

INTERNATIONAL COLLABORATION ON CO₂ SEQUESTRATION

Annual Report

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Principal Authors:
Howard J. Herzog and E. Eric Adams

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Massachusetts Institute of Technology
Energy Laboratory
77 Massachusetts Avenue
Room E40-455
Cambridge, MA 02139-4307
Telephone: (617) 253-0688
Fax: (617) 253-8013

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Abstract

The primary focus of this reporting period was to prepare for conducting the ocean carbon sequestration field experiment during the summer of 2002. We discuss four key aspects of this preparation:

- Design criteria for a CO₂ flow system mounted on a ship
- Inter-model comparison of plume models
- Application of a double plume model to compute near field mixing
- Evaluation of tracers

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Executive Summary

The main focus of our work during this time period (August 23, 2000 - August 23, 2001) was to:

- work with the international team through the technical committee (TC) and management team
- carry out numerical studies on CO₂ plumes
- support the infrastructure design effort
- lead the planning for the field experiment scientific plan
- contribute to the permitting process as needed

During this period, key events included:

- 7th TC meeting, January 15-16, 2001 in Victoria, British Columbia, Canada. Attended by Howard Herzog, Eric Adams, and Eric Wannamaker.
- 8th TC meeting, June 19-20, 2001 in Honolulu, HI. Attended by Howard Herzog, Eric Adams, and Eric Wannamaker.
- Submission of a chapter in *Environmental Fluid Mechanics: Theories and Applications* in January, 2001, entitled “Multi-phase plumes in uniform, stratified and flowing environments”
- Completion of PhD Thesis by Scott Socolofsky in February, 2001, entitled “Laboratory Experiments of Multi-phase Plumes in Stratification and Crossflow”.
- The First National Conference on Carbon Sequestration, May 14-17, 2001 in Washington, DC. A paper from this project was presented (attached).

This report deals with 4 main technical topics:

- Design criteria for a CO₂ flow system mounted on a ship.
- Summary of our input to an inter-model comparison carried out by the project
- We describe a numerical model of a steady-state plume in a quiescent, stratified, ambient, driven by a buoyant dispersed phase, such as bubbles or droplets. The model was developed specifically to simulate CO₂ sequestration plumes, and extends the hybrid double-plume model of Asaeda & Imberger (1993) by incorporating droplet dynamics (dissolution, hydrate formation, and phase changes), introducing a self-regulating detrainment criterion, and allowing multiple overlapping intrusions. The model is calibrated to data from the literature and our lab, and applied to predict plumes associated with a proposed CO₂ field study.
- We review six tracers that have been considered by participating scientists for measuring the rates of CO₂ mixing and dissolution, two processes which are important for

determining the concentrations of excess CO₂ and associated changes in pH. The comparison considers dissolved inorganic carbon (or total carbon, C_T), pH, labeled and natural carbon isotopes (¹³C and ¹⁴C) and two introduced tracers (fluorescent dye and SF₆). The tracers are compared with respect to their ability to trace the injected CO₂, the method of measurement, precision and response time, whether or not the measurement can be performed *in situ*, and other factors such as permitting.

Experimental

No experimental work was done during this reporting period.

Results and Discussion

A. Design criteria for a CO₂ flow system mounted on a ship.

Below we summarize the design criteria we developed:

We are soliciting the participation of an engineering/consulting firm to help in the design of the flow system to deliver the CO₂ from the supply ship, through the coiled tubing, to depths of 800 m at a steady flow. We would like to be able to operate at 2 flows: 0.1 kg/s and 1 kg/s. The exact value is not so important as long as we can determine its value and keep it steady. Because of concerns with hydrate formation, a nitrogen purge system is also envisioned.

The engineering/consulting firm will:

- a. Develop a conceptual design for the flow system in consultation with engineers from the international collaboration project.
- b. Write detailed specifications for the main equipment items, including the pumps and the valves.
- c. Develop operational procedures, including start-up and shut-down, in consultation with engineers from the international collaboration project.

Design Considerations: The delivery of a steady flow of liquid CO₂ to depths of 800 m gives rise to several engineering challenges in the area of flow control. The CO₂ will be liquid at the discharge point at 800 m depth (pressure of 80 bar, temperature about 5°C). However, surface temperatures will make CO₂ a gas, resulting in two-phase flow in the pipeline. In general, it is much easier to control one-phase flow in pipes as opposed to two-phase flow. We can avoid two-phase flow in the pipe by pressurizing CO₂ at the pipe inlet to above its critical pressure of about 73 bar (this is how commercial CO₂ pipelines work). However, when we compress the inlet CO₂ to such a high pressure, it may result in large pressure drops (tens of bars) at the discharge point, which can complicate the nozzle design.

Regardless of whether we design for one-phase or two-phase flow, keeping a steady outlet flow may be difficult. CO_2 is a compressible fluid, so if we control the flow at the inlet, it is not necessarily the same flow at the outlet over one km away. While this may not be a problem for commercial operations, for a controlled experiment we need a steady, measured flow rate. As a worst case scenario, oscillatory flow may develop in the pipe with a frequency on the order of minutes. One way to avoid this problem is to meter the flow at the outlet (at 800 m under the sea), but this complicates the equipment design.

