

Article



Experimental Study on the Effect of SDS and Micron Copper Particles Mixture on Carbon Dioxide Hydrates Formation

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Abstract: CO_2 hydrate formation and dissociation are the fundamental processes for investigating hydrate-based carbon storage. To better understand CO_2 hydrate phase behaviors in the presence of surfactant and solid additives, this study reports the effects of Sodium Dodecyl Sulfate (SDS) and micron Cu particles on the formation of CO_2 hydrates in the presence of porous quartz sands in a lab-scale reactor. This research is part of a wider study focused on defining the properties of solid additives, produced via gas-atomization, on the formation and dissociation of gas hydrates. The morphology of CO_2 hydrate formed in SDS solution shows dispersed crystal particles due to the increase of surface tension. SDS works as the kinetic promoter on CO_2 hydrates formation whereas the addition of Cu particles inhibits CO_2 gas consumption. The mixture additives show a faint kinetic inhibit effect, in which the Brownian motion restrictions may be responsible for the inhibition of CO_2 hydrate phase equilibrium.

Keywords: carbon dioxide hydrates; solid additives; kinetic promoter; SDS; micron Cu particles



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1. Introduction

Due to the rapid growth of the economy and population from the preindustrial era, anthropogenic carbon emissions have increased significantly. Especially since fossil fuels started to become the dominant source of anthropogenic emissions to the atmosphere in around 1950, their relative share has continued to increase until the present [1]. As extreme climate cases emerge and sustainable development is needed, the mitigation of associated Green House Gases (GHG) requires continual improvement and the achievement of the carbon emission neutrality objectives set by the Kyoto protocol, Paris Agreement in 2015 and The United Nations Climate Change Conference COP26 Glasgow in is also needed [2–4]. Since CO_2 is regarded as a significant GHG affecting climate change, carbon capture and sequestration (CCS) could play a prominent role in reducing emissions. In general, CCS methods can be categorized as a three-step process: capture of CO_2 (usually in pipelines) and underground injection and geologic sequestration (also referred to as storage) of the CO_2 into deep underground rock formations [5,6].

 CO_2 storage in hydrate form in geologic formations was firstly reported in the late 1990s [7]. Sequestering CO_2 as clathrate hydrates in oceanic sediments has been demonstrated as a long-term effective carbon storage method, in which the CO_2 molecules are trapped in crystal lattice formed by water molecules [8]. On the one hand, one unit volume of hydrates may theoretically hold up to 184 unit volume of gas (STP condition) [9,10]. On the other hand, gases trapped in hydrate-bearing sediments can be stable for a long geological period [11], for example, natural methane hydrates may be found in ocean sediments and permafrost, and they hold an estimated 1200–120,000 trillion cubic meters (TCM) of CH₄ that has been safely preserved for millennia by nature [12,13]. Furthermore, the potential of hydrate-based carbon storage has attracted more attention due to the advantages of enhanced oil recovery, and remaining seafloor stability [14].

To store CO_2 in the solid hydrates in sediments, several approaches have been simulated at the lab-scale. Qureshi et al. [15] injected liquid compressed CO_2 under high pressure to promote fast hydrate formation, achieving the overall water conversion of 82–98%. Song et al. [16] elucidated the high initial water saturation, as well as appropriate temperatures and pressures in marine sediments, and showed it to be conducive to highefficiency CO_2 storage. Additionally, additives were introduced to promote the hydrate formation kinetic or thermodynamic processes.

The study of hydrate formation in surfactant-containing systems began in the 1970s and was initially used mainly for hydrate inhibition studies. Kalogerakis et al. found that surfactants could also increase the rate of hydrate formation under certain conditions [17], and subsequently started to investigate this promotion effect. Surfactants have received much attention recently for their ability to promote hydrate formation without degrading gas storage performance [18]. Link et al. found that natural gas hydrate formed in pure water was not a high-efficiency method for gas storage due to insufficient storage capacity and low formation rate; however, adding surfactants to the system could increase the formation rate by a factor of 700 and methane uptake reached a theoretical maximum [19]. However, limited experimental data revealed the CO₂ hydrate crystals' morphology in SDS solution. Tetrahydrofuran (THF) and surfactant (sodium dodecyl sulfate, SDS) were found to be very efficient for promoting CO₂ capture [20]. Zheng et al. [21] reported that Tetra-n-butylammonium fluoride (TBAF) performed best among semi-clathrate promoters with stoichiometric concentration (3.38 mol%); the process could even be operated at near ambient temperatures. However, these common promoters are toxic in nature and might not be cost effective for use in the oil and gas industry. Biopromoters are renewable, biodegradable, ecologically friendly, non-toxic, and cost-effective, such as lignosulfonates (LSs), amino acids, biosurfactants, and biological porous structures, meriting more research for future applications [22–24].

