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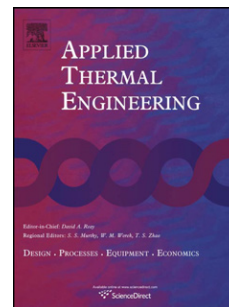
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ON THE EFFECTIVE THERMAL CONDUCTIVITY OF WETTED ZEOLITE UNDER THE WORKING CONDITIONS OF AN ADSORPTION CHILLER

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Abstract

This paper presents a theoretical model for predicting the effective thermal conductivity of wetted zeolite. The model comprises the thermal conductivities of the zeolite crystal as well as of the adsorbed water. The temperature dependence of both thermal conductivities is considered. Moreover, the contribution to the effective thermal conductivity due to vapor conductance is also taken into account. The effective thermal conductivity of 4A zeolite-water is measured by transient "hot wire" method under various conditions of vapor pressure, temperature and water loading. The measurement ranges are chosen according to the operating conditions of a typical adsorption cooling cycle. The experimentally measured data are fitted to the proposed theoretical model. The maximum deviation between the experimental results and the theoretical values is estimated to be $\pm 5.8\%$. The validated model is used to realize a zeolite 4A conductivity chart, which represents an useful tool for thermal design of adsorption machines.

Keywords: Adsorption Chiller, Thermal conductivity, Wetted zeolite

Nomenclature

A	area of heat transfer [m^2]
a	linear dependency on temperature [K^{-1}]
d	diameter of the micropores of zeolite [m]
I	electric current [amp]
k	ratio of the heat capacities of the vapor [-]
Kn	Knudsen number [-]
L	length [m]
p	pressure [Pa]
q	heating power per unit length of the wire [Wm^{-1}]
R	heat transfer resistance [$W K^{-1}$]
r	radius [m]
S	wire cross section [m^2]
T	temperature [$^{\circ}K$ or $^{\circ}C$]
t	time [s]
x	water uptake [$g g^{-1}$]

Greek letters

Λ	mean free path of molecule [m]
γ	accomodation coefficient [-]
ρ	density [kgm^{-3}], wire specific resistance [Ωm]
λ	conductivity [$Wm^{-1}K^{-1}$]
μ	tortuosoty factor [-]
ψ	void fraction [-]

Subscripts

c	zeolite crystal
eff	effective
w	water
wv	water vapor
x	trapped water in the zeolite structure
z	zeolite
0	reference condition

1. Introduction

The use of zeolite as an adsorbent for with natural refrigerants such as water and ammonia in adsorption heat pumps is an interesting alternative to traditional vapor compression heat pumps. Various adsorbent/adsorbate working pairs (zeolite/water, silica gel/water, activated carbon /ammonia, activated carbon/methanol, etc.) can be

employed in adsorption heating/cooling systems, as reported in [1, 2]. The zeolite-water working pair possesses a zero ozone depletion potential and a zero global warming potential. Possible applications of such an adsorption system include solar cooling, energy storage, automobile and residential space heating and air-conditioning [3, 4]. An efficient dynamic operation of a solid sorption unit requires high heat transfer properties of the sorbent layer [5]. Among the heat transfer properties, the thermal conductivity (λ) of the consolidated adsorbent layer is of primary importance. In several articles in the literature regarding the simulation of sorption cooling systems, the thermal conductivity is considered as a constant value [6-9]. However, clear evidence of dependence of λ on sorbent uptake, temperature and/or pressure can be found in references [10-14]. Freni et al. [15] presented experimental data on the thermal conductivity of the composite sorbents, $\text{CaCl}_2/\text{SiO}_2$ and LiBr/SiO_2 , measured by the ‘‘hot wire method’’ under various conditions of vapour pressure (p_{wv}), temperature (T) and water uptake (x). The measurement ranges were chosen according to the operating conditions of a typical sorption cooling cycle ($10 \text{ mbar} < p_{wv} < 70 \text{ mbar}$, $40 \text{ }^\circ\text{C} < T < 130 \text{ }^\circ\text{C}$). The obtained results show that the sorbent thermal conductivity increases considerably as the uptake of sorbate rises. Buonanno and Carotenuto [16] have developed a model to calculate the effective thermal conductivity of a porous medium. The procedure of volume averaging was applied to the process of steady-state heat conduction in a two-phase system. They have also examined the effects of particle shape, roughness and solid conductivity. McGaughey and Kaviany [17] have presented a molecular dynamic simulation-based analysis for the thermal conductivity of a porous structure. The applied molecular dynamic simulation is rather sophisticated to be utilized in adsorption heat pump system simulations.

In this work, a novel model for the effective thermal conductivity of wetted zeolite is presented together with its experimental validation. The model comprises the thermal conductivities of the zeolite crystal as well as that of the adsorbed water. The temperature dependence of both thermal conductivities has been also considered. A tortuosity factor for conductive heat transfer has been introduced in the model in analogy to the well known tortuosity factor for mass transfer in porous media [18]. Moreover, the contribution to the effective thermal conductivity due to vapor conductance has also been taken into account. In order to validate the model, the effective thermal conductivity of zeolite 4A-water has been measured by an on-purpose realized equipment based on the transient "hot wire" method. This equipment allows measuring the thermal conductivity under various conditions of vapor pressure, temperature and water loading. The measurement ranges were chosen according to the operating conditions of a typical adsorption cooling cycle. The measured thermal conductivity data of wetted zeolite 4A have been fitted to the presented model. The obtained parameters are the thermal conductivities of both zeolite crystal and adsorbed water along with the coefficients defining their temperature dependency. Moreover, the tortuosity factor for conductive heat transfer and the accommodation coefficient describing the effectiveness of heat transfer between the vapour molecules and the zeolite crystal have been estimated.

2. Theoretical Model

The theoretical model has been defined assuming that the zeolite is isotropic and has uniform porosity. Starting from the definition of the void fraction (Ψ) or the porosity of zeolite structures, the volume occupied by the zeolite crystals may be expressed as

indicated in equation (1) related to the total volume (V) of a certain zeolite structure [19].

$$V_z = (1 - \psi) \cdot V \quad (1)$$

As the volume is generally proportional to the third power of a characteristic length (L), the physical length of zeolite (L_z) can be derived from equation (1) as:

$$L_z = \sqrt[3]{(1 - \psi)} \cdot L \quad (2)$$

The void fraction for the zeolite 4A sample under test was measured by a mercury porosimeter to be $\psi = 0.24$.

