Article

An Aqueous CaCl₂ Solution in the Condenser/Evaporator Instead of Pure Water: Application for the New Adsorptive Cycle “Heat from Cold”

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Abstract: This paper addresses the analysis of the applicability of water as a working fluid for the new adsorptive heat transformation (AHT) cycle “Heat from Cold” (HeCol). The cycle proposed for cold countries operates at the ambient temperature below 0 °C. In this work, an aqueous solution of calcium chloride is proposed instead of liquid water to prevent the ice formation in the evaporator and condenser. The proposed water-based cycle is compared with the common methanol-based HeCol one in terms of the specific useful heat generated per cycle. The effect of the CaCl₂ solution on the cycle boundary pressures and its useful heat is studied both theoretically and experimentally. This approach can be extended to other adsorptive heat transformation cycles working at an evaporator or condenser temperature below 0 °C.

Keywords: adsorptive heat transformation; HeCol cycle; adsorption dynamics; water; calcium chloride aqueous solution

1. Introduction

Adsorption heat transformation (AHT) technology [1–3] is a promising way to utilize renewable and waste heat [4,5], which should replace fossil fuels in the immediate future. Closed AHT cycles operate by exchanging heat with the ambience. In essence, the heat of condensation/evaporation is rejected/absorbed to/from ambient thermal baths, such as air, soil, water reservoirs (sea, river, geothermal water, etc.). Therefore, the operating conditions of AHT cycles, first of all, the evaporator and condenser temperatures, are dictated by climatic conditions of the territory where AHT is used. The main AHT applications are cooling and air-conditioning [1,2], which are in demand in countries with warm or even hot climates. Water is basically used as a working fluid (adsorptive). It is ecologically sound and has a large evaporation enthalpy (ΔHₑ = 44.2 kJ/mol = 2.45 kJ/g at 20 °C [6]). This allows a high first law efficiency (or coefficient of performance, COP) to be obtained [3,7] as well as promotes a large specific useful heat Qₚᵤₛ per cycle. The principal disadvantages of water as a working fluid are:

1. A high freezing point of 0 °C. Ice formation in the evaporator/condenser at Tₑₑ < 0 °C is deemed to restrict the water application in AHT by the outdoor temperature above 0 °C;
2. Relatively low vapour pressure (Table 1) that can decelerate mass transport, which is determined by vapour pressure gradients in adsorbent bed or/and grain [8]. An intelligent compromise between reasonable values of COP and specific cooling power (SCP) has to be reached.
This analysis shows that it is very advantageous for gaining high SCP at the expense of lower COP and upgrading the ambient heat during the wintertime in cold countries [14]. A typical 3T HeCol cycle consists of two isosters and two isotherms (Figure 1). The regeneration (or desorption) phase occurs due to a drop of vapour pressure over adsorbent at its low and constant temperature \( T_M \) (stage 4–1 in Figure 1). The adsorption (or useful heat generation) phase is initiated by pressure jump at constant \( T_M \); the temperature of evaporator and adsorber is equal to the temperature of another natural thermal bath, namely a non-freezing water basin, such as a river, lake, sea, and underground water with \( T_M = 0\,\text{–}20\,\text{°C} \).

![Figure 1](image)

**Figure 1.** (a) P-T diagrams of a common isothermal (1–2–3–4) and non-isothermal (1–2–3′–4) 3T “Heat from Cold” (HeCol) cycles; (b) comparison of the HeCol cycles with pure water and a eutectic “CaCl₂ - water” solution in both evaporator and condenser.

If the ambient temperature \( T_{am} < 0\,\text{°C} \), methanol [10,11] and ammonia [12,13] are suggested as working fluids as they have a much lower melting temperature and higher vapour pressure (Table 1). The latter is advantageous for gaining high SCP at the expense of lower COP and \( Q_{us} \) due to a smaller evaporation heat of both methanol and ammonia. All these considerations are especially important for a novel AHT cycle “Heat from Cold” (HeCol), which has recently been proposed for upgrading the ambient heat during the wintertime in cold countries [14]. A typical 3T HeCol cycle consists of two isosters and two isotherms (Figure 1). The regeneration (or desorption) phase occurs due to a drop of vapour pressure over adsorbent at its low and constant temperature \( T_M \) (stage 4–1 in Figure 1). The adsorption (or useful heat generation) phase is initiated by pressure jump at constant (2–3, isothermal cycle) or raising (2–3′, non-isothermal cycle) temperature. The HeCol condenser is maintained at the ambient temperature \( T_L \); the temperature of evaporator and adsorber is equal to the temperature of another natural thermal bath, namely a non-freezing water basin, such as a river, lake, sea, and underground water with \( T_M = 0\,\text{–}20\,\text{°C} \).

