

## A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY ON THE EFFECT OF THE REACTOR CONFIGURATION AND OPERATIONAL PARAMETERS ON FORMATION, GROWTH AND DISSOCIATION OF CARBON DIOXIDE HYDRATE

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### ABSTRACT

Clathrate hydrate-based technologies have been considered as promising alternatives for the effective management of the climate change risks related to emissions of carbon dioxide produced by human activities. This work presents a combined experimental and computational investigation of the effects of experimental parameters, operational procedures, and experimental configuration characteristics on the phase behavior of CO<sub>2</sub>-H<sub>2</sub>O systems and CO<sub>2</sub> hydrates formation, growth and dissociation conditions. The operational modes involved (i) the incremental (step-wise) temperature cycling mode and (ii) the continuous temperature cycling processes, by applying the Isochoric Pressure-search method. Also, two different high pressure PVT configurations were used, of which one encompassed a stirred tank reactor of constant volume and the other incorporated an autoclave of constant volume with magnetic agitation. The determined (P-T) conditions for hydrate formation and dissociation, and the respective phase diagrams were compared with respect to the operational conditions, temperature cycling mode and utilized PVT configuration. The experimental findings were complemented by a thermodynamic simulation model, with the aim to resolve the phase diagrams including the CO<sub>2</sub> dissolution over the entire range of the applied (P-T) conditions.

**KEYWORDS:** CO<sub>2</sub> hydrates, CO<sub>2</sub> capture, phase diagrams, CO<sub>2</sub> hydrate formation and dissociation

### INTRODUCTION

The imperative need to eliminate the CO<sub>2</sub> emissions in the atmosphere has led to new advanced carbon capture technologies in order to keep the global temperature below 2°C<sup>[1]</sup>. Clathrates or Hydrates are non-stoichiometric ice-like compounds that are constructed with Van der Waals forces and could capture different gases. Three crystalline structures of Hydrates can be formed depending on the guest gas size, namely the sI structure hosting small molecules such as methane, carbon dioxide and ethane, sII for larger molecules such as propane iso-butane and others, and finally structure sH for methane+neohexane, methane+cycloheptane<sup>[2]</sup>. Hydrates can be found in shallow arctic sediments and in deep oceanic deposits in low-temperature and high-pressure conditions. Clathrates are considered as a possible energy resource with huge capacities of gas while the volume of gas stored in 1 m<sup>3</sup> of CO<sub>2</sub> hydrate is about 120-160 m<sup>3</sup><sup>[3]</sup>. The applications of gas hydrates include natural gas storage, capture of CO<sub>2</sub>, flow assurance and safe CO<sub>2</sub> pipeline transportations etc.<sup>[4,5]</sup>. Finally, clathrate gas separation technologies are considered to be energy-efficient techniques for capturing emitted CO<sub>2</sub> and can produce clean energy<sup>[6]</sup>. The environmentally friendly profile of the technique, the low energy costs, and its simplicity constitute some of the evident benefits of this process, compared to conventional methods for capturing CO<sub>2</sub><sup>[7,8]</sup>.

The objective of this work was to investigate the effect of various factors related to (i) the experimental parameters, (ii) operational procedures, and (iii) type of experimental configuration

on the CO<sub>2</sub> hydrates formation and dissociation conditions, and the form of phase diagrams. The experimental parameters included the feed pressure, H<sub>2</sub>O to CO<sub>2</sub> mole ratio in the feed, cooling rate, and temperature whereas the operational modes involved (i) the incremental (step-wise) temperature cycling and (ii) the continuous temperature cycling processes, in the framework of the Isochoric Pressure Search method. The two operational modes of the experiments proceeded through consecutive stages of initial equilibration, cooling, isothermal cooling, and heating of the studied CO<sub>2</sub>-H<sub>2</sub>O systems. Also, two different high pressure PVT configurations were used, of which one encompassed a stirred tank reactor and the other incorporated a magnetically agitated autoclave of constant volume. The determined (P-T) conditions for CO<sub>2</sub> hydrate formation and dissociation and the derived phase diagrams were compared in terms of the applied operational conditions, temperature cycling mode and utilized PVT configuration. The experimental findings were complemented by a thermodynamic simulation model, with the aim to resolve the phase envelopes including CO<sub>2</sub> dissolution, over the entire range of the applied (P-T) conditions.

