Fluid dynamics of sinking carbon dioxide hydrate particle releases for direct ocean carbon sequestration

by

Aaron C. Chow

Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the field of Environmental Fluid Mechanics at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 2008

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Abstract

One strategy to remove anthropogenic CO₂ from the atmosphere to mitigate climate change is by direct ocean injection. Liquid CO₂ can react with seawater to form solid partially reacted CO₂ hydrate composite particles (pure hydrate plus unreacted CO₂ and water) with densities several percent above ambient seawater. The most recent field injections at depths of 1500 m in Monterey Canyon resulted in long curved cylinders with diameters ~ 2.5 cm and lengths up to ~ 1 m that were observed to sink at ~ 4 cm/s. This thesis examines whether releasing the partially reacted hydrate particles into the ocean at ~ 100 kg/s of CO₂ (roughly the output of one 500 MW coal power plant) is able to create sufficient dilution to minimize the impact on marine life. We developed a drag coefficient model for cylindrical particles in free fall. Applying the new drag coefficient model to recently observed field injections to predict their descent, the recently produced field particles were estimated to have had a ~ 16% reaction efficiency and to have sunk 100 m before completely dissolving.

Ambient density stratification and currents will also affect particle descent, and in turn the dilution of dissolved CO₂. Three methods of injection of composite particles were evaluated, each with unique merits. Firstly, we can release hydrate particles (with a range of reaction efficiencies) continuously from a moving ship. This is shown to provide excellent dilution of the discharged CO₂. Second, we can release them from a stationary pipe to create a plume that generally sinks further than individual particles. However we show numerically that, while this method appears to be the most practical from an engineering standpoint, the dilutions and sequestration depths are highly dependent on ambient conditions. The third method involves constructing a shroud around a fixed source to shelter the plume from effects of ambient stratification and current. The shroud also serves as an inverted chimney, inducing a down draft that transports the dissolving particles to a depth of lower ambient disturbance. Laboratory measurements using particle image velocimetry (PIV) shows that the induced flow depends on the shroud length and diameter, as well as the particle buoyancy and size.
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Chapter 1

Motivation

1.1 Global climate change

The global atmospheric build-up of carbon dioxide (CO$_2$) and other greenhouse gases in recent history has been attributed to industrialization leading to increased fossil fuel combustion and deforestation. It is feared that rising concentrations of greenhouse gases will cause adverse changes in the climate, and that two-thirds of the change will be attributed to CO$_2$(Herzog et al. [29]). Possible effects include increased likelihood of extreme weather events, the rising of the mean ocean level, and even the cessation of large scale global climatological phenomena such as the North Atlantic Gulf Stream (Watson et al. (IPCC) [77]).

Carbon sequestration in the ocean has been suggested as an attempt to reduce the peak concentration of carbon dioxide levels, since even if overall CO$_2$ emissions were reduced today the climatic effects will manifest themselves long afterwards (as illustrated in Figure 1-1).
1.2 Ocean carbon sequestration

Ocean carbon sequestration has been studied as one method of curbing atmospheric buildup of anthropogenic carbon dioxide, believed to be responsible for global warming trends. The ocean is presently the dominant sink for atmospheric CO₂, taking up about 7 gigatons a year (The Intergovernmental Panel on Climate Change - Special Report on Carbon Capture and Storage, Metz et al. (IPCC-SRCSS) [44]). Since the industrial revolution, the ocean has already absorbed 500 GtCO₂ out of the total of 1300 GtCO₂ anthropogenic CO₂ emissions. The ocean will also be an important sink in the future: at about 70% of the earth’s surface and an average depth of 3800m, it has an enormous storage capacity (Figure 1-2).
Atmospheric CO$_2$ diffuses into the ocean through the air-ocean interface. Since the year 1800, the pH of the surface of the oceans has decreased about 0.1 pH units. The concentration of dissolved CO$_2$ at the surface is important, as noted by Knutzen [38], since dissolved CO$_2$ will lower the local ocean pH, and affect marine organisms. Metz et al. [44] cite several effects of elevated CO$_2$ levels on marine organisms: at acute levels CO$_2$ has a narcotic effect on animals and causes respiratory distress and death. Tamburri et al. [67] have observed the narcotic effects of increased CO$_2$ levels on mobile deep sea animals in the field; they also observe that while many tend to avoid CO$_2$ plumes, some may risk the narcotic effects to obtain food. Passive marine animals may experience depressed ion exchange capability and metabolism when exposed to lower, chronic levels CO$_2$. Examples of metabolic mechanisms that may be affect by lower pH levels are shown in Figure 1-3. The work of Auerbach et al. [8], Caulfield et al. [12] and Israelsson [33] that model the lowered pH on passive marine organisms such as zooplankton that spend varying times in and out of a CO$_2$ plume, and found that minimizing the local dissolved CO$_2$ and pH drops will reduce the mortality rate. As a guide, Metz et al. [44] uses a pH drop of 0.1 units as the threshold pH drop for insignificant marine life impact; it is also within the observed natural variability in the ocean.
Figure 1-3: Effects of added CO$_2$ on a generalized and simplified marine invertebrate or fish. The blue region on top refers to open water; the tan region represents the organism. Generalized cellular processes are depicted on the left and occur in various tissues like brain, heart or muscle; depression of these processes has consequences (depicted on the right and top). or + denotes a depression or stimulation of the respective function. Black arrows reflect diffusive movement of CO2 between compartments. Red arrows reflect effective factors, CO2, H+, HCO3 that modulate functions. Shaded areas indicate processes relevant for growth and energy budget. (Figure 6.26 of Metz et al. [44])
Figure 1-4 shows the long term effects of ocean absorption of atmospheric CO$_2$ (Caldeira and Wickett [11]). The top panel shows an emissions scenario showing a peak at about the year 2100, followed by a decrease to zero emissions. The middle panel shows that the corresponding expected atmospheric levels (pCO$_2$) will plateau at about 2000 ppm, just over 5 times the 2004 level of 380 ppm. The bottom panel of the figure shows the resulting change in the ocean pH levels with depth as it equilibrates with the atmosphere. The pH plot shows that, by relying solely on natural processes, anthropogenic CO$_2$ emissions will affect the top layer of the ocean the most. To counteract the lopsided oceanic CO$_2$ depth profile, any carbon to be sequestered must be stored in the deep ocean, or otherwise vertically distributed more evenly such that the surface does not gain the bulk of the CO$_2$. Deep ocean sequestration therefore serves another purpose: it will mitigate the acidification of the surface ocean through the diffusion of the CO$_2$ from the atmosphere.

![Figure 1-4: Model simulations of long term ocean pH changes, averaged horizontally, as a result of atmospheric CO$_2$ emissions shown in the top panel. The initial average ocean pH is about 8.2. (Caldeira and Wickett [11])](image)

CO$_2$ sequestration first involves capture from their sources, of which one major type is the coal-fired power plant. The CO$_2$ emissions are relatively pure from coal-fired power plants and can be isolated and injected into the ocean. A typical 500 MW power plant produces about 130 kg/s of CO$_2$ (Herzog et al. [30]). Technologies being
developed for CO$_2$ direct injection include positively buoyant liquid droplets (Brewer et al. [10]), dense gravity currents of CO$_2$-laden seawater (Haugen & Drange [27], Adams et al. [4], Saito et al. [58]), dry ice (Nakanishi et al. [50], Caulfield et al. [12]), and carbon dioxide hydrates (Holder et al. [31], Warsinzki et al. [76]). In addition, as shown in Figure 1-5, CO$_2$ can be pumped directly to the bottom of the ocean to form lakes.

![Figure 1-5: Different strategies for ocean carbon sequestration](image)

In comparing the methods above for effectiveness, one needs to consider both the persistence of the carbon dioxide once it is injected into the ocean, and also the dilution of CO$_2$ as it dissolves into the surrounding water. The former can be enhanced by injecting deeper under the ocean, or having a negative buoyancy source that sinks as far as possible. The latter will determine the dissolved inorganic carbon concentration, which has a bearing on the effects of the injection on the marine environment. Both factors depend largely on the fluid dynamics of the release condition.
1.3 Carbon dioxide hydrates: background

As outlined in Section 1.2, there is ongoing study of carbon dioxide hydrates as a possible vehicle for deeper ocean carbon sequestration. CO\(_2\) hydrates show promise for sequestration because they are denser than seawater, and will sink unaided while dissolving to promote dispersion in the ocean. This section provides some background information on hydrates, while the next section describes the work of our collaborators in creating hydrate particles in the ocean.

1.3.1 Hydrate formation

Figure 1-6 shows the pressure and temperature dependence of the observed phases of mixture of CO\(_2\) and water. Solid carbon dioxide hydrates (also known as clathrate hydrates) are thermodynamically stable at lower temperatures (below about 5° C) and high pressures, such as that found at ocean depths of 400 m or greater.

![Phase Diagram for CO\(_2\) with water](image)

Figure 1-6: Phase Diagram for CO\(_2\) with water (After Murray et al. [49])

Under stable conditions for carbon dioxide hydrates, the general stoichiometry of carbon hydroxide hydrate formation is as follows:

\[
CO_2 + nH_2O \rightleftharpoons CO_2 \cdot nH_2O
\]

(1.1)
$n$ is defined as the hydration number, the number of coordinating water molecules per CO$_2$ molecule. The molecular structure of a hydrate can be described as a cage of coordinating water molecules surrounding CO$_2$ molecules. Figure 1-7 shows the number of different cage structures that could exist for hydrates. In the light of the many different configurations, Rehder et. al [55] assumed an average hydration number of $n = 5.75$. The resulting solid has a density of 1143 kg/m$^3$ (Circone et al. [17]), about 10% greater than the ambient water density.

![Figure 1-7: Different structures for CO$_2$ hydrates (based on Sloan [61])]
1.3.2 Dissolution in seawater

CO₂ hydrates will also dissolve in the ambient seawater upon descent. There are two main reasons that the dissolution behavior requires study: the solute density effect and the contribution of dissolved CO₂ to the oceanic carbonate system.

1.3.3 Solute density effect

CO₂ hydrates will begin to dissolve in the ambient seawater upon release, due to the low concentration of CO₂ in the ambient water. The dissolution of CO₂ will increase the density of the seawater. Upon complete dissolution of the CO₂ the negative buoyancy flux \( B_{diss} \) of the solution can be determined as

\[
B_{diss} = \beta m
\]

where \( \beta \cong 0.0019 \text{ m}^4 \text{kg/s}^2 \), and \( m \) is the loading rate of CO₂ in kg/s (Haugen and Drange [27]).

1.3.4 Fate of dissolved CO₂

Once dissolved, aqueous CO₂ will exist in various charged forms in water according to these main reactions, known as the carbonate system (Morel and Hering [48]):

\[
\begin{align*}
\text{CO}_2(aq) + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3(aq) \\
\text{H}_2\text{CO}_3(aq) & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

The total dissolved inorganic carbon (DIC) is defined as ([48]):

\[
\text{DIC} = [\text{H}_2\text{CO}_3(aq)] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] 
\]

The result of this is that increasing dissolved CO₂ will shift the equilibria above to the right, and lower the local pH of the ambient seawater, which is expected to affect
passive marine organisms. (Alendal and Drange [5]).

**Alkalinity and pH**

To quantify the pH change of the ambient due to dissolved inorganic carbon, the carbon alkalinity $C - Alk$ is defined (Morel and Hering [48]):

$$C - Alk = - [H^+] + [OH^-] + [HCO^-_3] + 2[CO^{2-}_3]$$ (1.7)

The alkalinity is a measure of the buffering capacity of the water system to the addition of weak acids, such as carbonic acid from dissolved CO$_2$. Note $C - Alk$ remains a constant with added CO$_2$. With a known local DIC concentration and the alkalinity of the water, the resulting equilibrium pH value of the water can be determined. For the carbonate system at equilibrium shown in Equations 3.14 (which constitutes most of the alkalinity in seawater):

$$K_{a1}(T, S) = \frac{[H^+][HCO^-_3]}{[H_2CO_3(aq)]}$$ (1.8)

$$K_{a2}(T, S) = \frac{[H^+][CO^{2-}_3]}{[HCO^-_3]}$$ (1.9)

With Equations 3.17, 3.18, 3.19 and 3.20, and acid equilibrium constants available empirically for seawater (Zeebe et al. [79]), the concentrations of the four species, including the pH, can be solved.

**CO$_2$ partial pressure**

Tamburri et al. [67] note that increased partial pressure of carbon dioxide will also have a detrimental effect on marine organisms, such as causing slow respiratory distress and inducing a narcotic effect on fish. Therefore, the following plume behaviors of CO$_2$ are of importance: the depth of the resulting plume, the additional dissolved inorganic carbon (DIC) from the particles and the resulting decrease of ambient pH. These will act as markers of performance for the dilutions of CO$_2$ to minimize the
effect on aquatic life.

The partial pressure of CO$_2$ of a sample of water, denoted by $pCO_2$, is the pressure of gaseous CO$_2$ which, if allowed to equilibrate with water, will result in the same amount of dissolved CO$_2$ as observed in the sample. It is related to the solubility of CO$_2$, $C_s$ and the concentration of $H_2CO_3(aq)$ by the following:

$$pCO_2 = \frac{[H_2CO_3(aq)]}{C_s(T, S)}$$  \hspace{1cm} (1.10)

where $C_s(T, S)$ is dependent on the local temperature $T$ and salinity $S$. Dickson and Goyet [21] provide empirical relations to obtain $C_s$.

To illustrate the fate of the dissolved CO$_2$ in mean ocean conditions, Table 1.1 shows the relationship between changes in pH and the changes in pCO$_2$ and DIC and translates this to equivalent dilutions on an oceanic scale.

Table 1.1: Relationships between $\Delta$pH, changes in pCO$_2$, and dissolved inorganic carbon concentration calculated for mean deep-sea conditions. Also shown are volumes of water needed to dilute 1 tCO$_2$ to the specified $\Delta$pH, and the amount of CO$_2$ that, if uniformly distributed throughout the ocean, would produce this $\Delta$pH. (From Table 6.3 of IPCC [44])

<table>
<thead>
<tr>
<th>pH change $\Delta$pH</th>
<th>Increase in CO$_2$ partial pressure $\Delta$pCO$_2$ (ppm)</th>
<th>Increase in DIC $\Delta$DIC (μmol/kg)</th>
<th>Seawater volume to dilute 1 tCO$_2$ to $\Delta$pH (m$^3$)</th>
<th>GtCO$_2$ in entire ocean to produce $\Delta$pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-0.1</td>
<td>150</td>
<td>30</td>
<td>656,000</td>
<td>2,000</td>
</tr>
<tr>
<td>-0.2</td>
<td>340</td>
<td>70</td>
<td>340,000</td>
<td>3,800</td>
</tr>
<tr>
<td>-0.3</td>
<td>580</td>
<td>100</td>
<td>232,000</td>
<td>5,600</td>
</tr>
<tr>
<td>-0.5</td>
<td>1,260</td>
<td>160</td>
<td>141,000</td>
<td>9,200</td>
</tr>
<tr>
<td>-1</td>
<td>5,250</td>
<td>400</td>
<td>54,800</td>
<td>24,000</td>
</tr>
<tr>
<td>-2</td>
<td>57,800</td>
<td>3,260</td>
<td>6,800</td>
<td>190,000</td>
</tr>
<tr>
<td>-3</td>
<td>586,000</td>
<td>31,900</td>
<td>700</td>
<td>1,850,000</td>
</tr>
</tbody>
</table>
1.4 Continuous Jet Hydrate Reactor

The Oak Ridge National Laboratory has developed a small-scale continuous co-flow injector to create CO₂ hydrates in deep oceanic environments (Tsouris et al. [69]). The injector consists of an outer tube for CO₂ and an inner capillary tube for the water aligned concentrically within the reactor bore (Figure 1-8). The injector works by introducing a fast stream of ambient seawater into a coflowing stream of liquid CO₂. The capillary tube terminates some distance from the end of the outer tube, creating a zone in which the liquid CO₂ and water can mix before being discharged into the ambient water. Note that CO₂ and water are only sparingly miscible.

Figure 1-8: Schematic diagram of continuous coflow injector (from West et al. [78])
An injector was tested using a Hastelloy C-22 70 liter temperature-controlled, high-pressure Seafloor Process Simulator (SPS) that mimics conditions at ocean depths up to 2000 m (Figure 1-9). As confirmed by West et al. [78] and Lee et al. [40], the injection of water into the surrounding CO\textsubscript{2} stream increased the interfacial surface area between the two fluid phases and caused hydrates to form. Hydrate shells began to form on this interface and the result was a solid-like composite consisting of unconverted liquid CO\textsubscript{2}, CO\textsubscript{2} hydrate, and rejected brine from the seawater which was extruded from the injector tip into the surroundings (Figure 1-10). As shown in the figure, the extruded composite itself was a brittle solid, and the solid had weak points that lead to breaking off of cylindrical particles at the injector tip. The inhomogeneity of the reaction mixture and shear at the tip of the injector both contributed to the weak points in the extrusion.
Since the hydrate only formed in the interfacial area between the two phases, minimizing the droplet size of the water exiting the capillary tube into the CO₂ stream helped in increasing the contact area and thus the conversion efficiency of hydrate. Small droplets were achieved by keeping the water at jet spray or atomization mode, whereby the inertia of the fluid was sufficiently able to overcome the surface tension effects. The balance of inertia and surface tension is quantified by a jet Weber number, defined as

\[ We = \frac{\rho_w U_j^2 d_0}{\sigma_{cw}} \]  

(1.11)

where \( \rho_w \) is the water density, \( U_j \) the relative velocity of the jet and the CO₂ stream, \( d_0 \) the capillary diameter and \( \sigma_{cw} \) the surface tension between the water and CO₂. Based on Tang et al. [68], the criteria that indicates spray mode from the capillary water jet was \( We > 320 \). Tsouris et al. [71] reported that in practice a more consistent spray mode that led to a more steady solid composite production was obtained with \( We \) greater than 1000.

We define the conversion efficiency \( X \) of hydrate by the fraction of the mass of the
injected CO$_2$ that has converted into hydrate; a value of $X = 0$ denotes pure liquid CO$_2$ extruded while a value of $X = 1$ denotes pure CO$_2$ hydrate.

1.5 Field Observations

The coflow injector was tested in the field three times: in 2002 (Tsouris et al. [69]), in 2004 (Riestenberg et al. [56]) and in 2006 (Tsouris et al. [71]).

With each field testing, the size of the coflow injector prototype and the mass flow rate was increased. In addition to confirming hydrate formation in the field, the field experiments enabled better characterization of the extruded hydrate particles, as well as enable the measurement of particle descent velocities and in-situ hydrate particle dissolution rates that were not possible in the Seafloor Process Simulator.

1.5.1 Particle characterization

Figure 1-11 show particles emerging from the injector in the field. As the hydrate composite product stream extruded from the injector, the composite snapped at weak points of the extrusion, forming particles of typical length 10-100 cm. Particles emerge at a diameter similar to the internal bore diameter of the injector itself, and are long cylinders with some curvature. The particles produced in this injection showed a range of behavior: some were positively buoyant and rose, while others sank. This suggested a range of hydrate conversion rates using the same injector.

The cylindrical particles tend to fall horizontally in the water. The particles exhibit some rough edges, again suggesting an inhomogeneous mixture of solid hydrate, unreacted liquid CO$_2$ and ambient unreacted seawater. Some of the particles, which rise for a short while immediately after injection, are buoyed by some positively buoyant unreacted liquid CO$_2$. As the attached liquid CO$_2$ dissolves into the ambient and leaves the particle, the overall density of the composite increases due to the presence of the solid hydrate, and the particle starts to sink.

We are interested in determining the overall hydrate conversion efficiency of the extruded particles based on the ingredients and their observed fall velocity. Combined
with a suitable drag coefficient model for the curved cylindrical particles (addressed in Chapter 2), the correct characterization of the reaction efficiency will enable accurate prediction of the descent depth and the dissolved CO₂ concentrations due the particles.

Figure 1-11: Summary photographs of 2006 field injections. (a) The Remote operated vehible (ROV) *Tiburon* and (b) photograph of injector array assembly housed in a perspex cover. A release of curved cylindrical hydrate composite particles at 1500 m depth using the injector array of 2006: (c) view of injection at the injector and (d) view of a group of descending particles shortly afterward, from ROV *Tiburon*. 
1.5.2 Velocity measurement

In the three field experiments performed by the Monterey Bay Aquarium Research Institute (MBARI), the descent velocity of a particle was measured by following it with a remote operated vehicle (ROV) *Tiburón*, carefully keeping the particle stationary as the object of the underwater camera. The depth readings of the ROV thus served as the depth record of the particle it tracked. Typical particle trajectories are shown in 1-12. The ROV followed the particles for up to about 40 minutes after the injection, and not all the way until a single particle completely dissolved.

![Figure 1-12: Depth versus time profiles of CO$_2$ particles produced during experiment TO970 in 2006. From Tsouris et al. [71].](image)

The results of the field testing experiments are summarized in Table 1.2.
Table 1.2: Summary of field experiments 2002-6. Particle dimensions are representative of the particles generated in the field for each set of field observations. From Tsouris et al. [69], [71].

<table>
<thead>
<tr>
<th>MBARI particle</th>
<th>2002</th>
<th>2004</th>
<th>2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ mass loading (g/s)</td>
<td>0.2-0.8 (smaller injector)</td>
<td>0.4-0.5 (larger injector)</td>
<td>30 (larger outer bore)</td>
</tr>
<tr>
<td>reference</td>
<td>[69]</td>
<td>[56]</td>
<td>[71], [70]</td>
</tr>
<tr>
<td>release depth (m)</td>
<td>1300</td>
<td>1000-1200</td>
<td>1500</td>
</tr>
<tr>
<td>diameter d (cm)</td>
<td>0.5-0.6</td>
<td>0.8</td>
<td>2.2</td>
</tr>
<tr>
<td>length L (cm)</td>
<td>2-4</td>
<td>6-7</td>
<td>30</td>
</tr>
<tr>
<td>sinking rate U (cm/s)</td>
<td>2</td>
<td>5-6</td>
<td>4</td>
</tr>
<tr>
<td>shrink rate (mm/s)</td>
<td>4-7</td>
<td>4-7</td>
<td>6</td>
</tr>
<tr>
<td>Reynolds number (\frac{U d}{\nu})</td>
<td>80</td>
<td>310</td>
<td>630</td>
</tr>
</tbody>
</table>

1.6 Focus of current work

The project of ocean sequestration using CO₂ hydrates has been a collaborative work lasting over a decade with MIT, Oak Ridge National Laboratory (ORNL) and Monterey Bay Aquarium Research Institute (MBARI). As such, my thesis builds directly on the work of several key researchers. ORNL has spearheaded the development of a coflow injection method to produce a stream of hydrate particles by combining a slurry of CO₂ and ambient seawater (Holder et al. [31], Tsouris et al. [69]). Field studies have been initiated and conducted with MBARI (West et al. [78], Riestenberg et al. [56]). Parameters that characterize multiphase plumes were developed at MIT by Scott Socolofsky and E. Eric Adams (Socolofsky and Adams [63], [65], [64]). The carbon dioxide hydrate plume model was developed by Brian Crounse, Scott Socolofsky and Eric Wannamaker (Crounse et al. [20], Wannamaker and Adams [75]), also at MIT under the supervision of Eric Adams.
My direct contributions to the effort of understanding the behavior of hydrate particle releases are outlined below. This also serves as an overall outline of this thesis.

**Individual cylinder motion (Chapter 2)** Study of drag coefficient for straight and curved cylinders in free fall. The study is motivated by field observations of hydrate particles and the need to characterize and predict their descent.

**Hydrate particles for CO₂ sequestration (Chapter 3)** Prediction of hydrate composite particle descent depths and resulting dissolved CO₂ concentrations; scale-up of individual particles; discussion of a dispersal method of hydrate particles using a ship-towed pipe.

**Hydrate particle plumes (Chapter 4)** Use of a hydrate plume model to predict plume behavior of partially reacted hydrate composite particles; use of characteristic length scales to determine the relative effects of ocean current and stratification on plume behavior; hybrid two-staged model to account for strong crossflow effects on hydrate particle plumes.

**Shrouded plume (Chapter 5)** Assessment of the effectiveness of shrouded plume releases, long inverted chimneys that could be built to naturally convey hydrate particles downward and enhance dilution, while avoiding plume separation by crossflow.

