A High Pressure Carbon Dioxide Separation Process for IGCC Plants

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1.0 INTRODUCTION

Under separate contracts from the U.S. Department of Energy, Office of Fossil Energy (DOE-FE), Los Alamos National Laboratory, and a team of SIMTECHE and Nexant (a Bechtel Technology and Consulting Company) are jointly working to develop the proprietary process for capturing carbon dioxide (CO_2) from a shifted syngas stream (a mixture of mostly carbon dioxide and hydrogen) prior to combustion in an IGCC plant. This innovative approach, using the proprietary SIMTECHE Process, separates CO_2 from the shifted syngas with water at lower temperature than those in the existing absorption and adsorption approaches. The initial phase (18 months) of this four-phase, sixty six-month program consists of analytical and theoretical research and development studies as well as engineering analysis, both to further assess the efficiency and economic benefits of the SIMTECHE process and to better understand the micro- and macro-scale physics of the processes involved. The second phase (21 months) will consist of further laboratory-scale tests, which will be performed in parallel with the design and fabrication of a skid-mounted pilot plant. The third phase (15 months) will consist of laboratory-scale and pilot plant tests to further establish the proof-of-concept and to provide detailed design and operating data in preparation for pilot plant field tests. In the final phase (12 months), the pilot plant will be decommissioned and relocated to an existing IGCC power plant for final process evaluation with the shifted syngas from an industrial operating gasifier.

In this paper, the issue of carbon dioxide separation from shifted synthesis gas at elevated pressures is addressed. Focus is placed on the low temperature, high pressure SIMTECHE process. This process is based on formation of gas hydrates rich in carbon dioxide. The equilibrium thermodynamic limits of such a process are discussed and the results of equilibrium hydrate formation experiments are presented for selected shifted synthesis gas compositions. The enhancement of carbon dioxide hydrate formation and separation in the presence of gaseous and/or liquid promoters is also discussed. A bench-scale flow system for the continuous production of carbon dioxide hydrates is then described and operational issues associated with continuous hydrate production are identified. Finally, plans for continued development of the process are outlined.

Updated results on process evaluations of SIMTECHE's CO_2 hydrate separation process are presented. Performance projections are made using newly obtained experimental data. The results of several prior process evaluations indicated that the process is competitive with the existing commercial CO_2 separation processes, such as amine absorption. However, these prior studies were based on limited experimental data from the California Institute of Technology. The process configuration was revised to incorporate the lessons learned from the current R&D program. This paper summarizes the results of this latest process evaluation. The conceptual design of the SIMTECHE process, and its integration into an advanced IGCC plant, is presented. The previous capital and operating costs are updated for estimating the CO_2 capture cost in dollars per ton of carbon avoided. The future plan to design, fabricate, and operate a larger pilot plant is also discussed.

2.0 OBJECTIVES

The primary overall objective of the Phase 1 program is to analytically and experimentally confirm the feasibility of the proposed SIMTECHE Process, i.e. demonstrate the "Proof of Concept" performance. Other objectives in Phase 1 are to:

(1) Extend the previously developed process modeling to the latest proposed concept for the SIMTECHE Process,
(2) Assess the impacts of the experimental findings on the overall process economics and identify critical properties and critical parameters, and
(3 Determine ultimate reduction in carbon dioxide concentration that can be achieved and assess the potential influence of H_2S and other CO_2 hydrate promoters and elevated pressures on the process.

3.0 EXPERIMENTAL PROGRAM

The Phase 1 experimental program consists of "proof-of-concept" experiments and collection of data useful in the engineering analysis and design of the pilot plant in Phase 2. However, the main focus is in the "proof-of-concept". The main areas of investigation are:

- Equilibrium pressure/temperature of hydrate formation, and the effect of so-called “promoters”. This will enable the prediction of CO_2 removal performance of the process in the range of process conditions expected.
- Composition of the hydrate and the heat of formation of the mixed hydrates of interest. This will enable the prediction of the heat removal requirements of the hydrate formation reactors and the composition of the CO_2 gas stream to be sequestered.
- Performance of small-scale reactors in continuous-flow formation of hydrates. The main areas of interest are in the performance of the bench-scale reactors (versus ideal performance), in the cooling performance (heat transfer coefficients), and in assuring effective phase contacting (proper multiphase flow regime).