2.1. Thermal Conductivity of zeolite

The thermal resistance of zeolite is calculated according to following equation [20].

$$R_z = \frac{L_z \mu}{\lambda_c A_z} \quad (3)$$

In this equation, λ_c represents the thermal conductivity of zeolite crystal and A_z is the heat transfer area of zeolite. Since a zeolite structure contains micro and macro pores, the path traveled by heat is obviously longer than the physical path on a straight line. We have, therefore, introduced a tortuosity factor (μ) for the thermal conductivity in a similar way to that of the tortuosity factor known for mass transfer through porous media [18]. According to Fig. 1 and assuming spherical pores, the length of a straight path may be $2r$, while the length of the curved path equals $\pi \cdot r$. This gives a minimum tortuosity factor of $\pi/2$. Combining equations (2) and (3) will result in the following expression for the thermal resistance of zeolite.

$$R_z = \frac{L_z \mu}{\lambda_c A_z} = \frac{\sqrt[3]{(1 - \psi)} \cdot L \cdot \mu}{\lambda_c \sqrt[3]{(1 - \psi)^2} \cdot L^2} = \frac{\mu}{\lambda_c \sqrt[3]{(1 - \psi)} \cdot L} \quad (4)$$

For $L = 1$, the thermal conductivity of zeolite will be expressed as

$$\lambda_z = \frac{\lambda_c \sqrt[3]{(1-\psi)}}{\mu} \quad (5)$$

2.2. Thermal conductivity of the adsorbed water

Defining the water loading (x) as the mass ratio between the adsorbed water and the dry zeolite, the following equation may be simply deduced.

$$xL_z^3 \rho_z = L_w^3 \rho_w \cdot \quad (6)$$

Combining equations (2) and (6) leads to equation (7), which gives an expression for the characteristic length of the adsorbed water (L_w) in relation to the physical length of a certain zeolite structure (L).

$$L_w = \sqrt[3]{x(1-\psi) \frac{\rho_z}{\rho_w}} \cdot L \quad (7)$$

Where the density ratio between dry 4A zeolite (poreless) and adsorbed water $\frac{\rho_z}{\rho_w}$

amounts to 1.3 [19].

The thermal resistance of the adsorbed water may then be written as follows:

$$R_w = \frac{L_w \mu}{\lambda_w A_w} = \frac{\sqrt[3]{x(1-\psi) \frac{\rho_z}{\rho_w}} \cdot L \cdot \mu}{\lambda_w \sqrt[3]{\left[x(1-\psi) \frac{\rho_z}{\rho_w}\right]^2} \cdot L^2} = \frac{\mu}{\lambda_w \sqrt[3]{x(1-\psi) \frac{\rho_z}{\rho_w}} \cdot L} \quad (8)$$

For $L = 1$, the thermal conductivity of the adsorbed water will be expressed as

$$\lambda_x = \frac{\lambda_w \sqrt[3]{x(1-\psi) \frac{\rho_z}{\rho_w}}}{\mu} \quad (9)$$

Up to the moment, the addition of equation (5) to equation (9) will result in an expression for the combined thermal conductivity of both zeolite and the adsorbed water.

$$\lambda_{ZW} = \frac{\lambda_c \sqrt[3]{(1-\psi)}}{\mu} + \frac{\lambda_w \sqrt[3]{x(1-\psi) \frac{\rho_z}{\rho_w}}}{\mu} \quad (10)$$

2.3 Temperature dependence of the thermal conductivity of both zeolite crystal and of the adsorbed water

According to the experimental results of Freni et al. [15], the thermal conductivities of both composite sorbents have shown a small temperature dependence. We have, therefore, extended the model equation (10) to take the temperature dependence of the thermal conductivities of both zeolite crystal and adsorbed water according to the following equations (11 and 12).

$$\lambda_c = \lambda_{c,o} \cdot (1 + a_{\lambda_c} \cdot (T - T_o)) \quad (11)$$

$$\lambda_w = \lambda_{w,o} \cdot (1 + a_{\lambda_w} \cdot (T - T_o)) \quad (12)$$

In addition to the four parameters (λ_c , μ , λ_w and ρ_w) of equation 10, the two new parameters a_{λ_c} and a_{λ_w} are to be obtained through curve fitting to experimental data.

The reference temperature T_o has been fixed to 298,15 K through the curve fitting of the measured thermal conductivity data to the model equations (13-16).

2.4. Thermal conductivity of water vapor

As the pressure decreases the mean free path of the molecules becomes non-negligible compared to the mean pore diameter of a certain zeolite structure. The Knudsen

conductivity of the vapor phase has then to be taken into account [21, 22]. According to Kaganer [23], the thermal conductivity of water vapor is given as

$$\lambda_{wv} = \frac{\lambda_{wv,o}}{1 + 2 \cdot \beta \cdot Kn} \quad (13)$$

where $\lambda_{wv,o}$ is the thermal conductivity of water vapor at $p = 1$ bar,

$\beta = 2k(2 - \gamma)/(\gamma(k + 1))$, with k being the ratio of the heat capacities of the vapor and

Kn the Knudsen number. The accommodation coefficient (γ) describe the effectiveness

of energy transfer between the vapor molecules and the solid material. The value of the

accommodation coefficient is almost unknown and, therefore, it will be added to the

fitting parameters of the model. The ratio of the heat capacities of water vapor (k) and

the thermal conductivity of water vapor at 1 bar and 100 °C amount to 1.41 and 0.0248

$\text{W m}^{-1} \text{K}^{-1}$, respectively [24]. The Knudsen number gives the ratio between the mean

free path of a water vapor molecule (Λ_{wv}) to the mean pore diameter of the zeolite

structure (d).

$$Kn = \Lambda_{wv} / d \quad (14)$$

For the zeolite 4A under test, the mean pore diameter (d) has been measured by a

mercury porosimeter to be equal to $5e^{-7}$ m.

The mean free path of molecules is given by Kast [18] with

$$\Lambda_{wv} = \Lambda_{wv,o} \cdot \frac{p_o}{p} \cdot \frac{T}{T_o} \quad (15)$$

In this equation, p_o and T_o amount to 1 bar and 298.15 K, respectively. The mean free

path of water vapor under this reference condition ($\Lambda_{wv,o}$) amounts to 39.5 nm.

