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Abstract—Disposal of captured CO₂ in the deep ocean or in underground aquifers currently is being considered as a means to control atmospheric levels of this greenhouse gas. Long-term sequestration demands that CO₂ be released at depths where water temperatures and pressures foster the formation of a solid hydrate phase. Previous theoretical and experimental studies have demonstrated that the kinetics of formation of the CO₂ hydrate can proceed rapidly, with characteristic times of the order of a second. Under certain liquid CO₂ jet discharge scenarios, hydrate formation may have important implications related to jet instability. An analysis was performed to assess the nature and magnitude of these effects. It was determined that hydrate formation may pose problems under certain discharge conditions.

1. INTRODUCTION

Efforts to stabilize greenhouse gas emissions are underway in many industrialized nations. Carbon dioxide (CO₂) currently is the most important of these gas species, due to the preponderant quantities being released into the atmosphere by anthropogenic sources—largely through the combustion of fossil fuels. While CO₂ emissions from combustors may be reduced through fuel switching and efficiency improvements, direct control technologies also are being investigated which extract CO₂ from flue gases for reuse or disposal in the deep ocean or underground.

Modeling studies [1] have suggested that captured CO₂ must be discharged at depths greater than 500 m in the ocean in order adequately to forestall return to the atmosphere. Two primary disposal scenarios have been proposed wherein liquefied CO₂ is transported from the surface via a submerged conduit and released either at intermediate depths (typically between 500 and 1,500 m) or in the abyssal zone below 3,000 m. The former scenario acknowledges the current depth limitations of undersea pipeline deployment and maintenance. Disposal in the very deep ocean was conceived as a means to avoid potential problems related to buoyancy of the liquid CO₂ effluent at depths above 3,000 m (i.e., the CO₂ will rise toward the surface as it slowly dissolves).

Since CO₂ is a non-polar substance and water is strongly polar, liquid CO₂ is only slightly soluble in seawater; consequently, CO₂ released from a submerged pipeline (typically as jets issuing through discharge orifices) is hydrodynamically unstable and will break up into a dispersed droplet phase. The dynamics of this instability determine the distribution of droplet sizes which, in turn, can impact subsequent dissolution, coalescence (or agglomeration), and transport phenomena.

Although jet instability has been investigated extensively, earlier studies do not adequately address one important aspect of the liquid CO₂-seawater system: at conditions representative of the proposed marine disposal scenarios (i.e., pressures greater than 44.5 bar and temperatures less than 283 K), a solid hydrate phase will form at the CO₂-seawater interface. The effect of hydrate formation on discharge jet instability is poorly understood. The present theoretical study was undertaken as a response to this deficiency.

Naturally occurring CO₂ hydrates in the ocean were detected in a submersible study of a hydrothermal field in the Okinawa trough [2]. A CO₂ hydrate layer was observed to form rapidly at the interface between CO₂-rich fluid (containing approximately 86% CO₂), secreted from the seafloor at depths of 1,335-1,550 m, and the surrounding 3.8° C seawater. The solid tubes which resulted were fragile and easily fractured by hydrodynamic forces, resulting in a cylindrical pattern of break up. This study demonstrated that hydrate formation can influence jet instability—in some cases precluding droplet formation.

Laboratory investigations [3,4,5] of liquid CO₂ jets in high-pressure and low-temperature water report three patterns of jet break up corresponding to different degrees of influence by the hydrate phase. At very low jet velocity, droplets form at the discharge orifice and are immediately covered with a hydrate film. These droplets easily agglomerate (but do not coalesce) at the orifice if they are not removed quickly. Higher velocities result in a cylindrical jet. Hydrate formation on the surface of this jet may proceed rapidly enough to produce a tube-like solid structure. Further increase in jet velocity leads to normal break up into droplets. These droplets will be encased by a hydrate film that can assume a snow-like quality under certain conditions [3].

Conventional instability theory and related data predict that a liquid jet discharging into another dissimilar liquid will break up into a dispersed droplet phase. Observations made in the ocean and in the laboratory, however, suggest that other break up modes are possible and may be induced by a solid hydrate phase. This study investigates the phenomena of CO₂ jet break up in the deep

ocean and attempts to provide a theoretical basis to identify situations where jet instability may be affected by hydrate formation.