The slow rate of the formation of gas hydrates is one of the most significant drawbacks; therefore, many researchers have examined different methods to promote it, such as adding some solid particles or surfactants to the aqueous solution. Mohammadi et al. proved that the mixture of SDS and silver nanoparticles increased the water-to-hydrate conversion and the amount of gas consumption during the hydrate formation process [25]. Najibi et al. showed that SDS and CuO nanoparticles had no appreciable effect on the final gas storage capacity but decreased the induction times [26]. Nesterov et al. revealed that the oxide powders as the promoter (inducers) did not show any pronounced effect of the crystal structure of inducer powder on the induction time of hydrate formation [27]. Gambelli et al. reported that CuSn12 metallic powders worked as the inhibitor for carbon dioxide hydrates but as the promoter of methane hydrates [28].

It is known that metal particles provide numerous nucleation sites for gas hydrate crystallization, and also enhance hydrate heat transfer. Li et al. reported copper nanoparticles as kinetic hydrate promoters [29], and nanoparticles had a much larger relative surface and a high potential for heat transfer to promote hydrates formation [30]. Surfactants are usually used to stabilize nanofluid and prevent the particles coagulating. Additionally, the influence of different metal particles on the promotion or inhibition effects (thermodynamic and kinetic parameters) of hydrates depends on the nature of the metal, the size of the particles, the characteristics of the experimental systems [31,32], etc. There is currently a substantial lack of micron metal particles tests to better understand the interaction mechanism for the potential applications. Therefore, testing the effect of various metal particles on CO_2 hydrates formation is needed, especially in the presence of porous media, aiming to provide more experimental data for the development of hydrate additives and hydrate-based carbon storage.

The present research is part of a wider study focused on the utilization of solid metallic powders—produced via gas atomization and commonly used for applications in additive manufacturing—as additives capable of promoting and/or inhibiting the gas hydrate formation and dissociation processes. Previous studies allowed the characterization of these two processes in the presence of CuSn12 [28], Ti23 [33], Inconel 718 [34], FeSi3 [35] and Cu [36].

In particular, the experiments carried out with the addition of Cu particles to the porous quartz sediment confirmed the current literature on methane hydrates: the additive acted as kinetic promoter for the process and also improved the formation of hydrates under a thermodynamic point of view [36]. In 2015, Pahlavanzadeh and colleagues [37] produced methane hydrates by using Cu particles as an additive and proved the kinetic promotion as soon described. Similar research, carried out in the next years, produced the same conclusions [38].

Conversely, the additive was found to act as a weak thermodynamic inhibitor during the formation of carbon dioxide hydrates; moreover, this effect was found to increase with the concentration of Cu within the porous sediment. Unfortunately, there is a substantial lack of data about CO_2 hydrates' formation and dissociation in the presence of this additive.

In this work, the solid Cu-based additive was tested in conjunction with SDS, a wellknown promoter for the process. A similar combination of additives was previously studied in 2015, when Aliabadi and co-workers [39] tested the formation of methane hydrates in the presence of CuO + SDS. In this research, the concentration selected for SDS was 500 ppm, while the concentration of CuO ranged from 0.01 to 1.0 wt%.

More in general, the contemporary usage of promoters and inhibitors may find several advantageous applications. The inhibitors commonly reduce the water activity, thus hindering the hydrate phase stability. In practical applications, when the hydrates of methane are formed with the auxilium of TBAB and THF, the usage of chemical inhibitors can be required to generate their dissociation and the release of gaseous methane for their end use [40]. That explains the necessity of producing experimental data about hydrates formation in the presence of both promoters and inhibitors. Mech et al. [41] studied the phase equilibrium boundary conditions for ternary hydrate ($CH_4 + H_2O + THF$) systems in aqueous solutions containing sodium chloride, methanol and ethylene glycol, with different concentrations (0.03 and 0.1 mass fraction). They found that NaCl has a more inhibiting effect than MeOH and EG for CH_4 + THF hydrates, while the strongest inhibitor for CH_4 + TBAB hydrates is MeOH. They affirmed that the data produced and shown in their work could have been useful for the design of safe natural gas storage and transportation devices. Kumar et al. [42] proved that, even if NaCl is an inhibitor for gas hydrates, the contemporary application of it with THF allows a shift of the phase boundary equilibrium to milder thermodynamic conditions than pure methane hydrates. Finally, Sangway and Oellrich [43] formed semiclathrate hydrates of methane and TBAB in aqueous solutions containing NaCl (0.03 and 0.1 mass fraction). They observed that NaCl strongly inhibited the formation of methane hydrates in the presence of 0.2 mass fraction of TBAB. Conversely, a promoting effect was observed with 0.03 NaCl and 0.05 TBAB.

