

# USE OF CaO/ H<sub>2</sub>O REVERSIBLE REACTION FOR COOLING

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## Abstract

Common energy transformation systems, which are driven by natural gas, do not utilise the exergy of the combustion gases at the elevated temperature levels. In case of additional heat utilisation device, which would be placed, with regard to temperature levels, above the common system, an increase in the overall energy and exergy efficiency of the system is expected. This can be achieved with devices, which use reversible reactions for heat transformation. Research on reversible chemical reactions has been due to their interesting operational temperature levels and high energy storage capability intensified in the recent years. The reversible reaction process is used in a chemical heat pump, which can be used for a cooling or heating purposes, depending on the conditions in the reactor. In case of oscillation of external heat load, i.e. low heat demand over the night-time period, the chemical heat pump can have a heat storage function also.

In this work an experimental chemical heat pump operating with reversible reaction of calcium oxide and water is discussed. The experiments were performed at low vapour pressures, which are required in case of using chemical heat pump as a refrigeration device. Due to a low thermal conductivity of the reactive salts, an expanded graphite is used as a binding material in the reactor bed. To intensify mass transport to the reaction sites and to shorten the reaction phase we prepared the reactor bed with additional vapour channels. From the measurement results the expected heat and mass transfer intensification, which would be enough for thermally efficient heat pump, is observed. It is also concluded that an exact dimensioning of the matrix geometry is crucial for reaching a proper cooling or heating performance.

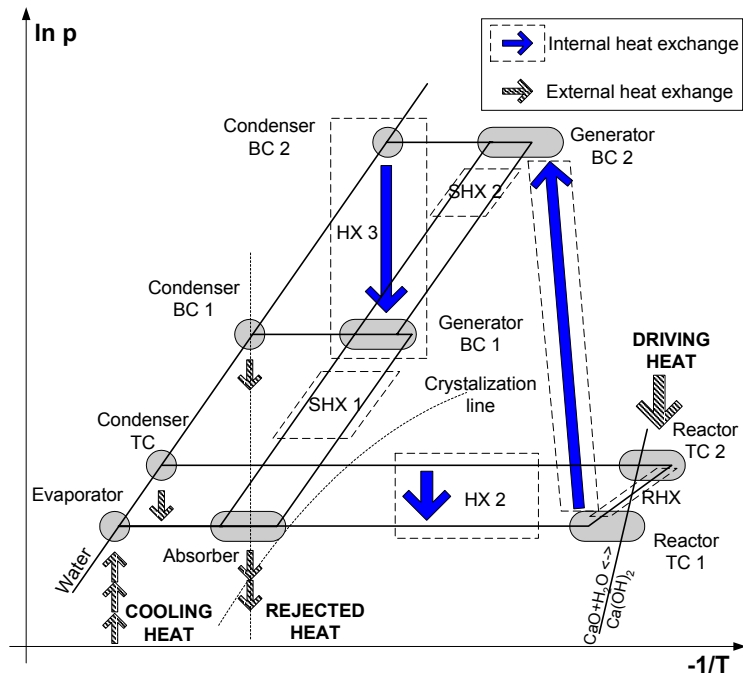
*Keywords:* calcium oxide, chemical heat pump, heat and mass transfer, expanded graphite

## Introduction

The basic reaction kinetics of calcium oxide reaction with water has already been presented (Hartman *et al.*, 1994). Fujii *et al.* have performed a basic measurements on calcium oxide as a heat storage medium and published the experimental results on hydration and dehydration process dynamics (1994). In addition, the same reaction has been examined experimentally for an application in a drying system (Ogura *et al.*, 1999).

The chemical heat pump could be used also as a supplementary system to the standard thermal systems, which encounter a typical heat peak loads over the daytime period (Kato and Yoshizawa, 1999; 2001b; Kato *et al.*, 2000; 2001a; 2002). One of such systems is a cogeneration plant, which produces in parallel electric and thermal energy.