Thus, the effective thermal conductivity of wetted zeolite may be expressed as the summation of equations (13) and (10) with the temperature dependence of the thermal conductivities of zeolite crystal and adsorbed water due to equations (11) and (12).

$$\lambda_{\text{eff}} = \frac{\lambda_{\text{wv},o}}{1 + 2 \cdot \beta \cdot Kn} + \frac{\lambda_{\text{c},o} \cdot (1 + a_{\lambda_c} \cdot (T - T_o)) \cdot \sqrt[3]{(1 - \psi)}}{\mu} + \frac{\lambda_{\text{w},o} \cdot (1 + a_{\lambda_w} \cdot (T - T_o)) \cdot \sqrt[3]{x \cdot (1 - \psi)} \cdot \frac{\rho_z}{\rho_w}}{\mu} \quad (16)$$

3. Experimental investigation

3.1 The “hot wire” method

The thermal conductivity of the wetted zeolite with water was measured by the transient “hot wire” method. According to the theory of the heat transfer from a linear heat source in an infinite solid, the thermal conductivity (λ) may be calculated from the temperature (T) rise of the heated wire that is closely in contact with the solid material [25]:

$$\lambda = \left(\frac{q}{4\rho} \right) \left(\frac{dT}{d(\ln t)} \right)^{-1} \quad (18)$$

where $q = \rho I^2 S^{-1}$ is the heating power per unit length of the wire, t is the heating time, I is the electric current, ρ is the wire specific resistance, S is the wire cross section.

During a typical test, the dependence of the wire temperature T on $\ln(t)$ appears, after a very short transient, to be a straight line. Consequently, the derivative $dT/d(\ln t)$ is constant and the thermal conductivity is determined from the slope of the line. More details on the “hot wire method” are found elsewhere [26].

3.2 The experimental set-up

The standard experimental set-up is shown in Figure 2: a constantan wire (1) of 0.127 mm diameter was placed between two sample bricks (2) and connected to the measuring circuit that includes a stabilized power supply (3), an electric resistance (4) and a PC controlled data acquisition system (5). A J-type thermocouple (6) soldered to the mid point of the wire, allowed to measure the wire temperature.

Two zeolite samples were prepared by molding commercial 4A powder (grain size about 20 μm) in rectangular bricks with size of 30x70x6 mm. Such geometry was specifically selected in order to minimize border-effects (i.e. heat loss to the ambient) which could affect the measurement reliability. A little amount of aluminium hydroxide is used as a binder in order to guarantee sufficient mechanical strength. The binder is loaded in minimum quantity (about 5 wt.%), allowing to maintain the adsorption capacity of the brick similar to that of the untreated 4A zeolite powder. The bulk density of the prepared bricks is about 800 Kg m^{-3} . Fig. 3 shows the on-purpose realized equipment for measurement of the effective thermal conductivity. The zeolite sample under test, together with the “hot wire” measuring circuit, is inserted inside a vacuum chamber which permits to carry out measurements at fixed conditions of pressure, temperature and water loading. The sample can be heated up to 150°C by an electric heater, evacuated down to 10^{-2} mbar, and is then allowed to come in equilibrium with water vapour at a constant pressure between 10 and 70 mbar. The water vapour is generated in an evaporator, whose temperature is fixed by means of a thermocryostat. The valves encountered allow switching between both evacuation and equilibrium regimes. The experimental set up was equipped with pressure and temperature sensors (uncertainty of the sensors was ± 1 mbar and ± 1 K, respectively) to analyze the evolution of relevant parameters during operation.

Obviously, the results of this test should be referred to an “effective thermal conductivity”, that includes the contribution of both the solid material and adsorbed water. Most of the measurements have been done at voltage 0.5-0.7 V and electric current through the wire 0.05-0.1 A. The corresponding rise of the hot wire temperature is limited to 2-3°C, which allowed to neglect the influence of water desorption from the sample during the measurements. A detail error analysis resulted in a typical experimental error of $\pm 0.004 \text{ Wm}^{-1}\text{K}^{-1}$.

The following procedure has been applied for sample saturation by water vapour: the sample with the known dry weight is placed inside the chamber and evacuated at 150°C. Then the sample is cooled down to the temperature $40^\circ\text{C} \leq T \leq 130^\circ\text{C}$, the chamber is disconnected from the pump and connected with the evaporator to fix the constant vapour pressure $10 \text{ mbar} < p_{\text{wv}} < 70 \text{ mbar}$. After the sample reaches equilibrium with water vapour, the "hot wire" measurements of the thermal conductivity is carried out. After each measurement the chamber is opened and weighed in order to check that the water uptake corresponds to that anticipated from the 4A zeolite isosteric chart.

4. Results and Discussion

The experimental measurements were carried out under normal operating conditions of an adsorption chiller ($10 \text{ mbar} < p_{\text{wv}} < 70 \text{ mbar}$, $40^\circ\text{C} < T < 130^\circ\text{C}$). Fig 4 shows the measured $\lambda(p, T, x)$ values, which are reported over the Zeolite 4A isosteric chart. Results obtained clearly prove that the effective thermal conductivity of Zeolite 4A varies with operating temperature and pressure. Indeed, referring to a typical thermodynamic cycle of an adsorption chiller, thermal conductivity ranges between $0.16\text{-}0.18 \text{ W m}^{-1} \text{ K}^{-1}$ during the adsorption phase ($p \sim 10 \text{ mbar}$, $T=30\text{-}80^\circ\text{C}$) and between

0.2-0.21 W m⁻¹ K⁻¹ during the desorption phase ($p \sim 70$ mbar, $T=60-150^\circ\text{C}$). The obtained values are in line with existing results in literature [27, 28]. The present experimental results confirmed that the zeolite 4A effective thermal conductivity is quite low (ranging between 0.16-0.21 W m⁻¹ K⁻¹). Subsequently, realization of an adsorbent bed using zeolite in powder or pellets is not recommended due to its poor thermophysical properties. Enhancement of heat transfer efficiency by utilization of highly conductive materials (expanded graphite, metal foams, carbon fibers etc.) could be an effective solution, as already demonstrated elsewhere [29-32]. From the obtained experimental data, the unknown parameters of the model were estimated by fitting the measured data to equation 16 with all its supporting equations (13-15) using MATLAB. In Table 1 the obtained values of all parameters are presented. The estimation was carried out using reference temperature ($T_o= 298,15$ K). The fitted value of the thermal conductivity of adsorbed water in zeolite structure is 0.41 W m⁻¹K⁻¹, which is lower than the conductivity of bulk saturated liquid water at e.g. 50 °C (0.64 W m⁻¹K⁻¹).

