Composite Materials Based on Zeolite 4A for Adsorption Heat Pumps

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Abstract. Some additives and binders were chosen for the preparation of 4A-zeolite-based composites with high equivalent thermal conductivity for heat pumps application. Additives (SiC, Si_3N_4, graphite) and binders (PTFE, $Al(OH)_3$) were tested for their effectiveness in terms of equivalent thermal conductivity and maximum water adsorption capacity of the composites. The influence of the equivalent thermal conductivity of the composite adsorbents on the specific power of the heat pump was also calculated. Results show a significant improvement in the equivalent thermal conductivity of the composite samples which are prepared using aluminum hydroxide as binder, over that of zeolite pellet beds. Such composite materials could be used to build adsorption heat pumps with higher specific power and, consequently, with lower investment cost.

Introduction

Zeolite-water is one of the most attractive adsorbent-adsorbate pair for adsorption heat pumps (Cacciola and Giordano 1986; Cacciola et al., 1987; Douss and Meunier 1989). The limiting factors for the complete development, that prevent the commercial viability of the system, are the low equivalent thermal conductivity of the adsorbent bed (Sahnoune and Grenier, 1989) and the modest heat transfer rate between the solid bed and the thermal vector fluid. The heat transfer rate depends on the geometry of the heat exchanger and of the solid adsorbent. Increasing the equivalent thermal conductivity and modifying the adsorbent shape for a better contact between adsorbent bed and heat exchanger surface may improve the specific power of a heat pump unit.

The main goal of this work is the preparation of new composite materials, based on zeolite 4A, in order to obtain an adsorbent bed whose equivalent thermal conductivity is higher with respect to the pellets bed and to the composite materials previously developed by the Authors (Cacciola et al., 1990). In a practical machine this type of materials must be supported or deposited on a continuous metallic structure such as the heat exchanger wall or an independent structure, with a good thermal conductivity, in contact with the adsorbent bed heat exchanger (e.g., metallic sponge or expanded graphite (Guilleminot et al., 1994, 1995). The equivalent thermal conductivity, the maximum water

adsorption capacity and the porosity characteristics of the zeolite doped with different binders and additives were then measured to evaluate the performance of the composites. The influence of the material equivalent thermal conductivity on the specific power of an adsorption heat pump was calculated based on a simple heat exchanger design.

Experimental

In previous papers (Cacciola et al., 1988, 1990) a new geometry of zeolite composite bound with 10 wt% of PTFE (polythetrafluoroethylene), characterized by a smooth surface, was proposed. The composite showed a better equivalent thermal conductivity compared to that of a pellet bed of the same adsorbent material; nevertheless further improvement of the equivalent thermal conductivity is required for an adsorption heat pumps. In this work, some additives with high equivalent thermal conductivity such as silicon carbide, silicon nitride and graphite, have been included using the consolidated procedure (Cacciola et al., 1988) for the preparation of PTFE-bound composites. Furthermore, samples with aluminum hydroxide or graphite binder in the loading range of 10–40% have been prepared and tested.

Samples Preparation

The general sample preparation procedure includes three phases: 1) the preparation of mixtures of zeolite, binder (PTFE, Al(OH)$_3$ or graphite) and, when PTFE is used as binder, additive (SiC, Si$_3$N$_4$ or Graphite); 2) shaping in brick form; 3) thermal treatment to vaporize the solvent.

A first group of samples has been prepared using Zeolite 4A as base material, in the sodium form (supplied by UOP Molecular Sieves-Reggio Calabria-Italy). A slurry constituted by fully hydrated zeolite and water, was homogenized at 50°C by ultrasonic

and mechanical stirring. Then, a PTFE dispersion (DuPont) containing the required amount to obtain 10 wt% of binder with respect to the anhydrous zeolite, was added. The mixture was successively dried under atmospheric pressure at 70°C for 15 hours; the powdered material obtained was milled. The powder was distributed into a mold, pressed at 250°C and 300 bar to obtain the final shape of bricks or cylinders; thereafter the samples were thermally treated in air following a program of temperature variation in order to remove the excess of water and allow the welding of the composite. To increase the equivalent thermal conductivity, the above described procedure was modified adding (10 wt% with respect of the anhydrous zeolite-PTFE) SiC (Lonza LTD), Si$_3$N$_4$ (UBE, Europe GmbH), synthetic graphite (The Asbury Graphite Mills Inc., # 4444), respectively. The samples composition and their characteristics are reported in Table 1.

