



## Monitoring of thermal properties of a composite material used in thermochemical heat storage

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### 1. Abstract

Thermochemical heat storage can be obtained using bromides or chlorides and the reversible water vapor sorption on them. These hygroscopic salts have sometimes such a high affinity for water that they suffer from spontaneous deliquescence, leading to an irreversible behavior and further degradation of their mass transport properties (i.e. water cannot migrate inside the bed within acceptable time spans). To address this problem, composite materials consisting of salt distributed inside a porous matrix were developed, but questions arise regarding their use in real-life conditions, especially concerning their thermal behavior. In this work, a protocol was proposed to assess the thermal conductivity of such a composite, when it is exposed to temperature or moisture transients. The device consists of a climate chamber with controlled temperature and moisture, wherein a balance and a vessel containing the solid bulk material were introduced. A probe measuring thermal conductivity was set inside the material and connected to a laptop to collect the data. The balance that was also exposed to the chamber atmosphere, allowed to control the occurring phenomena, and to correlate thermal conductivity variations with sorption properties and states of hydration. The material was exposed to two thermochemical cycles, at water partial pressures of 12.5 and 17 mbar. Each cycle began with hydration at 35°C, which was maintained until mass became stable. Then, temperature was increased stepwise to 50, 60, 70 and 80°C, that are realistic conditions for thermochemical heat storage. Mass and thermal conductivity were monitored as a function of time. In parallel, thermal conductivity measurements were made in dry conditions. With increasing temperature, water is desorbed and mass decreases. Because of a superposition of the thermal conductivities of the constituents and thermal convection effects, thermal conductivity apparently increases at the beginning of this process (apparent thermal conductivity:  $\lambda^{app}$ ). It converges to the new “equilibrium value” in the course of time. Phenomenologically this behavior can be explained by the fact that during transient (typically 1-2 days), desorbed water is entrapped inside the bed before escaping. Once water is released, the apparent conductivity  $\lambda^{app}$  decreases to the conductivity value  $\lambda$ . Measured conductivity data at equilibrium are in a range of  $\sim 0.155 \text{ Wm}^{-1}\text{K}^{-1}$  at 35°C and  $0.14 \text{ Wm}^{-1}\text{K}^{-1}$  at 80°C in “wet” conditions. In dry conditions,  $\lambda \sim 0.13 \text{ Wm}^{-1}\text{K}^{-1}$ ,



with a slightly increasing trend. These converging results can be used to feed automation models for thermochemical reactors and to evaluate the influence of the hydration state of the salt.

**Keywords:** Composite, thermal conductivity, salt, thermo-gravimetry, climate chamber

## 2. Introduction

One of the most promising ways to store low grade heat for central heating is to use reversible reactions involving salts and water vapor. Hydrates of  $\text{SrBr}_2$  [1-3],  $\text{MgSO}_4$  [4] and  $\text{CaCl}_2$  [5] have been studied, with heat storage densities reaching several hundreds of  $\text{kWh/m}^3$ . These salts are used either in a pure solid form or, more rarely, in aqueous solution [6, 7], the enthalpy of dissolution being used to store the heat.

When considering the scaling up of these systems, several phenomena must be accounted for:

- Even though they do not change physical state during the storage process, solid salts undergo major structural modifications that degrade the reversibility, i.e. the heat density or the heating power cannot be reproduced from cycle to cycle [5]. A critical parameter is the solubility in water [8].
- Transport phenomena are often rate limiting, so that heat power is not as high as predicted in laboratory experiments. Depending on the studies, authors invoke the heat transfer between the bed and heat exchangers [1].

Therefore, it is often necessary to entrap these salts into a porous solid matrix like zeolite [9, 10], carbon [11] or silicagel that participates marginally to the storage reactions.

To tackle the question of transport phenomena, models are available at the reactor scale [1, 12]. To be run, they need reliable data, especially thermal conductivity. However, these systems are complex to tackle, because of the presence of various phases (voids, matrix, salt) and possible anisotropies. The existence of two chemical states during the process leads to at least two different values of thermal conductivity [1].

There exist both experimental and theoretical studies on this “composite” conductivity. Authors use or develop devices that expose a sample to local heating (plate or wire) and monitor thermal transients, to get thermal conductivity and diffusivity ([13], “transient hot strip”: [14], “hot wire”: [15, 16]).

