Effect of Metal and Carbon Nanotube Additives on the Thermal Diffusivity of a Silica-Gel-Based Adsorption Bed

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Abstract: This article presents a study of the effect of metal particle and carbon nanotube additives on the thermal diffusivity of a silica-gel-based adsorption bed of an adsorption chiller. The structural properties of silica gel and carbon nanotubes were investigated using the volumetric method of low-pressure nitrogen adsorption. Thermal characteristic tests of the prepared mixtures based on a silica gel with 5 wt% and 15 wt% of aluminum, copper, or carbon nanotubes were carried out. The obtained results show that all the materials used as additives in blends in this study achieved higher thermal diffusivities in comparison with the thermal diffusivity of the parent silica gel. However, the best effect was observed for the mixture with 15 wt% aluminum.

Keywords: silica gel; thermal diffusivity; carbon nanotubes; adsorption chiller

1. Introduction

The planet’s ecological situation has long been forcing humanity to seek new, greener energy sources and industrial solutions. Globally, numerous branches of industry generate vast amounts of waste heat, which is not being used efficiently. One of the prospective solutions to this issue is adsorption cooling technology that can be powered using industrial waste heat [1–6] or renewable sources of energy. Refrigerants used in adsorption refrigeration, such as water, methanol, and ammonia, are natural substances that do not cause ozone layer depletion and global warming problems. Furthermore, adsorption cooling has more advantages in the form of its simple control, low operating costs, and lack of vibration [1,2,4,7–11].

The cooling capacity of the adsorption aggregate is obtained using thermal processes that take place during adsorption and desorption on porous media; the improvement of these phenomena is currently one of the most critical research challenges as adsorption chillers achieve lower coefficients of performance (COPs) in comparison to conventional compressor refrigerators. The maximum values for the COP of an adsorption chiller are usually between 0.5 and 0.6, while the COP of a compressor refrigerator is about 3–5 [2]. Since the main reason for the low COPs is the low thermal diffusivities of the adsorption beds, the study of the thermal properties of different bed component configurations is of high practical significance [2,12–16].
The most useful sorbents are the ones that adsorb water, including silica gel (SG) and zeolites. Natural and synthetic zeolites represent the most significant category of crystalline porous solids. The properties of zeolites concerning water sorption can be adjusted by modifying the framework composition, mainly the Si/Al ratio [17]. However, the disadvantage of zeolite adsorbents is their high desorption temperature (>200 °C) [18–20].

In addition to inorganic materials, porous coordination polymers (PCPs), also known as metal–organic frameworks (MOFs), have emerged as a new class of microporous materials [21–26]. MOFs are characterized by favorable properties, such as extraordinary porosity and a high degree of structural tunability, but the degradation of some earlier examples of highly porous MOFs in humid environments showed their lack of suitability for industrial implementation [27]. Apart from parent materials, a lot of studies show new types of composite materials composed of zeolites [28,29], silica gel (SG) [17,29,30], carbon nanotubes (CNTs) [31], and CNT-MOF [32].

Water adsorption cooling using silica gel is the most advanced adsorption cooling technology, which was successfully introduced to the market in the 1980s [33]. Silica gel has a colloidal silicic acid structure that is a porous polymer [34,35]. SG is often used in commercial applications, such as adsorption cooling [36–38], drying [39–41], separation [39,40], and desalination [42–44]. Silica gel has a low temperature of desorption (<100 °C) [17,45,46], making this material very suitable for use in adsorption chillers for waste heat utilization. Water adsorption on silica gel is a physical adsorption phenomenon, and SG’s adsorption capacity is very stable even in the case of a long period of operation. This material exhibits an excellent ability for the adsorption of water. The SG is also applied as an adsorbent because of its high uptake capacity, reliability, and low cost in comparison with other adsorbents [2].

