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GHGT-9

## Carbon dioxide hydrate particles for ocean carbon sequestration

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### Abstract

This paper presents strategies for producing negatively buoyant CO<sub>2</sub> 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 ~1500 m produced curved negatively buoyant cylindrical particles with diameters ~ 2.5 cm and lengths up to ~ 1 m. Accordingly we performed new laboratory experiments to determine the drag coefficient of such particles and, based on the measured drag coefficient and the initial settling velocity observed in the field, have concluded that the reactor efficiency (percentage of liquid CO<sub>2</sub> converted to hydrate) in the field was ~ 16%. Using the dissolution rates observed in the field, we conclude that such particles would ultimately sink to depth below discharge of ~ 115 m. We have also predicted the sinking depth of particles potentially produced from various scaled-up reactors and have shown that, for example, a 10 cm diameter particle produced with a hydrate conversion of 50 % could reach the ocean bottom before completely dissolving.

In a real sequestration scenario, we are interested in following large groups of hydrate particles released continuously. We have previously shown that increasing particle size and hydrate conversion efficiency enhances the sinking of hydrate particle plumes produced by the continuous release of CO<sub>2</sub> in a quiescent ambient, but that a sufficiently strong current will cause the entrained particles to separate from the plume and settle discretely. In the latter case, particles of different sizes and hydrate conversions (hence different settling velocities) will follow different settling trajectories as they dissolve. This particle fractionation, if employed deliberately, spreads the discharged CO<sub>2</sub> in the down current and vertical directions, enhancing mixing, while turbulent diffusion helps spread the CO<sub>2</sub> in the third direction. A numerical model that incorporates these processes is used to predict the downstream concentrations and changes in pH from such particle plumes in a 'strong' current. An extension of this model simulates hydrate particles that are released continuously from a moving ship. Because of the ship speed, such particles would never form a coherent plume, but the combination of particle fractionation and advection due to the ship motion produces excellent dilution of the discharged CO<sub>2</sub>.

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## 1. Introduction

Carbon dioxide hydrates are an attractive vehicle for deep ocean carbon sequestration, because they are denser than seawater and will sink unaided while dissolving to promote dispersion in the ocean. A CO<sub>2</sub>-seawater coflowing injection apparatus was developed to create cylindrical composite particles comprised of CO<sub>2</sub> hydrate, liquid CO<sub>2</sub> and seawater [1]. 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) [2-4]. The latest field observations of injections carried out at depths of about 1500m show that the particles produced are long (up to about 1 m), curved cylinders that descend at about 4 cm/s and shrink at a rate of about 6 μm/s.

We are interested in the strategies of employing the hydrate composite particles in a large scale release for CO<sub>2</sub> sequestration. Previously we have shown that, in a quiescent ambient, increased particle size and hydrate conversion efficiency enhances the sinking of hydrate particle plumes formed by the continuous large scale release CO<sub>2</sub> due to a combination of the plume effect and the solute density effect [5]. However, in a sufficiently strong current, the entrained particles would separate from the original plume and settle discretely some distance from the plume source. A schematic of the latter case is shown in Figure 1. Hydrate particles could separate from the initial plume at a separation depth  $h_s$  and fractionate as different particles with different settling speeds (depicted as Stage 1 in Figure 1). While most of the CO<sub>2</sub> mass loading ends up in Stage 1, some of the dissolved CO<sub>2</sub> from the original plume may form a separate single phase, positively buoyant plume (shown as Stage 2). Since Stage 2 accounts for less than ~5% of the total injected CO<sub>2</sub> mass for particles of 5 cm diameter or greater, it is not discussed in this paper (refer to [6] for a more detailed discussion). This paper presents our analysis of Stage 1 plume behavior when hydrate particles are released from a fixed pipe, and also if the particles are released from a moving source (e.g. a towed pipe).

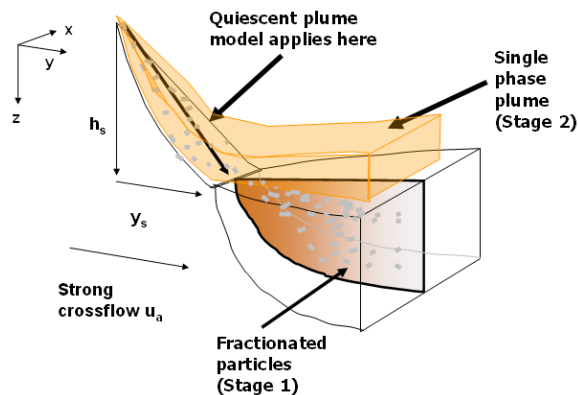


Figure 1: Schematic of a large scale hydrate particle release from a stationary source in a strong crossflow

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. Our laboratory measurements suggest that the shrouded hydrate release produces about half the draft provided by an idealized chimney driven by a distributed source of single-phase buoyancy. The shrouded plume approach is also discussed in more detail in [6].