Although we envision that anti-backflow valves will be installed immediately upstream of the nozzle discharge ports to prevent ingress of sea water, and the submerged conduit will be filled with dry gas during deployment, it is possible that some moisture will eventually intrude into the system. When CO_2 is dispersed in sea water, the hydrate phase typically is limited to a thin, often transient, film at the interface between the two fluids. When sea water is dispersed in CO_2 , however, complete conversion of the water into a solid, stable hydrate crystal often occurs. In the present application, this may lead to blockage of the pipeline or nozzle assembly. Procedures need to be developed to minimize the possibility of hydrate blockage during the field experiment. These procedures may include purging and drying the inside of the pipeline after deployment with nitrogen gas and heating the nozzles when starting and terminating the flow of CO_2 . If hydrate blockage does occur, it can be cleared by reducing system pressures by raising the diffuser assembly.

One final concern is what happens when the pipe is rapidly depressurized. If the CO_2 in the pipe is vented, it will flash into vapor and dry ice. The dry ice will plug the pipe and could take a substantial time (over a day) to sublimate. This type of delay is unacceptable, so procedures must be worked out to depressurize. Our current idea is to use nitrogen to push the CO_2 out the bottom of the pipe, and then depressurize with nitrogen in the pipe.

In summary, some of the design concerns that need to be addressed to assure a steady flow of CO_2 of approximately 1 kg/s and 0.1 kg/s are:

- Choice of pump
- Choice of pressure profile (one vs. two phase flow, pump outlet pressure)
- Choice of valves (anti-back flow, pressure regulation at outlet, flow control mechanism)
- Operational issues (start-up, shut-down, purging, hydrate avoidance)

B. Summary of our input to an inter-model comparison carried out by the project.

Case	Mass flow rate [kg/s]	Droplet Radius [cm]	Ambient Current [m/s]*	Rise Height (Sato) [m]	Rise Height (Alendal) [m]	Rise Height (MIT) [m]	Rise Height (Droplet) [m]
1	0.1	0.25	0.04	60	60	100	73
2	0.1	0.4	0.04	140	110	202	168
3	0.3	0.4	0.04	145	120	213	168
4	1.0	0.2	0.04	--	45	101	47
5	1.0	0.4	0.04	150	120	244	168
6	1.0	0.4	0	--	120	244	168

*Note: MIT model does not include ambient current effects.

Droplet dissolution height was calculated using the relation:

$$\frac{dm_b}{dt} = -pd_b^2 K (C_s - c_i) \quad (1)$$

where $K[L/T]$ is the mass transfer coefficient, $C_s [M/L^3]$ is the surface concentration (solubility) of CO_2 , and $c_i [M/L^3]$ is the concentration of dissolved CO_2 in the vicinity of the bubble. (Crounse, MS thesis) Inserting $z=U_s t$ into Equation 1 and assuming $c_i = 0$ gives:

$$\frac{dm_b}{dz} = \frac{-pd_b^2 K C_s}{U_s} \quad (2)$$

Using Equation 2 and the physical properties as described in the sub-model standardization memo, dissolution heights for single droplets were obtained.

Plume height results between the MIT model and the CFD models are significantly different. When these results are compared with a simple droplet model, it is clear that the CFD models estimate a plume height that is lower than the rise height for a single bubble, while the MIT model predicts a plume rise height higher than that of a droplet. In the MIT integral model, the droplets are part of a rising inner plume, yielding a total droplet velocity of $U_s + U_p$. This is related, in part, to the assumption that more dense fluid peels off of the outside of the plume. However, if this more dense fluid were to descend within the inner core, the droplet velocity would be reduced.

Additionally, the MIT model does not include current effects. It is uncertain what impact they may have on rise height.

C. Application of a double plume model to compute near field mixing.

The model was developed specifically to simulate CO_2 sequestration plumes, and extends the hybrid double-plume model of Asaeda & Imberger (1993) by incorporating droplet dynamics

(dissolution, hydrate formation, and phase changes), introducing a self-regulating detrainment criterion, and allowing multiple overlapping intrusions. The model is calibrated to data from the literature and our lab, and applied to predict plumes associated with a proposed CO₂ field study. Details of this model can be found in Appendix 1.

D. Evaluation of tracers.

We review six tracers that have been considered by participating scientists for measuring the rates of CO₂ mixing and dissolution, two processes which are important for determining the concentrations of excess CO₂ and associated changes in pH. The comparison considers dissolved inorganic carbon (or total carbon, C_T), pH, labeled and natural carbon isotopes (¹³C and ¹⁴C) and two introduced tracers (fluorescent dye and SF₆). The tracers are compared with respect to their ability to trace the injected CO₂, the method of measurement, precision and response time, whether or not the measurement can be performed *in situ*, and other factors such as permitting. Details can be found in Appendix 2.

Conclusion

We are on schedule in our technical preparation to conduct the ocean carbon sequestration field experiment in the summer of 2002. We have evaluated the following key components:

1. The infrastructure to deliver a steady and measurable flow of CO₂ is required. We have developed design criteria for this system to send out to a contractor for detailed design.
2. Models are being used to help in the design of specific experiments and measurements. We have developed plume models to conduct this task. In addition, our international collaborators have also developed models. An inter-model comparison was conducted to better integrate the model results.
3. The use of tracers is critical for making field measurements. We analyzed potential tracers to use in our experiment.