On the other hand, water is an ideal refrigerant because it is an environmentally friendly and non-toxic adsorbate. Thus, silica gel and water is the most applicable working pair for adsorption cooling technology [47]. In assessing the water sorption capacity and heat transfer efficiency of cooling with a moisture adsorbing material, its thermal and physical properties play an essential role. Parameters such as specific surface area, pore-volume, pore size distribution, and thermophysical properties, including the thermal diffusivity of the silica gel, are the most significant in the design and optimization of adsorption processes. Adsorbents with a larger surface have a higher sorption capacity. To design an effective adsorptive cooling system, a larger heat transfer surface area in the adsorption bed and a lower heat capacity of the silica gel are needed [48]. The SG’s structural parameters have various values, depending on the method of their production. In Islam et al. [49], the structure of six different silica gels was examined using the volumetric method. The tested gels had a specific surface area determined using the Brunauer–Emett–Teller (BET) model (SSA_{BET}) in the range of 490–780 m²/g and a total pore volume of 0.26–0.80 cm³/g, depending on the type of SG and its particle size. Mohammed et al. [50] examined the structure of two kinds of SG and obtained specific surface values in the range of 690–830 m²/g and a pore volume of 0.34–0.62 cm³/g.

Several modifications are used to improve the thermal properties of silica gels. Mixtures with various compounds, including nanomaterials, graphite, crystals, or chemical modifications involving the introduction of functional groups [51], may increase the gas and vapor adsorption capacity of silica gels. This relationship also applies to thermal and mechanical changes in other mesoporous and macroporous materials [52,53]. It is possible to improve the thermal properties by using a composition of silica gel and materials with a high thermal conductivity [14,54,55]. In Zheng et al. [56], the structural parameters and thermal diffusivity of a mixture of silica gel with expanded natural graphite treated with sulfuric acid (ENG-TSA) were examined in various proportions. The diffusivity of the created blends was closely related to the apparent density of ENG-TSA and the share of ENG-TSA in the SG. As the ENG-TSA share rose, the thermal diffusivity value increased from about \(1.75 \times 10^{-5} \text{ m}^2/\text{g}\) to about \(6 \times 10^{-5} \text{ m}^2/\text{g}\). The analysis of the thermal behavior of devices using a silica gel was studied by Gurgel et al. [57,58], among others. The authors showed that silica gel is very sensitive to heat and mass transfer rates inside the adsorbent beads. In the case of improving the thermal properties
of the silica gel as an adsorption bed, some authors analyzed the influence of metal additives to the silica gel adsorption bed [14,54]. Rezk et al. theoretically investigated the influence of metal additives on thermal performance and the overall cooling capacity of the adsorption chiller [14]. Based on these theoretical considerations, the authors reported an increase in cooling capacity and COP of modified chillers. Demir et al. [54] used a silica gel as a basis of the mixture and added spiral metal pieces, which were made of copper, brass, and aluminum, and sieved for separation into two fractions: 1–2.8 mm and 2.8–4.75 mm. They observed that the addition of 15 wt% aluminum wires to silica gel considerably enhanced the thermal diffusivity of a parent silica gel bed.

The effect of using metallic additives on the thermal conductivity of granular-activated carbon was investigated by Askalany et al. [55]. The theoretical considerations revealed that filings of iron, copper, and aluminum at different mass concentrations resulted in an increase of specific cooling power by 100%. Bahrehmand et al. observed that adding natural graphite flakes to a CaCl$_2$–silica gel composite adsorbent in a sorption cooling system can significantly enhance the overall thermal diffusivity while reducing the active material and increasing the mass transfer resistance [59]. The authors registered 500% and 17% increases in thermal diffusivity and COP, respectively, with a share of 20 wt% graphite flakes.

A detailed summary of these results is given in Table 1.

A CNT is one of the most interesting materials due to its unique properties and capability of being applied in different fields. First of all, it has a very high thermal conductivity [60–64]. Dasgupta et al. [60] used CNT in adsorption beds in a CNT–methanol adsorption pair since CNT is a useful adsorbent of methanol. However, CNTs also display functional water [65,66] and gas [67–69] transport capacities. CNTs may also have a well-developed pore structure. According to Peigney et al. [70], CNTs and nanofibers have surface area densities of 250 m$^2$/g to nearly 900 m$^2$/g, as determined using the microscopic characteristics. The CNTs manufactured using the CCVD method on a zeolite catalyst had an $SSA_{BET}$ (N$_2$, 77 K) in the range of 310–650 m$^2$/g [71], while the same parameter of the commercial CNT powder examined by Inoue using high-resolution episcopic microscopy [72] was found to be 200 m$^2$/g. In Pajdak et al. [73], the authors studied the structure of CNTs at various temperatures. They obtained $SSA_{BET}$ values of 170 m$^2$/g (N$_2$, 77 K) and 170–340 m$^2$/g (CO$_2$, 298–358 K).