## 2. Individual particle behavior

In Stage 1, the fractionated particles descend as discrete particles. We want to study individual composite particle behavior 1) to quantify the particle density and therefore the reaction efficiency of the extruded particles to

guide our design for the scale up of the injector for high CO<sub>2</sub> mass loadings; and 2) to predict individual particle descent depths, and therefore dilution of the dissolved CO<sub>2</sub>, as a way to evaluate injection strategies for hydrates.

In the field, the composite particle densities (and reaction efficiency, or fraction of injected CO<sub>2</sub> that forms hydrates, denoted by  $X$ ) cannot be directly measured, but are instead deduced from their fall velocities. We have therefore developed a drag coefficient model for Reynolds number above  $\sim 200$  based on laboratory experiments on cylindrical particles of varying density, aspect ratio and curvature [6]. We predict that the hydrate particles of densities of 1000–1140 kg/m<sup>3</sup> and high aspect ratios (greater than  $\sim 10$ , corresponding to field observations) have a drag coefficient of  $C_D \approx 1$ , regardless of curvature. Applying the drag coefficient to the descent velocity of a typical particle observed during the 2006 field study yields a reactor conversion efficiency of about 16%. Assuming a shrinkage rate and water content for the particles consistent with the field observations (about 6  $\mu\text{m/s}$ ; mass ratio of water to CO<sub>2</sub> about 2.45), we predict the descent depths of a hydrate composite particle as a function of its reaction conversion and particle size (Figure 2). In particular, the typical particle injected in 2006 would sink about 115 m before completely dissolving.

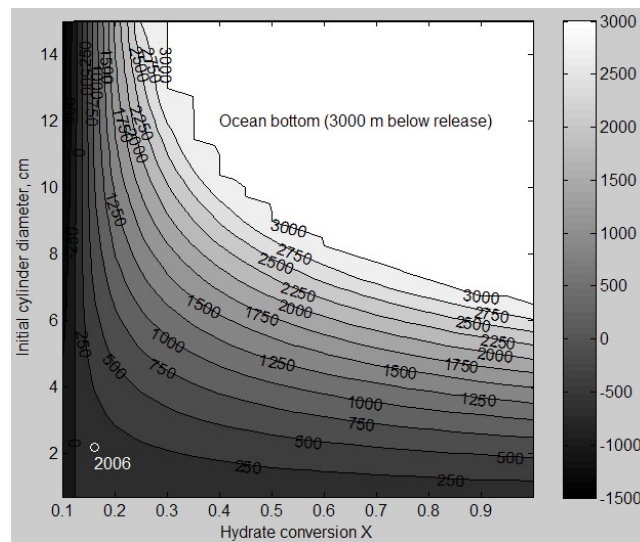


Figure 2: Predicted descent depths (below a release point at 1500 m depth) as a function of particle diameter and conversion efficiency  $X$ , for 30 cm long cylindrical CO<sub>2</sub> hydrate particles. Ocean bottom is at 3000 m below release point, at 4500 m. Diameter shrinkage rate is constant at 6  $\mu\text{m/s}$  and water to CO<sub>2</sub> ratio is about stoichiometric (mass ratio of water to CO<sub>2</sub> = 2.45). Predicted particle sinking depth for typical 2006 field injection indicated with a circle.

### 3. Fractionation in crossflow current

In the presence of an ambient crossflow current, hydrate composite particles of varying hydrate reaction efficiencies ( $X$ ) and initial diameters  $d_0$  will follow different trajectories to their dissolution depth (as predicted from Figure 2). The result of the fractionation is a vertical spread of dissolved CO<sub>2</sub> (Figure 3).

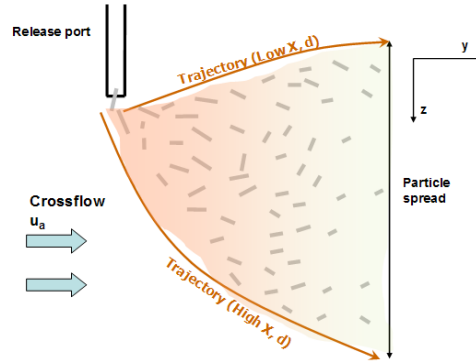


Figure 3: Schematic of trajectories of hydrate particles of differing reaction conversions and initial diameters in a crossflow current.