2. LIQUID CO₂ JET BREAK UP IN SEAWATER

When liquid CO₂ effluent is discharged through an orifice into seawater, droplets will form as a result of interfacial instability [6]. This instability arises from interfacial tension and/or differences in the velocities of the two fluids. At low jet velocities, break up always leads to a train of uniformly-sized droplets [4,5,7]. At high jet velocities, break up produces multiple non-uniformly-sized droplets [3,4].

The present study restricts its focus to the laminar instability flow regime [6] that is characterized by jet break up leading to a uniformly-sized droplet train. For these flows, closed form relationships can be derived for important instability parameters. Although turbulent jets are clearly relevant to the marine disposal problem, the associated mathematics are prohibitively complex and will not be pursued directly here.

For laminar flow, Rayleigh's maximum-instability theory [8] applies: break up is induced by the most unstable of numerous waves that can form on the jet surface from an initial disturbance. This "most-unstable wave" is identified by a maximum-growth-rate in amplitude. Jet instability can then be characterized by a break up time, t_b , which represents the induction period experienced by a quantity of jet fluid between discharge from the orifice and the formation of droplets.

Consider a liquid CO₂ jet in seawater. In the absence of a hydrate phase, jet instability is described by the following characteristic equation [6]:

$$1 + \frac{\rho_{seawater}}{2\rho_{CO_2}} \frac{K_0(kr_0)}{K_1(kr_0)} + 2Z^2 = \rho_{CO_2}^2 (1 - \rho_{CO_2}^2) + \frac{1}{2} W_e^3 \frac{K_0(kr_0)}{K_1(kr_0)} - N_s^2. \quad (1)$$

Here, ρ_i is the density of fluid i ($i = \text{CO}_2$ or seawater); k is the dimensionless disturbance wavenumber with k the dimensional disturbance wave number and r_0 the orifice radius; K_0 and K_1 are zeroth- and first-order modified Bessel functions of the second kind; $(2\rho_{CO_2}r_0^3/\rho_{seawater})^{1/2}$ is the dimensionless growth rate in disturbance amplitude with γ the dimensional growth rate in the disturbance amplitude and σ the interfacial tension; $Z = (3\mu_{CO_2} + \mu_{seawater})/(2\rho_{CO_2}r_0)^{1/2}$ is a modified Ohnesorge number with μ_i the viscosity of fluid i ; $W_e = 2\rho_{seawater}r_0U^2/\sigma$ is the Weber number with U the jet velocity; and $N_s = (C_s/d)(d/dC)$ is an interfacial tension number with C_s and C , respectively, the solubility and concentration of CO₂ in seawater. Based on Rayleigh's maximum-instability theory, a relationship may be derived for the jet break up time [6]:

$$t_b = [\ln(r_0/\delta_0)](2\rho_{CO_2}r_0^3/\rho_{seawater})^{1/2} / \gamma_m, \quad (2)$$

where δ_0 is the amplitude of the initial disturbance and γ_m is the dimensionless maximum-growth rate of the disturbance amplitude, which may be determined from equation (1).

Examination of equations (1) and (2) indicates that jet instability is affected by the discharge parameters, U and r_0 , and by fluid properties, ρ_i , μ_i , σ , C_s , and C . Over the range of depths being considered for liquid CO₂ disposal, fluid properties do not vary greatly. It is reasonable, therefore, to estimate the magnitude to t_b by adopting representative property values for substitution into (1) and (2). At a depth of 500 m, seawater temperature at most locations outside of major currents is about 279 K. Corresponding densities of seawater and CO₂ are approximately 1030 and 895 kg/m³, respectively. The interfacial tension number, N_s may be estimated as

$$N_s = \frac{d}{dC} \frac{C_s}{C_s} = \frac{\gamma_m - \gamma_m}{C_s},$$

where γ_m and γ_m are, respectively, values of interfacial tension with and without mass transfer (between the jet and the seawater). Thermodynamic theory can be applied to estimate interfacial tension [6]. At 279 K, $\gamma = 71.23 \times 10^{-3}$ N/m and $\gamma_m = 70.09 \times 10^{-3}$ N/m. Hence, $N_s = -0.016$, indicating that the system is tension-decreasing. For jets discharging from moderately-sized orifices (say, with diameters > 1 mm), the modified Ohnesorge number, Z , is of the order 10^{-3} , which implies that the damping term in (1) (i.e., the second term on the LHS of the equation) may be neglected. With this simplification, and assuming conditions at 500 m, (1) becomes

$$\rho_{CO_2}^2 = \rho_{CO_2}^2 \frac{1.016 - \rho_{CO_2}^2 + 0.5W_e^3 K_0(kr_0)/K_1(kr_0)}{1 + 0.577 K_0(kr_0)/K_1(kr_0)}. \quad (3)$$

