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1 **Experimental evaluation of the partial thermal energy compensation of hydrate**
2 **crystallization from cyclopentane-loaded porous activated carbon particles immersed in**
3 **brine**

4 Rafik Mallek,¹ Christelle Miqueu,² Matthieu Jacob,³ Christophe Dicharry^{1,*}

5 ¹ *CNRS/TOTAL/UNIV PAU & PAYS ADOUR, Laboratoire des Fluides Complexes et leurs*
6 *Réservoirs - IPRA, UMR5150, 64000, Pau, France.*

7 ² *CNRS/TOTAL/UNIV PAU & PAYS ADOUR, Laboratoire des Fluides Complexes et leurs*
8 *Réservoirs - IPRA, UMR5150, 64600, Anglet, France.*

9 ³ *Pôle d'Etude et de Recherche de Lacq (PERL), TOTAL SA, 64170 Lacq, France.*

10 *Corresponding author(s): christophe.dicharry@univ-pau.fr (C. Dicharry)

11

12 **Abstract**

13 Hydrate-based desalination (HBD) is a potential water desalination technology that has been
14 studied over the past decades. Recently, an HBD process based on hydrate formation from
15 cyclopentane (CP) loaded on porous activated carbon particles (PACP) was patented
16 (“Method for crystallizing clathrate hydrates, and method for purifying an aqueous liquid
17 using the clathrate hydrates thus crystallized”, EP3153606, 2017). It is thought that the
18 crystallization of CP hydrates from CP adsorbed on PACP might cause partial thermal energy
19 compensation. Actually, the heat released by the exothermic hydrate crystallization should be
20 partially balanced by the endothermic desorption of CP from the PACP. In order to
21 investigate this phenomenon, calorimetric and optical studies (heat flow and refractive index
22 measurements respectively) of hydrate formation in systems consisting of CP-saturated PACP
23 immersed in brines (3.5 wt% NaCl and 8 wt% NaCl) were performed. Comparison of the
24 thermal energy measured directly (through the calorimetric study) - i.e. the energy produced
25 by both hydrate crystallization and CP desorption - and the thermal energy measured

26 indirectly (deduced from the optical study) - i.e. the energy generated by hydrate
27 crystallization only - revealed a balanced energy ranging from 9 to 47 kJ/mol of
28 CP. Comparison of the latter with the differential enthalpy of CP desorption from PACP
29 suggests that the CP converted to hydrates was contained in the large pores of the PACP. It is
30 interesting to note that salinity had no significant impact on the degree of thermal energy
31 compensation obtained.

32

33 **Keywords: CP hydrates; CP-adsorption/desorption; activated carbon; energy**
34 **compensation; hydrate-based processes; desalination**

35

36

37 **1. Introduction**

38

39 Hydrate-based desalination (HBD) is a potential water-desalination technology that was first
40 proposed by A. Parker in 1942 [1] and has received marked attention since the 1960s in order
41 to strengthen the water-energy nexus [2]. It is based on the formation of gas hydrates which,
42 once formed, are separated and dissociated to obtain desalinated water due to the fact that salt
43 ions do not participate in the hydrate structure [3]. Gas hydrates are ice-like compounds
44 formed by the association of water cages and small chemical compounds known as guests.
45 They generally form at relatively high pressures and low temperatures [4]. Some of them,
46 such as cyclopentane (CP) hydrates, can however form at atmospheric pressure. Hydrate
47 crystallization has been widely studied in the literature in different contexts such as natural
48 sediments [5–7], flow assurance [8–10] and hydrate-based processes [2,3,11–15]. A
49 significant number of water-guest systems and experimental set-up designs have been studied,
50 mainly to describe hydrate formation mechanisms [16,17] or hydrate crystal morphology [18–

51 20], to promote [21,22] or inhibit [8,23] hydrate formation, and to reduce the energy required
52 for hydrate crystallization [24–28]. The optimization of energy consumption for hydrate
53 crystallization, which is an exothermic reaction, has essentially been studied in the context of
54 an economically viable hydrate-based desalination process. In the studies published, the
55 authors generally tried to make the most of the endothermic energy produced by a reaction
56 which is exogenous to the system. For instance, He et al. (2018) and Babu et al. (2020)
57 attempted to make use of LNG regasification to cool the water to be desalinated [24,25]. He et
58 al. (2018) achieved a decrease in specific energy consumption of 27.42% and 24.61% for
59 3.5wt% NaCl and 7 wt% NaCl brines respectively [25].

60 The hydrate formation stage of a recently patented HBD process [29], which has the
61 particularity to use porous activated carbon particles (PACP) loaded with CP, was studied in a
62 previous paper [22]. The main results showed that the PACP act as both kinetic promoters and
63 a source of CP for hydrate formation. However, a relatively small amount of hydrates was
64 obtained (< 50% of the theoretical maximum amount of hydrates that could be formed) [22].
65 This was proven to be related to the fact that the CP found in the small pores of the PACP
66 remains trapped [30,31]. Based on this observation, PACP with predominantly large pores
67 were recommended for enhancing the process. In the present work, we focus on the energy
68 aspect of the hydrate formation stage in this HBD process, in which the energy supplied by
69 hydrate crystallization - exothermic reaction (-115.4 kJ/mol of CP [32]) - could possibly be
70 partially compensated by a reaction endogenous to the system, namely the desorption of CP
71 from the PACP, which is endothermic (+28 to +57 kJ/mole of CP [30]).