References

None.

Appendices

Appendix A

Application of a Double Plume Model to Compute Near Field Mixing for the International Field Experiment on CO₂ Ocean Sequestration¹

ABSTRACT

We describe a numerical model of a steady-state plume in a quiescent, stratified, ambient, driven by a buoyant dispersed phase, such as bubbles or droplets. The model was developed specifically to simulate CO₂ sequestration plumes, and extends the hybrid double-plume model of Asaeda & Imberger (1993) by incorporating droplet dynamics (dissolution, hydrate formation, and phase changes), introducing a self-regulating detrainment criterion, and allowing multiple overlapping intrusions. The model is calibrated to data from the literature and our lab, and applied to predict plumes associated with a proposed CO₂ field study.

INTRODUCTION

Direct injection of CO₂ as a buoyant liquid at intermediate ocean depths has been proposed as one scenario for CO₂ sequestration. To study this situation, an international field experiment is planned for the summer of 2001, in which CO₂ will be released at rates of 0.1 to 1 Kg/s through various types of nozzles in water depths of order 800 m (Adams, et al., 1999). The experiment can be viewed as a full-scale test of one nozzle out of perhaps 100 to 1000 nozzles serving a 500 MW coal-fired electric power plant. Here we describe an integral model applicable to two-phase plumes in quiescent, stratified environments (Crounse, 2000), present some brief model calibration and sensitivity studies, and show results for the anticipated field study. Further information can be found in Crounse (2000).

MODEL FORMULATION

The model simulates the rise and dissolution of buoyant CO₂ droplets in an upward rising central core of the plume, sinking of negatively-buoyant CO₂-enriched seawater in the annular outer plume, “peeling” of water between the two regions, and intrusion of CO₂-enriched seawater at levels of neutral buoyancy. Integral models describe plume flow as one-dimensional by assuming that plume profile shapes are independent of height. Although this assumption is not strictly valid for two-phase plumes in stratification, similar models have been successfully applied to somewhat simpler flows by Asaeda & Imberger 1993, Wüest et al. 1992, and McDougall 1978. Here, we follow Asaeda & Imberger (1993) and choose top-hat profiles for both the inner, rising plume of water and droplets, and the outer, falling annular plume of water only.

The model is formulated in terms of flux variables. The mass flux of bubbles, W_b , is given by their number flux, N_b , their nominal diameter, d_b , and their density, ρ_b , yielding

$$W_b(z) = \frac{1}{6} \rho_b d_b^3(z) N_b(z) = Q_b(z) \rho_b(z). \quad (1)$$

¹ Proceedings of GHGT-5, Cairns, Australia, August 2000

The size and density of bubbles are tracked in a bubble sub-model that accounts for dissolution, hydrate formation and phase changes. Denoting X as the cross-sectional fraction of the inner plume occupied by bubbles, we define the volume flux, Q , of plume water as

$$Q_i(z) = \int_0^{b_i} (1 - X(z)) u_i(z) 2\pi r dr = \pi b_i^2 u_i \quad (2)$$

where u is the average water velocity and b is the plume width. The subscript i indicates an inner-plume value. The momentum flux, M , includes the momentum of both the bubbles and the droplets

$$M_i(z) = g \int_0^{b_i} (1 - X(z)) u_i^2(z) \pi r dr + g \int_0^{b_i} X(z) (u_i(z) + u_b(z))^2 \pi r dr \quad (3)$$

where u_b is the bubble slip velocity and g is a momentum amplification term, first introduced by Milgram (1983), that accounts for the fact that the model formulation implicitly ignores turbulent momentum transport. Because $X \ll 1$ and $u_b = O(u_i)$, the second term in (3) can be ignored giving $M_i = g \pi b_i^2 u_i^2 = g Q_i u_i$.

The buoyant forces generating the plume result from changes in density. For this model, density is tracked through changes in salinity flux, S , heat flux, J , and the dissolved CO_2 flux, C . The salinity flux is defined from the local plume salinity, s , such that

$$S_i(z) = Q_i(z) s_i(z) \quad (4)$$

The heat flux of the plume is defined from the local water temperature, T , yielding

$$J_i(z) = Q_i(z) \pi c_p(z) T_i(z) \quad (5)$$

where c_p is the heat capacity of the fluid. Finally, the dissolved CO_2 flux is defined from the local dissolved CO_2 concentration, c ,

$$C_i(z) = Q_i(z) c_i(z) \quad (6)$$

Thus, Eq. 2-7 define the model state variables for the inner plume.

The state variables for the outer plume are nearly identical. The primary difference is that, because the outer plume is assumed to be annular, the volume flux of the outer plumes is defined as

$$Q_o(z) = \pi (b_o^2 - b_i^2) u_o \quad (7)$$

where the subscript, o , indicates an outer plume value. Defining z as positive upward, and specifying that the outer plume flow is downward, the velocity u_o is negative and u_i is positive. Using Eq. 7 and changing the subscripts in Eqs. 1-6 from i to o yield the flux equations for the outer plume.

