DISCLAIMER

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ABSTRACT

This Technical Progress Report summarizes activities conducted over the period 8/16/96–2/15/97 as part of an investigation entitled "Laboratory Experiments to Simulate CO₂ Ocean Disposal," funded by the U.S. Department of Energy's University Coal Research Program. This investigation responds to the possibility that restrictions on greenhouse gas emissions may be imposed in the future to comply with the Framework Convention on Climate Change. The primary objective of the investigation is to obtain experimental data that can be applied to assess the technical feasibility and environmental impacts of oceanic containment strategies to limit release of carbon dioxide (CO₂) from coal and other fossil fuel combustion systems into the atmosphere. Critical technical uncertainties of ocean disposal of CO₂ will be addressed by performing experiments that: (1) characterize size spectra and velocities of a dispersed CO₂ phase in the near-field of a discharge jet; and (2) estimate rates of mass transfer from dissolving droplets of liquid CO₂ encased in a thin hydrate shell. Experiments will be conducted in a laboratory facility that can reproduce conditions in the ocean to depths of 600 m (1,969 ft).

Between 8/16/96–2/15/97, activities focused on modifications to the experimental apparatus and the testing of diagnostics. Following completion of these tasks, experiments will be initiated and will continue through the end of the 36 month period of performance. Major accomplishments of this reporting period were: (1) delivery, set-up, and testing of the PDPA (Phase Doppler Particle Analyzer), which will be the principal diagnostic of the continuous CO₂ jet injection tests; (2) presentation of research papers and posters at the 212th American Chemical Society National Meeting and the Third International Conference on Carbon Dioxide Removal; (3) participation in the 4th Expert Workshop on Ocean Storage of Carbon Dioxide; (4) execution of an Agreement with ABB Management, Ltd. to support and extend the activities of this grant; and (5) initiation of research collaborations with Dr. P.M. Haugen of the University of Bergen, Norway, and Dr. A. Yamasaki of the National Institute of Materials and Chemical Research, Japan.
EXECUTIVE SUMMARY

This investigation responds to the possibility that restrictions on greenhouse gas emissions may be imposed in the future to comply with the Framework Convention on Climate Change. The primary objective of the investigation is to obtain experimental data that can be applied to assess the technical feasibility and environmental impacts of oceanic containment strategies to limit release of carbon dioxide (CO₂) from coal and other fossil fuel combustion systems into the atmosphere. These strategies exploit the very large carbon storage capacity of the deep ocean. In most systems proposed to date, CO₂ extracted from a hydrocarbon combustion system is liquefied and transported to the deep ocean via a submerged conduit and discharged, usually as a jet. Hydrodynamic instability induces break-up of the jet into droplets which will be buoyant at depths above 3,000 m (9,843 ft). Dissolution of the rising droplets may be inhibited by a solid hydrate film that forms rapidly at the CO₂-seawater interface. The complex mechanisms of liquid CO₂ jet break-up, droplet dispersion and agglomeration, and dissolution in the deep ocean environment are not well-understood. The present investigation seeks to address several of the major technical uncertainties by conducting two categories of laboratory tests that will: (1) characterize size spectra and velocities of the dispersed CO₂ phase in the near-field of the discharge jet; and (2) estimate rates of mass transfer from dissolving droplets of liquid CO₂ encased in a thin hydrate shell.

Preparations for the experiments continued throughout the period 8/16/96–2/15/97. Additional facility modifications and hardware fabrication, which were not anticipated in the original work plan, as well as the repair of several electronic malfunctions, have delayed completion of Task 3.0 (Acquisition, Fabrication & Installation). As a consequence, Tasks 4.0 (Experimentation) and 5.0 (Analysis), which were scheduled to commence during this reporting period, have been postponed. It presently is anticipated that experimentation will begin in 5/97.

The major accomplishments of this reporting period were: (1) delivery, set-up, and testing of the PDPA (Phase Doppler Particle Analyzer), which will be the principal diagnostic for the CO₂ jet break-up tests; (2) presentation of a research paper and a poster at both the 212th American Chemical Society National Meeting and the Third International Conference on Carbon Dioxide Removal; (3) participation in the 4th Expert Workshop on Ocean Storage of Carbon Dioxide; (4) execution of an Agreement with ABB Management, Ltd. in 10/97 to support and extend the activities of the present grant; and (5) initiation of research collaborations with Dr. P.M. Haugen of the University of Bergen, Norway, and Dr. A. Yamasaki of the National Institute of Materials and Chemical Research (NIMCR), Japan.

