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Editorial

Adsorptive Systems for Heat Transformation and Heat Storage Applications

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1. Introduction

According to the BP Statistical Review of World Energy 2020 [1], the primary energy consumption growth slowed to 1.3% last year, less than half the rate of growth in 2018 (2.8%). Fossil fuel (oil, coal, and gas) remains the major primary energy source with a total share of 84%, leading to the growth by 0.5% of carbon emissions from energy use. Although a total share of renewables (solar, wind, biofuel) of 5.0% was very modest, it increased by a record amount, accounting for over 40% of the growth in primary energy in 2019.

Adsorption heat transformation and storage (AHTS) is gaining more and more attention in the scientific community as an emerging, environmentally benign technology utilizing renewable heat sources for cooling and heating. The Special Issue (SI) "Adsorptive Systems for Heat Transformation and Heat Storage Applications" aimed to provide an overview of the state-of-the-art technology in the AHTS field. The main aspects of AHTS technology were covered in this SI, including:

Development of novel and optimization of known AHTS applications and cycles.
Rational design of new adsorbents and testing of alternative working fluids.
Optimization of system design and performance.

Below we describe and briefly analyze the contributions in this SI, following this classification.

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2. A Short Review of the Contributions in This Issue

2.1. Development of Novel and Optimization of Known AHTS Applications and Cycles

Among various AHTS applications, adsorption cooling, heat pumping, and heat storage are at the most developed level yet; however, they are still far from practical applications. Therefore, the development and study of new cycles is an important direction for the development of AHCS.

Schamberger et al. [2] comprehensively described and analyzed a new Stratisorp cycle, which is an advanced version of the common adsorptive cycles with internal heat recovery [3]. The basic concept of the Stratisorp cycle is the connection of the adsorber with a well-insulated, stratified thermal storage tank, where the heat released during the adsorption phase is stored. The temperature of the fluid increases with the height of the storage bed due to buoyancy forces. The heat from each temperature level is stored separately in the storage bed needed in the next half (desorption) cycle. Thus, the new cycle can implement the internal heat recovery with a single adsorber instead of two, as is the case in the common concept [3]. In the Stratisorp cycle, the heat storage and release phases are separated in time; therefore, it can also be used in an intermittent mode, e.g., as short-term adsorptive heat storage.

To derive full advantage from the new cycle, (1) an innovative adsorber with improved heat and mass transfer characteristics was designed, built, and tested, and (2) a 1D dynamic model was developed to evaluate the entropy generation and the second law efficiency of the new cycle. It was shown that, due to lower driving temperature differences, the irreversibility caused by thermal coupling could be considerably reduced. However, it is reached at the expense of new irreversibility, due to convective mixing within the storage tank. Yet, the total entropy generation is reduced (see Figure 6 in [2]), thanks to the internal heat recovery in the storage tank.

Tokarev [4] experimentally studied a novel adsorption cycle, "Heat from Cold" (HeCol). It was proposed [5] for upgrading the heat of a natural basin of non-freezing water (ocean, sea, river, lake, underground water, etc.), available for free at temperatures from 3–15 °C to 30–40 °C, which is suitable for heating. This cycle's main feature is the use of ambient air at the temperature $-20 \div -40$ °C as a heat sink, which greatly helps in adsorbent regeneration. A laboratory-scale HeCol prototype, consisting of two adsorbers loaded with a composite sorbent LiCl/(mesoporous silica), was tested with methanol as a working fluid. The prototype ensured a continuous heat generation under steady-state cycling with a specific useful power of 350–390 W/kg and a thermal efficiency 0.44, showing good potential for a practical realization of the HeCol concept. The proposals for further unit improvements were outlined and discussed.