72 The main objective of the present work is to experimentally prove this partial thermal energy
73 compensation and determine its value. To do so, CP hydrates were crystallized from CP-
74 saturated PACP immersed in brines of 3.5 wt% NaCl and 8 wt% NaCl, at a subcooling
75 (difference between the hydrate equilibrium temperature and the experiment temperature) of

76 6°C. These salt concentrations mimic those of seawater [33] and produced water [11]
77 respectively. The experiments were carried out using both differential scanning calorimetry
78 (DSC) and refractive index measurements.

79

80

81 **2. Experimental section**

82

83 **2.1. Materials and Apparatus**

84

85 CP (purity of 97%) was supplied by Sigma Aldrich. Deionized water (resistivity of 18.2
86 MΩ.cm) was produced by a Purelab laboratory water-purification system. Sodium chloride
87 (NaCl) (purity of 99.5%) was purchased from Acros Organics. A grade of PACP called BGX,
88 supplied by Chemviron SA (Belgium), was used for the hydrate formation experiments. BGX
89 is granular activated carbon with an average particle size of about 1 mm and a pore size
90 distribution that has the specificity of being developed in both the meso- and macroporous
91 regions in addition to the more standard microporous range (see SM-1 and SM-2). Their CP-
92 adsorption capacity is 0.96 ± 0.02 g of CP/g of BGX at 1°C (see SM-3). A closed vessel and a
93 set of resealable glass flasks with a 5-ml capacity were used for the CP-saturated PACP
94 preparation. Plastic syringes (3-mL capacity) and cellulose acetate syringe filters (0.8-μm
95 mesh size), used to sample and filter the unconverted water at the end of the hydrate
96 formation experiments, were purchased from Sodipro.

97 A vacuum preparation apparatus called VacPrep™ (from Micromeritics) was used to purify
98 the PACP samples under primary vacuum at 200°C. The samples were weighed using an

99 ALC-110.4 balance (from Accurlab ®) with an uncertainty of 10^{-4} g. A universal convection

100 incubator (from Memmert®) was used to impose the chosen temperature on the closed vessel,

101 in which the PACP are placed to be saturated with CP (cf. paragraph 2.2.). Hydrate formation
102 was performed in the measurement cell (7-cm³ capacity) of a Tian-Calvet BT2.15 calorimeter
103 (from Setaram Instrumentation). The uncertainty with regard to the measured energy is 4%
104 (see SM-4).

105 The refractive index n_D (at a wavelength of 589.3 nm) of the water samples was measured
106 using an Abbemat 550 refractometer (from Anton Paar) with an accuracy of ± 0.00001 .

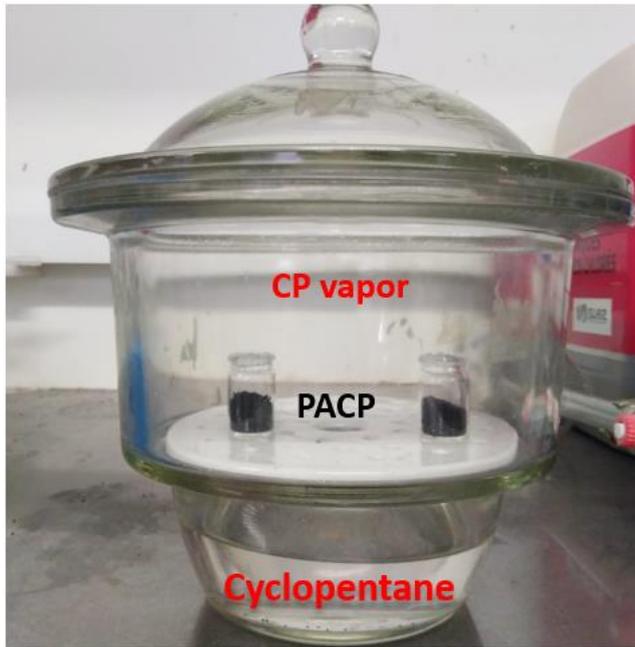
107

108 **2.2. Preparation of the CP-saturated PACP**

109

110 The saturation of PACP with CP was performed as follows: 0.54 g of BGX were purified at
111 200°C under primary vacuum for 12 hrs. Using a glass funnel, 0.500 ± 0.005 g of this hot
112 sample was immediately transferred to a resealable glass flask, which was then introduced
113 into the closed vessel partially filled with liquid CP (Fig. 1). This in turn was placed in the
114 incubator at $1.0 \pm 0.5^\circ\text{C}$. The PACP were left in contact with saturating CP vapor for 48 hrs to
115 saturate their pores with CP.