The approach used in the experimental program is to build on past work in characterizing CO_2 hydrates, small-scale continuous-flow experiments and engineering analysis. Equilibrium data was collected using a Parr Instruments high-pressure batch autoclave reactor, with conditions closer to the range of conditions expected in the SIMTECHE process. After confirming the

performance of the apparatus with pure CO_2 and water, experimental conditions have been focused on expected syngas compositions and pressures, and in the presence of proprietary hydrate promoters. The approach to the flow experiments has been to validate the performance of the system in repeating previous results, and then to develop continuous flow experiments with larger reactors and more complete measurement systems. The larger reactors are configured to yield data for design of a scaled-up system.

3.1 EQUILIBRIUM EXPERIMENTAL RESULTS

Results from $CO_2/H_2S/H_2$ experiments indicate that little, if any, hydrogen is involved in hydrate formation. Thus hydrogen behaves essentially as an inert and is not incorporated into the hydrate crystal. Batch equilibrium data experiments were then conducted with various binary gas mixtures as shown in Table 3-1. These experiments were planned to investigate the impacts of gas compositions and concentrations on the hydrate formation temperature and pressure.

Table 3-1 Composition (mole %) of Gas Mixtures in the Equilibrium Experiments

Gas Mixtures	H_2	H_2S	CO_2
A	**60**	**0**	**40**
B	**0**	**3**	**97**
C	**0**	**5**	**95**
D	**0**	**1**	**99**

One set of the results from gas mixture B is plotted in Figure 3-1. As shown, when the system is cooled from room temperature, the pressure drops linearly until clathrates begin to form. Then, a sharp spike in temperature is observed indicating initial clathrate formation. The system is cooled below this temperature and then slowly reheated to insure that the system is in equilibrium. The point at which the cooling curve and the heating curve become parallel is taken as the equilibrium pressure and temperature. These data show that the addition of 3 mole % H_2S significantly increases the clathrate equilibrium temperature or alternatively, reduces the equilibrium pressure compared to the phase line for pure CO_2. Figure 3-2 summarizes the results from the equilibrium experiments with the different gas mixtures.

At the time of preparing this paper, additional equilibrium experiments are underway to obtain data to determine the hydrate composition and effects of other hydrate promoters. Some of these additional results will be presented in the NETL Carbon Sequestration Conference. The current equilibrium data have confirmed the projected performance of CO_2 separation ratio in an impure shifted synthesis gas containing 1.1% H_2S by volume. The theoretical projections of minimum CO_2 hydrate formation pressures for various H_2S concentrations are generally within 10% of the experimental data.

