CO_2 can be achieved by the physical adsorption of the gas on high-surface-area solids in which the large surface area results from the creation of very fine surface porosity. Fine porosity is often created by a surface activation process (using steam), but some naturally occurring materials also show high surface areas (zeolite). Adsorption capacities and kinetics are governed by numerous factors including adsorbent pore size, pore volume, surface area and the affinity of the adsorbed gas for the adsorbent. Hydrogen production plants that presently use a pressure swing adsorption (PSA) process produce an impure CO_2 stream containing unrecovered hydrogen, methane, CO and nitrogen. Physical adsorbents suffer from low selectivity and low capacity, and they are limited to operation at low temperatures. A number of technological gaps are identified as needing to be resolved before physical adsorption can be seriously considered as a viable technology for CO_2 recovery. According to Reichle (1999) some of the technology gaps are: (1) adsorbents that can operate at higher temperatures in the presence of steam, (2) improved methods for effecting the adsorption-desorption process, and (3) stability of the sorbent needs to be demonstrated over thousands of cycles.

The IEA (1993) report discusses the use of physical adsorbents, as follows: Solid adsorption employs a physical attraction between the gas and "active sites" on the solid, as contrasted to solid absorption where a chemical reaction is employed to capture the gas. Pressure swing adsorption involves lowering the pressure in the vessel containing the saturated bed until trapped gases are pulled off the bed. Regeneration cycles are generally short (measured in seconds). Thermal swing adsorption employs high temperature regeneration to drive of the trapped gases. Regeneration cycles for TSA are long, usually measured in hours. Physical adsorption systems based on the use of zeolites operated in pressure swing adsorption (PDA) and thermal, or temperature swing adsorption (TSA) were evaluated. The IEA report concludes that PSA and TSA technologies are not attractive to the gas and coal-fired power systems in their present state of development, particularly the TSA mode with its large regeneration energy penalty.

Ito and Makino (1999) discusses the use of a physical adsorption process. Physical adsorption in the PSA mode was evaluated for CO_2 capture in an oxygen-blown IGCC. They concluded that in a pressurized condition with an equivalent partial pressure of CO_2 to coal gas, a molecular sieve zeolite showed a high effective capacity for CO_2 capture at 423 K. The potentially adverse effect of other adsorbates in the coal gas, relative to CO_2 adsorption became small at the high temperatures. The effect of H_2S in the coal gas, for example, was negligible in the 2000 hour test that was conducted.

However, given the objective of the subject project, Ito's promising results would not translate to a conventional pulverized coal-fired boiler application which operates at atmospheric pressure and has much lower CO_2 partial pressures than the oxygen blown IGCC.

Ishibashi, et al., (1998) evaluated a physical adsorption process that employed a combination of pressure and temperature swing adsorption (PTSA). A 5000-hour pilot scale test was carried out using a slipstream (0.1% of full gas flow) from TEPCO's Yokosuka Thermal Power Station (265 MW) which was burning a coal-oil-mixture (COM). A pelletized Ca-X (zeolite-based) adsorbent was used and test objectives of 90% CO_2 removal and 99% purity of the CO_2 were met. Energy requirements for CO_2 recovery were 40% of the power output, based on pilot test results. To decrease this large power requirement, reduced pressure drop is being evaluated by changing the adsorbent from pelletized to a honeycomb shape. It is also believed that the change in adsorbent shape will help reduce the size of the equipment, which is very large.

Ishibishi's results are technically promising, but energy costs and size of equipment required continue to be difficult challenges.

4.4 Recovery by Gas-Separation Membranes

The use of membranes for gas separation is a relatively new technology. Commercial membranes have been developed for O_2/N_2 separation, CH_4/CO_2 separation for the purification of natural gas, and H_2/N_2 separation for the recovery of H_2 from purge gases in ammonia plants (Hendricks, 1994). Recovery of carbon dioxide from flue gases is essentially a CO_2/N_2

separation; no commercial systems have yet been developed for this application (Hendricks, 1994).

Gas separation through a membrane is accomplished by selective transport of one of the two gases in the mixture, driven by a pressure difference across the membrane. Important characteristics of a membrane are its permeability and its selectivity for the gases involved.

There are two classes of membranes for gas separation: (1) organic (or polymer membranes), and (2) inorganic membranes. Examples of organic membranes suitable for CO_2/N_2 separation are based on materials like cellulose derivatives, polysulphone, polyamide or polyimide (Hendricks, 1994). Inorganic membranes are chemically stable and suitable for high pressures. Examples are porous inorganic membranes like ceramic membranes and metal oxide membranes, and non-porous inorganic membranes like metallic membranes (Hendricks, 1994).

IEA (1993): Review of this report points out that in addition to the organic and inorganic membranes, which essentially separate the gases because of differences in permeation through the membrane, gas absorption membranes are used as contacting devices between a gas flow and a liquid flow. Separation is caused by the presence of an absorption liquid on one side of the membrane that selectively removes certain components from a gas stream on the other side of the membrane. In contrast with gas separation membranes, it is not essential that the membrane has any selectivity at all. The membrane is merely intended to provide a contacting area without mixing gas and absorption liquid flow. Gas selectivity is derived from the sorbent. This report concluded that CO_2 removal using gas absorption membranes in conjunction with MEA were all significantly better than the membrane on its own.