## METHODOLOGY

***Experimental Setups:*** The phase behavior and gas hydrate formation conditions of the CO<sub>2</sub>-H<sub>2</sub>O system have been studied using two different experimental setups. The first high pressure PVT apparatus consists of two basic parts, namely a reactor cell (autoclave) inside an air bath-thermostated cabinet, and a gas preparation manifold. A detailed description of the PVT apparatus has been provided in the work of Kastanidis et al <sup>[9]</sup>. The second PVT configuration includes a high pressure stirred tank reactor immersed in a thermostated bath. The reactor shares the same gas preparation manifold with the first PVT apparatus, the description of which is given below. The gas preparation manifold is the system in which CO<sub>2</sub> or any other hydrate former can be stored and delivered to the PVT autoclave under high pressures.

### ***Description of the first PVT apparatus***

***High pressure PVT autoclave:*** The high-pressure PVT autoclave, which has an internal volume of approximately 325 ml, is constructed from a special alloy (Alloy 20). The PVT autoclave consists of a cup and a container that can be easily separated from each other. The autoclave is firmly mounted in an air-bath cabinet. Two feed-through connectors, each one bearing a K-type thermocouple, are mounted on top of the cup, to monitor the temperature of the gas and liquid phases inside the container. The top of the cup bears an optical window where an external camera is mounted. The camera video-monitors the gas/liquid interface during the experiments, allowing to optically invigilate the entire gas hydrate formation and dissociation processes. The bottom of the PVT autoclave is in contact with a magnetic agitator with controllable rotation speed.

***Thermostated air cabinet:*** The PVT autoclave is housed in an insulated cabinet with air circulation. The temperature in the cabinet is precisely controlled by a PID temperature controller and can be kept constant with an accuracy of  $\pm 0.1^\circ\text{C}$ . In addition, the cabinet contains the sampling loops for the gas and liquid phase with precisely defined volumes, and a pressure relief cell for the liquid sampling. All high pressure (24 MPa) diaphragm valves are accessible from the front panel of the cabinet. An overview picture of all the equipment located inside the insulated cabinet can be found in the work of Kastanidis et al <sup>[9]</sup>. A thermal bath with a water/ethylene-glycol mixture as coolant, and controlled by an automatic temperature controller, was used to thermostatize the PVT autoclave with a maximum deviation of  $\pm 0.02^\circ\text{C}$  over the temperature range of our measurements. The coolant from the bath circulates through a thermally insulated cooling coil which passes through the cabinet interior and is firmly mounted around the PVT autoclave.

### ***Description of the PVT configuration***

***Stirred reactor:*** A high-pressure stirred tank reactor has been used for the experimental investigation of CO<sub>2</sub> hydrates formation and Hydrates-Water rich liquid-Vapor (H-Lw-V) equilibrium. The configuration includes a Parr 4561 high-pressure stirred reactor, equipped with a magnetic drive

for internal stirring with controllable speed of the stirrer motor, a Parr stirring control unit, a refrigeration unit, a single piston sampling cylinder, and a high-pressure automated water pump. The stirred reactor encompasses an autoclave with inner volume of 100 ml, a mounted J-type thermocouple a part of which reaches to the cell interior, a pressure gauge and a burst disc. This reactor cell will be hereafter referred to as the “small” PVT autoclave. The pressure of the gas phase inside the autoclave is monitored by using an electronic pressure transducer, which is mounted on the outlet of the gas release valve. The same refrigeration bath which is connected to the first large PVT apparatus, is also used for thermostating the stirred reactor of the second PVT setup. In this case the Parr autoclave is immersed in the bath in direct contact with the coolant.

**Water supply configuration:** A high-pressure continuous flow pump has been used to deliver water into the autoclave of both PVT setups, with a precisely controllable flow rate and pressure. The water amounts were introduced to the reactor cell through the high-pressure single piston sampling cylinder, with inlet and outlet valves, which is connected to the water pump. The side of the cylinder that is fixed to the liquid sampling valve of the autoclave is filled with pressurized deionized and degassed water.