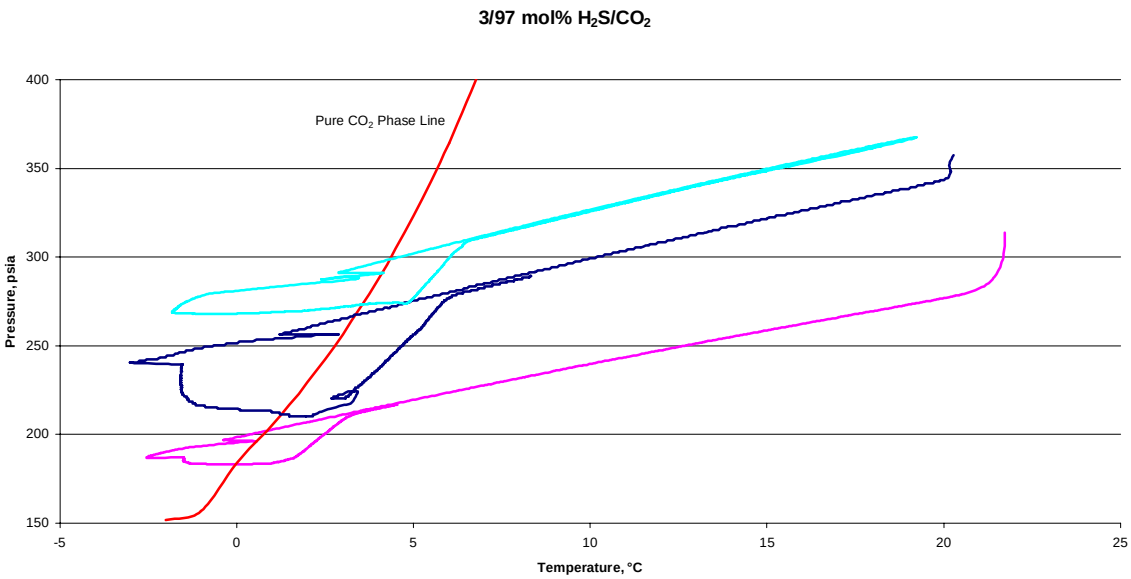

Figure 3-1 Equilibrium Experimental Data with a 3/97 mol% H_2S/CO_2 Mixture

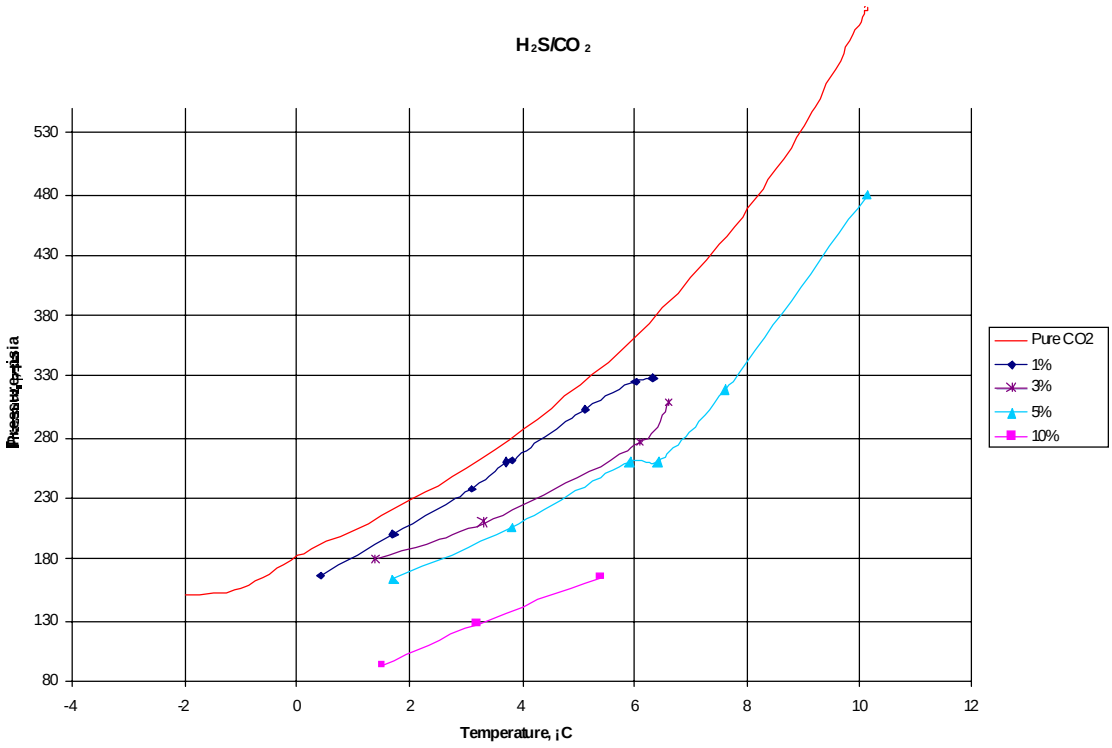

Figure 3-2 Measured hydrate formation pressure as a function of temperature for various H_2S percentages.

3.2 H_2S AS A HYDRATE PROMOTER

As shown in Figure 3-2, the equilibrium data also illustrate that the absolute partial pressure of H_2S is an important controlling variable that can be exploited. With constant mole fractions of H_2S and CO_2 in a shifted synthesis gas stream, the partial pressure of H_2S increases with increasing total system pressure; thus the minimum hydrate formation pressure decreases. Quantitatively, the final equilibrium point will depend on both the H_2S and CO_2 partial pressures. Generally, an increased system pressure should result in a greater separation of the hydrate formers from the gas stream as a result of both 1) the increased partial pressure of CO_2 and 2) a beneficial effect from a simultaneous increase in H_2S partial pressure that lowers the equilibrium hydrate formation pressure further. Measurements are underway to determine the composition of the resulting hydrates as a function of CO_2/H_2S partial pressures.