116



118 **Fig. 1.** Preparation of CP-saturated PACP

119

120 **2.3. Investigation into the CP desorption-CP hydrate crystallization thermal energy**
121 **compensation**

122

123 CP hydrates were formed in systems composed of CP-saturated BGX immersed in brine (3.5
124 wt% NaCl and 8 wt% NaCl). In order to evaluate whether or not the thermal energy
125 consumed by CP desorption from the PACP partially compensates the thermal energy
126 released by hydrate crystallization, the thermal energy compensation was assessed by
127 comparing the thermal energy measured in the DSC hydrate formation experiments (referred
128 to as direct measurement) with the value deduced from the refractive index measurements of
129 the unconverted water sampled at the end of the hydrate formation experiments (referred to as
130 indirect measurement). The former corresponds to the energy $E_{des+crys}$ generated by CP-
131 desorption and hydrate crystallization, whereas the latter corresponds to the energy E_{crys}
132 generated by hydrate crystallization only.

133 For this experiment, 0.500 ± 0.005 g of CP-saturated BGX and 4.15 g (or 4.35 g) of 3.5 wt%
134 NaCl (or 8 wt% NaCl) solution were introduced into the measurement cell of the BT2.15
135 calorimeter along with a few CP-hydrate crystals prepared beforehand (see Fig.2). These
136 hydrate crystals were added to initiate hydrate crystallization by using the so called
137 “memory effect”. Memory effect is a phenomenon resulting from the non-complete
138 dissociation of hydrate structure which reduces the time required to initiate hydrate formation
139 [4]. The PACP, NaCl solution and cell were all precooled to the equilibrium temperature T_{eq}
140 (5.5°C and 2.8°C for the 3.5 wt% NaCl and 8 wt% NaCl solutions respectively [22]). The cell
141 was then introduced into the calorimeter, which was set at a temperature 0.2°C above T_{eq} in
142 order to prevent (or at least limit) the added hydrate crystals from melting. The system was
143 maintained at this temperature for one hour (stage (a) in Fig. 3) so that the thermal signal
144 (heat flow) caused by the introduction of the cell into the calorimeter should reach the
145 baseline and the added hydrate crystals should melt slowly. Then, the system temperature was
146 decreased to the target temperature ($T_{eq} - 6^{\circ}\text{C}$), at a cooling rate of $1^{\circ}\text{C}/\text{min}$, and maintained
147 for 24 hrs (stage (b)). After 24 hrs of hydrate formation, the cell was removed from the
148 calorimeter, a sample of the residual (unconverted) NaCl solution was collected and filtered,
149 and its refractive index was measured (stage (c)).

150 $E_{des+crys}$, deduced from the direct measurements, was obtained by integrating the thermal
151 peak generated by subtracting the “blank” thermogram (obtained in a similar fashion but
152 without CP) from the “experiment” one (see Fig. 4). The “blank” thermogram (brown curve
153 in Fig. 4) only takes into account the heat flow deviations due to the temperature
154 programming and mass difference between the “measurement” and “reference” cells. Thus,
155 the resulting thermogram “Experiment minus Blank” (blue curve in Fig. 4) only shows the
156 heat flows due to both the CP desorption from the PACP and the hydrate crystallization, and
157 its integration gives $E_{des+crys}$.

158 E_{crys} , deduced from the indirect measurements, was obtained by first determining the salinity
 159 $[NaCl]_{24h}$ of the unconverted solution - concentrated with salt as hydrates formed - from the
 160 measured refractive index and a previously generated “nD-[NaCl]” calibration curve (see SM-
 161 5). Based on this, the water-to-hydrate conversion (WHC) and the water-to-hydrate amount
 162 (WHA) were determined using equations 1 and 2 respectively. The stoichiometric ratio of CP
 163 to water in the CP hydrates (1 mole of CP:17 moles of water) served to determine the amount
 164 of CP-to-hydrates obtained (CPHA) (equation 3). The hydrate formation energy was deduced
 165 from the CP-hydrate dissociation enthalpy ($115,400 \pm 7,600$ J/mole of CP (Delroisse et al.,
 166 2018)) using equation 4.

$$167 \quad WHC(\%) = 100 - \frac{100 * [NaCl]_i * (100 - [NaCl]_{24h})}{(100 - [NaCl]_i) * [NaCl]_{24h}} \quad (1)$$

$$168 \quad WHA (g) = m_{iw} * WHC (\%) \quad (2)$$

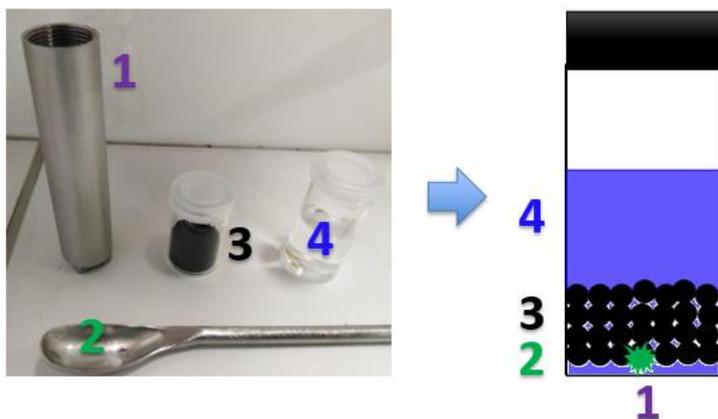
169 where $[NaCl]_i$, $[NaCl]_{24h}$ and m_{iw} are the initial water salinity (3.5 wt% NaCl or 8 wt%
 170 NaCl), the final water salinity (after 24 hrs.) and the initial pure-water mass respectively.