Models were also derived, to express the total apparent conductivity as a function of the conductivity of the individual components of similar systems. Some of them were reviewed in the case of silica gel with liquid water in the pores [14]. Aristov and coworkers completed these models to account for the presence of a solution of salt inside the pores [15, 17]. In parallel, Olives and Mauran introduced the concept of “thermal tortuosity”, in analogy to the tortuosity used in mass transfer in porous media. The concept was applied to an activated carbon- $\text{MnCl}_2$  composite that was anisotropic, because of previous compression [11].

In this work, the thermal conductivity of a matrix-salt composite is investigated in conditions close to the real system, by systematically varying the real-life control parameter, i.e. moisture in the reactor. The objectives are:

- 1.- To determine the thermal conductivity of the material in dry conditions (composite in anhydrous state).



- 2.- To determine the thermal conductivity as a function of temperature and relative moisture, to reproduce the state of the salt in “real life” conditions, to be used to model heat storage at the scale of a full heating system.
- 3.- To correlate the observed variations with mass changes of the composite.
- 4.- To verify the following assumptions:
  - Mass transfer is more limiting than heat transfer.
  - The same mass (i.e., the same hydration state) implies the same conductivity.

### **3. Materials and methods**

#### ***3.1 Conductivity measurements in dry conditions***

The studied material consists of salt entrapped in an inorganic matrix.

Thermal Conductivity Measurements were done with the Transient Hot Bridge Method (THB). The method bases on a specific solution of the thermal conductivity equation under transient temperature conditions [18-20]. Under ideal experimental conditions, two solid blocks with minimum one plan machined surface per each are available. The THB sensor foil is placed between these blocks – ensuring an ideal thermal contact to both of them. Studied composite material was available as bulk goods only. Nevertheless a sufficient thermal contact of both sides of the sensor foil to the bulk goods could be ensured. Measurements of sufficiently low uncertainty could be achieved.

The sensor operates in two different ways: as a heat source ensuring a constant heat flux and as a detector of the thermal response of the measured material. The method allows to measure thermal conductivity and thermal diffusivity as well. Two different phases of the detected thermal response of the measured sample are used therefore. The initial heating phase allows the examination of the thermal conductivity, the subsequent equilibrium phase from principle allows examination of the thermal diffusivity. A sufficient equilibrium state can only be achieved under ideal experimental conditions. Thus, for the studied material, only the thermal conductivity was measured.

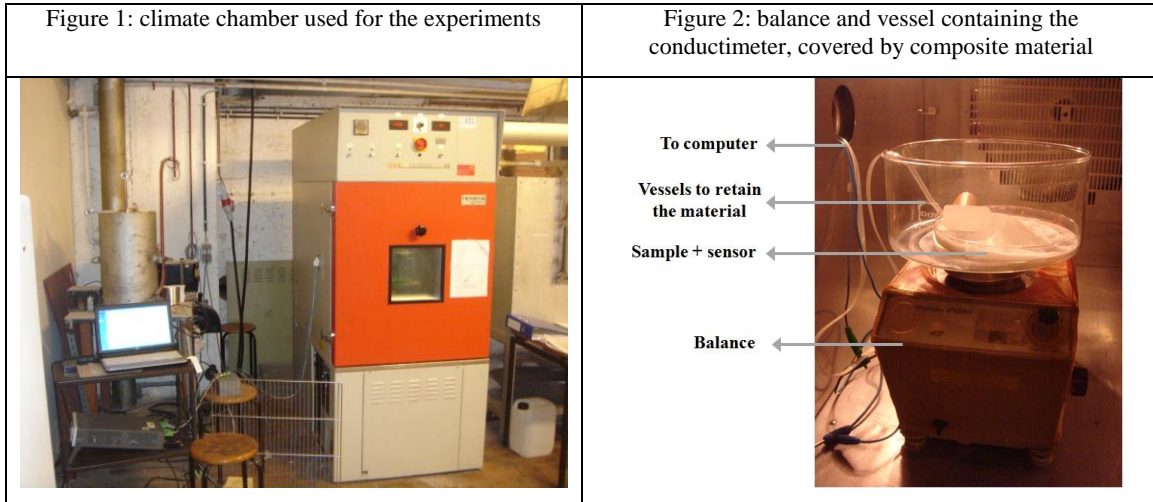
As it could be shown in a measurement campaign in a co-operation between AIT and ULB within the technologically relevant temperature interval on [0°C, 100°C], thermal conductivity can be seen as a quasi-constant property in terms of temperature. But measurements showed that conductivity is significantly dependent from the humidity level of the material. Thus in a first approach, conductivity measurements were mainly performed with pre-conditioned, dry material under ambient conditions.