Herein, micron cupper particles and SDS are selected and combined to investigate the effect on CO_2 hydrate formation of the existence of quartz sands in the lab-scale reactor, in which the hydrates had more nucleation sites and a highly porous internal lattice. Sodium Dodecyl Sulfate (SDS) is a well-known promoter of gas hydrates; its properties have been widely studied and experimental thermodynamic and kinetic data about gas hydrates formation and dissociation in its presence are available elsewhere in the literature [44,45]. In addition, the morphology characteristics of CO_2 hydrate in the micron silica tube are revealed to demonstrate the mechanism of surfactant facilitation promotion for hydrates crystals. Finally, the effect of the additive mixture is described, that is, adding SDS has a weakly kinetic promotion effect; however, it has no appreciable effect on the gas storage. The mixture shows a faint kinetic inhibit effect, in which the Brownian motion restrictions may be responsible for the inhibition of CO_2 hydrate formation.

2. Materials and Methods

Two separate experimental devices are mentioned in this section.

2.1. Experimental Apparatus

The laboratory-scale experimental apparatus was used to conduct hydrate formation and dissociation experiments in this work. The reactor consisted of a 316SS cylindrical chamber, with an internal volume equal to 949 cm³ (diameter 7.3 cm and height 22.1 cm). More specific data of the reactor can be seen in Table 1 [25].

Table 1. Specific information about the reactor.

Detailed Information about the Reactor			
Board height	21 cm	Internal pipe volume	1 cm ³
Internal height	22.1 cm	Volume of intake pipes	19 cm ³
Depth from the edge	18.5 cm	Gas volume from the high edge	90 cm ³
Depth edge to the network	18.3 cm	Total volume of free gas	109 cm ³
Weld thickness	1.1 cm	Water volume	236 cm ³
Thickness from the edge	1 cm	Sand pore volume	253 cm ³
Internal diameter	7.4 cm	Internal reactor volume	949 cm ³

As shown in Figure 1a, four type K thermocouples (T), with class accuracy 1, were installed at different depths in order to verify any temperature variation. In particular, thermocouples were positioned at depths of 2, 7, 11, and 16 cm, respectively, from the top. The temperature-monitoring system was established according to Wang et al., Yuan et al., and Yin et al. [46–48]. By placing the reactor in a thermostatic bath directly linked to a chiller, model GC-LT, temperature was regulated and adjusted from the outside. The thermostatic bath had a double copper coil to facilitate heat exchange between the bath and the refrigerating fluid (glycol).



Figure 1. Image of the lab-scale reactor used for hydrate formation: (**a**) Schematic of the experimental system. (**b**) Picture of the lab-scale reactor.

Another different apparatus was used to investigate the promotion effect of SDS on carbon dioxide hydrate, which had been widely used for the study of gas hydrate phase equilibrium [49,50]. The high-pressure optical cell (HPOC), made of silica tube ((ID = 300 μ m, OD = 90 μ m, and length \approx 24 cm) [51], was used to observe the formation and growth morphology of hydrates in situ. One end of the HPOC was sealed and put on the Linkam CAP 500 heating–cooling stage; the other end was attached to a high-

pressure line, allowing for pressure control via the pressure generator. More information regarding the experimental apparatus, shown in Figure 2, could be obtained in previous studies [52,53], as this element of the experiment was only utilized in this work for an auxiliary verification role.



Figure 2. Schematic diagram of the microscopic hydrate formation device, in which the CO₂ hydrates formed in the silica tube on the heating-cooling stage.

