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Evaluation of Options for CO₂ Capture/Utilization/Disposal

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OBJECTIVES

The primary objective of this project is to develop in-depth engineering evaluations of technologies for the capture, use, and disposal of carbon dioxide (CO₂). This project emphasizes CO₂-capture technologies combined with integrated gasification combined-cycle (IGCC) power systems. Complementary evaluations will address CO₂ transportation, CO₂ use, and options for the long-term sequestration of unused CO₂. Commercially available CO₂-capture technology will provide performance and economic baselines for comparing

innovative technologies. These results will then support recommendations for research and development to improve CO₂ capture and use, new process concepts, and optimized energy balances for CO₂ mitigation. Limited experimental research will provide data for evaluating new concepts.

BACKGROUND INFORMATION

The possibility of global climate change resulting from increasing levels of "greenhouse" gases is the subject of considerable debate and

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uncertainty. However, increasing atmospheric concentrations of CO₂ have the potential for significant impacts that may not be easily reversed. Because of these concerns, policies to limit CO₂ emissions are being discussed both in the United States and in various international forums (1). The options under consideration include calls for strong energy-conservation measures, the capture and sequestering of CO₂, and the substitution of nonfossil energy sources for fossil-fuel combustion. Discussion of the issues has drawn considerable interest to power generating systems that minimize the production of CO₂ and are amenable to CO₂ capture.

Integrated gasification combined-cycle systems, which are becoming an increasingly attractive option among the emerging technologies, combine several desired attributes. First, IGCC systems provide high energy-conversion efficiency, with the prospect of even higher efficiencies if higher-temperature turbines and hot-gas cleanup systems are developed. Second, very low emission levels for sulfur and nitrogen species have been demonstrated at such facilities as the Cool Water IGCC plant in California. Third, IGCC plants produce flue-gas streams with concentrated CO₂, and high levels of CO, which can be easily converted to CO₂.

Recovery of CO₂ in IGCC systems is potentially less expensive than in conventional combustion systems. CO₂ recovery now can be accomplished in conjunction with hydrogen sulfide (H₂S) removal by using several commercial technologies. At the same time, advanced process concepts now under development offer the prospect for further significant improvements.

PROJECT DESCRIPTION

Carbon Dioxide Recovery

System Definition. The evaluation of commercially available CO₂ recovery processes for application to IGCC plants will begin this project. The base case chosen is a 400-MW IGCC system using an air-blown KRW gasifier and in-bed sulfur removal. Detailed consideration of the design and costs for IGCC systems appeared in a recent METC report (2). A simplified schematic for this

process appears in Fig. 1; an expanded block diagram for the IGCC system from the METC report appears as Fig. 2.

A number of CO₂-removal technologies are commercially available for application to IGCC systems, including scrubbing processes based on amines, glycol (Selexol), or methanol (Rectisol). However, all of these options involve cooling or refrigerating the gas stream, with an attendant loss of thermal efficiency. After establishing a commercial baseline, the project will evaluate emerging technologies for both low-temperature CO₂ removal (e.g., facilitated transport membranes) and high-temperature removal (e.g., calcium- or magnesium-based sorbents and molten-carbonate cells). System definition for the CO₂-capture technologies includes the identification of plant or energy system boundaries and the selection of performance parameters to be used for the evaluation. Costs will be presented in the context of revenue requirements, including fixed charges, tax effects, and operating costs. The objective will be to determine those costs within a range of $\pm 30\%$. The cost analyses will be performed on a spreadsheet, allowing for recalculation under various sets of assumptions.

Net emissions, which are of interest in this project, will include more than unrecovered CO₂. Differences in plant materials and energy requirements will result in differences in the emissions of other pollutant species. Criteria pollutants, air toxics, solid wastes, and water emissions are of possible interest. Again, the issue of system boundary is important, since some of these emissions are associated with upstream processes.

Integration of the Gasifier and CO₂ Recovery Systems. The relationship between gasifier operating characteristics and CO₂-recovery system requirements will be examined in order to identify factors — such as operating temperature, product-gas composition, and plant scale — that could limit the applicability of certain recovery systems. It is necessary to recognize that this is a combined CO₂, H₂S, and heavier hydrocarbon recovery system for the IGCC plant. Hence, it is important to settle on a realistic base-case feed-stream composition. The product CO₂ from these systems will have to be of suitable quality for

long-distance pipeline transport. Again, it is necessary to establish standards for the trace components in the CO₂ product stream so that these systems can be evaluated for consistent specifications. The three systems described below are representative of current technology and are likely candidates for the evaluations, on the basis of previous analyses conducted for the Great Plains Gasification Plant.