**Summary and conclusions (Chapter 6)**
Chapter 2

Individual cylinder motion

2.1 Abstract

Laboratory experiments have been conducted to understand the behavior of negatively buoyant cylindrical particles of density $\rho$, length $L$, diameter $d$, with and without curvature, freely falling in a fluid of density $\rho_w$ at Reynolds numbers based on $d$ of 200-6000. We propose a parameter based on the cylinder density ratio $S = \rho/\rho_w$ and aspect ratio $E = L/d$ that is able to predict the onset of different modes of secondary motion ranging from oscillations to tumbling. The same parameter can also predict the maximum amplitude of the oscillations of the cylinder, based on comparing the magnitudes of the oscillation velocity with the fall velocity. Contrary to previous work which has treated the oscillations and drag coefficient dependence as independent phenomena, we argue that the secondary motion reduces the time-averaged projected surface area of the cylinder during its descent, leading to a lower observed drag coefficient $C_D$ computed using the nominal projected area of length times diameter, $Ld$. Curved cylinders adopt an average inclination to the horizontal and an oscillation pattern that depends on the curved particle’s arc angle as well as its specific gravity. The inclined particle has a smaller projected area compared with $Ld$, which, similarly to a straight cylindrical particle, leads to a reduced drag coefficient.
2.2 Introduction

Our study was motivated by the field injections of solid CO\textsubscript{2} hydrate particles into the ocean at depths of 1000 to 1500 m in order to assess their effectiveness for sequestering CO\textsubscript{2} from the atmosphere. It is feared that rising concentrations of greenhouse gases in the atmosphere will cause adverse changes in the climate, and that two-thirds of the change will be attributed to CO\textsubscript{2} (Herzog et al. [29]). There is ongoing study of carbon dioxide hydrates as a possible vehicle for deeper ocean carbon sequestration, because they are denser than seawater, and will sink unaided while dissolving to promote dispersion in the ocean. The field hydrate particles were created using a CO\textsubscript{2}-seawater coflowing injection apparatus, developed to create cylindrical composite particles, comprised of CO\textsubscript{2} hydrate, liquid CO\textsubscript{2} and seawater (Lee et al. [40]). Field tests were conducted on three occasions with differing co-flow injectors developed by ORNL in collaboration with the Monterey Bay Aquarium Research Institute (MBARI) (Tsouris et al. [69], Riestenberg et al. [56], Tsouris et al. [70] and Tsouris et al. [71]). The latest field observations show that the particles produced are long (up to \(~\sim 1\) m), curved cylinders of 2.2 cm in diameter that descend with Reynolds number of about 1000, and shrink at a constant rate of about 6 \(\mu\text{m/s}\) (Refer to Figure 1-11 and Table 1.2 from Chapter 1).

As a design guide for the scale up of the injector, it is important to determine the densities and therefore the reaction efficiency of the extruded particles. Since the densities of the particle cannot be directly measured, they must be deduced from their fall velocity, which requires an appropriate drag coefficient for the Reynolds number of interest (above \(~\sim 200\)).

2.3 Background

The average fall velocity of a straight cylinder in free fall can be dependent on the following 6 variables: the density of water \(\rho_{w}\), the water kinematic viscosity \(\nu\), the particle density \(\rho\), cylinder diameter \(d\), length \(L\), and gravity \(g\). In addition, if
the particle has curvature, its settling velocity can also depend on the arc angle, or circular arc length described by the particle, denoted as a 7th independent variable \( \theta \). \( \theta \) can also be expressed as \( L/R \) where \( R \) is the particle radius of curvature (See Figure 2-1).

![Figure 2-1: Definition sketch of straight and curved cylindrical particles.](image)

A straight cylinder therefore would have \( \theta = 0 \), while a cylindrical ring would have \( \theta = 2\pi = 360^\circ \). According to the Buckingham II theorem, with 3 dimensions, there are \( 8 - 3 = 5 \) independent dimensionless parameters that could determine the cylinder’s behavior. One possible set of parameters is

\[
C_D = \phi(Re, S, E, \theta) \tag{2.1}
\]

where \( Re = Ud/\nu \) is the Reynolds number based on the cylinder diameter, \( S = \rho/\rho_w \) is the density ratio of the cylinder and the fluid, and \( E = L/d \) is the cylinder aspect ratio. In contrast, in studies of drag on two-dimensional cylinders (Pruppacher et al. [54]) the drag force is only a function of \( Re \). \( C_D \) is the drag coefficient obtained by equating the drag force with the wet weight

\[
\frac{1}{2} C_D A_p U^2 = V_p \frac{\rho - \rho_w}{\rho_w} g \tag{2.2}
\]

where \( V_p = \frac{1}{4} \pi d^2 L \) is the particle volume and \( A_p \) the area of the particle projected in the direction of the fall. Nominally \( A_p = Ld \), the cylinder length times its diameter, and \( C_D \) can be written:
Using Equation 2.3, a drag coefficient model can be developed from laboratory experiments using particles of known density and dimensions and measuring their terminal velocities. Conversely a drag coefficient model can be used to determine the density of a particle whose steady fall velocity can be measured.

Clift et al. [18] and Michaelides [45] present a number of relationships of drag coefficient based on $S$, $E$ and $Re$ for irregularly shaped particles and straight cylinders in free fall. For straight cylindrical particles with aspect ratio $1 < E < 10$, a range of behaviors is reported depending on Reynolds number $Re$. For $0.01 < Re < 100$, they report that a cylinder falls flat, with its axis aligned steady in the horizontal direction. Heiss and Coull [28] and McKay et al. [43] provide $C_D$ as a function of $Re$ for free falling cylinders of $E = 0.2 - 5$ for low $Re$ (0.1 to 5). As mentioned earlier, Pruppacher et al. [54] studied infinitely long cylinders of different $Re$ up to 400 and report a drag force that is only dependent on $Re$. Jayaweera and Cottis [35] provided predictions for $C_D$ based on $E$ for $Re < 400$. In the Reynolds numbers of interest for hydrates, Isaacs and Thodos [32] and Marchildon et al. [41] have observed that cylinders falling at a $Re$ of about $200 - 60000$ and with $E > 1$ exhibit oscillations about the horizontal diameter that bisects the axis, in a see-saw motion. Particle oscillations will be discussed in section 2.5.

Isaacs and Thodos [32] experimentally determined a drag coefficient based on cylinder diameter and density in the following expression:

$$C_D = c S^{0.12} E^{-0.08}$$  \hspace{1cm} (2.4)

The drag coefficient relation was tested for values of $1 < E < 10$ and $1.05 < S < 12$. The proportionality constant was determined as $c = 0.99$, but their experiments showed a range from 0.8 to 1.2. The relation was not sensitive to Reynolds number for $200 < Re < 60000$.

Marchildon et al. [41] include tabulated data for measured drag coefficients $(1 <$
$E < 35$ and $1.05 < S < 13$) and report a dependence on $S$; however, since they focused on particle oscillations, they did not quantify a dependence of $C_D$ on $S$. A plot of their data (Figure 2-2) shows a weak dependence of $C_D \sim S^{-0.10}$.

![Figure 2-2: Drag coefficient plot versus density ratio $S = \rho/\rho_w$. Data from Marchildon et al. [41].](image)
2.4 Laboratory experiments

Since the hydrate particles can have values of $E$ larger than in previous studies (e.g. for a particle of 2.2 cm diameter and 1 m length, $E = 45$) and may also have curvature, we conducted experiments on straight cylinders with $E = 2–100$, $S = 1.1–8.5$ ($\theta = 0$) and on curved cylinders with $E = 2.5 – 50$, densities $S = 1.2 – 8.5$ and $\theta = 0 – 315^\circ$. We made the curved particles by cutting circular rings of different materials into desired arc angles $\theta$. In addition to fall velocities, we observed the orientation and oscillation of the falling particles. The main apparatus for the experiments is a glass-walled experimental tank at the R. M. Parsons Lab at MIT with dimensions 1.22 m by 1.22 m by 2.44 m tall (Figure 2-3).

![Figure 2-3: Elevation of experimental tank (from Socolofsky [62])](image-url)
Particle lengths were kept below one eighth of the tank width (15 cm) to reduce the effect of side walls on their descent (Marchildon et al. [41]).

2.4.1 Qualitative particle behavior

Our experiments with straight particles were consistent with Isaacs and Thodos [32] and Marchildon et al. [41] in that at high enough Reynolds number the particles began to oscillate in a see-saw motion (Figures 2-4 and 2-5). Marchildon et al. [41] report that the longer the particles and the lower the value of $S$, the slower the oscillation frequency and the lower the amplitude of oscillation. Short aspect ratio particles oscillated the most and, as $E$ approached 1, they began to tumble end over end. The onset of the tumbling motion differed with $S$ of the particle. However, while Isaacs and Thodos' [32] reported tumbling to occur only at about $E = 1$, tumbling was observed for denser particles with aspect ratio as high as 6.

![Image](image-url)

Figure 2-4: Time lapsed frames (superimposed at 0.62 second intervals) for a straight nylon cylinder ($S = 1.14, E = 15.6$) descending in the experimental tank.
Figure 2-5: Time lapsed frames (superimposed at 0.065 second intervals) for a straight aluminum cylinder ($S = 2.71, E = 6.1$) descending in the experimental tank.

For curved cylinders, we found that for mild curvature ($\theta < 180^\circ$) and low density ratio $S \sim 1$, particles tended to fall vertically (open side up), but their inclination decreased with increasing arc angle, such that for $\theta > 180^\circ$, they fell horizontally. Defining $\beta$ for the angle of inclination relative to horizontal, $\beta$ therefore ranges from $90^\circ$ for $\theta = 0^\circ$ and $90^\circ$ for $\theta > 180^\circ$ (see Figure 2-6). As with straight particles ($\theta = 0^\circ$), curved particles ($\theta > 0^\circ$) oscillated, but instead of a see-saw motion in a vertical plane, the oscillation occurred in the plane of curvature (Figures 2-7 and 2-8). As the density of the particle increased, the tendency for it to fall vertically increased. Whereas low density particles adopted a steady inclination angle $\beta$, heavier particles also oscillated about a new plane, causing the inclination angle $\beta$ to vary in time. The new oscillation is more pronounced with higher values of the arc angle $\theta$ and for higher $S$. Curved cylindrical particles will be discussed in Section 2.6.
Figure 2-6: Definition sketch for $\beta$ (inclination angle) and $\alpha$ (angular oscillation angle) for a curved cylindrical particle.

Figure 2-7: Time lapsed frames (superimposed at 0.195 second intervals) for a curved Teflon cylinder ($S = 2.13$, $E = 6.3$, $\theta = 90^\circ$) descending in the experimental tank. The alignment of the particle is ($\beta \approx 60^\circ$).
Figure 2-8: Time lapsed frames (superimposed at 0.65 second intervals) for a curved Teflon cylinder \((S = 2.13, E = 6.3, \theta = 180^\circ)\) descending in the experimental tank. The alignment of the particle is close to horizontal \((\beta \approx 0^\circ)\).

2.4.2 Velocity measurement

Particles were released at the center of the top of the tank. A force balance (confirmed by experiments) showed that the experimental particles would achieve a steady fall velocity at a maximum of 50 cm below the release position, so velocity measurements and observations of the particles were made well below 50 cm, at 100-180 cm below the surface. Images were taken with a Prosilica EC640 1/2 inch CMOS Firewire (IEEE1394A) camera with resolution 659x493 pixels and a maximum frame rate of 100 frames per second. This was interfaced with the MATLAB (The MathWorks, Natick, Massachusetts) and the Image Acquisition toolbox using a generic DCAM driver for MATLAB. In order to force the camera to accept user-defined exposure times on the camera, the images taken were set to 648x485 pixels. Using this method of interfacing the maximum frame rate for the camera was 77 frames per second. A series of time stamped images taken at approximately 50 frames per second was made for each released particle for the duration of its descent. Figure 2-9 illustrates the method used to measure particle velocity from the images. A piece of tape was affixed horizontally to the glass wall and the camera was adjusted so that the center
of the image coincided with the level of the black tape. This was used as the first reference height (starting line) for the particle. A second reference level (finish line) for the particles was created by shining a horizontal laser sheet (1 cm thick, covering the cross-section of the tank) about 40 cm below the level of the black tape, which was also recorded in the camera image. The laser used was a Coherent Innova 70 Argon-ion laser at 4 Watts continuous output power, attached to an optical fiber with a cylindrical lens affixed at its end that created the light sheet. We determined from the series of recorded images the two images where the particle crosses both of the reference heights as it falls. While the vertical distance traveled can be measured by the distance between the top of the laser sheet and the top of the black tape, the time elapsed was obtained by comparing the time stamps on the two images. The above method eliminates the parallax error that arose from the particle drifting away from the plane of focus as it fell.

Figure 2-9: Determination of fall velocity from images. (a) Image where particle centroid falls to the middle of the image at the level of the tape (highlighted with long black line: 140 cm below water surface); (b) Image where particle crosses laser sheet (measured as 40.8 cm below the horizontal line in (a)). The time difference between the two frames was 2.68 s, leading to a fall velocity of 15.2 cm/s.

Values of $C_D$ were computed from Equation 2.3 using the nominal projected area of the particle. Error in velocity measurement resulting from errors in elapsed time and measured vertical displacement together led to an error of 2-5% in the determination
of $C_D$. Variability of up to 10% of the value $C_D$ for the same particle arose from the random lateral drift during descent as illustrated in Figure 2-10.

Figure 2-10: Trajectories of 20 different releases of one curved particle ($S = 1.2$, $E = 21$, $\theta = 180^\circ$) in the tank, showing variability in path lengths.
<table>
<thead>
<tr>
<th>Particle</th>
<th>Material</th>
<th>d (mm)</th>
<th>S</th>
<th>E</th>
<th>θ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU</td>
<td>Polyurethane</td>
<td>19.4</td>
<td>1.13</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>NY</td>
<td>Nylon</td>
<td>1.6 - 9.6</td>
<td>1.14</td>
<td>8 - 16</td>
<td>0</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
<td>6.7</td>
<td>1.21</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>TF</td>
<td>Teflon</td>
<td>3.2 - 9.6</td>
<td>2.17</td>
<td>3 - 47</td>
<td>0</td>
</tr>
<tr>
<td>AL</td>
<td>Aluminum</td>
<td>2.4 - 12.8</td>
<td>2.71</td>
<td>2 - 63</td>
<td>0</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steel</td>
<td>1.6 - 3.0</td>
<td>8.41</td>
<td>5 - 95</td>
<td>0</td>
</tr>
<tr>
<td>BR</td>
<td>Brass</td>
<td>2.9 - 4.8</td>
<td>8.51</td>
<td>1 - 25</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>Rubber</td>
<td>7.7</td>
<td>1.19</td>
<td>4 - 26</td>
<td>40 - 270</td>
</tr>
<tr>
<td>LO</td>
<td>Rubber</td>
<td>7.2</td>
<td>1.30</td>
<td>4 - 42</td>
<td>60 - 240</td>
</tr>
<tr>
<td>TF</td>
<td>Teflon</td>
<td>3.6 - 5.4</td>
<td>2.13</td>
<td>3 - 49</td>
<td>45 - 315</td>
</tr>
<tr>
<td>ST</td>
<td>Steel</td>
<td>4.5 - 5.8</td>
<td>7.87</td>
<td>3 - 21</td>
<td>45 - 240</td>
</tr>
</tbody>
</table>

Table 2.1: Characteristics of experimental particles.

Our experimental $C_D$ plotted against aspect ratio in the range $1 < E < 100$ (Figure 2-11) resulted in $C_D$ that generally increased with $E$, contrary to the results of Isaacs and Thodos [32] for straight particles in the range $1 < E < 10$. The model adopted by Isaacs and Thodos, Equation 2.4, would therefore underestimate the drag coefficient of a particle of $E \sim 100$ by a factor of 2. The next section discusses our prediction method of secondary motion and also our development of a new drag coefficient model for straight and curved particles.

**Experimental particles**  The particles used for our experiments were cylinders of $1.4 < S < 8$ and $1 < E < 100$, and are tabulated in Table 2.1.
Figure 2-11: Drag coefficient as a function of cylindrical aspect ratio $E$. "I&T" lines refers to the predicted drag coefficient from Isaacs and Thodos [32] at various values of $S$. Characteristic error bars show variability of fall velocities for each particle.
2.5 Particle Oscillation

At Re>200, wakes shed from the cylinder at regular intervals, causing a deflection of the cylinder orientation. In turn the deflection creates a lengthwise variation in the fore pressure distribution. The pressure distribution creates a resultant torque about the axis normal to the cylinder axis which restores the particle to the horizontal (See Figure 2-12). The result is that a cylinder is observed to oscillate in a see-saw motion upon descent.

![Figure 2-12: Schematic showing the angular deflection of a cylinder α. Arrows indicate the fore pressure distribution; large arrow shows the resultant force creating a moment about the cylinder centerline.](image)

Fage and Johansen [23] performed experiments on the pressure distributions against flat rigid two-dimensional plates fixed at different inclination angles to the stream direction. Due to the periodic shedding of wakes on either side of the plate, the pressure distribution at the fore side of the plates varies with time, with a maximum total pressure of 44% of the total drag force. The aft pressure distribution remains fairly constant and independent of the inclination angle.

Marchildon et al. [41] adapts the time-varying pressure field described by Fage and Johansen [23] to cylindrical particles at different inclination angles to the horizontal direction. The distance between the center of the pressure distribution and the middle of the particle, of the moment arm x, varies with the inclination angle as follows:

\[
x = \frac{3}{4} \sin \alpha \left(4 + \pi \cos \alpha \right) L \approx \frac{3}{4 \pi} \frac{\alpha \pi}{L}
\]

where \(\alpha\) is the inclination angle, \(L\) the length of the particle, and the approximation
for the trigonometric expression accurate to within 10% in the range $0^\circ < \alpha < 90^\circ$.

Marchildon et al. [41] proposed that the particle angular displacement is described by the ODE

$$I \frac{d^2\alpha}{dt^2} + C\alpha = 0. \quad (2.6)$$

For a cylinder, the moment of inertia about the center $I$ is given by

$$I = \frac{\pi}{16} \rho_d L d^2 \left( \frac{L^2}{3} + \frac{d^2}{4} \right) \quad (2.7)$$

For $E > 1$ the second term in the brackets is negligible, thus yielding

$$I = \frac{\pi}{16} \rho_d L d^2 \frac{L^2}{3} \quad (2.8)$$

The torque as a function of the inclination angle $\alpha$ based on the experiments by Fage and Johansen [23] on flat inclined plates: it is 44% of the wet weight (which balances the drag force), acting at the distance $x(\alpha)$ from the cylinder center (Equation 2.5).

$$\text{Torque} = 0.44 \times (\rho - \rho_w) g \frac{\pi}{4} d^2 L \times \frac{3}{4} \frac{\alpha}{2\pi} L$$

$$= C\alpha \quad (2.9)$$

where

$$C = 0.44 \times (\rho - \rho_w) g \frac{\pi}{4} d^2 L \times \frac{3}{4} \frac{1}{2\pi} L \quad (2.10)$$

The predicted frequency of oscillation as a solution of Equation 2.6 is

$$T_{osc} = 2\pi \sqrt{\frac{I}{C}} \quad (2.11)$$

Substituting the values of $I$ (Equation 2.8) and torque (Equation 2.9) for a cylinder and rearranging yields the oscillation frequency $T_{osc}$:
\[ T_{osc} = 2\pi \sqrt{\frac{\pi}{0.44 \times 6}} \sqrt{\frac{4}{3} \frac{SL}{g'}} \]  
(2.12)

which simplifies to the expression

\[ T_{osc} = 7.91 \sqrt{\frac{SL}{g'}} \]  
(2.13)

where the reduced gravity of the particle is \( g' = \frac{\rho - \rho_w}{\rho_w} g \). The angular deflection of a falling cylinder that undergoes oscillations can therefore be expressed as a function of time as

\[ \alpha(t) = \alpha_{max} \sin \left( \frac{2\pi t}{T_{osc}} \right) \]  
(2.14)

Our experiments also showed that straight particles oscillated with a frequency which decreased with particle length. The oscillation of curved particles was similar as long as \( \theta < 180^\circ \) and \( S \sim 1 \). Our data for the oscillation of straight and mildly curved particles, as well as data on the oscillation of straight particles reported by Marchildon et al. [41] agree with the theory and are plotted in Figure 2-13.
Figure 2-13: Oscillation frequency plot: observed vs. predicted by Equation 2.13. Data from laboratory experiments and from Marchildon et al. [41].
2.5.1 Angular deflection

Because a particle’s actual projected area depends on its deflection, it is useful to observe the amplitude of deflection. Belmonte et al. [9] studies the oscillation of flat 2D sheets (e.g. falling pieces of paper) and we adapt a similar approach in our study of falling cylinders. The oscillation velocity $u_{osc}$ of the ends of the cylinders scales as its excursion over its period, i.e.

$$u_{osc} = \frac{L \alpha_{max}}{T_{osc}}$$  (2.15)

where $\alpha_{max}$ is the maximum angular displacement. Since the motion is induced by the falling motion, we argue that the oscillation velocity of the particle should be the same order of magnitude as the fall velocity itself, which, following our definition of drag coefficient, scales as

$$u_{fall} \sim \sqrt{g'd}.$$  (2.16)

i.e.,

$$\frac{u_{fall}}{u_{osc}} \sim 1.$$  (2.17)

Substituting Equations 2.13-2.16 into Equation 2.17, we obtain

$$\frac{\sqrt{g'd}}{\alpha_{max} \sqrt{\frac{g'L}{S}}} = \sqrt{\frac{S}{E}} \frac{1}{\alpha_{max}} \sim 1$$  (2.18)

The maximum deflection angle induced by the falling motion can be determined as

$$\alpha_{max} \sim \sqrt{\frac{S}{E}}$$  (2.19)

From our experiments we determined $\alpha_{max}$ for each particle from their digitized images and plot them as a function of $\sqrt{S/E}$ (Figure 2-14).
2.5.2 Onset of tumbling

Figure 2-14 shows that \( \alpha_{\text{max}} \) plotted against \( \sqrt{S/E} \) shows an increasing trend. When \( \sqrt{S/E} \) increases to about \( \sqrt{S/E} = 1.5 \), such that \( \alpha_{\text{max}} \) increases to about \( 70^\circ \), the particle will begin to tumble as well as oscillate. Furthermore, tumbling behavior is the dominant mode of motion at \( \sqrt{S/E} \) larger than about 2. Particles that tumbled were assigned a value of \( \alpha_{\text{max}} = 90^\circ \) in Figure 2-14. While Isaacs and Thodos [32] only reported tumbling for \( E = 1 \), we observe that the value of \( E \) that triggers tumbling is also dependent on the density, and the criterion for tumbling is \( \sqrt{S/E} > 1.5 \). For example, while aluminum cylinders \( (S = 2.7) \) of aspect ratio \( E = 3.2 \) did not tumble \( (\sqrt{S/E} = 0.92) \), a brass cylinder of \( S = 8.5, E = 3.4 \) did tumble since \( \sqrt{S/E} = 1.6 \). A similar transition from fluttering to tumbling behavior of a flat sheet was also noted by Belmonte et al. [9] as a function of the sheet’s Froude number.

![Figure 2-14: Plot of maximum particle deflection from horizontal \( \alpha_{\text{max}} \) versus \( \sqrt{S/E} \).](image)

Figure 2-14: Plot of maximum particle deflection from horizontal \( \alpha_{\text{max}} \) versus \( \sqrt{S/E} \).
Belmonte et al. [9] performed experiments on the maximum deflection angle of flat plates of mass \( M \), length \( L \) width \( w \), and observed a similar dependence of maximum deflection angle to a Froude number, defined as

\[
F_R = \left( \frac{M}{\rho_w L^2 w} \right)^{\frac{1}{2}}. \tag{2.20}
\]

Substituting \( M = \rho d L w \) for the mass, where \( d \) is the thickness of the flat plate, the Froude number can be expressed as

\[
F_R = \left( \frac{\rho d L w}{\rho_w L^2 w} \right)^{\frac{1}{2}} = \left( \frac{\rho}{\rho_w} \frac{d}{L} \right)^{\frac{1}{2}} \tag{2.21}
\]

which is the same parameter as \( \sqrt{S/E} \) but with \( L \) defined as the length along the axis of rotation rather than the direction of the moment arm.

### 2.5.3 Effect on drag coefficient

We argue that as the particle undergoes oscillations of higher amplitude, the time averaged projected area of the particle is decreased. The projected area of a particle oscillating in its plane of descent is obtained based on Equation 2.14:

\[
A_p(t) = L d \cos \alpha(t) = L d \cos \left( \alpha_{\max} \sin \left( \frac{2\pi t}{T_{osc}} \right) \right) \tag{2.22}
\]

The ratio of the drag coefficient computed with the time averaged projected area, \( C_{D,\text{actual}} \) compared with \( C_D \) computed with the nominal area \( Ld \) is

\[
\frac{C_D}{C_{D,\text{actual}}} = \frac{A_{p,\text{actual}}}{Ld} = \frac{1}{T_{osc}} \int_0^{T_{osc}} \cos \left( \alpha_{\max} \sin \frac{2\pi t}{T_{osc}} \right) dt = J_0(\alpha_{\max}) \quad 0 < \alpha_{\max} < \frac{\pi}{2} \tag{2.23}
\]

where \( J_0(x) \) is the Bessel function of the first kind, order 0.