Girnik et al. [6] theoretically studied a novel adsorption method, VentireC, which was proposed for heat and moisture recuperation in ventilation systems in cold countries. The VentireC unit comprises two thermally coupled adsorbent beds (AB) and two isolated heat-storing beds (HSB). Indoor air passes through AB1 and HSB1, where indoor moisture and heat are absorbed. Simultaneously, outdoor air passes in AB2 and HSB2 in the opposite direction, extracting the stored heat and moisture, thus maintaining the indoor temperature and humidity balance. Thermal coupling of two ABs allows the heat released during moisture adsorption in one adsorber to be transferred to another one to facilitate water adsorption/desorption and to promote better adsorbent regeneration. The VentireC offers the following advantages: (1) inflow air relative humidity is maintained at a comfortable level of 40–45%; (2) freezing of moisture in the unit outlet at outdoor temperatures above -12 °C is avoided. At a lower outdoor temperature, better dehumidification can be achieved with a longer contact time between air and the adsorbent.

A passive method for regulating the temperature and relative humidity of the air inside museum display cases was suggested and theoretically studied by Yu et al. [7]. The concept of using composite materials for temperature and humidity control was proposed. They consist of the porous silica gel as a humidity-regulating material and a phase change material as a temperature-regulating element. Its temperature-regulating capacity was higher as compared with using only silica gel. The moisture buffering capacity is close to that of the silica gel; however, it was lower than for silicas modified by hygroscopic salt, as proposed in [8]. Thus, the proposed method and materials could effectively improve the stability of the temperature and relative humidity in museum display cases.

A specific feature of AHTS is that its performance can be susceptible to the cycle operating conditions determined by four boundary temperatures of adsorption, desorption, condensation, and evaporation. They, in turn, are determined by climatic conditions, AHTS application, and the heat source available for desorption. In the literature, there are many different methodologies to define these temperatures that make difficult the comparison of the performance of AHTS units and adsorbents. Frazzica et al. [9] suggested a unified methodology to identify the boundary working conditions, under which, long-term, seasonal thermal energy storage (STES) in buildings operates. This methodology is based on features of building envelop, heating system for desorption (solar thermal collectors), space heating distribution, heat source/sink for evaporation/condensation, climatic conditions of the place where the STES is installed, and space heating demands. Based on this methodology, winter and summer operating conditions were thoroughly identified for two locations (Regensburg and Stockholm), representing the climates of Central and North Europe, respectively, considering the ambient temperature variations through the year. Finally, the potential of two adsorbents (composite LiCl/MWCNT and AQSOA FAM-Z02) was assessed in terms of the needed adsorbent volume as a function of the heating demand fraction covered by STES.

2.2. Rational Design of New Adsorbents and Testing of Alternative Working Fluids

Since the pair "adsorbent–working fluid" is a keystone of AHTS technology, the study of novel working pairs with advanced properties and their adsorption equilibrium is one of the effective routes for improving AHTS performance.

Common working fluids are water, methanol, ethanol, and ammonia. A systematic scanning of "adsorbent–working fluid" pairs (258 pure fluids and 16 adsorbents) was reported in [10]. It confirmed the thermodynamic advantages of the four mentioned fluids and explained why. For the first three fluids, the operating pressure is much lower than atmospheric pressure; whereas, for ammonia, it can be much higher. From dynamic, safety and cost issues, it is convenient to use working fluids with the operating pressure around atmospheric one. This opportunity was investigated by Luberti et al. [11], who analyzed a mixture "ammonia–ethanol" instead of pure fluids. The authors found that the total pressure around atmospheric one could be obtained using ethanol/ammonia mixtures with the ethanol mole fraction between 0.70 and 0.75. A decrease in COP was observed for these mixtures compared with pure fluids, which is a cost for the advantages mentioned above.