Beside this the calcium oxide/water reaction can be used for cooling purposes also (Satzger, 1993; Nettinger, 1996; Cerkvėnik, 1998). If the ability to utilise energy at elevated temperature levels is applied, it can be used as a topping cycle of a gas-driven cascading sorption cooling device (Cerkvėnik *et al.*, 1999; 2000). As an example a cascade of standard absorption double-effect absorption cooling device as a bottoming cycle and a chemical heat pump as a topping cycle is presented in **Figure 1** (Cerkvėnik *et al.*, 1999; Cerkvėnik, 2001a). With this step a higher heating/cooling ratios - *COP* can be reached as with a stand-alone absorption cooling device. The theoretical cooling *COP* of the topping cycle could be as high as 0.4. This results in a total practical system *COP* of about 1.8, under a consideration of a burner efficiency (Cerkvėnik *et al.*, 2000). This is still 25% better than the commercial gas-fired double-effect LiBr/H<sub>2</sub>O absorption cooling device.



**Figure 1** Application of calcium oxide chemical heat pump in a cascade with a standard double-effect absorption chiller. HX – internal heat exchanger, SHX – solution heat exchanger, RHX – reactor-reactor heat exchange, BC – bottoming cycle, TC – topping cycle.

The critical point in such a cascade is coupling of continuously operating absorption and periodically operating chemical heat pump. In the first successful coupling (Berlitz, 1996; Cerkvėnik, 2001a; Cerkvėnik *et al.*, 2001b) this problem has been solved. In spite of all that, due to a complex dynamic conditions in the chemical heat pump, a commercial application is not possible yet.

The present study attempts to show the applicability of the reversible reaction of calcium oxide and water in the chemical heat pump, which is used for cooling. The specific reaction is chosen due to a satisfactory repeatability and suitable temperature and pressure range, which can be used for cooling and heating purposes (Satzger, 1993; Nettinger, 1995). First, methods for an intensification of heat and mass transfer in the reactor bed will be presented. Then, experimental device and measurement results will be discussed. Due to the application at low operating pressures, emphasis will be laid on improvement in reactivity at low vapour pressures during the hydration phase.

## Heat and mass transfer in reactor bed

Reactor bed is usually carried out as a single cylindrical vessel, where the reactive material is placed in a bulk form. Due to the fact that a thermal conductivity of salts in a bulk phase is low, the heat transfer to reactive sites in interior of the reactor bed is limiting the reaction process. As a result, the bed diameter is kept small to reach a satisfactory reaction rate. Beside this, due to a reversible reaction process a volume of reactive salt constantly changes, which influences on the repeatability of chemical reaction. In addition, a perceivable decrease in reactivity and porosity of reactive material is expected in subsequent reaction cycles.

The main transfer resistances in a common reactor bed can be divide into thermal resistance due to the low thermal conductivity of the reactor bed, mass resistance to the interior of the reactor bed and mass resistance to salt crystals in the salt particles.

To overcome the heat transfer problems and also to stabilise the salt structure a support matrix is introduced (Mauran *et al.*, 1991). It can be a metal or graphite matrix with high thermal conductivity, which increases the overall conductivity of the reactor bed. In the recent years the use of expanded graphite material has been intensified (Cerkvėnik, 1998, 2001a; Fujioka *et al.*, 1998). The thermal conductivity of the matrix depends mostly on a density and quantity of expanded graphite in the matrix (Lebrun and Spinner, 1990). Due to the low density of the expanded graphite  $3 \text{ kg/m}^3$  it can be pressed to any optional form, with the resulting densities between  $100\text{-}500 \text{ kg/m}^3$ .