For the first theoretical [15] and experimental [16,17] studies of the HeCol cycle, methanol was used as an adsorptive because of its low freezing temperature. These studies demonstrated that the proposed HeCol cycle is feasible and the generated useful heat can be suitable for heating low-energy buildings in countries with a cold climate (northern parts of Canada, Europe, Russia, the USA, etc.), as well as for the Arctic zone. However, the specific useful heat was found to be quite modest (300–400 \( \text{kJ/g} \)-adsorbent), which could be mostly due to the low evaporation heat of methanol, which is half of that for water (Table 1). It leads to the enhanced size of HeCol units, which, in its turn, increases inert thermal masses [18] of a HeCol unit and can further reduce the COP and the useful heat. Therefore, it is worthy of performing a thermodynamic evaluation of the HeCol useful heat, if water

| Working Fluid | \( T_m, °C \) | \( \Delta H_e \), kJ/mol (kJ/g) | \( P (0 \,\text{°C}), \text{mbar} \) | \( P (−10 \,\text{°C}), \text{mbar} \) | \( P (−20 \,\text{°C}), \text{mbar} \) |
|---------------|----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Water (pure)  | 0              | 44.2 (2.45)                     | 6.1                             | 2.6                             | 1.03                            |
| Methanol     | −97.6          | 37.5 (1.17)                     | 39.8                            | 19.9                            | 9.6                             |
| Ammonia      | −77.3          | 23.3 (1.37)                     | 4180                            | 2850                            | 1880                            |
| Eutectic \( \text{CaCl}_2 + \text{H}_2\text{O} \) | −55.5          | 45.4 (2.52)                     | 3.9                             | 1.8                             | 0.8                             |

\( ^1 \) at \( 20\,\text{°C} \); \( ^2 \) estimated from [9].

**Table 1.** Thermodynamic parameters of various working fluids.
would be used as adsorptive, and compare it with that with methanol [15,17]. In this hypothetical
analysis (Section 2), we neglect ice formation in the condenser. This analysis shows that it is very
attractive to use water vapour as adsorptive in the HeCol cycle; therefore, special measures should be
made to avoid ice formation in the condenser. For instance, it was proposed in [19] to mix pure water
with ethylene glycol as an anti-freezing agent. The glycol remains in the evaporator and, hence, water
is used as a refrigerant.

In this communication, we propose to use in the condenser and evaporator of the HeCol unit
an aqueous salt solution instead of pure water. It is well-known that the freezing point of a solvent
(water) is decreased upon the addition of a non-volatile solute (salt) [20]. The depression of the freezing
temperature depends on the salt nature and its concentration in solution. The lowest possible melting
temperature corresponds to the eutectic mixing ratio of the salt and water. The eutectic temperature for
different "salt–water" mixtures can vary in a wide range (Table 2) to cover possible winter conditions.
Further decline of the melting temperature can be reached by water [21] or solution [22] confinement
to small pores of a host matrix. Since the salt is non-volatile, only water vapour is in the gas phase over
the aqueous salt solution and serves as adsorptive.

**Table 2.** Salt content in the selected “water and salt” eutectic solutions and their melting temperature $T_m$.

| Salt     | Salt Content (wt.%) | $T_m$, °C | Reference |
|----------|---------------------|-----------|-----------|
| MgCl$_2$ | 21.8                | −33.5     | [23]      |
| CaCl$_2$ | 29.9                | −55.5     | [9]       |
| LiBr     | 39.1                | −67.5     | [24]      |

The proposed substitution of pure water with the salt solution leads to lower vapour pressure over
the salt solution (Table 3) caused by interaction of water molecules with anions and cations of the salt
dissociated in solution. The substitution can affect the cycle boundary pressures, the uptake variation,
and a driving force for adsorption and desorption. These issues are considered theoretically in Section 3.
As for HeCol cycle based on water as adsorptive, sorption dynamics is of crucial importance, we
have also performed an experimental measurement of water uptake/release curves under the reduced
vapour pressure typical for a eutectic (CaCl$_2$ – H$_2$O) solution in the evaporator/condenser. The dynamic
tests in Section 4 have aimed to evaluate whether the ad/desorption rate under these severe conditions
is acceptable for HeCol cycles.

**Table 3.** Vapour pressure (in mbar) over pure water/ice and eutectic (CaCl$_2$ – H$_2$O) solution at a
low temperature.

| $T_r$, °C | Pure Water | Eutectic CaCl$_2$ – H$_2$O |
|-----------|------------|---------------------------|
| 20        | 23.6       | 14.8                      |
| 10        | 12.4       | 7.8                       |
| 0         | 6.1        | 3.8                       |
| −5        | 4.0        | 2.7                       |
| −10       | 2.6        | 1.8                       |
| −15       | 1.65       | 1.2                       |
| −20       | 1.0        | 0.8                       |
| −25       | 0.63       | -                         |
| −30       | 0.38       | -                         |
| Reference | [25]       | [9]                       |
2. Effect of Methanol Substitution with Water