Both H₂S and CO₂ may be directly recovered in a simple amine absorber-stripper system. Using tertiary amines, such as MDEA (methyldiethylamine), it would be necessary to cool the feed gas below the hydrocarbon dewpoint. The first tower of the absorber system would operate at low pressure (approximately 50 psig) to recover as much CO₂ as possible. Further polishing could be done by dehydrating and cooling the CO₂-lean off gas and then contacting it with MDEA in a second tower at high pressure (600 psig). The CO₂-rich solution would then be taken to the amine stripper for recovery of a high-purity CO₂ stream. Hydrogen sulfide could be recovered separately, if required.

The Selexol glycol-based recovery process has been used at the Cool Water IGCC plant to separate H₂S from CO₂. Both sulfur and saleable CO₂ can be produced. The Selexol process operates by using a glycol-based solvent to strip out both CO₂ and H₂S and then recovers them as two separate streams. In an IGCC application, heat exchangers would be used to cool the raw sulfur-laden synthesis gas, which would then be diverted and fed upward through an absorber column, where it would contact a counter-current flow of chilled lean Selexol solvent. (This is a glycol-based solvent not unlike automobile radiator fluid.) Rich solvent from the absorber would then be fed to a second column, where the absorbed H₂S would be stripped off and routed to a sulfur-treatment system. Subsequently, the CO₂ would be stripped off and recovered as a product stream. Regenerated (or lean) Selexol solvent is then successively cooled by heat exchange with rich solvent and supplemental ammonia refrigeration so that it can be recycled to the absorber.

The Rectisol methanol-based recovery process uses methanol as a physical solvent for the H₂S and CO₂ in the IGCC gas stream. For

acid-gas removal, the absorption step is preferentially carried out below ambient temperature (-40°F) at pressures near 400 psig to take advantage of the high solvent capacity at low temperatures. The acid-gas-rich methanol is then flash-regenerated for recovery of the H₂S and CO₂. The process can also be configured so that the acid gases are recovered separately.

Selection of Emerging CO₂-Recovery Technologies. The final step in this task will be the selection and evaluation of emerging CO₂-recovery technologies on the basis of their potential for improved system performance and/or CO₂ capture, preliminary cost estimates, and developmental status. The economics of three different emerging technologies will be compared on a consistent basis using available reference data and a scoping process-design. Three potential technologies for the evaluation are:

1. High-temperature CO₂ separation with calcium- or magnesium-based sorbents.
2. High-temperature molten-carbonate membranes for acid-gas removal.
3. Ambient-temperature facilitated-transport membranes for acid-gas removal.

The product CO₂ from these systems will need to be of suitable quality for long-distance pipeline transport (typically less than 2 ppm H₂S).

Transportation, Utilization, and Disposal of Carbon Dioxide

Once the CO₂ has been recovered from the fuel-gas stream, its transportation, utilization, and/or disposal remain as significant issues. It represents a large-volume, relatively low-value by-product that cannot be sequestered in the same way as most coal-utilization wastes (i.e., by land-filling). The objective of this task is to evaluate, on a consistent technical and economic basis, options for the transportation and utilization/disposal of CO₂ recovered from IGCC systems.

The large volume of recovered CO₂ is likely to be moved by pipeline. In some cases, existing pipelines could be used, perhaps in a shared mode with other products. In other cases, new pipeline construction would be required. Costs for pipeline construction and use vary greatly on a regional basis within the United States.

The CO₂ can be utilized for enhanced oil recovery (EOR) or sequestered in depleted gas/oil reservoirs and nonpotable aquifers. Proposals have been made to dispose of the CO₂ in the ocean depths, as is currently being investigated by the Japanese. However, many engineering and ecological and regulatory concerns associated with such options remain unanswered.

Numerous technologies for the sequestering or use of recovered CO₂ have been suggested. Biological fixation is technically challenging due to the large volumes of gas that must be processed; the concept is only of value if the resulting biomass provides either long-term sequestration, can be used as a fuel, or has some other significant market value. Initial work under this task will evaluate three options for their technical feasibility, costs, and potential impacts on reducing CO₂ emissions to the atmosphere. Candidate concepts for the initial evaluation include the following:

- Sequestering CO₂ in depleted oil/gas reservoirs.
- Biological fixation using algae and other plants.
- Enhancement of concrete properties using CO₂.

Limitations on the scope of this project preclude analysis of all possible options. Instead, the focus must be on options that appear to be most suitable for IGCC systems with respect to volume of CO₂, purity of the CO₂, and location of the IGCC system.