The plume develops by exchanging fluid with the ambient and by exchanging fluid between the inner and outer plumes. The entrainment hypothesis, introduced by Morton et al. (1956), states that the entrainment flux across a turbulent shear boundary is proportional to a characteristic velocity in the turbulent layer. In this model, we have defined three entrainment fluxes: E_i entrains from the ambient or from the outer plume into the inner plume, E_o entrains from the inner plume into the outer plume, and E_a entrains from the ambient into the outer plume. The entrainment relationship for counterflows is not well known. Here, we adopt the relationship used by Asaeda & Imberger (1993):

$$E_i(z) = 2pb_i \mathbf{a}_i (u_i - u_o) \quad (8)$$

$$E_o(z) = 2pb_o \mathbf{a}_o u_o \quad (9)$$

$$E_a(z) = 2pb_o \mathbf{a}_a u_o \quad (10)$$

where the \mathbf{a} 's are entrainment coefficients.

The final exchange equation accounts for buoyant detrainment, which has been modeled in a variety of ways. Liro (1992) assumed that a fixed fraction of plume fluid was ejected when the net buoyancy flux across the plume approached zero. Asaeda & Imberger (1993) assumed that all of the plume fluid detrained when the net momentum approached zero. Based on experiments, peeling is better predicted when the net momentum approaches zero. For this model, a self-regulating peeling criterion is introduced. We know that peeling occurs when the drag from the bubbles can no longer support the negative buoyancy of the fluid. The simplest parameterization that behaves similarly to experiments gives the peeling flux as

$$E_p(z) = \epsilon \left(\frac{u_b(z)}{u_i(z)} \right)^2 \left(\frac{B_i(z)}{u_i^2(z)} \right) \quad (11)$$

where ϵ is a non-dimensional fitting parameter of order 0.01, and B is the buoyancy flux, defined as

$$B_i(z) = gQ_i(z) \frac{\mathbf{r}_a(z) - \mathbf{r}_i(z)}{\mathbf{r}_i} \quad (12)$$

where \mathbf{r}_a is ambient density. The form of Eq. 11 makes it possible for outer plumes to overlap and allows simulation of continuous peeling (Type 3) plumes, defined by Asaeda and Imberger (1993).

With these definitions, plume conservation equations can be defined, including mass conservation:

$$\frac{dQ_i}{dz} = E_i + E_o + E_p \quad (13)$$

$$\frac{dQ_o}{dz} = E_i + E_o + E_p + E_a \quad (14)$$

momentum conservation:

$$\frac{dM_i}{dz} = g \left(\frac{Q_b}{(u_i + u_b)} (\mathbf{r}_a - \mathbf{r}_b) + \mathbf{p} b_i^2 (\mathbf{r}_a - \mathbf{r}_i) \right) + E_i \mathbf{r}_o u_o + E_o \mathbf{r}_i u_i + E_p \mathbf{r}_i u_i \quad (15)$$

$$\frac{dM_o}{dz} = -g \mathbf{p} (b_o^2 - b_i^2) (\mathbf{r}_a - \mathbf{r}_o) + E_i \mathbf{r}_o u_o + E_o \mathbf{r}_i u_i + E_p \mathbf{r}_i u_i + E_a \mathbf{r}_a u_a \cdot \quad (16)$$

and the conservation of salt, heat and dissolved CO₂ flux for the inner plume:

$$\frac{dS_i}{dz} = E_i s_o + E_o s_i + E_p s_i \quad (17)$$

$$\frac{dJ_i}{dz} = c_p \mathbf{r}_r (E_i T_o + E_o T_i + E_p T_i) + \frac{dW_b}{dz} \Delta H_{diss} \quad (18)$$

$$\frac{dC_i}{dz} = E_i c_o + E_o c_i + E_p c_i \quad (19)$$

and for the outer plume:

$$\frac{dS_o}{dz} = E_i s_o + E_o s_i + E_p s_i + E_a s_a \quad (21)$$

$$\frac{dJ_o}{dz} = c_p \mathbf{r}_r (E_i T_o + E_o T_i + E_p T_i + E_a T_a) \quad (22)$$

$$\frac{dC_o}{dz} = E_i c_o + E_o c_i + E_p c_i + E_a c_a \quad (23)$$

The last term in Eq. 18 accounts for energy released by dissolving CO₂. Densities \mathbf{r}_i and \mathbf{r}_o are determined by an equation of state as a function of s , T , and c . dW_b/dz is calculated by the bubble sub-model.

The model begins with integration of the inner plume from the point of release to the point where the droplets disappear or the water surface is reached. Once the inner plume integration is complete, the outer plume segments are integrated. The integration of each outer plume section continues until the momentum flux approaches zero. Then, the next outer plume section is initialized and integrated. This cycle repeats until the solution converges to a steady result (typically 10 iterations).

MODEL VALIDATION

The model has been successfully compared against measurements in plumes of varying complexity (Crounse, 2000). In general, optimal agreement requires slight adjustment of model entrainment coefficients, suggesting some uncertainty in model formulation, but acceptable agreement is obtained using constant values. Literature data include velocities for an air bubble plume in unstratified surroundings (Milgram 1983), and trap heights for single phase plumes in linear stratification (Turner, 1986). For both cases an outer plume does not develop, so only values for \mathbf{a}_i could be calibrated. The model best matched the observed trend and magnitude of plume velocities using $\mathbf{a}_i = 0.12$, and the classical trap height relationship, $h_T = 3.8(B/N^3)^{1/4}$, where N is the ambient stratification frequency, was reproduced for $\mathbf{a}_i = 0.11$.