ABB Management, Ltd. has agreed to provide $25,000 to the University of Hawaii (UH) to extend the test matrix for the planned CO₂ jet break-up/nozzle performance experiments and to initiate a study to evaluate dissolution rates of pure, sinking CO₂ hydrates. The latter study is being considered as a possible topic of collaboration with Dr. Yamasaki of NIMCR, who currently is developing an in situ hydrate crystallizer.

Statoil (Norway) also was solicited as a corporate partner for the ongoing research. In response to this inquiry, Mr. Olav Kaarstad proposed that Statoil would indirectly participate by funding Dr. P.M. Haugen to collaborate with UH. Discussions with Dr. Haugen have identified the testing of an Acoustic Doppler Velocimeter (ADV) in the UH experimental facility as the first initiative of this cooperative research. Dr. Haugen is scheduled to visit the UH facility in 5/97 and will bring an ADV system from the University of Bergen with him at that time.

NIMCR, a laboratory of the Agency of Industrial Science and Technology of the Ministry of International Trade and Industry (MITI) of the Government of Japan, has been conducting research on ocean disposal of CO₂ for over six years. In 2/97, the UH PI was informed that approval had been granted from MITI for NIMCR to collaborate with UH. Approval from U.S. DOE had been received earlier. Discussions have been initiated to define the research project.
INTRODUCTION

This investigation responds to the possibility that restrictions on greenhouse gas emissions may be imposed in the future to comply with the Framework Convention on Climate Change. The primary objective of the investigation is to obtain experimental data that can be applied to assess the technical feasibility and environmental impacts of oceanic containment strategies to limit release of carbon dioxide (CO$_2$) from coal and other fossil fuel combustion systems into the atmosphere. These strategies exploit the very large carbon storage capacity of the deep ocean. In most systems proposed to date, CO$_2$ extracted from a hydrocarbon combustion system is liquefied and transported to the deep ocean via a submerged conduit and discharged, usually as a jet. Hydrodynamic instability induces break-up of the jet into droplets which will be buoyant at depths above 3,000 m (9,843 ft). Dissolution of the rising droplets may be inhibited by a solid hydrate film that forms rapidly at the CO$_2$-seawater interface. The complex mechanisms of liquid CO$_2$ jet break-up, droplet dispersion and agglomeration, and dissolution in the deep ocean environment are not well-understood. The present investigation seeks to address several of the major technical uncertainties by conducting two categories of laboratory tests that will: (1) characterize size spectra and velocities of the dispersed CO$_2$ phase in the near-field of the discharge jet; and (2) estimate rates of mass transfer from dissolving droplets of liquid CO$_2$ encased in a thin hydrate shell.

During Year-1 (8/15/95–8/15/96) of the project, activities focused on modifications to an existing experimental apparatus and the design, fabrication, and testing of diagnostics. These tasks are scheduled for completion in Year-2, after which experiments will be initiated and will continue through the end of the 36 month period of performance. This report summarizes technical progress made during the first six month period of Year-2 (8/16/96–2/15/97). Individual Tasks identified in the Statement of Work are reviewed in the following section.

The scope of the present investigation has expanded as a result of supplemental funding received recently from corporate sponsors. This private sector support and planned international collaborative studies also are discussed below.

RESULTS AND DISCUSSION

Preparations for the experiments continued throughout the period 8/16/96–2/15/97. Additional facility modifications and fabrication of adapters and optical mounts for the instrumentation, which were not anticipated in the original work plan, as well as the repair of several electronic hardware malfunctions, have delayed completion of Task 3.0 (Acquisition, Fabrication & Installation). As a consequence, Tasks 4.0 (Experimentation) and 5.0 (Analysis), which were scheduled to commence during this reporting period, have been postponed. It presently is anticipated that the experimentation phase of the project will begin in 5/97.