The IR-Measurements of Shen et. al [33] as well as Frohnsdorf and Kington [34] have shown that the first adsorbed water molecules in the framework of zeolite Na-Y are adsorbed on the Na-cations. A maximum of two water molecules could be coordinated to each cation. Besides, those first adsorbed water molecules have shown more rotational and vibrational degrees of freedom compared to the three- or four molecules-coordinated bulk water molecules. The investigations of Shen et. al [33] have shown also that hydrogen bonds between the H-atoms of the adsorbed water molecules and the O-atoms of the zeolite crystal play the dominant role in binding the sorbed water molecules in the medium uptake range. Moreover, X-Ray Diffraction measurements of Mortier and Bosmans [35] have shown that the cations leave their fixed places in the

zeolite crystal and that the translational, rotational and vibrational degrees of freedom of the adsorbed molecules approach those of bulk liquid molecules as the uptake increases up to the saturation level. It means that the adsorbed molecules should have properties between bulk vapour and liquid molecules depending on the uptake. In the working range of adsorption chillers, both very low and very high water uptake ranges shall be avoided, in order to avoid the need to very high regeneration temperatures (corresponding to very low uptakes) and the negative consequences of Hysteresis at higher uptake values closer to saturation (leading to very high process times and consequently low specific power values). This may justify the assumption of a constant thermal conductivity of the adsorbed water, which should then lie between those of bulk vapour and liquid phases.

Chakraborty et. al [36] have introduced a very detailed thermodynamic model for deriving the thermal and calorific properties of single-component adsorbent-adsorbate systems. It reveals that, the estimated specific volume data are highly dependent on the parameters of the applied adsorption equilibrium theory. Assigning the specific heat capacity of bulk water to the adsorbed phase results in model values, which match well with the measured data of Aristov et. al [37] only at higher uptake values.

The previous discussion reveals that, more and more attention should be paid to the properties and to the state of the adsorbed phase as well as on the uptake dependency of those properties. The authors are willing, therefore, to explore this dependency for the thermal conductivity in coming investigations.

Increasing the working temperature results in increasing the kinetic energy of water molecules, consequently the conductivity of adsorbed water increases with temperature.

Figure 5a-e represent the comparison between theoretical and experimental results.

Effective thermal conductivity values are presented as a function of the water loading and for various temperatures, showing almost linear dependence.

It is evident from the Figures that the theoretical and experimental values are in a good agreement. The maximum deviation of theoretical result to experimental was $\pm 5.8\%$.

The validated model was used to extrapolate the obtained results for the zeolite 4A/water working pair and to construct a thermal conductivity chart, as shown in Fig. 6. In this chart, isothermal and isobaric lines, calculated by the equilibrium equation of Na-A zeolite/water reported in [38], were plotted for various water loadings. Effective thermal conductivity values were determined – based on the correlations (13)-(16) – for a wide interval of pressure, temperature and water uptake (0.01-200 mbar, 25-200°C, 0.02-0.2 g/g), which allows to appreciate the variation of thermal conductivity for different applications and working conditions of the adsorption machine. Subsequently, this effective thermal conductivity chart can be considered as a useful tool for thermal design of adsorption chillers/heat pumps.

5. Conclusions

A simple model to describe heat transfer phenomenon through wetted zeolite layer was developed and experimentally verified. With this aim, the effective thermal conductivity of 4A zeolite-water was measured by transient "hot wire" method under various conditions of vapor pressure, temperature and water loading. The zeolite 4A effective thermal conductivity was $0.16\text{-}0.21\text{ W m}^{-1}\text{ K}^{-1}$, depending on the temperature and pressure imposed over the sample. Experimental data were successfully fitted, indicating that the developed model is competent in describing such phenomenon. A

conductivity chart for the zeolite 4A/water working pair was also constructed using the developed model. As dynamic evolution of adsorption / desorption is largely dependent on the heat transfer characteristics of zeolite, the model presented in this paper would help to describe the dynamics of adsorption / desorption cycle more accurately. The presented model can be simply adapted to estimate the effective thermal conductivity of metal foams, which will be the subject of future investigations by the authors.

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Figure captions

Figure 1: A schematic layout for the heat transfer path through a typical zeolite crystal

Figure 2: Circuit for the measurement of thermal conductivity by the “hot wire” method

Figure 3: Experimental setup for the “hot wire” thermal conductivity measurement

Figure 4: Experimental values of effective thermal conductivity $\lambda(p, T, x)$ reported over the Zeolite 4A isosteric chart

Figure 5a-e Comparison between theoretical and experimental results: effective thermal conductivity vs. water uptake for various temperatures in the range 50-125°C

Figure 6: Thermal conductivity chart of wetted zeolite 4A

1. A model for effective thermal conductivity of wetted zeolite is presented.
2. Thermal conductivity of zeolite 4A-water is measured to validate the model.
3. Effective thermal conductivity of Zeolite 4A varies with temperature and pressure.
4. Low effective thermal conductivity of zeolite is found ($0.16\text{-}0.21 \text{ Wm}^{-1}\text{K}^{-1}$).
5. A conductivity chart for the zeolite 4A/water working pair is provided.

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Table 1: Various parameters of eq. (16) estimated by fitting the experimental data

Parameter	Units	Corresponding values
$\lambda_{c,0}$	$\text{Wm}^{-1}\text{K}^{-1}$	0.1797
a_{λ_c}	K^{-1}	1001.85×10^{-6}
$\lambda_{w,0}$	$\text{Wm}^{-1}\text{K}^{-1}$	0.41
a_{λ_w}	K^{-1}	2.67004×10^{-6}
μ	[-]	2.59
γ	[-]	1.95