Here, we evaluate how the substitution of methanol with water can affect the performances of the typical HeCol cycle in terms of the specific useful heat $Q_{us}$ [J/g adsorbent] generated for a consumer. It should be noted that the specific useful heat $Q_{us}$ is equal for both isothermal and non-isothermal cycles. This heat is equal to the adsorption heat $Q_{ads}$ released at stage 2-3 minus the sensible heat $Q_{sen}$ consumed at stage 1-2 related to the adsorbent mass $m_a$

$$Q_{us} = Q_{ads} - Q_{sen} = \Delta H_{ads} \Delta w - CM(T_H - T_M)/m_a,$$

where $\Delta H_{ads}$ is the specific adsorption heat [J/g adsorbate], $\Delta w$ is the specific adsorbate mass exchanged in the cycle [g adsorbate/g adsorbent], $C$ and $M$ are the overall specific heat capacity and the mass of inert components, $T_H$ and $T_M$ are the temperatures of adsorption and regeneration (Figure 1a). In Equation (1), the specific heat of vapour in the gas phase is neglected as its mass is very small.

The overall specific heat capacity $C$ and mass $M$ of inert components concern the adsorbent, adsorbate, and metal heat exchanger that can be called as an "adsorbent – heat exchanger" unit (AdHEx). As seen from Equation (1), there is a threshold exchange $\Delta w^* = [C \cdot (T_H - T_M)] / (\Delta H_{ads} \cdot m_a)$, at which the adsorption heat just compensates sensible heating of the AdHEx unit.

The specific useful heat is compared for water and methanol as adsorptive for the HeCol unit tested in [17]. It consists of a plate-tube finned heat exchanger loaded with a composite sorbent LiCl/(silica gel), which is promising for sorbing both water [26] and methanol [27]. For this composite, $\Delta H_{ads} = (2.86 \pm 0.25)$ kJ/g for water [26] and $(1.30 \pm 0.08)$ kJ/g for methanol [27]. A fined flat-tube HEx (Yamaha Aerox) made of aluminum with the dimensions 190 x 200 x 30 mm$^3$ ($M_{Al} = 0.50$ kg and $m_a = 0.25$ kg) [17] is considered. Equation (1) can be re-written as:

$$Q_{us} = Q_{ads} -(Q_{sen}^{adsorbent} + Q_{sen}^{adsorbate} + Q_{sen}^{metal}) = \Delta H_{ads} \Delta w - [C_{LiCl} \omega_{LiCl} + C_{SiO2}(1 - \omega_{LiCl}) + C_{adsorbate}(\Delta w/2 + w_1) + C_{Al}M_{Al}/m_a](T_H - T_M),$$

where $\omega_{LiCl} = 0.21$ is the mass fraction of the salt in the composite, $w_1$ is the initial adsorbate content (0.1 g/g and 0.01 g/g for water and methanol, respectively); $T_H = 313$ K and $T_M = 293$ K (Figure 1b). The specific heat capacity $C$ of inert components is presented in Table 4.

| Component           | $C$, J/kg K | Reference |
|---------------------|-------------|-----------|
| Aluminum            | 903         | [28]      |
| Water               | 4180        | [28]      |
| Methanol            | 2490        | [28]      |
| Silica gel          | 740         | [29]      |
| Lithium Chloride    | 1130        | [29]      |

The useful heat of the HeCol cycle is generated only if $\Delta w > \Delta w^* = 0.023$ and 0.044 g/g for water and methanol (Figure 2). The heat linearly increases at larger adsorbate exchange $\Delta w$ and would be much larger if water is used as adsorptive instead of methanol. Therefore, the use of salt solutions instead of pure water is deemed to lead to significantly increasing the HeCol useful heat.
The released adsorption heat 

\[ Q_{\text{ads}} = \Delta H_{\text{ads}} \cdot m_a \cdot \Delta w \]

is consequently decreased. For the LiCl/silica, this reduction is acceptable as the specific useful heat \( Q_{\text{us}} = \Delta H_{\text{ads}} \cdot m_a \cdot (\Delta w - \Delta w^*) = 850 \text{ J/g}_2 \text{O} \) is only slightly lower than that for pure water (1020 J/g). Thus, it remains much larger as compared with methanol as adsorptive (490 J/g), at least, for the HeCol prototype tested in [16,17]. Although for the CaCl2/silica composite the uptake changes are significantly smaller (Table 5), a similar relation between the useful heats is found: 710 J/g > 480 J/g > 350 J/g.