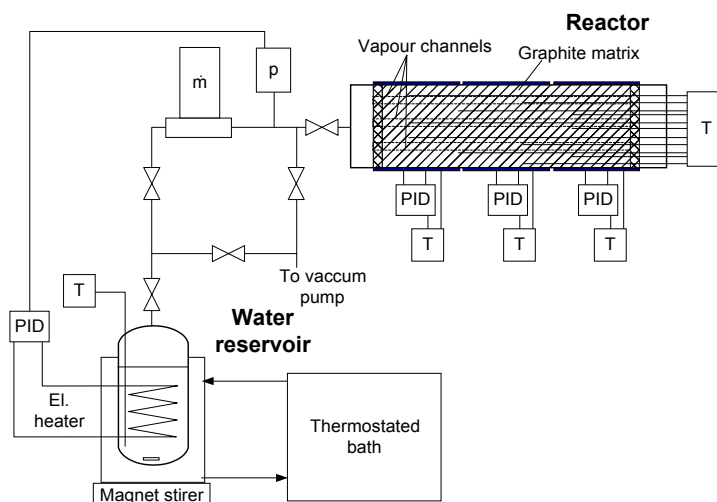
Until now, two methods of matrix preparation have been used, a suspension and impregnation method. In the previous experiments both preparation methods have been tested with the MgO and CaO as the reactants and better results have been gained with the matrices produced by the suspension method (Nettinger, 1995). Thus the suspension method is used in the preparation of the reactor bed for our experimental device. With this method the salt is dissolved and mixed together with the expanded graphite. The mixture is dried and pressed into desired forms. The disadvantage of the drying procedure is a consolidation of small salt particles with a diameter as large as 10-500  $\mu\text{m}$ . Consequently, the influence of the particle size on the dynamics of the reaction process must be considered. As a result of using the expanded graphite and the suspension method the thermal conductivity of 2  $\text{W/m}^2\text{K}$  is expected (Lebrun and Spinner, 1990).

With the use of graphite matrix the mass transfer into the matrix can be intensified also. This can be done, if the blocks of pressed mixture are prepared with a desired density. The other way is to change geometry of the reactor bed, e.g. with the introduction of several vapour channels for a direct vapour transport into the interior of the matrix (Depta, 1994). Beside this the matrix structure serves as a compensation structure for constant volume change of the reactive salt during the repetitive reversible reactions.

On the other side the mass transfer into the salt particles can be intensified with a proper grinding and preparation of the reactive salts.

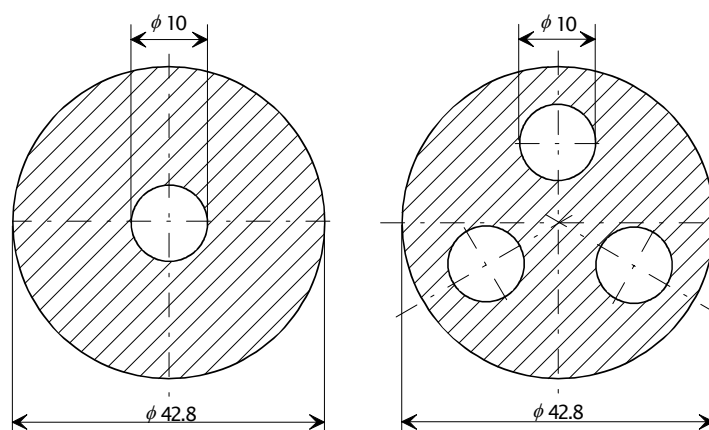
## Experimental device

To investigate a possibility of using calcium oxide as the salt in the chemical heat pump an experimental device has been set up (Depta, 1994). It is a small scale laboratory device with two vessels: reactor with the graphite matrix and a water reservoir, which performs a function of an evaporator and condenser (Figure 2). The graphite matrix in the first reactor (Depta, 1994) had a single inlet vapour channel (left, Figure 3). Due to the fact that the reaction rate was too low an improvement in structure of the matrix is made (right, Figure 3).



**Figure 2** Scheme of experimental device. Measurement points for temperature  $T$ , pressure  $p$  and mass flow  $\dot{m}$  are presented also. PID – controller.

As it can be seen, the novel graphite matrix has two additional inlet channels, which positively influence on the reaction rate. Thus, a more intense mass transfer in the reactor bed is expected. Reactor tube is made of stainless steel, length 750 mm, outer diameter of 48.3 mm. The graphite matrix with length of 139 mm is inserted in the middle of reactor tube. On the both sides of the graphite matrix is a pressed block of insulation material. Together with a safety distance to the both ends of the reactor tube it serves for adequate cooling due to a high operating temperature.



