Solid Sorption Refrigeration With Calcium Chloride Methanolates on Technical Scale

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Abstract—**Thermochemical solid/gas sorption systems are known for their environmental benefits. They can use low-grade temperature sources for supplying cold storage and cooling of buildings. The thermochemical working pair calcium chloride/methanol is well suited for sorption refrigeration and storage due to low costs, high energy density and good cyclability. The energy storage capacity results from the reversible sorption of methanol by the salt. Heating up the salt (desorption) stores thermal energy. Refrigeration results from the endothermic methanol evaporation which is induced by the salt reabsorbing the methanol and thus lowering the methanol vapor pressure. This study presents results from a 2 kW technical scale demonstrator of a closed thermochemical process with calcium chloride/methanol. The demonstrator consists of two alternatingly working sorption reactors to enable continuous operation. The operation was done under atmospheric pressure using fans for the mass transport of methanol. Overall functionality is demonstrated by supplying up to 5 kWh of stored cooling energy from a reactor containing 9.7 kg dried calcium chloride. Optimization potentials are identified in desorption temperatures of around 90°C and/or condenser temperatures around 15°C, reduction of pressure and the use of mechanical compression.**

Keywords—*Chemisorption refrigeration, calcium chloride, methanol, technical scale, thermochemical storage*

I. Introduction

In the light of global warming, the relevance of the production of cold is increasing. Legal obligations such as phasing out of refrigerants with high global warming potential (GWP) [1] and rising building standards [2] call on less energy-intensive flexible cold production which replaces hazardous refrigerants and which utilizes unexploited (relatively low-temperature) waste heat. A candidate technology for this objective is thermochemical refrigeration which is based on reversible chemical solid/gas reactions. Before highlighting the advantages and shortcomings, the terminology has to be clarified as it is inconsistent in the field [3]. A sorption

system is classified to be a thermochemical sorption system if it involves solid/gas reactions. Often, no differentiation is made between the principles physisorption (no chemical bonding) and chemisorption (chemical reaction between the gaseous sorbate and the solid sorbent [3], [4]. Some authors use the controversial term "solid absorption" interchangeably for chemisorption, stressing that the sorbate is incorporated into the crystal lattice of a salt [3]. For solid/gas refrigeration systems as a whole, many authors use the term "chemical heat pump" [5], [6]. Closed thermochemical refrigeration systems consist of a thermodynamic cycle [3]. A detailed explanation of the basic thermodynamic cycle is given in Cot-Gores et al. and Kuznik/Johannes [4], [7]. The generic equation for reversible heterogeneous solid/gas reactions can be written as follows (1) [3]:

$$MX_{(s)} + vCH_3OH_{(g)} \rightleftharpoons MX \cdot vCH_3OH_{(s)} + \Delta_r H \quad (1)$$
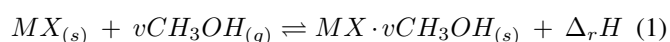
with:

v	= stoichiometric coefficient
$MX_{(s)}$	= solid reactant forming the solid product $MX \cdot v\,CH_3OH$

Thermochemical refrigeration can use a variety of heat sources for the regeneration of the sorption materials e.g. waste heat [8], heat from combined heat and power plants (CHP) [8], solar thermal/electrical energy [8], [9] or combustion engines [8]. The regeneration of the sorbens is also referred to as 'charging' of the reactor. The application spectrum of thermochemical refrigeration ranges from dehumidification, air conditioning, ice making, food and medicine chilling and preservation, electronic appliance and data center cooling, etc. [3], [8]. The most studied application is the use for buildings as this is an important leverage point to reduce energy consumption [7].

This paper studies solid sorption refrigeration with calcium chloride methanolates on the laboratory scale and on technical

scale using a closed demonstrator. First, we point out properties of the utilized storage salt, calcium chloride (sorbens), and the utilized refrigerant, methanol (sorbate). Subsequently, pioneering works from the literature and from experimental works of this research group are referred to.