If the particles are advected by a constant ambient current  $u_a$  with weak stratification, the depth of the particle  $h$  as a function of the downcurrent distance  $y$  is given by

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

where  $l_d$  is the downcurrent distance of particle dissolution,

$$l_d = \frac{u_a}{\frac{dd}{dt}} d_0 \quad (2)$$

and the total descent depth  $h_d$  is obtained from Figure 2.

Field observations [4] have shown that particles with a range of  $X$  are ejected due to the inhomogeneity of mixing within the co-flow reactor, and that all the particles emerge with an initial diameter  $d_0$  comparable to the ID of the reactor. Figure 4 shows the ranges of trajectories of 4 different initial particle diameters (different injectors) ejecting particles with varying  $X$  in a crossflow. A large vertical particle spread is possible: for example, particles of 5 cm initial diameter (top right panel) would be dispersed over a water column range of 1200 – 2800 m. Larger diameter particles are predicted to have longer trajectories in the  $y$  (downcurrent) direction, and also a larger final sinking depth.

We are interested in calculating the resulting pH drop induced by the dissolved inorganic carbon (DIC) that is added from the proposed injection scenarios. The efficiencies are assumed to be distributed between  $X=12\%$  (a neutrally buoyant trajectory at a release depth of 1500m) and a maximum of 55% (the approximate maximum deduced from earlier field experiments). We also 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 (shaded regions in Figure 4). Furthermore, the distribution of  $X$  is assumed to yield an increase in DIC concentration that is uniform over the depth  $h_{max}(y)$  for each downcurrent distance  $y$ , where  $h_{max}(y)$  is computed using Equation 1 for the deepest sinking particle (e.g.  $X=50\%$ ). The plume therefore reaches a maximum depth of  $h_{dmax}$ , also computed for the heaviest particle, 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.

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 5). The added dissolved carbon concentration can therefore be expressed as

$$c(x, y) = \frac{\dot{m} f_d(y)}{u_a} \frac{1}{\sqrt{2\pi}\sigma_x(y)h_{\max}(y)} e^{-\frac{x^2}{2\sigma_x(y)^2}} \quad (3)$$

where  $h_{\max}(y)$  is the downcurrent depth of sinkage determined by Equation 1 for the heaviest particle,  $\dot{m}$  is the CO<sub>2</sub> mass loading, and  $f_d$  is the fraction of the hydrates that have dissolved, given by

$$f_d = 1 - \left( \frac{d(y)}{d_o} \right)^2 \quad (4)$$

where

$$d(y) = d_o - \frac{dd}{dt} \left( \frac{y}{u_a} \right) \quad (5)$$

and  $d_o$  is the initial particle diameter. The value of  $\sigma_x(y)$  is based on oceanic diffusion data from Okubo [7], modified for deep ocean conditions, and assumes that multiple injectors of diameter  $d_o$  are closely spaced in the direction normal to the ambient current). Assuming a hydrate release velocity of 4 m/s, the initial standard deviation is given by  $\sigma_{x0} = (b_0/\sqrt{12})$  where  $\sigma_{x0}$  is in m and  $b_0$ , the total width of the injectors 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. See [6] for more details. Figure 6 shows the calculated centerline pH drops resulting from the four releases in crossflow depicted in Figure 4 at a CO<sub>2</sub> 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. [8] and [9] discusses the effects of lowered pH on marine life in greater detail.

#### 4. Towed pipe scenario

To promote more rapid mixing, a ship could be used to tow the hydrate source perpendicular to the ambient current, as shown in Figure 7. The concentration distribution is given by Equations 3, 4 and 5 except that  $u_a$  is replaced by  $u_s$ . The greater dilution with this scenario comes from the fact that  $u_s \gg u_a$ . A plot of the calculated pH drop as a function of downcurrent distance  $y$  for the towed pipe scenario is shown in Figure 8 for the particle release scenarios from Figure 4, 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).

#### 5. 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 ~ 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 CO<sub>2</sub> 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, travelling perpendicular to the ambient current, can enhance the dilution of CO<sub>2</sub> to levels that are expected to have minimal impact on marine life.