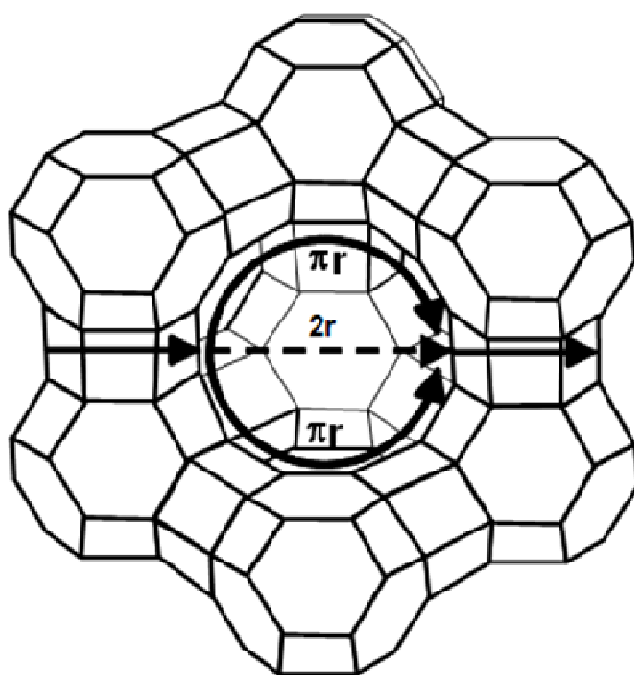


Figure 1

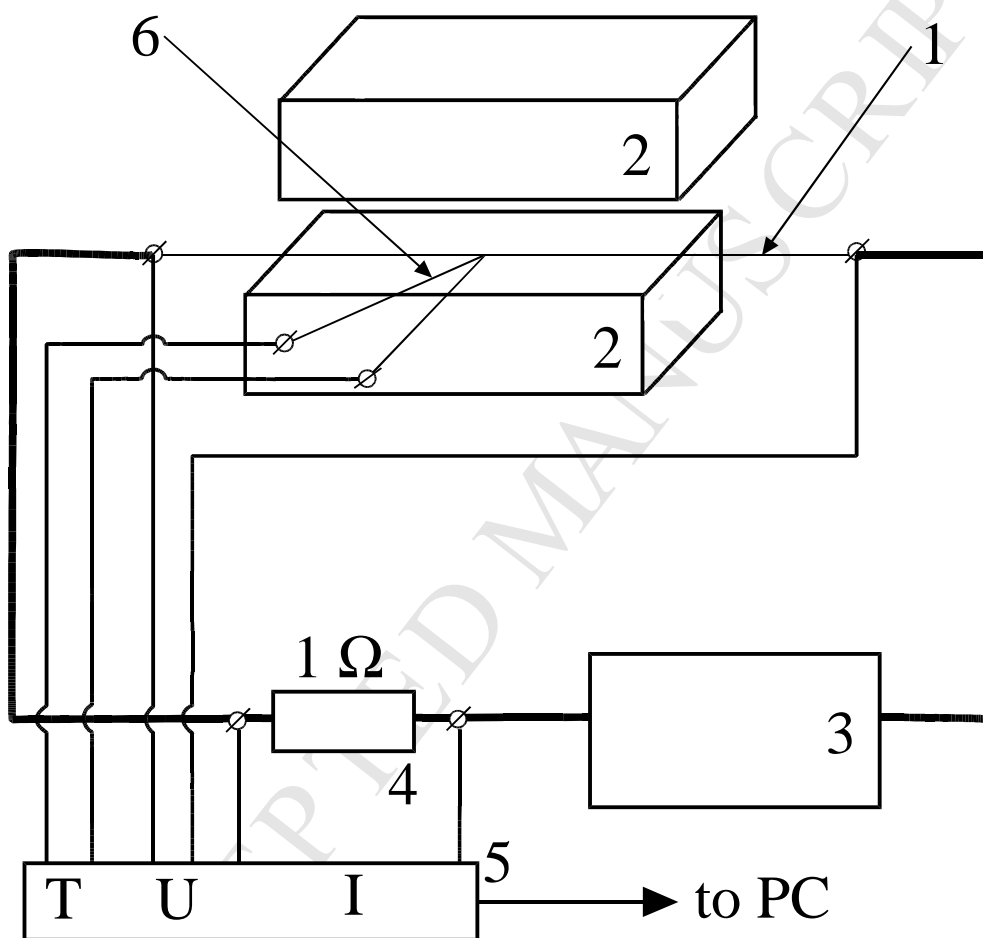
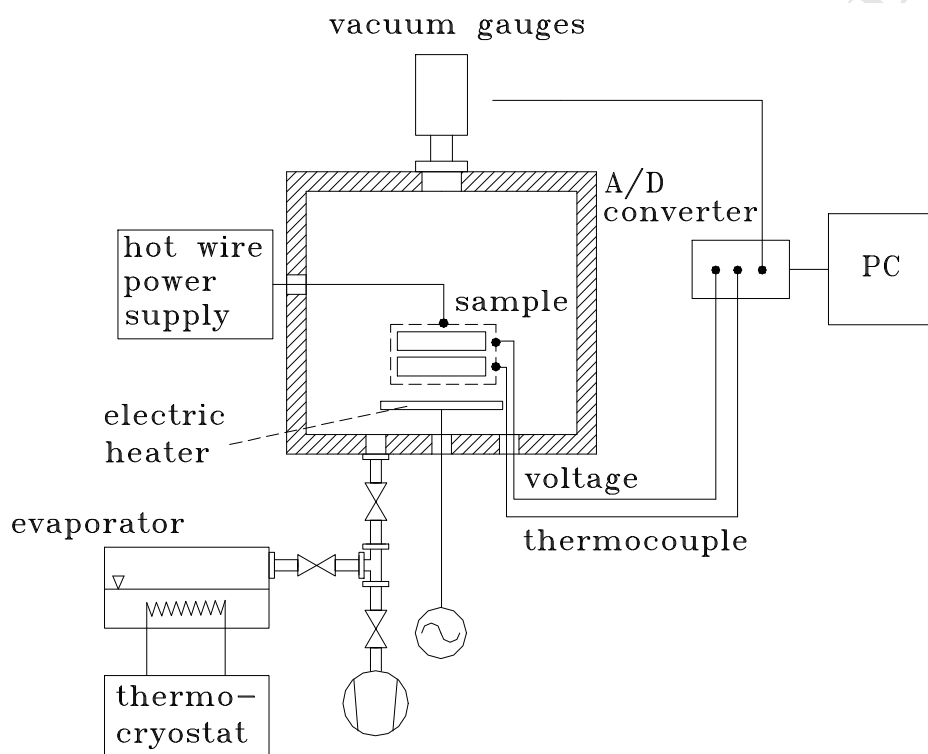