The second group of samples consists of the replacement of the PTFE with other binders (Al(OH)$_3$ or graphite) without any additive. A set of samples was prepared following the same procedure, replacing the PTFE with synthetic graphite as binder; the graphite loading ranging between 10 and 40 wt%. The brick form was obtained by self-pressing (300 bar) at room temperature and by a thermal treatment at 240°C. Alternatively, aluminum hydroxide was used as a binder. In this case, an aqueous solution containing 40 wt% sodium aluminate (Carlo Erba) was mixed with an aqueous solution of urea (35 wt%, Carlo Erba) and added to a fixed amount of zeolite, in order to reach a 10–40 wt% loading of binder. The sodium carbonate, formed by reaction between sodium aluminate and urea, was not eliminated. Drying was carried out at 50°C for 5 hours; the powder was then pressed at room temperature and 300 bar. Finally, the brick was thermally treated at 200°C for 2 hours. The characteristics of the samples of zeolite bound with graphite or with Al(OH)$_3$ are reported in Table 2 and compared with an analogous set of samples bound with PTFE.

Table 1. Zeolite based composite samples with additives: composition and characterization.

Samples	Component weight ratio					Sample characterization		
	Zeolite %	PTFE %	SiC %	Si$_3$N$_4$ %	Graphite %	V_p mm^{3}g^{-1}	W_{cs} wt%	λ_{eq} Wm^{-1}K^{-1}
A1	90	10				360.8	21.30	0.15
B	80	10	10			439.3	19.70	0.15
C	80	10		10		597.9	20.05	0.12
D	80	10			10	356.9	18.90	0.18

Table 2. Zeolite based composite samples with different binders: composition and characterization.

Samples	Component weight ratio				Sample characterization		
	Zeolite %	PTFE %	Graphite %	Al(OH)$_3$ %	V_p mm^{3}g^{-1}	W_{cs} wt%	λ_{eq} Wm^{-1}K^{-1}
A1	90	10			360.8	21.30	0.15
A2	80	20			300.0	18.82	0.19
A3	70	30			217.2	17.96	0.22
A4	60	40			208.2	14.13	0.25
E1	90		10		365.8	17.85	0.18
E2	80		20		309.2	18.79	0.26
E3	70		30		349.7	17.36	0.34
E4	60		40		377.0	14.74	0.36
F1	90			10	351.8	23.20	0.25
F2	80			20	225.7	22.40	0.35
F3	70			30	202.8	22.18	0.43
F4	60			40	200.9	23.27	0.43

Samples in cylinder form (final dimensions: diameter = 14 mm, height = 17 mm) were used for water adsorption capacity and porosity measurements, and samples in brick form (final dimensions: 70 × 30 × 15 mm) were used for equivalent thermal conductivity measurements.

Sample Characterization

Sample characterization includes the determination of pore volume, equivalent thermal conductivity and maximum water adsorption capacity. Pore volume (V_p) were determined by means of a Carlo Erba Porosimeter 2000. To measure the equivalent thermal conductivity (λ_{eq}) the so called "hot wire" method was used (Cacciola et al., 1990; Liu et al., 1990; Outzourhit and Trefny 1994; Takegoshi et al., 1982; Woodside et al., 1961). This method is a transient one and it is based on the theory of heat transfer from a liner heat source in an infinite homogeneous medium as proposed by Carslaw and Jaeger (1959). According to the theory, the equivalent thermal conductivity of a brick can be calculated from the temperature rise of the heated wire that is closely in contact with the solid material:

$$\lambda_{eq} = \frac{q/4\pi}{dT/d(\ln t)} \qquad (1)$$

where $q = \rho i^2/S$ is the heating power per unit length of the wire, t is the heating time, i is the electric current,

ρ is the wire (constantan) electrical resistivity and S the wire section.

Tests were carried out at room temperature and atmospheric pressure. A specific expedient involving silicon grease (Donati et al., 1987) was adopted to improve the thermal contact between the probe and the sample. Before testing, the bricks were saturated with water vapor. The measured values of the equivalent thermal conductivity, included the contribution of both solid material and adsorbed water. This measurement procedure was verified (Liu et al., 1990) and validated with materials of known equivalent thermal conductivity; it was also verified that during the measurements, desorption does not take place because of the small temperature rise.

