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Thermal conductivity of composite sorbents “salt in porous matrix” for heat storage and transformation

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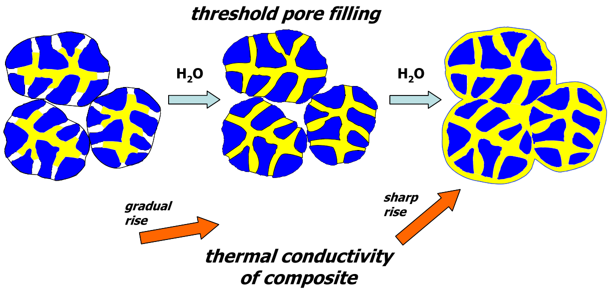
HIGHLIGHTS

- The thermal conductivity of composites “salt in porous matrix” is measured vs. the water uptake.
- The salts are $CaCl_2$, $MgCl_2$, and LiBr, and the matrices are mesoporous silica gel and alumina.
- A sharp conductivity rise is found near a threshold water uptake.
- This threshold uptake corresponds to a complete filling of the matrix’s mesopores by the salt solution.

GRAPHICAL ABSTRACT



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ABSTRACT

The thermal conductivity of composites “inorganic salt in porous matrix” was measured as function of the water uptake w by a “hot wire” method. Three hygroscopic salts ($CaCl_2$, $MgCl_2$, LiBr) were confined to the pores of a commercial KSK silica gel. For $CaCl_2$, an alumina was used as host matrix, too. Similar dependencies $\lambda(w)$ were found for the three silica based sorbents: a smooth rise at $w < w^* = 0.4–0.55$ and a sharp increase within the narrow w-range near the threshold uptake w^*. Regardless the salt confined, this increase occurs at the same fraction ν of the pore volume occupied by the salt solution, $\nu^* = 0.60–0.64$. At $\nu > \nu^*$ the solution starts to leak out of the pores to form a liquid film on the external surface of silica particles that strongly facilitates the heat transfer between adjacent particles and enhances the heat conductivity of the whole bed. No such threshold behaviour was found for $CaCl_2$/alumina composites. The data obtained can be used for analysing open and closed adsorptive units for heat transformation, gas drying, extraction of potable water from the atmosphere, etc. For user friendliness, the experimental $\lambda(w)$-dependences were approximated by polynomial equations.

1. Introduction

The increasing demand for efficient heat/cold sources that do not add more CO_2 to the environment has resulted in increased attention worldwide to the adsorptive heat transformation [1] and storage [2] (AHTS). Many common [3] and innovative [4] adsorbents have been suggested and studied for this application. Among them, composites “salt in porous matrix” (CSPM) have been proven to be promising for adsorptive cooling [5], heating [6], thermal energy storage [7], desiccant cooling [8] and dehumidification [9]. Hydroscopic metal halides are the most popular salts confined to matrix pores as an active CSPM filling [10], $CaCl_2$ [5] and LiBr [11] being more particularly used.

The thermal conductivity λ is a fundamental characteristic of materials that may strongly affect the dynamic performance of AHTS units [12]. Therefore, it has to be experimentally determined and further used as an input parameter for heat and mass transfer models of AHTS units [13]. The coefficient of thermal conductivity λ

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of a multiphase system at constant temperature and pressure is mainly determined by the thermal conductivity and volume fraction of each single component, the composite porosity, the average pore size [14], and the presence of adsorbable gases [15]. If the composite is hygroscopic, one of the components is sorbed water, and its fraction can change in time due to the sorption process. The influence of sorbed water on the λ-value of single-component porous materials was investigated for silica gels [16], expanded clays [17], zeolites [18], building materials [19], etc. Appropriate models were developed to describe the conductivity of a moist porous medium.

The CSPMs may essentially differ from the mentioned single-component adsorbents, because the water sorption on the composites is accompanied by phase changes of the dispersed salt. At initial stage of sorption, crystalline hydrates of the confined salt may appear in the matrix mesopores [20]. Further sorption results in the formation of salt aqueous solution until the whole pore volume is filled. Therefore, the composite thermal conductivity may depend on the moisture content w in a complicated manner. It was confirmed by the first measurements of the $\lambda(w)$-dependence of the two-component sorbent "silica gel + calcium chloride" performed in Ref. [21] by a "hot wire" method [22]. The sample was prepared as rectangle bricks of $70 \times 30 \times 10$ mm^3 size. Four regions of the λ-evolution with the uptake increase were observed, namely, smooth rise, approximate constancy, steep rise and monotonous increase. This evolution was discussed on the basis of the interplay between the salt phase transformation and a gradual filling of the pore voids. It was suggested that the steep λ-rise may be due to a percolation effect, when the confined salt solution forms an infinite cluster inside the pores. Experimental data on the thermal conductivity of the two composite sorbents, namely, $CaCl_2$/(silica gel KSK) and LiBr/(silica gel KSK) were measured by the "hot wire" method under conditions typical of an adsorptive cooling cycle (10 mbar $< PH_2O <$ 70 mbar, 40 °C $< T <$ 130 °C) in Ref. [23].