### ***Experimental procedure***

The Isochoric Temperature-Search method is applied in both PVT set-ups to determine the (P-T) conditions for the formation and dissociation of gas hydrates. This method allows the construction of the phase diagram of the studied CO<sub>2</sub>-H<sub>2</sub>O system including the point (P-T) of the complete thermal dissociation of the formed gas hydrates. At first, the PVT apparatus and the autoclave are being thoroughly evacuated along with the gas feed line while pressure and temperature data are recorded. The temperature of the thermal bath is set to 23-25°C and the empty reactor cell of the small PVT setup is immersed in the bath, whereas in the large PVT apparatus the temperature of the autoclave is regulated by the coolant circulating through the cooling coil in firm contact with the cell. Subsequently, pure CO<sub>2</sub> is fed into the reactor cell and pressurized to a selected target pressure, at bath temperature, by using the gas booster. The (P-T) data are recorded and after remaining stable for 3 hours, their average values are taken as the feed (P-T) conditions.

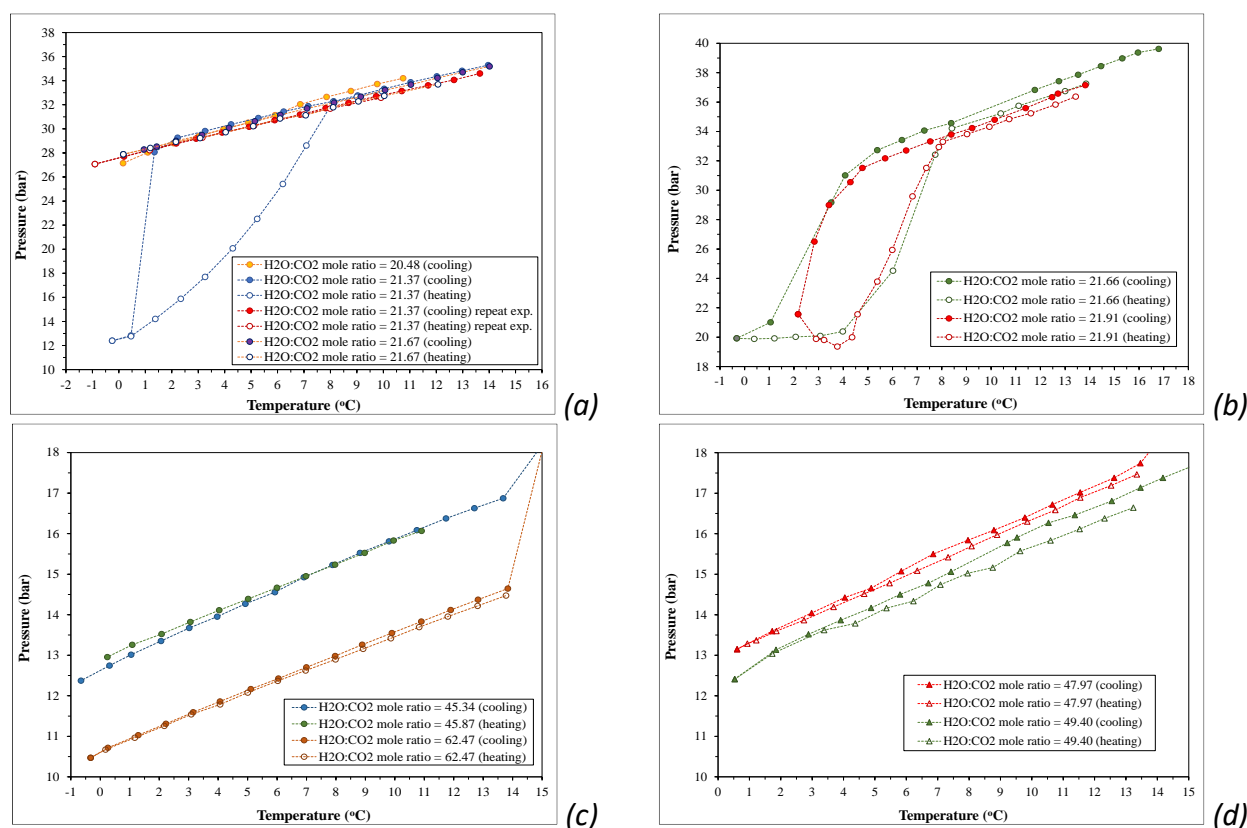
Subsequently, a certain volume of deionized and degassed water is loaded into the autoclave through the single piston sampling cylinder which is connected to the high-pressure water pump. Then, the contained liquid is stirred either by using a magnetic agitator in the large PVT configuration or via the magnetic drive bearing an impeller when the small PVT setup is used. The temperature is kept constant and the pressure begins to decrease as a result of gas dissolution in water, until absorption equilibrium is reached, as indicated by the stabilization of the pressure.