Investigation of CO₂-Enhanced Concrete

Concrete is the most widely used material in the construction business, with road construction being one of the biggest applications. The

economics of concrete use in road construction would be considerably enhanced if its strength, durability, and resistance to freeze-thaw cycles could be improved and if its curing time could be reduced. It has been shown that carbonation of cement pastes both improves strength and reduces curing time considerably. The use of CO₂ captured from the combustion products of coal would improve the quality of the concrete and provide long-term sequestration of the CO₂. The objective of this task is to conduct an experimental investigation of the concept in order to better understand the CO₂-binding mechanisms, determine the degree of enhancement of concrete properties, and provide the basis for an economic evaluation of the concept.

RESULTS: PUBLICATIONS FROM RELATED ARGONNE RESEARCH

As a new project, the work described in this plan has not yet generated any publications. However, numerous conference papers and reports have been published in connection with other Argonne research on CO₂-capture/utilization and global climate issues. The following is a very abbreviated sampling of those publications, intended only to convey the breadth and general thrust of those efforts.

Limiting Net Greenhouse Gas Emissions in the United States, Volumes I and II, R.A. Bradley, E.C. Watts, and E.R. Williams (eds.) [contribution by ANL staff to Chapters 2, 6, and 7 of Vol. I and Chapters 4, 7, and 9 of Vol. II], U.S. Department of Energy Report DOE/PE-0101 (Sept. 1991).

Streets, D.G., C.N. Bloyd, G.A. Boyd, D.J. Santini, and T.D. Veselka, *Climate Change and US Energy Policy*, *Energy* 16(11/12):1437-1466 (1991).

South, D.W., A.L. Fish, and R.L. Kane, *Coal Utilization and CO₂ Emissions: What Are the Control Options?*, in P.F. Dugan, D.R. Quigley, and Y.A. Attia (eds.), *Processing and Utilization of High Sulfur Coals IV, Proceedings of the Fourth International Conference on Processing and Utilization of High Sulfur Coals*, Idaho

Falls, Idaho, Elsevier Science Publishing Co., Inc., New York, N.Y. (Aug. 1991).

South, D.W., *Clean Coal Technologies: Their Role in Determining Future Electric Utility Emissions*, Engineering Foundation Conference, Environmental and Economic Impacts of Coal Utilization, Santa Barbara, Calif. (Jan. 1991).

South, D.W., et al., *A Fossil Energy Perspective on Global Climate Change*, U.S. Department of Energy Report DOE/FE-0164 (Jan. 1990).

Berry, G.F., et al., *New Method for Carbon Dioxide Recovery from the Combustion of Fossil Fuel*, 109th Winter Annual Meeting of the American Society of Mechanical Engineers, Chicago, Ill. (1988).

Recovery and Use of Waste CO₂ in Enhanced Oil Recovery: Proceedings of a Workshop in Denver, March 19-20, 1987, A.M. Wolsky and C. Brooks, compilers, Argonne National Laboratory Report ANL/CNSV-TM-186 (1988).

Ford, Bacon & Davis, Inc., *Technical and Cost Evaluation of Use of Idle Pipelines for Reverse CO₂ Service*, Argonne National Laboratory Report ANL CNSV-TM-159 (1985).

Jankowski, D.J., and A.M. Wolsky, *The Permissible Cost of Carbon Dioxide Used for Enhanced Oil Recovery*, Argonne National Laboratory Report ANL/CNSV-51 (1985).

Recovering Carbon Dioxide from Man-Made Sources: Proceedings of a Workshop Held in Pacific Grove, California, February 11-13, 1985, A.M. Wolsky and C. Brooks, compilers, Argonne National Laboratory Report ANL/CNSV-TM-166 (1985).

Taber, J.J., *Fate of Small Concentrations of SO₂, NO_x, and O₂ When Injected with CO₂ into Oil Reservoirs*, Argonne National Laboratory Report ANL/CNSV-50 (1985).

Wolsky, A.M., K. Stern, and M. Hyland, *Status of CO₂ Recovery from Waste Gases and Its Application to Enhanced Oil Recovery*, Spring National Meeting of the American Institute of

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FUTURE WORK

The National Energy Strategy Environmental Analysis Model (NESEAM) accounts for emissions in the five main economic sectors: electric utility, transportation, residential, commercial, and industrial (3). By taking advantage of the existing data base for the electric-utility sector, it will be feasible to assess the actual pipeline routes required between newly installed IGCC systems and likely host sites for CO₂ sequestering. These projections will be based on existing forecasts for utility plant replacement and expansion within the model. Recent studies from the United Kingdom have suggested that a CO₂ pipeline alone may cost one-third of the installed power-plant cost (4).

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Figure 1. Integrated Gasification Combined Cycle System with KRW Gasification 1/m Simplified Schematic

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Figure 2. Integrated Gasification Combined Cycle System with KRW Gasification 1/m Block Diagram

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