The major accomplishments of this reporting period were: (1) delivery, set-up, and testing of the PDPA (Phase Doppler Particle Analyzer), which will be the principal diagnostic for the CO$_2$ jet break-up tests; (2) presentation of a research paper and a poster at both the 212th American Chemical Society (ACS) National Meeting and the Third International Conference on Carbon Dioxide Removal (ICCDR-3); (3) participation in the 4th Expert Workshop on Ocean Storage of Carbon Dioxide; (4) execution of an Agreement with ABB Management, Ltd. in 10/97 to support and extend the activities of the present grant; and (5) initiation of research collaborations with Dr. P.M. Haugen of the University of Bergen, Norway, and Dr. A. Yamasaki of the National Institute of Materials and Chemical Research (NIMCR), Japan.

Support from ABB Management, Ltd. was solicited with the approval of the U.S. DOE CO$_2$ Subprogram Manager. ABB Management, Ltd. has agreed to provide $25,000 to the University of Hawaii (UH) to extend the test matrix for the planned CO$_2$ jet break-up/nozzle performance exper-
ments and to initiate a study to evaluate dissolution rates of pure, sinking CO\textsubscript{2} hydrates. The latter study is being considered as a possible topic of collaboration with Dr. Yamasaki of NIMCR, who currently is developing an \textit{in situ} hydrate crystallizer. A copy of the Statement of Work of the Agreement with ABB is provided as an Appendix of this report.

Statoil (Norway) also was solicited as a corporate partner for the ongoing research. In response to this inquiry, Mr. Olav Kaarstad proposed in a letter dated 7/3/96 that Statoil would indirectly participate by funding Dr. P.M. Haugen to collaborate with UH. Discussions with Dr. Haugen to identify a joint project have been ongoing since that time. It has been decided that the first initiative of the cooperative research will involve testing an Acoustic Doppler Velocimeter (ADV) in the UH experimental facility. The ADV is expected to be the primary velocity diagnostic in future field tests of CO\textsubscript{2} ocean disposal. Since ADVs typically are employed in water containing relatively low concentrations of small particulates, there is concern that a dense CO\textsubscript{2} droplet phase, characteristic of the near-field of ocean disposal systems, may compromise instrument performance. Dr. Haugen is scheduled to visit the UH facility in 5/97 and will bring an ADV system from the University of Bergen with him at that time.

At the beginning of this reporting period, NIMCR was approached via a letter from the U.S. DOE CO\textsubscript{2} Subprogram Manager (issued at the request of the UH Principal Investigator) to initiate an international collaborative research project with UH on CO\textsubscript{2} ocean disposal. NIMCR is a laboratory of the Agency of Industrial Science and Technology of the Ministry of International Trade and Industry (MITI) of the Government of Japan. NIMCR has been conducting research on ocean disposal of CO\textsubscript{2} for over six years and currently is hosting Dr. H. Teng, a U.S. National Science Foundation/Japan Science and Technology Agency fellow, who previously was employed by the UH CO\textsubscript{2} program as a Graduate Research Assistant (GRA). In a correspondence dated 9/30/96, NIMCR indicated that it was interested in collaborating but required official approval from MITI. The UH PI was informed by NIMCR in 2/97 that approval had been granted and discussions were initiated to define the cooperative project.

The status, as of 2/15/97, of individual Subtasks identified in the Statement of Work is reviewed below.

**Task 1.0 Project Management and Reporting**

Management and reporting tasks pursued during the period covered by this Technical Progress Report were consistent with the requirements of the project Statement of Work. Highlights of this Task include: executing an Amendment to the U.S. DOE UCR grant; executing an Agreement for supplemental financial support from a private sector research sponsor; presentation of research papers and posters at technical meetings and workshops; and the initiation of international collaborative research projects.

**Subtask 1.1 Management:**

Funding for Year-2 and Year-3 of this investigation was obligated in Modification No. A001 of the current grant Agreement. This Modification was fully executed on 10/8/96.

**Subtask 1.1.1 Planning, Budgeting and Control:**

Work on this Subtask is proceeding in accordance with the project Statement of Work.