**Figure 4** Distribution of the vapour channels in the graphite matrix with single (Depta, 1994) and three vapour channels (Cerkvenik *et al.*, 1999).

The graphite matrix, which represents a reactor bed, is made of 15 pressed blocks (reactor bed in Fig. 3), which are by the assembly pressed together into the reactor tube. Because the CaO partly reacts with the water vapour from air, the Ca(OH)<sub>2</sub> is used in the preparation of the pressed blocks instead. First, it has to be precisely ground so that the particles are not larger than 50 μm in diameter (Satzger, 1993). As a binding material an expanded graphite with the bulk density of 3 kg/m<sup>3</sup> is used. To diminish the problem with the nonuniform distribution of the salt particles and the flakes of the expanded graphite, the solution of Ca(OH)<sub>2</sub> in the distilled water has been prepared (ratio of 1 to 10). After that the solution is dried in electric oven at temperature of 200°C for several hours. At the end it is pressed into the carefully prepared forms of 1 cm height. The density of the blocks is fixed over the mass ratio between the graphite and salt. This is set at 1 to 1 to simplify the production of the mixture. Before the pressed blocks were inserted into the reactor tube, they were also perforated at the 11 points for the insertion of thermocouples. A detailed data of the graphite matrix is presented in Table 1. For the comparison with the former realisation of the graphite matrix (Depta, 1994) both data are compared.

**Table 1** Geometry data of the graphite matrix, with single and three vapour channels.

GRAPHITE MATRIX	Single vapour channel (Depta, 1994)	Three vapour channels
Length	150 mm	139 mm
Diameter of the reactor bed	42.8 mm	42.8 mm
Vapour channel diameter	10 mm	10 mm
Volume	0.204 l	0.188 l
Ca(OH) <sub>2</sub> mass	20,593 g	18.673 g
Graphite mass	20.012 g	18.401 g
Total mass	40.605 g	37.074 g
Total density	199 kg/m <sup>3</sup>	222 kg/m <sup>3</sup>
Porosity of the matrix	0.912	0.901
Max. mass of reacted water	5.00 g	4.53 g

Pressure transducer MKS, type Baratron 122, with a range from 10 to 10000 Pa and accuracy ±0.5% of measured value (m.v.), was for a better accuracy of the results calibrated with the pressure calibrator DH Instruments PPC2 (accuracy: ±0.01% full scale (f.s.), ±0.005% m.v.). The mass transport to / from the water reservoir is measured with the mass flow meter from the UNIT Instruments, type UFC-9350, with the range 0-40 mg/s and accuracy of ±1.0% m.v. The total mass, which is transported between the reactor and water reservoir is controlled with the weighing of the water reservoir before and after the each reaction phase. With the resulting difference between the both masses a conclusions about measurement accuracy and reactivity of the salt in the reactor bed are drawn. Temperature in graphite matrix is

measured with thermoelements, class 1, type K, with accuracy of  $\pm 1$  K. The control of the external reactor temperature and the temperature of the connection tubes, which are heated during the operation to prevent the condensation, is performed with the temperature controllers. The external temperature of the reactor tube represents a reaction temperature.