Figure 2-15 shows that Equation 2.23 is a reasonable fit for \( C_D \) with \( \alpha_{\max} \) for particles that oscillate and not tumble. As \( \alpha_{\max} \) increases beyond a value of 60-70°
the particle will begin to transition to tumbling. Particles that exclusively tumbled are denoted as having $\alpha_{\text{max}} = 90^\circ$.

Figure 2-15: Drag coefficient plot versus $\sqrt{S/E}$.
Since the maximum deflection angle $\alpha_{\text{max}} \sim \sqrt{S/E}$ we may also plot $C_D$ against $\sqrt{S/E}$. As shown in Figure 2-16 $C_D \sim J_0\left(\sqrt{S/E}\right)$ until tumbling occurs at $\sqrt{S/E} \sim 1.5$.

The series expansion of $J_0(x)$ is

$$J_0(x) = \sum_{k=0}^{\infty} \frac{(-1)^k x^{2k}}{2^k (k!)^2} = 1 - \frac{x^2}{4} + \frac{x^4}{32} - \ldots$$

which compares with the expansion of the expression

$$\frac{1 + \cos(x)}{2} = 1 - \frac{x^2}{4} + \frac{x^4}{48} - \ldots$$

Thus, $J_0(\alpha_{\text{max}}) \approx \frac{1 + \cos(\alpha_{\text{max}})}{2}$ to within 11% for $0 < \alpha_{\text{max}} < \frac{\pi}{2}$. Physically the cosine expression approximates the particle as spending half of the time at the maximum deflection $\alpha_{\text{max}}$ and the other half of the time at zero deflection. Figure 2-16 shows that both expressions predict the observed drag coefficients well in the oscillation regime.

Beyond the value of $\sqrt{S/E} = 1.5$, the drag coefficient does not follow Equation 2.23 since the time average projected area does not go to zero. Instead, in the tumbling mode, the projected area varies with time as

$$A_p(t) = Ld \left| \cos \frac{2\pi t}{T_{\text{tumble}}} \right|$$

where $T_{\text{tumble}}$ is the rotation period. This is a lower bound area since the projected area of the ends is neglected. The ratio of the drag coefficient computed with the time averaged projected area $C_{D,\text{actual}}$ compared with the drag coefficient computed with the nominal area $Ld$ for the tumbling particle, $C_D$, is thus

$$\frac{C_D}{C_{D,\text{actual}}} = \frac{A_{p,\text{actual}}}{Ld} = \frac{1}{T_{\text{tumble}}} \int_0^{T_{\text{tumble}}} \left| \cos \frac{2\pi t}{T_{\text{tumble}}} \right| \, dt$$

$$= \frac{2}{\pi}$$

(2.27)
The tumbling limit of $C_D$ from Equation 2.27 is also plotted in Figure 2-16 and shows agreement with the experimental results of Isaacs and Thodos [32] and with our experiments. From the points taken from Isaacs and Thodos $E = 2$, there could well have been particles in their data that tumbled ($\sqrt{S/E} > 1.5$), and for this regime the drag coefficient could appear to be increasing with $\sqrt{S/E}$, consistent with the empirical relationship proposed by Equation 2.4.

Figure 2-16: Drag coefficient plot versus $\sqrt{S/E}$. Open triangles denote data from Isaacs and Thodos [32], with $E = 2$. Regimes of particles exhibiting tumbling and oscillation/tumbling are labeled. The tumbling regime is indicated by $\sqrt{S/E} > 1.5$. 
2.6 Curved particles

This section presents our experiments on curved particles to mimic the often curved hydrate particles extruded in the field experiments. We are interested in describing their behavior and the effect of their secondary motion on their drag coefficient. As mentioned in Section 2.4.1, we found that cylinders of $S \sim 1$ adopted steady inclination angles, starting with mildly curved cylinders that fall vertically (open side up). As the arc angle of the particle $\theta$ increases, their inclination decreases with increasing arc angle, such that above an arc angle $\theta$ of 180° degrees, they fall horizontally. This behavior can be reasonably fit by the relationship, for $S \sim 1$:

$$\beta = \frac{\pi}{4} (1 + \cos \theta) \quad 0^\circ < \theta < 180^\circ$$
$$= 0 \quad \theta \geq 180^\circ$$

(2.28)

where $\beta$ is the inclination above horizontal and $\theta$ is the arc angle, both measured in degrees. Figure 2-17 shows the fit of Equation 2.28 with experimental data.

Curved particles are observed to oscillate within the plane of curvature in a see-saw motion, like straight particles ($\theta = 0$) (as shown by $\alpha$ in Figure 2-6), and the period of these oscillations can be predicted by Equation 2.13. However, for curved particles, the oscillation of the particle within its plane of curvature does not necessarily affect the time averaged projected area, and for $\beta = 0$, the drag coefficient is unaffected by $\alpha(t)$. Instead, the time-averaged projected area is a function of the inclination angle $\beta$:

$$A_p = 2Rd \int_0^{\theta} \cos \left( \frac{2\theta' \beta}{\pi} \right) d\theta'$$

$$= \frac{\pi Rd}{\beta} \sin \frac{2\theta \beta}{\pi}$$

(2.29)

(2.30)
Figure 2-17: Inclination angle $\beta$ versus arc angle $\theta$ for Rubber particles (M/LO in Table 2.1), $S = 1.2$. 
The ratio of the drag coefficient inclined at $\beta$, $C_{D,\text{actual}}$, to $C_D$ as computed with nominal projected area $Ld$ also decreases with $\beta$.

$$\frac{C_D}{C_{D,\text{actual}}} = \frac{A_{p,\text{actual}}}{Ld} = \frac{\pi}{\beta \theta} \sin \frac{2\theta \beta}{\pi}$$ (2.31)

When applied to particles of $S \sim 1$, this means that replacing the actual projected area of an inclined falling curved particle ($\beta > 0$) with the nominal projected area (particle length times diameter) involves an approximation of less than 3% in the inferred drag coefficient, which is within the range of variability in measured drag coefficient (Figure 2-18.)

![Figure 2-18: Ratio of actual to nominal projected area of curved cylinders as a function of arc angle $\theta$, using Equation 2.28 to determine particle inclination.](image)

Curved cylinders of higher densities ($S \rightarrow 10$) showed increasing mean inclination $\beta$ and oscillations of $\beta$ during their descent, with mean values that tended towards $\beta \rightarrow 90^\circ$. The measured values of the mean inclinations are plotted in Figure 2-19. A change from oscillations to tumbling was also observed for a curved particle of $\sqrt{S/E} > 1.5$, suggesting a similar mechanism of secondary motion as for straight cylinders.

A lower limit of $C_D$ can be taken with a circular ring of $\theta = 360$, aligned at the vertical $\beta = 90^\circ$. Its radius of curvature is $R$, and thickness is $d$, consistent with our
Figure 2-19: Inclination angle $\beta$ versus arc angle $\theta$. Error bars show the range of oscillations of $\beta$ observed for each particle. Densities of particles: Rubber (M/LO in Table 2.1): $S = 1.2$), TF (Teflon: $S = 2.2$), ST (Steel: $S = 8.5$).

straight and curved particles. If its circumference is taken as $L = 2\pi R$, The limiting value of the the ratio of the actual and projected area for this particle is

$$\frac{C_D}{C_{D,\text{actual}}} = \frac{A_{p,\text{actual}}}{Ld} = \frac{2Rd}{2\pi Rd} = \frac{1}{\pi}$$ (2.32)

The effect of the curvature on of the drag coefficient as compared to straight particles is plotted in Figure 2-20, which shows a marked decrease in $C_D$ for particles of higher densities whose inclination angle $\beta$ are closer to vertical. The smaller observed value of $C_D$ was slightly above the lower limit of $C_D = 1/\pi$. 

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Figure 2-20: Drag coefficient $C_D$ plotted against $\sqrt{S/E}$ for curved cylinders. The lower bound is $C_D = 1/\pi$, while the upper bound is provided by the straight cylinder approximations. In the tumbling regime ($\sqrt{S/E} > 1.5$), $C_D \to 2/\pi$. Error bars show typical variability in $C_D$. 
2.6.1 Conclusions

Based on experimental observations on straight and curved cylinders at $Re > 200$ the parameter $\sqrt{S/E}$ is able to predict the prevalence of oscillation or tumbling as a secondary motion. We propose a drag coefficient model for cylinders in free fall: For straight cylinders,

$$C_D = J_0 \left( \sqrt{\frac{S}{E}} \right) \approx \frac{1}{2} \left( 1 + \cos \sqrt{\frac{S}{E}} \right) \quad \sqrt{S/E} < 1.5$$

$$\approx \frac{2}{\pi} \quad \sqrt{S/E} > 1.5 \quad (2.33)$$

For curved cylinders of densities close to 1, applying the formulation as if they were straight cylinders (Equation 2.33) will suffice. Curved particles of higher density ratio ($S \rightarrow 10$) will tend to free fall in a vertical inclination, and based on the actual projected area, will have a minimum value of $C_D \sim 1/\pi$. Curved particles of $\sqrt{S/E} > 1.5$ will tumble, and have a value of $C_D$ close to $2/\pi$.

Extruded hydrate particles observed in the field had density ratios $S$ of 1 to 1.15, and aspect ratios $E > 10$. For the field particles $\sqrt{S/E}$ would have a maximum value of about 0.3, and thus lie in the regime predicted to have weak or no oscillations. Equation 2.33 would therefore apply to the hydrate particles regardless of curvature.
Chapter 3

Hydrate particles for $\text{CO}_2$
sequestration

This chapter serves as an update to the information presented in Tsouris et al. [71], Adams et al. [3] and Chow et al. [15])

3.1 Abstract

This paper presents strategies for employing negatively buoyant $\text{CO}_2$ hydrate composite particles for ocean carbon sequestration. Our study is based on recent field observations showing that a continuous-jet hydrate reactor located at an ocean depth of $\sim 1500$ m produced curved negatively buoyant cylindrical particles with diameters $\sim 2.5$ cm and lengths up to $\sim 1$ m. Using a drag coefficient model developed for such particles and the initial settling velocity observed in the field, we have concluded that the reactor efficiency (percentage of liquid $\text{CO}_2$ converted to hydrate) in the field was $\sim 15$–$20\%$. Using the dissolution rates observed in the field, we conclude that such particles would ultimately sink to a depth below discharge of $\sim 115$ m. We have also predicted the sinking depths of particles potentially produced from scaled-up reactors and have shown that, for example, a $10$ cm diameter particle with a hydrate conversion of $50\%$ could reach the ocean bottom before completely dissolving.

In an ambient ocean with a sufficiently strong crossflow current that precludes
plume formation, or at least prevents a plume from being sustained over a long trajectory, particles of different sizes and hydrate conversions (hence different settling velocities) will follow different settling trajectories as they dissolve. The differential settling results in vertical and downcurrent spreading. This may be used to advantage by releasing hydrate particles continuously from a moving ship which would provide dilution in the third dimension, resulting in excellent dilution of the discharged CO₂.

3.2 Introduction

Our study was motivated by the field injections of solid CO₂ hydrate particles into the ocean at depths of 1000 to 1500 m in order to assess their effectiveness for sequestering anthropogenic CO₂ from the atmosphere. It is feared that rising concentrations of greenhouse gases in the atmosphere will cause adverse changes in the climate, and that two-thirds of the change will be attributed to CO₂ (Herzog et al. [29]). There is ongoing study of carbon dioxide hydrates as a possible vehicle for deeper ocean carbon sequestration, because they are denser than seawater, and will sink unaided while dissolving to promote dispersion in the ocean. The hydrate particles were created using a CO₂-seawater coflowing injection apparatus, developed to create cylindrical composite particles, comprised of CO₂ hydrate, liquid CO₂ and seawater (Lee et al. [40]). Field tests were conducted on three occasions with differing co-flow injectors developed by ORNL in collaboration with the Monterey Bay Aquarium Research Institute (MBARI) (Tsouris et al. [69], Riestenberg et al. [56], Tsouris et al. [70] and Tsouris et al. [71]). The latest field observations show that the particles produced are long (up to ~1 m), curved cylinders that descend with Reynolds number of about 1000, and shrink at a constant rate (Refer to Figure 1-11 from Chapter 1).

As a design guide for the scale up of the injector, it is important to quantify the particle density and therefore the reaction efficiency of the extruded particles. In addition, the ability to predict particle descent depths and dilution of the CO₂ is vital to evaluate injection strategies for hydrates.
### Table 3.1: Masses of components of CO₂ composite as expressed by reaction efficiency \((X)\) and mass ratio of water:carbon dioxide \((W)\). The masses have been normalized by the mass of CO₂. Note \(MW_h = MW_{CO₂} + nMW_w\); \(MW CO₂ = 44\); \(MW_w = 18\); \(n = 5.75\).

<table>
<thead>
<tr>
<th>Component</th>
<th>Initial mass</th>
<th>Reacted mass</th>
<th>Density</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1</td>
<td>(M_c = 1 - X)</td>
<td>(\rho_c)</td>
<td>(V_c = \frac{M_c}{\rho_c})</td>
</tr>
<tr>
<td>Water</td>
<td>(W)</td>
<td>(M_w = W - \frac{nMW_w}{MW CO₂}X)</td>
<td>(\rho_w)</td>
<td>(V_w = \frac{M_w}{\rho_w})</td>
</tr>
<tr>
<td>Hydrate</td>
<td>0</td>
<td>(M_h = \frac{MW_h}{MW CO₂}X)</td>
<td>(\rho_h)</td>
<td>(V_h = \frac{M_h}{\rho_h})</td>
</tr>
</tbody>
</table>

3.3 Hydrate reaction efficiency

The general stoichiometry of carbon hydroxide hydrate formation is given by Equation 3.1:

\[
CO₂ + nH₂O \rightleftharpoons CO₂ \cdot nH₂O
\]

with \(n\) the average hydration number of 5.75 (Rehder et al. [55]). The above reaction does not go to completion, resulting in CO₂ composite particles consisting of hydrates, combined with unreacted CO₂ and ambient seawater. A measure of the performance of the injectors from the field, and a useful guide for future injector design, is the reaction efficiency of the reactor \(X\), which is defined here as the mass fraction of liquid CO₂ converted to hydrate. \(X = 0\) therefore represents pure liquid CO₂, density about 970 kg/m³ while \(X = 1\) represents pure hydrate, density about 1140 kg/m³.

The quantity of ambient water that is to be used to react with the liquid CO₂ in the injector can be expressed as a mass ratio of water and carbon dioxide, \(W = M_w/M CO₂\). It is assumed that all unreacted components stays attached in the composite to conserve mass. It has also been convenient to express the initial water to CO₂ ratio in terms of the the CO₂ to water volume ratio \(\lambda\), which is related to \(W\) by the following relation:

\[
\lambda = \frac{V_{CO₂}}{V_w} = \frac{\rho_w M_{CO₂}}{\rho_{CO₂} M_w} = \frac{\rho_w}{\rho_{CO₂}} \frac{1}{W}
\]

Table 3.1 shows the masses of each of the components as a function of \(X\) and \(W\), based on the the stoichiometry of Equation 3.1.
\[ \rho_p = \frac{M_{CO_2} + M_w + M_h}{V_t} \]  

(3.3)

where \( V_t \) is the total volume of the three components in the composite particle,

\[ V_t = \frac{M_{CO_2}}{\rho_{CO_2}} + \frac{M_w}{\rho_w} + \frac{M_h}{\rho_h} \]  

(3.4)

Using Table 3.1 and Equations 3.3 and 3.4, the density of the composite particle can be solved as a function of \( X \) and \( W \). Figure 4-4 plots the resulting densities of composite particles as a function of \( X \) and \( W \). Note that a range of value pairs of \((X, W)\) can achieve a certain hydrate composite density. Conversely, if the value of \( \rho \), and \( W \) are known, Figure 4-4 can be used to determine the reaction conversion of the particle.

![Graph showing density as a function of hydrate conversion (X) and water to CO2 mass ratio (W). The densities of the phases at 1500 m depth were used. The surface \( \rho_w = 1035 \) is plotted to indicate the composite compositions which result in a negatively buoyant particle (above surface) and positively buoyant particles (below surface).](image-url)
3.3.1 Particle shrinkage

Hydrate composites formed from the injector were followed by the ROV Tiburon and by sonar measurements for up to an hour. The particles were observed to shrink along their descent as they dissolve into the ocean. (Refer to Figure 1-12 and Table 1.2.) The particle shrinkage rate was determined by measuring the particle aspect ratio from digitized images at different times. On average, the particle shrinkage rate was determined as about $6 \pm 2 \mu m/s$.

3.3.2 Particle water content

Figure 4-4 shows that the density of the hydrate particle depends on the water content, $W$. An initial approximation for $W$ can be obtained by assuming mass conservation and taking the ratio of the flow rates of water and liquid CO$_2$ fed into the injection reactor. However, observations of the injector in the high pressure vessel at ORNL indicated that seawater was ejected from the injector assembly without being incorporated into the composite particle. This suggests that the actual value of $W$ is less than the ratio for the composite particle is not identical to the ratio of the input mass flow rates of the reactants. We conducted experiments at ORNL in July 2005 in collaboration with Costas Tsouris, Scott McCallum and Eric Adams, where we inverted the hydrate injector assembly within the Seafloor process simulator (SPS). The hydrate composite was extruded upwards into a high pressure nitrogen atmosphere instead of downwards into the tank. Figure 3-2 shows the schematic of the apparatus used for measurement of $W$. The setup allowed any liquid not incorporated into the composite to flow along the outside of the injection reactor into a collection funnel leading outside pressure vessel. The hydrate particle was allowed to slide off the top sloping exterior (Figure 3-3.)

In one experiment conducted using the above method, about 2/3rds of the water was incorporated into the hydrate, thus reducing $W$ by one third. Figure 4-4 shows that for a sinking particle of the same density, a lower value of $W$ results in lower conversion $X$. Based on this preliminary measurement, a hydrate particle previously
Figure 3-2: Schematic of hydrate composite reactor arranged to collect and measure volumes of unreacted water.

Figure 3-3: Right: Image of hydrate produced in the high pressure vessel (SPS). The water not incorporated into the hydrate is seen at the tip of the injector.
assumed to have $x_h$ 55%, due to the absence of some of the water, would have a conversion closer to 43%. Further experiments (October 2005) based on 16 separate measurements of unreacted water leakage from the hydrate injector by Costas Tsouris and Scott McCallum at ORNL have shown the average water leakage of 32%. Using this value of $W$, the computed conversion is 41%. In general, the findings suggest that for a particle of a known density the actual hydrate efficiency could be about 10% lower than the hydrate efficiency computed using the ratio of the reactants.

3.4 Prediction of particle descent

Since the composite particle densities cannot be directly measured, but instead deduced from their fall velocity, we have developed a drag coefficient model for the Reynolds number of above ~ 200 based on laboratory experiments (Chapter 2), and showed that the hydrate particles of low density and high aspect ratio have a drag coefficient of $C_D \approx 1$. Using the drag coefficient model discussed in Section 2.5.3, and assuming a shrinkage rate for the particles consistent with the field observations, it is possible to predict the descent depths of a hydrate composite particle as a function of its reaction conversion $X$, water content $W$ and particle size.

A typical ocean density profile from Keahole point, Hawaii (Miller et al. [47]) was used to describe the ambient density as a function of depth. The total particle descent depth $h_d$ was obtained numerically by computing the velocity of the particle using the drag coefficient model, advancing the particle downwards and shrinking the particle over the time step, and repeating until the particle shrinks to zero diameter. The result of the simulations for hydrate particles in a range of reaction efficiencies and cylindrical particle diameters are plotted in Figure 3-4. A typical cylinder length of 30 cm and a shrinkage rate of 6 $\mu$m/s was used for the simulation.
Figure 3-4: Predicted descent depths (below a release point at 1500 m depth) as a function of particle diameter and conversion efficiency $X$, for 30 cm long cylindrical CO$_2$ hydrate particles released at 1500 m depth. Ocean bottom is at 3000 m below release point, at 4500 m. Diameter shrinkage rate is constant at 6 $\mu$m/s.
As a particle shrinks its Reynolds number is reduced so a separate drag coefficient model was employed (Wadell [73]) if the particle Reynolds number was below $Re < 200$.

$$Re = \frac{Ud}{\nu} = \left( \frac{\pi}{2 C_D} g'(X, W)d \right)^{\frac{1}{3}} \frac{d}{\nu} < 200 \quad (3.5)$$

This may be written

$$(g'(X, W))^{\frac{1}{3}} d^\frac{3}{2} < 200\nu \left( \frac{2}{\pi} C_D \right)^{\frac{1}{2}} \quad (3.6)$$

However, it is noted that the fraction of the trajectories at which a particle has $Re > 200$ represents 80-90% of the trajectories of the majority of hydrate particles as shown in Figure 3-5. This shows that the drag coefficient model of Chapter 2 is sufficient for estimation of the trajectories of the hydrate composite particles.

![Figure 3-5: Percentage of total distance traveled at $Re > 200$ as a function of particle diameter and conversion efficiency $X$, for 30 cm long cylindrical CO$_2$ hydrate particles released at 1500 m depth. Ocean bottom is at 3000 m below release point, at 4500 m.](image)
Table 3.2: Summary of field experiments 2002-6. Particle dimensions are representative of the particles generated in the field for each set of field observations. From Tsouris et al. [69], [71].

Table 3.2

<table>
<thead>
<tr>
<th>MBARI particle</th>
<th>2002</th>
<th>2004</th>
<th>2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ mass loading (g/s)</td>
<td>0.2-0.8</td>
<td>0.4-0.5</td>
<td>30</td>
</tr>
<tr>
<td>Reference</td>
<td>[69]</td>
<td>[56]</td>
<td>[71], [70]</td>
</tr>
<tr>
<td>Release depth (m)</td>
<td>1300</td>
<td>1000-1200</td>
<td>1500</td>
</tr>
<tr>
<td>Init. diameter ( d ) (cm)</td>
<td>0.5-0.6</td>
<td>0.8</td>
<td>2.2</td>
</tr>
<tr>
<td>Init. length ( L ) (cm)</td>
<td>2-4</td>
<td>6-7</td>
<td>30</td>
</tr>
<tr>
<td>Init. sinking rate (cm/s)</td>
<td>2</td>
<td>5-6</td>
<td>4</td>
</tr>
<tr>
<td>Shrink rate (mm/s)</td>
<td>4-7</td>
<td>4-7</td>
<td>6</td>
</tr>
<tr>
<td>Reynolds number ( Re = \frac{ud}{v} )</td>
<td>80</td>
<td>310</td>
<td>630</td>
</tr>
<tr>
<td>Using cylindrical drag coefficient model (Refer to Section 2.33):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated density ( \rho ) (g/cm³)</td>
<td>1.03</td>
<td>1.05-1.06</td>
<td>1.04</td>
</tr>
<tr>
<td>Calculated ( X ) (%)</td>
<td>15-20</td>
<td>45-60</td>
<td>16</td>
</tr>
<tr>
<td>Predicted descent depth ( h_d ) (m)</td>
<td>10</td>
<td>40-70</td>
<td>115</td>
</tr>
</tbody>
</table>

Table 3.2 shows the result of applying the numerical model to determine the reaction efficiencies of the past field-scale injectors, and to predict the descent depths of the sample particles. Applied to the most recent 2006 field study particles, the reaction efficiency was about 20%, significantly lower than the 45-60% deduced from the 2002 and 2004 field studies. We attribute the lower efficiency to reduced mixing over the larger diameter reaction bore. Nonetheless, because the release depth (~1500 m) was greater than that used previously (1000 to 1200 m), the constituent unreacted water and CO₂ phases are denser, and the particles still sank as a result.

3.5 Scaleup Guidelines

This section describes an approach for the practical scale-up of hydrate particle releases from the current 30 g/s to the 100 kg/s required for sequestration of the emissions of a typical power plant. Figures 3-6 and 3-7 show the possible methods of scale-up. Increasing the diameter of the individual particle can be achieved by increasing the reactor bore (Panel (b)). In the light of the most recent scale-up, larger reactors may suffer from reduced mixing, so the design could incorporate multiple
capillaries injecting into a wide reactor (Panel (c)). Finally, an array of many identical hydrate injectors can be harnessed to eject a large number of particles from one release port, as shown in Figure 3-7.

Figure 3-6: Schematic of injector scale-up guidelines for larger diameter, showing (a) the original coflow injector, (b) an increased diameter of both the capillary and the outer bore and (c) multiple capillaries injecting into a wide outer bore.

Figure 3-7: Schematic of a particle release plume with multiple coflow injectors.