Review of the DOE “working paper” (Reichle,1999) reveals the following:
Diffusion mechanisms in membranes are numerous and differ greatly depending on the type of membrane used. An example is given stating that polymeric membranes transport gases by a solution-diffusion mechanism (the gas is dissolved in the membrane and transported through the membrane by a diffusion process). Polymeric membranes, while effective, typically achieve low gas transport flux and are subject to degradation. On the plus side polymer membranes are inexpensive and can achieve large ratios of membrane area to module volume. Conversely,

porous inorganic membranes can be 100 to 10,000 times more permeable than polymer membranes, which translates to a much greater gas volume throughput per unit of membrane area. Other advantages of inorganic membranes are long life, ability to withstand high pressures and temperatures and resistance to wastage in corrosive environments. However, the cost for inorganic membranes is high and the ratio of membrane area to module volume is 100 to 1000 times smaller than for polymer membranes.

Most of the papers reviewed on this technology (Hendricks, 1994; Reichle, 1999; IEA, 1993) concluded that the use of membrane separaton has potential, but at the present state of development cannot match the economics of an alkanolamine-based absorbent system. Hendricks (1994) states that polymer membrane separation cannot compete economically with other technologies with respect to recovery of CO_2 from flue gases. He claims that to make membrane separation systems a serious competitor with other technologies membranes are required with a CO_2/N_2 selectivity higher than 200 (currently, the best commercial value is 67). Hendricks (1994) states that the lowest cost per ton CO_2 avoided with an SMS-V (single membrane stage, nitrogen vented to atmosphere) system was $51, versus $34 for an MEA-based system. Reichle (1999) believes that it is likely that an inorganic membrane can be made that will be useful for separating CO_2 from almost any other gas if appropriate operating conditions can be achieved. However, he states that for multiple gas mixtures, several membranes with different characteristics may be required to separate and capture high-purity CO_2.

4.5 Recovery by Low Temperature Distillation

Under certain conditions with respect to temperature and pressure, components of a gas mixture can exist in different phases. This phenomenon can be used to separate carbon dioxide from flue gases. When a gas mixture, such as flue gas, is cooled down, gaseous CO_2 will liquefy or solidify, given correct conditions of temperature and pressure. If a flue gas at atmospheric pressure is sufficiently cooled solid CO_2 will form directly from the gas phase. Liquid CO_2 is formed if the partial pressure of CO_2 is above the triple point (518kPa), the triple point being the conditions of pressure and temperature (518 kPa, -56.6 °C, respectively) where all three phases, gaseous, liquid and solid converge. Therefore, depending on the pressure and concentration of CO_2 when it is cooled down, a certain amount of CO_2 will condense either to the liquid phase or to the solid phase.

Hendricks (1994) discusses the following options: To obtain liquid CO_2 with low-temperature distillation, the condensation temperature must be higher than the temperature of the triple point (-57 °C). High pressures must be applied to get reasonably large fractions of the CO_2 liquefied. For example to liquefy 90% of the CO_2 from flue gases with a CO_2 content of 15% (typical for a coal-fired boiler), the flue gas would have to be compressed to 35,000 kPa (~5080 psi). Some methods have been used for reducing required pressures in other applications (separating CO_2 from natural gas), such as the use of a multi-column system and the use of additive, which must be recycled in the recovery process. High pressures for gas mixtures with low concentrations of CO_2, like flue gas, are still required. A low temperature distillation process to separate CO_2 from nitrogen (main component of flue gas) has not yet been found. To avoid high pressures (lower by a factor of almost 10 compared to liquefaction) CO_2 could be separated by solidification. The disadvantage is that solid CO_2 is more difficult to handle than liquid CO_2. A low- pressure system is described for recovering CO_2 from flue gases of a conventional coal-fired power plant where the CO_2 is collected in the solid phase. For a 600 MW unit having an efficiency starting at 41%, 90% CO_2 recovery will cause the overall plant efficiency to decrease by 11.1% to 29.9%. The cost of electricity would increase from 3.7 cents/kWh to 6.0 cents/kWh. Hendricks believes most of the equipment is commercially proven; the technology for handling solid CO_2 represents the area of greatest uncertainty.

Reichle (1999) discusses the following: Recovery of lean CO_2 streams is best accomplished by low temperature refrigeration and solids processing below the triple point (-57 C). It is pointed out that distillation processes generally show good economies of scale and can be cost effective for large plants. Trace combustion by-products like NO_x and SO_x must be removed before the stream in introduced to the low temperature process. The need to remove trace constituents, coupled with the energy intensity of low-temperature refrigeration, tend to make distillation less economical than other processes. Application of low-temperature distillation is best suited to sources at high pressure and with high concentrations of CO_2, such as is found in natural gas wells.