$$171 \quad CPHA (g) = \frac{WHA * (17 * 18)}{70.13} \quad (3)$$

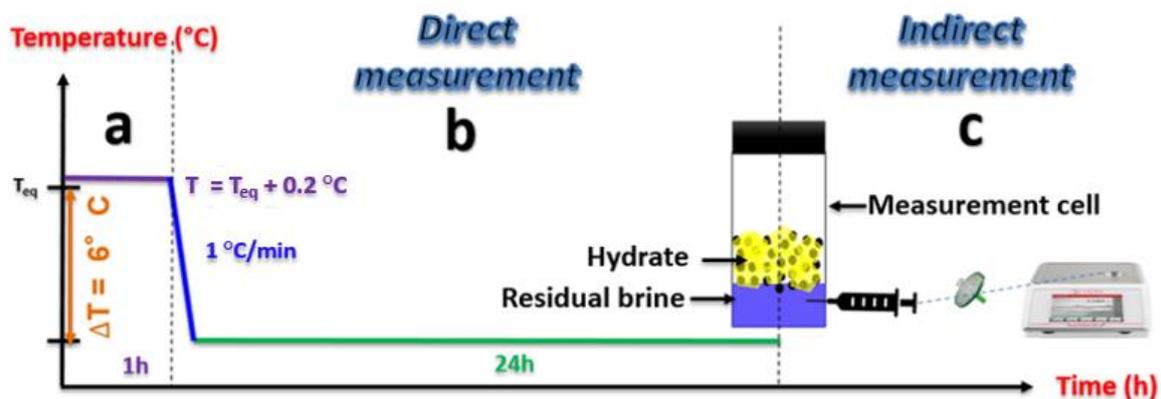
$$172 \quad E_{crys} (J) = \frac{CPHA * 115400}{70.13} \quad (4)$$

173 The uncertainties as regards $E_{des+crys}$ were determined as the sum of experiment repetition
 174 and calibration-control deviations, whereas the uncertainties as regards E_{crys} were calculated
 175 from the experiment-repetition deviation, the calibration curve deviation, the refractometer
 176 accuracy, and the uncertainty regarding the dissociation enthalpy.

177



178
 179 **Fig. 2.** Preparing the system for the hydrate formation experiment in the calorimetric cell of
 180 the BT2.15 apparatus. 1) The measurement cell, 2) hydrate seed, 3) CP-saturated PACP, and
 181 4) brine
 182



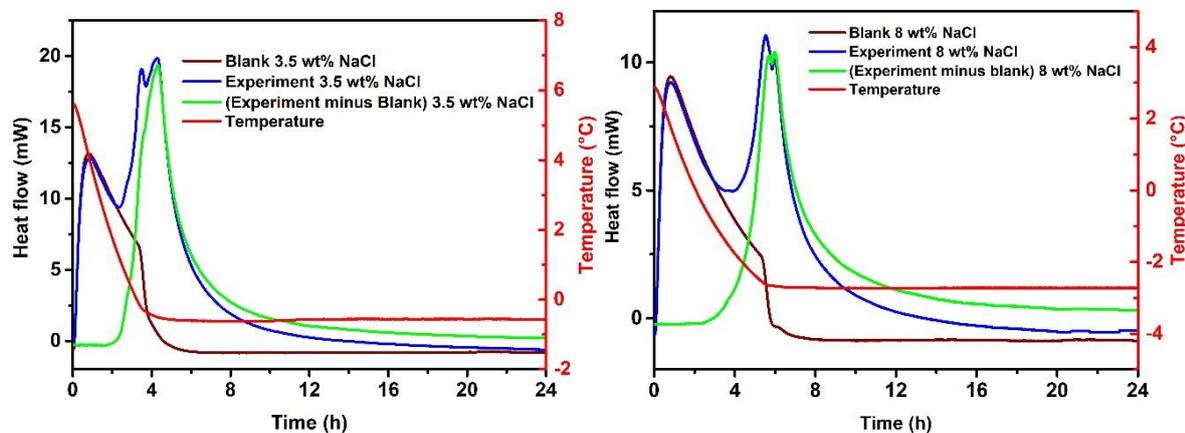
183
 184 **Fig. 3.** Experimental procedure to determine thermal energy compensation
 185
 186

187 **3. Results and discussion**

188
 189 Fig. 4 shows the resulting thermal peak (green curve) obtained after subtracting the “blank”
 190 thermogram (brown curve) from the “experiment” one (blue curve) for both NaCl solutions.
 191 The superposition of the thermal peaks obtained in experiments 1 and 2 shows a good

192 reproducibility for each salinity (Fig. 5). The average values of $E_{des+crys}$ obtained by
 193 integrating the thermal peaks are also given in Fig. 5.