In addition to pure demineralized water and pure quartz sands, ultra-high purity (UHP) methane and carbon dioxide with purity levels of 99.997% and 99.999% were utilized to produce gas hydrates. This latter composition was made up of 100-m-diameter pure quartz spheres. The grain porosity was tested with a porosimeter, model Thermo Scientific Pascal 140, and it was reported to be 34%. More specifically, the reactor was filled with 744 cm³ sand and 236 cm³ water, with the remaining space reserved for gas injection (as seen in Table 1). The amount of dodecyl sulfate (SDS) used in this experiment was chosen according to the current literature [39]; thus, we opted for 300, 500 and 1000 ppm. Micro Cu powders, the characteristics of which are specified in the following section, were also employed in addition to those compounds.

2.2. Materials

The materials were used in HPOC system as shown in Table 2.

Table 2. Materials used in HPOC experiments.

Materials	Purities	Suppliers
Carbon dioxide	99.9 mol%	Hainan Jiateng Gas Co., Ltd. (Haikou, China)
Ultrapure water	18.25 Ω·m	Sichuan Ulupure Technology Co., Ltd. (Chengdu, China)
Dodecyl sulfate (SDS)	>99.0%	Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China)

Pure copper powder, produced via gas-atomization, was considered in this work. The occurrence of partial oxidation must be considered, due to the insertion of such compound in a sand-water mixture. The additive was provided by the University of Perugia and more details can be found in [54,55].

The morphological characterization of this compound was carried out by means of high-resolution electronic scanning microscope (FE-SEM Zeiss LEO-1530). The shape of Cu particles appears to be generally spherical (as seen in Figure 3).



Figure 3. Morphology of Cu particles, SEM images (magnification: 70× at left and 200× at right).

The specifications of the device used for the two high-resolution images shown in Figure 3 are presented in Table 3.

Table 3. Main properties of the high-resolution electronic scanning microscope (FE-SEM Zeiss LEO-1530).

Resolution	1.7 nm (15 kV) and 3.5 nm (1 kV)
Magnification	12–500×
Acceleration Voltage	0.5–20 kV
Probe Current	4 pA-10 nA
Std Detectors	High efficiency In-lens detector

The concentration of Cu particles within the porous medium was chosen according to previous research, where carbon dioxide hydrates were formed with only the presence of this additive at different concentrations, in order to define the role of Cu particles during the process and also the variation of this effect with the concentration [36].

In particular, the concentration selected for this work was equal to 18.01 wt%.

2.3. Procedure

The experimental *P-T* procedure was carried out following the profile shown in Figure 3, which is similar to our previous study [56]. Quartz sands, metal particles and ultrapure water were put in the reactor at the volume mentioned above before carrying out the experiments. The first step was cooling the reactor and excluding the air inside, followed by gas injection. After injecting CO_2 gas up to the required pressure of about 3.6 MPa, we closed all valves. Then, the temperature was decreased and CO_2 hydrates formed in the pore space between quartz sand and metal particles as shown in Figure 4 (the blue region). As the temperature decreased, CO_2 gas and bulk water were gradually consumed and converted to hydrate phase. It was worth noting that hydrates started to form in large quantities, accompanied by a sharp drop in pressure. Subsequently, the system was kept in low temperature conditions for enough time to confirm the hydrate formation process had been completely finished. The last step was to increase the temperature, leading to CO_2 hydrate dissociation. The complete process and more detailed information can be found in Gambelli et al. [57].

For the HPOC experiments, first, ultrapure water (or the additive solution) was injected into the closed end as part of the samples loading procedure. After centrifuging the tube and expelling the air, CO_2 gas was injected to the tube. At the other end, mercury was used to seal the entire reaction system and conduct the pressure from the stainless-steel high-pressure line. The formation and dissociation of hydrate was observed through a small drillhole between the silver platform and the silver cover when the HPOC was

connected to the Linkam cooling–heating stage. The morphology of CO_2 hydrate was observed via in situ experiments.



Temperature

Figure 4. Experimental *P-T* profile of CO₂ hydrate formation and dissociation.