The IEA (1993) report stated that cryogenics would only be considered for the IGCC and combustion in O_2/CO_2 cases. They reported that water presents a problem in cryogenic systems and must be removed before the flue gas is cooled.

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5.0 Potential Utilization of CO_2

5.1 Overview

Utilization of the CO_2 from flue gas for useful industrial products is a potential alternative to other disposal methods. Numerous researchers have explored this subject, as this literature review yielded about 50 references on the potential utilization of CO_2.

Following other reviews on this subject (IEA, 1995; Herzog, 1993; Arresta, 1992; Arresta, 1997), CO_2 utilization methods can be divided into the following areas:

- Enhanced Oil Recovery (EOR) or Enhanced Gas Recovery (EGR)
- Industrial Uses
- Chemical Conversion (Chemical manufacturing or fuels)
- Biological Methods

The last category, biological methods was not considered in this review, and the reader is referred to a recent IEA summary on CO_2 utilization methods (IEA, 1995), and to reviews conducted in 1993 and 1997 by MIT researchers (Herzog, et al.,1993; Herzog, et al.,1997) . Be that as it may, these authors note that biological methods for CO_2 utilization can be divided into two categories: (1) Direct Fixation: e.g., algae uptake of carbon dioxide into photo bio-reactions, and (2) Indirect Fixation: e.g., the storage of carbon dioxide in biomass as forests and the utilization of forest biomass as fuel.

Before a review of the literature in first 3 areas of potential CO_2 utilization, it is important to note that, for any of these potential utilization methods, one should look at the "big picture" if a particular process is to be considered as a viable method for large-scale carbon dioxide utilization. As an example of this type of detailed assessment procedure, one should consider the work of Audus and Oonk (1997), which was also summarized by Herzog, et al. (1997). In summary, this procedure should include the following criteria:

- Net emissions of CO_2: The proposed utilization method has to reduce the net emissions of carbon dioxide to the atmosphere. Here, mass and energy balances for the process can provide the basis for an accurate assessment of the carbon balance. Specifically, does the process consume carbon? (i.e., is the C/H ratio of the stable products greater than that of the raw material?).

- Energy input for Conversion: For chemicals that are predominately carbon and hydrogen, the heat of reaction of the process should not be more than 1.25 times the heat of combustion of the reference fuel.
- Process Characteristics: When alternate utilization processes are being compared, the better choice will usually involve:

    1) A reduction in the number of processing steps
    2) Milder operating conditions
    3) Fewer discontinuities in operating conditions
    4) Improved possibilities for process integration
- Favorable Reaction Equilibrium Chemistry: Negative or slightly positive free enthalpy change (ΔG) indicates that the equilibrium for the reaction favors the desired product
- Effectiveness: This performance parameter is defined by:

    1) Significant storage lifetime (e.g., time scales of 100 to 1000 years or more)
    2) Market size (sufficient to sequester 10 million tons of CO_2 per year)
    3) Availability of co-reagents (to process at least 10 million tons of CO_2 per year).

Examples of the use of the assessment procedure methodology are given in the paper of Audus and Oonk (1997) for two case studies:

1) Fixation of CO_2 as an inorganic carbonate
2) Production of methanol by an alternative process

In summary, it should be noted that, once a process meets these criteria, the economic feasibility still must be determined. This subject is addressed in a number of the following reviewed publications on CO_2 utilization. For example, Appendix B of a 1993 MIT review (Herzog, et al., 1993) contains some useful examples of economic evaluation criteria that are currently in use for CO_2 sequestration processes.

5.2 Enhanced Oil Recovery (EOR) or Enhanced Gas Recovery (EGR)

5.2.1 Enhanced Oil Recovery

Comprehensive overviews of the potential use of CO_2 for enhance oil recovery (EOR) are given in the references of Sparrow (1987) and Bondor (1992), with the most detail given in a general MIT review (Herzog, et al., 1993). Furthermore, a number of publications (IEA, 1995; Herzog, 1993; Arresta, et al., 1992; Arresta and Tommasi, 1997) point out that enhanced oil recovery (EOR) is the largest current user of carbon dioxide, with stated amounts ranging up to 80% mentioned.

The literature review produced a number of technical publications on worldwide applications of this subject, including the following:

- Berman, Winter, and Chen, 1997 (US DOE, Burns and Roe, SAI): This paper examines the utilization of depleted oil and gas reservoirs in Texas for power plant generated CO_2. In addition to technical factors, the authors present the results of economic studies using this concept for storage, and for EOR. One of their conclusions is that oil reservoirs are economically preferred to gas reservoirs since operators are willing to buy the CO_2 for enhanced oil recovery.

- DeMontigny, et al., 1997 (University of Regina, Canada): In this paper the authors show how cogeneration concepts can be used to reduce energy production costs by simultaneously producing electricity, CO_2, and steam for EOR applications. The paper presents the design concept for the combined power system, some key design output specifications, and a summary of the economic results for three variations of the basic system. Under favorable conditions (a market for the power outputs of the combined system) the economic results show the advantages of this proposed system.