If we extrapolate our model to particles extruded through reactors with diameters of 5 and 10 cm, assuming similar dissolution rates and reaction conversion efficiencies as those found for the 2006 particles, such particles are predicted to sink to depths of 300 and 640 m, respectively. Furthermore, if improved reactor design can boost the reaction efficiency back up to 50%, the sinking depth increases to 2800 m. Table 3.3 presents the anticipated behavior of the scaled-up particles. It seems possible that
Table 3.3: Numerically predicted enhancement of individual particle descent depths with scale-up of a particle produced in the 2006 field experiment (Particle 'T0970-4' in Tsouris et al. [71].) Particles '2006+' and '2006++' refer to particles with increased diameter, but otherwise the same characteristics as particle 'T0970-4'. Particle '2006+++ has an increased diameter and an increased reaction conversion from 16% to 50%. Boldface values indicate the changed values to the original particle.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Release depth (m)</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Init. diameter d (cm)</td>
<td>2.2</td>
<td>5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Init. length L (cm)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Init. sinking rate (cm/s)</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>27</td>
</tr>
<tr>
<td>Shrink rate (μm/s)</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Reynolds number $Re = \frac{Ud}{v}$</td>
<td>630</td>
<td>2100</td>
<td>5700</td>
<td>19300</td>
</tr>
<tr>
<td>Calculated density $\rho$ (g/cm$^3$)</td>
<td>1.04</td>
<td>1.04</td>
<td>1.04</td>
<td>1.08</td>
</tr>
<tr>
<td>Calculated $X$ (%)</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>50</td>
</tr>
<tr>
<td>Predicted descent depth $h_d$ (m)</td>
<td>115</td>
<td>345</td>
<td>745</td>
<td>3000</td>
</tr>
</tbody>
</table>

Individual particles could be produced that would be large and dense enough to sink all the way to the seafloor. While depositing the particles onto the seafloor may be desirable, the next sections explore how particles can be made to distribute evenly over the water column by virtue of the variation in hydrate reactor efficiencies $X$.

3.6 Particle releases in crossflow

One way to exploit sinking composite hydrate particles is to release them in the presence of a crossflow current. These particles would sink discretely as if they were released from a fixed point, but the dissolving CO$_2$ would be distributed downcurrent, resulting in smaller added CO$_2$ concentrations.

3.6.1 Vertical particle spread

We have shown in Figure 3-4 that a range of particle sinking depths is possible as a function of hydrate particle diameter and conversion efficiency. Field observations (Tsouris et al. [71]) have shown that particles with range of $X$ are ejected from a single injector due to the inhomogeneity of mixing within the co-flow reactor. As the particles have a range of efficiencies and initial diameters, their differing vertical
descent will fractionate them in the presence of crossflow, resulting in vertical spread of CO₂ (Figure 3-8).

![Diagram of particle trajectories](image)

Figure 3-8: Trajectories of hydrate particles of differing reaction conversion in a crossflow current

### 3.6.2 Particle trajectories

To determine particle trajectories, we can obtain expression (in negligible ambient stratification) for the particle's vertical position $h$ as a function of time after injection $t$ by integrating the local velocity $U(t)$:

$$h(t) = \int_0^t U(t') dt'$$

$$= \int_0^t \left( \frac{\pi}{2 C_D} g'(X, W) d(t') \right)^{\frac{1}{2}} dt'$$

(3.7)

where $g'(X, W)$ is the reduced gravity which depends on the particle density, assumed to stay constant throughout dissolution. Since the particles are observed to shrink at a constant rate of about $\frac{dd}{dt} = 6 \text{ μm/s}$, the diameter of the particle varies with time as
\[ d(t) = d_0 \left( 1 - \frac{t \, dd}{d_0 \, dt} \right) \]  

(3.8)

where \( d_0 \) denotes the initial particle diameter. Substituting into Equation 3.7, and taking a drag coefficient of \( C_D \approx 1 \) (from Chapter 2) for \( Re > 200 \):

\[
\begin{align*}
  h(t) &= \int_0^t \left( \frac{\pi}{2 \, C_D} \frac{g'd_0}{d_0} \right)^{\frac{1}{2}} \left( 1 - \frac{t' \, dd}{d_0 \, dt} \right)^{\frac{1}{2}} \, dt' \\
  &= \frac{2}{3} U_0 \frac{d_0}{dt} \left[ 1 - \left( 1 - \frac{t \, dd}{d_0 \, dt} \right)^{\frac{3}{2}} \right]
\end{align*}
\]

(3.9)

where \( U_0(X, W) \) is the initial fall velocity. The total descent depth \( h_d \) can be determined by setting \( t = \frac{d_0}{dd} \) to give

\[ h_d = \frac{2}{3} U_0 \frac{d_0}{dt} \]  

(3.10)

If the particle is advected along by a constant ambient current of \( u_a \), i.e. \( y = u_a t \), then the trajectory \( h(y) \) is given as

\[
\begin{align*}
  h(y) &= \frac{2}{3} u_a \frac{d_0}{dd} \left[ 1 - \left( 1 - \frac{y \, dd}{d_0 u_a \, dt} \right)^{\frac{3}{2}} \right]
\end{align*}
\]

(3.11)

This can also be expressed more illustratively in non dimensional terms as

\[
\begin{align*}
  \frac{h(y)}{h_d} &= 1 - \left( 1 - \frac{y}{l_d} \right)^{\frac{3}{2}} \quad y \leq l_d \\
  &= 1 \quad y > l_d
\end{align*}
\]

(3.12)

where \( l_d \) is the downcurrent distance of particle dissolution,

\[ l_d = \frac{d_0 u_a}{dd} \]  

(3.13)

Equation 3.12 indicates that the trajectory is dependent on the initial fall velocity.
$u_{e,0}$ which is in turn dependent on initial particle diameter $d$ and reactor parameters $X$ and $W$. The trajectories of particles of a range of diameters and reaction efficiencies are shown in Figure 3-9, assuming a water to CO$_2$ ratio that is sufficient for stoichiometric hydrate formation $W = 2.45$.

![Particle trajectories for different diameters](image)

**Figure 3-9:** Trajectories of particles of different diameters in a typical crossflow current of 0.05 m/s. Release depth = 1500 m. (a) initial particle diameter $d_0=2.5$ cm; (b) $d_0=5$ cm (c) $d_0=10$ cm (d) $d_0=15$ cm. Particles of each diameter have length 30 cm; range of reaction efficiencies $X=10$-$55\%$ and stoichiometric water $W = 2.45$. Ocean bottom is at 4500 m depth.

The different panels in Figure 3-9 show that increasing the diameter of the particle prolongs their lifetime since the shrinkage rate is assumed constant for all particles (similar to observed behavior). For example, particles of 5 cm diameter (top right panel) shows that the particles, and thus the CO$_2$, would be dispersed over a water column range of 1200 to 2800 m. Larger diameter particles are predicted to have longer trajectories in the $y$ (downcurrent) direction, and also a larger final sinking
3.6.3 Fate of dissolved CO₂

We are interested in calculating the resulting dissolved inorganic carbon (DIC) concentration that is added from the proposed injection scenarios. Once dissolved, aqueous CO₂ will exist in various charged forms in water according to these main reactions, known as the carbonate system (Morel and Hering [48]):

\[
\begin{align*}
CO_2^{aq} + H_2O & \rightleftharpoons H_2CO_3^{aq} \quad (3.14) \\
H_2CO_3^{aq} & \rightleftharpoons H^+ + HCO_3^- \quad (3.15) \\
HCO_3^- & \rightleftharpoons H^+ + CO_3^{2-} \quad (3.16)
\end{align*}
\]

The total dissolved inorganic carbon (DIC) is defined as ([48]):

\[
DIC = [H_2CO_3^{aq}] + [HCO_3^-] + [CO_3^{2-}] \quad (3.17)
\]

The result of this is that increasing dissolved CO₂ will shift the equilibria above to the right, and lower the local pH of the ambient seawater, which is expected to affect passive marine organisms. (Alendal and Drange [5]).

Alkalinity and pH

To quantify the pH change of the ambient due to dissolved inorganic carbon, the carbon alkalinity \( C - Alk \) is defined (Morel and Hering [48]):

\[
C - Alk = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad (3.18)
\]

The alkalinity is a measure of the buffering capacity of the water system to the addition of weak acids, such as carbonic acid from dissolved CO₂. Note \( C - Alk \) remains a constant with added CO₂. With a known local DIC concentration and the alkalinity of the water, the resulting equilibrium pH value of the water can be
determined. For the carbonate system at equilibrium shown in Equations 3.14 (which constitutes most of the alkalinity in seawater):

\[ K_{a1}(T, S) = \frac{[H^+][HCO_3^-]}{[H_2CO_3(aq)]} \]  \hspace{1cm} (3.19)

\[ K_{a2}(T, S) = \frac{[H^+] [CO_3^{2-}]}{[HCO_3^-]} \]  \hspace{1cm} (3.20)

With Equations 3.17, 3.18, 3.19 and 3.20, and acid equilibrium constants available empirically for seawater (Zeebe et al. [79]), the concentrations of the four species, including the pH, can be solved.

### 3.7 Environmental Impacts

Metz et al. [44] cite several effects of elevated CO₂ levels on marine organisms: at acute levels CO₂ has a narcotic effect on animals and causes respiratory distress and death. Tamburri et al. [67] have observed the narcotic effects of increased CO₂ levels on mobile deep sea animals in the field; they also observe that while many tend to avoid CO₂ plumes, some may risk the narcotic effects to obtain food. Passive marine animals may experience depressed ion exchange capability and metabolism when exposed to lower, chronic levels CO₂. Examples of metabolic mechanisms that may be affect by lower pH levels are shown in Figure 1-3. Auerbach et al. [8], Caulfield et al. [12] and Israelsson et al. [34] have modeled the lowered pH on passive marine organisms such as zooplankton that spend varying times in and out of a CO₂ plume, and found that minimizing the local dissolved CO₂ and pH drops will reduce the mortality rate.

As a guide, Metz et al. [44] uses a pH drop of 0.1 units as the threshold pH drop for insignificant marine life impact; it is also within the observed natural variability in the ocean.
3.7.1 Dissolved mass flux

We are interested in calculating the resulting dissolved inorganic carbon (DIC) concentration that is added from the proposed injection scenarios. From the DIC concentration we can also derive the induced pH drop, another measure of the environmental impacts of the injection. To this end, we assume a more simplified geometry of the downcurrent area covered by the particle trajectories by taking only the particles of a given diameter that sink and do not reach seafloor (highlighted by Figure 3-10.) Using a slightly smaller area will also result in a slightly conservative added DIC concentrations.

![Figure 3-10: Wedges (shaded regions) based on the particle trajectories taken from Figure 3-9 used for determining dissolved CO2 resulting from the particle releases. The wedges are described by: (a) $d=2.5$ cm, $X=0.12-0.55$ (b) $d=5$ cm, $X=0.12-0.55$ (c) $d=10$ cm, $X=0.12-0.50$ and (d) $d=15$ cm, $X=0.12-0.30$.](image)

Different particle trajectories and sinking depths are also achievable by a particle release of the same conversion $X$ and different initial diameters $d$. However, our
analyses here use ranges in $X$ rather than $d$ to achieve differential settling trajectories. If the ranges of reaction are approximated as equally spread between $X = 12\%$ (a neutrally buoyant trajectory) and a maximum either of $50\%$ (the current maximum achievable) or $X$ that leads to particles that just reach the seafloor, then the DIC gain for a given downcurrent distance $(y)$ is spread vertically (in the $z$ direction) over $h_{dmax}(y)$. This would be computed using Equation 3.12 for the deepest sinking particle (e.g. $X = 50\%$.) The plume therefore reaches a maximum depth of $h_{dmax}$, and vertical spreading of the plume beyond the dissolution of the particles is neglected. The use of a slightly smaller area than the predicted particle trajectories results in slightly conservative added DIC concentrations.

Figure 3-11: Depiction of lateral (crosscurrent, $x$) spreading of dissolved CO$_2$ by turbulent diffusion.

The particles are expected to diffuse in the lateral (cross-current, $x$) direction by turbulent diffusion. We characterize the lateral diffusion with the plume's standard deviation $\sigma_x(y)$ which grows with downcurrent distance (See Figure 3-11). The added dissolved carbon concentration can therefore be expressed as

$$c(x, y) = \frac{\dot{m} f_d(y)}{u_a} \frac{1}{\sqrt{2\pi\sigma_x(y) h_{max}(y)}} e^{-\frac{x^2}{2\sigma_x(y)^2}}$$

(3.21)

where $h_{max}(y)$ is the downcurrent depth of sinkage determined by Equation 3.12 for the heaviest particle, $\dot{m}$ is the CO$_2$ mass loading, and $f_d$ is the fraction of the hydrates that have dissolved, given by
where

\[ d(y) = d_0 - \frac{dd}{dt} \left( \frac{y}{u_a} \right) \]  

(3.23)

and \( d_0 \) is the initial particle diameter.

Okubo [51] collected the data from two dimensional field patch diffusion studies, including those on the surface and in oceanic thermoclines, and obtained a relationship of the lateral spread, reflected by a standard deviation \( \sigma_x(t) \) that grows with time as

\[ \sigma_x(t) = a(t_0 + t)^n \]  

(3.24)

where \( \sigma_x \) is in m and \( t \) is in seconds. Using \( y = u_a t \), Equation 3.24 becomes

\[ \sigma_x(y) = a \left( t_0 + \frac{y}{u_a} \right)^n \]  

(3.25)

Equation 3.24 assumes that multiple injectors of diameter \( d_0 \) are closely spaced in the direction normal to the ambient current. The initial standard deviation is given by

\[ \sigma_{x0} = a(t_0)^n = \frac{b_0}{\sqrt{12}} \]  

(3.26)

where \( \sigma_{x0} \) is in m and \( b_0 \), the total width of the injectors, is in m. The value of \( b_0 \) is determined by varying the number of injectors and the total flow rate out of each injector. In our analysis we use \( b_0 \) of 10 meters (on the order of the width of a ship), \( a = 0.00071/\sqrt{10} \) and \( n = 1.15 \). \( a \) was reduced by a factor of \( \sqrt{10} \) to account for reduced mixing expected in deeper waters.

Figure 3.7.1 shows the calculated centerline pH drops resulting from the four releases in crossflow depicted in Figure 3-10 at a CO₂ mass loading of 100 kg/s. Using a pH drop of 0.1 units as a threshold pH drop for insignificant marine life
impact (also within the observed natural variability in the ocean), the impact from the plumes cease at a distance of 2700-12500 m downcurrent, or after 15-70 hours of advection by the current.

Figure 3-12: Plot of centerline added DIC concentrations downcurrent of the four particle group release scenarios ($\dot{m} = 100$ kg/s) in an ambient crossflow of 0.05 m/s, as a function of downcurrent distance resulting from the four particle release scenarios from a fixed source shown in Figure 3-10. Elapsed time is 96 hours (4 days). The background DIC level used was approximately 0.1 kg/m³.
Figure 3-13: Centerline pH drop as a function of downcurrent distance resulting from the four particle release scenarios from a fixed source shown in Figure 3-10. Elapsed time is 96 hours (4 days). Horizontal dashed line indicates the threshold pH drop of 0.1 units for insignificant marine life impacts.

3.8 Towed source

To promote more rapid mixing, a ship could be used to tow the hydrate source perpendicular to the ambient current, as shown in Figure 3-14.
Figure 3-14: Depiction of a towed pipe injection from a ship.

The concentration distribution is given by Equations 3.21, 3.22 and 3.23 except that \( u_a \) is replaced by \( U_{ship} \). The greater dilution with this scenario comes from the fact that \( U_{ship} \gg u_a \). A plot of the calculated added DIC and pH drop as a function of downcurrent distance \( y \) for the towed pipe scenario is shown in Figures 3-15 and 3-16 for the particle release scenarios from Figure 3-10, but with added towing by a ship at 3 m/s (about 6 knots). Again using a pH drop of 0.1 units as a threshold pH drop for insignificant marine life impact, it is clear that the towed method achieves a very high dilution. Within 1800-18000 m downcurrent of the towed pipe, the added DIC results in pH drops of about 0.1 units. Moreover, the dilution is achieved in a much shorter time (less than 2 hours).
Figure 3-15: Centerline added DIC as a function of downcurrent distance \( y \) resulting from four particle release scenarios from a towed pipe. Elapsed time is 96 hours (4 days). CO\(_2\) mass loading is 100 kg/s, ambient current speed \( u_a = 0.05 \) m/s, ship tow rate \( U_{ship} = 3 \) m/s. Horizontal dashed line indicates a typical background DIC of approximately 0.1 kg/m\(^3\).

Figure 3-16: Centerline pH drop as a function of downcurrent distance \( y \) resulting from four particle release scenarios from a towed pipe. Elapsed time is 96 hours (4 days). CO\(_2\) mass loading is 100 kg/s, ambient current speed \( u_a = 0.05 \) m/s, ship tow rate \( U_{ship} = 3 \) m/s. Horizontal dashed line indicates the threshold pH drop of 0.1 units for insignificant marine life impact.
3.9 Onset of plume behavior

The above analysis assumes that the particles that are released from the towed source have minimal inter-particle interactions and will descend as discrete particles. This section studies the approximate criteria required for particles to begin to interact together to form plumes, whose behavior will be studied in Chapter 4.

Interactions between different particles have been studied for the purpose of understanding the dynamics of bubble coalescence and breakup due to collisions. Among the studies, observations have been made for pairs of bubbles (Crabtree and Bridgewater [19]), chains of bubbles (Tsuchiya et al. [72]), groups (Stewart [66]) and bubble swarms (Otake et al. [52]).

Tsuchiya et al. [72], in experiments performed in a 2D cell simulating a fluidized bed, investigated air bubbles ($Re = 2000 - 13000$) to determine behavior between bubbles and wakes. They found that if a trailing bubble is at a spacing of about 5-7 times the leading bubble breadth behind, it will catch up with the leading bubble (due to suction by lower pressure of first wake) and cause bubble pairing side by side, or coalescence. The critical bubble spacing is not sensitive to $Re$. Lazarek and Littman [39] measured the pressure field around a single spherical capped air bubble in water ($Re=26700$) and showed that there is a pressure minimum directly behind the bubble at about 2 bubble diameters downstream.

We evaluated whether towed hydrate particles would show any group effects by calculating their average particle spacing from the magnitude of the vector sum of the fall velocity $u_s$, ambient current $u_a$ and ship towing speed $U_{ship}$:

$$\text{Particle spacing} = \frac{\left(u_s^2 + u_a^2 + U_{ship}^2\right)^{\frac{1}{2}}}{N}$$  \hspace{1cm} (3.27)

where $\dot{N}$ is the particle number rate obtained by dividing the hydrate composite volume flux (equivalent to a CO$_2$ mass loading of $\dot{m}$ by the individual particle volume:

$$\dot{N} = \frac{\dot{m}(1+W)}{\rho \frac{1}{4} \pi d^2 L}. \hspace{1cm} (3.28)$$
Table 3.4: Predicted inter-particle separations (in boldface) for field particles in Table 3.3.

We used a particle spacing of approximately 10 particle diameters as a conservative criterion for the onset of particle to particle interactions. Table 3.4 shows the predicted particle separations for a CO₂ mass loading of 100 kg/s. Due to an ambient crossflow of 0.05 m/s and ship tow speed of 3 m/s, particles emerging from the injector would have an average particle spacing of over 30 particle diameters. The lateral towing by a ship therefore spreads particles laterally and allows them to settle as discrete particles.

3.10 Conclusions

Descent depths of hydrate composite particles are numerically predicted as a function of the hydrate reaction efficiency and particle diameter, and show that particles observed in previous field experiments are able to descend typically \( \sim 115 \) m on their own. We anticipate that scale-up of the injector is technically feasible with minor modifications to the prototype and can produce particles that could potentially sink to the bottom of the ocean. Although it is still to our advantage to improve hydrate reactor efficiency, we present a numerical analysis that shows that an inhomogeneous mixture of hydrate efficiencies (and therefore differing particle densities) will in fact help in vertical spreading of the dissolved injected CO₂ by creating particles of different settling velocities. To further take advantage of the differential settling, we
could use a ship to tow a stream of hydrate composite particles. The ship, traveling perpendicular to the ambient current, can enhance the dilution of CO₂ to levels that are expected to have minimal impact on marine life.
Chapter 4

Carbon Dioxide Hydrate Plumes

This chapter serves as an update to information presented in Tsouris et al. [70], [71], Adams et al. [3] and Chow et al. [15])

4.1 Abstract

This paper studies negatively buoyant CO₂ hydrate composite particle plumes for ocean carbon sequestration. Our study is based on recent field observations showing that a continuous-jet hydrate reactor located at an ocean depth of ~1500 m produced curved negatively buoyant cylindrical particles with diameters ~ 2.5 cm and lengths up to ~1 m. Applying a drag coefficient model (described in Chapter 2) on observed initial settling velocity and dissolution rates, we have concluded that the reactor efficiency (percentage of liquid CO₂ converted to hydrate) in the field was ~15-20% and that such particles would individually sink to a depth below discharge of roughly 115 m. Even greater sinking could be achieved if the particles are released in a larger continuous stream forming a dense plume. A double plume model (Wannamaker and Adams [75]; Crounse et al. [20]) was used to simulate the behavior of continuous streams of composite particles released to a quiescent ocean, with typical ambient stratification, at CO₂ loadings of 0.01 to 1000 kg/s. Results showed that, for a CO₂ release of 100 kg/s, a plume composed of 2.2 cm diameter composite particles with 16% reaction efficiency would sink about 1000 m, a plume composed of similar
particles, but with a diameter of 5 cm, would sink about 2000 m, while plumes composed of larger particles, or particles exhibiting higher reaction efficiency, would reach the seafloor.

In an ambient ocean with a current strong enough to cause separation of the dispersed phase from the plume, particles of different sizes and hydrate conversions (hence different settling velocities) will follow different settling trajectories as they dissolve. The particle fractionation spreads the discharged CO\textsubscript{2} in the down-current and vertical directions, enhancing mixing, while turbulent diffusion helps spread the CO\textsubscript{2} in the lateral direction. We developed a numerical model that approximates the effect of separation in the presence of crossflow and predicts the downstream concentrations and changes in pH from such particle releases.

4.2 Introduction

Our study was motivated by the field injections of solid CO\textsubscript{2} hydrate particles into the ocean at depths of 1000 to 1500 m in order to assess their effectiveness for sequestering anthropogenic CO\textsubscript{2} from the atmosphere. It is feared that rising concentrations of greenhouse gases in the atmosphere will cause adverse changes in the climate, and that two-thirds of the change will be attributed to CO\textsubscript{2} (Herzog et al. [29]). There is ongoing study of carbon dioxide hydrates as a possible vehicle for deeper ocean carbon sequestration, because they are denser than seawater, and will sink unaided while dissolving to promote dispersion in the ocean. The hydrate particles were created using a CO\textsubscript{2}-seawater coflowing injection apparatus, developed to create cylindrical composite particles, comprised of CO\textsubscript{2} hydrate, liquid CO\textsubscript{2} and seawater (Lee et al. [40]). Field tests were conducted on three occasions with differing co-flow injectors developed by ORNL in collaboration with the Monterey Bay Aquarium Research Institute (MBARI) (Tsouris et al. [69], Riestenberg et al. [56], Tsouris et al. [70] and Tsouris et al. [71]). The latest field observations show that the particles produced are long (up to a few meters in length), curved cylinders that descend with Reynolds number of about 1000, and shrink at a constant rate (Refer
Using a drag coefficient model developed for such particles and the initial settling velocity and dissolution rates observed in the field (Chapter 2), we conclude that such particles would ultimately sink to a depth below discharge of \(\sim 115\) m. We have also predicted the sinking depths of particles potentially produced from scaled-up reactors and have shown that, for example, a 10 cm diameter particle with a hydrate conversion of 50% could reach the ocean bottom before completely dissolving.

4.3 Qualitative plume behavior

In a real sequestration scenario where it is necessary to attain a \(\text{CO}_2\) mass loading of about 100 kg/s, we are interested in the behavior of the field hydrate composite particles in a large scale release. Releasing particles in a plume serves to enhance ocean sequestration in a number of ways: particles in a group sink faster (thus deeper in the case of dissolving particles) than individual particles; a plume will entrain surrounding fluid, enhancing dilution of dissolved \(\text{CO}_2\) from the particle; and the dissolved \(\text{CO}_2\), via the solute density effect, will increase the density of the ambient fluid, causing an additional source of negative buoyancy.