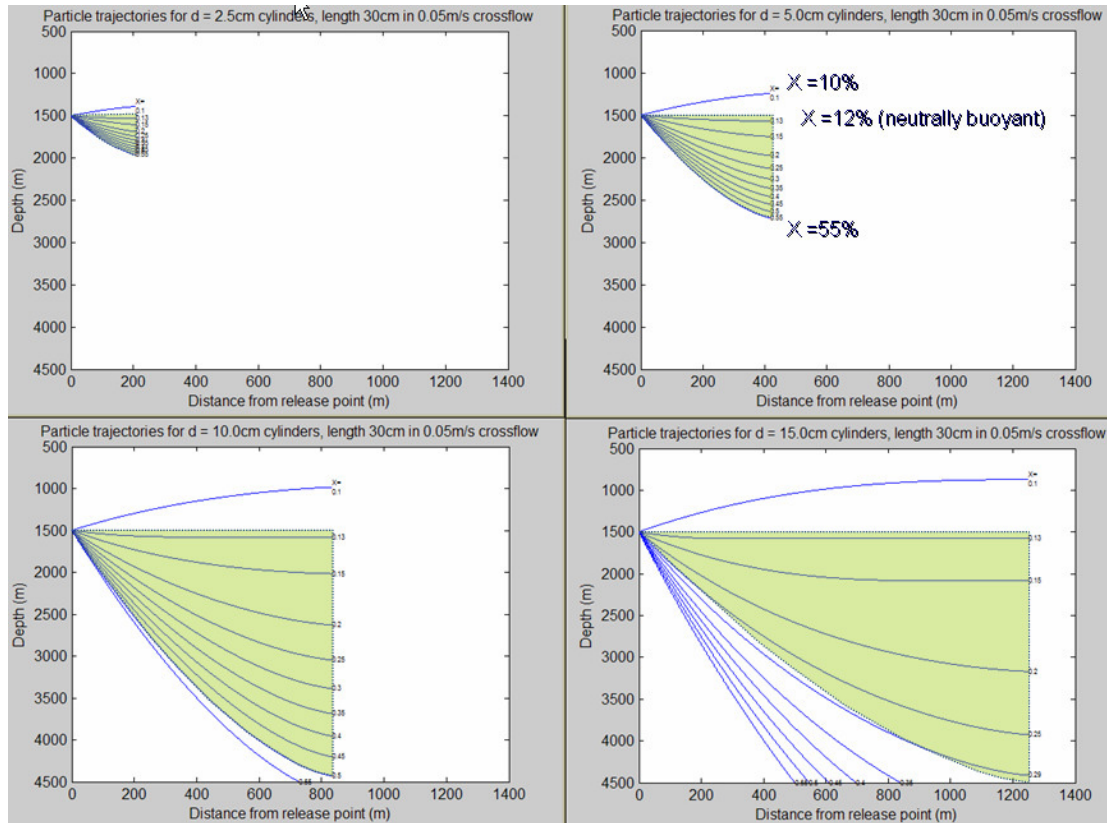


Figure 4: Trajectories (solid blue lines) of particles of different diameters in a typical crossflow current of 0.05 m/s. Release depth = 1500 m. Top left: initial particle diameter  $d_0=2.5$  cm; top right:  $d_0=5$  cm; bottom left:  $d_0=10$  cm; bottom right:  $d_0=15$  cm. Particles of each diameter have length 30 cm; range of reaction efficiencies  $X=10\text{--}55\%$  and stoichiometric water to CO<sub>2</sub> mass ratio of 2.45. Ocean bottom is at 4500 m depth. Wedges (shaded regions) based on the particle trajectories are used for determining dissolved CO<sub>2</sub> resulting from the particle releases. The wedges are described by:  $d_0=2.5$  cm,  $X=0.12\text{--}0.55$ ;  $d_0=5$  cm,  $X=0.12\text{--}0.55$ ;  $d_0=10$  cm,  $X=0.12\text{--}0.50$ ;  $d_0=15$  cm,  $X=0.12\text{--}0.30$ .

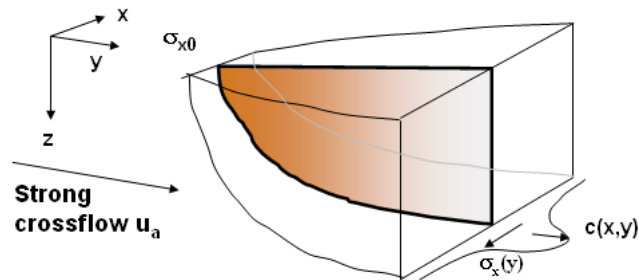


Figure 5: Depiction of lateral ( $x$ ) spreading of dissolved CO<sub>2</sub> by turbulent diffusion.