Since water is the best working fluid from the thermodynamic point of view, recent attempts have been made to use it for AHCS cycles performing at T < 0 °C, which is the water freezing temperature. To prevent ice formation in the evaporator/condenser and expand the temperature range for water application below 0 °C, the authors of [12] suggested adding ethylene glycol to water. In this SI, Girnik et al. [13] proposed to use an aqueous salt solution instead of pure water. The solution has a lower freezing point and higher evaporation heat, both being profitable from the thermodynamic point of view. The effect of $CaCl_2$ solution on the boundary pressures and useful heat of the new HeCol cycle [5] is studied both theoretically and experimentally. Such a substitution is found to be kinetically acceptable for this low temperature. Yet, further study of prototypes is necessary. In a broader sense, this approach can be extended to other AHTS cycles working at an evaporator or condenser temperature below 0 °C [14].

The adsorption isotherm of working pairs is the most important feature in characterizing an AHTS system. According to IUPAC classification [15], there are eight types of adsorption isotherms and many theoretical and empirical models for their description. The selection of a suitable model could be an issue. Rahman et al. [16] suggested optimal models for describing each isotherm type. Fifteen models, including traditional (Langmuir, Toth, Henry, BET, etc.) and novel (universal isotherm model by Ng et al., Sun and Chakraborty, Yahia et al.) are considered for the description of adsorption isotherms of thirteen adsorbent–adsorbate pairs, which include all eight isotherm types. The study provides a universal approach for selecting the optimal model for any experimental data on adsorption isotherms.

Chemical heat pumps operate based on the same working principles as adsorption heat pumps [17]. Searching for stable and cheap materials for CHP is an essential issue for practical realization of this technology. Lai et al. [18] evaluated the potential of Ofunato limestone, in comparison with Kawara and Garrou natural limestones (Japan), as a calcium oxide source for $CaO/H_2O/Ca(OH)_2$ chemical heat pump. The effect of impurities (quartz and clay minerals) on the CaO reactivity was examined. Although the high temperature sintering of impurities in the Ofunato limestone occurs easy and could inhibit hydration reaction of CaO particles, this effect can be minimalized by controlling the decarbonization temperature and process time. For practical chemical heat pump development, the cheap Ofunato limestone can be utilized instead of the high quality and expensive Kawara limestone.

2.3. Optimization of System Design and Performance

The system design and performance optimization are prerequisites for making the AHTS more competitive with common absorption and vapor compression technologies.

A crucial element of any AHTS is an integrated unit "adsorbent—heat exchanger" (AdHEx). For this unit, the ratio M_{HEx}/M_{ad} = (HEx mass)/(Ad mass) characterizes the effect of HEx thermal masses (TM) [19]. The TM definition was considered in this SI by Gluesenkamp et al. [20]. It depends on the control volume chosen, which is affected by the type of HEx and AHTS cycle, and, for instance, can include the heat transfer fluid inside the HEx channels, connecting pipes, valves, etc. The authors reported detailed data on the TM for many typical AdHExs, including flat tube–fins, round tube–corrugated fins, modular finned tube, hell–tube, plate–shell, and other HEx types. Experimental data on TM were collected from many research laboratories around the world and presented in terms of the specific thermal mass STM = <TM>/<Ad mass> and the effective specific heat $C_{p.eff}$ = <TM>/<HEx mass>. Both indicators are useful for analyzing and modeling the AHTS performance. The TM impact on system performance and the contribution of the heat transfer fluid to the overall effective thermal mass are also briefly discussed.

The paper of Kulakowska et al. [21] was also concerned AdHex and its thermal masses. The authors proposed introducing into the silica gel bed special additives—metal particles (aluminum and copper) or carbon nanotubes—which are inert from the adsorption point of view, but capable of improving heat transfer in the bed. As follows from the previous papers [19,23], such an approach can improve heat transfer, adsorption rate, and specific cooling power; however, these advantages are at the expense of lower AHTS efficiency (COP). The obtained results show that all the additives lead to higher thermal diffusivity compared with that of the parent silica gel bed. The best effect was observed for the mixture with 15 wt% aluminum, probably due to the more homogeneous mixing of the silica gel grains with the additive particles.