In the present study, carbon nanotubes (CNTs), as well as copper (Cu) and aluminum (Al) particles, were used as additives to improve the thermophysical properties of a silica gel (SG). These additives were selected since they have the highest thermal conductivities among metals. The main objective of the research was to select a sorption material that has good adsorption and thermal properties for use in a low-pressure adsorption chiller. For this reason, silica gel was selected as a parent material since it is a widely available adsorbent with good adsorption properties. Aluminum and copper powders, as well as carbon nanotubes, were chosen as additives to allow for improving the thermal properties of adsorption beds and thus increasing the cooling capacity of adsorption chillers.

The significant novelty of the presented research is the comparative analysis of the thermal diffusivity of a silica-gel-base adsorption bed with carbon nanotubes and metals additives.
| Parent Material | Particle Diameter of Parent Material | Additive | Content | Thermal Conductivity | Improvement | Ref. |
|-----------------|-------------------------------------|----------|---------|----------------------|-------------|------|
|                 | mm                                  |          |         | % W/mK               | %           |      |
| Silica gel      | 3–5                                 | Al       | 5       | 0.34                 | 72          | [14] |
|                 |                                     |          | 10      | 0.498                | 152         | [14] |
|                 |                                     |          | 15      | 0.675                | 241         | [14] |
|                 | 3–5                                 | Cu       | 5       | 0.305                | 54          | [14] |
|                 |                                     |          | 10      | 0.424                | 114         | [14] |
|                 |                                     |          | 15      | 0.557                | 181         | [14] |
| Activated carbon| 1–2                                 | Al       | 10      | 10                   | 100         | [55] |
|                 |                                     |          | 20      | 8                    | 80          | [55] |
|                 |                                     |          | 30      | 16                   | 160         | [55] |
|                 |                                     | Cu       | 10      | 12                   | 120         | [55] |
|                 |                                     |          | 20      | 12                   | 120         | [55] |
|                 |                                     |          | 30      | 12                   | 120         | [55] |
| CaCl₂ + silica gel | 150 μm × 1.3 mm *; 250–500 μm ** | Carbon flakes | 20 | 0.78 | 136 | 17 | [59] |

* For CaCl₂ fine-length, ** for silica gel; COP: Coefficient of Performance.
2. Methods and Materials

The solid samples were sieved on a vibrating Analysette 3 Spartan shaker screen (FRITSCH GmbH, Idar-Oberstein, Germany), and then the fraction of particles in the range of 100–160 µm was selected for the study.

Structural analyses of the materials were performed with an ASAP 2020 volumetric analyzer (Micromeritics, Norcross, Georgia, USA) using low-pressure nitrogen adsorption (LPNA) at 77 K. The measurements were carried out under isothermal conditions in the absolute pressure range of 0–0.1 MPa, corresponding to a relative pressure range of 0 < p/p₀ < 0.996.

Before measurements were made, each sample was degassed under vacuum at 378 K for 4 hours. LPNA measurements consisted of filling the pore volume of the tested materials with adsorbate particles (N₂) due to the interactions occurring at the solid–gas interface under vacuum. The analysis aimed to record the volume of gas accumulated in the sample pore space and the pressure around the sample. By knowing the volume of the adsorbed gas, the structural parameters SG and CNT were determined, such as the specific surface area (SSA), pore volume (V), and pore size distribution (PSD). The pore space of materials in the range of micropores and partly mesopores was characterized. The theoretical models of Brunauer–Emmett–Teller (BET) [74], t-plot, and non-localized density functional theory (NLDFT) [75,76] were employed in the calculations. The t-plot calculations were made based on the BET specific surface area and using the Broekhoff–de Boer thickness equation (silica gel) and carbon black STSA thickness equation (CNT). For the calculations of the NLDFT model, it was assumed that the tested materials had pores with a cylindrical shape. The skeletal density of the SG and CNT were defined using an AccuPyc II 1340 analyzer (Micromeritics, Norcross, Georgia, USA). The density was determined based on the sample skeletal volume by measuring the amount of helium that penetrated the open pores in the samples at 298 K. High purity gases were used for the porosimetric and densimetric analyses, namely helium 6.0 (pycnometer method) and nitrogen 6.0 (LPNA method).