3.3 CONTINUOUS FLOW HYDRATE REACTOR

A bench-top continuous flow apparatus has been set up and tested. This unit involves CO_2 flows on the order of one gram-mole/min (in excess water) and has been run for continuously for periods of many minutes (as opposed to seconds, as was done in the earlier experimental program). With proper control of phase contacting, a significant amount of hydrate can be formed in the flow system. Specifically, with proper mixing, the kinetics of hydrate formation appears to be quite favorable. In fact, plugging of the small-scale system with hydrate has been observed. Preliminary energy balances suggest that conversions as high as 35% to hydrate can be obtained and separate analysis indicates that global performance of the unit may be heat transfer-limited with the current design. Detailed heat and material balance data will not be presented until the unit is fully commissioned. Operationally, key issues appear to be phase contacting and preservation of favorable multiphase flow regimes, effective heat transfer for removal of the heats of solution and formation, and operating strategies which avoid formation of hydrate plugs. We are currently assessing the impact scale-up to larger diameter equipment will have on these operational issues.

4.0 ENGINEERING ANALYSIS

In a separate 1999 DOE study, Nexant evaluated the feasibility of the SIMTECHE Process in an IGCC plant with different advanced power plant configurations. The current study revises the base case design in the 1999 Study in light of new experimental data and lessons learned in order to assess their impacts on the overall process economics, to identify critical properties and critical parameters, and to develop the sensitivity of the cost of sequestration to variances in design parameters.

Conceptual designs of the IGCC plant with and without CO_2 capture are developed, and then capital and operating costs are estimated which enable a cost of sequestration to be quantified. Important design parameters are varied and the impact upon the cost is estimated. These provide indication of the areas in which accurate laboratory data is most crucial, and areas for which design optimization will be the most beneficial. Table 4-1 lists the parameters and their ranges investigated in the sensitivity study.

Table 4-1
Design Parameters for Cost Sensitivity Study

Design Parameters	Base Case	Variation
Reactor Feed Pressure, psia	1,000	-200
Hydrate Heat of Formation, Btu/lb hydrate	490	343 - 520
Reactor Efficiency	95	80 - 100
Slurry Concentration, wt% hydrate	61	40
H_2S Concentration in Reactor Feed Gas, mol%	1.1	2.2**
Hydrate Flash reactor Temperature, ^0F	54	43

Note: ** 600 psia reactor feed, 95% efficiency, with H_2S recycle.

In this paper, the base case IGCC plant configuration and a summary the results of the 1999 engineering analysis are presented as the background information. Then, the preliminary results of the current engineering analysis are discussed.

4.1 IGCC PLANT CONFIGURATION

The conceptual design of the IGCC plant includes the following major process steps:

A. a high pressure Texaco gasifier, with the required feed handling and preparation facilities, to generate the syngas,
B. a radiant cooler followed with water quench of the syngas to maximize sensible heat recovery from the gasifier,
C. an air separation unit to produce 95% purity oxygen required for gasification,
D. a two stage catalytic shift reactor to produce a predominantly H_2- CO_2 rich gas,
E. the SIMTECHE CO_2 hydrate separation process to remove nearly all the CO_2 ,
F. additional product gas cleaning, i.e. H_2S removal and sulfur recovery, and
G. power generation using an advanced syngas-fueled gas turbine power cycle with Praxair's Elevated Pressure(EP) ASU with full air extraction from the GT.

Figure 4-1 shows the overall block flow diagram of the SIMTECHE Process. While the overall SIMTECHE plant configuration is similar both in the 1999 and present engineering analysis, performance and operating conditions for the latest analysis are consistent with the LANL experimental data. The block flow diagram of the IGCC plant with and without the SIMTECHE Process is shown in Figure 4-1. Two IGCC plant configurations without CO_2 capture are shown: (1) Base Case with an independent air separation unit, and (2) Case 2 with air extraction from the ASU air compressor. The IGCC plant with the SIMTECHE Process (Case 3) is integrated with the ASU plant for air extraction.