4.3.1 Trapping

When buoyant particles descend and entrain fluid along their way in an ambient density stratification, a fraction of the fluid, sinking below its neutrally buoyant depth, will ‘peel’ away from the particles in the core, resulting in an intrusion (or trapping). A number of peeling events are likely to occur upon descent, resulting in outer intrusion layers of varying lateral width (Figure 4-1).
Socolofsky and Adams [65] predict the first plume trap depth $h_t$, based on experimental observations and dimensional analysis, as

$$h_t = \left(2.8 - 0.27 \left[ \frac{u_s}{(BN)^{1/4}} \right] \right) \left( \frac{B}{N^3} \right)^{1/4} \quad (4.1)$$

where $u_s$ is the slip velocity of the dispersed phase droplets or particles, $B$ the initial kinematic buoyancy flux, and $N$ the Brunt-Väisälä frequency, or stratification frequency of the ambient. $B$ is the initial kinematic buoyancy flux of the plume (dimensions $[L^4 T^{-3}]$), and is given by

$$B = \dot{N}_p V g \frac{\Delta \rho}{\rho} \quad (4.2)$$

where $\dot{N}_p$ is the number of particles released per unit time, $V$ is the particle volume, $g$ is gravity and $\Delta \rho / \rho$ is the normalized excess density of the particles. In an arbitrary stratification, a numerical model could be used to predict the trap depth.

**Plume structure**

For a two-phase plume, the dispersed phase is generally able to travel vertically beyond the intrusion, resulting in the continuous phase 'peeling' away from the intrusion, restarting the cycle of peeling and trapping any number of times depending
on the dispersed phase particle size (Asaeda and Imberger [7]). The different possible observed plume structures are shown in Figure 4-2, for the analogous situation of a positively buoyant plume.

![Plume Types Diagram](image)

Figure 4-2: Stagnant multiphase plume structure types (after Socolofsky [62]). The plumes depicted are positively buoyant.

Socolofsky and Adams [65] define a non-dimensional slip velocity $U_N$, that relates the observed plume type with the initial plume source and ambient conditions. $U_N$ is defined as

$$U_N = \frac{u_s}{(BN)^{1/4}}$$  \hspace{1cm} (4.3)

The denominator, $(BN)^{1/4}$, is a characteristic plume fluid velocity. It is found by that Type 1* plume behavior (as shown in Figure 4-2) is observed for $U_N < 1.4$, Type 2 for $1.4 < U_N < 2.4$, and Type 3 for $U_N > 2.4$.

### 4.3.2 Numerical modeling

We are interested in numerically predicting large scale behaviors of the plume (its depth and dilution of dissolved inorganic carbon (DIC)) using a two phase plume model that reflects the behavior of CO$_2$ hydrate composite particles. A number of computational models have addressed bubble plumes in quiescent conditions. While some have solved the full three dimensional Navier-Stokes equations for liquid droplets (Alendal and Drange [5], Chen [13], Sato and Hama [57]), the thin geometry of the
plume flow conditions have allowed for a one dimensional cross-sectionally-averaged integral initial value model. In their study of bubble plumes, Asaeda and Imberger [7] adopted a counter-flowing double plume structure, in which the bubbles are confined to an inner core, surrounded by an outer core of plume fluid to simulate peeling events observed in bubble plume experiments (Socolofsky and Adams [64]). Because of the interaction of the outer and inner plume layers, the initial value problem must be iterative. Crounse et al. [20] used the same approach of a double plume structure, and adapted it for a liquid CO$_2$ release. The presence of dissolution and salinity called for integral conservation equations for mass, momentum, salt, heat and dispersed phase concentrations in each integral control volume. Wannamaker and Adams [75] adapted the model to allow for negatively buoyant, pure solid hydrate particles, and for a mixture of spherical particle sizes. This work adapts Wannamaker’s version of the model to simulate the behavior of partially reacted hydrate particles that are cylindrical in shape.

Two phase plume model

The carbon dioxide hydrate plume model was developed by Brian Crounse, Scott Socolofsky and Eric Wannamaker (Crounse et al. [20], Wannamaker and Adams [75]), also at MIT under the supervision of Eric Adams. We made modifications to account for partially reacted hydrate cylindrical particles, as described in Chapter 1. The features of the model are:

- One dimensional, steady state – assumes axisymmetry about plume centerline.
- Initial value problem – the model integrates mass, momentum, buoyancy, thermal energy, dissolved and dispersed phase fluxes, starting from a small distance downstream, known as the zone of flow establishment, for which fluxes are known.
- One dispersed phase is allowed (e.g. air, hydrate or CO$_2$). Hydrates are characterized by their water to CO$_2$ ratio $W$ and their reaction efficiency $X$, defined as the fraction of liquid CO$_2$ that reacts to form hydrate.
• Double plume structure – an inner core and outer region are modeled. First used by Asaeda and Imberger [7], this reflects observations of real bubble plumes. Entrainment between the two regions, and that between the outer plume and the ambient, are accounted for. This also requires iteration between the inner and out plume calculations until the interactions among the two plume regions and with the ambient are steady.

• Accounts for peeling of dispersed phase from the plume fluid, depending on fall velocity of the individual particles, and detrainment of plume fluid into intrusion layers.

• Solute density effect, whereby the dissolved CO₂ from liquid CO₂ or hydrates imparts a density increase in the ambient seawater.

Model outputs

The modeling outputs of interest are the final plume depth, trap depth $h_t$, the concentration of increased dissolved inorganic carbon (DIC) added to the plume, and the resulting changes of pH values in the intrusions, or peeling layers of the plume.

Plume depth

The inner plume depth at which the total mass flux of particles has decreased to less than 1% of the original particle flux represents the depth at which the particles have dissolved, and this is taken to be the final plume depth.

Trap depth

While Equation 4.1 can be used to predict the trap depth $h_t$ of a plume in a linear stratification, the model predicted trap depth $h_t$ is calculated with the ambient density profile of the modeled ocean. The trap depth will be used to determine the effects of ambient crossflow, described in Section 4.5.1.

Dissolved carbon and pH change

The additional dissolved inorganic carbon (DIC) concentration is calculated by the output flux of DIC (kg/s) divided by the total plume fluid volume flux (m³/s) in the outer plume. Having established the local DIC concentration by adding the calculated the value to the background DIC
concentration, the change in pH of the plume fluid is calculated using an alkalinity in the modeled water body. Calculations herein are based on measurements in Hawaii’s Keahole Point reported by Miller et al. [47]. The determination of pH from added DIC and alkalinity is outlined in Section 1.1. For the model calculations, the background DIC concentration used was 4410 μmol/kg or 0.102 kg/m³, and the alkalinity was \( Alk = 2260 \, \mu \text{mol/kg}. \)

A typical ocean density profile from Keahole point, Hawaii (Miller et al. [47]) was used to describe the ambient density as a function of depth. Figure 4-3 shows typical outer and inner plume structures from a model simulation.

![Figure 4-3: Typical model result for the structure of hydrate plume release. Model inputs: Release depth = 800 m; depth of water body = 4500 m; dispersed phase: spherical pure hydrates, diameter 1 cm, density 1143 kg/m³; mass loading: 100 kg/s of CO₂. The resulting additional DIC throughout the intrusions (outer layers) was 0.02 kg/m³ resulting in a pH decrease of 0.8 units.](image-url)
When used for solid, pure spherical CO$_2$ hydrate particles, the model showed that hydrate particle plumes of large mass loadings can sink up to 10 times the distance by individual particles in a quiescent environment (Wannamaker [75]).

4.3.3 Effect of composite particle composition

As illustrated in Chapter 3 and in Figure 4-4, the density of the composite particle can be determined as a function of the hydrate reaction efficiency $X$ and initial water content $W$, expressed as the ratio of initial water mass to initial CO$_2$ mass. Figure 4-4 plots the resulting densities of composite particles as a function of $X$ and $W$. The present two phase plume model is able to take the composition of the particle as a model input.

Figure 4-4: Density of hydrate composite, as a function of conversion efficiency ($X$) and water to CO$_2$ mass ratio ($W$). The densities of the phases at 1500 m depth were used. The surface $\rho_w = 1035$ is plotted to indicate the composite compositions which result in a negatively buoyant particle (above surface) and positively buoyant particles (below surface)
The two phase plume model was tested using spherical hydrate particles to be able to compare the results to those of Wannamaker and Adams [75]. Figure 4-5 shows the model outputs for trap depth for different mass loadings of CO₂ under stratified conditions, varying X. There is an increasing trend of plume depth with X, due to increased particle density. As outlined in Section 4.3.1 the plume structure and the number of peeling events are related to the slip velocity of the particles, resulting in the relatively sharp increases in plume depth at certain values of X. However, even at low conversion efficiencies, the plume does descend to a great depth. This is attributed to the solute density effect by the dissolution of CO₂ into the ambient. The model suggests that the solute density effect alone can cause a plume to sink to a depth 40% of the depth attained with pure hydrate particles.

Figure 4-5: Model plume depths of test releases of CO₂ for four CO₂ mass loadings, varying conversion efficiency X. Model inputs: Spherical particles 1 cm in diameter, release depth 800 m. The water/CO₂ mass ratio is $W = 2.45$, the stoichiometric ratio required to create 100% hydrate with no excess.
Figure 4-6 shows the change in plume depth with hydrate particle water to CO₂ ratio, \( W \). Increasing \( W \) decreases the composite particle density, and this results in a decrease in the final plume depth for all mass loadings.

![Image of Figure 4-6 showing model plume depths plotted against diameter for different water to CO₂ mass ratios \( W \), and for different mass loadings 1-1000 kg/s CO₂. Release depth: 800 m.]

**4.3.4 Effect of mass loading**

Figures 4-5 and 4-6 also show that increased mass loading of CO₂ will predictably increase the plume sinking depth, due to the larger initial buoyancy flux of the release and a greater plume effect. Again, for reference, a typical power plant outputs about 100 kg/s of CO₂. The results favor a larger scale release for deeper sequestration.

**4.3.5 Effect of particle diameter**

Changing the particle diameter increases both the slip velocity of the dispersed phase and time for particles to completely dissolve, both contributing to higher plume depths. Plume depths for different \( X \) and \( W \) values, and at different mass loadings, while changing the diameter, are shown in Figures 4-7-4-9. As the maximum depth
of the modeled water body is 4500 m, in many high-diameter model runs the particles are able to sink to the bottom.

Figure 4-7: Model plume depths plotted against reaction efficiency $X$, for various spherical particle diameters. Model inputs: Spherical particles, release depth 800 m, $W = 2.45$. 
Figure 4-8: Model plume depths plotted against diameter, for different CO$_2$ mass loadings. Model inputs: Spherical particles, release depth 800 m, $W = 2.45$.

Figure 4-9: Model plume depths plotted against diameter, for different reaction efficiency $X$. Model inputs: Spherical particles, release depth 800 m.
4.4 Cylindrical particles

Having established that the model behaves qualitatively as expected using spherical particles of varying composition, we apply the model to particles of different geometry, in particular to particles shaped like those observed in the field experiments.

The drag coefficient model used to determine the local dispersed phase slip velocity is outlined in Chapter 2. The cylindrical particles in the field were determined to have a constant shrinkage rate of about 6 μm/s. Assuming that the composition of the hydrate does not change upon dissolution, the mass of dissolved CO₂ transferred to the inner plume fluid can be determined by the initial ratio of the water and CO₂.

The particles used in the simulations are shown in Table 4.1, and reflect both particles previously observed in the field and particles we believe can be produced with current technology by scaling up the reactor. Figure 4-10 shows the resulting plume descent depths for the four simulated hydrate particles.
Table 4.1: Numerically predicted descent depth of individual particles assuming scale-up of a particle produced in the 2006 field experiment (Particle 'TO970-4' in Tsouris et al. [71]). Particles '2006+' and '2006++' refer to particles with increased diameter, but otherwise the same characteristics as particle 'TO970-4'. Particle '2006+++ ' has an increased diameter and an increased reaction conversion from 16% to 50%. Boldface values indicate the changed values from the original particle.

In the limit of small mass flow rate, plume descent depths approach those of single particles. Figure 4-11 illustrates the "plume effect", defined as the descent depth of the plume release divided by that of an individual particle, resulting from the particle releases. The greatest plume effect occurs with the smallest particles delivered at the largest \(\text{CO}_2\) injection rates. For example, with a release of 100 kg/s (one large power plant), the smallest particles are predicted to sink \(\sim 9\) times further as part of a plume (a depth of around 1000 m), rather than as individual particles (which sink to about 115 m below release depth). With the largest anticipated scaled-up particles "2006+++", since the individual particles will sink to the bottom of the ocean, a plume of any mass loading, discharging in a quiescent ambient, will also sink to the bottom, resulting in a plume effect of 1 for all mass loadings.

Figures 4-12 and 4-13 show the resulting average added DIC concentration and pH drop due to the plume releases. An individual particle has negligible effect of the ambient DIC concentration and pH drop. As expected, the larger mass loading of \(\text{CO}_2\) will result in a larger added DIC and therefore higher pH changes from the plume. Note that the added DIC and pH values are near field dilution values that are found close to the source point.
Figure 4-10: Depth of particle plume descent as a function of mass loading for the four particles with characteristics described in Table 4.1. Ocean bottom is located 3000 m below discharge.
Figure 4-11: Plume effect as a function of mass loading and for the particle releases shown in Figure 4-10.
Figure 4-12: Added DIC concentration as a function of mass loading and for the particle releases shown in Figure 4-10. Background DIC concentration of 0.1 kg/m³ shown.
Figure 4-13: pH drop as a function of mass loading and for the particle releases shown in Figure 4-10.
4.5 Crossflow

Ambient ocean currents are known to cause phase separation, whereby the continuous fluid in the plume is swept downstream of the particles which sink more directly. While Figure 4-14 shows a remarkably constant density profile at depths below about 1500 m, Figures 4-15 and 4-16 by contrast indicate that typical ambient ocean currents could range from 0-40 cm/s and are more variable with depth and global position than the ambient density profile.

Figure 4-14: Plot of potential density versus depth for 3000 different locations (shown in inset map). Data taken from the World Ocean Circulation Experiment (WOCE) [59]
Figure 4-15: Plot of typical ambient ocean currents in an area of the North Atlantic Ocean. Upper left - area of measurements (Longitude 50-70° W, Latitude 20-32° N); upper right - points showing the northerly (V) and easterly (U) current velocity values at each measurement point; lower left - ambient current velocity (denoted here as $U_s$) as a function of water depth; lower right - ambient current velocity as a function of latitude. Data taken from the World Ocean Circulation Experiment (WOCE) [59].
Figure 4-16: Plot of typical ambient ocean currents in an area of the South Atlantic Ocean. Upper left - area of measurements (Longitude 15-25° W, Latitude 20-30° S); upper right - points showing the northerly (V) and easterly (U) current velocity values at each measurement point; lower left - ambient current velocity (denoted here as $U_s$) as a function of water depth; lower right - ambient current velocity as a function of latitude. Data taken from the World Ocean Circulation Experiment (WOCE) [59]
4.5.1 Plume separation

Socolofsky and Adams [63] described a criterion to determine the significance of the crossflow current compared to the plume buoyancy in a stratified environment. The separation depth $h_s$ predicts the vertical distance from the source at which the continuous phase would begin to be advected away from the dispersed phase (Figure 4-17). $h_s$ is determined based on dimensional analysis, predictions of the plume centerline trajectory and from experimental measurements:

$$h_s = \frac{5.1B}{(u_au_s^{2.4})^{0.88}} \quad (4.4)$$

where $B$ is the initial kinematic buoyancy flux, $u_a$ the ambient current velocity, and $u_s$ the dispersed phase slip velocity.

Figure 4-17: Effect of crossflow current on a particle plume, showing the separation depth $h_s$ from the source.

Socolofsky and Adams [63] determined that a crossflow is strong, and will result in the separation of the phases as shown in Figure 4-17, when the ratio of the first trap depth and the separation depth $h_t/h_s > 1$. When $h_t/h_s < 1$, the crossflow is considered weak, the dispersed phase stays within the plume, and the plume release acts more like a stagnant plume in stratification.

The criterion for determining strong or weak crossflows provides a basis for a hybrid model in which composite particles released continuously into an ocean current
descend initially as a coherent plume, then separate, with the remaining descent taking place by individual particle settling. Model results shown in Figure 4-18 indicate total descent depths that are intermediate between those for individually released particles (dotted lines), and continuously released particles without phase separation (solid black lines).

Following [3], we assume that if the depth of the first trap depth $h_t$, as predicted by the quiescent two-phase particle model, is less than the separation depth $h_s$ calculated for the plume by Equation 4.4, then the quiescent plume calculations are valid, whereas if the separation depth is less, the particles are assumed to sink individually following separation. The descent depths and plume effects predicted by the hybrid model are depicted in Figures 4-18 and 4-19, respectively. The results show that as reactor size (and thus particle diameter) increases, the plume effect diminishes. In addition, increasing particle diameter reduces the of plume separation caused by an ambient current.

Section 4.6 discusses the the development of a model to predict the resulting added DIC and pH drops for a plume separated by a crossflow.
Figure 4-18: Depth of particle plume descent as a function of mass loading and ambient current speed for four particles (from left to right): Typical observed field experiment 2006; scaled up particle 2006+, 2006++ and 2006+++. Ocean bottom is located 3000 m below discharge.
Figure 4-19: Plume effect as a function of mass loading and ambient current speed for four particles described in Figure 4-18.
4.6 Dissolved inorganic carbon

Whereas the two-phase plume model predicts the added DIC concentrations and pH drops for a plume released in a quiescent ambient, a strong crossflow current (where \( h_s < h_t \)) will remove the axisymmetry of the plume beyond the separation depth \( h_s \). A new method for estimation of the added DIC is thus required beyond the plume separation depth for plumes in a strong current. A schematic of the plume after separation is shown in Figure 4-20.

![Figure 4-20](image)

Figure 4-20: The 3-dimensional spread of particles from a plume in the presence of an ambient current. (Not to scale)

The schematic shows two regions that arise after separation: \textbf{Stage One}, the region occupied by the particles that have separated from the original plume; and \textbf{Stage Two}, the remainder of the original plume consisting mainly of the dissolved inorganic carbon continuous phase. The coordinate system is defined by the following: \( z \) is the depth (positive downwards); \( y \) is the direction along the prevailing current; \( x \) is the direction lateral to the current.
Conditions at plume separation

Stage One consists of hydrate composite particles falling out of the original plume. Following the approach for the particles that separate from a towed source (Section 3.8), if the particles exhibit a range of reaction efficiencies ($X$) or diameters, they will follow different settling trajectories. The particle fractionation could be conceived to begin at a separation depth $h_s$, creating a vertical particle distribution advected downcurrent. As a simplification, it is assumed that, if the current is strong enough to cause separation, all of the particles in the plume leave at one separation depth $h_s$ from the discharge point and enter Stage One. The remainder of the plume in Stage Two is therefore a single continuous phase plume. Since the two phase plume model only allows for a single density for the particles, the models were run using an average value for the conversion efficiency $X$. Since a reactors has been shown to create particles with the same diameter equal to the reactor internal diameter, each simulation is performed with only one diameter size.

Separation mass flux  Since the particles are partly dissolved upon separation, the output of the plume model is used to determine the mass loading that will take part in the post-separation region. The fraction of the initial mass loading of CO$_2$ found at the separation depth $h_s$ is plotted as a function of initial mass loading and ambient current speed (far from the particles) in Figure 4-21. Note that if the current is weak, the mass fraction in post separation becomes zero and the quiescent plume model applies to the entire CO$_2$ mass loading.
Figure 4-21: Fraction of CO$_2$ retained in plume at separation depth $h_s$, as a function of mass loading and ambient current speed for four particles described in Figure 4-18.
Down-current separation location  A plot of the separation depth $h_s$, calculated with Equation 4.4 as a function of mass loading and ambient current speed for four particles is shown in Figure 4-22. As Equation 4.4 indicates, an increased mass loading results in an increased buoyancy flux $B$ which also increases the separation depth.

![Plot](Image)

Figure 4-22: Separation depth $h_s$, calculated with Equation 4.4 as a function of mass loading and ambient current speed for four particles described in Figure 4-18.
The time delay, denoted by $t_0$, between the particle release from the injection port to the separation depth causes the separation to occur a certain distance downstream of the release, denoted by $y_s$. In an ambient current of $u_a$ the downcurrent location where separation occurs can be calculated by

$$y_s = u_a t_0 = u_a \int_0^{h_s} \frac{dz}{u(z)}$$

(4.5)

where $u(z)$ is the plume velocity as a function of depth given by the output of the two-phase plume model. Figure 4-23 shows the simulation predictions of downcurrent separation distance as a function of mass loading and ambient current speed for the four model particles. Note that if the particles do not separate, as indicated by $h_s > h_t$, then $y_s = \infty$.

Similar to the prediction of the separation depth $h_s$, the downstream separation location is assumed to occur at one location, calculated for a particle of a mean conversion efficiency $X$.

**Continuous phase** Figure 4-24 shows the prediction of added DIC at the separation depth taken from two-phase model simulations. The curves show two opposing effects of $h_s$ on the DIC concentration: as CO$_2$ mass loading increases, $h_s$ increases, as calculated in Equation 4.4. The increased time spent in the plume results in higher dissolved mass from the particles, contributing to a higher DIC. On the other hand, as the separation depth approaches the trap depth $h_t$ in the ambient stratification, the plume increases in width at an increasing rate contributing to additional dilution. The curves clearly show that as the separation depth approaches the trap depth the DIC concentrations are reduced.
Figure 4-23: Downcurrent location of separation $y_s$, as a function of mass loading and ambient current speed for four particles described in Figure 4-18. Plume-like releases for which $h_s > h_t$ are shown as having a very large value of $y_s$. 
Figure 4-24: Added dissolved inorganic carbon (DIC) concentration at the separation depth, as a function of mass loading and ambient current speed for four particles described in Figure 4-18.
Table 4.2: Initial conditions used in hybrid crossflow separation model. Common parameters for the simulation are: CO₂ mass loading 100 kg/s, particle cylinder length 30 cm, diameter shrinkage rate 6 µm/s.

**Initial conditions** A selection of initial conditions used for the model obtained by the above considerations are shown in Table 4.2 for a moderately high ambient current of 0.2 m/s and a high ambient current of 0.4 m/s. Common parameters for the simulation are: CO₂ mass loading 100 kg/s, particle cylinder length 30 cm, diameter shrinkage rate 6 µm/s.

<table>
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<th>Ambient current 0.2 m/s</th>
<th>Ambient current 0.4 m/s</th>
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<td><strong>Diam at h_s (cm)</strong></td>
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<td>9.98</td>
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<td>15</td>
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</table>
4.6.1 Stage One

This section illustrates the approach used in modeling the added DIC concentration of Stage One: the volume covered by the fractionated descending particles after separation. (Refer to Figure 4-20 and Figure 4-25 below).

Figure 4-25: Schematic of Stage 1 of the hybrid model, showing the 3-dimensional spread of particles in the presence of an ambient current, and with the centerline plane \((x = 0)\) highlighted.

Vertical particle spread

In Chapter 3, it was found that groups of individual particles of different sizes and hydrate conversions (hence different settling velocities) follow different settling trajectories as they dissolve (Figure 3-10). The particle fractionation spreads the discharged CO\(_2\) in the down-current and vertical directions, enhancing mixing, while the movement by the ship releasing the particles in the lateral direction helps spread the CO\(_2\) in the lateral direction. This approach was used in Chapter 3 to assess the effect on the ocean of a particle release from a towed source.

Here we rely on turbulent diffusion to provide lateral mixing, as characterized by the plume’s standard deviation in the lateral \((x)\) direction, \(\sigma_x(y)\). The added DIC concentration thus can be expressed analytically as
\[ c(x, y) = \frac{\dot{m}}{u_a} \frac{1}{\sigma_x(y) h(y)} \exp \left( \frac{-x^2}{2\sigma_x^2(y)} \right) \]  

(4.6)

where \( \dot{m} \) is the CO₂ mass loading in kg/s.

We adopt the same set of trajectories as in the towed case (Equation 4.7) to model the vertical spread \( h(y) \) of Stage One particles, using the diameters of the particles at the separation depth as the initial diameters.

\[
\frac{h(y)}{h_d} = \begin{cases} 
1 - \left(1 - \frac{y}{l_d} \right)^{\frac{3}{2}} & y \leq l_d \\
1 & y > l_d 
\end{cases}
\]  

(4.7)

where \( l_d \) is the downcurrent distance of particle dissolution,

\[
l_d = \frac{d_0 u_a}{dd} \]  

(4.8)

**Lateral spread**  Instead of spreading the plume laterally using advection from a ship as in the towed example (Section 3.8), the lateral turbulent diffusion of the particles (in the \( x \) direction) results in a lateral distribution of variance \( \sigma_x \) that increases with time. Figure 4-25 shows the expected 3-dimensional spread of the particles.