Thermal diffusivity is a material-specific property that characterizes heat conduction in transient conditions. This value allows for determining how quickly a given material reacts to temperature changes. To define the coefficient of thermal diffusivity dependence, the laser flash method was applied in this study. The method allows for determining the thermal diffusivity factor based on the specific heat, density, and thermal conductivity coefficient according to Equation (1):

$$a = \frac{\lambda}{\rho C_p}$$  (1)

The thermal diffusivity of material is related to the time to reach thermal equilibrium under variable thermal conditions. The tests were carried out on an LFA 457 MicroFlash (Netzsch-Gerätebau GmbH, Selb, Germany). A sample of a test plate-shaped material was placed in a holder and “closed” from the outside with spacers made of a material with known properties, e.g., aluminum. The sample was subjected to a heater to determine the desired measurement temperature, and then a laser light pulse of known energy was directed toward the sample. From the moment of exposure, the time and temperature on the other side of the sample were recorded. The scheme of thermal diffusivity measurement using the laser flash method is shown in Figure 1.

Knowing the temperature change rate allows for determining the heating rate (heat diffusion in the material). The coefficient of thermal diffusivity was calculated by the camera automatically based on the built-in relationship; the coefficient is proportional to the square of the sample thickness and inversely proportional to the time for the expected temperature rise to occur. The measurement conditions of thermal diffusivity are shown in Table 2.

Seven different samples were prepared for studying the thermal diffusivity, as seen in Table 3.

As previously mentioned, silica gel was selected for the study as a base adsorbent material. It is the typical adsorbent used in adsorption chillers. Copper (Cu) and aluminum (Al) particles were applied to increase the thermal diffusivity of the adsorption bed. Carbon nanotubes (CNTs) were also selected
due to their excellent thermal conductivity. The commercial silica gel and nanotubes were supplied from Fuji Silysia Chemical Ltd (Greenville, South Carolina, USA) and 3D-nano (Cracow, Poland), respectively. According to the manufacturer’s data, the metals used in the study were of high purity. Materials were delivered by the manufacturers and mixed as powders after weighing. The main properties of the samples are shown in Table 4.

![Temperature change detector](image)

**Figure 1.** The operating principle of the laser flash method apparatus.

| Dimensions of Sample (ø/h) | Reaction Atmosphere | Gas Flow Rate | Reference Temperature | Measurement Temperatures |
|---------------------------|---------------------|---------------|-----------------------|-------------------------|
| mm                       | cm³/min             | K             | K                     |
| 13/4                      | Ar                  | 50            | 293                   | 298–358, every 10       |

**Table 2.** Parameters for the measurement of thermal diffusivity.

| SG content in the sample (wt%) | 100 | 95 | 95 | 95 | 85 | 85 | 85 |
| An additive content in sample (wt%) | 0   | 5  | 5  | 5  | 15 | 15 | 15 |

| Additive | Al | Cu | CNTs | Al | Cu | CNTs |
|----------|----|----|------|----|----|------|
|          |    |    |      |    |    |      |

**Table 3.** Sample compositions for measurement. CNTs: Carbon nanotubes.

| Material               | Granulation | Thermal Conductivity | Thermal Diffusivity |
|------------------------|-------------|----------------------|---------------------|
| Silica gel (SG)        | 100–160     | 0.1760 [51]          | 0.137 [51]          |
| Aluminium (Al)         | 45–425      | 237 [51]             | 97.1 [54]           |
| Copper (Cu)            | <150        | 401 [51]             | 117 [54]            |
| Carbon nanotubes (CNTs) | Ø = 3 nm, l = 10 nm | 3000 [54] (by length) | 460 [61] |

**Table 4.** Physical properties of the used materials.

3. Results

3.1. The Structural Analyses

The N₂ equilibrium adsorption points were determined using the LPNA method. From these measurements, the adsorption isotherms were plotted, which are shown in Figure 2a,b. The silica gel adsorption isotherm (Figure 2a) represents a type I adsorption material, according to International Union of Pure and Applied Chemistry (IUPAC) [77], and is similar to a Langmuir isotherm. This shape
of the isotherm indicates that as the concentration of the N$_2$ adsorbate increased, the active centers became gradually saturated, and the adsorption process decreased. This isotherm shape is typical for materials with many micropores in their porous structure. Carbon nanotubes, which were added to the silica gel, produced a type II isotherm (Figure 2b) [77].