The maximum adsorption capacity (W_{cs}) measurements was carried out by first outgassing the sample at 250°C for 24 hours. Subsequently a flux of air (R.H. about 60%) was allowed to flow through the sample. The time-weight increase was recorded up to saturation. The adsorption capacity was defined as the maximum amount of water adsorbed referred to dry solid weight. The characterization results are reported in Tables 1 and 2.

Table 1 shows the composition and the results of characterization for samples prepared with PTFE binder and some high thermal conductivity additives. The sample without additive is considered as base case. In term of maximum adsorption capacity, the additives slightly reduced the adsorption capacity probably

because of the reduced amount of adsorbent material (80% zeolite) on the global composite. For equivalent thermal conductivity, only the graphite showed the ability to increase the brick equivalent thermal conductivity. The addition of the SiC and Si_3N_4 resulted in a slight decrease of the λ_{eq} values. Probably the latter two materials are very rigid and do not contribute to a good mechanical contact between zeolite and additive particle; on the contrary, the graphite is a rather soft material that is likely to improve the equivalent thermal conductivity. These initial results obtained with graphite led us to increase its concentration even if it could result in decrease of adsorption ability. We expected a considerable increase in equivalent thermal conductivity when the amount of graphite is enough to create the interconnected graphite network favorable for heat transfer. For this reason the zeolite-graphite bricks (samples E1–E4) pressed without PTFE binder were prepared.

With the aim to maximize the particle interconnections without lowering the adsorption capacity, another series of bricks, (samples F1–F4, see Table 2) using $Al(OH)_3$ as binder were prepared. Composites samples (E1–E4 and F1–F4) have been compared with PTFE bound zeolite (A1–A4) in order to choose the best binder.

Figure 1 shows the increasing behaviour of the equivalent thermal conductivity of the bricks with the increasing binder loading. Furthermore, the values of the equivalent thermal conductivity of the composite materials, particularly that bound with aluminum hydroxide, are very promising in comparison with the equivalent thermal conductivity of traditional materials

based on the same zeolite. In fact, the equivalent thermal conductivity of a zeolite pellet bed is about 0.09 $Wm^{-1}K^{-1}$ as reported in literature (Guilleminot et al., 1992). All samples demonstrated good mechanical strength and hardness which is very important to prevent the material losses during operation. On the contrary, the zeolite-graphite samples prepared for this set of test were very fragile. This could be due to the not yet optimized preparation procedure for such kind of components. The low values of the equivalent thermal conductivity of these materials indicate that λ_{eq} of bi- or poly-dispersed composites is primarily dependent upon geometrical consideration related to the contact between additive and adsorbent + binder particles rather than only the intrinsic equivalent thermal conductivity of additives and binders.

A comparison in the adsorption capacity of bricks as a function of the binder load is reported in Fig. 2. There is clearly a better behavior for samples prepared with aluminum hydroxide as binder. This was expected due to the adsorption property of the aluminum hydroxide with respect to both graphite and PTFE, which are hydrophobic and non porous. Among the proposed materials, $Al(OH)_3$ as a binder seemed to be the best with respect to both PTFE and graphite. The samples bound with $Al(OH)_3$ had the highest equivalent thermal conductivity and adsorption capacity. In addition, graphite is an anisotropic material. Therefore, the equivalent thermal conductivity of the resulting brick will be different in the two directions (parallel or perpendicular to the direction of the pressure applied during preparation of composites, which could
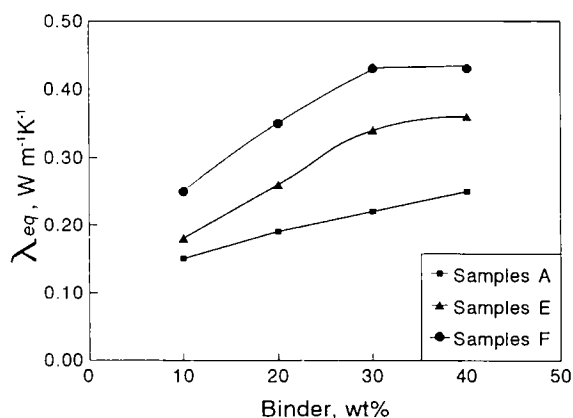
Figure 1.   Influence of the different binders content (●—$Al(OH)_3$; ▲—graphite; ■—PTFE) on the equivalent thermal conductivity of the zeolite based composite samples.
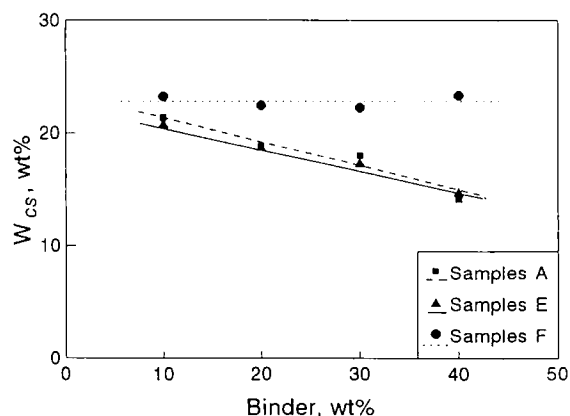
Figure 2.   Influence of the different binders content (●—$Al(OH)_3$; ▲—graphite; ■—PTFE) on the maximum adsorption capacity of the zeolite based composite samples.