Accordingly, each CO<sub>2</sub>-H<sub>2</sub>O binary system is slowly cooled down to 13.7-13.8°C, and kept under isothermal conditions to reach absorption equilibrium. Then, the system is further cooled to ~0°C or -1°C to study CO<sub>2</sub> dissolution and form gas hydrates by applying either an incremental (step-wise, SW) mode or a continuous cooling (CC) mode. The system is kept at the lower temperature limit for 24 or 48 hours. Subsequently, a step-wise or continuous heating stage is conducted to thermally decompose the formed hydrate phase and close the phase envelope. The applied H<sub>2</sub>O:CO<sub>2</sub> mole ratios (denoted hereafter as MR) were assorted as “low” mole ratios, in the range of 20.48-21.91, and “high” mole ratios, in the range of 45.34-62.47.

## **RESULTS AND DISCUSSION**

### ***Experimental runs performed in incremental temperature cycling mode***

The experimental (P-T) data acquired from the studied CO<sub>2</sub>-H<sub>2</sub>O systems have been used to identify the three-phase (H-L<sub>w</sub>-G) equilibrium conditions and construct the phase envelope of the studied systems. The phase envelope consists of all (P-T) values which are determined during the cooling, isothermal and heating stage in each experiment. The experimental (P-T) results at equilibrium conditions, acquired at the cooling, isothermal, and heating stage, are presented in **Figure 1**.

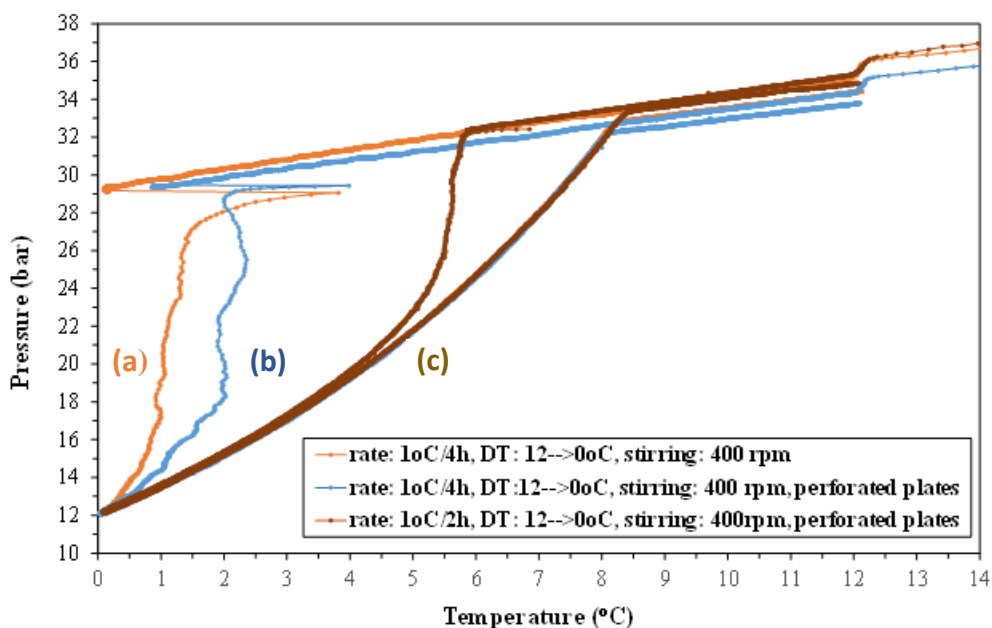


**Figure 1.** Equilibrium pressure vs. Temperature diagram for the CO<sub>2</sub>-H<sub>2</sub>O system including the cooling and heating cycles, for the H<sub>2</sub>O:CO<sub>2</sub> mole ratios (a) 20.48-21.67, small reactor, (b) 21.66-21.91, large reactor, (c) 45.34-62.47, small reactor, and (d) 47.97-49.40, large reactor.