The paper by Krzywanski [22] addressed the design and optimization of HEx that is one of the most critical components of any AHTS unit. To reach this goal, the author used an AGENN model, a combination of genetic algorithms and artificial neural networks. Its application was illustrated on a falling film evaporator, as one of the most promising units for adsorption cooling–desalination systems. A broad range of operating conditions and geometric configurations were considered, e.g., different tube pass arrangements—top–bottom, bottom–top, and side by side. The total heat transfer rate of the evaporator was predicted by the model with a maximum error of less than 3%. This provides a solid basis for using the developed model in practice and considers it a cost-effective and universal methodology for researchers working in adsorption, power engineering, and environmental science, etc.

It is known that the adsorption rate and specific power of closed AHTS systems can be greatly reduced by a non-condensable gas (NCG). Donkers et al. [23] studied the effect of NCG on the performance of the reactor for thermochemical energy storage. The theoretical and experimental study of the water evaporation/condensation process and (K_2CO_3 hydration)/($K_2CO_3 \cdot 1.5H_2O$ dehydration) was performed. The main findings were as follows: (1) even a small amount of NCG in a vacuum setup can significantly reduce or even stop the evaporation/condensation, due to a high concentration of NCG located over the condensation surface [24]; (2) the decrease in performance is related to the water transport process, which is convection at low NCG content and transforms into a diffusion at high NCG content. To design a robust AHTS system, strict demands on leak tightness of the reactor/Ad-HEx unit have to be imposed. Significant progress achieved by the authors in comparison with previous studies is associated with the development of a mathematical model that allows acceptable levels of NCG in an AHTS unit to be calculated.

Chemisorption systems produce more heat per kg of adsorbed refrigerant and have potentially higher COP than adsorption systems. Hinmers and Critoph [25] performed modeling of the barium chloride ammoniation, keeping in mind this process for chemical heat transformers/heat pumps. $BaCl_2$ was confined to a conductive matrix of expanded natural graphite to enhance the bed thermal properties. The model was built using semi-empirical equations from the literature [26] and was validated with the kinetic tests performed by a large temperature jump method. The authors mentioned that this method best tests sorption systems with transient processes, such as supersaturation, overheating, and subcooling, etc. A reasonable prediction for solid/gas reactions dynamics is possible with the suggested model if kinetic constants are known. In addition, the results provide enough evidence and knowledge to produce a detailed design for a resorption bed or adsorption generator.

Chorowski et al. [27] analyzed the AHTS applicability in countries with an essential portion of CHP in total electricity production and well-developed district heating networks, such as Poland, Russia, Ukraine, etc. The authors proposed modifications to increase the COP by better software control of an existing large-scale (90 kW cooling power), three-bed, two-evaporator adsorption chiller. The suggested changes were related to a sequence of the switching valves, which enabled mass and heat regeneration to be implemented without any changes in the chiller's hardware. This resulted in significant improvement of the COP (up to 0.7) and the cooperation of the chiller and heating source. The latter is of great importance in the case of district heating supply. In the authors' opinion, the presented modifications could potentially lead to similar improvements in the AHTS performance.

Artificial neural networks (ANN) offer a modern way for modeling complex problems, which cannot be described with simple mathematical approaches. The ANN is widely used to model renewable energy systems [28]; however, their application for AHTS is still scarce. This gap has partially been filled in by Halon et al. [29], who used a multi-layer ANN to predict the cooling capacity and COP of a real adsorption chiller, built and operated in Wroclaw, Poland.

First, the ANN was trained using experimental data, collected over several years of testing the mentioned chiller. Then, the model was applied to accurately assess the unit's performance when driven by only partially predictable energy sources. As a result, the cooling capacity of the adsorption chiller can be predicted with reasonable accuracy; whereas, to achieve a similar accuracy of COP predictions, a substantially bigger experimental database is required. The obtained results can be used to develop a flexible system to control AHTS chillers.