- Deshun, Chen, and Lihui, 1997 (Tsinghua University, People's Republic of China (PRC)): These researchers have investigated the feasibility of CO_2 from power plants based EOR in the PRC. For this initial feasibility study, the primary emphasis was on a case study that used CO_2 injection in the Jilin oil field. An overall flow chart of the proposed system is presented along with some initial economic results (via incremental costs for the CO_2 mitigation). The authors also summarize the technical and economic barriers facing this type of project.

- Iijima, 1999 (MHI): This work presents an analysis for the cost of flue gas CO_2 recovery using new MHI developed technology (new energy saving absorbent) for the purpose of enhanced oil recovery. Material balance and overall economic results are presented for two power plant designs (a 600 MW natural gas boiler and a two unit 90 MW gas turbine design).

- Tanaka, Hakuta, and Haino , 1992 (University of Tokyo, Japan): This paper presents the results of a case study system for the utilization of CO_2 in an EOR system. The system involves separation and recovery of CO_2 from fixed sources in Japan, liquefaction and transportation to the oil fields in oil producing countries, injection to the reservoir, and eventual recovery and recycling. At the time of completion of this paper, however, all the tasks of the project were not completed.
- Holt, Jensen, and Lindeberg, 1995 (IKU Petroleum Research, Norway): These investigators reviewed the potential for EOR in light of Norwegian oil field experience.

In another work discussing the potential of CO_2 utilization for EOR, IEA (1995) researchers concluded that CO_2 application in EOR could be applied more extensively than previous researchers had envisioned. They concluded that the barrier preventing current extensive use of CO_2 for EOR is economics, and that oil prices do not justify EOR, unless CO_2 is available at a cost of less than $20/t (yielding a 10% return on investment). They also note that transportation of CO_2 to oilfields can be a problem and another potential problem here is the integrity of long term storage. The economics of CO_2 used for EOR is also discussed by Bondor (1992).

Herzog, et al., (1993) point out that there were literally 100's of papers and technical books that were focused on EOR operations, with many directed specifically towards the optimization of CO_2 miscible displacement. At this time, they also concluded that a comprehensive review involving EOR technology from industry and academia should be used as a first step to define non-redundant research tasks to improve fundamental understanding and to refine modeling and simulation capabilities to reduce uncertainties in technical and economic feasibility estimates.

5.2.2 Enhanced Gas Recovery (EGR)

Another application of CO_2 utilization occurs when carbon dioxide is used for enhanced gas recovery (EGR). Currently, work in this area consists of two major variations:

1) Use of CO_2 injection for enhanced recovery of natural gas.
2) Use of CO_2 for enhancement of the production of natural gas from coal deposits.

In an example of the first case, the enhanced recovery of natural gas is summarized in a paper by Blok, et al. (1997). This study deals with the use of EGR combined with the production of hydrogen from natural gas. In addition to schematics of the proposed system, the paper presents economic results for three variations of the base case design. One conclusion of this study is that, taking credit for enhanced natural gas recovery, the penalty for gas sequestration is reduced to a net incremental cost of about 2%.

The second case, the enhancement of coal bed methane, is described in two recent papers (Gunter, et al., 1997; Bryer and Guthrie, 1997). It should be noted that unlike the CO_2 injection EOR process where CO_2 breakthrough eventually occurs, in this process the injected CO_2 is sequestered in the reservoir by sorption to the coal surface. The two papers just describes the overall concept and no mass, energy, or economic calculations for the viability of the process are presented. Also, a summary of recent publications in this area is given in the recent MIT general review (Herzog, et al., 1997). They note that, although the process is still in the development stage, the process has been tested in pilot scale field studies conducted by Amoco and Meridan in the San Juan Basin (Colorado).

5.3 Industrial Uses

For this literature review, this subject is limited to industrial uses that do not convert carbon dioxide into other chemicals. Under this category, some authors (e.g., Arresta, et al., 1992; Arresta and Tommasi, 1997) include enhanced oil recovery (EOR); however, this application was reviewed in the previous section.

A summary of industrial uses of carbon dioxide is included in the following references:

- IEA (1995)
- Arresta, et al. (1992)
- Arresta and Tommasi (1997)
- Herzog, et al. (1997)

As reviewed by these authors, they include the following applications

- Waste water treatment
- Food packaging and freezing
- Additive for beverages and food
- Extraction (e.g., extraction of flavors from plants, of caffeine from coffee, etc)
- Welding
- Refrigeration
- Fire extinguishers

Herzog, et al., (1997) note that, even in a vigorous CO_2 mitigation effort, many small industrial activities could be converted to power plant feed streams (as compared to natural wells in use today (Arresta, et al., 1992)). The total impact, however, would still be much less than 1% of the total power plant CO_2 generated. Furthermore, researchers at IEA (1995) emphasize that the CO_2 utilized in these industrial applications still returns to the atmosphere.

5.4 Chemical Conversion (Chemical manufacturing or fuels)

As evidenced by the amount of technical information in the open literature, this subject is one of the current CO_2 utilization favorites. In general this potential CO_2 utilization method can be divided into two categories:

1) Chemical conversion to fuels
2) Conversion of carbon dioxide to other chemicals

Both these categories are discussed in the following sections.

