OCEAN SYSTEMS FOR MANAGING
THE GLOBAL CARBON CYCLE

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ABSTRACT
Carbon dioxide is formed in all processes utilizing fossil fuels. Controlling the emissions of CO2 from a number of processes by forming CO2 hydrates (clathrates), may be an effective approach for both absorbing CO2 from multicomponent gas streams (Flue gases, Anaerobic digester gases, etc.) and sequestering CO2 in the deep oceans. Further, ocean marine farms may be an effective process for extracting CO2 from the atmosphere and forming both valuable products and rejecting excess CO2, in the form of clathrates, to the deep ocean. Preliminary engineering analyses indicates that clathrate formation for controlling both conventional fossil fuel gaseous CO2 emissions and those associated with marine farm anaerobic digester gases may provide a meaningful control strategy for CO2. © 1997 Elsevier Science Ltd

KEYWORDS
Carbon dioxide clathrates; extraction from multicomponent gases; oceanic sequestration; marine farm systems.

INTRODUCTION
Over the last 20 years, increasing global emissions of carbon dioxide from fossil resources, and the potential impacts on the earths' atmosphere, have become a subject of intense scientific investigation. Major emphasis has been placed on assessing the range of impact of these increased emissions and methods to reduce or restrict the increasing use of fossil fuels.

Much less emphasis is being placed on the research, development, and demonstration of engineered systems to manage and control CO2 emissions, particularly from stationary fossil sources, such as powerplants, chemical plants, petroleum refineries, etc.
The purpose of this paper is to summarize key new fundamental research on the formation of CO$_2$ clathrates from pure CO$_2$ gas streams and to discuss the potential for CO$_2$ clathrate formation from multi component gas streams. Typical emission streams including powerplant stack gases, coal or petroleum coke synthesis gases, natural gas/carbon dioxide mixtures, etc. are all potential sources for carbon dioxide extraction and fixation, in the form of CO$_2$ clathrates.

Once formed, these solid clathrates can be injected, in slurry form, into the ocean or deep aquifers for CO$_2$ sequestration. Finally, an active CO$_2$ management and control system will be discussed which a) extracts CO$_2$ from the atmosphere, at a distributed level, i.e. non-point source, b) converts the marine carbon to natural gas and carbon dioxide, c) sequesters the carbon dioxide in the deep ocean, and d) provides liquified natural gas, as well as other high valued products, as articles of commerce.

FORMATION OF CARBON DIOXIDE CLATHRATES

It is well known that liquid or gaseous carbon dioxide when mixed with water at temperatures below 10°C and pressures in the range of 10-70 bars, form solid clathrates (Takenouchi and Kennedy, 1965). These clathrates typically have 2 to 8 CO$_2$ molecules, bound into a matrix of 46 water molecules. If full lattice occupancy is achieved, 8 CO$_2$ molecules are trapped within the matrix of 46 water molecules. This produces a mole fraction of CO$_2$ of only 0.148, but a weight fraction of 0.36.

The purpose of a research program, undertaken at Caltech and sponsored by the Electric Power Research Institute, was to determine how such clathrates could be formed under minimal pressure conditions; thus reducing compression requirements for CO$_2$, or CO$_2$ containing gaseous mixtures. This work was reported in a number of EPRI progress reports (North, et al., 1993; North, et al., 1995) and in a paper (North, et al., 1993).

Initial experiments were conducted in a batch chamber, at temperatures of 4-6°C and pressures of 65 to 200 bars. Through a series of experiments, stable CO$_2$ clathrates with greater than 25% by weight can now be formed at -1 to 0°C (salt water) and pressures of 12 to 14 bars. These greatly reduced formation conditions have been achieved by developing an empirical model of CO$_2$ clathrate formation, which indicates three distinct phases in the development of stable clathrate formation, namely a) CO$_2$ dissolving in water, b) hydrate precursors forming, i.e. structured water, and c) final hydrate formation with the introduction of additional CO$_2$.

The research then moved to the use of two interconnected semi continuous flow bubbling reactors for clathrate formation and formation pressures were reduced to the 12 to 14 bar levels. These reduced formation conditions are achieved by stepwise
formation/decomposition of the clathrate. Each subsequent clathrate formation step occurs at a lower pressure, indicating that the nucleated water has a "memory" from the previous formation. Stable formation pressures of 13 bar were achieved, at reactor temperatures slightly below zero centigrade.