Calcium chloride is a non-toxic and cheap substance with a high energy density [3], [5], [10]. It acts as a soft Lewis acid and forms strong complexes with methanol [3]. Calcium chloride is a waste product in the production of fertilizers (e.g. from acidulation of apatite with HCl. It is undesired for making the fertilizer hygroscopic and unsuitable for storage and handling in the field) [11]. Calcium chloride is of high interest in applied thermal engineering as a phase change material (PCM) and in thermochemical applications and sorption, as reviewed by N'Tsoupkpoe et al. [10]. It is stated that the use of $CaCl_2$ as PCM for thermal storage is widely demonstrated [10]. However, more research efforts concerning the use of $CaCl_2$ in sorption and thermochemical units are suggested [10].

The major refrigerants for solid sorption refrigeration which are studied and applied are natural working fluids with no GWP and ozone depletion potential (ODP): water, ethanol, methanol, and ammonia [12]–[14]. Methanol is one of the favored refrigerants [12]. The high latent heat of vaporization makes it remarkably energy efficient. CH_3OH is suitable for applications operating below the freezing point of H_2O and for subatmospheric conditions; it is a less toxic and less corrosive refrigerant compared to NH_3 [12].

There are few experimental works studying the working pair $CaCl_2 \cdot xCH_3OH$. Advantages of this pair are that the thermodynamic properties match low-level temperature refrigeration applications and that common low-grade heat sources can be used for desorption (charging of the reactor) [3]. Experimental works with $CaCl_2$ and CH_3OH include e.g. the studies by Offenhartz et al. who performed tests in a finned tube heat exchanger system [15] and by Lai and Li [5] investigating the system performance of a periodic flow reversal fixed-bed reactor [5]. An overview of various physisorption refrigeration systems at prototype level, including commercially available adsorption chillers, and the respective efficiency performance is given in [8]. Further reviews are presented in [3]. For experimental works with other workings pairs see e.g. [16]. An overview over working pairs tested in prototypes under practical conditions is given in [4] and a list of salts for solid / water vapor chemical sorption can be found in [7]. Other works use the water vapor / zeolite pair with low pressure (10 ppm) and solar power (temperature of 150°C) for the charging process, producing a temperature drop to 0°C. The cooling energy produced was 250 kJ per kg of zeolite [17].

Korhammer et al. studied the potential of the working pair $CaCl_2$/methanol for solid sorption refrigeration using TGA/DSC (thermogravimetric analysis / differential scanning calorimetry) [3]. The pair possesses a good cyclability and reproducible cooling output [3]. Specific cooling power (SCP) values are stated to be up to 1029 W/kg (between 157 W/kg and 366 W/kg on average) [3]. Cooling power is calculated as follows (2):

$$SCP \;/\; \mathrm{kW\ kg^{-1}} = \frac{dm}{dt} \cdot \Delta_v H_{(CH_3OH)} \cdot \frac{1}{3600} \quad (2)$$

with:

$\frac{dm}{dt}$ = specific methanolation rate / mol h^{-1} kg$_{(salt)}^{-1}$

$\Delta_v H_{(CH_3OH)}$ = latent heat of vaporization (at T=298.15 K) / kJ mol^{-1} ; value from [18]

Thermal coefficient of performance (COP, here for a cooling system with solid/gas reactions) is the ratio of the cooling power output ΔQ_{out} to the heat power input ΔQ_{in}. This fraction equals the vaporization enthalpy of the gaseous absorbate $\Delta_v H$ divided by the desorption enthalpy of the solid absorbent $\Delta_r H$ [19] (3):

$$COP = \frac{\Delta Q_{out}}{\Delta Q_{in}} = \frac{|\Delta_v H|}{|\Delta_r H|} \quad (3)$$

Thermal COP (see 3) are stated to be between 0.67 and 0.75 [3]. The relation of temperature and partial pressure for calcium methanolates can be seen in Fig. 1. The methanolates are stable at the right of the curve, at the left side of the curve they decompose. The green plot separates the liquid state of methanol (above the plot) and the gaseous state (below the plot).
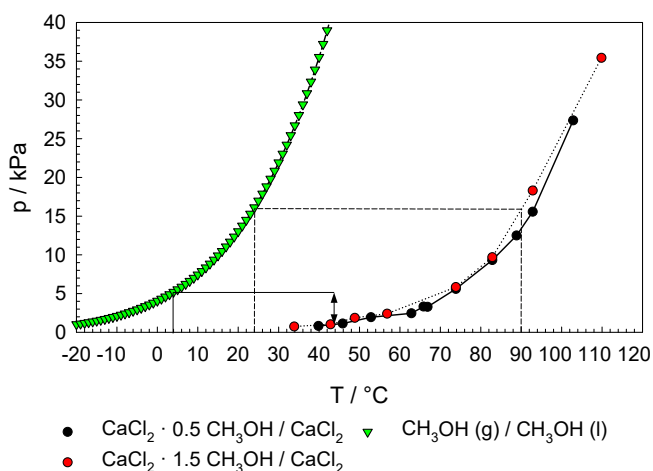