5.4.1 Chemical Conversion to Fuels

As detailed by Herzog, et al., (1997), a large use that could begin to meet power plant emissions of CO_2 would be to ‘recycle” the CO_2 back to a fossil fuel that could reduce the use of virgin fossil fuels. They note, however, that reducing CO_2 back to carbon requires at least 80% of the energy that is generated from burning a typical coal, and that when losses and efficiencies are considered, this type of process could result in a net energy loss. Unless this energy comes from non-fossil sources, additional CO_2 is generated. Thus, any scheme that includes the chemical conversion of CO_2 to fuels must include a detailed mass and energy balance before hand.

In this light, numerous researchers have carried out studies regarding the possibility of converting CO_2 to methanol, which could be used as a transportation fuel. A majority of these investigators are from various institutions in Japan. For example, the literature review yielded the following Japanese-based references that explored various phases of the conversion of CO_2 to methanol:

- Inui, 1999 (Kyoto University): Discusses recent work on several schemes to use CO_2 for the production of methanol.
- Arakawa, Dubois, and Sayama, 1992 (National Chemical Laboratory for Industry): Proposed a catalytic hydrogenation system for recycling CO_2 combined with hydrogen energy production system requiring a solar energy (PV, photocatalyst) input.
- Sugawa, et al., 1995 (RITE, National Institute of Materials and Chemical Research): Studied the catalytic hydrogenation of CO_2 to methanol using a silver catalyst.
- Fan and Fujimoto, 1995 (University of Tokyo): Worked on the development of noble metal catalysts for the hydrogenation of CO_2 to methanol.
- Hagihara, et al., 1995 (RITE, Mitsui-toatsu Chemicals, NIRE): Proposed a liquid phase methanol synthesis using liquid-liquid separation
- Hirano, et al., 1995 (Kansai Electric Power, MHI): Studied the possibility of methanol synthesis from CO_2 using $CuO\text{-}ZnO\text{-}Al_2O_3$ catalysts.
- Saito, et al., 1995; 1997a, 1997b (NIRE, RITE): Studies methanol synthesis from CO_2 and H_2 using a Cu/ZnO based catalyst.
- Mabuse, et al., 1997 (RITE, NIRE): Investigated a liquid phase catalyst for methanol synthesis from CO_2 and H_2.
- Kanai, et al., 1995 (RITE, NIRE): Studied the role of ZnO in promoting methanol synthesis over a physically mixed Cu/SiO_2 and ZnO/SiO_2 catalyst.

Other work on methanol synthesis from CO_2 also includes the work of Bill, et al., (1997) and work on a natural gas decomposition process using CO_2 (Steinberg, 1997). The later process, presently under investigation is of particular interest from an energy utilization standpoint (see Herzog, et al., 1997).

It should be noted that many of these researchers have concentrated on the development of improved catalysts and catalytic pathways, both liquid and gas phase, to achieve high conversion and minimal energy losses in using H_2 to convert CO_2 to methanol (see Herzog, et al., 1997). However, as pointed out by such researchers as Herzog, et al. (1997) and Audus and Oonk (1997), however efficient the conversion, the fundamental energy requirements to recycle CO_2 to methanol still make the conversion very limited from an energy utilization standpoint.

In addition, other researchers from Japan (Inui, et al., 1992, 1997) have studied processes that convert CO_2 to gasoline. In this light, Inui (1999) summarizes work on the selective synthesis of gasoline or light olefins from CO_2-H_2 mixtures by one pass conversion via methanol synthesis. Fujimoto, et al., (1992) also studied the selective synthesis of liquid hydrocarbons from CO_2 and methane. None of this work, however, has reached even the pilot plant stage.

5.4.2 Chemical Conversion of CO_2 to Other Chemicals

The use of carbon dioxide as source of carbon for the large-scale synthesis of chemicals has been investigated by a number of research groups in recent times. In a 1992 review of this subject, Aresta, Quaranta, and Tommasi (1992), review a number of potential chemical products that could result from the large scale utilization of CO_2. These included:

- Agrochemicals
- Carboxylated products
- Polymers
- New Materials

In dealing with possible chemical conversion pathways, they note that several evaluation criteria are possible, including:

- Added value of the product
- Market size of the product
- Energy requirements for the synthesis of the product
- Rate of carbon dioxide conversion (yield and selectivity towards the product)
- Lifetime of the product

In their review, they also point out that several new CO_2 based synthesis procedures had been developed.

In more recent work on this subject, Arresta and Tommasi (1997) expand on the classification of carbon dioxide chemical conversion by grouping all possible conversion of CO_2 by the following:

1) Fixation of the entire molecule into organic products (synthesis of species in which the _COO-moiety is present: RCOOH, RCCOOR', ROC(O)OR', polycarbonates, polyurethane,etc. (Urea, H_2NCOHN_2, and its derivatives are also included in this list).
2) Fixation into inorganic carbonates (synthesis of Group 1- 2-element carbonates that already find industrial applications, and interaction of carbon dioxide with natural basic silicates (mimicking the "silicate weathering" process that produces carbonates).
3) Reduction to other C1 molecules (HCOOH, CO, H_2CO, CH_3OH, CH_4) or fixation of a reduced form (synthesis of Cn-alcohols and hydrocarbons, formamides, etc.).