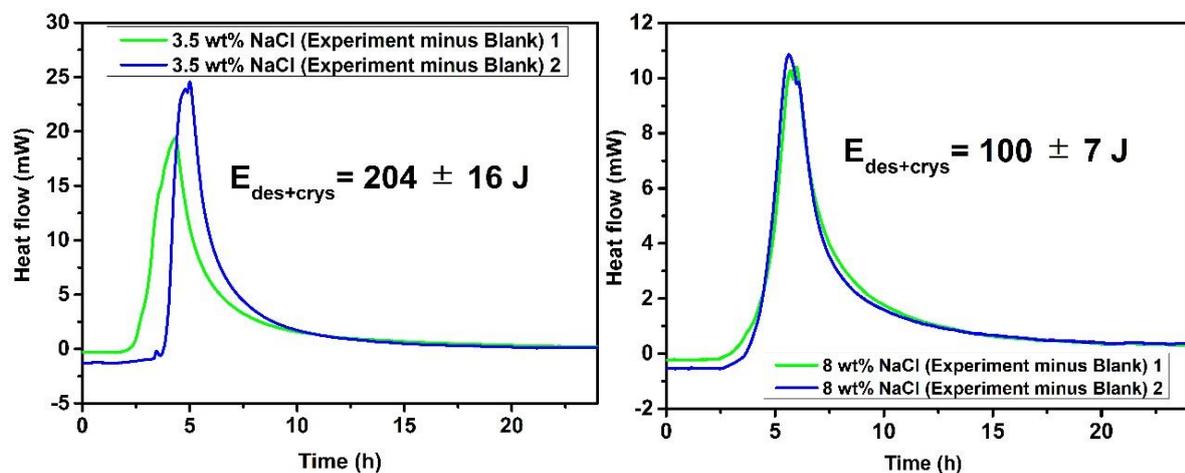
194



195

196 **Fig. 4.** Thermal energy peak (green curve) generated by subtracting the “blank” thermogram
 197 (brown curve) from the “experiment” thermogram (blue curve) for the 3.5 wt% NaCl solution
 198 (left) and 8 wt% NaCl solution (right)

199



200

201 **Fig. 5.** Comparison of the thermal energy peak obtained in two repeated experiments with the
 202 3.5 wt% NaCl solution (left) and the 8 wt% NaCl solution (right). The values of $E_{des+crys}$ were
 203 obtained by integrating the peaks.

204

205 The thermal energy values E_{crys} deduced from the indirect measurements for the same
 206 systems are given in Table 1. The refractive indexes (nD) measured after 24 hrs of hydrate
 207 formation in experiments 1 and 2 are in good agreement which indicates a good
 208 reproducibility (difference of less than 0.002%).

209

210 **Table 1.** Indirect measurement of hydrate formation energy

		3.5 wt% NaCl	8 wt% NaCl
nD	Exp. 1	1.340402	1.348213
	Exp. 2	1.340376	1.348220
	Average	1.340390 ± 0.00001	1.34822 ± 0.00001
[NaCl] _{24h} (wt%)		4.23 ± 0.01	8.71 ± 0.01
WHC (%)		18.0 ± 0.4	8.70 ± 0.25
WHA (g)		0.72 ± 0.02	0.35 ± 0.01
CPHA (g)		0.160 ± 0.004	0.080 ± 0.002
E_{crys} (J)		271 ± 24	131 ± 12

211

212 As can be seen in Table 2, $E_{des+crys}$ is lower than E_{crys} . The difference in energy ($E_{crys} -$
 213 $E_{des+crys}$) is in fact the balanced energy. Since the PACP are initially saturated with CP,
 214 meaning that the CP is found only within the pores, the balanced energy can thus be fully
 215 attributed to CP desorption. While assuming that all the CP desorbed from the PACP is
 216 converted to hydrates (i.e. the desorbed-CP amount is equal to CPHA), the balanced energy
 217 value, calculated as the ratio of ($E_{crys} - E_{des+crys}$) to CPHA (in mol), is between 9 (=28-19)
 218 kJ/mol of CP and 47 (=28+19) kJ/mol of CP. The balanced energy can be compared to the
 219 differential enthalpy of CP desorption (the opposite of the differential enthalpy of CP
 220 adsorption on PACP), which ranges from 28 to 57 kJ/mol of CP. The differential enthalpy of

221 CP desorption was measured in a previous paper for two different activated carbons (see SM-
 222 6) [30] using the calorimetric-manometric technique [34]. The similarity of the curves
 223 indicates a general range of values for CP adsorbed on an activated carbon. For the sake of
 224 comparison, the balanced energy range and the differential enthalpy of CP desorption from
 225 PACP are plotted in the same figure (Fig. 6).