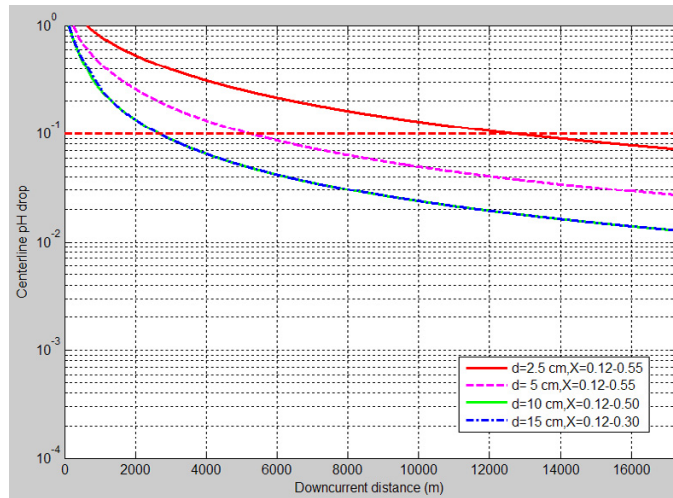


Figure 6: pH drop as a function of downcurrent distance resulting from the four particle release scenarios from a fixed source shown in Figure 4. The CO<sub>2</sub> mass loading is 100 kg/s. Ambient current speed  $u_a=0.05$  m/s. Elapsed time is 96 hours (4 days). Horizontal dashed line indicates the threshold pH drop of 0.1 units for insignificant marine life impact.

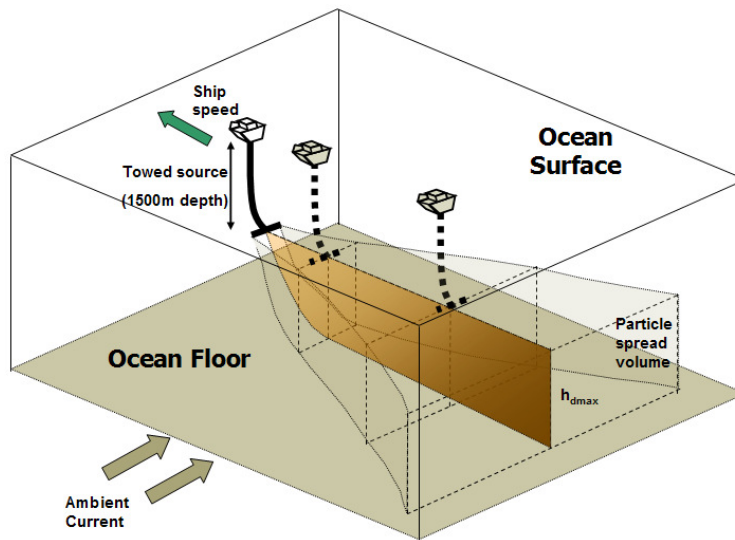


Figure 7: Depiction of a towed pipe injection from a ship.



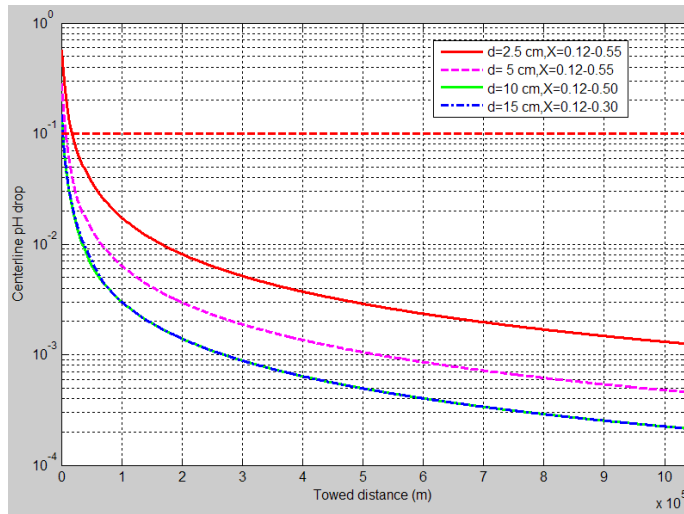


Figure 8: Centerline pH drop as a function of downcurrent distance  $y$  resulting from the four particle release scenarios shown in Figure 4, released from a towed pipe. Elapsed time is 96 hours (4 days). The  $\text{CO}_2$  mass loading is 100 kg/s. Ambient current speed  $u_a=0.05$  m/s, and ship tow rate is 3 m/s. Horizontal dashed line indicates the threshold pH drop of 0.1 units for insignificant marine life impact.

## 6. Acknowledgements

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