Furthermore, in the conclusion of their work they state that CO_2 is used by the chemical industry at the rate of 100 Mt/year and that this limit must be expanded before carbon dioxide utilization can be a significant technology. They also conclude that an assessment of the real potential of this technology requires an inventory of feasible processes and the definition of the conditions for exploitation.

Other potential chemical products from carbon dioxide have been proposed or reviewed by a number of investigators. They include:

- Lipinsky, 1992 (Battelle): Conducted a research study for a consortium of Canadian companies. The work considered opportunities in the paper and pulp industry, and polymers.
- IEA Researchers (IEA, 1995): Reviewed the use of CO_2 in the chemical manufacting of: CO_2 polymers, Dimethyl Carbonate (DMC), and replacement of chemical and solvents used commercially. Their summary results did not indicate a large market for any of these applications.
- MIT Researchers (Herzog, et al., 1993, 1996, 1997): In their review of chemical utilization options they evaluate the use of carbon dioxide for the production of plastics. They conclude that this option would not have a major impact.
- Baiker, 1999 (Swiss Federal Institute of Technology): This researcher emphasizes the belief that catalysts provide a number of opportunities to convert CO_2 to valuable chemicals. Specifically, the following resulting chemical products are identified: 1) Carbonates, 2) Carbamates, 3) Urethanes, 4) Lactones, 5) Pyrones, and 6) Formic acid and derivatives.

5.5 Bibliography

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6.0 CO_2 Sequestration

6.1 Overview

In this section, the technical literature dealing with the sequestration of CO_2 will be reviewed. In recent years, the potential sequestration or storage of CO_2 recovered from large scale utility generation has been the subject of numerous publications. Specifically, during the course of this work, about 45 technical references on the subject were reviewed. In addition, it should be pointed out that (see IEA, 1994), the calculation of large scale storage potentials for carbon dioxide is fraught with numerous assumptions and made difficult by the differing concepts associated with various storage options.

A number of research groups have produced technical reports or portions of books on the general subject of CO_2 sequestration. These include the following:

- Herzog, et al. from the MIT Energy Laboratory (Herzog, et al., 1993; 1995; 1996; 1997; 1999a; 1999b; 1999c; 1999d). In addition to a general overview of the carbon dioxide emissions problem from large-scale utility generation, these papers and reports give a comprehensive review of the existing and potential CO_2 sequestration issues and technologies.
- U.S. Department of Energy Researchers (Reichle, et al. 1999). This recent working paper (book length) gives a detailed overview of the current status of carbon sequestration science and technology.
- IEA Greenhouse Gas R&D Programme (IEA, 1994). This European based organization has produced a number of 'white' papers dealing with carbon dioxide emissions. The one of most interest here specifically addressed the subject of carbon dioxide disposal from power stations.
- Hendricks (1994). This textbook includes a chapter on the underground storage of carbon dioxide
- Holloway (1997a, 1997b). In addition to a general overview of the underground disposal of carbon dioxide, this author addresses the safety aspects of this sequestration process.

Based on a consensus of the work of these references and others, various researchers have examined the following potential options for large-scale carbon dioxide sequestration:

1) Ocean Sequestration of CO_2
2) Land (Geological) Storage in Active Oil or Gas Reservoirs

3) Land (Geological) Storage in Depleted Oil or Gas Reservoirs
4) Land (Geological) Storage in Coal Formations
5) Land (Geological) Storage in Deep Aquifers
6) Land (Geological) Storage in Salt Domes or Rock Caverns
7) Land Storage in Thermally Insulated Respositories
8) Sequestering of CO_2 in Mineral Form.

The first option, ocean sequestration, was beyond the scope of this work and the literature was not reviewed in detail. For a detailed review of this segment, however, the reader is referred to a recent DOE white paper (Reichle, 1999), the work of Herzog, et al. at the MIT Energy Laboratory (Herzog, et al., 1993; 1995; 1996; 1997; 1999a; 1999b; 1999c; 1999d), and other selected technical papers (Haugen and Drange, 1992; Fujioka, 1997).

Geological storage in active oil or gas reservoirs (know as Enhanced Oil Recovery (EOR) or Enhanced Gas Recovery (EGR) was reviewed in the previous section under CO_2 utilization methods. Thus, it will not be included in this section.

The sixth option, geological storage in salt domes or rock caverns, is discussed in references from the MIT Energy Laboratory (Herzog, et al., 1993; 1997). These researchers point out that despite the high technical feasibility of such a carbon dioxide storage process, without a major breakthrough, the costs of excavating rock caverns are too high to be practical. For this reason, and since no recent technical references were found on this subject, this potential storage method will not be reviewed in detail here.