Finally, two continuous flow reactors, designed by D. Johnson, a project subcontractor, were operated in late 1995. Our previous studies had shown that CO₂ hydrate formation at 12-14 bars pressure would most likely require two or three reactor stages, to ensure that an adequate quantity of precursors occurred in the stream of CO₂-water entering the final stage.

The Johnson Fluidic Venturi consists of two converging cylindrical chambers, the eductor tube and plenum, discharging into a common terminal space, the tail tube. Two Fluidic Venturis were constructed. The second unit produced excellent gaseous CO₂, water mixing at flow rates of 0.36 liters per second. Unit 2 could accommodate about 120 grams of CO₂ per second and produce 1.7 metric tons of hydrates per hour. This represent near full saturation of the lattice, as the CO₂ weight fraction is 0.33.

Optimal operation occurred when the water pressure in the plenum was approximately 6.7 bars greater than the CO₂ gas pressure i.e. the water educts the CO₂ into the Fluidic Venturi. Therefore, it may be possible to further reduce the CO₂ compression requirements for second stage injection, if the Fluidic Venturi is used as the clathrate formation reactor. In a fully engineered system, it is likely that a two stage reactor system would be employed. The first to form the clathrate precursors, and the second for clathrate production. Approximately 25% of the CO₂ is absorbed in the precursor stage, so this portion might be compressed to 20 bars. The remaining 75% would be compressed only to 12-14 bars, and perhaps less, if the eductor tube provides 6-7 bars of suction. With these low pressures for stable clathrate formation, one can consider hydrate formation from atmospheric pressure CO₂ streams, such as flue gases, as well as pressurized streams, such as found in synthesis gas production from natural gas, coal, petroleum, coke, etc.

CLATHRATE FORMATION FROM MULTI COMPONENT GAS STREAMS

All of the clathrate formation research performed to date has been with pure CO₂ gases. In order to obtain a pure CO₂ stream from a multi component gas, conventional separaton techniques subject the multi-component gas to a number of energy consuming steps, namely (1) absorption of the CO₂ from the gaseous stream by a host solvent e.g. monoethanolamine or Selexol, (2) removal of CO₂ from the host solvent e.g. by steam stripping, and (3) compression and cooling of the stripped CO₂ for clathrate formation or alternatively, (4) compressing or liquifying the pure CO₂ gas stream for pipelining or injection into the ocean.

Recently, one of us (Spencer), has conceived an approach for CO₂ clathrate formation from multicomponent gas streams, including
a) Powerplant Flue Gases, b) Turbo Charged Boiler Flue Gases, c) Coal Gasification Product Gases, d) Shifted Coal Gasification Product Gas, and e) Anaerobic Digester Product Gas. In these applications, the exhaust (flue) gas from processes a and e are at atmospheric pressure, and processes b, c, and d at pressures from 10 to 60 bars. Mole fractions of CO₂ in the multi component gas streams vary from 0.02 to 0.50 over the range of these applications.

Due to the extremely high preferred solubility of carbon dioxide in water, and even higher preferred CO₂ solubility in nucleated water, a single step process for extracting CO₂ from these gaseous streams, forming CO₂ clathrates, and clathrate slurries, has been designed. The CO₂ is now ready for injection as a CO₂-water slurry into either the ocean or a deep aquifer system. A U.S. patent application has been filed (Spencer, 1996), earlier this year.

At this point, only theoretical separation efficiencies have been developed. Comparisons of the energy efficiency for separating and pipelining CO₂ using conventional amine scrubbing/stripping techniques e.g. monoethanolamine, with the new process of forming CO₂ clathrates directly, have been developed for both a 500 Mwe conventional coal fired powerplant and utilizing Selexol for CO₂ separation in an integrated coal gasification combined cycle (IGCC) powerplant. The base energy losses for both of these systems are taken from Smelser (1991). The energy loss associated with separation and pipelining of CO₂ using conventional technology from a conventional coal fired powerplant is estimated to consume 35 percent of the power output. The similar loss for an integrated coal gasification combined cycle powerplant is 12 percent.

Theoretical estimates of these losses, if the new clathrate formation process is utilized for both separation and slurry pipelining, are 9.0 and 4.4 percent respectively for the conventional coal plant or the IGCC powerplant. Thus, the energy losses, as well as process simplification, are much more attractive utilizing the new clathrate separation process.