2.4. Data Processing

To analyze the properties of CO₂ hydrate formation and dissociation processes, the related parameters were calculated as follows. Some thermodynamic parameters in the experiment were measured in real time, such as the initial pressure P_i , initial pressure T_i , final pressure P_f at the end of the experiment, and final temperature T_f . The time interval between the occurrence of P_i and P_f is denoted by t. Taking into account the pressure and temperature variations, the internal volume fraction available to contain the gaseous compound, and the compression coefficients, the total amount of gas (n_{INJ}) entering the reactor and the gas involved in hydrate formation (n_{HYD}) were calculated. The number of moles of gas and hydrate formed in this process was calculated using Equations (1) and (2), respectively [58].

$$n_{INJ} = \left[\frac{P_i V}{Z_i R T_i}\right]_{t=0} (\text{mol})$$
(1)

$$n_{HYD} = \frac{V_{PORE} \left(P_i Z_f - P_f Z_i \right)}{Z_f \left(RT - \frac{P_f}{\rho_{HYD}} \right)}$$
(mol). (2)

The V_{PORE} refers to the total free volume made up of sand pores open to harboring hydration. It was easily determined by taking into account the porosity of the sand and the total volume that it occupied. The compression coefficients *Z* before and after the reaction were Z_i and Z_f , respectively, calculated from the Peng–Robinson equation of state [59]. The gas constant was written with the letter *R*. Subscripts take on the same meaning as previously defined. The ideal hydrate molar density, ρ_{HYD} , was calculated under the assumption that all available cages would be occupied [60,61].

For the description, the CO₂ hydrate formation kinetic characteristic, $n_{gas \ consumption}$ was calculated by Equation (3) to characterize CO₂ hydrate formation kinetics. Finally, the gas conversion was clarified based on the proportion of $n_{gas \ uptake}$ and n_{INJ} as listed in Equation (4).

$$n_{gas\ consumption} = \left[\frac{PV}{ZRT}\right]_{t=0} - \left[\frac{PV}{ZRT}\right]_t (\text{mol})$$
(3)

$$gas \ conversion \ (\%) = \frac{n_{gas \ uptake}}{n_{INJ}} * 100\%. \tag{4}$$

Carbon dioxide dissolved in water is still considered captured carbon because, as time proceeds during the experiment, it will form hydrates once the thermodynamic conditions change; so, here we ignored dissolved gas changes when calculating hydrates based on gas consumption.

3. Results and Discussion

3.1. Morphology of CO₂ Hydrate Formed in SDS Solution

In addition to the kinetic and thermodynamic analyses, we conducted in situ visual experiments on CO_2 hydrate formation in an SDS solution of 200 ppm.

Figure 5 shows the morphology of CO_2 gas and CO_2 hydrate crystals in the silica tube. Both gas and hydrate exist in a dispersed state. It is worth noting that the hydrate crystals formed in the SDS solution differ from the common morphology of hydrate previously reported [49,62,63]. Gas disperses into small bubbles and hydrate crystals cannot aggregate into large clumps, which is similar to a study finding that hydrate grows as a porous surface, allowing efficient water-to-gas contact for better conversion [64]. As suggested in the literature survey by Watanabe et al. [65], in a hydrate forming rector with a surfactant solution, hydrate migrated to the vertical reactor sidewall and formed a relatively thick, porous layer. The morphology of hydrate crystals provides microscopic experimental evidence to reveal the promotion mechanism of SDS. Before CO₂ hydrate formation and after hydrate dissociation, the dispersed gas bubbles increase the gas-liquid interface. The mechanism can prove the deduction of Kumar et al.-reduced surface tension in the presence of surfactants not only enhances the mass transfer but also changes the morphology of hydrate formation, which in turn enhances gas-water interactions for a faster hydrate growth rate [66]. In general, the addition of surfactant benefits fast hydrate crystallization; additionally, the use of such additives can achieve recycling for hydrate formation and decomposition cycles.



Figure 5. CO_2 gas and hydrate crystals formed in 200 ppm SDS aqueous solution. (a) CO_2 gas existed as small bubbles rather than concentrated into one large bubble in liquid phase because of the presence of SDS, which increased the gas–liquid contact area. (b) The CO_2 hydrate formed in SDS solution in the form of dispersed small particles, which is different from the crystal form, formed in pure water.