To complete the formulation of the added DIC concentration, we require an expression for the lateral spread, \( \sigma_x \). Okubo [51] collected the data from many two dimensional field patch diffusion studies, including those on the surface and at depth on thermoclines, and obtained a relationship of the lateral spread, reflected by a radial variance \( \sigma_r \) that grows with time as

\[
\sigma_r^2 = (1.0 \times 10^{-6}) t^{2.3}
\]  

(4.9)

where \( \sigma_r^2 \) is in \( \text{m}^2 \) and \( t \) is in seconds. Using \( y = u_a t \) and \( \sigma_x^2 = \frac{1}{2} \sigma_r^2 \) the form of Equation 4.9 becomes
\[ \sigma^2_x = \frac{1}{2} (10^{-6}) \left( \frac{y}{u_a} \right)^{2.3} . \]  

Equation 4.9 applies to a point source. Because the lateral diffusion begins at a distance downstream from the separation, we must account for the initial plume at separation, denoted \( \sigma_{x0} \), i.e.,

\[ \sigma^2_x = \sigma^2_{x0} + \frac{1}{2} (10^{-6}) \left( \frac{y}{u_a} \right)^{2.3} \]  

(4.11)

where \( \sigma_{x0} \) can be approximated as a quarter of the plume width at separation:

\[ \sigma_{x0} = \frac{1}{4} b_{hs} \]  

(4.12)

where \( b_{hs} \) can be determined from the output of the plume model.

Equations 4.11 and 4.6 were used to predict the added DIC concentrations resulting in the four injection scenarios using particles depicted in Figure 3-10 from Chapter 3, and are shown in Figures 4-35 and 4-36. The mass loading of CO\(_2\) is 100 kg/s. The values shown are the centerline values of the concentration distribution, i.e., \( x = 0 \).

**Stage One plume behavior** Section 3.9 discusses the criterion of particle spacing that causes particles to interact each other in a towed ship release. In the absence of lateral spreading of a towed ship, the particles are expected to have a smaller particle spacing (refer to Table 4.3). In particular, the expected spacing of the larger particles is about 2 particle diameters. This shows that if the particles were all to separate from the plume at a single separation depth (as assumed in the analysis), they would form a new plume that would descend further than an individual particle. In an actual release of particles with a range of \( X \), the particles would not separate at one location, and therefore would have an initial downcurrent spread that is likely to increase their particle spacing. Since it is likely that the downcurrent spread could increase particle spacing to further than 10 particle diameters (refer to Section 3.9), we have assumed that the particles do descend as individual particles in Stage One.
Table 4.3: Predicted inter-particle separations (in boldface) for field and scaled-up field particles from Table 3.3 in Chapter 3, for a current speed of 0.2 cm/s and without lateral spreading by a ship.

### 4.6.2 Stage Two

Stage Two comprises only the continuous phase of the original plume, without particles (Refer to Figure 4-26).

![Figure 4-26: Schematic of Stage 2 of the hybrid model.](image)

Figure 4-26: Schematic of Stage 2 of the hybrid model.
The Stage Two discharge has some initial momentum in the $y$ and $z$ directions, imparted from the sinking particles and the ambient current. Here we used the commercially available numerical model CORMIX (The Cornell Mixing Zone Expert System), developed by the DeFrees Hydraulics Laboratory at Cornell University, for studying aqueous pollutant discharges into a range of water bodies (Jirka et al. [36]). CORMIX was chosen since it can model, among many other things, effects of initial single phase momentum and account for all possible transitions of a discharge from a momentum jet, to a buoyant jet or a pure plume. We ran simulations on the CORMIX1 model (signifying a single port discharge) using the initial conditions of the two-phase plume model that have been adapted to suit the requirements of CORMIX1 while preserving the characteristics of the Stage Two flow. The initial conditions for the plumes in Stage Two are shown in Table 4.4. The CORMIX1 input interface only allows for a water depth of 1000 m. Restrictions on the port location within the 1000 m domain meant that the model was run with the top of the model 770 m above and 230 m below the separation depth $h_s$ of each case from the two-phase model. In addition, CORMIX1 only accepts a linear stratification, so a top and bottom density that matched the density gradient found around the depth of interest (1500 m) from the quiescent model was used as shown in Figure 4-27. In the example shown in the figure, since $h_s = 230$ m corresponded to an actual ocean depth of 1730 m for the separation depth, the modeled top and bottom of the CORMIX model (0-1000 m depth) corresponded to the density conditions at depths 770 m above and 230 m below, i.e. 960-1960 m. The discharge port area and and volume flux rate for CORMIX were taken from the model outputs at $h_s$ for the continuous phase from the quiescent plume model: since both used a top hat plume profile, their momentum fluxes are matched. To match the initial angle of inclination of the initial plume in Stage Two, we determined the inclination angle using the crossflow current speed and the average plume velocity at the separation depth from the quiescent model. The CORMIX1 model will accept discharge angles between 90 degrees (pointing vertically upward) to -45 degrees (pointing diagonally downward). Discharges with a calculated inclination angle of $-45 - -90$ degrees (as occurs in a weaker current) were made to
have an inclination angle of -45 degrees.

Figure 4-27: Approximate linear density profile used for CORMIX1 model compared to that used in the two-phase model. In this example, $h_s = 230\ m$ below discharge. The dashed line shows the CORMIX1 input density gradient, over the depths modeled by CORMIX1 (960-1960 m).
<table>
<thead>
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<th>Simulation description</th>
<th>CORMIX1 inputs</th>
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<td>Init.particle diam d (cm)</td>
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<td>0.12-0.55</td>
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<td>0.12-0.50</td>
</tr>
<tr>
<td>15</td>
<td>0.12-0.30</td>
</tr>
</tbody>
</table>

Table 4.4: Initial conditions used for CORMIX in determining the dilution of plumes in Stage Two of the hybrid model. Common parameters for all simulations: CO₂ mass loading 100 kg/s; laterally unbounded domain

The CORMIX1 model determines the class of flow based on the length scales of momentum, buoyancy and volume, and on water body geometry. An algorithm flowchart for stratified flows used by CORMIX1 is shown in Figure 4-28. The simulations made for Stage 2 resulted in flows that were of classes 'S4' and 'S5' in CORMIX, meaning that the end plumes trap well below the surface of the model. As a result, CORMIX ignored the effects of its surface and a bottom for the model body, making it equivalent to the Stage 2 plume conditions.
FLOW CLASSES FOR AMBIENT STRATIFICATION

NEGATIVELY BUOYANT JET
for Downward Oriented All

AMBIENT STRATIFICATION

UNIMPORTANT with Vertical Mixing

AMBIENT STRATIFICATION

IMPORTANT

Terminal Height

Z_t

CLASS 5 for 55
4.6.3 Results

Qualitative behavior  The hybrid model simulations are run using the initial conditions listed in Table 4.2 and Table 4.4, and the simulated resultant plume structures are depicted in Figures 4-29 (for a fairly strong ambient current $u_a = 0.2$ m/s) and 4-30 (for a strong ambient current $u_a = 0.4$ m/s). The figures show that Stage One occupies a much larger ocean volume, allowing for a higher dilution opportunity. On the other hand, as the particles leave the plumes at the separation point, the single phase remainder of the plumes entering Stage Two are positively buoyant and begin to rise from the separation point while being advected downcurrent. They form a thin vertical layer at a depth of neutral buoyancy, which could be about 100 m above the release depth.

The fraction of the mass loading that end up in each Stage depends on the initial diameter of the particles. The smaller the particles, the larger the collective surface area to volume ratio of the hydrate particles. Since all of the modeled particles shrink at the same rate, the smaller particle plumes therefore dissolve more quickly, causing more of the original plume to enter Stage 2. In the case of particles of diameter 2.5 cm (about the same order as the particles created in recent field experiments), in a moderately strong crossflow (0.2 m/s), up to 26% (or 26 kg/s) of the total CO$_2$ is in the dissolved phase at the separation depth. This fluid enters Stage Two to trap at a depth close to the release depth. On the other hand, more than 99% of the largest particles of 15 cm diameter separate from the plume and descend as individual particles, leaving behind less than 1% of the plume to trap at around 1500 m.
Figure 4-29: Depiction of Stage One and Stage Two plumes, viewed normal to the ambient crossflow direction. Ambient current = 0.2 m/s. Numbers in the plot windows indicate the fraction of the mass loading in Stage Two (top value) and in Stage One (bottom value).
Figure 4-30: Depiction of Stage One and Stage Two plumes, viewed normal to the ambient crossflow direction. Ambient current = 0.4 m/s. Numbers in the plot windows indicate the fraction of the mass loading in Stage Two (top value) and in Stage One (bottom value).
**Added DIC**  The hybrid model was run for two ambient current speeds (0.2 and 0.4 m/s, fairly strong to strong current). Stage One, comprised of fractionating particles, creates fairly good dilution by spreading out over a large volume as they differentially settle and dissolve (however not as efficient at spreading the particles as seen in the towed pipe case). Stage Two, the continuous remainder of the plume, on the other hand, lifts off since it is initially positively buoyant, and traps at depths close to the injection depth. The limited spread of the continuous phase plume results in high expected values of DIC for the plumes in Stage Two. A particle plume of 100 kg/s comprising of particles of similar size as those observed in the field (2.5 cm diameter) will have over a quarter of its original mass loading trapping at around 1500 m. The added DIC concentration changes due to the two stages of the hybrid model are shown in Figures 4-31 to 4-34 for the two ambient current speeds.
Stage One added DIC

Figure 4-31: Plot of added DIC concentrations downcurrent of the four particle group release scenarios (\( \dot{m} = 100 \text{ kg/s} \)) in an ambient crossflow of 0.20 m/s, as a function of the downcurrent distance for Stage One (fractionated particles). The background DIC level of 0.1 kg/m\(^3\) is indicated on the plot (dashed line).
Figure 4-32: Plot of Stage One (fractionated particle) added DIC concentrations downcurrent of the four particle group release scenarios in an ambient crossflow of 0.40 m/s.

The results show that the DIC concentrations decrease fairly rapidly downstream, with not much variation between the two cases with two current speeds. Note that the particles of 10 cm diameter (bottom left panels) have a conversion efficiency range of $X = 0.12 - 0.55$, compared to the 15 cm diameter particles ($X = 0.12 - 0.30$). While the ranges were chosen such that the heaviest particles just reach the bottom, a consequence of assuming a smaller range of $X$ for the large particles is a smaller total volume occupied downstream (Figures 4-29 and 4-29), and therefore a lower dilution for the largest particles.
Stage Two added DIC The Stage Two added DIC concentrations are shown in Figures 4-33 and 4-34. Compared to Stage One, the Stage Two plume dilutions are more affected by the ambient current since a higher current will result in a smaller fraction of the original mass loading entering Stage Two. In general, the DIC concentrations found in the Stage Two plumes are higher than those in Stage One.

Figure 4-33: Plot of added DIC concentrations downcurrent of the four particle group release scenarios ($\dot{m} = 100$ kg/s) in an ambient crossflow of 0.20 m/s, as a function of the downcurrent distance for Stage Two (continuous phase). The background DIC level of 0.1 kg/m$^3$ is indicated on the plot.
Figure 4-34: Plot of added DIC concentrations downcurrent of the four particle group release scenarios in an ambient crossflow of 0.40 m/s, for Stage Two (continuous phase).

**pH change**: The corresponding pH changes due to the two stages of the hybrid model are shown in Figures 4-35 to 4-38 for the two ambient current speeds.

**Stage One pH drop** Figures 4-35 and 4-36 show the pH drops of due to the particles that have separated from the plume and have entered Stage One. The results show that the larger volume occupied by the particle trajectories upon descent causes the pH drop to decrease quite rapidly downcurrent. As described in Section 3.7, a pH drop of 0.1 is considered as a threshold for insignificant impact to marine life.
Figure 4-35: Plot of Stage One pH drop downcurrent of the four particle group release scenarios in an ambient crossflow of 0.20 m/s, as a function of the downcurrent distance.

Stage Two pH drop
Figure 4-36: Plot of Stage One pH drop downcurrent of the four particle group release scenarios in an ambient crossflow of 0.40 m/s, as a function of the downcurrent distance.

Figure 4-37: Plot of Stage Two pH drop downcurrent of the four particle group release scenarios of Figure 4-33.
Figure 4-38: Plot of Stage Two pH drop downcurrent of the four particle group release scenarios of Figure 4-34.

The resulting plumes in Stage 2 shown in Figures 4-37 and 4-38 shows regions of higher pH drop. These plumes may contain up to a quarter of the total mass loading for weaker current and smaller particles. For example, a particle plume of 100 kg/s comprising of particles of similar size as those observed in the field (2.5 cm diameter) will have over a quarter of its original mass loading trapping at around 1500 m, and shows pH drops of > 0.3 within 15 km downstream. Meanwhile for the same plume, the separated particles in Stage One have attained a pH drop of less than 0.1 after about 5000 m downstream.

4.7 Conclusions

Numerical simulations of partially reacted hydrate composite particles in quiescent and a crossflow situation indicate the following:

- Plumes of low hydrate conversion (but sufficient to impart negative buoyancy) descend to about 40% of the depth attained by pure hydrates due to the solute density effect.
• Plumes are beneficial for smaller particles (similar to those created in the field to date) and will enhance sinkage by about a factor of 10 if scaled to meet the sequestration needs of one power plant (100 kg/s CO$_2$).

• Plumes composed of larger particles have a smaller plume effect for a given mass loading, but they are less affected by crossflow currents.

• Having a range of particle conversions and sizes in a strong crossflow may enhance dilution due to differential settling of the individual particles. However, a current could cause separation of the plume resulting in a significant fraction of the CO$_2$ to linger at around the separation depth.

• Dilutions of added DIC due to the separated particles causes pH drops to fall to less than 0.1 units beyond around 2-5 km downcurrent. For the separated continuous phases on the other hand, the pH drops fall below 0.1 only after about 15 km downcurrent.
Chapter 5

Shrouded plume release

5.1 Abstract

An additional approach to promoting hydrate particle plume sinkage involves constructing a shroud around the particle source to shelter the plume from effects of ambient stratification and current. The shroud also serves as an inverted chimney, inducing a down draft that will transport the dissolving particles to a depth of lower ambient disturbance. The induced draft, and thus dilution of dissolved CO₂ emerging from the bottom of the shroud, depends on the shroud length and diameter, as well as the particles’ buoyancy and size. Laboratory measurements using particle image velocimetry (PIV) are compared to an idealized chimney that is long, frictionless and is driven by a single phase source of buoyancy distributed uniformly over the chimney base. Results indicate that the efficiency is dependent on the ratio the slip velocity of the dispersed phase compared to the idealized average induced draft velocity: the faster the particles fall in relation to the surrounding fluid, the lower the chimney efficiency.

5.2 Introduction

Our study was motivated by the field injections of solid CO₂ hydrate particles into the ocean at depths of 1000 to 1500 m in order to assess their effectiveness
for sequestering anthropogenic CO₂ from the atmosphere. It is feared that rising concentrations of greenhouse gases in the atmosphere will cause adverse changes in the climate, and that two-thirds of the change will be attributed to CO₂ (Herzog et al. [29]). There is ongoing study of carbon dioxide hydrates as a possible vehicle for deeper ocean carbon sequestration, because they are denser than seawater, and will sink unaided while dissolving to promote dispersion in the ocean. The hydrate particles were created using a CO₂-seawater coflowing injection apparatus, developed to create cylindrical composite particles, comprised of CO₂ hydrate, liquid CO₂ and seawater (Lee et al. [40]). Field tests were conducted on three occasions with differing co-flow injectors developed by ORNL in collaboration with the Monterey Bay Aquarium Research Institute (MBARI) (Tsouris et al. [69], Riestenberg et al. [56], Tsouris et al. [70] and Tsouris et al. [71]). The latest field observations show that the particles produced are long (up to a few meters in length), curved cylinders that descend with Reynolds number of about 1000, and shrink at a constant rate (refer to Figure 1-11 from Chapter 1).

Numerically predicted depths of sinking for composite particle plumes of different diameters and reactor efficiencies were made for CO₂ injection rates of 0.01-1000 kg/s. Results showed that, for a CO₂ release of 100 kg/s in a quiescent ambient, a plume composed of 2.2 cm diameter composite particles with 16% reaction efficiency would sink about 1000 m, about 10 times the individual particle sinking depth. A plume composed of similar particles, but with a diameter of 5 cm, would sink about 2000 m (~5 times individual particle sinkage), while plumes composed of larger particles, or particles exhibiting higher reaction efficiency, would reach the seafloor (as would the individual particles).

5.3 Background

As discussed in Chapter 4, the release of particles in a plume enhances sinking and dilution compared with individual particles. However, two ambient effects reduce the performance of a plume: ocean currents and stratification. Plume sinkage is hampered
by strong ambient stratification which causes trapping at intermediate depths below release. Figure 5-1 shows that a remarkably weaker density stratification is found at depths below 1500 m throughout the ocean. From the perspective of reduction of plume trapping, the deeper regions of the ocean are thus potentially favorable for depositing CO₂.

Figure 5-1: Plot of potential density versus depth for 3000 different locations (shown in inset map). Data taken from the World Ocean Circulation Experiment (WOCE) [59]
Ambient ocean currents are known to cause a different type of phase separation, whereby the continuous fluid in the plume is swept downstream of the particles which sink more directly. Figures 5-2 and 5-3 show that typical ambient ocean currents could range from 0-40 cm/s and are more variable with depth and global position than the ambient density profile. As discussed in Chapter 4, a plume release in the presence of a crossflow current may be prone to plume separations, and in a typical current will result in lower dilution and sinking depths. This chapter discusses the possible use of a shroud that could prevent such separations.

Figure 5-2: Plot of typical ambient ocean currents in an area of the North Atlantic Ocean. Upper left - area of measurements (Longitude 50-70° W, Latitude 20-32° N); upper right - points showing the northerly (V) and easterly (U) current velocity values at each measurement point; lower left - ambient current velocity (denoted here as $U_s$) as a function of water depth; lower right - ambient current velocity as a function of latitude. Data taken from the World Ocean Circulation Experiment (WOCE) [59]
Figure 5-3: Plot of typical ambient ocean currents in an area of the South Atlantic Ocean. Upper left - area of measurements (Longitude 15-25° W, Latitude 20-30° S); upper right - points showing the northerly (V) and easterly (U) current velocity values at each measurement point; lower left - ambient current velocity (denoted here as $U_s$) as a function of water depth; lower right - ambient current velocity as a function of latitude. Data taken from the World Ocean Circulation Experiment (WOCE) [59]
5.3.1 Shroud definition

Figure 5-4 shows a schematic of a shroud, or an inverted chimney, that could be constructed around a plume release in order to reduce the two ambient effects. The shroud, intended to be stationary and fixed, is of length $h$ below the plume release and diameter $d$. As the particles are released into the shroud, the particles induce a down draft from the ambient seawater at the top of the shroud. Releasing particles into a stationary shroud will therefore negate the effects of an ambient current and density stratification, delivering the sinking particles to their intended depth.

![Figure 5-4: Schematic of shrouded release (inverted chimney). Left: before - plume affected by ambient current and stratification. Right: after - plume released in shroud, creating a down draft $Q$.](image)
5.3.2 Ducted flows

This section outlines some past applications of confined duct flow similar to a shroud that promote dilution and transport.

Jet diffuser arrays

Adams 1982 [2] and Parr and Melville [53] studied two dimensional jet diffuser arrays for thermal discharges into a water body. The flow is momentum induced and two dimensional and the sources are distributed over the cross section. The construction of a duct or shroud around the source points reduces contraction of the jets, encouraging a larger dilution.

Water jet pumps

Silvester [60] and Argaman et al. [6] studied the momentum induced, 3D axisymmetric discharge from a central submerged sewage source. A shroud is introduced to set up a pressure gradient and to lengthen the plume trajectory, increasing horizontal momentum and dilution of the effluent. The situation is akin to a water jet pump and results in enhanced dilution compared with a free jet especially if the entrance loss is reduced by building a flared opening. Dilution increases with the square root of the ratio between the shroud and the nozzle diameter.

Chimneys/Cooling towers

Buoyant chimneys and cooling towers have been used since antiquity to set up a pressure gradient to induce a draft, either for drawing in oxygen to sustain a fire as in the former, or to remove heat as in the latter. The flows are buoyancy induced, usually with the buoyancy source distributed over cross section. Cooling towers are usually hyperbolic in shape partly to reduce entrance losses, but also because the shape offers structural integrity under wind forcing with a small volume of construction material (Cheremisinoff [14]).
Buoyant gas lift pump

Air lift pumps are commonly used to induce an upward flow using a highly buoyant second phase. The pumps are buoyancy induced, 3D axisymmetric releases, with sources distributed over cross section. The flow through ducts by bubbles has been well investigated with applications flow of droplets in vertical pipes. The dispersed phase size is also dependent on the flow conditions and therefore the dispersed phase velocities are not known a priori (Wallis [74]). Govier et al. [25] report different regimes of flow (bubbly flow, slug flow, annular flow) due to the relative flow rates of the dispersed and continuous phases. Kajishima et al. [37] and Adams et al. [4] have also studied the use of the gas lift pumps in the present context of dissolving CO$_2$ droplets for ocean carbon sequestration whereby the CO$_2$.

5.4 Ideal shroud

Our release for hydrates is a buoyancy induced, downward flow that is to be shielded from ambient effects using a shroud. In this section we assume an ideal case where a single phase, negatively buoyant source is distributed uniformly across the top of the chimney. In addition, there is no friction within the shroud interior. The shroud is a wide fixed vertical pipe with constant cross sectional area $A$, diameter $d$ and height $h$ below the release (refer to the right hand panel of Figure 5-4). A Bernoulli equation for flow along a streamline entering the shroud yields

$$\frac{\Delta p}{\rho_w g} = \frac{1}{2} \frac{u_{\text{shroud}}^2}{g} (1 + K)$$

(5.1)

where $u_{\text{shroud}}$ is the mean induced velocity $u_{\text{shroud}} = \frac{Q}{A}$, $\rho_w$ is the ambient fluid density, $g$ is gravity and $\Delta p$ is the pressure difference between the inside and outside of the bottom of the shroud. $Q$ is the flow rate induced by the shroud. $K$ is an entrance loss coefficient for the shroud. Mays [42] discusses entrances losses for a range of fittings and valves. For example, $K = 1$ for an reentrant orifice (e.g. a Borda mouthpiece) and $K \sim 0$ for a flared entrance.
The pressure difference driving the flow ($\Delta p$ in the LHS of Equation 5.18) can be taken as the excess weight per unit area of the column of denser fluid (density difference $\Delta \rho$) within the shroud:

$$\Delta p = \frac{1}{A} \int_0^h \Delta \rho g Adz$$

$$= \Delta \rho gh$$  \hspace{1cm} (5.2)

Substituting Equation 5.2 into Equation 5.18, and using $B = \frac{\Delta \rho g Q}{\rho_w}$ for the kinematic buoyancy flux and $Q = u_{\text{shroud}} A$,

$$\frac{\Delta \rho gh}{\rho_w g} = \frac{1}{2} \frac{u_{\text{shroud}}^2}{g} (1 + K)$$

$$Bh = \frac{1}{2} \frac{Q^2}{A^2} (1 + K)$$  \hspace{1cm} (5.3)

which yields the expression for the induced flow rate:

$$Q = \left( \frac{2BA^2h}{1 + K} \right)^{\frac{3}{2}}$$  \hspace{1cm} (5.4)

For a straight shroud opening the entrance loss coefficient can be taken as $K = 1$, yielding a relation for the theoretical shroud induced flow $Q = Q_{\text{theo}}$:

$$Q_{\text{theo}} = \left( BA^2h \right)^{\frac{3}{2}}$$  \hspace{1cm} (5.5)

The shroud induced draft therefore increases with cross sectional area and shroud length, i.e. a wider and taller shroud will induce more flow.
5.4.1 Comparison with free plume

A free plume of the same buoyancy in a quiescent unstratified ambient will have a flow rate at the depth of the shroud exit in the following form (Fischer et al. [24]):

\[ Q_{free} = 0.15B^{\frac{1}{3}}z^{\frac{2}{3}} \quad (5.6) \]

Taking the ratio of the free plume flow rate and the induced flow from an theoretical chimney,

\[ \frac{Q_{free}}{Q_{theo}} = \frac{0.15B^{\frac{1}{3}}z^{\frac{2}{3}}}{B^{\frac{1}{3}}h^{\frac{1}{3}}A^{\frac{2}{3}}} = \frac{0.15z^{\frac{2}{3}}}{h^{\frac{1}{3}}(\frac{\pi}{4}d^2)^{\frac{2}{3}}} = 0.18 \left(\frac{h}{d}\right)^{\frac{4}{3}} \left(\frac{z}{h}\right)^{\frac{2}{3}} \quad (5.7) \]

The outlet plume flow rate for both cases is given by \( z = h \)

\[ \left| \frac{Q_{free}}{Q_{theo}} \right|_{z=h} = 0.18 \left(\frac{h}{d}\right)^{\frac{4}{3}} \quad (5.8) \]

Solving for \( Q_{free}/Q_{theo} = 1 \), the idealized flow for a chimney induced draft \( Q_{theo} \) exceeds that of a free plume where the aspect ratio \( h/d \) less than about 3.7. A plot with theoretical induced flow normalized by \( Q_{theo} \) is shown in Figure 5-5. Most significant is that a shroud with aspect ratio \( h/d > 3.7 \) is predicted to create a smaller entrainment flow than a free plume. However, a free plume in stratification and cross current also may not perform as well as \( Q_{free} \). In addition, for \( h/d < 3.7 \) wall effects from the short shroud can also be expected to affect the free plume behavior.
5.5 Non-ideal shroud

5.5.1 Effect of central buoyancy source

The flow predicted by Equation 5.5 applies to a buoyancy source that is distributed evenly across the top of the chimney. In scenarios where the buoyancy source is released from a central port, the suction near the top of the chimney is less than in the ideal case as the plume itself has not yet spread over the cross section.