Table 5. Comparison of the boundary pressures \( P \) (mbar), uptakes \( w \) and \( \Delta w \) (g/g) for the analyzed HeCol cycle with various fluids in the evaporator/condenser.

| Fluid           | \( P_1 \) | \( P_2 \) | \( P_3 \) | \( P_4 \) | LiCl/ (Silica gel) | CaCl2/ (Silica gel) |
|-----------------|----------|----------|----------|----------|-------------------|-------------------|
|                 | \( w_1 \) | \( w_2 \) | \( \Delta w \) | \( w_1 \) | \( w_2 \) | \( \Delta w \) |
| Water           | 1.0      | 3.8      | 22.4     | 5.8      | 0.10              | 0.48              |
| Eutectic solution | 0.8      | 3.1      | 14.2     | 3.7      | 0.06              | 0.38              |
| Methanol        | 11.2     | 35.3     | 130.1    | 45.1     | 0.01              | 0.43              |

Thus, from the thermodynamic point of view, the usage of eutectic (CaCl2 – H2O) solution in both evaporator and condenser could essentially increase the specific useful heat generated in the HeCol cycle as compared with methanol. However, the water boundary pressures are more than ten times lower than those for methanol (Table 5), and dynamic analysis is strictly necessary to realize whether the application of the salt solution is feasible. In this case, it seems difficult to make a relevant theoretical evaluation, which properly accounts for various heat and mass transfer resistances in this

Figure 2. Useful heat for water and methanol as adsorptive and LiCl/(silica gel) as adsorbent (see details in the text).

3. Effect of Aqueous Salt Solution on the HeCol Cycle

Here, we compare how the substitution of pure water with a eutectic (CaCl2 , H2O) solution affects the cycle boundary pressures and its useful heat \( Q_{\text{us}} \). The analysis is performed for the typical HeCol cycle with \( T_L = -20 ^\circ \text{C} \), \( T_M = 20 ^\circ \text{C} \), and \( T_H = 40 ^\circ \text{C} \) (Figure 1b). The composites (21 wt.% LiCl/ (silica gel) and (33 wt.%) CaCl2/ (silica gel), which are advanced sorbents of both methanol and water vapour [30], are considered here.

As the vapour–liquid (solid) equilibrium line for the solution lies below the line for water (ice), the proposed HeCol cycle is also shifted to lower pressure (Figure 1b and Table 5). It can be disadvantageous for ad/desorption dynamics; this issue is discussed in Section 4. The equilibrium uptake reduces so that the specific exchange \( \Delta w \) in the cycle changes from \( \Delta w = 0.38 \text{ g/g} \) to \( 0.32 \text{ g/g} \). The released adsorption heat \( Q_{\text{ads}} = \Delta H_{\text{ads}} \cdot m_a \cdot \Delta w \) is consequently decreased. For the LiCl/silica, this reduction is acceptable as the specific useful heat \( Q_{\text{us}} = \Delta H_{\text{ads}} \cdot m_a \cdot (\Delta w - \Delta w^*) = 850 \text{ J/g}_2 \text{O} \) is only slightly lower than that for pure water (1020 J/g). Thus, it remains much larger as compared with methanol as adsorptive (490 J/g), at least, for the HeCol prototype tested in [16,17]. Although for the CaCl2/silica composite the uptake changes are significantly smaller (Table 5), a similar relation between the useful heats is found: 710 J/g > 480 J/g > 350 J/g.

Table 5. Comparison of the boundary pressures \( P \) (mbar), uptakes \( w \) and \( \Delta w \) (g/g) for the analyzed HeCol cycle with various fluids in the evaporator/condenser.
system. For this reason, we have performed an experimental dynamic study of water sorption and desorption under the reduced water vapour pressures.

4. Experimental Study of Water Sorption Dynamics Under the Reduced Vapour Pressure

The dynamic tests aim at evaluating whether the rate of water sorption/desorption under these severe conditions is acceptable for HeCol cycles and which factors affect the dynamics. The composite SWS-1L (CaCl₂ in mesoporous silica gel) [30], commercial microporous silica gels Fuji RD [31] and Siogel (Oker Chemie) [32] are tested in this Section to elucidate the effect of the adsorbent properties. Their specific surface \( S_{sp} \) and pore volume \( V_{sp} \), the average size of pores \( d \) and grains \( D \) are displayed in Table 6.

Table 6. Textural characteristics of the sorbents tested.

| Sorbent          | \( S_{sp}, \text{m}^2/\text{g} \) | \( V_{sp}, \text{cm}^3/\text{g} \) | \( d, \text{nm} \) | \( D_{gr}, \text{mm} \) |
|------------------|---------------------------------|---------------------------------|---------------|-----------------|
| SWS-1L           | 230                             | 0.51                            | 15            | 0.3–0.35        |
| Silica Fuji RD   | 820                             | 0.40                            | 2.2           | 0.4–0.5         |
| Silica Siogel    | 800                             | 0.40                            | 2.0           | 0.4–0.5         |