**Subtask 1.1.2 Contract Management:**

Upon execution of Modification No. A001 of the current grant Agreement, which obligates funds for the project through Year-3, applications were prepared and submitted to the Office of Procure-
ment, Property, and Risk Management (OPPRM) of UH to extend the term of the three Consultant Agreements with E.E. Adams, H.J. Herzog, and D.S. Golomb through 8/14/98 to ensure uninterrupted participation by these individuals. The amounts of the Agreements will be increased to provide compensation for services during Year-2 and Year-3. The applications were undergoing review as of 2/15/97. Approval is expected on or before 4/31/97.

Subtask 1.1.3 Financial Management:

Expenses are being tracked on a regular basis. With the exception of Subtask 3.1.2, activities are proceeding within budget. As reported previously, completion of Subtask 3.1.2 requires additional funds to meet higher-than-estimated component costs. These funds became available with the execution of an Agreement between ABB Management, Ltd. and UH on 10/18/96. Per this Agreement, ABB Management, Ltd. will provide $25,000 to support and extend the present laboratory investigation of CO$_2$ ocean disposal. A portion of this award will be applied to complete Subtask 3.1.2. The ABB grant also will be used to initiate a study to evaluate dissolution rates of pure, sinking CO$_2$ hydrates. This study may be pursued in cooperation with NIMCR.

The collaboration with Dr. P.M. Haugen of the University of Bergen will require an additional commitment of time by the PI and project GRA and will incur expenses for equipment and supplies. Statoil is expected to provide funds for equipment and supplies via Dr. Haugen. Efforts are underway to secure contributions to cover PI and GRA salaries from private sector donors in the State of Hawaii.

Subtask 1.2.1 Financial/Property/Environmental/Other Reports:

The Federal Assistance Reporting Checklist for this grant called for submission of SF-272 "Federal Cash Transaction Report" during the period 8/16/96–2/15/97. SF-272 is prepared and submitted to U.S. DOE by the University's CGMO on a regular basis.

Subtask 1.2.2 Technical Reports:

The Federal Assistance Reporting Checklist for this grant called for submission of the second semi-annual Technical Progress Report during the period 8/16/96–2/15/97. A Technical Progress Report was submitted to AAD Document Control (PETC) on 9/5/96.

Subtask 1.2.3 Papers & Publications:

The Principal Investigator (PI) presented a technical paper entitled "The Effect of Hydrate Formation on CO$_2$ Jet Instability" and an associated poster at the 212th American Chemical Society (ACS) National Meeting held on 25-29 August 1996 in Orlando, Florida. A technical paper entitled "Dispersion of CO$_2$ Droplets in the Deep Ocean" and a poster entitled "Laboratory Experiments to Simulate CO$_2$ Ocean Disposal" were presented at the Third International Conference on Carbon Dioxide Removal (ICCDR-3) held on 9–11 September 1996 at the Massachusetts Institute of Technology. The papers were published in the proceedings of these meetings. Support by the U.S. DOE UCR grant was acknowledged.

The PI was invited by the IEA Greenhouse Gas R&D Programme to participate in the 4th Expert Workshop on Ocean Storage of Carbon Dioxide–Practical and Experimental Approaches held on 29-30 October in Tokyo, Japan. The PI presented a review of laboratory experiments related to CO$_2$ ocean disposal, an outline of the present investigation, and recommendations for future work. A related manuscript was submitted which will appear in an upcoming IEA publication. All papers produced under this Subtask are listed at the end of this report.
Task 2.0 Design of Experiments

As discussed in the first Technical Progress Report, this Task was expanded to include several activities related to facility modifications. The majority of work proposed for this Task has been completed in accordance with the Project Schedule. The portions of Subtasks 2.1.2, 2.1.3, and 2.2.3 which were deferred for reasons discussed below will be completed during the second half of Year-2.

Subtask 2.1 Modifications to Facility:

Many of the activities of Subtasks 2.1.1 and 2.1.2 have been consolidated. Work on Subtasks 2.1.2 and 2.1.3 resumed following execution of the Agreement with ABB Management, Ltd. that secured funds to procure the high-pressure circulation pump and to pursue an expanded range of nozzle performance tests.

Subtask 2.1.1 Static Dissolution Experiments:

The work proposed for this Subtask in the project Statement of Work has been completed.

Subtask 2.1.2 Dynamic Dissolution Experiments:

Work resumed in 2/97 to finish remaining design integration tasks for the high-pressure water circulation ancillary system of the diffuser flow device. This Subtask will be completed once a specific pump is identified in the ongoing procurement activity and information is obtained on its operating characteristics.