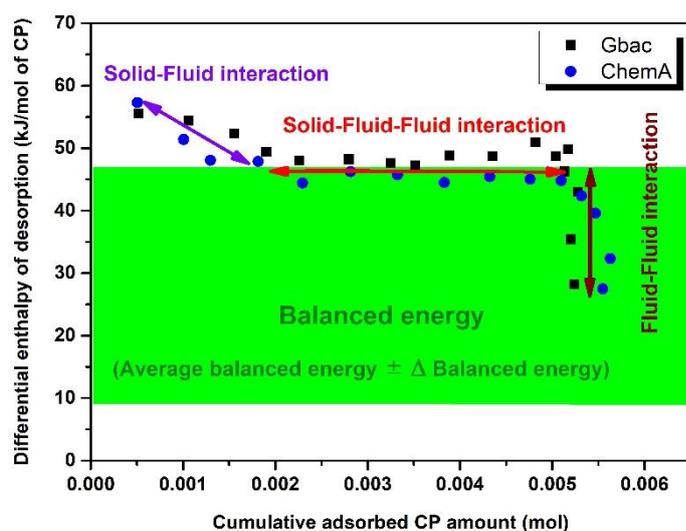
226

227 **Table 2.** Determination of the balanced energy per mole of CP

	3.5 wt% NaCl	8 wt% NaCl
$E_{des+crys}$ (J)	204 ± 16	100 ± 7
E_{crys} (J)	271 ± 24	131 ± 12
CPHA (g)	0.16	0.08
	$(2.3 \cdot 10^{-3})^*$	$(1.1 \cdot 10^{-3})^*$
Balanced energy (J)	67 ± 40	31 ± 19
Balanced energy (kJ/mol CP)	29 ± 17	28 ± 19

228 * value of CPHA in mol

229



230

231 **Fig. 6.** Comparison of the balanced energy obtained in the case of hydrate formation from CP-
232 saturated PACP (green area), and differential enthalpy of CP desorption from PACP (blue and
233 black dots) [30]

234
235 As can be seen in Figure 6, the former (green area) does not cover the entire range of the latter
236 (dots), which confirms that part of the CP did not desorb from the PACP (and therefore did
237 not participate in the formation of hydrates). The high enthalpy values (48 to 57 kJ/mol of CP)
238 of the uncovered dots correspond to the filling of pores at the lowest pressures ($0 < P_{eq}/P_{sat} < \sim$
239 0.02) [30] *i.e.* the smallest pores, mainly micropores, where the prevailing interactions are
240 fluid-solid. The non-desorbed CP was therefore trapped in these pores. The enthalpy values of
241 the covered dots (28 to 48 kJ/mol of CP) correspond to medium-to-high-pressure filling of the
242 meso- and macropores ($\sim 0.02 < P_{eq}/P_{sat} < 1$) [30]. Hence, CP that desorbed from the PACP to
243 form hydrates was contained in these pore ranges where the prevailing interactions are solid-
244 fluid-fluid and fluid-fluid interactions. One can see that the balanced energy range obtained
245 was almost the same for both salinities (3.5 wt% NaCl and 8 wt% NaCl), suggesting no
246 significant effect of salt on this phenomenon. This result makes sense since the balanced
247 energy was found to be related to the CP-desorption energy. The balanced energy (+9 to +47
248 kJ/mol of CP) implied a thermal energy compensation of between 8% and 40% of the energy
249 supplied by hydrate crystallization. The (positive) balanced energy (+9 to +47 kJ/mol of CP)
250 implied a thermal energy compensation of the (negative) energy supplied by the hydrate
251 crystallization (-115.4 kJ/mol of CP). Its value, calculated as the ratio of the balanced energy
252 to the dissociation enthalpy of CP hydrates, is between 8% ($=100 \times 9:115.4$) and 40%
253 ($=100 \times 47:115.4$).

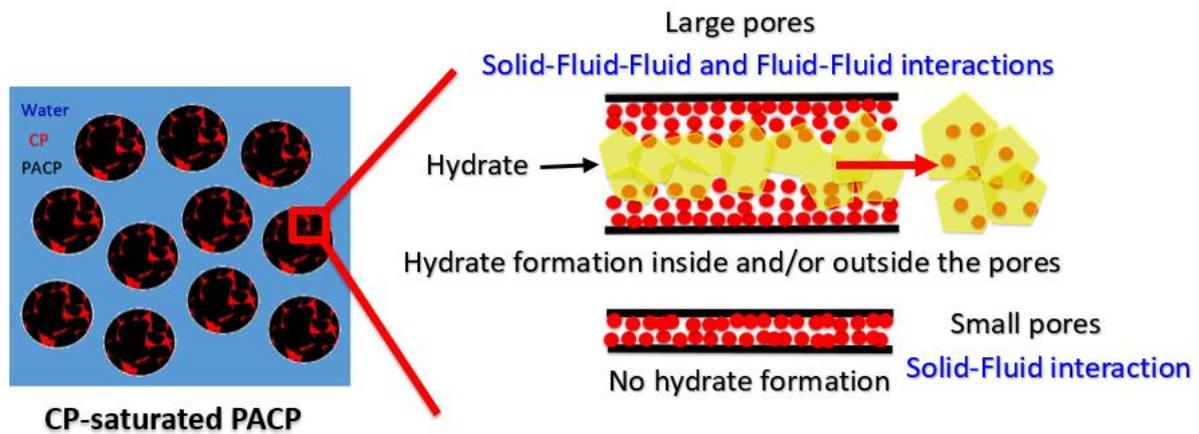
254 The investigation into the thermal energy compensation together with the assumption that
255 (some) water molecules can enter the pores of PACP [16,31] lead us to propose a mechanism

256 for CP-hydrate formation from CP-saturated PACP (Fig. 7). In the smallest pores, the fluid-
257 solid interactions prevent CP from desorbing and thus from participating in hydrate formation.
258 In larger pores, the prevailing interactions (solid-fluid-fluid and fluid-fluid interactions) allow
259 the desorption of CP (or at least part of it). In this case, hydrate formation can occur outside
260 and/or inside the pore.