4.1. Experimental

The dynamics of water sorption was studied under both adsorption and desorption modes by a volumetric Large Pressure Jump method with an experimental set-up described elsewhere [33]. The adsorbent loose grains were mounted on metal support inside a Teflon ring (diameter 23 and 16 mm for composite and silica gels, respectively). The dry adsorbent mass \( m_a = 180 \) and 90 mg for SWS and silica gels, so that the ratio \( S/m = \) (heat transfer surface area)/(adsorbent mass) = 2.3 and 2.15 m²/kg (Table 7). This value is typical for real AdHEx used for AHT [3]. For drying the adsorbents and removing residual air, the metal support was heated to 100 °C under continuous pumping. The temporal evolution of the water uptake and release \( w(t) \) was calculated from the change in the vapour pressure over the adsorbent as described in [33]. The pressure was recorded every 1 s by a pressure sensor MKS Baratron® type 626A (accuracy ± 0.01 mbar). As the pressure drop/jump \( \Delta P \) is a driving force for vapour transfer, the selected adsorbents were tested for larger and smaller \( \Delta P \)-values, namely 20.3 and 11.1 mbar for adsorption, 6.1 and 2.9 mbar for desorption (Table 7). The metal support temperature was maintained constant at 20 °C for desorption and 40 °C for adsorption (Figure 1b).

Table 7. Conditions of the dynamic tests.

| Sorbent          | \( \Delta w_{eq}, \text{g/g} \) | \( S/m_a, \text{m}^2/\text{kg} \) | Adsorption | Desorption |
|------------------|--------------------------------|---------------------------------|------------|------------|
|                  | \( T_i, ^\circ \text{C} \) | \( P_{in} \rightarrow P_{fin} \) | \( T_f, ^\circ \text{C} \) | \( P_{in} \rightarrow P_{fin} \) |
| SWS-1L           | 0.26                           | 2.3                             | 40         | 3.1 → 23.4 | 20 | 6.9 → 0.8 |
| Silica Fuji RD   | 0.13                           | 2.3                             | 40         | 3.1 → 23.4 | 20 | 6.9 → 0.8 |
| Silica Siogel    | 0.085                          | 2.15                            | 40         | 3.1 → 14.2 | 20 | 3.7 → 0.8 |

4.2. Water Adsorption Dynamics

The selected kinetic curves for water adsorption and desorption are presented in Figures 3 and 4. At short times, both processes are quite fast, the exponential function satisfactorily describes an initial part of the curves (up to the dimensional conversion \( \chi = 0.4–0.6 \))

\[
\chi = 1 - e^{d/\tau},
\]

with the characteristic time \( \tau \) presented in Table 8. It is quite short for adsorption and increases from 12 s to 41 s when the larger water mass is adsorbed (from 0.05 g/g to 0.21 g/g). Interestingly, the initial adsorption rate is almost equal for these cases, which results in the same initial (maximal)
power $W_{\text{max}} = \Delta H_{\text{ads}} \cdot \Delta w_{\text{exp}} / \tau = 11.3 \pm 0.4$ kW/kg (Table 8). It is quite large despite such low vapour pressures and small driving force $\Delta P$ for mass transfer. The driving force for the water desorption is even smaller, and the desorption temperature is only 20 °C. As a result, desorption (Figure 4) is slower than adsorption (Table 8): the exponential time varies from 30 to 81 s, and the maximal power varies from 2.1 to 3.7 kW/kg.

At longer times (or larger conversions), both adsorption and desorption become slower, so that the time $\tau_{0.7}$ corresponding to $\chi = 0.7$ is significantly longer than the exponential one. This slowdown can be due to adsorbent heating/cooling caused by heat release/absorption during the adsorption/desorption

### Table 8. Results of the dynamic tests.

| Sorbent       | $\Delta w_{\text{exp}}$ | $\tau$, s | $\tau_{0.7}$, s | $W_{\text{max}}$, kW/kg | $W_{0.7}$, kW/kg | $\Delta w_{\text{exp}}$, g/g | $\tau$, s | $\tau_{0.7}$, s | $W_{\text{max}}$, kW/kg | $W_{0.7}$, kW/kg |
|---------------|--------------------------|-----------|-----------------|--------------------------|-----------------|-------------------------------|-----------|-----------------|--------------------------|-----------------|
| SWS-1L        | 0.21                     | 47        | 105             | 10.9                     | 3.4             | 0.025                         | 30        | 34              | 2.1                      | 1.3             |
| Silica Fuji RD| 0.13                     | 30        | 60              | 11.7                     | 4.1             | 0.11                          | 81        | 315             | 3.7                      | 0.7             |
| Silica Siogel | 0.05                     | 12        | 126             | 11.7                     | 0.8             | 0.03                          | 33        | 112             | 2.5                      | 0.5             |

![Figure 3](image3.png)  
**Figure 3.** Dimensionless water uptake curves (■) for SWS-1L (a) and Fuji silica RD (b). Solid lines—exponential approximation (3).

![Figure 4](image4.png)  
**Figure 4.** Dimensionless water release curves (■) for silica gels Fuji RD (a) and Siogel (b). Solid lines—exponential approximation (3).
tests, as revealed by numerical modeling in [34]. This rate reduction could be alleviated by enhancing heat transfer between the adsorbent and the metal support, e.g., by consolidating them with a binder.