![N$_2$ sorption isotherms of (a) SG and (b) CNTs.](image)

This shape of isotherms is typical for mesoporous materials but its shape for CNTs is also due to adsorbate (N$_2$)–adsorbent interactions. CNTs are not highly selective compared to, e.g., hard coal. Nevertheless, if one compares the measurements from the adsorption of N$_2$ and CO$_2$ to the CNTs, one can see a significant difference in the sorption capacity, and the structural parameters determined using a CO$_2$ adsorbate have much higher values [72]. Capillary condensation of the adsorbate occurred in the samples in the multilayer area. The desorption curves did not reproduce the adsorption curves, and slight hysteresis loops were observed.

The structural parameters of SG and CNT materials calculated based on the sorption isotherms are given in Table 5. The amount of nitrogen adsorption in the tested silica gel at 0.1 MPa was 125.4 mmol/g. The multilayer specific surface area, determined using the BET model ($SSA_{BET}$), was 753 m$^2$/g. Based on the t-plot model, the SSA value of the silica gel was divided into micropores ($micrSSA$) and pores larger than the micropores, namely external pores ($extSSA$). The value of $micrSSA$ was 128 m$^2$/g, and the $extSSA$ was 625 m$^2$/g. This suggests that in the tested silica gel, the pore surface area was mostly formed by mesopores rather than by micropores. Based on the NLDFT model, the participation of the volume of the smallest pores in the silica gel was very low. The volume of pores with diameters below 3.6 nm was 0.02 cm$^3$/g, while the total volume of pores was 0.45 cm$^3$/g.

![Figure 2. N$_2$ sorption isotherms of (a) SG and (b) CNTs.](image)

For the tested CNTs, the adsorption volume at 0.1 MPa was 27.7 mmol/g. The specific surface parameters of the CNTs, regardless of whether BET or t-plot models were used for the calculation, were much lower than for silica gel. The specific surface area $SSA_{BET}$ was 208 m$^2$/g. Almost all carbon nanotubes had inner diameters above 0.2 nm. This was indicated by the $extSSA$ value, which was 198 m$^2$/g, while the $micrSSA$ was only 9 m$^2$/g. The total volume of the nanotubes was 0.26 cm$^3$/g, and the volume of CNT with inner diameters below 0.36 nm, according to the NLDFT model, was negligible.

![Figure 3 contains the incremental and cumulative pore volume distribution as a function of pore diameter according to the non-localized density functional theory (NLDFT).](image)

| Sample | $A$ (mmol/g) | $SSA_{BET}$ (m$^2$/g) | $micrSSA_{t-plot}$ (m$^2$/g) | $extSSA_{t-plot}$ (m$^2$/g) | $micrV_{NLDFT}$ (cm$^3$/g) | $V_{NLDFT}$ (cm$^3$/g) |
|--------|--------------|-----------------------|------------------------------|---------------------------|-----------------------------|------------------------|
| SG     | 125.43       | 753                   | 128                          | 625                       | 0.02                        | 0.45                   |
| CNTs   | 27.74        | 208                   | 9                            | 199                       | 0.01                         | 0.26                   |

Figure 3 contains the incremental and cumulative pore volume distribution as a function of pore diameter according to the non-localized density functional theory (NLDFT). This theory is based on...
the Tarazona approach [75,76], which is used to calculate the pore size distribution of carbon, zeolites, pillared clays, and other porous materials. In silica gel, the pores with a diameter in the range of 2–6 nm had the largest volume (Figure 3a), which puts them within the range of the narrowest mesopores (2–50 nm). In the CNTs, the largest increase in pore volume was in the range of 11-18 nm, which is shown in Figure 3b.