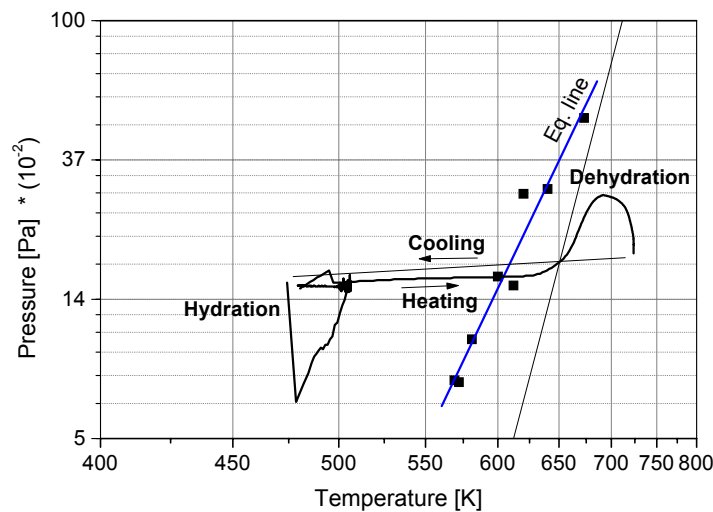
## Measurement results

### Equilibrium line determination

To follow the reaction process in the pressure-temperature diagram the equilibrium line at low pressures below 5000 Pa has to be estimated. Measurements for estimation of the equilibrium state are performed for both directions of the reaction separately. First, the dehydrated reactor bed is slowly heated up with keeping the vapour pressure constant. When the dehydration reaction started, e.g. when a change in the mass flow could be measured, the reaction temperature is noted. The same is done at the same pressure level for the dehydration reaction. In such a way it could be assumed that the equilibrium line at the selected pressure is found between the two noted temperatures (**Figure 4**). The resulting reaction equilibrium line equation can be written as

$$\ln\left(\frac{p}{100}\right) = -7155.9/T + 14.61 \quad p \text{ [Pa]}, T \text{ [K]}. \quad (1)$$

In **Figure 4** a single reversible reaction cycle, operating at water vapour pressure  $p = 1500$  Pa, is presented also. Basically, it consists of a hydration (on the left of the equilibrium line) and dehydration phase (on the right of the equilibrium line). To start with the dehydration phase the reactor bed has to be heated up over the equilibrium line. In **Figure 4**, the direction of the heating phase is noted. On the other side, to start with the hydration phase, the reactor bed is cooled down to the conditions, which allow the reaction of the calcium oxide with water.



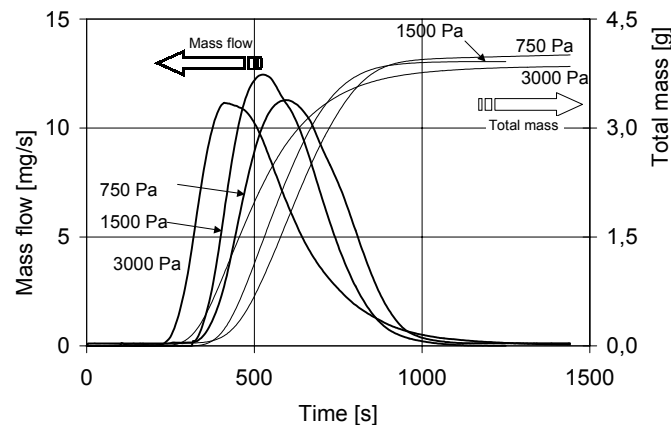
**Figure 4** Estimated reaction equilibrium line for the reversible reaction  $\text{CaO} + \text{H}_2\text{O} \leftrightarrow \text{Ca}(\text{OH})_2$ . In addition, a single reversible cycle, which consists of hydration and dehydration process, is plotted also. Cooling phase is not measured and is noted with an arrow line between two operating points.

At the beginning and the end of each reaction phase the weight of the water reservoir is measured to perform a check of the calculated mass of transported vapour, which is given by the mass flow meter. This did not allow a continuous operation of the chemical heat pump. Nevertheless, due to a possibility of setting up the vapour pressure in the reservoir a several repetitive reaction cycles are performed for the same reaction pressure and temperature conditions. The control of the vapour pressure can be noted in **Figure 4** also. In the first minutes of the hydration phase it can be seen that when the connecting valve is opened a pressure drop occurs. The pressure control switch the electric heater on and increases the temperature and thus also the vapour pressure in the water reservoir.

## Dehydration reaction process

The dehydration of  $\text{Ca}(\text{OH})_2$  starts, when at the constant pressure the temperature of the reactor bed exceeds the equilibrium temperature. The kinetics of the reaction process depends on the distance from the equilibrium state.