261 It should be noted that the surface chemistry of the PACP is reported to impact (promote or
262 inhibit) hydrate crystallization [8,16,35]. However, in the case of our investigated system, the
263 low-size pores of PACP, where the specific surface is significant and thus also the surface
264 chemistry effects could be, do not participate to hydrate formation as previously explained.
265 Therefore, the role of surface chemistry is probably not critical compared to that of pore size.

266

267



268

269 **Fig. 7.** Proposed prevailing mechanisms of hydrate formation from CP-saturated PACP

270 immersed in water

271

272

273 **4. Conclusions**

274

275 In this work, the partial thermal energy compensation that may occur during hydrate
276 formation from CP adsorbed in PACP was investigated in brines with salt concentrations
277 typical of seawater (3.5 wt% NaCl) and produced water (8 wt% NaCl). A combination of
278 differential scanning calorimetry and refractive index measurements were used to determine
279 the thermal energies released by both the hydrate crystallization and CP desorption from the
280 PACP ($E_{des+crys}$), and by the hydrate crystallization alone (E_{crys}). The balanced energy
281 ($E_{crys} - E_{des+crys}$) was found to range between 9 and 47 kJ/mol of CP for both salinities,
282 which means that it might be possible to save 8% to 40% of the energy required by hydrate
283 crystallization in hydrate-based desalination processes. This energy can be attributed to the
284 desorption of CP from the large pores of the PACP. This result demonstrates that the CP
285 converted to hydrates was contained by the largest pores of the PACP, and that the part of CP
286 adsorbed in the smallest ones remained trapped. In the light of these results, a mechanism of
287 hydrate formation in these types of CP-saturated PACP has been proposed.

288

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295

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297

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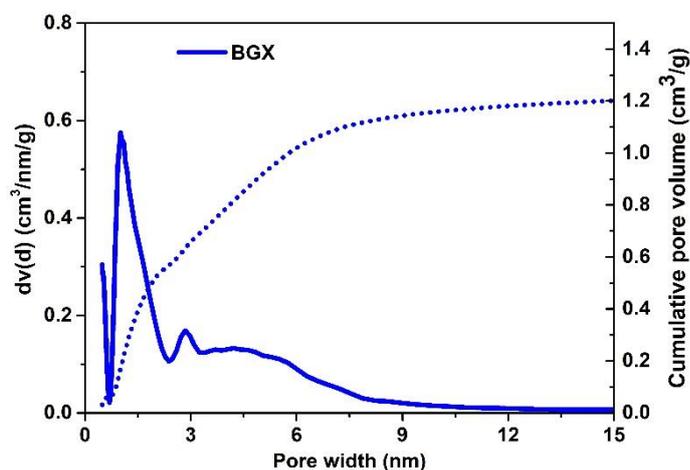
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403

404 Supplementary Material

405

406 SM-1

407 **Fig. S1.** PSD and cumulative PV determined using gas porosimetry (Ar isotherms at 87K on
408 Quantachrome IQ)

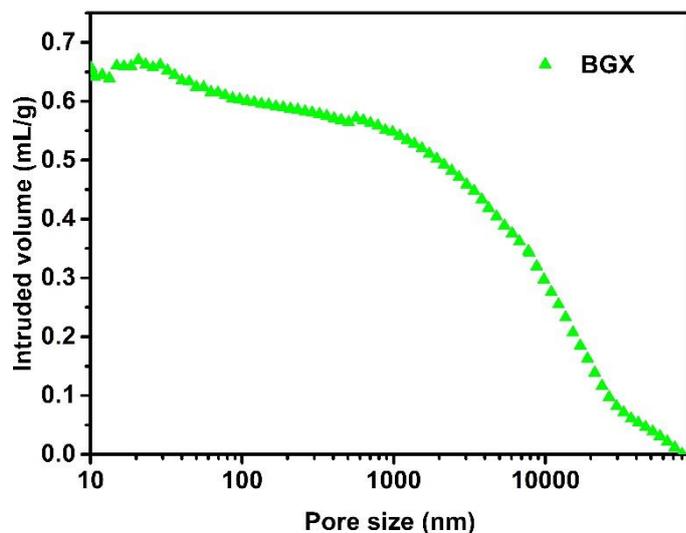


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411 SM-2

412 **Fig. S2.** cumulative PV determined using mercury intrusion porosimetry (Micromeritics
413 Autopore IV)