#### ***3.2 Conductivity measurements in wet conditions***

A VTRK 300 climate chamber (Heraeus Vötsch) was used to impose predefined conditions of temperature and dew point (that can be directly converted into water partial pressure) in its atmosphere (figure 1). Prior calibration was made around the working conditions of present paper.

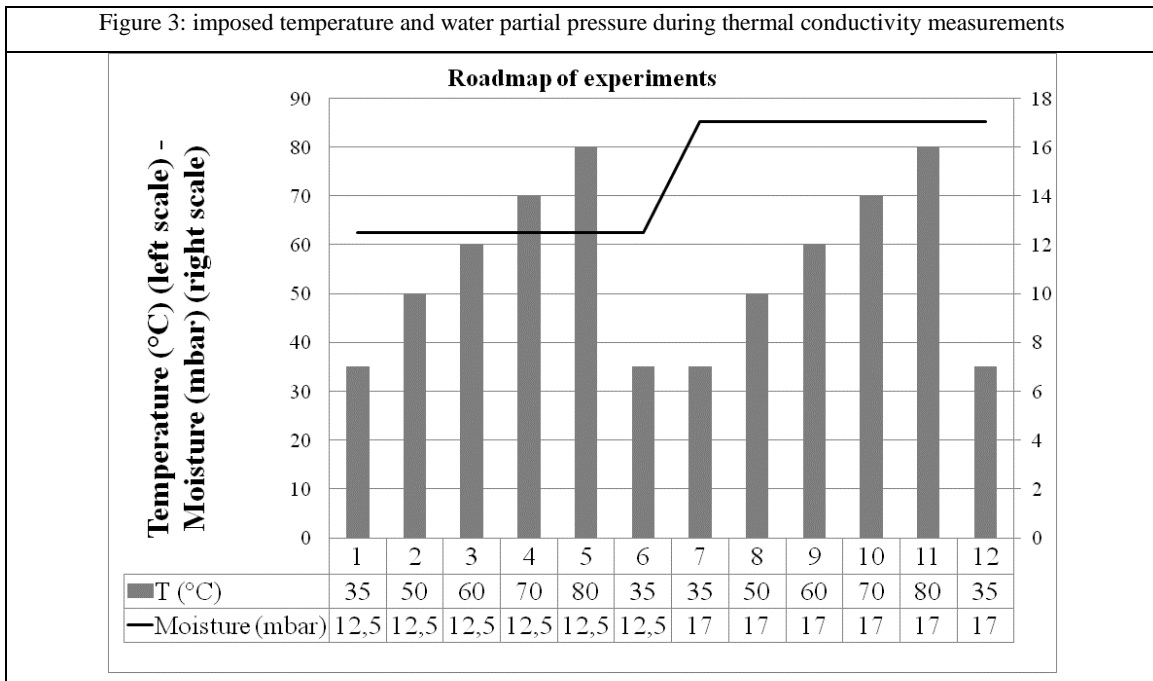
A balance able to withstand a temperature of 80°C was inserted into the chamber, with a vessel containing the composite material to be tested and the sensor already described in § 3.1 (figure 2). Since the fan might blow away some composite, the vessel is chosen to be high enough.

The mass of composite could then be monitored by subtracting the tare and the mass of the conductimeter from the mass measurement.