A conceptual scheme for storing CO_2 from a 500 MW coal fired power station in solid form was presented in an IEA report on carbon dioxide storage (IEA, 1994). These researchers concluded that such a scheme for the storage of solid CO_2 was prohibitively expense. Thus, this storage method will not be examined any further here.

The last CO_2 storage option, sequestering of CO_2 in mineral form, has been the recent subject of a number of researchers at Los Alamos National Laboratory (see Butt, et al., 1998; Goff, et al., 1998, Lackner, et al.,1997, 1999). Since this method of carbon sequestration is still in a conceptual form, and also since it could be classified under chemical utilization of CO_2 (see

Reichle, et al.,1999), this potential sequestration method was also not reviewed further at this time.

This leaves three sequestration methods that will be reviewed in more detail in the following sections:

- Land (Geological) Storage in Depleted Oil or Gas Reservoirs
- Land (Geological) Storage in Depleted Coal Formations
- Land (Geological) Storage in Deep Aquifers

In addition, due to its special application in the state of Ohio in particular, the literature regarding the potential geological storage of CO_2 in Ohio will be reviewed in a separate section.

For geological storage, Herzog, et al., (1993) point out that there are several common geotechnical performance issues that should be addressed. These include:

- Resource assessment
- CO_2 transportation and placement methods
- Displacement behavior of CO_2 within the reservoir/cavity
- Storage capacity
- Containment with long-term environmental integrity
- Engineering economic factors

Also, before reviewing the current literature on these three sequestration methods, it is important to note that any comparison of CO_2 sequestration methods should include a review of technical and economic factors in two areas: 1) Overall Feasibility, and 2) Operational Drivers. The recent U.S. Department of Energy report on this subject (Reichle, et al., 1999), subdivides these areas into the following (following Figure 5.5 of their report):

1) Overall Feasibility
    - Co-Located Capacity
    - Industrial Experience
    - Beneficial Uses of CO_2
    - Natural Analogues for Sequestration
    - Safety and Cost Analysis

2) Operational Drivers
   - Monitoring
   - Performance Assessment and Prediction
   - Injection, Drilling, and Completion Technology
   - Formation Characterization
   - CO_2 Waste Stream Characteristics
   - Trapping Mechanisms

A discussion of these subjects is beyond the scope of this review, but this list does illustrate the complexity of the problem faced by the proponents of any large-scale carbon dioxide sequestration process.

6.2 Land (Geological) Storage in Depleted Oil or Gas Reservoirs

For a starting point, excellent sources of technical and economic information on the subject of geological storage of CO_2 in depleted oil or gas reservoirs are found in the general CO_2 sequestration work of the U.S. Department of Energy (Reichle, et al., 1999), the IEA (1994), the MIT Energy Laboratory (Herzog, et al., 1993, 1997), and the textbook of Hendricks (1994). Furthermore, Reichle, et al., (1999) present a detailed section on the subject of R&D needs and priorities for advancing the technology and acceptability of CO_2 sequestration in oil and gas reservoirs.

In addition to these combined sources of information, a number of individual technical papers that have examined the subject of the storage of CO_2 in depleted oil or gas reservoirs were reviewed. Ones of particular interest include the following:

- Hendricks, Blok, and Turkenburg, 1992 (University of Utrecht, The Netherlands): This paper combines the storage of CO_2 with an integrated-gasifier, combined-cycle power plant. The economic calculations are based on a system sited in the Netherlands.
- Koide, et al., 1992 (Geological Survey of Japan, Kanto Natural Gas, Electric Power Development, MHI, and National Chemical Laboratory): These Japanese researchers investigated the feasibility of long term storage of carbon dioxide in depleted natural gas reservoirs. The system feasibility is investigated on a worldwide basis.
- van der Burgt, Cantle, and Boutkan, 1992 (Shell Oil Company): This paper, prepared by researchers from The Netherlands examines the technical and

economic feasibility of CO_2 sequestration in small and large depleted gas fields in the Netherlands.
- Hendricks and Blok, 1995 (Utrecht University): This paper summarizes the potential for carbon dioxide storage in natural gas and oil fields on a worldwide basis.
- Tanaka, Koide, and Sasagawa, 1995 (ENAA, Japan): These researchers addressed the problem of carbon dioxide sequestration in oil and gas reservoirs in Japan.

6.3 Land (Geological) Storage in Depleted Coal Formations

There are not as many technical references on the sequestration of carbon dioxide in depleted coal formations as the other two geological storage options. However, some recent initial sources of technical and economic information on the subject of geological storage of CO_2 in depleted coal formations are found in the general CO_2 sequestration work of the U.S. Department of Energy (Reichle, et al., 1999), and the MIT Energy Laboratory (Herzog, et al.,1997).

Reichle, et al. (1999) note that coal formations provide an opportunity to simultaneously sequester CO_2 and increase the production of natural gas. In this process, methane production from deep unmineable coal beds can be enhanced by injecting CO_2 into coal beds where the adsorption of carbon dioxide causes the desorption of methane.