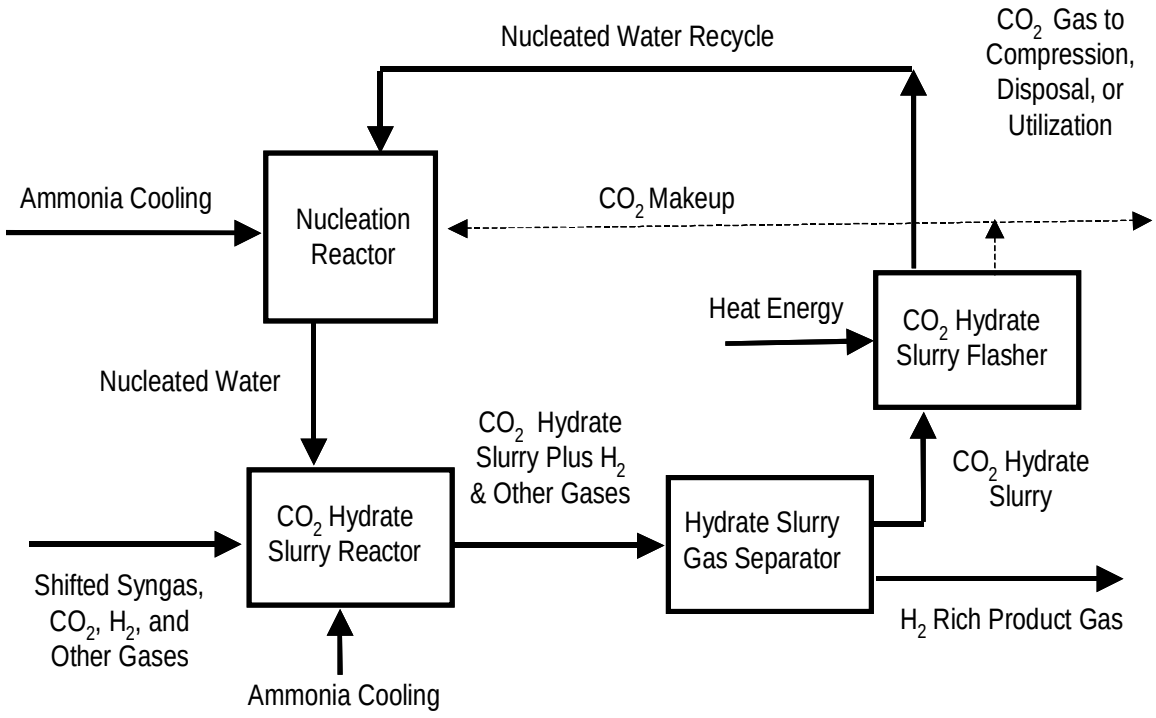

Figure 4-1 CO_2 Hydrate Process For Gas Separation From A Shifted Synthesis Gas Stream (High Pressure CO_2 Regeneration for Disposal or Utilization)