induce some graphite layer orientation). Furthermore composites bound with graphite showed a considerable mechanical instability.

Prospects on the Heat Pump Performance

The performance of an adsorption heat pump can be described by two coefficients: the Specific Power (Ps) and the Coefficient of Performance (COP). The former is related with the size and the investment cost of the machine, while, the second gives information about the energy efficiency and consequently the operating cost of the machine.

As described in the introduction, the low heat transfer properties of the solid adsorbent bed limits the performances of the adsorption heat pump and in particular the specific power, Ps. The relation between these heat transfer properties, as the solid adsorbent equivalent thermal conductivity, and the Ps is not simple to generalize, as in fact it depends both on the dynamic behavior of the global machine and on the geometry and the flow dynamic characteristic of the sub-system heat exchanger-solid adsorbent bed.

In order to compare the composites for their application is heat pump sector, the influence of the equivalent thermal conductivity λ_{eq} and of the coefficient of heat transfer at the wall h_w on the global heat transfer coefficient U has been calculated for a simple but realistic solution as shown in Fig. 3. The adsorbent bed is placed on the metallic surface of the heat exchanger using oil as thermal vector fluid.

The model presented in Fig. 3 is symmetric. It represents either a tube or a flat plate coated with a thickness (s_a) of adsorbent bed. In this study we fix our attention on the flat plate configuration, while the tube configuration is object of another scientific program that the authors are developing (Cacciola et al., 1996).
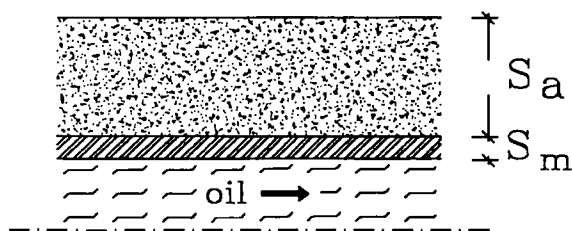

Figure 3. Scheme of a consolidated bed-heat exchanger surface contact.

Referring to the geometry of Fig. 3, the U value can be calculated by:

$$U = 1/(1/h_w + s_a/\lambda_{eq} + s_m/\lambda_m + 1/h_f) \qquad (2)$$

The following data have been chosen for the model here considered:

$h_w = 1500 \ \text{Wm}^{-2}\text{K}^{-1}$, for consolidated adsorbent (Guilleminot et al., 1994)
$h_w = 25 \ \text{Wm}^{-2}\text{K}^{-1}$, for unconsolidated adsorbent i.e., pellets (Guilleminot et al., 1994)
$h_f = 500 \ \text{Wm}^{-2}\text{K}^{-1}$
$s_a = 3 \ \text{mm}$
$s_m/\lambda_m = \text{negligible}$

Using the above mentioned data and the experimental results on λ_{eq} obtained for each type of material, the values of U have been calculated. In order to put in evidence of influence of λ_{eq} and h_w on the global heat transfer coefficient U, Fig. 4 shows the U values of the materials here presented calculated at two values of h_w (25 and 1500 $\text{Wm}^{-2}\text{K}^{-1}$). As can be seen with low h_w, generally related to unconsolidated adsorbent bed, the influence of λ_{eq} on U is very little. This depends on the ratio s_a/λ_{eq} which is of the same order of magnitude of $1/h_w$. For consolidated samples with $h_w = 1500 \ \text{Wm}^{-2}\text{K}^{-1}$, the global heat transfer coefficient U is considerably higher and more sensitive to λ_{eq} variation. Figure 4 shows that among consolidated samples, those bound with aluminum hydroxide are the most interesting.