For the desorption runs, the experimental conversions for SWS-1L and the Siogel (Table 8) are much smaller than the equilibrium ones (Table 7), although, for the Fuji RD, they are equal. For the composite, it can be caused by a quite large heat of desorption due to a strong interaction between water molecules and the salt. It is likely to make the water removal at low desorption temperature and small pressure drop extremely slow. It was assumed in [35] that, for the composite LiCl/silica, an additional driving force might need to initiate the reaction between the salt and water. This can be true for any chemical reaction systems, e.g., composites "salt in porous matrix" [30]. These sorbents are very good for HeCol cycles from the thermodynamic point of view but may have severe dynamic restrictions. A trade-off between these issues is obligatory, especially if water is used as adsorptive.

The subtle driving force for desorption ($\Delta P = 2.9$ mbar) can also be a reason for small conversion for the Siogel. For a major part of the adsorbed water, the desorption time is much longer than 1000-1500 s because of the very small pressure gradient in the adsorbent bed of grain. If the driving force increases to 6.1 mbar, complete water desorption is observed for the silica Fiji RD, which is very similar to the Siogel silica from both dynamic and thermodynamic points of view [36]. The pressure drops providing acceptable dynamics under these severe conditions should be the subject of future analysis. At present, the practical recommendation is obvious: to make the drop as large as possible because the desorption rate seems very sensitive to its value. In the real HeCol units, the pressure drops $\Delta P = P_4 - P_1$ are gradually reducing in time because the salt solution in the condenser is getting less concentrated; hence, the condensation pressure $P_1$ is increasing. For moderating this effect, the volumes of the condenser and evaporator should be enlarged.

5. Summary

A new cycle "Heat from Cold" (HeCol) has recently been proposed for upgrading the ambient heat in cold countries [14]. The useful heat of this cycle essentially increases at lower temperature of the ambient air [15], which is far below 0 °C. For this reason, methanol was used as a working fluid for the first theoretical and experimental investigations of the HeCol cycle. These studies confirmed that the cycle is feasible; however, its specific useful heat is restricted by 300–400 J/g_adsorbent [17] due to the relatively low evaporation heat of methanol. This paper has aimed to analyze whether water, having much larger evaporation heat, can be applied as a working fluid for HeCol cycle.

First, a thermodynamic evaluation showed that the HeCol useful heat would be much larger if water is used as adsorptive instead of methanol (Figure 2). This heat is generated only if the uptake change in the cycle is larger than a threshold value $\Delta w^*$, at which the adsorption heat just compensates the sensible heating of the AdHEx unit. For the particular HeCol unit tested in [16,17], this value is estimated for water and methanol as $\Delta w^* = 0.023$ and $0.044$ g/g.

To use water as adsorptive, it is necessary to avoid ice formation in the condenser. Here, we propose to use in the condenser and evaporator of a HeCol unit an aqueous salt solution instead of pure water. For instance, the freezing point of a eutectic CaCl$_2$ solution is as low as $-55.5$ °C and the solution remains liquid above this temperature. The salt addition results in lower vapour pressure over the salt solution (Table 3) so that the cycle boundary pressures (Figure 1b and Table 7) and the uptake variation (Table 5) reduce appropriately. Despite this decrease, the specific useful heat still remains much larger as compared with methanol as adsorptive; e.g., 870 J/g versus 520 J/g for the HeCol prototype tested in [16,17]. Thus, the proposed substitution is very advantageous from the thermodynamic point of view.

The dynamic tests were performed to evaluate whether the adsorption and desorption rates under the reduced vapour pressure are acceptable for the HeCol cycle. The dynamics are studied by a volumetric LPJ set-up described in [33] for three selected adsorbents under larger and smaller pressure drops $\Delta P$ (Table 7). The adsorption dynamics is quite fast and ensures the initial useful power as large as 11.3 ± 0.4 kW/kg (Table 8). The driving force for water desorption is smaller than for adsorption;
therefore, it is slower, and the initial power varies from 2.1 to 3.4 kW/g. However, the experimental desorption conversion can be smaller than the equilibrium one due to the large desorption heat (for the composite "CaCl$_2$ in mesoporous silica") and/or subtle driving force for desorption (for the silica Siogel). The composites "salt in porous matrix" [30] are promising for the HeCol cycle from the thermodynamic point of view; however, an intelligent compromise between the useful heat and specific power has to be reached.

It is worth noting that a eutectic aqueous solution of CaCl$_2$ provides a very low freezing point of $-55.5^\circ\text{C}$ that can cover almost all possible winter conditions. For most of the cold countries, a higher freezing temperature is sufficient, e.g., $-33.5$ or $-21.2^\circ\text{C}$ for eutectic aqueous solutions of MgCl$_2$ or NaCl. In this case, the reduction of the water vapour pressure is smaller and leads to the enlargement of both uptake change $\Delta w$ and driving force $\Delta P$ for desorption; hence, higher specific useful heat and power can be expected. Thus, a choice of the proper salt can be an effective tool to manage these basic outputs of the HeCol cycle.

