

Droplets of Dry Ice and Cold Liquid CO₂ for Self-Transport of CO₂ to Large Depths

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ABSTRACT

In this work we discuss a specific approach for the self-sending of CO₂. In this concept, slurry balls of liquid and solid CO₂ are released at the 200-m depth. The main focus of this work is this concept's thermodynamic issues. We present a general theory for the kinetics of phase transitions and apply this to the calculation of phase transitions for the formation of a thin hydrate layer, and the subsequent growth of ice on the outside of this thin hydrate layer. This kinetic rate of ice growth, and the corresponding heat flux, represent an integral part of the heat transfer dynamics between the sinking balls and the surrounding seawater. The estimates show that the rapid ice growth on balls of dry ice requires balls of approximately 47 cm in order to reach depths where CO₂ is heavier than water. The ice thickness at this depth is, however, estimated to be 65 mm. If the balls do not break mechanically by colliding with the ocean floor at these depths, and as a consequence release the CO₂, then the overall density of the balls will turn the transport of CO₂ upwards again. Similar estimates of sinking slurry balls with solid fractions of 0.3 and 0.5 show more promising trends. Results from simulations using different sizes of these slurry balls indicate a significant potential for adjusting ball size and solid fractions so as to meet the requirements for different sinking depths, according to either sequestration in the ocean or for transport to depths corresponding to the CO₂ lake option.

INTRODUCTION

The oceans are undersaturated with respect to CO₂, and it is estimated that the storage capacity of the oceans may be in the order of 1000 GtC (Cole et al., 1993; Herzog et al., 1997). Sequestration and disposal of CO₂ in the ocean is one option for reducing the greenhouse effect related to disposal of CO₂ into the air.

CO₂ deposited at depths beyond 2800 m will be in the liquid form, and storage beyond these depths is considered the best ocean storage option, with estimated recirculation rates in the order of 1000 to 2000 years (Herzog et al., 1997). For this reason, much of the focus on the storage of CO₂ in the sea is related to these depths. The question is how to get the CO₂ down to these depths. While pipelines from an onshore plant would be one option, this would require some new technology for these great depths. The cost related to such installations is also substantial. Thus, most of the focus during the last decade has been on the development of technologies that can make use of natural gravity in parts of the transport of the CO₂ to great depths.

Self-transport of CO₂ to great depths in the form of hydrate or very cold, large (~1-m diameter) liquid CO₂ droplets according to the COSMOS (CO₂ Sending Method for Ocean Storage, Aya et al., 1998) concept was discussed in a recent paper (Kvamme, 2001). CO₂ hydrate will not be thermodynamically stable with respect to seawater with a background concentration of CO₂ (~2000 μmoles/kg seawater) and will melt during the sinking process. A layer of ice will form around the large CO₂ droplets, which will reduce the leakage of CO₂ to the surrounding seawater. Work is currently in progress on the experimental verification

of the concept as well as on the theoretical evaluation of the system's mechanical stability during transport towards great depths.

Another option would be to drop the CO₂ into the sea in solid form, i.e., dry-ice blocks. The extra costs related to production of solid CO₂ from liquid CO₂ make it rather uncertain as an economically feasible solution compared to the cost of pipelines. The growth of ice on the outside of solid CO₂ will reduce the overall system density and result in lower sinking velocity and possibly even turn it towards the surface again at a certain depth.

Aya (2000) proposed an extension of the COSMOS concept. In this paper, I examine an extension of the COSMOS idea where slurry balls of CO₂ are deposited from a ship at a given depth. The CO₂ dry-ice droplet will of course only sink as long as the overall density of the system composed of CO₂ dry ice and the surrounding ice is higher than the density of seawater. This relationship gives a delicate balance between the need for a sufficiently thick layer of ice to maintain the droplet's mechanical stability after the CO₂ has melted, and the need for an overall density that is at least larger than seawater density. I use the MDIT (Multi-component Diffuse Interface Theory) nucleation theory (Kvamme, 2000) to estimate the initiation and growth of ice on the outside of the dry-ice droplets under the constraints of the maximum possible heat transport capacity for the whole system.

The calculation involves the estimation of an initial layer of hydrate, followed by the initiation and growth of ice outside this layer. The hydrate layer is extremely thin, as also visualised in the paper by Brewer et al. (1998, 1999). From video-clips of these different sets of experiments, it is evident that there is no sign of any significant increase in the film thickness. This is due to the conditional stability of the hydrate at the actual conditions, as discussed by Kvamme (2001). The hydrate equilibrium curve plotted in Fig. 1 in the paper by Brewer et al. (1999) is, according to this, incomplete, since it does not contain the limits of hydrate stability with respect to the dissolved CO₂ in seawater. Unconditional stability for hydrate facing seawater is only possible if the

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