A number of individual technical papers have discussed the storage of CO_2 in coal formations. Ones of particular interest include the following:

- Bryrer and Guthrie, 1997, 1998, 1999 (U.S. Department of Energy, FETC): These authors provide an overviews assessment of the worldwide potential of this CO_2 sequestration technology.

- Stevens, et al., 1999 (Advanced Resources, Inc, and IEA): This paper, sponsored by the IEA Greenhouse Gas R&D program, presents a summary of pilot results and the worldwide potential of CO_2 sequestration in deep coal seams.

6.4 Land (Geological) Storage in Deep Aquifers

As with a previous section, excellent initial sources of technical and economic information on the subject of geological storage of CO_2 in deep aquifers are found in the general CO_2

sequestration work of the U.S. Department of Energy (Reichle, et al., 1999), the IEA (1994), the MIT Energy Laboratory (Herzog, et al., 1993, 1997), and the text book of Hendricks. These references also include comparisons of the three options, and estimates of the worldwide CO_2 storage potential.

It is interesting to note that there are many more technical publications on this subject than the other two previously summarized geological storage options. A number of examples obtained during this literature review include:

- van der Meer, 1992, 1995 (TNO Institute of Applied Geosciences, The Netherlands): This paper summarizes the results of investigations on the technical feasibility of storing carbon dioxide in aquifers. In addition, the physical processes, geothermal aspects, and environmental aspects that occur when CO_2 is stored in an aquifer were investigated. Also, the underground storage capacity of the Netherlands was estimated.

- Bergman and Winter, 1995 (U.S. Department of Energy, PETC): These authors have investigated the potential capacity of deep saline aquifers in the U.S. In addition to an estimate of the storage potential, they note that saline aquifers underlie the regions in the U.S. where most utility power plants are sited.

- Holt, Jensen, and Lindeberg, 1995 (IKU Petroleum Research, Norway): These investigators reviewed the potential for CO_2 storage in aquifers on a general basis.

- Hendricks and Blok, 1995 (Utrecht University): This paper summarizes the potential for carbon dioxide storage in aquifers on a world-wide basis.

- Koide, et al., 1995 (AIST/MITI, Japan): This paper concentrates on the subject of the potential self sealing mechanisms of CO_2 in aquifer reservoirs.

- Tanaka, Koide, and Sasagawa, 1995 (ENAA, Japan): These researchers addressed the potentia for carbon dioxide sequestration in aquifers in Japan.

- Weir, White, and Kissling, 1995 (Industrial Research, Ltd, New Zealand): This paper summarizes the computational modeling of CO_2 storage in deep aquifers.

- Gupta, Herlihy, and Sass, 1997; Gupta, et al., 1997; Gupta,Naymik, and Bergman, 1998 (Battelle Columbus): In addition to a general overview of aquifer based CO_2 storage, a major part of this work presents a literature review of the feasibility of aquifer storage in the Midwestern U.S. More details of these researchers work will be presented in the next section.

- Lindberg and Wessel-Berg, 1997 (IKU Petroleum Research, Norway): This work examines the potential for vertical convection, which influences the storage capacity of CO_2 in aquifers.

- Lindeberg, 1997 (IKU Petroleum Research, Norway): This paper addresses the problem of CO_2 escape from aquifers.

- Otto, 1998 (CSIRO): This paper summarizes work that investigated the storage of CO_2 in deep aquifers in Australia.

- IEA, 2000 (International Energy Agency, Europe): This reference summarizes the current status of the first large-scale process for the storage of carbon dioxide in aquifers. In this system, CO_2 is injected into a deep saline reservoir 800 m below the bed of the North Sea.

6.5 Land (Geological) Storage in Deep Aquifers: Applied to the State of Ohio

One of the objectives of this literature review was to address the potential utilization of CO_2, especially as it is related to Ohio coals. In this respect, it was considered appropriate to review the literature on CO_2 sequestration as specifically applied to the State of Ohio.

As reported by researchers from Battelle and the U.S. Department of Energy (Gupta, Naymik, and Bergman, 1998), the National Energy Technology Laboratory of DOE has sponsored a project that uses data from an existing hazardous waste disposal injecting into the Mt. Simon Sandstone aquifer in Ohio to evaluate hydrogeologic, geochemical, and social issues related to CO_2 disposal.

One result of major interest on this subject was a detailed literature review on the feasibility of underground carbon dioxide injection in the midwestern U.S. (Gupta, Herlihy, and Sass, 1997). In addition to containing an annotated bibliography of technical references on CO_2 storage, this report contains separate chapters on the following subjects (including many that contain a detailed technical review of a subject):

- Carbon Dioxide Disposal in Deep Aquifers and Oil Fields
- Deep Well Disposal of Waste and Gases
- Modeling
- Regional Hydrogeology of Deep Aquifers in the Midwest
- Regulations and Status of Underground Injection Wells in Ohio
- CO_2 Emissions Inventory throughout Ohio

It is expected that this report will provide an excellent starting point for a specific study that would consider CO_2 storage in a deep saline aquifer for application to an Ohio based power plant.

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7.0 General Bibliography

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