Figure 2

**Figure 3**

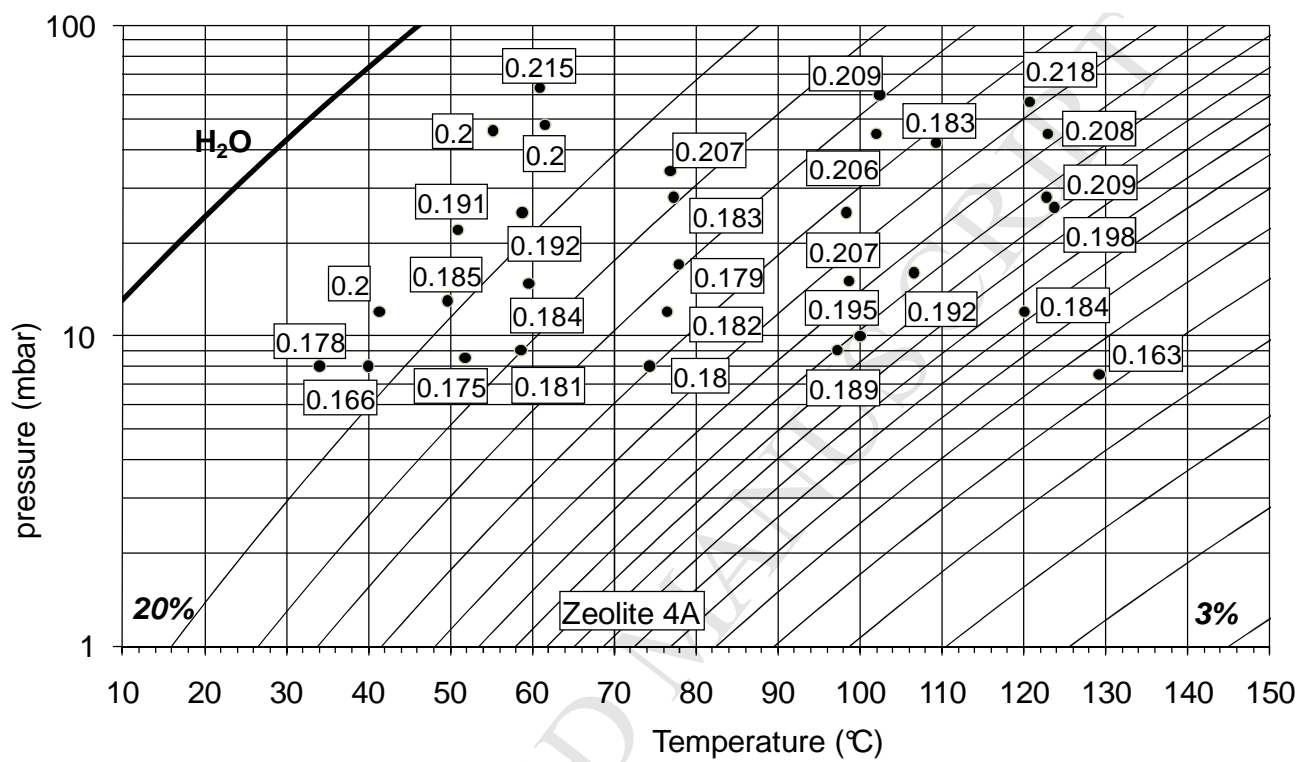


Figure 4

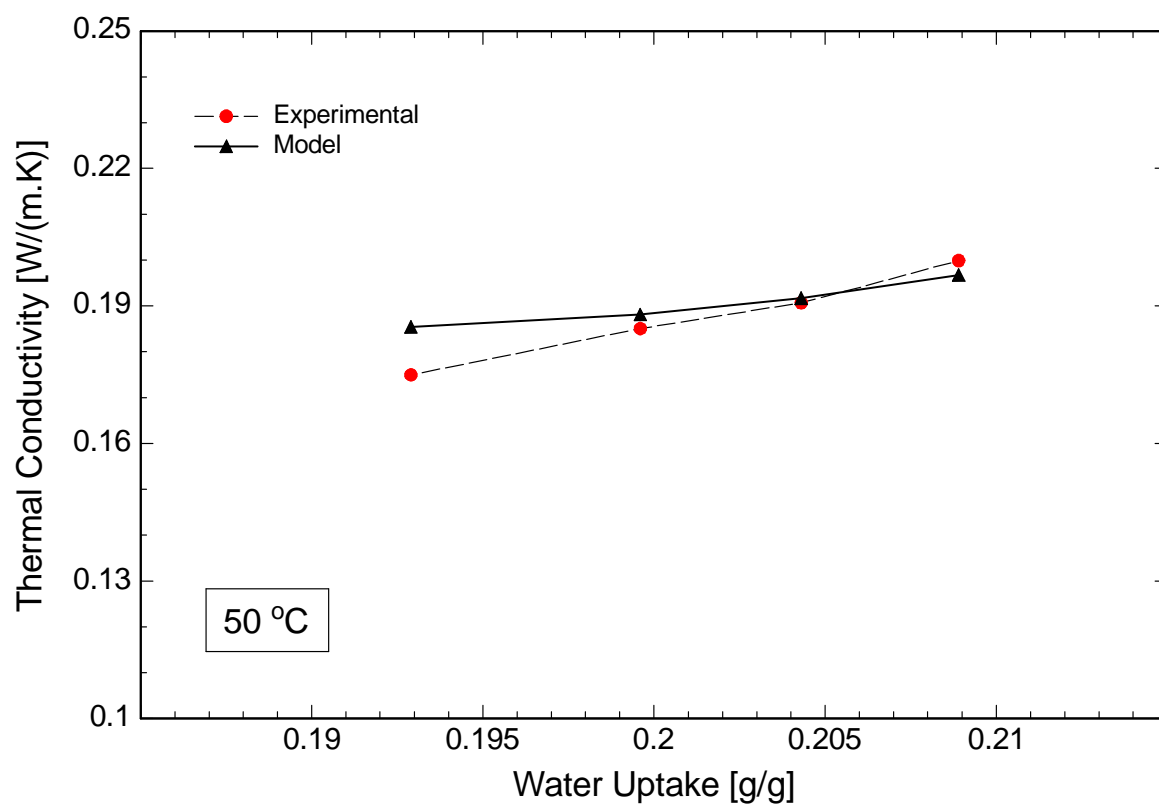
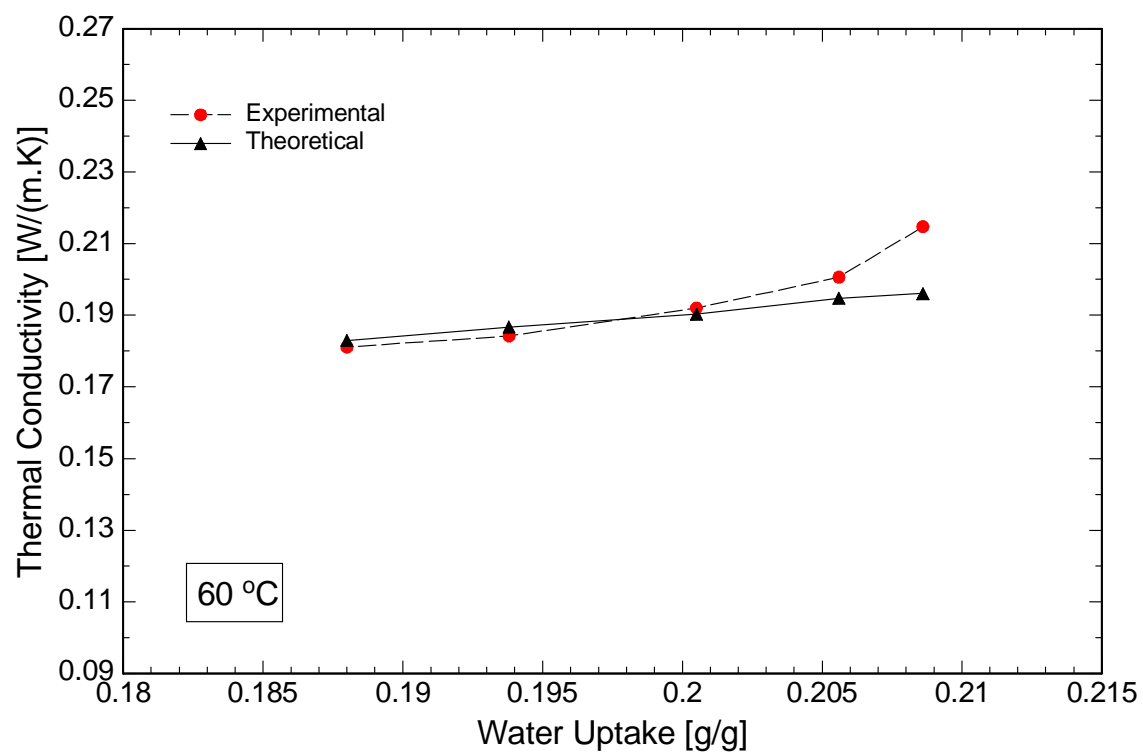