Table 5. Structural parameters of SG and CNTs.

| Sample | SSA (m²/g) | Micron SSA (m²/g) | Density (mmol/g) | Volume (cm³/g) |
|--------|------------|-------------------|-----------------|----------------|
| SG     | 125.43     | 753               | 128             | 0.02           | 0.45           |
| CNTs   | 27.74      | 208               | 9               | 0.01           | 0.26           |

Figure 3. Incremental and cumulative pore volume as a function of pore width using the non-localized density functional theory (NLDFT) model of (a) SG and (b) CNTs.

3.2. The Influence of Metal Additives on the Thermal Diffusivity of the Adsorption Bed

The influence of metal additives on the thermal diffusivity of the SG-based adsorption bed is given in Figures 4–6.

The increase in temperature and the additive content improved the thermal diffusivity of all solids mixtures. Since the thermal diffusivity of each additive, i.e., Al, Cu, and CNTs, was much higher than the thermal diffusivity of silica gel, all materials contributed to the increase in thermal diffusivity with comparison to the parent silica gel.

The highest thermal diffusivities were reached for additive contents making up 15 wt% of the mixture, and were equal to 0.444 mm²/s, 0.535 mm²/s, and 0.467 mm²/s, for Cu, Al, and CNTs, respectively (Figures 4–6). Thus, the highest thermal diffusivity of the blend was obtained for the addition of 15 wt% alumina particles.
Figure 4. Effect of Cu additives on the thermal diffusivity of the SG-based adsorption bed.

Figure 5. Effect of the Al additives on thermal diffusivity of the SG-based adsorption bed.

Figure 6. Effect of CNT additives on the thermal diffusivity of the SG-based adsorption bed.

For a precise comparison of the thermal diffusivity, its increase for the considered mixtures, compared to the one of the parent silica gel, was determined and is shown in Figure 7. The applied measurement methodology allowed for obtaining thermal diffusivities with an absolute uncertainty of 0.001 mm²/s. On the other hand, the approximation of the measured data depicted in Figures 4–7 was performed using the exponential fitting curve. The error bars express relative uncertainties ranging from 5% to 12%, depending on the sample.

The increase of the additives shares in the SG-based adsorption bed promoted a significant increase in its thermal diffusivity. The highest increase was observed for the mixture with 15 wt% aluminum. The effect of adding 15 wt% Al was the highest and reached 121% at 308 K. However, the importance of the metal share in the solids mixture decreased with the temperature.

The influence of temperature on the thermal diffusivity of the blends, as depicted in Figures 4–7, was the result of the mutual dependence between the thermal conductivity and specific heat capacity of the mixtures, according to Equation (1).

The above-obtained results can also be explained by taking into account the observations made during the preparation process of the considered solids mixtures. During the preparation of the samples for analysis, certain phenomena were observed that could significantly affect the use of
porous material with additives. One of the most severe problems was the difficulty in obtaining a homogeneous mixture of materials, which is concerning given the purpose of mixing was to achieve a relatively even distribution of the substance within the entire volume.

The sample with 15 wt% aluminum was characterized by a high homogeneity of components in the mixture. Aluminum has a density of 2.7 g/cm³, which is close to the density of silica gel (2.1 g/cm³); this allowed for obtaining a high homogeneity of the blend.

The sample with 15 wt% copper had an inhomogeneous structure. The reason for this was a significant difference in density between the copper particles (8.96 g/cm³) and silica gel. The lack of material homogeneity deteriorated the heat transfer processes within the bed.

A similar situation existed for the solids mixture with 15 wt% carbon nanotubes. The agglomeration of nanotube particles caused similar problems as the inter-particular attraction force played an essential role in the CNTs’ behavior. For a particle size of 10 µm, the inter-particle forces became of the same order of magnitude as those of gravity [60]. Moreover, the CNT material tended to accumulate on the surface of the silica gel during mixing. From the viewpoints of functionality and application, this type of mixture as a filling of the adsorption bed may have also induced the uneven heat flow between the exchanger and the silica gel. However, according to the literature, the use of carbon nanotubes can be beneficial in the case of a fluidized bed adsorption chiller as the mixing of the materials may facilitate their fluidization [15,78,79].