Regarding the small PVT reactor, with the exception of one experiment performed with MR<sub>21.37</sub>, in all other cases no hydrate formation has taken place at all during the experimental runs, for both low and high H<sub>2</sub>O:CO<sub>2</sub> mole ratios. On the other hand, regarding the experiments performed in the large PVT configuration, application of low H<sub>2</sub>O:CO<sub>2</sub> mole ratios allowed for gas hydrate formation, in opposition to the experiments at which high H<sub>2</sub>O:CO<sub>2</sub> mole ratios were applied. Formation and growth of gas hydrates was deduced by the steep and drastic pressure reduction at the cooling stage, owing to formation and growth of CO<sub>2</sub> hydrate crystals which exhibit substantially higher capacity for CO<sub>2</sub> absorption compared to liquid water. For the runs with MR<sub>21.66</sub> and MR<sub>21.91</sub>, the pressure drop became rapid and prominent below ~3°C.

#### **Experimental runs performed in continuous temperature cycling mode**

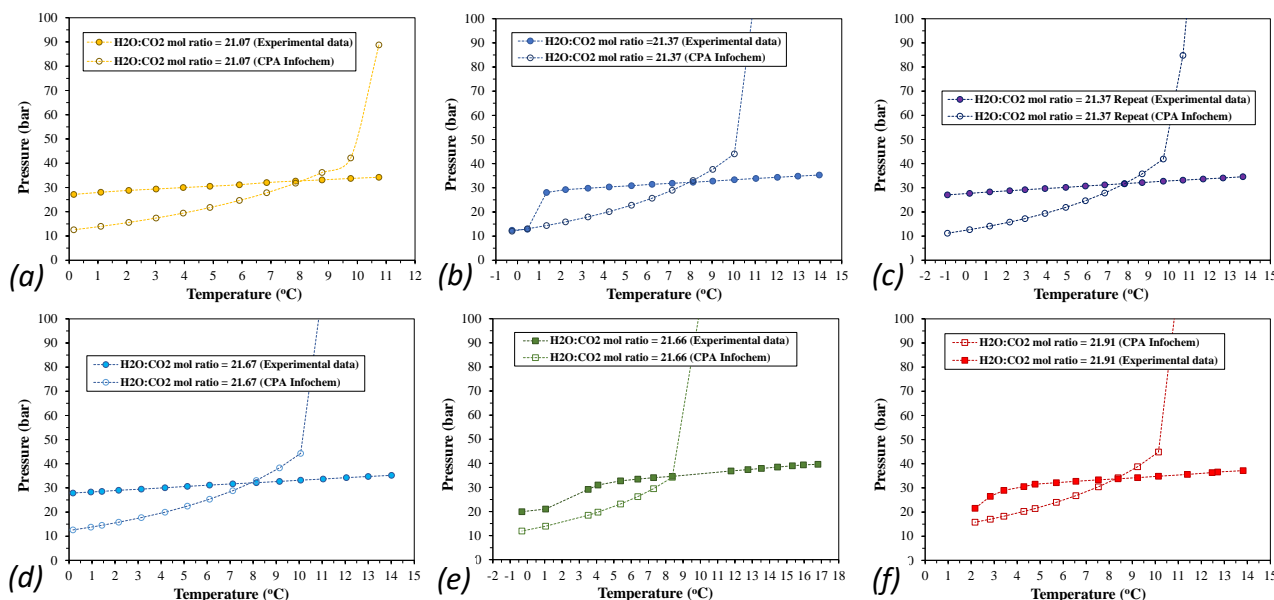
The (P-T) diagrams derived from the experiments conducted in the continuous temperature cycling mode are presented in **Figure 2**. The steep and drastic pressure drop steps which imply the extensive formation of CO<sub>2</sub> hydrates were affected by the cooling rate and the presence of perforated plates on the rotation axis of the magnetic drive, in what concerns their onset temperatures and pressure reduction profile, and reached to the same equilibrium pressure at the isothermal temperature limit at 0.1°C (i.e. the same (P<sub>eq</sub>, T<sub>eq</sub>) equilibrium point). It is worthy to mention that the faster applied cooling rate (1°C/2h) significantly promoted the CO<sub>2</sub> hydrates growth. In all experiments performed in the continuous mode, the pressure increased as soon as the heating stage commenced and kept increasing smoothly up to the point where the heating curve joint the cooling curve. The evolution of pressure with raising temperature during the heating stage was common in the three runs. Furthermore, the temperature at which the hydrate thermal dissociation and cooling curves joint, ranged between 8.15-8.45°C. Another important finding is the different thermal dissociation profiles obtained from the two PVT configurations. This dissimilarity could arise from the different characteristics of the crystallization reactors including their internal design and the agitation mode.