Additional data for bubble and sediment plumes in stratification were available from Asada and Imberger (1993), Lemckert and Imberger (1993), Reingold (1994) and Socolofsky et al. (2000). The measured height of the first peeling event, h_T , and the volume flux in the resulting intrusion, Q_i , both decrease with the dimensionless slip velocity $u_b / (BN)^{1/4}$. Calibrating to the trap-height relationship gives values of $a_i = 0.07$, $a_o = 0.11$, and $a_a = 0.11$. **Figure 1** shows the model predictions for trap height and intrusion layer flux, compared to experimental data.

Finally, to simulate rising CO₂ droplets in a downward stream of CO₂-enriched seawater, we introduced a stream of air bubbles at the bottom of a water tank, and observed their upward rise against a falling stream of dense brine released near the tank surface. The goals were to test the postulated model structure in which plume water and bubbles rise upward in the inner core, and to compare modeled and observed plume velocities. Injected dye clearly showed the entrained water rising within the central core, and **Fig. 2** indicates reasonable agreement between measured and modeled plume velocities in both inner and outer plumes.

MODEL SENSITIVITY

A number of model sensitivity studies have been performed (Crounse, 2000) using, as a base case, 1 Kg/s of liquid CO₂, released as 0.5 cm diameter droplets with a density of 940 Kg/m³ into linear stratification ($N = 0.0032 \text{ s}^{-1}$; characteristic of the W. coast of Hawaii, at 800 m). The droplets act as if they are solid particles, with a 50% reduction in mass transfer due to hydrates (Hirai, 1996).

Fig. 3 depicts modeled volume flux, CO₂ flux and buoyancy flux as a function of elevation.

Three sensitivity studies are presented: the first, illustrated in **Tab. 1** and **Fig. 4**, is to the ambient density gradient, characterized by N .

Figure 4 shows that a factor of two variation in stratification causes little change in total plume rise height (the droplets dissolve at the same height), but the intrusion levels and fluxes differ. The volume flux to the intrusion layers decreases with increasing stratification because their descent is arrested more quickly in higher stratification, which leads to less cumulative entrainment and less total dilution. The mean concentration of excess CO₂ and the resulting change in pH in the intrusions are summarized in Table 1. Over the range of buoyancy frequencies sampled, the concentration of CO₂ in the intrusion layers is nearly proportional to the buoyancy frequency. **Figure 5** shows that plume concentrations are also a strong function of CO₂ discharge rate, suggesting that environmental effects can be minimized by injecting the CO₂ through a large number of separated discharge ports.

Table 1: Sensitivity to ambient stratification.

Variable	Decreased Stratification	Base Case	Increased Stratification
Buoy. Freq., N	0.0016 s^{-1}	0.0032 s^{-1}	0.0064 s^{-1}
Intrusion excess CO ₂	0.03 Kg/m^3	0.06 Kg/m^3	0.13 Kg/m^3
Intrusion pH change	1.1	1.5	1.9

Figure 6 shows sensitivity to a factor of **xxx** variation in initial droplet diameter, and a factor of **xxx** in the rate of CO₂ dissolution (the factor labelled **xxx** represents the base case). Note that droplet diameter is a design parameter, while the mass transfer rate is a model parameter, reflecting uncertainty in, among other things, the effects of hydrates. Maximum dilution is obtained by dispersing the CO₂ into as large a volume as possible, which means the droplets should ascend a reasonable height before dissolving. A wide range in plume heights appears to be feasible by designing droplet size to compensate for the effects of mass transfer. An additional run was made with a single droplet. **Figure 7** shows that the full plume always rises higher than individual droplets, and by a ratio which increases with decreasing droplet size, because droplet velocity is the sum of slip velocity plus the upward water velocity in the inner core.

ACKNOWLEDGEMENTS

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Appendix B: Evaluation of Tracers for Use in the International Field Experiment on CO₂ Ocean Sequestration²

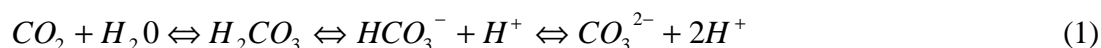
INTRODUCTION

An international field experiment is scheduled to take place off of the west coast of the big island of Hawaii during the second half of 2001 (Adams, et al., 1999; Herzog, et al., 2000). Scientists representing some dozen institutions in five countries on four continents are expected to participate. The experiment will involve several sub-experiments in which CO₂ will be released at a depth of 800 m as a buoyant liquid at rates of 0.1 to 1.0 kg/s. The releases will each be made for a duration of about one hour using nozzles with differing diameters and numbers of ports. Moored and mobile platforms will be used to measure ambient physical, chemical, biological and sedimentary properties, and the changes in these properties, if any, due to the CO₂ release over a spatial scale of about 100 m. The experiment can be viewed as a full-scale test of one nozzle out of perhaps 100 to 1000 nozzles that could serve a 500 MW coal-fired electric power plant whose total CO₂ flow rate would be of order 100 kg/s.