In a broader sense, this approach can be extended to other AHT cycles working at the evaporator or condenser temperature below 0 °C. It is notable if a large adsorption heat is crucially important, as for adsorptive heat storage and, first of all, for its long-term (seasonal) version. For this application, the useful heat actually supplied to a consumer is dramatically lower than the theoretical value [37]. This is due to the fact that the sensible heat of the storage unit is completely lost and has to be recovered.

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**Nomenclature**

| Symbol | Definition                                      |
|--------|-------------------------------------------------|
| C      | specific heat capacity, J/(g K)                 |
| D      | average size of grains, mm                      |
| d      | average size of pores, nm                       |
| H      | enthalpy, J/mol                                 |
| $M, m$ | mass, g                                         |
| $p$    | pressure, mbar                                  |
| $Q$    | specific heat, J/g                              |
| $S$    | surface, m$^2$                                  |
| $S_{sp}$ | specific surface area, m$^2$/g                 |
| $T$    | temperature, K, °C                             |
| $t$    | time, s                                         |
| $V_{sp}$ | specific pore volume, cm$^3$/g                |
| $W$    | specific power, W/g                             |
| $w$    | specific adsorbate mass, g/g                   |
| wt.%   | weight %                                        |

**Greek symbols**

| Symbol | Definition                                      |
|--------|-------------------------------------------------|
| $\tau$ | characteristic time                             |
| $\chi$ | dimensionless uptake                            |
| $\omega$ | dimensionless salt fraction                     |

**Subscript**

| Symbol | Description                      |
|--------|----------------------------------|
| 0.7    | 70% conversion                   |
| a      | adsorbent                        |
| ads    | adsorption                       |
| Al     | aluminum                         |
| am     | ambient                          |
con condensator
des desorption
e evaporation
eq equilibrium
ev evaporator
exp experimental
fin final
H high
in initial
L low
M medium
m melting
max maximal
sen sensible
us useful

Abbreviation
3T three temperature
AdHEx adsorbent – heat exchanger
AHT adsorption heat transformation
COP coefficient of performance
HeCol Heat from Cold
LPJ Large Pressure Jump method
SCP specific cooling power