3. Conclusions

On the one hand, the Special Issue "Adsorptive Systems for Heat Transformation and Heat Storage Applications" clearly demonstrates the increasing attention which this technology has attracted. This is due to its potential contribution to smoothing global climate changes, rational use of renewable and waste energy, and its reduced consumption of fossil fuel [30]. Another AHTS advantage is its modest consumption of electricity that is especially important in places with electricity deficit or/and high costs of electricity. On the other hand, the share of AHTS technology is almost negligible compared with traditional systems—vapor compression and absorption chillers [31]. Therefore, there is still room for improving AHTS units and making them more competitive [32]. We hope that this SI will contribute to further development and dissemination of this promising technology. For ensuring its future progress, intensive R&D programs are still necessary, including the international collaboration of experts in materials science, thermal and chemical engineering, adsorption technology, and related fields.

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References

1. *Statistical Review of World Energy 2020*, 69th ed.; Available online: bp.com/statisticalreview (accessed on 9 January 2022).
2. Schamberger, V.; Desai, A.; Schmidt, F. Novel Adsorption Cycle for High-Efficiency Adsorption Heat Pumps and Chillers: Modeling and Simulation Results. *Energies* **2020**, *13*, 19. [CrossRef]
3. Pons, M.; Poyelle, F. Adsorptive machines with advanced cycles for heat pumping or cooling applications. *Int. J. Refrig.* **1999**, *22*, 27–37. [CrossRef]
4. Tokarev, M.M. A Double-Bed Adsorptive Heat Transformer for Upgrading Ambient Heat: Design and First Tests. *Energies* **2019**, *12*, 4037. [CrossRef]
5. Aristov, Y.I. Adsorptive transformation of ambient heat: A new cycle. *Appl. Thermal. Eng.* **2017**, *124*, 521–524. [CrossRef]
6. Girnik, I.S.; Yang, T.; Gordeeva, L.G.; Wang, W.; Ge, T.; Aristov, Y.I. New Adsorption Method for Moisture and Heat Exchange in Ventilation Systems in Cold Countries: Concept and Mathematical Simulation. *Energies* **2020**, *13*, 1386. [CrossRef]
7. Yu, M.; Zhang, X.; Zhao, Y.; Zhang, X. A Novel Passive Method for Regulating Both Air Temperature and Relative Humidity of the Microenvironment in Museum Display Cases. *Energies* **2019**, *12*, 3768. [CrossRef]
8. Glaznev, I.S.; Salnikova, I.V.; Alekseev, V.N.; Gordeeva, L.G.; Elepov, B.S.; Kundo, L.P.; Shilova, I.A.; Aristov, Y.I. ARTIC-1: A New Humidity Buffer for Showcases. *Stud. Conserv.* **2009**, *54*, 133–148. [CrossRef]
9. Frazzica, A.; Brancato, V.; Dawoud, B. Unified Methodology to Identify the Potential Application of Seasonal Sorption Storage Technology. *Energies* **2020**, *13*, 1037. [CrossRef]
10. Santori, G.; Di Santis, C. Optimal fluids for adsorptive cooling and heating. *Sustain. Mater. Technol.* **2017**, *12*, 52–61. [CrossRef]
11. Luberti, M.; Di Santis, C.; Santori, G. Ammonia/Ethanol Mixture for Adsorption Refrigeration. *Energies* **2020**, *13*, 983. [CrossRef]
12. 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]
13. Girnik, I.S.; Aristov, Y.I. An Aqueous CaCl2 Solution in the Condenser/Evaporator Instead of Pure Water: Application for the New Adsorptive Cycle "Heat from Cold". *Energies* **2020**, *13*, 2904. [CrossRef]