Subtask 2.1.3 Discharge Nozzle Performance Experiments:

Tests are being devised to investigate hydrate fouling phenomena in discharge nozzles. This investigation will be pursued with partial support from ABB Management, Ltd. The design of associated orifices will be completed during the second half of Year-2.

Subtask 2.2 Instrumentation Design:

All instrumentation design activities related to the particle sizer and imaging optics and sizing program have been completed. The development of the high-pressure pH probe has been assigned a low priority and will be pursued on a time-available basis.

Subtask 2.2.1 Particle Sizer:

The work proposed for this Subtask in the project Statement of Work has been completed.

Subtask 2.2.2 Imaging Optics and Sizing Program:

The work proposed for this Subtask in the project Statement of Work has been completed.

Subtask 2.2.3 pH Probe:

This instrument is not critical to the performance of the planned experiments. Resources initially allocated to this Subtask have therefore been applied to address other project needs of higher priority; activity proceeds on a time-available basis.

In 8/96, a potential supplier (Ocean Optics) of an off-the-shelf high-pressure pH probe was contacted and technical and price information was requested. The vendor did not respond to this
request. Mr. K. Yamane of the Ship Research Institute of the Ministry of Transportation of the Government of Japan identified another supplier (IDRONAUT Srl) during his visit to the UH CO$_2$ experimental facility in 2/97. This vendor subsequently was contacted and has provided technical information on a pH probe, designed for use at depths to 7,000 m (22,966 ft), which appears to be appropriate for the planned experiments. A cost estimate has been requested.

**Task 3.0 Acquisition, Fabrication, and Installation**

Modifications to the facility and the fabrication or procurement and installation of instrumentation comprised the primary technical effort of this reporting period. Additional modification and fabrication tasks, which were not anticipated in the original work plan, were identified and pursued following delivery of the Phase Doppler Particle Analyzer upgrade in 9/96.

**Subtask 3.1 Facility Modifications:**

Modifications to the existing facility continued during this reporting period. The scope of these modifications was expanded to accommodate integration of the diagnostics and the pressure vessel. The portion of Subtask 3.1.2 that had been suspended while additional funds were being solicited to procure the high-pressure centrifugal pump was resumed following execution of the Agreement with ABB Management, Ltd.

**Subtask 3.1.1 Modifications for Static Dissolution Experiments:**

These modifications have been consolidated with Subtask 3.1.2.

**Subtask 3.1.2 Modifications for Dynamic Dissolution Experiments:**

As reported previously, the proposal budget underestimated the cost of the high-pressure circulation pump employed by the diffuser flow device by several thousand dollars. Additional funds from ABB Management, Ltd. became available during this reporting period to purchase the pump. Procurement activities were initiated in 2/97 and delivery is expected in the second half of Year-2.

**Subtask 3.1.3 Modifications for Discharge Nozzle Performance Experiments:**

This short-lead-time activity was suspended during this reporting period to focus on other higher priority Subtasks.

**Subtask 3.2 Diagnostics:**

Acquisitions of the primary diagnostics, the optical particle sizer and imaging system (including software), were completed according to schedule. Fabrication of the CO$_2$ injector traversing system continued during this reporting period. Acquisition of the pH probe proceeds on a time-available basis.

**Subtask 3.2.1 Optical Particle Sizer:**

The PDPA (Phase Doppler Particle Analyzer) upgrade to an LDA (Laser Doppler Anemometer) system purchased in 1995 with University funds was delivered on 9/16/96. The vendor, Aero-metrics, Inc., provided several days of on-site technical support to assemble and to test the system. The GRA subsequently customized the analysis software and fabricated an external traversing system that allows the transmitter and receiver modules to be aligned and moved between the bottom two rows of pressure vessel viewports. Electronic failures in the laser power supply and controller resulted in delays in this Subtask.
Procurement and fabrication of the CO$_2$ injector traversing system continued during this reporting period.

Subtask 3.2.2 Imaging System:
The work proposed for this Subtask in the project Statement of Work has been completed.

Subtask 3.2.3 Sizing Program:
The work proposed for this Subtask in the project Statement of Work has been completed.