References
1. Wang, R.; Wang, L.; Wu, J. Adsorption Refrigeration Technology: Theory and Application; John Wiley & Sons, Singapore Pte. Ltd.: Singapore, 2014.
2. Saha, B.B.; Ng, K.S. Advances in Adsorption Technologies; Nova Science Publishers: Hauppauge, NY, USA, 2010.
3. Sapienza, A.; Frazzica, A.; Freni, A.; Aristov, Y.I. Dynamics of Adsorptive Systems for Heat Transformation; Springer: Cham, Switzerland, 2018.
4. Deng, J.; Wang, R.Z.; Han, G.Y. A review of thermally activated cooling technologies for combined cooling, heating and power systems. *Prog. Energy Combust. Sci.* 2011, 37, 172–203. [CrossRef]
5. Gordeeva, L.G.; Aristov, Y.I. Adsorptive heat storage and amplification: New cycles and adsorbents. *Energy* 2019, 167, 440–453. [CrossRef]
6. Wexler, A. Vapor Pressure Formulation for Ice. *J. Res. Natl. Bur. Stand.—A Phys. Chem.* 1977, 81, 5–20. [CrossRef]
7. Freni, A.; Maggio, G.; Sapienza, A.; Frazzica, A.; Restuccia, G.; Vasta, S. Comparative analysis of promising adsorbent/adsorbate pairs for adsorptive heat pumping, air conditioning and refrigeration. *Appl. Therm. Eng.* 2016, 104, 85–95. [CrossRef]
8. Ruthven, D.M. *Principles of Adsorption and Adsorption Processes*; John Wiley & Sons: New York, NY, USA, 1984.
9. Conde, M.R. Properties of aqueous solutions of lithium and calcium chlorides: Formulations for use in air conditioning equipment design. *Int. J. Therm. Sci.* 2004, 43, 367–382. [CrossRef]
10. Douss, N.; Meunier, F. Effect of operating temperatures on the coefficient of performance of active carbon-methanol systems. *Heat Recovery Syst. CHP* 1998, 8, 383–392. [CrossRef]
11. Pons, M.; Meunier, F.; Cacciola, G.; Critoph, R.E.; Groll, M.; Puigjaner, L.; Spinner, B.; Ziegler, F. Thermodynamic based comparison of sorption systems for cooling and heat pumping. *Int. J. Refrig.* 1999, 22, 5–17. [CrossRef]
12. Vasiliev, L.L.; Kanonchik, L.E.; Antujh, A.A.; Kulakov, A.G. NaX Zeolite, Carbon Fibre and CaCl2 Ammonia Reactors for Heat Pumps and Refrigerators. *Adsorption* 1996, 2, 311–316. [CrossRef]
13. Tamainot-Telto, Z.; Metcalf, S.; Critoph, R.E.; Zhong, Y.; Thorpe, R. Carbon–ammonia pairs for adsorption refrigeration applications: Ice making, air conditioning and heat pumping. *Int. J. Refrig.* 2009, 32, 1212–1229. [CrossRef]
14. Aristov, Y.I. Adsorptive transformation of ambient heat: A new cycle. *Appl. Therm. Eng.* 2017, 124, 521–524. [CrossRef]
15. Okunev, B.N.; Voskresensky, N.M.; Girmik, I.S.; Aristov, Y.I. Thermodynamic analysis of a new adsorption cycle for ambient heat upgrading: Ideal heat transfer. J. Eng. Thermophys. 2018, 27, 524–530. [CrossRef]
16. Tokarev, M.M.; Gordeeva, L.G.; Shkatulov, A.I.; Aristov, Y.I. Testing the lab-scale “Heat from Cold” prototype with the “LiCl/silica–methanol” working pair. Energy Convers. Manag. 2018, 159, 213–220. [CrossRef]
17. Tokarev, M.M. A Double-Bed Adsorptive Heat Transformer for Upgrading Ambient Heat: Design and First Tests. Energies 2019, 12, 4037. [CrossRef]
18. Gluesenkamp, K.R.; Frazzica, A.; Velte, A.; Metcalf, S.; Yang, Z.; Rouhani, M.; Blackman, C.; Qu, M.; Laurenz, E.; Rivero-Pacho, A.; et al. Experimentally Measured Thermal Masses of Adsorption Heat Exchangers. Energies 2020, 13, 1150. [CrossRef]
19. Seiler, J.; Hackmann, J.; Lanzerath, F.; Bardow, A. Refrigeration below zero °C: Adsorption chillers using water with ethylene glycol as antifreeze. Int. J. Refrig. 2017, 77, 39–47. [CrossRef]
20. Cengel, Y.A.; Boles, M.A. Thermodynamics: An Engineering Approach, 4th ed.; McGraw-Hill Inc.: New York, NY, USA, 2002.
21. Brun, M.; Lallemend, A.; Quinson, J.-F.; Eyraud, C. A new method for the simultaneous determination of the size and shape of pores: The thermoporometry. Thermochim. Acta 1977, 21, 59–88. [CrossRef]
22. Aristov, Y.I.; Di Marco, G.; Tokarev, M.M.; Parmon, V.N. Selective water sorbents for multiple applications: 3. CaCl2 solution confined in micro- and mesoporous silica gels: Pore size effect on the “solidification-melting” diagram. React. Kinet. Catal. Lett. 1997, 61, 147–160. [CrossRef]
23. National Research Council of the USA. International Critical Tables of Numerical Data, Physics, Chemistry and Technology; National Research Council: Washington, DC, USA, 1928; Volume 4.
24. Kirgintsev, A.N.; Trushnikova, L.N.; Lavrentieva, V.G. Vapor Pressure of Ice. Available online: https://www.lyotechnology.com/vapor-pressure-of-ice.cfm (accessed on 11 April 2020).
25. Gordeeva, L.G.; Shkatulov, A.I.; Huininik, H.; Girmik, I.S.; Aristov, Y.I. Adsorption method for moisture and heat recuperation in ventilation: Composites “LiCl/matrix” tailored for cold climate. Energy 2020, 201, 117595. [CrossRef]
26. Gordeeva, L.G.; Aristov, Y.I. Composite sorbent of methanol “LiCl in mesoporous silica gel” for adsorption cooling: Dynamic optimization. Energy 2011, 36, 1273–1279. [CrossRef]
27. Lide, D.R. Handbook of Chemistry and Physics, 84th ed.; CRC: Boca Raton, FL, USA, 2004.
28. Rabinovich, V.A.; Khavin, Z.Y. Solubility of Inorganic Substances in Water: Handbook; Chemistry: Leningrad, Russia, 1972. (In Russian)
29. Chua, H.T.; Ng, K.C.; Chakraborty, A.; Oo, N.M.; Othman, M.A. Adsorption characteristics of silica gel + water systems. J. Chem. Eng. Data 2002, 47, 1177–1181. [CrossRef]
30. Sapienza, A.; Velte, A.; Girmik, I.; Frazzica, A.; Füldner, G.; Schnabel, L.; Aristov, Y.I. “Water—Silica Siogel” working pair for adsorption chillers: Adsorption equilibrium and dynamics. Renew. Energy 2017, 110, 40–46. [CrossRef]
31. Palomba, V.; Sappienza, A.; Aristov, Y.I. Dynamics and useful heat of the discharge stage of adsorptive cycles for long term thermal storage. Appl. Energy 2019, 248, 299–309. [CrossRef]