With regard to the other two contributions in Eq. (2), the value of s_m/λ_m is generally negligible, whereas h_f is an important parameter which is also connected with the characteristics of the thermal vector fluid. Since the exact calculation of h_f is out of the aim of this paper, two possible cases ($h_f = 500 \ \text{Wm}^{-2}\text{K}^{-1}$ and $h_f = 1000 \ \text{Wm}^{-2}\text{K}^{-1}$) have been considered to put in evidence their influence of U. As shown in Fig. 5 in case of consolidated bed ($h_w = 1500 \ \text{Wm}^{-2}\text{K}^{-1}$), h_f does not affect too much the final U value, in fact, when h_f increases from 500 to 1000 $\text{Wm}^{-2}\text{K}^{-1}$ the increase of U ranges between 10 and 15%.

In order to have an idea about the influence of the heat transfer characteristics of the adsorbent materials on the machine performances, the specific power in heating mode, Ps, was calculated using a simulation program previously developed (van Benthem et al., 1995). The simulation model referred to an adsorption heat pump
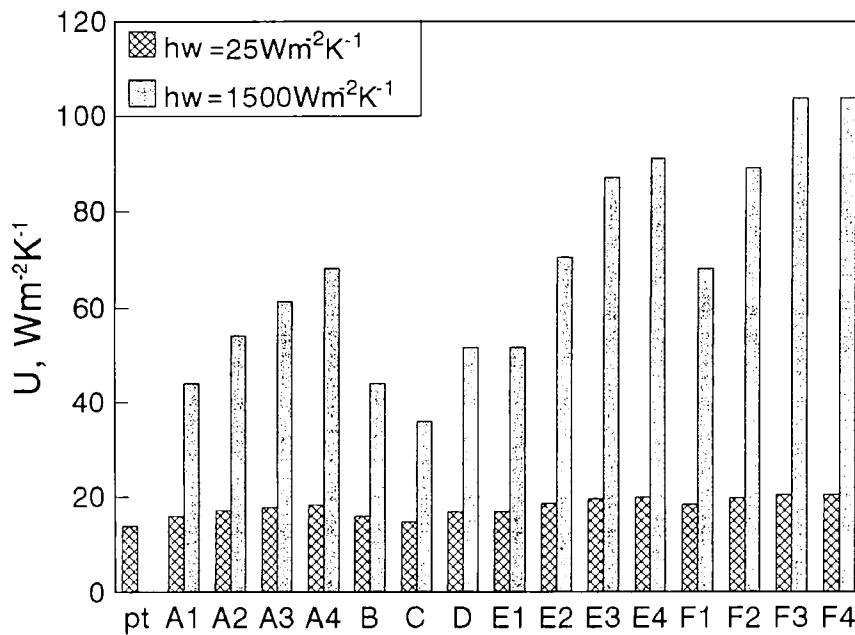
Figure 4. Influence of the wall heat transfer coefficient h_w on the global heat transfer coefficient U (calculated with $h_f = 500$ Wm^{-2}K^{-1}).

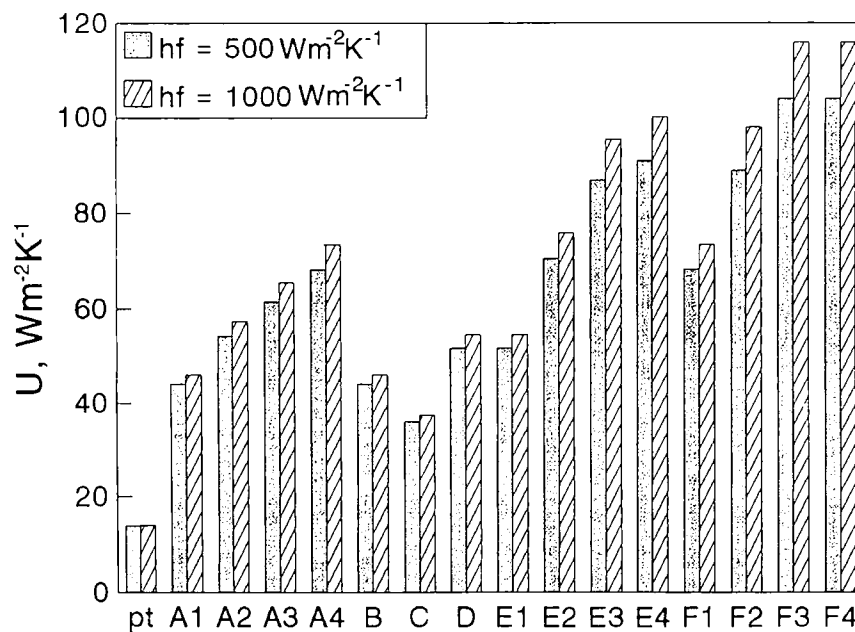*Figure 5.* Influence of the fluid heat transfer coefficient h_f on the global heat transfer coefficient U ($h_w = 1500$ Wm^{-2}K^{-1} for consolidated samples and $h_w = 25$ Wm^{-2}K^{-1} for pellets).