In **Figure 5** reacted water mass flow and sum of the total transported mass at three different operating pressures and for dehydration temperature of  $440^\circ\text{C}$  are presented. The preceding hydration phase has been performed at the temperature of  $200^\circ\text{C}$ , except in case of vapour pressure of 3000 Pa, where it was  $280^\circ\text{C}$ . The reason for the exception is the measurement of mass flow. At the hydration temperature of  $200^\circ\text{C}$  and pressure of 3000 Pa the upper limit of  $40\text{ mg/s}$  is exceeded. The influence of a different starting temperature at the end of the hydration phase for the pressure of 3000 Pa can be noted as a time drift to the lower values.



**Figure 5** Mass flow and a total mass of transported vapour during the dehydration phase at different pressure levels.

The dehydration and hydration temperatures represents the external temperature of reactor tube, which were controlled to the selected reaction temperature. The total mass could be represented as a reacted quantity, if the total mass of  $4.53\text{ g}$  is considered (**Table 1**).

The typical duration of the dehydration phase, together with the heating phase is of about  $1400\text{ s}$ . It would be expected that with an increase in the pressure the decomposition reaction rate would be lower at the constant dehydration temperature. Due to a satisfactory distance to the equilibrium pressure is a difference in the results for different operating pressures hardly to recognise. From the results at lower pressure of  $750\text{ Pa}$ , it can be seen that the gradient of reaction rate is similar to that at  $p = 1500\text{ Pa}$ . A slight difference can be noted at higher pressure of  $3000\text{ Pa}$ , especially to the end of the reaction process.

In case of higher dehydration temperatures the pressure difference to the equilibrium would increase again, which would result in a higher reaction rate and shorter reaction phases.

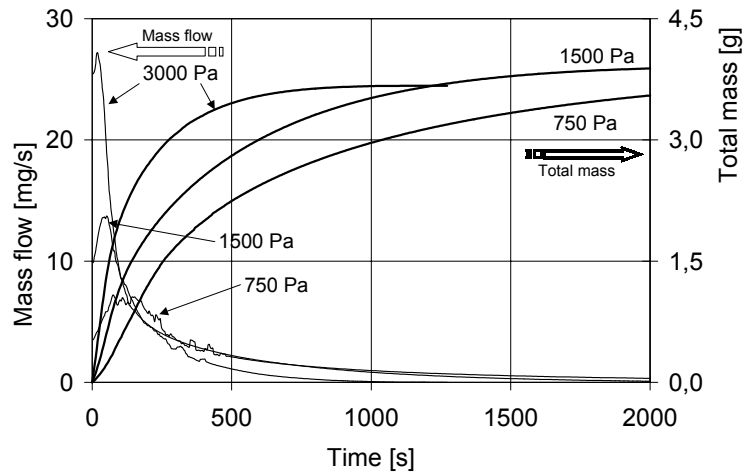
## Hydration reaction process

During the hydration phase, the  $\text{CaO}$  reacts with water vapour, which is evaporating in the water reservoir. In the following the reaction at the hydration temperature of  $200^\circ\text{C}$  will be discussed more detailed. The reaction rate is at the selected hydration temperature in relation to the pressure difference to the equilibrium, which is limited with the low operating pressure. The hydration temperature level is chosen to be high enough for further use of rejected heat in the bottoming absorption cooling device (Cerkvenik *et al.*, 1999). If the hydration phase would occur at higher temperature levels the heat transfer would become limiting again and a different construction of the reactor bed would be required.

In **Fig. 7** the measured mass flow into the reactor bed and total reacted mass of water during the hydration phase are presented. It can be seen that with increase in pressure the mass flow increases. At the same time the initial gradient of the total mass increases also. Both is expected due to the increase in difference to the equilibrium with increase in the vapour pressure.