414

415

416 **SM-3**

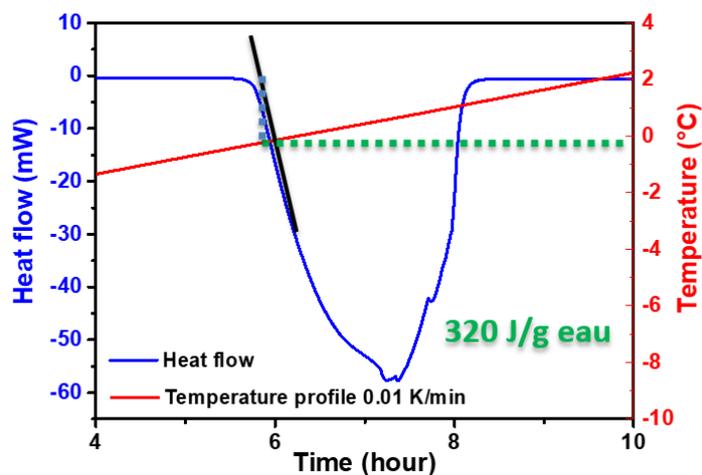
417 Determination of the CP-adsorption capacity of BGX

418 To perform CP-adsorption capacity measurements, the PACP were purified at 200°C for 12
 419 hrs under primary vacuum. Using a glass funnel, the hot purified sample was directly
 420 transferred into a small closable flask (5-mL capacity), which was then weighed and
 421 introduced into the CP adsorption chamber (closed-vessel partially filled with a flask of liquid
 422 CP). The PACP were only in contact with CP vapor (cf. Figure S1). The CP adsorption
 423 chamber was placed in the incubator at $1.0 \pm 0.5^\circ\text{C}$. After 48 hrs of adsorption, the flask was
 424 weighed again and the CP-adsorption capacity of the PACP was determined. The experiment
 425 was repeated 3 times to check the results.

426

427 **SM-4**

428 **Fig. S3.** dissociation of ice used to determine the uncertainties associated with the DSC
 429 measurements

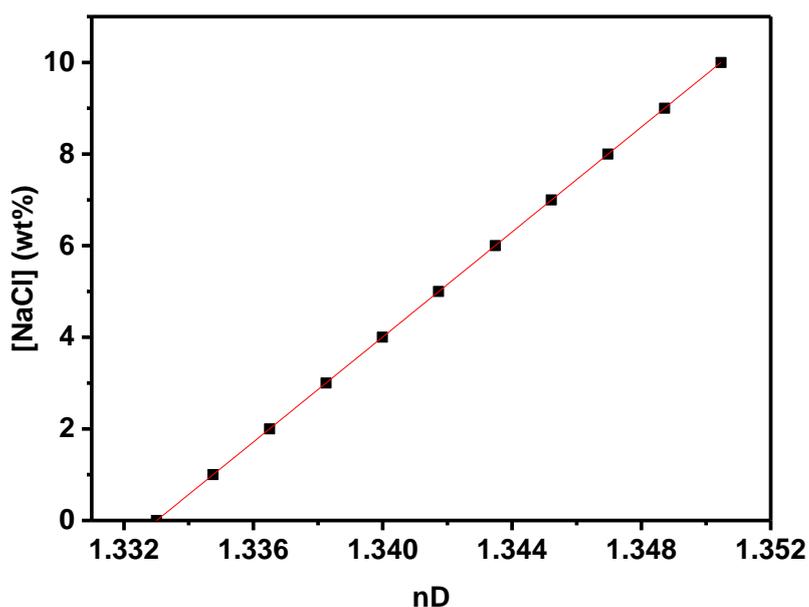


430

431

432 SM-5

433 Fig. S4. [NaCl]-nD calibration curve



434

435

436 The calibration curve [NaCl] vs. nD was obtained by measuring the refractive index (nD) of

437 previously prepared NaCl solutions of known concentrations [NaCl]. The linear regression of

438 the [NaCl] vs the nD plot gave the following equation: $[NaCl] = 573.044 \times nD - 763.87$. The

439 uncertainties regarding the slope and the offset were determined using the DROITEREG

440 function method ($\Delta a = 0.18704$; $\Delta b = 0.25096$). The uncertainties $\Delta[\text{NaCl}]$ and ΔWHC
 441 regarding the salinity determined and the water-to-hydrate conversion (WHC) respectively,
 442 were obtained by differentiating the calibration equation and equation 1. Finally, ΔE_{cryst} was
 443 obtained in a similar fashion after determining ΔWHA , ΔCPHA from the differentiation of
 444 equations 2 and 3.

445

446 **SM-6**

447 Gbac and ChemA are the notation used for G-BAC-G70R and Chemviron-A, which are two
 448 different PACP manufactured by Keruha GmbH and Calgon, respectively. The differential
 449 enthalpies of CP-adsorption on these PACP were measured in a previous work [30], and they
 450 showed almost the same values despite their different origins and characteristics. The
 451 similarity of the obtained results indicates a general range of values for CP adsorption on
 452 activated carbons.

453 Table S1. Origin and characteristics of Gbac and ChemA

	Gbac	ChemA
Origin	Petroleum pitch	Coconut
Particle size (μm)	700	<177
Principal pore size (nm)	5.5 ; 0.79	5.5 ; 0.79; 1.3

454

455