Two successive programs of experiments were applied, at  $p_{\text{water}} = 12.5 \text{ mbar}$  and  $17.04 \text{ mbar}$  respectively. The composite is initially dehydrated. Each program consists of the following steps (figure 3):

- Hydration of the sample at low temperature ( $35^\circ\text{C}$ ). Since this step is very slow, the composite material is frequently stirred. After this preconditioning, the sample is poured in a flat vessel and not stirred anymore (like in figure 2).
- Dehydration in 4 steps ( $50, 60, 70$  and  $80^\circ\text{C}$ ). Mass and conductivity are monitored during each step, until they reach a constant value. Since the sample is somewhat massive, a small control sample is controlled as well, so as to determine the expected relative mass loss.
- Rehydration of the sample ( $35^\circ\text{C}$ ), to verify the reversibility of the cycle.

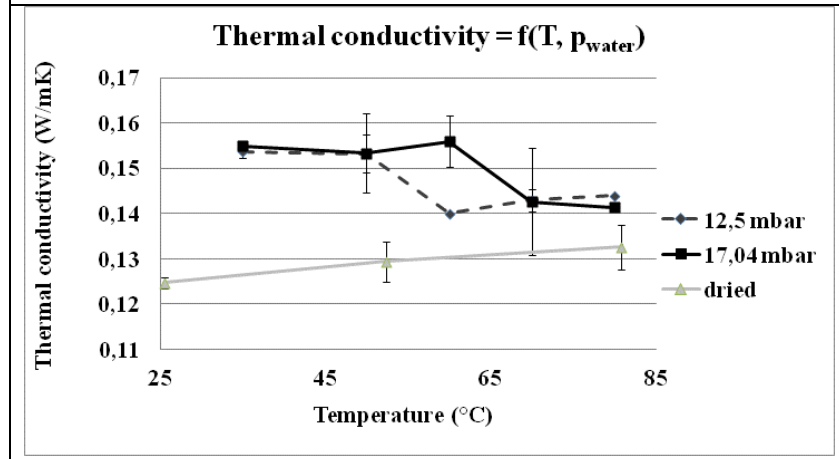


## 4. Result and discussion

### 4.1 In dry conditions

Thermal conductivity in dry conditions is given in figure 4, light grey curve. The value is nearly independent from temperature in the studied range, since the variations are within the error bar. The apparent value is  $\sim 0.13 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ .

Figure 4: thermal conductivity, steady state value, as a function of T and moisture: steady-state values