In this paper we review six tracers that have been considered by participating scientists for measuring the rates of CO₂ mixing and dissolution, two processes which are important for determining the concentrations of excess CO₂ and associated changes in pH. The comparison considers dissolved inorganic carbon (or total carbon, C_T), pH, labeled and natural carbon isotopes (¹³C and ¹⁴C) and two introduced tracers (fluorescent dye and SF₆). The tracers are compared with respect to their ability to trace the injected CO₂, the method of measurement, precision and response time, whether or not the measurement can be performed *in situ*, and other factors such as permitting.

THE TRACERS

When CO₂ is added to seawater it reacts to form aqueous CO₂ and bicarbonate, carbonate and hydrogen ions,



The distribution among the dissociation species is governed by equilibrium constants that depend on temperature and salinity, as well as ambient carbon chemistry parameters such as C_T and alkalinity (Morel and Hering, 1993). While the kinetics of CO₂ dissociation in isolation are quite fast, Zeebe et al. (1999) suggests that the carbon chemistry couples with other chemical systems in the ocean [e.g., H₂O, B(OH)₃] such that the time constant of the CO₂ dissociation reaction may be much larger than the time constant of any single reaction in the system. They estimate the relaxation time for CO₂ equilibrium at the ocean surface (25°C) is about 16s. While still relatively quick, this time-scale approaches that of some plume processes.

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Following dissociation, the carbon that is actually discharged can be found in one of four states, CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-} , the sum of which is termed dissolved inorganic carbon or total carbon, C_T . Because C_T is conserved, it is a fundamental measure of the perturbation to the system, and hence a logical tracer of the injected CO_2 . C_T is best measured in the lab (on board ship) using coulometry to a precision of about 1-2 μM , which is comparable to ambient variability (see further discussion below). pCO_2 sensors are also available for *in situ* measurements, but their response time appears too slow (Walt, 1993).

Along with possibly pCO_2 itself, pH (the negative log of the H^+ concentration) is one of the important variables determining biological response of injected CO_2 (Angel, 1996; Auerbach et al., 1997). Hence it is also a fundamental tracer. But unlike C_T , pH can be easily measured *in situ*, using, for example, a glass electrode probe (e.g., SeaBird SB-18) or the solid state ISFET probe developed recently by CRIEPI. Probe precision is about 0.03 and 0.01 respectively, and each has a reported time constant of order seconds, though lab experiments by IOS suggest the response time of the SeaBird probe may be closer to 30 s (C.S. Wong, personal communication). *In situ* pH measurements may be complemented by more precise shipboard measurement using photometric techniques with precision of about 0.001. Like C_T , the accuracy of measured pH may be limited by ambient variability in carbon chemistry.

Carbon isotopes can also be used as direct measures of injected CO_2 . ^{13}C is a stable isotope whose concentration, relative to ^{12}C , varies with the source of carbon. The isotopic fraction is written as

$$f = \frac{^{13}\text{C}}{^{12}\text{C}} \quad (2)$$

or, with relationship to a standard isotope fraction,

$$d = \left(\frac{f}{f_{std}} - 1 \right) \times 1000 \quad (3)$$

While the injected ^{13}C is initially associated with the CO_2 , it rapidly becomes equilibrated with the other carbon species, and hence becomes a measure of C_T . Hence by measuring the isotopic fraction, using mass spectrometry, one can infer the concentration of excess CO_2 . The precision in the measurement of delta ^{13}C is about 0.1 per mil, similar to ambient variability.

Radiocarbon, ^{14}C , can also be used as a tracer, and is measured onboard using mass spectrometry. The concentration of ^{14}C in fossil sources of CO_2 is zero so, like ^{13}C , measurements of natural ^{14}C can be used to trace plume concentrations of C_T . However, the precision of such measurements is less than using natural ^{13}C or C_T . Much greater sensitivity can be obtained if ^{14}C is added to the discharge by labeling some of the injected CO_2 . Although the resulting radioactivity is small compared with ambient radioactivity, e.g., from ^{40}K , a drawback of using labeled ^{14}C is the public perception of adding radioactivity to the ocean.

Water-soluble fluorescent dyes such as fluorescein and Rhodamine WT are frequently used as tracers. Illuminated by incident light of a specified excitation frequency, they re-emit light at a lower emission frequency. Fluorometers can be used to rapidly measure fluorescent tracers *in situ* as part of a standard instrument package (i.e., along with temperature, conductivity, pressure, pH) with a precision of order 0.1 ppb. If injected passively as a neutrally buoyant solution near the nozzle, the dye will become entrained in the rising plume, and provide a useful measure of plume entrainment/dilution. However, the CO₂ droplets and the entrained seawater eventually separate, due to effects of ambient stratification (Asaeda and Imberger, 1993; Socolofsky and Adams, 2001a) and/or current (Hugi, 1993; Socolofsky and Adams, 2001b). After separation, the dye will mark the water and not the CO₂. Indeed, it can be envisioned that, after a certain elevation, most of the entrained seawater will have detrained (peeled) from the plume, taking the dye with it, thus leaving much of the CO₂ droplets to rise without dye. Thus dye is not a good measure of CO₂ fate. However, it can be used as a diagnostic: models that purport to describe plume behavior must be able to represent phase separation and hence measurements of both dye and pH (or C_T) are complementary. Injecting dye in the early part of plume ascent (before peeling) can also serve to determine the rate of CO₂ dissolution, by measuring both pH and fluorescence, as dual tracers. Before peeling, the integrated flux of dye should be conserved, while the integrated flux of excess C_T should increase with elevation, reflecting dissolution of CO₂. The variation of this ratio can be used to measure variation in CO₂ dissolution with height and, with the help of models, the rate of dissolution with time. Such an experiment is being planned by researchers from CRIEPI.