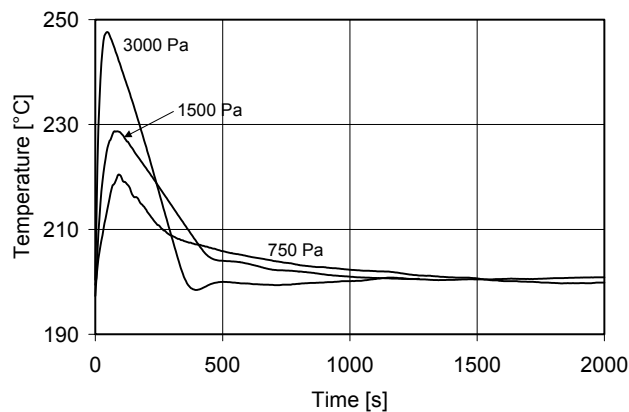
The heat transfer would be a limiting mechanism, if the temperature difference to the equilibrium temperature at the operating pressure would decrease to such a level that it would influence on the

reaction rate. In other words, if the heat rejection from the reactor bed would be inefficient the reactor bed temperature would increase and influence on the reactivity of the bed.



**Figure 6 Comparison of hydration phase at different pressure conditions.**

From the comparison of mean reactor bed temperature, which is calculated as an average temperature of the reactor bed, it can be noted that it is brought to the set value of 200°C in less than 500 s (**Figure 7**). From a comparison of temperature peaks it can be seen that the heat rejection from the reactor bed is quick enough so that it has a small influence on the reaction process. As it can be seen at the pressure  $p = 750$  Pa, which is normally used for refrigeration, the temperature peak of 20 K is measured. This is, if compared with the difference to the equilibrium line (equilibrium temperature at this pressure is of about 330°C), small enough to be neglected.

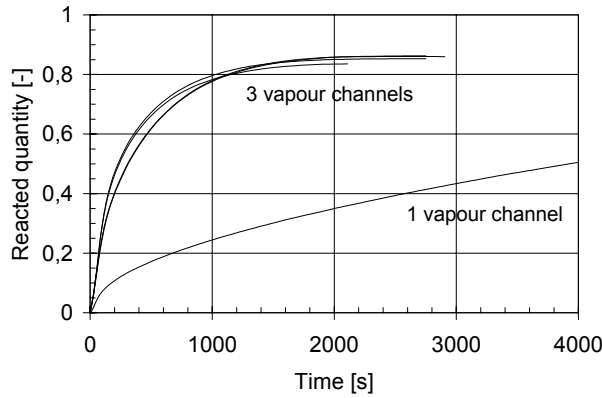


**Figure 7 Comparison of reactor bed temperature for different operating pressure conditions.**

In case of using the same reactor bed at elevated pressure levels, the heat transfer would have a stronger influence on the reaction kinetics, so that a modified structure of the reactor bed should be used.

## Comparison of measurement results

In **Figure 8**, the reaction rates for both graphite matrix structures, with one and three vapour channels, are compared. The hydration phases are performed at  $T_{syn} = 200^\circ\text{C}$  and  $p = 1500$  Pa. To present the repeatability of the hydration phase, several measurements are presented for the same conditions (different plots for 3 vapour channels, **Figure 8**).



**Figure 8 Comparison of measurement results for different matrix structures.**

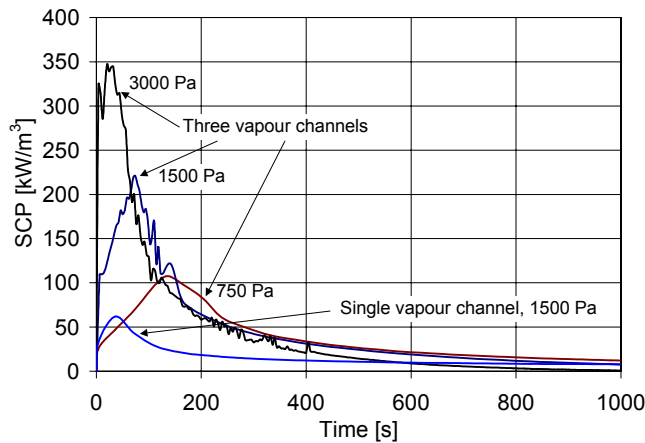
It can be clearly seen that a major improvement in the mass transfer has been achieved. It can be also seen that about 85% of the salt reacts repetitively during the successive cycles. This corresponds to the 15% of not decomposed  $\text{Ca}(\text{OH})_2$ , which is determined by Hartman *et al.* (1994).