Fig. 1. Methanol vapor pressure curve and partial pressure of decomposition curves of two calcium chloride methanolates (desorption). The upper help lines illustrate the relation of desorption and condensing, the lower help lines illustrate the relation of evaporation and sorption. The arrows show the difference in partial pressure which is required for mass transport. Data from Ambrose & Sprake [20], Bonnel & Jones [21] and Offenhartz et al. [15].

II. MATERIAL AND METHODS

A. Salt preparation

For the intended experiments there was the option to either work with dry $CaCl_2$ and start with methanolation in the first cycle or to fill the reactor with $CaCl_2 \cdot 2\,CH_3OH$ and start with the desorption phase. When using dried salt, it was unclear if the increase of volume during methanolation

leads to salt spill over. Using $CaCl_2 \cdot 2\,CH_3OH$ to fill the demonstrator would require the production of adequate amounts e.g. by passive transport. To find out if the required amounts of $CaCl_2 \cdot 2\,CH_3OH$ could be produced within a reasonable time, a simple test in a desiccator with two separate containers with methanol from Merck (methanol, anhydrous, max. 0.003 % H_2O, analytical reagent) and thermally dried $CaCl_2$ from VWR Chemicals (calcium chloride 90-98 %, technical) was performed. The completeness of sorption to $CaCl_2 \cdot 2\,CH_3OH$ was assessed by determining mass changes. It took 14 days for complete sorption of the provided CH_3OH and thus production of $CaCl_2 \cdot 2\,CH_3OH$. Regular manual mixing did not substantially shorten the sorption time (still ≈ 14 days). Therefore, it was not feasible to produce enough $CaCl_2 \cdot 2\,CH_3OH$ and it was decided to use dried $CaCl_2$. The $CaCl_2$ was dried for 24 hours at 200°C in a laboratory oven (VO 500, Memmert).

B. Preliminary test with methanol at laboratory scale

For preliminary tests, five cycles with the working pair of $CaCl_2$ and CH_3OH were performed in the laboratory. The set-up was as follows: Two round aluminum honeycomb plates with a diameter of 180 mm, a height of 20 mm and a diameter of the honeycombs of 3.2 mm and a bottom plate of 1 mm thickness were filled with 689.54 g dried $CaCl_2$ in total and mounted on a u-pipe made from aluminum, serving as a heat exchanger (Fig. 2).

This absorber set-up was installed into a vacuum tight stainless steel cylinder of 200 mm diameter. Inlet and outlet of the u-pipe heat exchanger were connected to a laboratory thermostat (Unistat 405, Huber) through the closure head. Pressure was measured inside the void volume of the reactor space with an analogue pressure sensor. Temperature was measured inside the void volume and inside the salt of both aluminum plates via Pt100 temperature sensors. Evacuation of the reactor chamber was facilitated by a vacuum pump connected to the top of the reactor by a ball valve. Pressure was decreased to the level when evaporation started. A round-bottom flask, serving as the methanol evaporator/condenser was placed in a thermal bath and connected to the bottom of the reactor by a ball valve.

For the used amount of dry $CaCl_2$, sorption of methanol to $CaCl_2 \cdot 2\,CH_3OH$ stoichiometrically yields an sorption of 398.14 g methanol. For the sorption phase, the respective amount of methanol necessary for stoichiometric uptake plus 100 g methanol was filled into the flask. The findings from the preliminary tests in the laboratory were taken into account in designing the demonstrator.