Finally, SF₆ is another introduced tracer. Using gas chromatograph with electron-capture detection, it can be measured in volumes down to about 10⁻¹⁷ mole (Ledwell et al., 1998) or in concentrations about one million times smaller than fluorescent dye. Like dye there is essentially no background concentration. Because of its strong sensitivity, SF₆ has been used to measure oceanic mixing over time scales of a year or more (Ledwell et al., 1998). However, SF₆ must be analyzed on board and hence is not suitable for rapid plume surveying. Like dye, if injected into the entrained seawater, it will mark entrained seawater and not excess C_T *per se*. However, because SF₆ is more soluble in CO₂ than in seawater, it could conceivably be incorporated into CO₂ before injection so as to more directly track injected CO₂ (van Scoy, 1996). In the early phases of our experimental planning (Adams and Herzog, 1997) it was envisioned that an SF₆ experiment would make a nice complementary study of far field mixing and such a study would still be useful as part of a later, more comprehensive, field survey.

THE CONCEPT OF DILUTION

Because a major objective of a tracer is to measure dilution, we must define dilution. The dilution S of a volume V_o of discharged fluid, mixed with a volume $V_m - V_o$ of ambient fluid, can be written

$$S = \frac{V_m}{V_o} \quad (4)$$

Assuming conservative behavior (no reactions or decay), the concentration of mixed fluid is a weighted average of the discharge concentration and the ambient concentration or

$$C_m = \frac{C_o V_o + C_a (V_m - V_o)}{V_m} \quad (5)$$

Combining with Eq. 4,

$$S = \frac{C_o - C_a}{C_m - C_a} \quad (6a)$$

Eq. 6a can be used directly with C_T , using appropriate values for C_o , C_m and C_a . Since $C_o \gg C_a$, Eq. 6a can be approximated as

$$S \approx \frac{C_o}{C_m - C_a} \quad (6b)$$

Eqs 6a and 6b would also pertain to the introduced tracers (dye and SF_6), to the extent that these trace C_T (see above discussion).

Using pH as a tracer, the change in measured pH relative to ambient, $\Delta\text{pH} = \text{pH}_a - \text{pH}_m$, can be related to the change in C_T (excess C_T), $\Delta C_T = (C_m - C_a)$, as

$$\Delta\text{pH} = a\Delta C_T \quad (7)$$

so that Eq. 6b can be written

$$S = \frac{aC_o}{\Delta\text{pH}_m} \quad (8)$$

where C_o refers to the discharged concentration of C_T .

If C represents the concentration of $^{12}\text{C} \cong C_T$ and fC represents the concentration of ^{13}C or ^{14}C then the fraction of ^{13}C (or ^{14}C) in a mixture can be expressed

$$f_m = \frac{V_o f_o C_o + (V_m - V_o) f_a C_a}{V_o C_o + (V_m - V_o) C_a} \quad (9)$$

Assuming $S \gg 1$, S can be evaluated as

$$S = \frac{V_m}{V_o} = \frac{C_o (d_o - d_m)}{C_a (d_m - d_a)} \quad (10)$$

MAXIMUM DILUTION

The accuracy and sensitivity of the various tracers depends on the accuracy with which the concentrations/pH/isotopic fraction can be measured, and with the associated ambient variability of the concentration/pH/isotope fraction. For example, denoting uncertainty in measured concentration by σ_m and variability in ambient concentration by σ_a , the maximum dilution which can be determined to within a precision of p from measuring C_T , dye or SF_6 concentration, can be determined from Eq. 6b as

$$S_{\max} = \frac{pC_o}{\sqrt{s_m^2 + s_a^2}} \quad (11)$$

When pH is used to measure changes in C_T , the maximum dilution depends on the ambient variability of C_T (denoted by σ_a), the accuracy of the pH measurement (denoted by $\sigma_{\Delta\text{pH}}$) and the uncertainty in the relationship between ΔpH and ΔC_T (denoted by σ_α), or

$$S_{\max} = \frac{pC_o}{\sqrt{s_a^2 + (as_{\Delta\text{pH}})^2 + (s_a \Delta\text{pH})^2}} \quad (12)$$