Equation (3) indicates that $\gamma_m = \gamma_m(\rho_{CO_2}, W_e)$. In general, γ_m increases with W_e (and, hence, with increasing jet velocity, U , and orifice size, r_0). From experiments reported in literature [6], it is

estimated that, for the CO₂/seawater system, $\ln(r_0/r_0) = 10.7$. Employing this value in (2), a representative jet break up time is given by $t_b = (1.7 \times 10^3)(r_0)^{1.5}/m$.

The preceding developments are predicated on the assumption that the formation of an interfacial, solid hydrate phase during the induction (i.e., pre-break up) period of the jet exercises a negligible influence on the amplification of surface disturbances. While, in reality, this must not be true under certain flow conditions (otherwise the unconventional break up modes noted in the preceding section could not occur), it is acceptable for the purpose of this study which, as discussed below, seeks to compare characteristic times of (unimpeded) jet break up and hydrate formation to establish regimes where the hydrate effect may be neglected or may be significant.

3. HYDRATE FORMATION AT THE CO₂-SEAWATER INTERFACE

The CO₂ hydrate is a clathrate compound having a body-centered structure formed by linkage of 46 water molecules. The clathrate has two pentagonal-dodecahedral cavities and six tetrakaidecahedral cavities. When all cavities are occupied by CO₂ molecules, the hydrate has a chemical formula of 8CO₂ • 46H₂O or CO₂ • 5.75H₂O. In reality, all cavities cannot be occupied [9], so the hydrate always contains fewer than the stoichiometric number of CO₂ molecules [10].

Hydrate formation is a physiochemical process. During this process, water molecules form a hydrogen-bonded framework (i.e., the clathrate) and CO₂ molecules enter the cavities of the clathrate as "guests." The hydrate framework is formed with geometric distortions and, therefore, the clathrate is unstable unless a large percentage of the cavities are filled with CO₂ molecules [10]. Hydrate formation at the CO₂-seawater interface can be expressed as



where n is the hydrate number ($n = 5.75$ at stoichiometric conditions). The kinetics of interfacial CO₂ hydrate formation have been investigated in previous modeling studies [11,12]. It was concluded that hydrates would form rapidly at conditions representative of the deep ocean and that the resulting solid layer would be very thin. These predictions agree reasonably well with the limited experimental results reported in the literature.

The CO₂-seawater hydrate kinetics may be characterized by a formation time, t_f , which corresponds to the period required for a solid layer to develop after a liquid CO₂ phase and seawater phase are brought into contact. The theoretical expression for the hydrate formation time is [12]

$$t_f = 6.91 \left(\frac{k_h}{M_h} \right) / (C_s), \quad (5)$$

where k_h is the effective rate constant of the formation reaction and k_h and M_h are, respectively, the CO₂ hydrate density and molar mass. It can be argued that, under the near-isothermal conditions of the deep ocean, the parameters in (5) remain essentially constant [6,12]. An estimate of t_f that can be compared with t_b can then be obtained utilizing representative values of these parameters: for $C_s = 0.91$ kmol/m³ [13], $k_h = 30$ s⁻¹, $\rho_h = 1.112 \times 10^3$ kg/m³, and $M_h = 147.5$ kg/kmol [11], the hydrate formation time in the deep ocean is $t_f = 1.91$ s.

4. HYDRATE EFFECTS

Expressions for the characteristic times of jet instability, i.e., break up, and surface hydrate formation were obtained in the preceding sections. It is proposed that the relative magnitudes of these characteristic times can be utilized to indicate whether hydrate formation will exercise an effect on liquid CO₂ jet instability. The physical reasoning is as follows: if t_b is much shorter than t_f , then hydrates will not form in significant quantity on the jet surface prior to break up and, hence, jet instability will be unaffected; if, on the other hand, t_b is much longer than t_f (or of comparable magnitude), then a thin, solid hydrate layer will encase the jet, inhibiting the surface deformation required to induce jet break up. These two regimes are considered below.