Figure 5a

**Figure 5b**

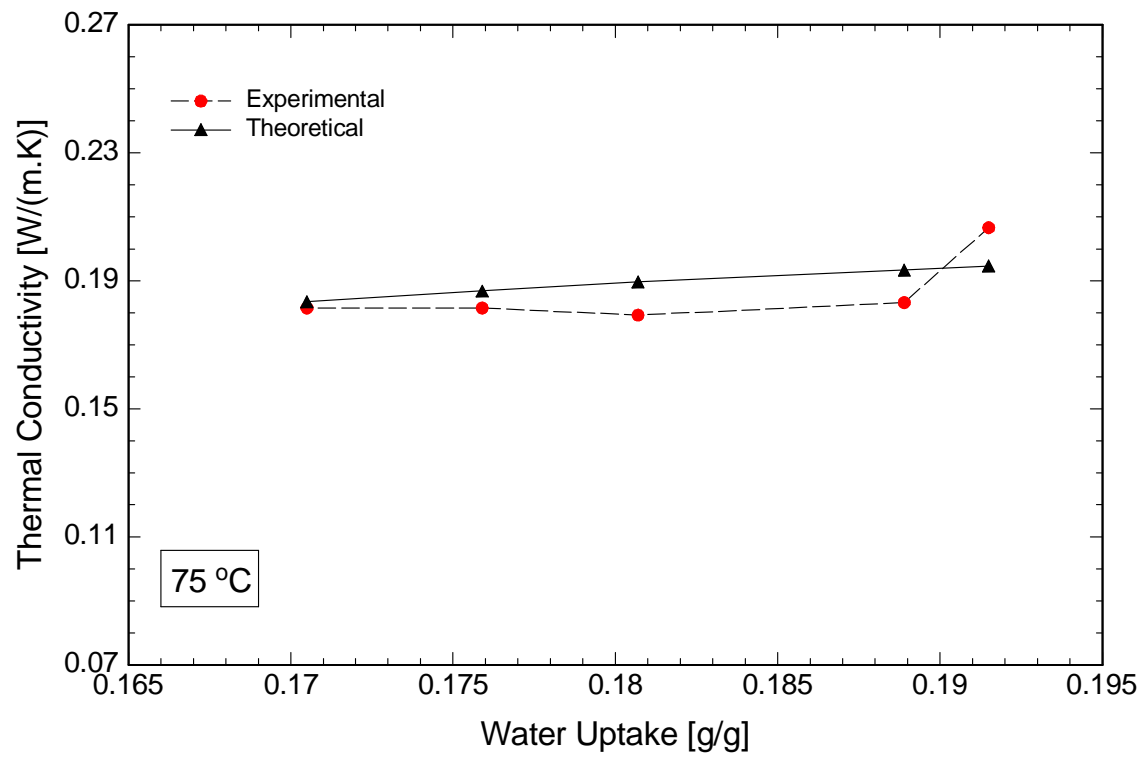
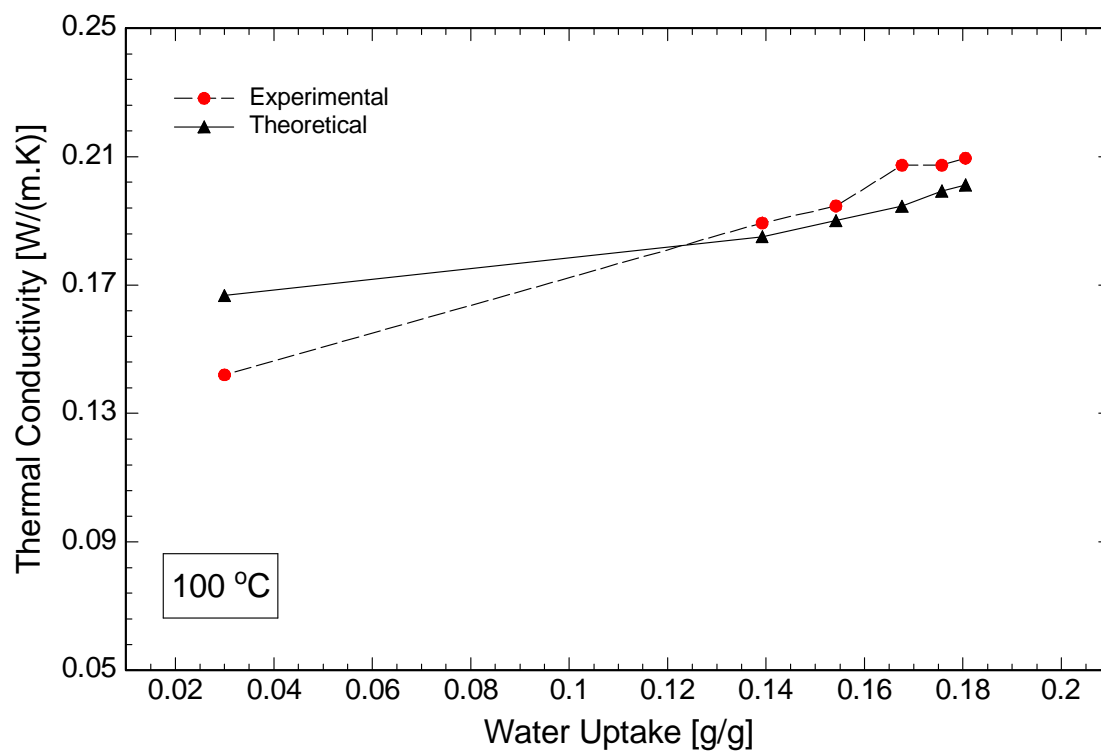
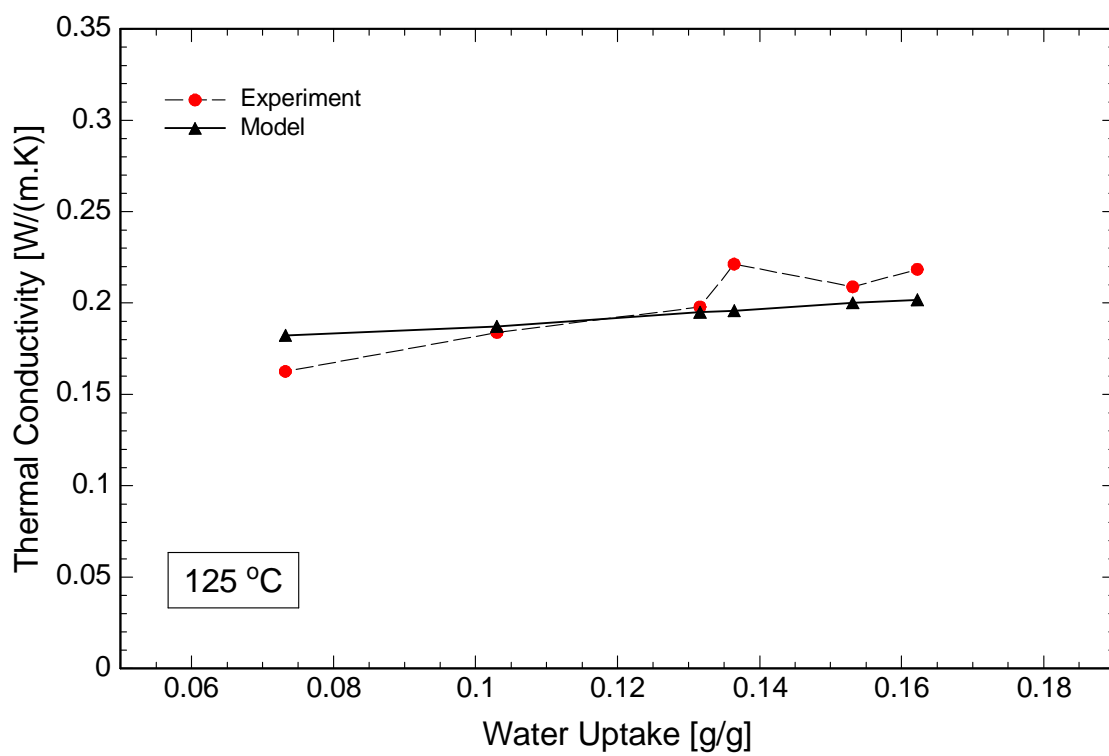