3.2. Effect of SDS on CO₂ Hydrate Formation

By evaluating the kinetic process of hydrate generation from the SDS solution, Tang et al. [67] found that the shortest induction time was observed at an SDS concentration of 0.03 wt% and the maximum hydrate growth rate was observed at 0.01 wt%. Molokitina et al. [68] showed experimentally that hydrate induction time increased with concentration in 0.01, 0.1, and 0.5 wt% SDS solutions. For the optimal concentration of SDS on promoting CO₂ hydrate formation, we experimentally tested CO₂ hydrate formation and dissociation with SDS concentration varying from 0 to 1000 ppm in the presence of quartz sands as shown in Figure 6. Six tests were carried out: two attempts for each selected SDS concentration. To better analyze the kinetic effect of SDS on CO_2 hydrate formation, the mole of CO_2 gas uptake via time (as the same quality of water is injected) and the final gas conversion rates were calculated and are presented in Figure 7. It can be observed in Figure 7, for this study, that SDS promotes CO_2 hydrate formation kinetically with an optimal concentration of 300 ppm. Additionally, the gas conversion rate is about 61~65% with and without SDS, as some studies have proved that SDS did not show any clear influence on gas recovery [69]. Moreover, with certain surfactants, hydrate formation can even be inhibited. One disadvantage of this study in the reactor without stirring is that a small amount of hydrate (no more than 0.8 mol) is formed in the reactor. For future investigations, a stirred tank reactor should be considered to enhance the CO_2 hydrate formation process and total gas conversion rate.



Figure 6. Pressure, temperature and gas uptake evolution over time for carbon dioxide hydrates in the presence of three different SDS concentrations: 300, 500 and 1000 ppm.



Figure 7. Comparison of kinetic parameters of CO_2 hydrate formation in solutions with different SDS concentrations. (a) CO_2 gas uptake profile via time during CO_2 hydrate formation process and (b) final gas conversion rate of CO_2 formation in the presence of 0–1000 ppm SDS.

The trend shown in Figure 7 clearly proved that SDS acted as kinetic promoter, independently from the concentration in the aqueous solution used for the specific experiments. If the diagrams are compared among each other during the first five hours of formation, it clearly appears that the lowest gas uptake value was obtained in the absence of SDS. Conversely, the variation in concentrations of this additive seemed to not be relevant in terms of the increase/decrease of gas uptake.

Figure 8 shows CO_2 hydrate dissociation curves with slow heating rate as the phase equilibrium curves. The process of hydrate decomposition is accompanied by a very slow temperature increase and is thought to remain in dissolution equilibrium. Compared with CO_2 hydrate phase equilibrium data from previous literature [70] and the experimental data of this study, the SDS solution shows no significant thermodynamically promotion effect and only serves as a kinetic promoter. The difference between the phase equilibrium curve and previous data at higher temperatures is due to the limited initial experimental gas injection. The results are consistent with the results of previous studies on surfactant as a kinetic promoter; it is concluded that in the presence of silica sands the surfactant can only be used as the kinetic promoter without the thermodynamic promotion effect.



Figure 8. Phase equilibrium curves of CO₂ hydrate in SDS solution.

3.3. Effect of SDS + Micron Cu on CO₂ Hydrate Formation

Nanometallic particles have been studied as hydrate promoters due to their large specific surface area, excellent heat transfer performance, and ability to reduce induction time [71]. One of the disadvantages of nanometals as additives is their high price. In addition, nanomaterials will agglomerate in the solution and weaken their promoting effect. The typical approach is to dope surfactants to improve the dispersion of nanomaterials in solution [33,72]. A similar effect of micron metallic particles on hydrate formation has been studied; for example, Ti₂₃ particles were found to reduce the induction [34] and Inconel 718 particles acted as inhibitor on CO₂ hydrate. The effect of Cu nano and micro particles on the formation and dissociation of hydrates has been previously explored; however, the experimental results are almost exclusively focused on methane hydrates. Li and co-workers studied the effect of Cu nanoparticles on the two processes and discovered that this additive improves the heat and mass transfer process of hydrate formation [19]. In addition, an upward shift of the dissociation pressure was observed below the critical dissociation point. Said explored the effect of copper nanoparticles on a binary mixture made with methane (25 mol%) and carbon dioxide (75 mol%). He found that, even at low concentrations (0.1-0.3 wt), these particles acted as a kinetic promoter for the process [73]. Conversely, recent studies proved that Cu particles may have a weak inhibiting effect on the formation of pure CO_2 hydrates.