Observations of single phase turbulent plumes show that the top hat plume width increases linearly with vertical distance, with a proportionality constant of about 0.2. Using the approach of Equation 5.2, the pressure difference at the top of the shroud now becomes

\[
\Delta p = \frac{1}{A} \int \Delta \rho g A dz \\
= \frac{g}{A} \int \Delta \rho_{plume} A_{plume} dz + \frac{g}{A} \int \Delta \rho_w (A - A_{plume}) dz \tag{5.9}
\]
Since the density difference of the water is \( \Delta \rho_w = 0 \), Equation 5.9 becomes

\[
\Delta p = \frac{g}{A} \int \Delta \rho_{\text{plume}} A_{\text{plume}} dz
\]

(5.10)

From here let \( \Delta \rho = \Delta \rho_{\text{plume}} \). The cross sectional area of the plume accounting for plume width growth is given by

\[
A_{\text{plume}} = \begin{cases} 
A & 0.2z \geq d \\
A \left( \frac{0.2z}{d} \right)^2 & 0.2z < d
\end{cases}
\]

(5.11)

The entrance pressure difference is therefore

Case \( 0.2h < d \) (or \( h/d < 5 \))

\[
\Delta p = \frac{g}{A} \int \Delta \rho_{\text{plume}} dz = \frac{g}{A} \int \Delta \rho A \left( \frac{0.2h}{d} \right)^2 dz
\]

\[
= \Delta \rho g \int_0^h \left( \frac{0.2h}{d} \right)^2 dz
\]

\[
= \Delta \rho g \left( \frac{0.2h}{d} \right)^2 \frac{h}{3}
\]

(5.12)

Case \( 0.2h \geq d \) (or \( h/d \geq 5 \))

\[
\Delta p = \frac{g}{A} \int \Delta \rho_{\text{plume}} dz = \frac{g}{A} \int_0^{0.2h} \Delta \rho A \left( \frac{0.2h}{d} \right)^2 dz + \frac{g}{A} \int_{0.2h}^h \Delta \rho Adz
\]

\[
= \Delta \rho g \frac{d}{3} \frac{0.2}{0.2} + \Delta \rho g \left( h - \frac{d}{0.2} \right)
\]

\[
= \Delta \rho g \left( h - \frac{d}{3\alpha} \right)
\]

(5.13)

Substituting both cases into Equation 5.18:

Case \( 0.2h < d \) (or \( h/d < 5 \))

\[
\frac{\Delta \rho g \left( \frac{0.2h}{d} \right)^2 \frac{h}{3}}{\rho g} = \frac{1}{2} \frac{u^2}{g} (1 + K)
\]
\[ 2BA^2 \left( \frac{0.2h}{d} \right)^2 \frac{h}{3} = Q^3(1 + K) \]  \hspace{1cm} (5.14)

Case \(0.2h \geq d\) (or \(h/d \geq 5\))

\[
\frac{\Delta \rho g}{\rho g} \left( h - \frac{d}{3a} \right) = \frac{1}{2} \frac{u^2}{g} (1 + K) \\
2BA^2 \left( h - \frac{d}{3a} \right) = Q^3(1 + K) \hspace{1cm} (5.15)
\]

Normalizing the two new predicted flows (Equations 5.14 and 5.15) by \(Q_{\text{theo}}\), using 
\(K = 1\), results in the efficiency of the shroud with a central buoyancy source as a function of aspect ratio \(Q_c/Q_{\text{theo}}\):

\[
\frac{Q_c}{Q_{\text{theo}}} = \frac{Q_c}{(BA^2 h)^{\frac{1}{3}}} = \begin{cases} 
\left( \frac{1}{3} \left( \frac{0.2h}{d} \right)^2 \right)^{\frac{1}{3}} \frac{h}{d} & \frac{h}{d} < 5 \\
\left( 1 - \frac{2}{3} \frac{1}{0.2h} \right)^{\frac{1}{3}} & \frac{h}{d} \geq 5
\end{cases} \hspace{1cm} (5.16)
\]

Figure 5-6 plots shroud efficiency as a function of aspect ratio, for a plume released from a central source.

![Figure 5-6: Plot of normalized \(Q_c\) with shroud aspect ratio.](image)

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Images showing the qualitative behavior of shrouds of different aspect ratios are shown in Figures 5-9 - 5-11.

Since at aspect ratios lower than about 5, we do not expect the plume to fill the shroud cross section, the flow is more likely to behave like a free plume (refer to Section 5.4.1). Moreover, the confinement of the shroud near the top may cause Coanda effects whereby the plume interacts with the shroud forming a "wall plume". This non-ideal behavior suggests that both $Q_{\text{free}}$ and $Q_{\text{theo}}$ are upper bounds for the flow induced at the respective ranges of $h/d$. 
5.5.2 Effect of pipe friction

In a real shrouded plume release scenario, the flow through the shroud interior is subjected to pipe friction that increases with the shroud height. A Darcy-Weisbach friction factor is commonly used to define the pipe head loss in a pipe (shroud) as

\[ h_{pipe} = f \frac{h u_{shroud}^2}{d} \frac{2g}{2g} \]  

(5.17)

Incorporating the effect of friction, the formulation of the pressure head balance (Equation 5.18) becomes

\[ \frac{\Delta p}{\rho \omega g} = \frac{1}{2} \frac{u_{shroud}^2}{g} (1 + K + f \frac{h}{d}) \]  

(5.18)

A value for \( f \) can be determined from a Moody diagram based on the Reynolds number and relative roughness. The Reynolds number of the induced flow based on the shroud diameter and \( Q_{theo} \) ranges from 5000-10000. Using a roughness range of \( 10^{-6} \) (essentially smooth) to 0.02 (a conservatively high value: 2% of the shroud diameter ) for this range of \( Re \), \( f \) will vary from 0.03 (for smooth full flow) to 0.055 (Mays [42]).

With pipe friction the induced draft (distributed single phase buoyancy source), denoted \( Q_f \), becomes:

\[ Q_f = \left( \frac{1 + K}{1 + K + f \frac{h}{d}} A^2 B h \right)^{\frac{1}{3}} \]  

(5.19)

Taking the ratio of the prediction of the induced draft with and without friction yields

\[ \frac{Q_f}{Q_{theo}} = \left( \frac{(1 + K)}{(1 + K + f \frac{h}{d})} \right)^{\frac{1}{3}} \]  

(5.20)

Note that the ratio given by Equation 5.20 can apply to a central or distributed plume source. Figure 5-7 illustrates the reduction in efficiency of the shroud with increasing friction.
5.6 Effect of buoyant particle size

Instead of a single phase buoyancy analyzed above, our release scenario involves a negatively buoyant solid phase (CO$_2$ hydrates). This section details the potential effect of negatively buoyant particles on the induced shroud draft.

5.6.1 Dimensional analysis

The induced draft by buoyant particles in a shroud $Q$ depends on the following physical quantities: the shroud height $h$, shroud diameter $d$, the initial kinematic buoyancy $B$, and buoyant particle slip velocity $u_s$ which embodies particle characteristics (density, diameter, inter-particle separation distances with a given buoyancy).

$$Q = f(h, d, B, u_s)$$  \hspace{1cm} (5.21)

The entrance loss coefficient $K$ can also be a variable in the above functional dependence but in the analysis below we take $K = 1$ to study a cylindrical shroud only.
From dimensional analysis three non-dimensional quantities may be used, yielding the following relation:

\[
\frac{Q}{Q_{\text{theo}}} = f \left( \frac{h}{d}, \frac{u_s}{u_{\text{theo}}} \right) \tag{5.22}
\]

where the theoretical induced draft is given by

\[
Q_{\text{theo}} = (BA^2h)^{\frac{1}{3}} \tag{5.23}
\]

\[
A = \pi d^2/4 \]

is the shroud cross sectional area and \( u_{\text{theo}} \) is the theoretical mean shroud induced fluid velocity, equal to \( Q_{\text{theo}}/A \).

### 5.6.2 Onset of plume behavior

The presence of the term \( u_s/u_{\text{theo}} \) in Equation 5.22 has implications on whether the groups of particles are interacting with each other to form a plume. The numerical predictions from and Chapter 4 and the theoretical analysis presented earlier in the chapter assume that the resulting release will behave as a turbulent plume, regardless of particle number frequency and size.

Table 5.1 shows that the expected particle release rates for the field particles and scaled-up field particles could range from 130 to 2800 particles per second. The number release rate can be translated to an estimated particle spacing by dividing the particle number rate by the slip velocity. While the particles are closer than 10 particle diameters and are therefore expected to interact with each other (refer to Section 3.9), the particle spacing can vary by a factor of 30 (0.03 to 1 particle diameters) for different particle sizes. Therefore we are interested in the effect of particle size on the induced flow.
Table 5.1: Predicted particle number release rates and particle spacing for field and scaled-up field particles from Table 3.3 in Chapter 3.

5.6.3 Plume spreading

One consequence of increased slip velocity on a plume is the effect on plume spreading. The above discussion assumes that the spread of particles is the same as that of a continuous phase tracer in a regular single phase plume (entrainment coefficient \( \alpha \sim 0.1 \)). In reality particles (or bubbles) or in a multi-phase plume will only occupy a central core which is smaller than the liquid portion of the plume, as has been observed by Milgram [46] and Asaeda and Imberger [7]. For bubble plumes, Socolofsky and Adams [65] obtained a relation between the plume spreading ratio (width of bubbles versus total plume width, \( \lambda \)) as a function of the bubble characteristics, by measuring the edge of the inner particle core with a dyed edge of the plume fluid. They found

\[
\lambda = 1 - 0.19U_N^{0.61}
\]  

(5.24)

where \( U_N = u_s/(BN)^{1/4} \) is the slip velocity, normalized by a characteristic plume speed in stratification. We can use a similar non-dimensional slip velocity, this time in the following form:

\[
\frac{u_s}{u_{theo}} = \frac{u_s}{Q_{theo}} = \frac{u_s}{(BN)^{1/3}}
\]  

(5.25)

The plume spreading ratio is taken into account in the predictions by replacing
0.2 with 0.2λ in Equation 5.16 to give

\[
\frac{Q}{(BA^2h)^{\frac{1}{3}}} = \begin{cases} 
\frac{1}{3} (0.2\lambda)^2 \left(\frac{h}{d}\right)^2 & \frac{h}{d} < \frac{1}{0.2\lambda} \\
1 - \frac{2}{3} (0.2\lambda) \frac{d}{h} & \frac{h}{d} \geq \frac{1}{0.2\lambda}
\end{cases}
\]  

(5.26)

where we adapt Equation 5.24 for the plume spreading ratio

\[
\lambda = 1 - 0.19 \left(\frac{u_s}{u_{theo}}\right)^{0.61}
\]

(5.27)

\(u_s/u_{theo}\) values for our experiments ranged from 0 - 3.8, resulting in \(\lambda\) values of about 0.57 - 1 using Equation 5.27. Figure 5-8 shows the reduction of the shroud efficiency as a result of both friction and a reduced plume spreading rate corresponding to \(\lambda = 0.5\).

![Plot of normalized plume flow rate including friction (f = 0.055) and accounting for reduced plume spreading with \(\lambda = l = 0.5\)](image)

Figure 5-8: Plot of normalized plume flow rate including friction (\(f = 0.055\)) and accounting for reduced plume spreading with \(\lambda = l = 0.5\)

The above analysis assumes that the particles in the plume, although behaving less like the continuous phase, are still part of a turbulent plume. For more sparsely spaced particles, the induced flow of the shroud may be further decreased. This is explained in the following sections experimentally.
5.7 Experimental measurements

The purpose of the experiments is to determine whether a shrouded plume indeed induces a draft, and whether aspect ratio and particle size affect shroud efficiency as discussed in the previous sections.

The main apparatus for the experiments is an experimental tank in the R. M. Parsons Lab at MIT with dimensions 1.22 m by 1.22 m by 2.44 m tall (Figure 2-3 in Chapter 2). Shrouds were constructed of PVC pipes or rigid sheets of plastic rolled into a cylindrical shape. The shrouds ranged in diameter from 7.5 cm to 30 cm and ranged from 30 cm to 157 cm. The aspect ratios used were from \( h/d = 1 - 21 \). The shrouds were suspended in the tank by four strings from the four top corners of the tank. In order to reduce spurious effects from either the water surface or the bottom of the tank the top of the shroud was always at least 3 diameters from the surface and the bottom of the shroud was at least 3 diameters from the tank bottom.

5.7.1 Buoyancy sources

Four buoyancy sources were used: brine, small glass beads and plastic balls of two different densities (made by filling hollow polystyrene spheres with brine and molasses). The glass beads used were Ballotini impact glass beads (From Potters Industries), available in various sizes, used for finishing smooth metal surfaces in industry. Table 5.2 shows the characteristics of the four buoyancy sources. The size distribution of the small glass beads and polystyrene seeding particles were obtained by sieve analysis and their slip velocities calculated by an empirical relation based on a spherical particle by Dietrich [22] (also refer to Clift et al. [18] and Chow [16]).

For the balls, the slip velocity \( U \) was obtained by releasing the particles into the tank and measuring the time taken to cross a start and finish line, as described in Chapter 2. The corresponding particle buoyancy flux is obtained using the slip velocity and the number flow rate \( \dot{N} \), both measured using experimental images:
\[
B = \frac{\Delta \rho}{\rho_w} g Q_0 \\
= \frac{\Delta \rho}{\rho_w} g V_{ball} \dot{N}
\]  
(5.28)

where \( V_{ball} \) is the ball volume. Using the balance of buoyancy and drag force, 
\[
\frac{\Delta \rho}{\rho_w} g V_{ball} = \frac{1}{2} C_D A_{ball} U^2,
\]
where \( A_{ball} = \pi d^2/4 \) is the projected ball surface area and \( C_D(d, U) \) is the drag coefficient for a sphere taken from Clift et al. [18]. The buoyancy flux can be expressed as

\[
B = \frac{1}{2} C_D A_{ball} U^2 \dot{N} = \frac{1}{2} C_D \left( \frac{\pi d^2}{4} \right) U^2 \dot{N}.
\]

Equations 5.28 and 5.29 can then be used to calculate the density difference of the particle.

<table>
<thead>
<tr>
<th></th>
<th>( \rho ) (kg/m(^3))</th>
<th>( d ) (mm)</th>
<th>( u_s ) (cm/s)</th>
<th>Typical ( N ) (particles/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std. dev.</td>
<td>Mean</td>
<td>Std. dev.</td>
</tr>
<tr>
<td>Brine</td>
<td>1100-1360</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Beads</td>
<td>2450</td>
<td>0.15</td>
<td>0.016</td>
<td>1.2</td>
</tr>
<tr>
<td>Ball (low density)</td>
<td>1050</td>
<td>18.8</td>
<td>0.05</td>
<td>21.3</td>
</tr>
<tr>
<td>Ball (high density)</td>
<td>1180</td>
<td>18.8</td>
<td>0.05</td>
<td>33.0</td>
</tr>
<tr>
<td>Polystyrene (PIV seeding particles)</td>
<td>1050</td>
<td>0.32</td>
<td>0.027</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 5.2: Buoyancy sources used in shroud experiments, with typical particle number release rates \( \dot{N} \).

The release mechanisms for each buoyant discharge type are described in Appendix A. For consistency we sought a constant initial buoyancy flux \( B \) among the experiments. Actual initial buoyancy fluxes for the experiments had a mean of \( B = 1530 \text{ cm}^4/\text{s}^3 \), standard deviation \( 470 \text{ cm}^4/\text{s}^3 \) (31%). Since the measured flow rates are normalized by \( Q_{theo} \) which includes \( B \), the variation in \( B \) is not of importance.
5.7.2 Qualitative behavior

Figures 5-9 to 5-12 show images of the steady buoyant releases in shrouds of different aspect ratios ($h/d = 2, 4$ and $10$). Due to the thickness of the transparent PVC of the shroud, the actual plume widths within the shroud cannot be measured quantitatively, but inspection shows that the plume does spread to fill the shroud cross section by about 4 or 5 shroud diameters. Figure 5-12 shows that by 10 shroud diameters, brine and bead plumes are fully spread over the shroud cross section.

Conversely, Figure 5-9 for $h/d = 2$ shows a plume that has clearly not completely spread over the cross section. Although not discerned in the figure, some releases showed evidence of the Coanda effect, with the plume attaching to one side of the shroud walls at random. The right hand panels of each figure show the release of the heaviest particles. Although a plume effect is not immediately apparent in these figures, typical particle spacings for the balls shown were about 8.4 diameters, close enough for particles to interact with each other for group behavior, as described in Section 3.9 from Chapter 3. As a result, the ball releases do show a significant induced flow.

![Figure 5-9: Buoyant releases in a shroud of aspect ratio $h/d = 2$. Each release is of comparable initial kinematic buoyancy flux $B$. Left: dyed brine release; center: glass bead release; right: high density ball release.](image)
Figure 5-10: Buoyant releases in a shroud of aspect ratio $h/d = 4$. Left: dyed brine release; center: glass bead release; right: high density ball release.

Figure 5-11: Buoyant releases in a shroud of aspect ratio $h/d = 10$. Left: dyed brine release; center: glass bead release; right: high density ball release.
Figure 5-12: View from the shroud exits of aspect ratio $h/d = 10$ to show plume spreading over their cross sections (Same shrouds as Figure 5-11)

5.8 Particle image velocimetry

Particle Image Velocimetry (PIV) was used to measure the induced flows into the shroud for all particle and brine releases, and is described below.

5.8.1 Equipment

Images of the shroud flow were taken with a Prosilica EC640 1/2 inch CMOS Firewire (IEEE1394A) camera with resolution 659x493 pixels and a maximum frame rate of 100 frames per second. This interfaced with MATLAB (The MathWorks, Natick, Massachusetts) and the Image Acquisition toolbox using a generic DCAM driver for MATLAB. In order to force the camera to accept user-defined exposure times on the camera, the images taken were set to 648 $\times$ 485 pixels. Using this method of interfacing the maximum frame rate for the camera was 77 frames per second. Timestamps of each image were made with each image acquired, and were used to determine the time elapsed between frames. Typically 900 to 2400 images were taken in succession with a frame rate of about 50 frames per second (limited by the memory available on the computer), resulting in a velocity record of 18-48 s of the duration for each shroud experiment.

In order to illuminate a slice of the flow into the shroud, a vertical laser light sheet with thickness of about 0.5 cm was directed radially into the center of the shroud.
The laser used was a Coherent Innova 70 Argon-ion laser at 4 Watts continuous output power, attached to a long (25 foot) optical fiber. A cylindrical lens affixed at its end created the light sheet. Polystyrene seeding particles of average diameter 315 microns obtained by sieve analysis (corresponding to slip velocity of 0.17 cm /s using the equation of Dietrich [22]) were used to seed the flow for the laser (refer to Table 5.2 and Chow [16]).

5.8.2 PIV Velocity determination

Particle image velocimetry (PIV) has been used extensively as an unobtrusive method to measure instantaneous flow fields. For the experiments, MATPIV was used in conjunction with MATLAB. Gui and Merzkirch [26] analyzed different correlation methods used for PIV, and concluded that the minimum quadratic difference (MQD) method is best for images with non-uniform lighting.

The basic algorithm for determining the displacement of particles between two images is as follows. The two images are split into numerous regions of interest (ROIs), each of which is used to determine the fluid velocity at the center of the ROI. Let each ROI have a size $M \times N$ pixels. The intensity of pixels in the ROI in the first image (intensity $a_1$) is compared to the corresponding pixels of an ROI in the second image (intensity $a_2$) that is of the same size ($M \times N$ pixels) but displaced by $(m \text{ and } n)$ pixels in position from the first. The square of the differences of corresponding individual pixel intensities is added up over the ROI, and the result is normalized by the dot product $M \cdot N$. The displacement is determined by the value of $m$ and $n$ between the two ROIs that results in the minimum of the sum (a least squares fit of the displacement). The above description can be reiterated as finding the value of $m$ and $n$ which satisfies

$$\min_{m<M,n<N} \left[ \frac{1}{M \cdot N} \sum_{i=0}^{M-1} \sum_{j=0}^{N-1} [a_1(i,j) - a_2(i + m, j + n)]^2 \right]$$  \hspace{1cm} (5.30)

Figure 5-13 illustrates an example displacement determination. The result, expressed in pixels, can be converted to an instantaneous velocity using the scale of the image.
(cm per pixel) and the time elapsed between the two images (s). In the current shroud experiments the size of an ROI is $64 \times 64$ pixels. The total image size of $648 \times 485$ pixels results in many ROIs available per image to generate a velocity field as shown in Figure 5-15.

Figure 5-13: Example of a correlation of pixel displacement using the minimum quadratic difference (MQD) method. The two images at region of interest (ROI) for consecutive frames are shown in the inset. The surface plot indicates the displacement resulting in the minimum quadratic difference in the pixel intensity.
5.8.3 Induced flow determination

This section outlines the method of using the images to determine an induced flow into the shroud. Images of the top of the shroud are used (rather than images at the bottom of the shroud) due to the lower effect of the high reflectivity particles on the image contrast in the former. The laser illuminates a radial slice of the shroud to the center as shown in Figure 5-14.

![Example image of top of shroud for use in determining draft velocities by PIV, showing a radial slice illuminated by the laser sheet.](image)

Figure 5-14: Example image of top of shroud for use in determining draft velocities by PIV, showing a radial slice illuminated by the laser sheet.

A steady state flow field is calculated by PIV over the course of the relevant image acquisition period (shown in Figure 5-15). The determination of the steady state will be described in Section 5.8.4.

Figure 5-16 shows the rectangular 2D control volume used to determine the flow entering the shroud. The control volume is bounded by the injection pipe with radius $R_0$, and has the same radius as the shroud $R = d/2$, and a height $H$ extending immediately above the shroud. Assuming axisymmetry, the value of $Q$ is determined by integrating the velocities crossing into control volume and around the shroud:
Figure 5-15: Steady state flow field calculated by PIV over shroud. Pipe radius $R_0 = 1.2$ cm, Shroud radius $R = d/2 = 15$ cm, Shroud height $h = 91$ cm. Coordinate axis defined by arrows shown (positive $h$ upwards, positive $r$ away from shroud center).

\[
Q = - \left( 2\pi \int_{R_0}^{R} v(r, H) r dr + 2\pi R \int_{0}^{H} u(R, z) dz \right) \tag{5.31}
\]

$v(r, H)$ and $u(R, h)$ are the steady state values of the vertical (positive upward) and horizontal (positive in the $r$ direction) velocities. Multiple control volumes (i.e. different values of $H$) are used in each experiment to determine $Q$ (Figure 5-17).
Figure 5-16: A control volume used to measure the inflow into a shroud. The calculated velocities are integrated using Equation 5.31 to obtain a flow rate $Q$.

Figure 5-17: Multiple control volumes used per experiment to measure the inflow into a shroud.
5.8.4 Steady state velocities

Velocity measurements taken over time at a discrete point indicate that the shroud takes some time to set up a steady siphon effect following the initiation of continuous particle release. In addition, there are velocity fluctuations which indicate that the siphon effect is not constant with time, as shown in Figure 5-18. The steady state velocities were determined over periods of time after the initial velocity ramping. For the example in Figure 5-18, the steady state was attained after \( \sim 31 \text{ s} \).

Figure 5-18: Plot of the downward velocity time series at four points at the height of the lip of the shroud for one experiment, showing the ramping up of downward velocities as the siphon effect builds up after the start of the continuous particle release at time=0 seconds. Steady state was attained after about 31 s.

The time averaged velocity vector entering the different control volumes for a brine release, used for obtaining the induced flow rates \( Q \) by integration using Equation 5.31 are shown in Figure 5-19.
Figure 5-19: Steady velocities used to calculate $Q$ for one experiment. While there is only one set of horizontal velocities entering the control volumes, the top panel shows the various radial vertical velocity profiles for the different control volumes. The location of the delivery pipe is at 1.2 cm radially from the center.
Figure 5-20: Example shroud flow rate for experiment with brine. The mean induced flowrate $Q = 2150$ cm$^3$/s, standard deviation $= 25$ cm$^3$/s between the different control volumes.