Hidy and Spencer have submitted a grant application to the U.S. Environmental Protection Agency for a 3 year research program entitled, "Exploratory Design and Evaluation of a New CO₂ Removal Process" (Hidy, et al., 1996). This work is planned to performed at the University of Riverside Center for Environmental Research and Technology, in conjunction with Dr. North of Caltech. At least, two fundamentally different reactor configurations will be tested, one a con-current flow reactor, the second, a countercurrent flow reactor.

CLATHRATE SEQUESTRATION IN THE OCEAN

As discussed above, it is envisaged that slurries of CO₂ clathrate will be formed for injection into the ocean or deep aquifers. With a slurry concentration of 50 percent by weight clathrate, the CO₂ content of the slurries is approximately 16-


17 percent. The specific gravity of the clathrates are approximately 1.16, so that the hydrate should slowly settle through sea water after injection and will either redisolve or sink to the ocean floor. (Cole, et al., 1993) have shown that the deep ocean can be a repository for at least 1200 gigatons of CO₂, with minimal change in oceanic acidity. This amount is equivalent to approximately 2 pre-industrial atmospheric CO₂ contents.

If the clathrates reach the sediments, it is estimated that an additional 2800 gigatons of carbon could be sequestered. Of course, these estimates assume uniform dispersal over the sea floor or injection in a deep advection zone such as the North Atlantic Deep Water flow. In any case, there is clearly a large repository potential in the deep oceans. Pumping clathrate slurries to depth of 700 meters or so and discharging the slurries in a downward flow direction should allow complete sequestration of the CO₂ for many centuries, if not permanently.

**MARINE FARM SYSTEMS FOR GLOBAL CARBON MANAGEMENT**

One of us, (Spencer, 1991), has proposed large scale floating macroalgal systems for CO₂ fixation from the atmosphere. These "so called" marine farms, each some 100,000 acres in extent, would not only fix airborne CO₂, but also, produce valuable byproducts. By harvesting and processing species such as Macrocystis Pyrifera, e.g. by anaerobically digesting these species to form approximately a 50:50 mixture of methane and carbon dioxide, a portion of the carbon is used to produce clean fuels and the remainder of the carbon can be sequestered. The carbon dioxide, representing approximately 50 percent of the anaerobic digester gas, would be stripped from the methane in the form of CO₂ clathrates and injected as a slurry into the ocean. The methane would be liquified and become an article of commerce. Other coproducts can also be produced from these marine farms.

A 100,000 acre marine farm fixes approximately 1 million tons of carbon per year, of which 50 percent is recycled as fuel (methane) and 50 percent is sequestered as CO₂ clathrates in the ocean. Thus; 1000 such marine farms would be necessary for managing 1 gigaton of carbon annually.

By utilizing anaerobic digestion of the harvested macro algal species, such as Macrocystis Pyrifera, 90-95 percent of the nutrients (nitrogen and phosphorus) are retained in the digester liquors and can be recycled to the farm to provide the necessary nutrients. Upwelled seawater would provide the "makeup" nutrients necessary for equilibrium macro algal production.

Overall system and process designs have been developed (SIMTECHE Proprietary Information); however a full preliminary design of the system has not yet been conducted. Very preliminary performance and costs indicate that such a system could be economically viable, if a broad product slate of high value products can be established.

Such a multi-component product slate could include a) Food-
algae, fish and invertebrate polycultures, b) Biopolymers, such as agar, algin, carogens, c) Organics, such as acetone, and organic acids, d) Fuels, such as alcohols, in addition to methane, etc. This type of floating, tended farm system could serve many useful purposes, and assist in the distribution of CO$_2$ clathrates being injected over large ocean areas.

**SUMMARY**

This paper summarized some recent experimental work focused on controlling CO$_2$ emissions from stationary sources. It has shown that systematic study of the properties of CO$_2$-H$_2$O mixtures and conditions, can greatly reduce the energy necessary to fix and sequester CO$_2$.

Further, recent advances have shown that a) stable, high mole fraction CO$_2$ clathrates can be formed in continuous reactors, b) CO$_2$ clathrate formation from a range of multi component gaseous streams is feasible and for some gases, very easily achieved, and c) system concepts which include global CO$_2$ management can be integrated with productive marine farm systems for fuels, chemicals, etc. and clathrate injection of the CO$_2$ waste stream.

Although this is only the beginning of the search for meaningful engineered systems to manage CO$_2$, the efforts to date, are both promising and exciting. Although the cost effectiveness of these systems must yet be determined, the fundamental reductions of energy losses associated with these systems, compared to conventional techniques, indicate that this cost effectiveness should be achieved, as engineering and operational data are obtained.

**REFERENCES**