Figure 5c

**Figure 5d**

**Figure 5e**

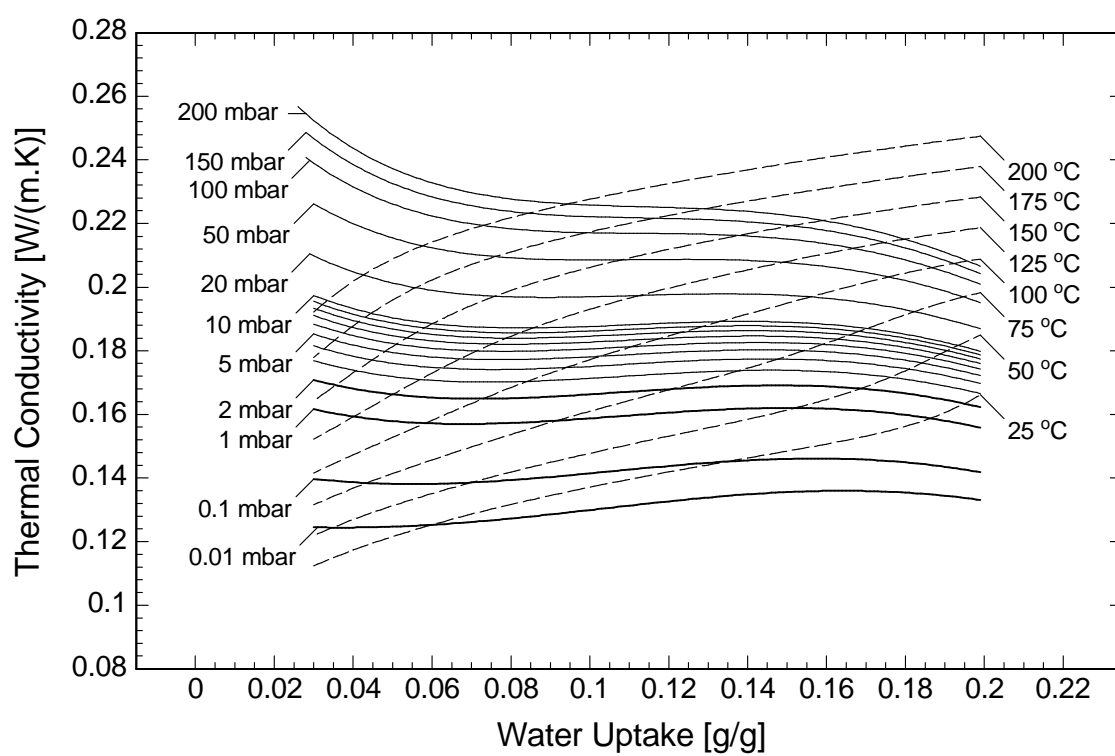


Figure 6