4. Discussion and Conclusions

This study examined silica gel (SG) in the context of its practical use in adsorption cooling technology along with adsorbing water vapor. Tests of the thermal diffusivity of silica gels with carbon nanotubes (CNTs) and selected metal (Cu, Al) additives of high thermal diffusivity were carried out. Since the primary purpose of the study was to investigate the influence of additives on the thermal diffusivity of the bed, implementation of the idea was outside the scope of the paper. Nevertheless, it was possible to apply a so-called coated bed, or nets, which are already used in some industrial applications, to keep loose grains in place.

For this work, materials were delivered by the manufacturers and mixed after weighing. These additives were used to improve the thermo-physical properties of the SG. Since the pore size is essential in determining the rate of water vapor flow through porous media in the adsorption process, the SG and CNT structural characteristics were investigated. Characteristics of the silica gel pore space showed that it had a micropore surface area of 128 m²/g and a mesopore (external) surface

![Figure 7. The effect of Al, Cu, and CNT additives to silica gel on the thermal diffusivity of the SG-based adsorption bed.](image-url)
area of 625 m²/g. The total pore volume was 0.45 cm³/g, and the largest volume was in the pores with diameters in the range of 2–6 nm. The nanotubes used as the additive had a mesoporous structure. The extSSA−plot of the CNTs was 199 m²/g, and the volume of the pores was 0.26 m²/g. The metals had negligible surface areas, but they had a high thermal diffusivity.

The mixture containing aluminum gave the best results. The addition of 5 wt% aluminum allowed for a 90% increase in thermal diffusivity compared to the parent silica gel, and the inclusion of 15 wt% aluminum powder increased the thermal diffusivity level by 121%. The effect of adding copper and nanotubes to silica gel was not as significant as it was for the aluminum-containing solids mixture.

Even though aluminum has the lowest thermal diffusivity, its addition produced the highest effect. An important reason for this was that the density of aluminum is similar to silica gel. Copper had the highest density of the additives, four times higher than the silica gel. This affected the homogeneity of the silica gel blend with the additive material. Moreover, the agglomeration tendencies of carbon nanotubes caused a lack of homogeneity of the adsorption bed. Thus, the high homogeneity of aluminum and silica gel mixtures allowed for obtaining the best thermal diffusivities of silica gel-based adsorption beds.

The addition of metal or nanotubes, i.e., inert material, reduced the mass exchange in the bed from the sorption point of view. However, significant improvement in heat transfer processes within the adsorption beds, caused by the existence of these additives, emerged at the same time. Both of these factors affected the COP of the adsorption chillers but the resultant effect led to an increase in COP. Summarizing, the key to improving the COP is the intensification of heat transfer. Mass transfer, although important, has less of an impact on the COP of an adsorption chiller.

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**List of Symbols and Abbreviations:**

- \( A \) adsorption capacity in pressure 0.1 MPa (mmol/g)
- \( BET \) Brunauer–Emett–Teller method
- \( CCVD \) Catalytic Chemical Vapor Deposition method
- \( CNT \) carbon nanotubes
- \( COP \) coefficient of performance
- \( ENG-TSA \) expanded natural graphite treated with sulfuric acid
- \( extSSA_{t-plot} \) external surface area according to the t-plot model (m²/g)
- \( IUPAC \) International Union of Pure and Applied Chemistry
- \( LPNA \) low-pressure nitrogen adsorption method
- \( micrSSA_{t-plot} \) micropore area according to the t-plot model (m²/g)
- \( micrV_{NLDFT} \) micropore volume according to the NLDFT model (cm³/g)
- \( MOF \) metal–organic framework
- \( NLDFT \) non-localized density functional theory
- \( V_{NLDFT} \) total volume in pores according to the NLDFT model (cm³/g)
- \( p_0 \) saturation pressure of the adsorbate in the gas phase
- \( SG \) silica gel
- \( SSA_{BET} \) specific surface area according to BET model (m²/g)
- \( STSA \) Statistical Thickness Surface Area method
- \( \alpha \) thermal diffusivity (mm²/s)
- \( \lambda \) thermal conductivity (W/m-K)
- \( \rho \) density, g/cm³
- \( C_p \) specific heat capacity (J/kg-K)
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