**Figure 2.** Pressure vs. Temperature diagram for the CO<sub>2</sub>-H<sub>2</sub>O binary system in the continuous temperature cycling mode, for the H<sub>2</sub>O:CO<sub>2</sub> mole ratios (a) 20.09, (b) 20.28, and (c) 20.21.

### Computational results on the incipient conditions for CO<sub>2</sub> hydrate formation

In parallel to the experimental investigation of the phase behavior and CO<sub>2</sub> hydrate formation and dissociation conditions, the incipient conditions for CO<sub>2</sub> hydrate formation at each equilibrium temperature studied have been computationally determined using a commercial thermodynamic simulation software (Multiflash v.6.1). The simulation model used for calculating the incipient conditions was the CPA Infochem EoS available in the simulator. **Figure 3** depicts a collocation of the experimental ( $P_{eq}$ - $T_{eq}$ ) equilibrium diagrams for the cooling stage with the ( $P_{incipient}$ - $T_{eq}$ ) diagrams that have been calculated by applying the CPA Infochem model and for the same temperatures.



**Figure 3.** Juxtaposition of Experimental pressure vs. Temperature curves and calculated Incipient pressure vs. Temperature curves for the experiments with (a)-(d) H<sub>2</sub>O:CO<sub>2</sub> mole ratios of 20.48, 21.37, 21.37 (repeated run), and 21.67; (e)-(f) H<sub>2</sub>O:CO<sub>2</sub> mole ratios of 21.66, and 21.91. The experimental results (a)-(d) have been performed in the small reactor. The experimental result (e) and (f) have been performed in the large reactor

configuration.

According to the simulation results presented in **Figure 3**, there is a temperature threshold at which the experimental equilibrium ( $P_{eq}$ - $T_{eq}$ ) curve intersects the calculated ( $P_{incipient}$ - $T_{eq}$ ) curve, below which the experimental pressures exceed the predicted incipient pressure at any equilibrium temperature,  $T_{eq}$ . This intersection point is detected at different temperature depending on the  $H_2O:CO_2$  mole ratio. For all experiments with low  $H_2O:CO_2$  mole ratios (20.48-21.91) the intersection point ranges between  $\sim 7.8$ - $8.38^\circ C$  and thus, it coincides to the “hydrate decomposition point” of the respective phase envelopes. At the experimental pressures above the calculated incipient ones (at the same temperatures), the  $CO_2$ - $H_2O$  systems are two-phase gas hydrate-aqueous liquid (H- $L_w$ ) systems, and thus, the gas phase should have been completely depleted and  $CO_2$  would only be distributed between the hydrate phase and the aqueous liquid.

The intense shear and heat exchange in the stirred tank reactor did not favor the formation of a mechanically and thermally stable hydrate phase. In opposite, the moderate stirring and the slower heat transfer conditions in the large PVT apparatus resulted in formation of a thermally stable  $CO_2$  hydrate phase up to the threshold of  $4^\circ C$ . It is likely that the stability of the pressure over this temperature range is due to the growth of a thick dense hydrate layer on the gas/liquid interface rather than to a slow dissociation rate of large  $CO_2$  hydrate crystals dispersed in the bulk liquid.

## CONCLUSIONS

In this work the phase behavior, and gas hydrates formation and dissociation conditions of  $CO_2$ - $H_2O$  systems have been experimentally investigated with respect to (i) the applied temperature cycling procedures, (ii) operational parameters, and (iii) characteristics of the experimental PVT configuration. The experimental parameters included the gas feed pressure,  $H_2O:CO_2$  mole ratio in the feed, cooling rate, and operating temperature whereas the operational procedures involved (i) the incremental temperature cycling mode and (ii) the continuous temperature cycling process, in the framework of the Isochoric Pressure Search method.

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