C. Demonstrator design and experimental runs

The technical design of the demonstrator for solid sorption refrigeration with calcium chloride and methanol was based on experimentally determined thermodynamic and kinetic data by Korhammer et al. [3] to give ≈ 2 kW of continuous cooling power and a temperature level around 10°C, which is suitable for the cooling of buildings [3]. Fig. 3 shows a
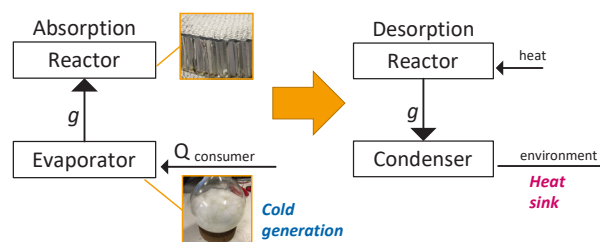

Fig. 2. Scheme of the lab-scale set-up.

photograph, Fig. 4 a schematic drawing of the demonstrator. Continuous operation is ensured by two alternatingly working sorption reactors (A and B). Each reactor consists of a welded

Fig. 3. Technical scale demonstrator during construction with the two reactor cassettes (1 and 2), the evaporator (3) and condenser (4) with the corresponding fans (5 and 6).

cuboid steel housing with four aluminum honeycomb plates (496 mm x 500 mm x 15 mm with an honeycomb diameter of 3.2 mm and a bottom plate of 1 mm thickness) glued onto commercially available universal flat radiators (type 10, 600 mm x 600 mm, unpainted, glue agent: 4486 CV Thermal Adhesive, Dow Corning).

The flat radiators are pressure-resistant, dimensionally stable and they are supposed to ensure an efficient heat transfer. The dried $CaCl_2$ is filled into the honeycombs (Fig. 5) with each reactor containing $\approx 9.7 \pm 0.1$ kg $CaCl_2$ in total.

Each of the 8 honeycomb plates (4 per reactor) is fitted with two Pt100 temperature sensors: one in the center and one at the edge in the back corner of the plate. This is meant to to be able to assess the uniformity of the temperature. Temperature data was logged digitally every 5 seconds. The evaporator was
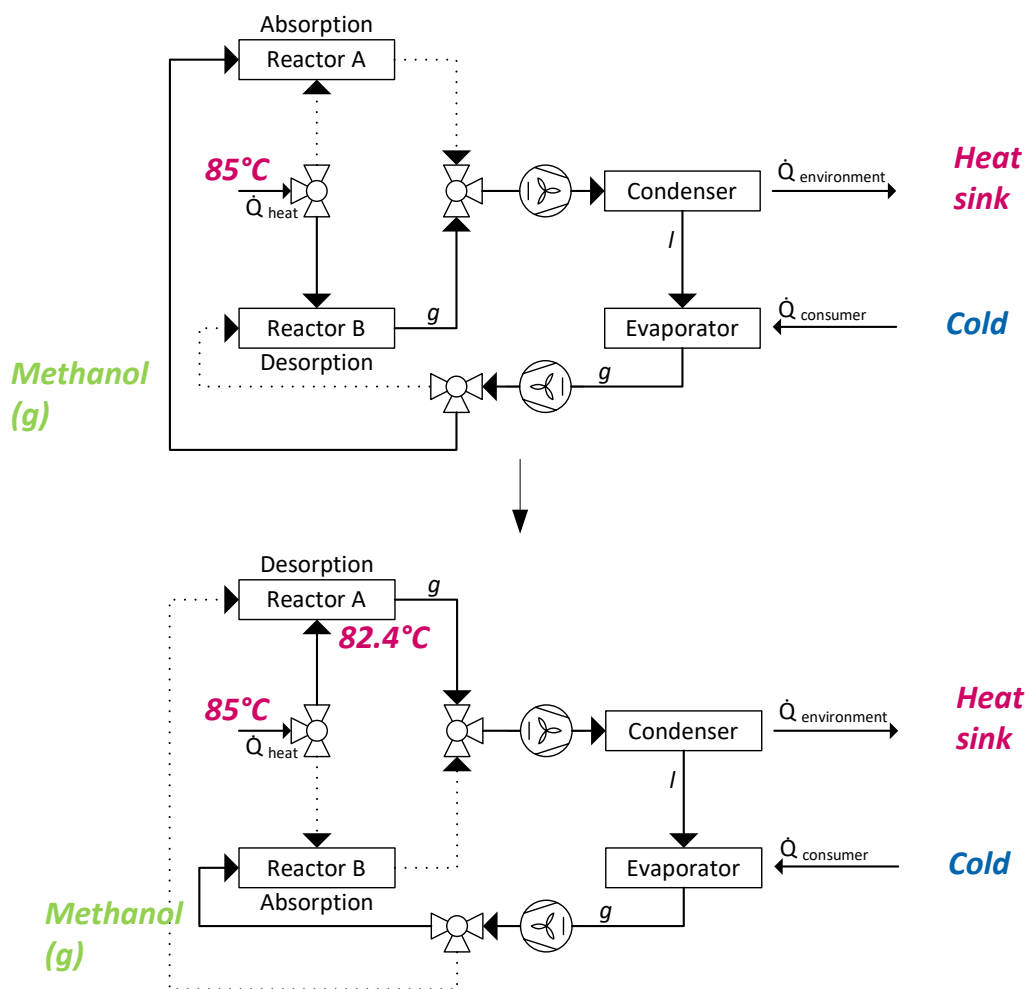
Fig. 4. Schematic drawing of the used demonstrator for solid sorption refrigeration on technical scale. Top: state of methanolation in reactor A, desorption in reactor B; bottom: vice-versa.
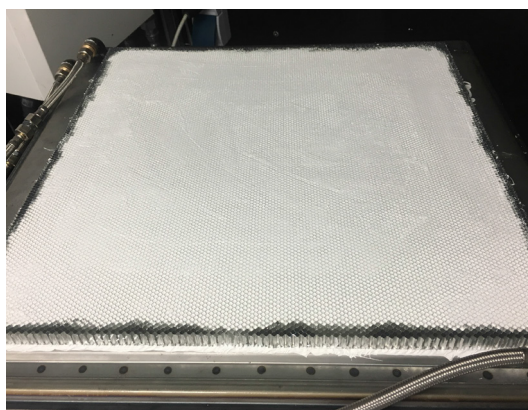