Considering these factors, herein different concentrations of SDS solutions were chosen to mix with micron-sized copper particles to investigate their effect on CO_2 hydrate. Figure 9 shows pressure-temperature evolution curves of CO₂ hydrate formation in a micron Cu and SDS solution of concentrations varying from 0 to 1000 ppm; the mole of gas uptake is also included. To better compare the effect of SDS and micron Cu particle mixture on CO_2 hydrate formation, the CO_2 gas uptake profile is presented in Figure 10. The results show that, after the addition of Cu particles, the rate of gas consumption is slower than when only SDS is present as the additive. Additionally, the final gas conversion also shows the trend of reduction in the system containing the mixed additives. In all the experiments, the best promotion effect of gas consumption is when the CO_2 hydrate formed in the 300 ppm SDS solution. Although metal particles are considered to be potential hydrate promoters, in this study our experimental results suggest that the addition of micron Cu not only does not promote hydrate formation but, on the contrary, hinders the gas absorption rate during hydrate formation. This is a significant difference from the general perception that the addition of particles promotes hydrate nucleation. For example, SDS and CuO nanoparticles were demonstrated to promote methane hydrate formation by reducing the induction time but have no appreciable effect on the final gas storage capacity in a batch stirred reactor [26]. It was believed that the effect of reducing induction time and promoting growth rate is due to the continuous Brownian motion of nanoparticles [74]. However, in our experiments, the micron-sized particles are used and the no-stirred reactor is filled by quartz sands; the restricted Brownian motion could lead to the kinetic inhibition of CO₂ hydrate formation by the addition of micron Cu powders.

Differently from the tests carried out with only SDS as an additive, here, a secondary peak of temperature was always observed. This means that the process had a slower evolution and the solid additive hindered the formation of the first nuclei of hydrates. With time, the formation process also involved the remaining regions and the consequent formation of further nuclei of hydrates caused these secondary peaks of temperature.

The thermodynamic process of CO_2 hydrate formation has also been tested, as the *P*-*T* trajectory shown in Figure 11. What differs from the previous study is that the micron Cu particles have no significant effect on CO_2 hydrate phase equilibrium [25]. As reported by Mohammadi et al. [75], the nano ZnO showed an inhibition effect on hydrate formation, which could be caused by the insoluble layer of zinc hydroxide according to the Zn(OH)₂ formation in the experimental process [30]. Based on the results from this study, we speculate that micron cupper particles have no impact on the equilibrium of the CO_2 hydrate phase due to its inactivity.



Figure 9. Pressure-temperature evolution curves of CO₂ hydrate formation in micron Cu and SDS solution of concentrations varying from 0 to 1000 ppm.



Figure 10. CO₂ gas uptake profile during CO₂ hydrate formation in the presence of SDS and micron Cu particles.



Figure 11. Pressure-temperature trajectory of CO₂ hydrate formation and dissociation in the presence of SDS and micron Cu mixture.

4. Conclusions

The article deals with hydrates formation in the presence of a liquid and a solid additive, having opposite properties on the formation and dissociation processes. While the liquid additive is capable of establishing a more intimate contact with water and guest molecules, thus having a higher effect, the solid one is easier to recover and reuse, with consequent lower costs and reduced effects on the surrounding environment. Moreover, the solid additive chosen for this research was realized via gas atomization and is commonly destined for applications in additive manufacturing.

In summary, the formation of CO_2 hydrates was tested in the presence of SDS and micron copper particles; the effect of mixed additives on CO_2 hydrate are reported kinetically and thermodynamically.

The coupled usage of a promoter in conjunction with an inhibitor has several promising applications, especially in the gas storage and transportation sectors, or in situations where hydrates are formed in the presence of promoters and the following dissociation, required for the end use of the gas contained in them, needs an appropriate inhibitor to be competitive and technically feasible.

Direct crystallographic evidence of SDS promoting CO_2 hydrates is revealed. SDS increases the surface tension of water and inhibits hydrate aggregation into clusters. SDS does not affect the phase equilibrium, and the kinetic optimum concentration is 300 ppm in the range of 0 to 1000 ppm in this study. The addition of micron Cu particles affected the kinetics of hydrate formation by inhibiting gas consumption, and the mixed additive was less effective than facilitation by SDS alone, with elongation showing inhibition kinetically. We speculate that this is due to the restricted Brownian motion, which could lead to the kinetic inhibition of CO_2 hydrate formation. Previous studies proved that micron Cu powders are capable of affecting the thermodynamic phase equilibrium curve of CO_2 hydrate. Even if the pure metals are more inactive than metal oxide particles such as ZnO and CuO, a weak thermodynamic inhibition was observed. This result differs from the current literature, which describes Cu almost exclusively as a kinetic promoter, even if the research behind this conclusion was carried out exclusively for methane hydrates. The results

provide experimental data for subsequent selection and optimization of hydrate promoters. However, more factors need to be considered for future CO₂ hydrate-based storage.

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