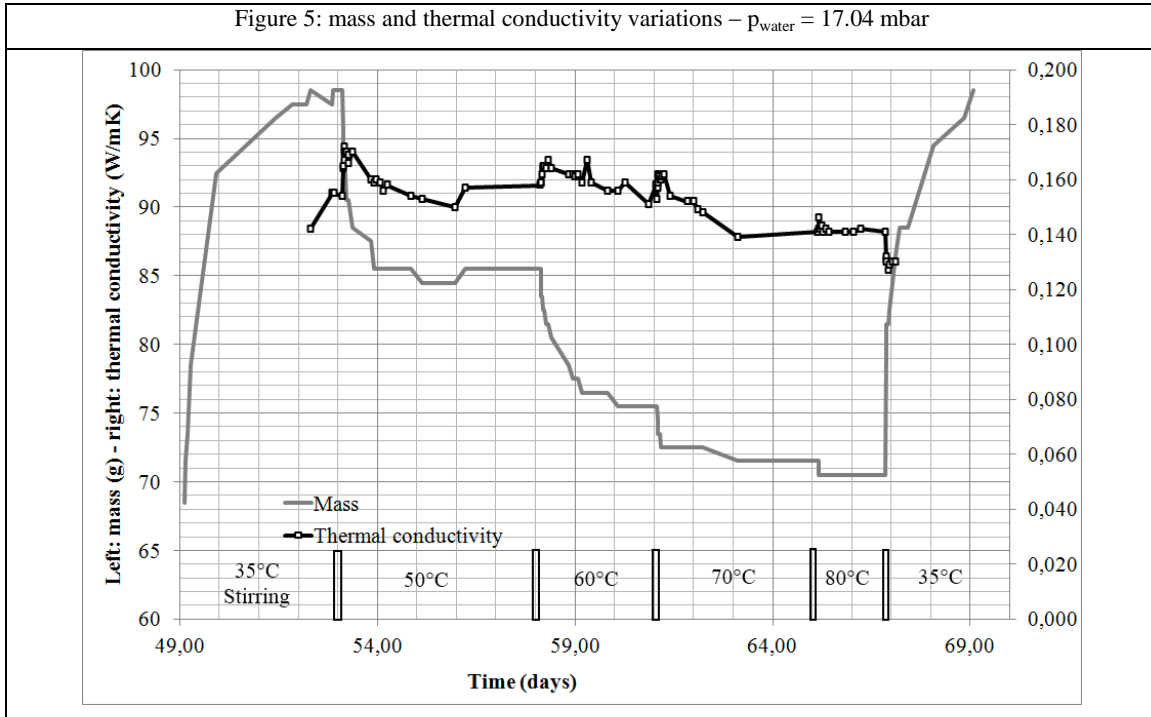


### 4.2 In wet conditions

Mass and thermal conductivity measurements as a function of time are given in figure 5 in the case of a moisture content of 17.04 mbar. Water uptake is a very long lasting process, extremely dependent on the stirring conditions and the sample geometry: in the first trial at 12.5 mbar, this process took  $\sim 26$  days because frequent stirring was not planned initially. This illustrates that adsorption of water is a very slow process, with mass transfer limitation. This time was reduced during the next trial, see figure 5, thanks to a better sample geometry. At each temperature jump, mass roughly follows a decreasing exponential curve, until a new plateau in mass is reached. The amplitude of the mass decrease is higher at 50 and 60°C than at 70 and 80°C. This is better sketched on figure 6, where the values at each plateau are given.

At each new temperature step, thermal conductivity undergoes some variations after reaching a new plateau value (figure 5). These steady-state values are given on figure 4 and do not differ significantly from more than 10 %. A decrease in conductivity appears at  $\sim 60^\circ\text{C}$ . This variation is significant, but not much higher than the uncertainty. Conductivity is significantly higher in wet conditions than in dry conditions, at least until  $\sim 60^\circ\text{C}$ .

Figure 5: mass and thermal conductivity variations –  $p_{\text{water}} = 17.04$  mbar



Transient values of apparent thermal conductivity are represented on figures 7 and 8. In the conditions of (12.5 mbar, 50°C), (12.5 mbar, 60°C), (17.04 mbar, 50°C), (17.04, 60°C) and (17.04 mbar, 70°C), conductivity first increases, then decreases to the new plateau value. These transient values are observed during less than 2 days and plateau values are clearly reached after 3-4 days. Variations during the transient episode are always of less than  $0.2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ .

Figure 6: mass variations at the end of each step, relative value (100 = mass at  $T = 35^\circ\text{C}$  and  $p_{\text{water}} = 12.5$  mbar)