Using carbon isotopes, the limiting dilution comes from Eq. 10. Assuming $(\delta_o - \delta_m) \gg (\delta_m - \delta_a)$, the maximum dilution is

$$S_{\max} = \frac{p(C_o / C_a) d_o}{\sqrt{s_{d_m}^2 + s_{d_a}^2}} \quad (13)$$

AMBIENT VARIABILITY

As indicated above, precision in the measurement of dilution by a given tracer reflects spatial and temporal variability in the ambient concentration of the particular tracer. In principle, temporal variability can be eliminated by measuring ambient concentrations during the experiment. Spatially, we focus on vertical variability because it is expected to be much more significant than horizontal variability over the respective scales of the plume. We assume that the plume may mix over a height of order 100 m and that the ambient tracer concentration varies linearly over this height. Because of uncertainty regarding the exact vertical distribution of entrainment into the plume, the associated uncertainty in the average concentration of entrained seawater is taken as 10-20 percent of the plume height (10-20 m) times the gradient in ambient concentration. Measurements collected by IOS during the ambient survey of August 1999

suggest gradients of ambient C_T concentration of about 0.1 $\mu\text{M}/\text{m}$ (Miller et al., 2000), while corresponding gradients of ambient ^{13}C fraction analyzed by NRL were about 0.1 per mil (Coffin, et al., 1999). The estimated gradient in ambient ^{14}C fraction is 2 per mil (K. Grabowski, personal communication).

COMPARISON

Table 1 uses Eqs. (11-13) to estimate S_{max} for each of the six tracers, assuming $p = 0.1$. A number of other tracer attributes are also summarized, from which we can draw the following conclusions:

While the source strength of fluorescent dye and (particularly) SF_6 can be adjusted at will to provide any reasonable level of sensitivity, these tracers monitor the entrained seawater, and not excess C_T ; hence they are not suitable as the primary tracer of the plume. However, by measuring dye along with pH, one has a useful field measurement of CO_2 dissolution, as well as a complementary diagnostic of overall plume behavior.

With 10% precision, measurement of excess C_T can resolve dilution up to about 10^6 . This corresponds to an estimated average dilution (Eq. 4) in a volume 100m long by 40m wide by 50m high, containing CO_2 discharged at a “low” volume flow rate of $10^{-4}\text{m}^3/\text{s}$ (0.1kg/s) for a period of 2000 s in a current of 5 cm/s. This volume is consistent with 3D numerical predictions of CO_2 plume behavior in a current made (Alendal and Drange, 2001; Sato, 2000). Assuming the same mixing volumes, the estimated average dilution for a “high” volume flow rate of $10^{-3}\text{m}^3/\text{s}$ (1 kg/s) is 10^5 . Thus 100m downstream from the discharge, C_T could resolve the spatial features of a high flow rate plume, but possibly not a low flow rate plume.

Based on the measured ambient variability and measurement precision of ^{13}C , slightly lower dilutions ($\sim 3 \times 10^5$) can be resolved using natural ^{13}C . The ambient variability of ^{13}C needs to be checked during the actual survey.

Because the discharge concentration can be adjusted at will (and it traces excess C_T directly) ^{14}C offers considerably more sensitivity. Using a discharge enrichment factor of 100 yields an order of magnitude greater sensitivity than that obtained with C_T or with natural ^{13}C . However, there are several “issues” associated with the use of ^{14}C : how to introduce it to the tank, permitting, and public perception concerning use of radioactive materials. ^{13}C , ^{14}C and C_T can not be measured *in situ*, or with real time output, so they must be supplemented with other measurements.

A pH probe can provide *in-situ*, real time measurements. With in-place calibration, such probes can provide accuracy of 0.01 units, yielding similar dilution sensitivity as obtained with C_T (i.e., accuracy will be limited by spatial variability in C_T). The finite response time of the pH probes could limit spatial resolution somewhat, but any error can be corrected during data analysis. Shipboard measurements of pH should provide useful calibration, but it appears that ambient variability in C_T will control the sensitivity of pH.

Consistent with the above discussion, our experiment will include four of the six tracers discussed herein: C_T , pH, natural ^{13}C and dye.

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Table 1. Tracer Comparison

Tracer	Method	<i>In-situ?</i>	Real time?	Disch Conc	Amb Conc	Precision	Ambient Var	Max. Dil. S_m	Response Time	Cost/effort
DIC	coulometry	no	no	$C_o \cong 20M$	$C_a \cong 2mM$	$s_m \cong 1 - 2mM$	$s_a \cong 1 - 2mM$	1E6	NA	moderate
pH	SeaBird	yes	yes	NA	NA	0.03	related to	3E5	15-45s	low
	CRIEPI	yes	yes	NA	NA	0.01	variability	1E6	< 10 s	low
	photometric	no	no	NA	NA	0.001	in C_T	1E6	NA	moderate
Nat ^{13}C in C_T	MS	no	no	$d_o \cong -24$ to -32	$d_a \cong 0$	$s_{dm} \cong 0.1$	$s_{da} \cong 0.1$	3E5	NA	moderate
Dead ^{14}C	MS	no	no	$d_o \cong -1000$	$d_a \cong -200$	$s_{dm} \cong 10$	$s_{da} \cong 2$	E5	NA	moderate
Lab ^{14}C (100x)	MS	no	no	$d_o \cong 10^5$	$d_a \cong -200$	$s_{dm} \cong 10$	$s_{da} \cong 2$	E7	NA	high
Dye	fluorometer	yes	yes	adjustable	small	.01 to .1ppb	small	adjustable	fast	moderate
SF ₆	GC	no	no	adjustable	v. small	v. high	v. small	v. high	NA	high