To compare the chemical heat pump with other sorption cooling devices, it is required to estimate the specific power of the reactor bed (Cerkvenik *et al.*, 1999)

$$SCP = \frac{\dot{Q}_{ev}}{V} \quad (2)$$

The volume of the reactor bed  $V$  indicates the specific volume, which allow us a comparison with other sorption cooling devices, i.e. adsorber bed of adsorption device or volume of absorber of absorption device. If the  $SCP$  is defined relatively to the mass of reactant (Pons *et al.*, 1999) we can not compare the different structures of bed.

In the first measurements the matrix had been prepared with only one vapour channel and very low reaction rates have been achieved (Figure 8). Consequently, the  $SCP$  of such a structure is low if compared with enhanced structure with three vapour channels ( $p = 1500 \text{ Pa}$ , Figure 9). The reaction rate is higher and therefore the cycle time is about 4 times shorter than with one channel only.



**Figure 9 Comparison of specific cooling power  $SCP$  for a hydration phase at hydration temperature of  $200^\circ\text{C}$  and different operating pressures.**

It can be clearly seen that with increase in pressure the hydration phase is shorter and thus the average  $SCP$  is higher. At the pressure level of  $750 \text{ Pa}$ , which is normally used in case of refrigeration, an average  $SCP$  of  $50 \text{ kW/m}^3$  can be achieved, if cycle is limited to  $1000 \text{ s}$ . In this period about 70% of salt, which is used in the matrix, is reacted (Figure 6). The rest of the reaction process should be neglected, due to the low  $SCP$ , which negatively influence on the size and performance of the chemical heat pump. The given average  $SCP$  of  $50 \text{ kW/m}^3$  corresponds to specific reactor volume of  $20 \text{ l/kW}$  cooling power. This is already comparable with the results from advanced absorption cooling devices (Pons *et al.*, 1999).



## Conclusion

The main disadvantage for the practical use of chemical heat pumps is their low cooling efficiency and specific cooling power, which are limiting the size and cost of the device. An improvement in specific cooling power can be achieved with the intensification of the heat and mass transfer in the reactors using a specially designed graphite matrix. With this structure the main problems of the common reactor bed - reactivity of the salt in the interior of the bed and the mechanical stability of matrix are diminished. In addition, due to the use of expanded graphite the thermal conductivity is increased.

From the previous measurements of the temperature gradients over the reactor bed with single vapour channel it was concluded that the heat transfer is not limiting resistance any more, if the chemical heat pump is used for cooling. Thus the mass transfer into the matrix and into the salt particles had to be intensified. In our case the mass transfer is improved with the introduction of two additional inlet vapour channels. As a result, the average *SCP* of reactor bed is gained, which is comparable to that of the advanced absorption device. If compared with the previous matrix geometry the mass transport is increased to a satisfactory level. It is also determined that in the case of cooling at 750 Pa the hydration phase can be shorter than 20 min, which is enough for an efficient chemical heat pump.

It is also concluded that an exact dimensioning of the matrix geometry is crucial for the determination of the cooling or heating performance of the reactor bed. In case of commercial application, the reactors could be constructed of several reactor tubes, which are mounted in parallel or with a larger reactor bed, which geometry could be optimised for the specific conditions. At this stage, the measurement results are useful for the future research on the large-scale chemical heat pumps.

## Acknowledgements

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## Nomenclature

$\dot{m}$	= mass flow	[g/s]
$p$	= vapour pressure	[Pa]
$\dot{Q}_{ev}$	= cooling power	[kW]
<i>SCP</i>	= specific cooling power	[kW/m <sup>3</sup> ]
$T$	= temperature	[°C]
$V$	= volume of reactor	[m <sup>3</sup> ]

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