4.1 Pre-Jet-Breakup Effects

The structure of the CO₂ jet will be affected when significant quantities of surface hydrates form prior to break up. Since hydrate formation time in the deep ocean is essentially constant, jet break up time becomes the relevant parameter. To be conservative, only maximum predicted values of this parameter, $t_{b,max}$, will be considered here; hence, low jet velocity cases are of interest (i.e., $W_e = 0$). Employing the expression $t_b = (1.7 \times 10^3)(r_0)^{1.5}/m$ and solving (3) to determine m when $W_e = 0$ [6], it can be shown that $t_{b,max} = t_f = 1.91$ s when $r_0 = 6.7$ mm. This implies that the pre-jet-breakup hydrate effects may become non-negligible when discharge orifice size exceeds a critical value, here, about 14 mm diameter.

If $t_f \ll t_{b,max}$, then rapid hydrate formation will establish a solid layer on the surface of the jet at the early stage of instability. This layer will inhibit surface deformation; thus, the jet remains stable and a solid tube can grow to encase the jet. Since the hydrate tube is very thin and fragile [2], it is easily broken by hydrodynamic forces. The breaking of hydrate tubes results in the cylindrical instability mode observed in the ocean at hydrothermal fields [2].

In reality, jet velocities are finite and, therefore, $t_b < t_{b,max}$. Figure 1 presents a comparison of t_f and t_b calculated for a range of jet velocities and discharge orifice diameters under deep ocean conditions. From this figure, it is observed that jet break up time increases with increasing orifice diameter and decreases with increasing jet velocity. The results imply that, for a given orifice diameter, interference by hydrates can be avoided by appropriate selection of jet velocity. To minimize pre-jet-break up effects, relatively small values of orifice diameter should be selected and/or velocities should be maintained at moderately high values.

4.2 Post-Jet-Breakup Effects

If $t_b \approx t_f$, then hydrate formation effects only are significant during the latter stages of jet instability, i.e., near to the end of the jet. Here, break up produces droplets covered with a hydrate layer. If $t_b \ll t_f$, then a conventional droplet break up pattern will be observed; however, the rapid kinetics of formation ensure that these droplets also will quickly be encased by a hydrate film.

Although hydrate formation does not significantly affect jet instability when $t_b < t_f$, it can impact the subsequent dissolution and dispersion of the droplet phase. The hydrate layer on the droplet surface is chemically stable [10] and will remain on the droplet (albeit undergoing cycles of collapse and regeneration) as it dissolves and is transported in space by buoyancy, currents, or turbulence [3,12]. Since water molecules at the hydrate surface have broken hydrogen bonds (note that each water molecule can form four hydrogen bonds) arranged toward the seawater phase [10,14], they will rapidly establish a bond when encountering a similar hydrate surface. Hence, CO₂ droplets brought in contact by hydrodynamic forces will easily agglomerate to form a droplet cluster [5,6,7,9,15]. The hydrate interphase, however, prevents the liquid CO₂ of the individual droplets from contacting and, therefore, inhibits coalescence into a single, larger droplet. This agglomeration phenomena has been observed in the laboratory.

5. CONCLUSIONS

A study was conducted to assess the effects of hydrate formation on the stability and break up of jets of CO₂ effluent released in the deep ocean. Within the laminar instability flow regime, a relationship was obtained for a characteristic jet break up time that could be applied for comparison with a hydrate formation time. It was proposed that two regimes exist which are defined by the relative magnitudes of t_b and t_f . When $t_b \ll t_f$, instability phenomena occur much faster than hydrate formation and jet break up is determined purely by hydrodynamics. When $t_b \gg t_f$, a thin hydrate layer forms on the jet surface at the early stage of instability. Since this layer separates the CO₂ and seawater phases, surface deformation of the jet is impeded and, thus, the jet remains stable. The resulting tube-like hydrate structure is fragile and easily fractured by fluid forces, producing the cylindrical mode of jet break up observed near hydrothermal vents in the ocean.