Figures 5-21 - 5-23 show the same information as Figures 5-18 - 5-20, but for a ball release. Figure 5-21 shows large fluctuations in local velocities that correspond to the descent of the discrete balls into the shroud. Nevertheless, a significant induced flow was measured by taking the time-averaged velocities into the control volumes at the top of the shroud (Figure 5-22).
Figure 5-21: Plot of the downward velocity vectors along the lip of the shroud as a function of time for one experiment with a ball release.
Figure 5-22: Steady velocities used to calculate $Q$ for an experiment with a ball release. The location of the delivery pipe is at 1.8 cm radially from the center.

**Velocity measurement compared with individual particle tracking** In order to verify that the velocities calculated with PIV match those observed, velocities of groups of particles from a typical set of images were tracked by eye by measuring their individual particle displacements. The average velocity of the particles within the region of interest matched the PIV result, and the variability in the velocities determined by both methods were comparable. An example of the comparison of individual particle tracking and PIV is shown in Section B.1 in the Appendix.

**Flow measurements compared with dye dilution study** Additionally, comparison to concurrent dye studies for several experiments show that the flow rate measured by the integration of the velocities determined by the PIV method matches the flow rate computed by the dilution of dye measured by a fluorometer at the shroud bottom. The dye dilution study was found to have a similar variability as the PIV method. The details of the dye study, performed mainly with brine as the buoyant
Figure 5-23: Example shroud flow rate for experiment with balls. The mean induced flow rate $Q = 700 \text{ cm}^3/\text{s}$, standard deviation $= 20 \text{ cm}^3/\text{s}$ between the different control volumes.

phase, are included in Section B.2 of the Appendix.

5.9 Results

5.9.1 Shroud efficiency

The experimental results for the induced shroud flow rates $Q$ are presented in Figure 5-24.

The plots show that brine (a single phase flow) and beads that resemble a single phase buoyancy source, as indicated by their low non-dimensionalized slip velocity, behave very closely to the predictions.

However, releases due to larger particles are more intermittent in creating an entrainment flow into the shroud, resulting in lower performance compared to the theoretical predictions. As expected from the discussion in Section 5.6.2, the larger the slip velocity in relation to the theoretical induced flow velocity, expressed as
Figure 5-24: Plot of experimentally measured shroud flows normalized by the theoretical single phase induced flow $Q_{theo} = (BA^2h)^\frac{2}{3}$, as a function of shroud aspect ratio $h/d$. The plot has been superimposed onto Figure 5-8 which contains the various induced flow predictions. Typical standard deviations for multiple measurements of $Q$ are shown as vertical error bars.
\( u_s/u_{theo} \), the smaller the induced flow rate efficiency (Figure 5-25). Furthermore, the large balls in the shroud underperform even compared to the relation described by a two phase plume, as plotted in the line labeled \('l=0.5'\) in Figure 5-24. This suggests that the particles, though showing group effects and entraining the ambient fluid, are no longer fully plume-like.

Figure 5-25: Plot of experimentally measured shroud flows normalized by the theoretical single phase induced flow \( Q_{theo} = (BA^2h)^{\frac{1}{3}} \), as a function of the dimensionless slip velocity \( u_s/u_{theo} \). Results are from experiments of a shroud aspect ratio \( h/d = 10 \).
5.9.2 Implications for shrouded release in ocean

While results presented above show that the flow induced by shrouds of small aspect ratios are low compared with the theoretical (idealized) values, the flow is still quite large in absolute terms, as the induced flow is dependent on the shroud cross sectional area \( A \) (see Figure 5-26).

![Absolute induced shroud flowrate \( Q/Q_{\text{theo}} = 0.6 \)](image)

Figure 5-26: Plot of predicted absolute shroud flows \( Q \) as a function of aspect ratio, for a shroud efficiency of \( Q/Q_{\text{theo}} = 0.6 \). For \( h/d < \sim 4 \) the induced flow at the shroud exit is the same as that of a free plume.

Table 5.3 shows values of \( u_s/u_{\text{theo}} \) for experimental particle releases and for potential field scale hydrate releases, which lie in a comparable range. From the previous section, on the high density balls showed reduced plume-like behavior. In order for the shrouded plume to show reduced plume behavior at the scale of the '2006+++' hydrate release, the slip velocity of the particles would need to be about 40-50 cm/s as compared with a calculated value of 26 cm/s. We concluded that scaled up hydrate particle releases are most likely to behave like a plume. Despite the reduced
plume-like behavior, the induced flow is still predicted to be about 55-60% the value of $Q_{\text{theo}}$.

The CO$_2$ of the particles will ultimately dissolve into the dispersed phase. At the bottom of the shroud, assuming that the particles are dissolved, the added dissolved inorganic carbon (DIC) concentration $\Delta DIC$ emerging from the bottom of the shroud is determined by

$$\Delta DIC = \frac{m}{Q(h/d, u_s/u_{\text{theo}})} \tag{5.32}$$

The corresponding pH drop at the exit of the shroud are determined using the method outlined in Section 1.1. For a 100 kg/s CO$_2$ release into a shroud with diameter of 100 m and height of 1000 m, the predicted added DIC and pH drops are shown in Table 5.4.

---

Table 5.3: Typical values of $u_s/u_{\text{theo}}$ for experiments and expected values for shrouded hydrate plumes. Expected hydrate plume characteristics: 100 kg/s CO$_2$ mass loading, shroud diameter $d = 100$ m, height $h = 1000$ m. Hydrate particle characteristics are found in Table 3.2.

<table>
<thead>
<tr>
<th>Buoy source</th>
<th>Slip velocity $u_s$ cm/s</th>
<th>$B$ m$^4$/s$^3$</th>
<th>$u_{\text{theo}}$ cm/s</th>
<th>$u_s/u_{\text{theo}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiments:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brine</td>
<td>0</td>
<td>1.5e-5</td>
<td>11</td>
<td>0.00</td>
</tr>
<tr>
<td>Beads</td>
<td>1.2</td>
<td>1.5e-5</td>
<td>11</td>
<td>0.10</td>
</tr>
<tr>
<td>Ball (low density)</td>
<td>21</td>
<td>1.5e-5</td>
<td>11</td>
<td>1.76</td>
</tr>
<tr>
<td>Ball (high density)</td>
<td>33</td>
<td>1.5e-5</td>
<td>11</td>
<td>2.80</td>
</tr>
<tr>
<td>Hydrate particles:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td>4</td>
<td>0.015</td>
<td>12</td>
<td>0.32</td>
</tr>
<tr>
<td>2006+</td>
<td>6</td>
<td>0.015</td>
<td>12</td>
<td>0.48</td>
</tr>
<tr>
<td>2006++</td>
<td>8</td>
<td>0.015</td>
<td>12</td>
<td>0.64</td>
</tr>
<tr>
<td>2006+++</td>
<td>27</td>
<td>0.132</td>
<td>26</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Table 5.4: Typical dilutions achieved by shrouded hydrate plumes. Expected hydrate plume characteristics: 100 kg/s CO₂ mass loading, shroud diameter \(d = 100\) m, height \(h = 1000\) m. Hydrate particle characteristics are found in Table 3.2. Estimated shroud efficiencies obtained by inspection of the plot in Figure 5-25.

It is important to note that the pH drops listed in Table 5.4 are the average values of pH leaving the shroud and that further dilution will occur beyond the exit.

### 5.10 Conclusions

We investigated a strategy of sequestration of CO₂ hydrates by injecting them into a shroud (a tall inverted chimney). The goal of the shroud is to protect the hydrate release from ambient stratification and crossflow currents, and thus giving better control of CO₂ plume placement. Predictions based on physical arguments and experimental observations show that a long shroud will induce a draft that increases with shroud cross sectional area and shroud length. Very large particles that show reduced plume-like behavior may not be as efficient in inducing draft, but they will still induce at least half of the theoretical flow.
Chapter 6

Summary and conclusions

Liquid CO₂ can be reacted with seawater to form solid, partially-reacted sinking composite CO₂ hydrate particles comprised of CO₂ hydrate plus unreacted CO₂ and seawater. When released in the ocean at a depth of 1000-1500 m, the negative buoyancy of the composite particles causes them to sink and disperse, two qualities that make them attractive as a method to sequester CO₂ from the atmosphere. This thesis examines with fluid mechanics of such particles and attempts to determine if releasing them in large quantities (~100 kg/s of CO₂, roughly the output of one 500 MW coal power plant) is able to create sufficient dilution to minimize their impact on marine life.

We developed a drag coefficient model that is applicable to long cylindrical particles, and from which we estimated that particles created during a 2006 field study was roughly 10-20% reacted and sank ~ 100 m before completely dissolving. Larger particles of higher reaction efficiency, for example of initial diameter 15 cm and conversion of $X = 50\%$, are predicted to sink to the ocean bottom.

Ambient density stratification and currents will affect the particle descent, and in turn the dilution of dissolved CO₂. Three methods of injection of composite particles were evaluated, each with their unique merits and demerits. Table 6.1 compares the three hydrate release methods in terms of three criteria: dilution in the near field, minimum sinking depth and ease of engineering implementation.
Table 6.1: Comparison of the three hydrate particle release methods

<table>
<thead>
<tr>
<th>Method of hydrate particle release</th>
<th>Near field dilution</th>
<th>Minimum sequestration depth</th>
<th>Engineering Implementation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Towed pipe</td>
<td>Best</td>
<td>Release depth</td>
<td>Fair</td>
</tr>
<tr>
<td>Fixed pipe</td>
<td>Variable</td>
<td>Release depth</td>
<td>Easiest</td>
</tr>
<tr>
<td>Shrouded pipe</td>
<td>Fair</td>
<td>Deepest</td>
<td>Challenging</td>
</tr>
</tbody>
</table>

A towed pipe has the advantage of creating the best dilution, since the spreading of the particles is deliberately introduced by towing the source with a moving ship. Within a short distance of the release, the high dilution is able to reduce perturbations in DIC concentrations and pH to values well below thresholds that characterize marine fauna impacts. By contrast, the fixed pipe and the shrouded pipe rely on passive fluid dynamical effects, and achieve relatively less, though still good, dilutions. The other side of the coin is that ships need to be deployed and maintained constantly in order to generate the moving source. The energy and manpower expended by the potential dispatch process would make it fairly challenging to implement.

A plume released from a stationary source will create pretty good dilution, but not as much as the towed case, since it relies on passive turbulent diffusion to effect lateral spreading. Furthermore, dilution is hampered by potential separation of the continuous phase and dispersed phases of the plume when the ambient current exceeds a threshold. We developed a numerical model that approximates the effect of plume separation in the presence of crossflow and predict the downstream concentrations and changes in pH from such particle releases. For smaller particles, the plume effect enhances sinking tenfold compared to the sinking of an individual particle. However, in a strong crossflow current, plumes with smaller particles face a higher risk that up to a quarter of the mass of dissolved CO₂ will form a separate plume and trap near the release depth. Plumes with larger diameter particles will exhibit less of a plume effect compared to the individual particles (since the particles themselves sink further), but they have the advantage of being less affected by a crossflow current. While the release of hydrate particles from a stationary port is most easily implemented from an engineering standpoint, the dilutions and sequestration depths are highly dependent
on ambient conditions.

The third method involves constructing a shroud around the source to shelter the plume from effects of ambient stratification and current. The shroud also serves as an inverted chimney, inducing a down draft that transports the dissolving particles to a depth of lower ambient disturbance. The induced draft, and thus dilution of dissolved CO₂ emerging from the bottom of the shroud, depends on the shroud length and diameter, as well as the particle buoyancy and size. Laboratory measurements suggest that the shrouded hydrate release produces at least half of the draft provided by a theoretical chimney driven by a distributed source of single-phase buoyancy. The shroud release method provides the best control of the sequestration depth, since all of the particles exit through the bottom of the shroud. However, a practical implementation of the method involves constructing a fixed shroud of ~ 150 m in diameter and ~ 1500 m around the fixed release point, which could potentially be a large engineering undertaking.

The three methods all involved particles produced by hydrate reactors which have been scaled up from existing reactors tested in the field. While beyond the scope of this thesis, such scale-up is believed to be possible employing modest modification to the existing design. Furthermore, while the three methods have relative advantages and disadvantages, each method generated CO₂ dilution in the near field that is sufficient for minimal environmental impact. Ocean carbon sequestration using direct injection of sinking hydrate particles should therefore not be dismissed on the grounds of harm to marine fauna.
Appendix A

Buoyancy release mechanisms

A.1 Brine release

In order to deliver a steady flow of brine, a 6 gallon carboy was modified to become a large Mariotte siphon (Figure A-1), as described in Fischer et al. [24]. The density of the brine was determined by a hydrometer, which gives a specific gravity compared to water at 60°F to the nearest 0.001 units. The tube leading from the carboy entered the vertical PVC delivery tube into the top of the shroud.

A.2 Bead release

Figure A-2 shows a schematic of the glass particle release method. The glass beads used were Ballotini impact glass beads (From Potters Industries), available in various sizes, used for finishing smooth metal surfaces in industry. Glass beads were released from a 1 L plastic bottle by gravity. An agitator powered by a 3 V DC transformer was also placed at the top of the bottle, to facilitate steady bead flow, which was confirmed by timing the funnels’ output onto an analytical balance. The funnel rested on a PVC pipe setup, that spanned across the top of the tank as shown in Figure A-2, and that acted as a conduit for flushing water to prevent clogging in the vertical pipe. The average mass flux was determined by measuring the mass of beads dispensed over time, from which the initial kinematic buoyancy flux was calculated.
Figure A-1: Mariotte siphon used to deliver brine.
A.3 Ball release

To achieve particle densities that were close to those of hydrates, hollow polystyrene balls (density 970 kg/m³) were filled with brine and molasses to create particles of low density (1060 kg/m³) and high density (1210 kg/m³), relative to water. Both sets of balls were dispensed in the shroud using an auger mechanism made by attaching a large masonry drill bit to a 7.2-volt hand drill. The thread of the masonry bit was about 2 cm, slightly larger than the diameter of the balls. The balls were made to line up with the thread of the auger, and the auger rotated to push the balls downward. The set up schematic is shown in Figure A-3. Upstream of the auger the balls were queued up in PVC pipes which were used to feed the auger mechanism one ball at a time. To deliver a specified ball delivery rate, the drill was attached to a variable DC power supply. While keeping the voltage constant, the electrical current supplied to the drill was varied to cause the drill bit to rotate at different rates. Figure A-4
shows a plot of the particle delivery rate with electrical current. The particle delivery rates used were about 2 and 7 particles per second for the high and low density balls respectively.

Figure A-3: Schematic of auger mechanism for the release of balls.

In order to reduce the initial momentum of the balls, after leaving the auger mechanism but before descending into the shroud, the balls traveled through an elbow connector submerged under the water surface. Despite the constant flow rate observed while testing the auger delivery of particles in air, the observed particle delivery rate in water was more erratic, since each particle underwent slightly different initial conditions due to the turbulence within the delivery pipe. The actual particle release rate was therefore measured by counting particles emerging from the pipe from the images and using the image time stamps to determine elapsed time.
A.4 Initial Flow and Momentum

In a pure plume, the initial momentum and volume flow rate of the plume fluid is zero, but in practice the experimental releases introduced some momentum and initial volume flux. The initial volume flux of the plume was obtained by the sum of the flow rates of brine and/or particles at the discharge, $Q_0 = Q_{w0} + Q_{br0}$. The mean kinematic momentum flux $M$ of the particles was determined by

$$M = (u_{pipe}^2 a_{pipe})_{water} + (u_s + u_{pipe}) q_{solid}$$  \hspace{1cm} \text{(A.1)} \nonumber$$

where $u_{pipe}$ is the fluid velocity in the delivery pipe of cross section area $a_{pipe}$. Here we made two conservative exaggerations in the momentum flux: (1) the momentum of the fluid phase occupied the whole cross section of the pipe, including the area occupied by the dispersed phase; (2) the particles were already at terminal slip velocity $u_s$ at the onset relative $u_{pipe}$.

Fischer et al. [24] provides a test for the determination of whether the volume and momentum fluxes are significant to cause a buoyant jet to form rather than a pure plume. The momentum length scale which indicates the vertical distance within which the momentum and buoyancy of the release (with a negligible volume flux) are
comparable is given by

\[ l_m = \frac{M^3}{B^{1/2}}. \]  \hspace{1cm} (A.2)

where \( B = \Delta \rho g / \rho \) For \( z \gg l_m \) the flow is plume like.

The volume length scale \( l_q \) determines the regime where the initial pipe volume flux and the momentum flux are also comparable, and is determined by

\[ l_q = \frac{Q_0}{M^{1/2}} \]  \hspace{1cm} (A.3)

For the experimental releases \( l_m \) is 1-10 mm from the source, insignificant compared with the shroud depths of 30-150 cm, implying the flow is plume like. \( l_q \) is on the order of 4-26 mm, much smaller than shroud depths, suggesting negligible influence of the initial flow.
Appendix B

PIV velocity verification

B.1 PIV comparison with particle tracking

In order to verify that the velocities calculated with PIV match those observed, velocities of groups of particles from a typical set of images for one velocity vector were tracked by eye by measuring their individual particle displacements. Particles were analyzed from the entire region of interest (ROI), a 64×64 pixel square from which the PIV takes the pixel correlations for one velocity vector (Example shown in panel (a) of Figure B.1).

It was found that the variations in the individual particles within the ROI were large enough to investigate velocity differences within the ROI. Figure B.1 shows the result of particle tracking of only the particles at the top half of the ROI in a typical shroud velocity vector, and Figure B-2 shows the same using only the particles in the bottom half of the ROI. As expected, the particles in the top half of the ROI was measured to have a lower mean velocity since it is further from the buoyancy source and the lip of the shroud. While the velocity obtained for the entire ROI by PIV is 4.51 cm/s, the mean of the particle velocities of the two regions gives 4.85 cm/s, within 10% of the PIV result. The histograms of the distributions of the velocities determined by PIV and particle tracking over the same time period (panel (d) of the two figures) show that in general the particle tracking method had higher variability.
Figure B-1: Example of particle tracking comparison with PIV. (a) Location of ROI at the shroud. Particle tracking is done only for the particles in the TOP half of the ROI, while PIV is performed for the whole ROI. (b) Downward PIV velocities plotted with individual particle tracking results (crosses). (c) zoomed in image of (b) where particle tracking was performed. (d) Top: histogram of downward velocities for PIV (mean=4.51 cm/s over entire ROI); Bottom: histogram of individual particle velocities at the top half of ROI (mean=3.57 cm/s). Compare figure with Figure B-2, which shows a higher average particle tracking velocity.
Figure B-2: Example of particle tracking comparison with PIV. (a) Location of ROI at the shroud. Particle tracking was done only for the particles in the BOTTOM half of the ROI, while PIV was performed for the whole ROI. (b) Downward PIV velocities plotted with individual particle tracking results (crosses). (c) zoomed in image of (b) where particle tracking was performed. (d) Top: histogram of downward velocities for PIV (mean=4.51 cm/s); Bottom: histogram of individual particle velocities at the top half of ROI (mean=6.13 cm/s). Compare figure with Figure B.1, which shows a lower average particle tracking velocity.
B.2 Dye dilution study for shrouded plume

Dye dilution measurements were made for brine induced flow emerging from the shroud to verify that the flow rate calculated by the PIV velocities matched the observed flowrate. Rhodamine WT dye was used as a fluorescent tracer whose intensities were measured by a Rhodamine WT fluorometer, by Seapoint Sensors, Inc., of Exeter, New Hampshire. The fluorometer was connected to the Ocean Sensors, Inc., OS200 conductivity temperature and depth (CTD) probe that interfaces with the computer, and gives fluorescence voltage outputs at 7 readings per second. The intensities were converted to a dye concentration and a dilution to determine flow rates. Figure B-3 shows the calibration curve of voltage reading to concentration of Rhodamine WT. There was a linear relationship in log-log space between the concentration of the dye and the voltage registered by the fluorometer. Figure B-4 shows the corresponding dilution from the original batch of dye as a function of the voltage reading.

![Figure B-3: Calibration curve (concentration against voltage) for Seapoint Sensors fluorometer, with linear fit equation](image)

\[
\log C = 0.9816 \log V + 1.7409 \\
R^2 = 0.9993
\]
Figure B-4: Calibration curve (dilution against voltage) for Seapoint Sensors fluorometer, with best fit line.

The Rhodamine WT was dispensed by a 1 L Mariotte bottle (see Figure A-1) to maintain a constant pressure head, and was introduced inline with the brine delivery for the buoyancy source. The density of the dye solution matched the brine density for each experiment and thus was included to the initial buoyancy flux. The dye flow rate was measured for each experiment by dividing the volume of dye dispensed over the total time, and was about 1.8 ml/s.

To minimize obstructing the shroud flow, samples of the fluid traveling out of the shroud exit were pumped continuously through the fluorometer using a peristaltic pump via a flexible plastic tube. The opening of tube that fed to the fluorometer was at the center of the shroud exit, and stretched about 4 cm horizontally. Many holes were made in the plastic tube exposed to the dyed sample so that the sample was drawn with minimal disturbance from all directions at the shroud exit. The presence of the tube resulted in a time lag of the fluorometer dye reading of roughly 30 seconds.

Some experiments resulted in more steady fluorometer readings than others, as the dye dilution method relies on the constancy of the dye or brine flowrates.
Figure B-5: Example of a fluorometer time series for a shroud experiment where the fluorometer readings were steady. Upper left panel: voltage reading with time; Lower right: Dilutions calculated for steady state region of voltage readings; Upper left: corresponding flow rates. The ideal chimney flow calculated by Equation 5.5 is $Q_{theo} = 1752 \text{ cm}^3/\text{s}$; the Flow measured by dye study $= 1729 \text{ cm}^3/\text{s}$
Examples of fluorometer dye dilution measurement compared with the PIV predicted measurement for the induced flow rate $Q$ are shown in Figures B-5, B-6, and B-7.

Figure B-6: Example of an fluorometer time series for a shroud experiment where the fluorometer readings were fairly steady. Upper left panel: voltage reading with time; Lower right: Dilutions calculated for steady state region of voltage readings; Upper left: corresponding flow rates. The theoretical chimney flow calculated by Equation 5.5 is $Q_{\text{theo}} = 2156 \text{ cm}^3/\text{s}$; the Flow measured by dye study $= 2400 \text{ cm}^3/\text{s}$; Flow measured by PIV $= 2263 \text{ cm}^3/\text{s}$. 

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Figure B-7: Example of an fluorometer time series for a shroud experiment where the fluorometer readings were poor. Upper left panel: voltage reading with time; Lower right: Dilutions calculated for steady state region of voltage readings; Upper left: corresponding flow rates. The theoretical chimney flow calculated by Equation 5.5 is $Q_{theo} = 1896 \text{ cm}^3/\text{s}$; the Flow measured by dye study = 3401 cm$^3$/s
The results for six experiments with brine and bead releases using both a dye study and PIV are presented in Table B.2. They predict a similar magnitude for the induced flow, and also show a similar variability of prediction of the flow $Q$.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Buoy. Source</th>
<th>$Q_{\text{theo}}$ cm$^3$/s</th>
<th>$Q_{\text{fluor}}$ cm$^3$/s</th>
<th>$\frac{Q_{\text{fluor}}}{Q_{\text{theo}}}$</th>
<th>Quality of Fluorometer reading</th>
<th>$Q_{\text{PIV}}$ cm$^3$/s</th>
<th>Quality of PIV reading</th>
<th>$\frac{Q_{\text{PIV}}}{Q_{\text{theo}}}$</th>
<th>$\frac{Q_{\text{PIV}}}{Q_{\text{fluor}}}$</th>
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<tr>
<td>20080709a</td>
<td>Brine</td>
<td>2156</td>
<td>2400</td>
<td>1.11</td>
<td>Fair</td>
<td>2263</td>
<td>Good</td>
<td>1.05</td>
<td>0.94</td>
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<tr>
<td>20080709b</td>
<td>Brine</td>
<td>1752</td>
<td>1729</td>
<td>0.99</td>
<td>Good</td>
<td>2290</td>
<td>Good</td>
<td>1.31</td>
<td>1.32</td>
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<td>20080709d</td>
<td>Brine</td>
<td>1872</td>
<td>1484</td>
<td>0.79</td>
<td>Good</td>
<td>1567</td>
<td>Fair</td>
<td>0.84</td>
<td>1.06</td>
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<tr>
<td>20080709e</td>
<td>Brine</td>
<td>1882</td>
<td>1780</td>
<td>0.95</td>
<td>Fair</td>
<td>1929</td>
<td>Fair</td>
<td>1.02</td>
<td>1.08</td>
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<tr>
<td>20080709f</td>
<td>Beads</td>
<td>2040</td>
<td>1549</td>
<td>0.76</td>
<td>Fair</td>
<td>1527</td>
<td>Fair</td>
<td>0.75</td>
<td>0.99</td>
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<td>Average</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.08</td>
</tr>
</tbody>
</table>

The average ratio between the PIV calculated flowrate and the flowrate measured by the dye study was 1.08, which confirms that both methods are equivalent from a flow measurement standpoint.
Bibliography