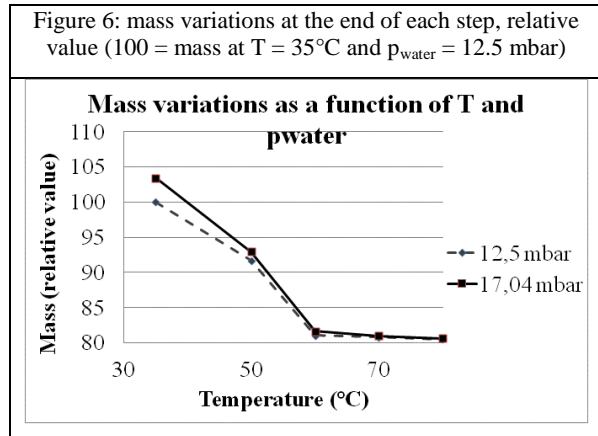


Figure 7: transient measured values of thermal conductivity – 12.5 mbar

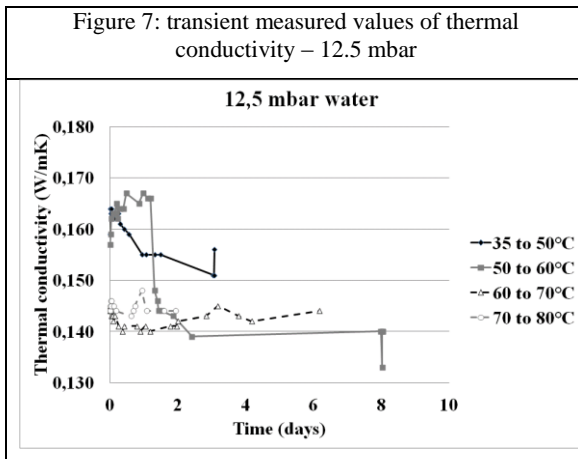
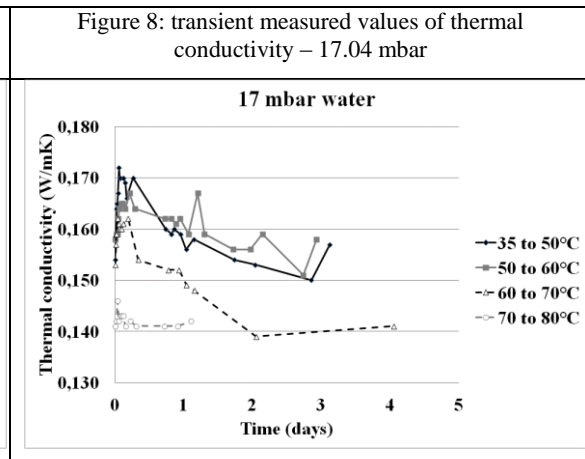


Figure 8: transient measured values of thermal conductivity – 17.04 mbar





### 4.3 Interpretations

The relationship between temperature, water pressure and mass is typical of a salt with at least two different hydrates. When  $T$  increases or when  $p_{\text{water}}$  decreases, the salt loses molecules of water. In present material, most molecules of water are lost between 35 and 60°C. Changes are hardly significant at higher temperatures.

In dry conditions, there is presumably no change in water content inside the material and conductivity increases with  $T$ . This is a typical trend for insulating materials.

In the presence of water, an opposite trend is observed. Thermal conductivity is higher and decreases with temperature. This can be mainly attributed to:

- Desorption of water from the matrix and subsequent increase of the voids.
- Changes in the state of hydration of the salt: different hydrates are expected to have different intrinsic conductivities.
- Modifications in the convection process.

The biggest gap of conductivity appears at a higher  $T$  at 17 mbar than at 12.5 mbar, because chemical equilibrium is shifted towards a higher hydrate.

At 80°C, there is very few dependence of thermal conductivity on  $p_{\text{water}}$ , because of water desorption: at 80°C, the three samples are in a quite similar state, because most of the water has desorbed in all the cases. They only differ by the fact that heat transfer by convection is a bit higher at higher pressure.

Transient values of conductivity must be considered with extreme caution for two reasons:

- Because of the evidence of consumption and release of vapor, the basic assumption in the heat balance of a body lasting to the thermal conductivity equation (absence of heat sources and sinks) is not fulfilled at any time. Thus, an increased deviation of individual measurements from the average conductivity is noticeable.
- Relative moisture is measured only in the atmosphere of the climate chamber. There is no sensor able to measure moisture inside the material during these transients. Such sensors exist, however, in the technical literature, and their use would be an improvement to present experiment [21, 22].

Despite these limitations, measurements clearly show the limitations of existing models for thermal conductivity, that generally focus only on the amount of adsorbed water inside the pores. A more comprehensive approach would be:

- To apply existing models to individual grains of composite.
- To model convection around the grains.
- To account for thermal transfer at contact points between grains.

## 5. Conclusions

An experiment able to measure practical values of thermal conductivity inside the bed of a thermochemical reactor was proposed. The main observations are:

- That dehydrated bed shows nearly no variation in thermal conductivity.
- That in the presence of moisture, conductivity decreases with an increasing temperature, showing that a part of the phenomenon is correlated to the number of molecules of water linked to the salt. Conductivity is slightly higher than in the dry state.

However, transient phenomena occur, due to a shift in chemical equilibrium after each temperature change. When desorbing water, the measurement is altered by the presence of



additional thermal transport caused by water vapor between the grains (convection) and by the heat of desorption.

From the practical point of view, it appears that:

- Measured conductivity is comprised between 0.12 and 0.17 W.m<sup>-1</sup>.K<sup>-1</sup>.
- Mass transfer phenomena are much more detrimental to the reactor, especially during the adsorption step, i.e., heating during the winter.

Further experimental work should focus:

- on the measurement of conductivity in the presence of an endo/exothermal reaction;
- on the measurement of relevant thermal properties during transients (presence of convection);
- on the reduction of mass transfer in “real life” conditions.

## 6. Acknowledgement

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