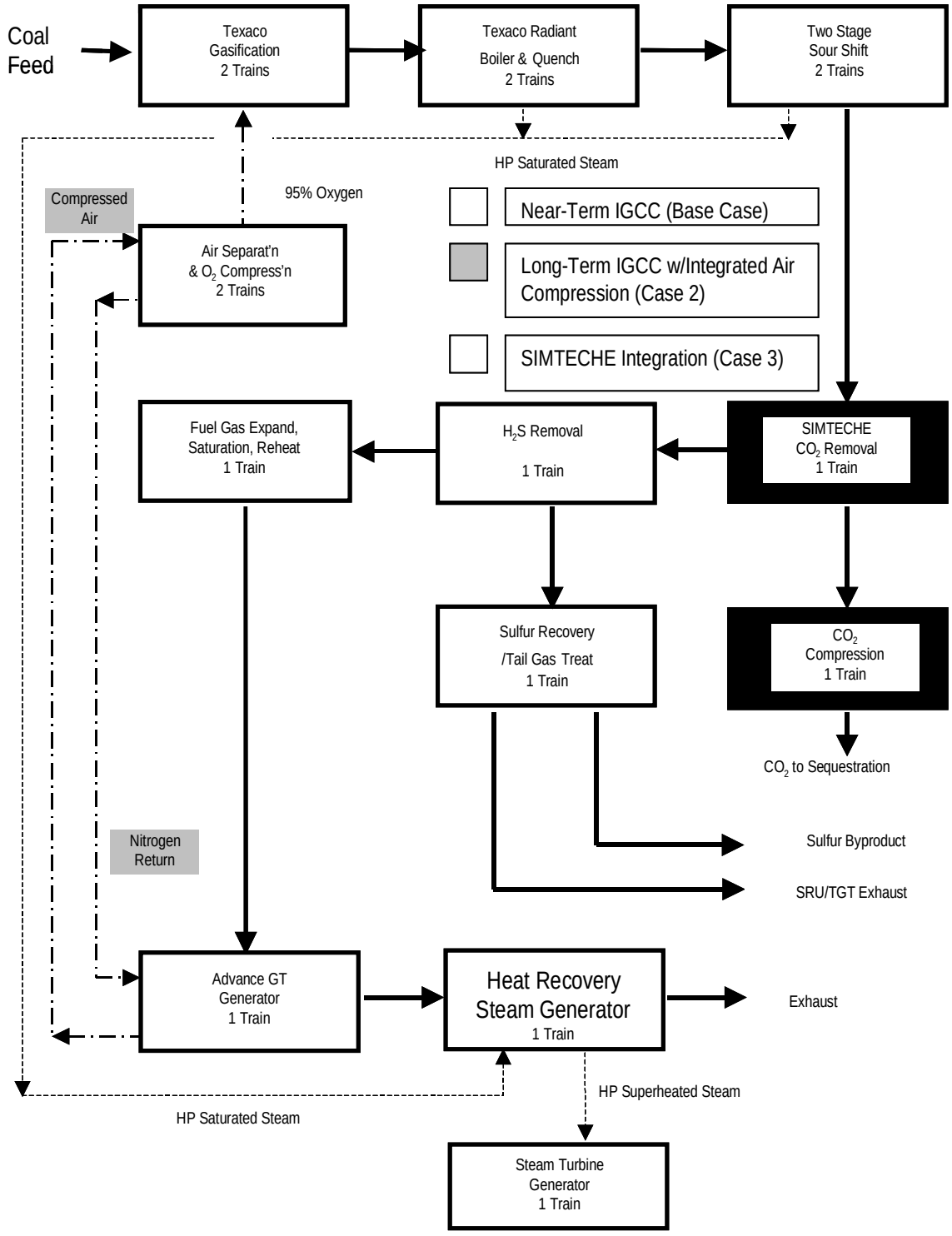

Figure 4-2 IGCC Plant Configurations With and Without CO_2 Capture

4.2 RESULTS OF 1999 ENGINEERING ANALYSIS

The following are the results from the 1999 engineering analysis. These will be updated with the results of the Phase 1 LANL laboratory data and lessons learned. Table 4-2 lists the estimated power generation cost for each case. The capital charge at 75% capacity factor is assumed at 18%. The coal cost is $1.0/MM Btu (HHV). The Base Case is an IGCC plant with an independent ASU and without any CO_2 capture. Case 2 is an advanced IGCC plant with air extraction via integration with the ASU. Case 3 is an advanced IGCC plant with CO_2 capture.

Table 4-3 shows the cost of carbon control in reference to the near-term Advanced GT-based IGFC without CO_2 control, based on a power worth of 3.95 cents/kW-Hr and 4.2 years return of investment (equivalent to 18% capital charge at 75% capacity factor). These are in-plant costs for carbon control, and do not include pipelining and sequestration costs.