Table 3. Comparison of calculated values of U and Ps of pellets and F2 samples.

	Pelletized beds pt	Composite sample F2
Global heat transfer coefficient U (Wm^{-2}K^{-1})	14	89
Heating specific power Ps (Wkg^{-1})	100	400

composed of two reactors with uniform temperature distribution and operating with internal heat recovery. This calculation was done for commercialized pellets and for consolidated samples F, which showed the highest U value. In particular, sample F2 was chosen because of the same binder content of commercialized zeolite pellets (20%). Thus, with the hypothesis that the adsorption characteristics of the zeolite were not affected by the binder, the equilibrium curves (Cacciola et al., 1993) of zeolite 4A in pellets (Grace 514) were used in the model for both cases. A comparison of the results for zeolite pellets and zeolite brick F2, is presented in Table 3. As can be seen, the heating specific power Ps increased from 100 W/kg, for pellets, to 400 W/kg for zeolite bricks bound with aluminum hydroxide. It should be pointed out that the validity of these results must be confined to the aim of this work and any extrapolation of different systems or different processes may incur error.

Conclusions

The feasibility of zeolite-based composite materials has been demonstrated. Several binders or additives with high thermal conductivity had been tested. A comparison of samples A1 with C, D and E (Table 1 and Fig. 5) demonstrates that the use of additives with PTFE as binder would not be convenient because the global heat transfer coefficient remains constant or decreases. Furthermore, the additive reduces from 90 to 80% the adsorbent content in the composite material. The results show that the improvement of the thermal conductivity of adsorbents is valid only if a geometry of adsorbent different from pellets is considered. In fact, changing from pellets to composite adsorbents with planar geometry, the global heat transfer coefficient increases 3–8 times depending on the thermal conductivity of the binder.

A general conclusion is that bi-dispersed composite materials (zeolite + binder with good ther-

mal conductivity) are preferable over three-dispersed materials composed of zeolite, binder and additive. Moreover, the use of composite bricks here proposed can increase the performances of the adsorption machine with respect of the realized with pellet beds. Among the composite materials here proposed, those prepared with aluminum hydroxide as binder show the highest thermal conductivity and global heat transfer coefficient. This produces an increase in the specific power of the adsorption heat pump to a value of about 400 W/kg for aluminum hydroxide bound composites with respect to the 100 W/kg obtainable with pelletized bed. This considerable increase of the specific power of adsorption heat pumps can be translated into a lower weight and a lower investment cost for the total system.

Nomenclature

COP	coefficient of performance	
h_w	wall heat transfer coefficient	Wm^{-2}K^{-1}
h_f	fluid heat transfer coefficient	Wm^{-2}K^{-1}
i	electric current	A
Ps	specific thermal power	WKg^{-1}
q	heating power per unit length of the wire	W
S	constantan wire section	m^2
s_a	solid adsorbent bed thickness	m
s_m	metal (heat exchanger) thickness	m
T	temperature	°C
t	time	sec
U	global heat transfer coefficient	Wm^{-2}K^{-1}
W_{cs}	maximum water adsorption capacity of consolidated samples	g g^{-1}
W_p	maximum water adsorption capacity of pellets	g g^{-1}
Z_{cs}	zeolite content in the consolidated samples	g g^{-1}
Z_p	zeolite content in the pellets	g g^{-1}
λ_{eq}	equivalent thermal conductivity of the adsorbent bed	Wm^{-1}K^{-1}
λ_m	thermal conductivity of the metal (heat exchanger)	Wm^{-1}K^{-1}
η	ratio of the water adsorption capacity of consolidated samples and pellets	
ρ	wire (constantan) electrical resistivity	Ωm

Acknowledgments

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