Hydrate formation effects on jet instability are believed not to be significant when $t_b \approx t_f$ or $t_b \ll t_f$; in this regime, jet break up produces a train of droplets. Rapid formation kinetics ensure that these droplets will quickly be encased by a thin hydrate shell. This hydrate phase is chemically stable and will remain on the droplets, inhibiting dissolution and promoting agglomeration.

Since, over the range of depths proposed for marine CO₂ disposal, t_f is predicted to vary only slightly, the sole determining parameter to assess the importance of hydrate formation on instability is t_b . It was shown that jet break up time depends on fluid properties, jet velocity, and orifice diameter. Large orifices result in long break up times, which increase the probability that hydrate formation will induce non-conventional instability phenomena. Low jet velocities tend to produce the same effect. Although the present results do not consider the important category of turbulent flows, they can be applied to evaluate a range of discharge conditions relevant to the ocean disposal concept.

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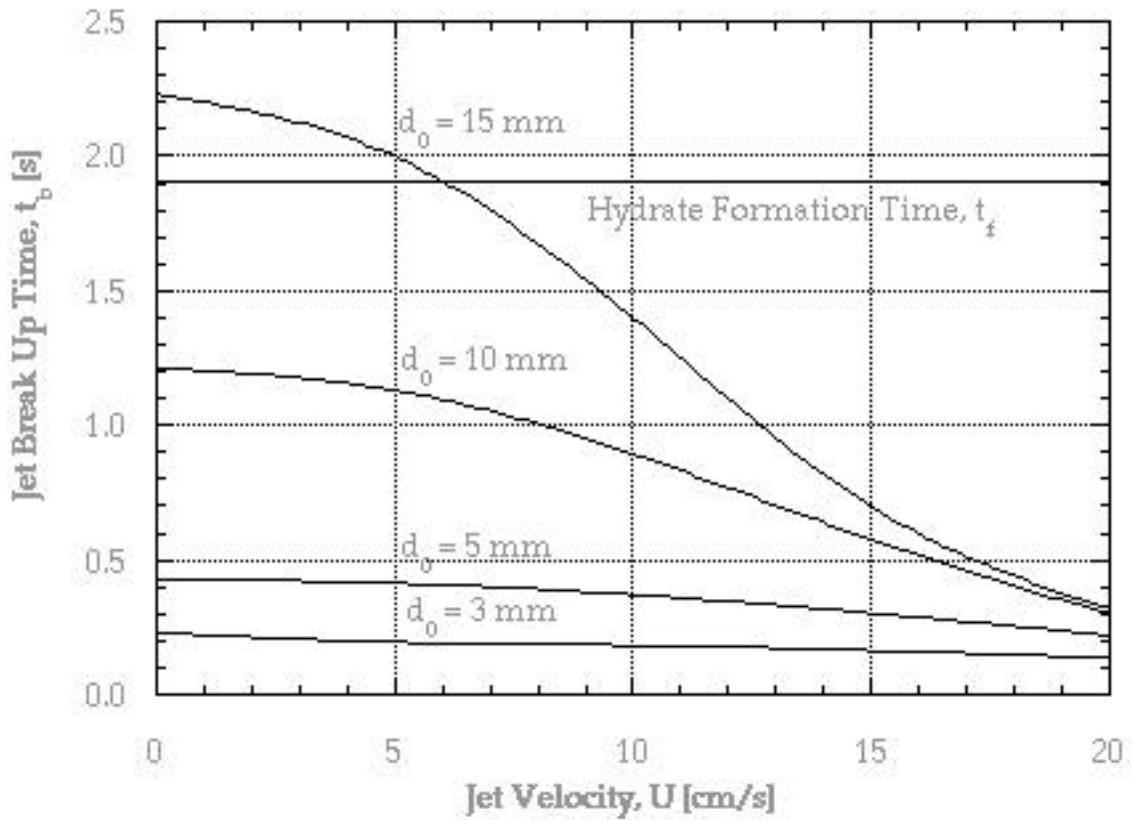


Figure 1. Comparison of hydrate formation times, t_f , and liquid CO₂ jet break up times, t_b , calculated for different discharge orifice diameters, d_0 , under deep ocean (500 m) conditions.