Table 4-2
Estimated Power Generation Cost Comparison

	Advanced GT		
Case:	**Base**	**2**	**3**
Integrated Air Compression	No	Yes	Yes
SIMTECHE Carbon Separation	No	No	Yes
Coal Feed, STPD (As-Received)	5,000	5,000	5,000
Coal Feed HHV, MMBtu/Hr	4,540	4,540	4,540
CO_2 Sequestered, STPD (100%)	0	0	8,365
Equivalent Carbon, STPD	0	0	2,280
Installed Cost, $/kW	1,110	1,050	1,310
Net Plant Efficiency, %HHV	40.1	41.6	37.2
Power Generation Cost, ¢/kW-Hr.			
Capital Cost	3.04	2.88	3.59
Feed Cost	0.85	0.82	0.92
O&M Cost	0.06	0.06	0.07
Total Generation Cost	3.95	3.76	4.58

Table 4-3
Estimated Cost Of Carbon Control, 1999 US$
(Reference to the Base Case IGCC Plant)

	Advanced GT		
Case:	**Base**	**2**	**3**
Integrated Air Compression	No	Yes	Yes
SIMTECHE Carbon Separation	No	No	Yes
CO_2 Sequestered, STPD (100%)	0	0	8,365
CO_2 Sequestered, STPH (100%)	0	0	348
Equivalent Carbon, STPD	0	0	2,280
Equivalent Carbon, STPH	0	0	95
Net Power Exported, Mwe	533	553	496
Export Power Loss, kwe	Base	-20,000	37,000
Hourly Revenue Loss (1)	Base	-$790	$1,462
Total Install Cost, $MM	591.0	582.0	649.0
Added Capital Cost, $MM	Base	- 9.0	58.0
Total Hours in 4.17 Yrs	36,500	36,500	36,500
Hourly Capital Charges	Base	- $250	$1,590
Total Hourly Revenue Loss	Base	-$1,040	$3,050
Carbon Control Cost:			
$/ton of CO_2	Base	N/A	$8.75
$/ton of Carbon	Base	N/A	$32

Notes: (1) Based on electricity worth of 3.95 cents/kW-Hr.

4.3 STATUS OF CURRENT ENGINEERING ANALYSIS

The conceptual plant design of the Base Case has been updated. The revised major equipment list indicates that the overall equipment cost should not be different from that of the previous study. Energy requirements from the refrigeration system, CO_2 hydrate reactor, hydrate flash drum, and CO_2 pipeline compressors are expected to be different from those of the previous study. However, the net change in energy requirement is uncertain. Complete results of the updated engineering analysis will be available at the time of the Conference.

5.0 CONCLUSIONS

The preliminary results of the experimental program confirm the results and observations from the earlier experiments performed in California Institute of Technology. Preliminary results from the updated engineering analysis and the sensitivity study indicate that incorporation of the recently obtained experimental data into the conceptual plant design should not change the previous conclusion that SIMTECHE process holds promise as a superior method of carbon dioxide separation and delivery of high-pressure gas for sequestration in IGCC electric power generation. Parasitic power losses can be less than conventional carbon capture methods, and the capital cost may also be considerably lower. More quantitative comparisons will be presented as additional experimental data become available and are subsequently incorporated into the engineering analysis.

6.0 FUTURE ACTIVITIES

Phase 1 has been completed, with results that warrant further development in phase 2. Design of the pilot plant has begun. Key areas of development for a successful pilot plant include:

- Hydrate reactor design. The hydrate formation reactors require adequate residence time and gas/liquid mixing for hydrate formation, and large heat removal duty.
- CO_2 Regenerator design. Regeneration of the CO_2 requires accurate regulation of heat input to recover the CO_2 and retain residual nucleation sites (also referred to as subcritical nuclei) in the recycled water.
- Continuous measurement systems for process diagnostics. Evaluation of the performance of the system must be adequately measured to enable a thorough evaluation of the process, as well as for troubleshooting and optimization. Due to the large refrigeration requirement, the performance of the process will depend heavily on accurate measurement of the hydrate characteristics and the characteristics of the recycled nucleated water.

The SIMTECHE pilot plant is being designed as a modular unit, to be initially operated during Phase 3. Upon successful demonstration of the system, phase 4 will be implemented. This will include relocation of the pilot plant to a gasification facility for operation in an industrial evironment.