14. Girnik, I.S.; Aristov, Y.I. Water as a working fluid for adsorptive cycles operating at temperature below 0 °C. *Energy* **2020**, *211*, 119037. [CrossRef]
15. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [CrossRef]
16. Rahman, M.M.; Muttakin, M.; Pal, A.; Shafiullah, A.Z.; Saha, B.B. A Statistical Approach to Determine Optimal Models for IUPAC-Classified Adsorption Isotherms. *Energies* **2019**, *12*, 4565. [CrossRef]
17. Raldow, W.M.; Wentworth, W.E. Chemical heat pumps—A basic thermodynamic analysis. *Sol. Energy* **1979**, *23*, 75–79. [CrossRef]
18. Lai, L.; Imai, T.; Umezu, M.; Ishii, M.; Ogura, H. Possibility of Calcium Oxide from Natural Limestone Including Impurities for Chemical Heat Pump. *Energies* **2020**, *13*, 803. [CrossRef]
19. 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]
20. 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]
21. Kulakowska, A.; Pajdak, A.; Krzywanski, J.; Grabowska, K.; Zylka, A.; Sosnowski, M.; Wesolowska, M.; Sztekler, K.; Nowak, W. Effect of Metal and Carbon Nanotube Additives on the Thermal Diffusivity of a Silica Gel-Based Adsorption Bed. *Energies* **2020**, *13*, 1391. [CrossRef]
22. Krzywanski, J. A General Approach in Optimization of Heat Exchangers by Bio-Inspired Artificial Intelligence Methods. *Energies* **2019**, *12*, 4441. [CrossRef]
23. Donkers, P.; Gao, K.; Houben, J.; Huinink, H.; Erich, B.; Adan, O. Effect of Non-Condensable Gasses on the Performance of a Vacuum Thermochemical Reactor. *Energies* **2020**, *13*, 362. [CrossRef]
24. Nusselt, W. Surface condensation of water vapor. *Z. Ver. Deut. Ing.* **1916**, *60*, 541–546.
25. Hinmers, S.; Critoph, R.E. Modelling the Ammoniation of Barium Chloride for Chemical Heat Transformations. *Energies* **2019**, *12*, 4404. [CrossRef]
26. Mazet, N.; Amouroux, M.; Spinner, B. Analysis and Experimental Study of the Transformation of a Non-Isothermal Solid/Gas Reacting Medium. *Chem. Eng. Commun.* **1991**, *99*, 155–174. [CrossRef]
27. Chorowski, M.; Pyrka, P.; Rogala, Z.; Czupryński, P. Experimental Study of Performance Improvement of 3-Bed and 2-Evaporator Adsorption Chiller by Control Optimization. *Energies* **2019**, *12*, 3943. [CrossRef]
28. Kalogirou, S.A. Artificial neural networks in renewable energy systems applications: A review. *Renew. Sustain. Energy Rev.* **2001**, *5*, 373–401. [CrossRef]
29. Halon, T.; Pelinska-Olko, E.; Szyc, M.; Zajaczkowski, B. Predicting Performance of a District Heat Powered Adsorption Chiller by Means of an Artificial Neural Network. *Energies* **2019**, *12*, 3328. [CrossRef]
30. Wang, R.; Wang, L.; Wu, J. *Adsorption Refrigeration Technology: Theory and Application*; John Wiley & Sons Singapore Pte. Ltd.: Singapore, 2014.

31. Jacob, U. Is Thermal Cooling a Sleeping Giant or Just Wishful Thinking? Presentation "Friends of Sorption" Workshop, 2018, Pisa, Italy. Available online: https://www.sorptionfriends.org/presentations-keynotes/keynote-is-thermal-cooling-a-sleeping-giant-or-just-wishful-thinking-uli-jakob-green-chiller-association-for-sorption-cooling-e.v/ (accessed on 28 June 2021).
32. Aristov, Y.I. Adsorption processes for energy conversion and storage: What have we learned over the past decade of this century? *Energy* **2022**, *239*, 122142. [CrossRef]