The aim of the present paper is to study the effect of impregnated salt (calcium and magnesium chlorides as well as lithium bromide) and of host matrix (silica gel and alumina) on the composite thermal conductivity. For these adsorbents the λ-value was measured at $T = 293$ K and atmospheric pressure over a wide range of water content (up to the complete pore filling with the salt solution). The results obtained were satisfactorily described by the model of heat transfer in a porous wetted medium developed by Luikov [14] and modified by Bjurstrm [16]. The experimental $\lambda(w)$-dependences were approximated by polynomial equations and the fitting coefficients were tabulated for ease of handling.

2. Experimental

2.1. Samples preparation

Commercial KSK silica gel or IK-02-200 alumina was used as a porous host matrix. Some matrix's texture properties are summarised in Table 1. The average pore size R_{av} was determined by a standard BET method as $R_{av} = 4V/S$ where V is the specific pore volume and S is the specific pore surface. The dry matrices were impregnated with aqueous solutions of $CaCl_2$ (SWS-1L [5] and SWS-1A based on silica and alumina), or LiBr (SWS-2L [11]) or $MgCl_2$ (SWS-3L) (see Table 2). After impregnation, the powder samples were moulded under the pressure $P = 150$–200 bar into rectangle bricks of $70 \times 30 \times 10$ mm^3 size for 30 min. No binder was used. The bricks were dried at $T = 423$ K until their weight was constant. After drying, the samples were kept in contact with water vapour until the desired equilibrium water content w was reached. The water content w was determined as $w = M_{H_2O}/(M_{hm} + M_s)$, where M_{H_2O} is the mass of sorbed water, M_{hm} the mass of host matrix, and M_s the mass of salt. The amount of sorbed water can be also presented as the number of water molecules with respect to 1 molecule of the confined salt $N = [M_{H_2O}/\mu(H_2O)]/[M_s/\mu(\text{salt})]$, where μ is a molecular weight. The fraction of silica pore volume occupied by the salt solution $v = V/V_p$ was also calculated, where V is the volume of system "salt + water", V_p is the volume of the matrix pores.

Table 1
Characteristics of the host matrices used.

Porous matrix	Mesopore volume V_μ volume, cm^3/g	Pore size, nm		
		Min	Max	Average
Silica gel	1.0	1	60	15
Alumina	0.75	1	100	7

Table 2
Characteristics of the impregnated samples.

Matrix	Solution used for impregnation		M_s/M_{hm}	v_o[a]	w_μ[b]	w_m[c]	Sample symbol
	Salt	wt.%					
Silica gel	$CaCl_2$	42	0.55	0.14	0.51	0.96	SWS-1L
Silica gel	LiBr	48	0.75	0.13	0.46	0.85	SWS-2L
Silica gel	$MgCl_2$	33	0.46	0.13	0.62	1.15	SWS-3L
Alumina	$CaCl_2$	31	0.30	0.105	0.54	1.08	SWS-1A

[a] The volume of salt related to the brick pore volume at $w = 0$.

[b] The water content corresponding to complete filling of mesopores inside a single matrix grain.

[c] The water content corresponding to complete filling of pore volume inside a brick ($v = 1$).

2.2. Thermal conductivity measurement

To measure the thermal conductivity we used a "hot wire" method [22] that is based on a closed form solution of the equation for heat transfer from a linear heat source in an infinite medium. The thin constantan wire of 0.127 mm diameter is placed between two bricks of a studied sorbent and heated by an electric current (Fig. 1). The wire temperature T_w is registered by an iron-constantan thermocouple that is welded to the wire. According to the theory [22], the thermal conductivity may be calculated from

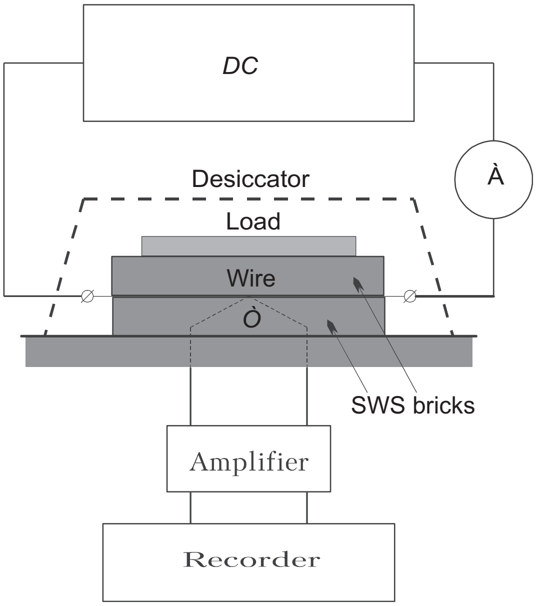

Fig. 1. Schematics of the experimental set-up.