Subtask 3.2.4 pH Probe:
Requests for technical and cost information on a submersible pH probe from Ocean Optics were submitted in 8/96 and 10/96. The vendor did not respond to these requests. Acquisition of the high-pressure pH probe resumed in 2/97 after identification of an alternative supplier.

Discussions were initiated via a 11/96 correspondence from the PI to Dr. T. Ohsumi of the Central Research Institute of Electric Power Industry (CRIEPI) in Japan to test a fast-response pH probe developed by CRIEPI in the UH facility. This probe is based on a IS-FET (Ion Sensitive Field Effect Transistor) sensing element and will be marketed by a Japanese manufacturer sometime in 1997.

Task 4.0 Experimentation

This Task was postponed due to delays in completing elements of Task 3.0. Experiments are expected to commence in 5/97.

Task 5.0 Analysis

This Task was postponed due to delays in completing elements of Task 3.0.

CONCLUSION

Preparations for the experiments continued throughout the period 8/16/96–2/15/97. Additional facility modifications and hardware fabrication, which were not anticipated in the original work plan, as well as the repair of several electronic malfunctions, have delayed completion of Task 3.0 (Acquisition, Fabrication & Installation). As a consequence, Tasks 4.0 (Experimentation) and 5.0 (Analysis), which were scheduled to commence during this reporting period, have been postponed. It presently is anticipated that the experimentation will begin in 5/97.

The major accomplishments of this reporting period were: (1) delivery, set-up, and testing of the PDPA (Phase Doppler Particle Analyzer), which will be the principal diagnostic for the CO$_2$ jet break-up tests; (2) presentation of research papers and posters at the 212th American Chemical Society National Meeting and the Third International Conference on Carbon Dioxide Removal; (3) participation in the 4th Expert Workshop on Ocean Storage of Carbon Dioxide; (4) execution of an Agreement with ABB Management, Ltd. in 10/97 to support and extend the activities of this grant; and (5) initiation of research collaborations with Dr. P.M. Haugen of the University of Bergen, Norway, and Dr. A. Yamasaki of the National Institute of Materials and Chemical Research, Japan.
REFERENCES/PUBLICATIONS

The following articles were prepared with partial support from the present UCR grant.


APPENDIX A

ABB Management Grant: Statement of Work

Project Title: International Support for Laboratory Experiments to Simulate CO\textsubscript{2} Ocean Disposal

Effective Dates: 10/18/96 to 08/14/98
Total Amount Requested: $25,000.00

Principal Investigator: Stephen M. Masutani
Affiliation: University of Hawaii
Hawaii Natural Energy Institute

Sponsoring Agency: ABB Corporate Research, Department of Energy and Global Change

STATEMENT OF WORK

This project will support and complement the ongoing study entitled "Laboratory Experiments to Simulate CO\textsubscript{2} Ocean Disposal" that is being conducted by the Hawaii Natural Energy Institute of the University of Hawaii under U.S. Department of Energy (USDOE) Grant No. DE-FG22-95PC95206. Specifically, the test matrix for the jet break-up/nozzle performance experiments to be conducted in the USDOE-sponsored study will be extended to include a preliminary investigation of hydrate fouling of discharge nozzles and disposal pipelines. A study also will be performed to design an experiment to evaluate the dissolution rates of pure, sinking CO\textsubscript{2} hydrates utilizing the existing High-Pressure CO\textsubscript{2} Mixing Facility (HCMF). This hydrate dissolution experiment is relevant to an alternative concept to sequester CO\textsubscript{2} in the ocean by generating pure solid hydrates from captured fossil CO\textsubscript{2}, either at the ocean surface or in-situ, and releasing these crystals in mid-ocean. The hydrates will subsequently sink and dissolve in the unsaturated seawater.

The requested funding will be applied to: (1) compensate for labor required to pursue the technical effort described above; (2) procure supplies and equipment needed to conduct the proposed (additional) tests; and (3) disseminate information to the sponsoring agency and present results at technical meetings.

Per direct request by the funding agency, all relevant reports or technical articles produced as a result of the present effort and the associated USDOE-sponsored study will be transmitted promptly to ABB Management, Ltd., contingent upon approval by USDOE. ABB Management, Ltd. will also be offered the opportunity to review progress and provide suggestions regarding the direction of the project.