Fig. 5. Calcium chloride in honeycomb plates (Al, 15 mm high).

the risks of unintended combustion of methanol and corrosion. Controllable explosion protected ventilation was used as an energy saving compromise between compression and passive transport. This is linked to the finding from the preliminary test (see III)) that passive transport towards the storage salt and also desorption are challenging (heat transfer from u-pipe into the aluminum plate was non-optimal). Volumetric flow rate was calculated for the target cooling power value ($P_{demonstrator}$) of 2 kW (4).

$$\dot{V} = \frac{P_{\text{demonstrator}} \cdot V_m}{\Delta_v H_{(\text{CH}_3\text{OH})} \cdot \chi_{(\text{CH}_3\text{OH})}}$$

$$= \frac{2000 \text{ W} \cdot 0.02247 \text{ m}^3 \text{ mol}^{-1}}{10.4 \text{ Wh mol}^{-1} \cdot 0.16} \quad (4)$$

$$\approx 27 \text{ m}^3 \text{ h}^{-1}$$

with:

$\dot{V}$ = volumetric flow rate / $\text{m}^3 \text{ h}^{-1}$

$\Delta_v H_{(\text{CH}_3\text{OH})}$ = latent heat of vaporization / Wh mol^{-1}

filled with 10 L methanol per reactor, providing a higher volume than stoichiometrically required. The stoichiometrically required methanol volume for $CaCl_2 \cdot 2\,CH_3OH$ and the used amount of salt per reactor is $\approx$ 7 L. After filling, the system was purged with N_2 ($N_2 > 99{,}8\%$, Air Liquide) to eliminate

V_m = molar volume of an ideal gas at 1 bar and 25°C / m³ mol⁻¹

$\chi_{(\text{CH}_3\text{OH})}$ = $f(T_{(reactor)}, T_{(condenser)}, T_{(evaporator)})$ mole fraction of methanol

The radial blower on the condenser side of the demonstrator was running at $\approx$ 10 m³ h⁻¹ during the charging phase. The condenser is situated above the evaporator so that the condensed medium flows into the evaporator via a siphon. The experimental runs were performed in an uninsulated vehicle trailer which was exposed to daily and seasonal temperature fluctuations.

III. Results

A. Preliminary tests in the laboratory

In the preliminary tests with calcium chloride and methanol in the stainless steel cylinder, one of the observations was an volume expansion of the salt (Fig. 6).
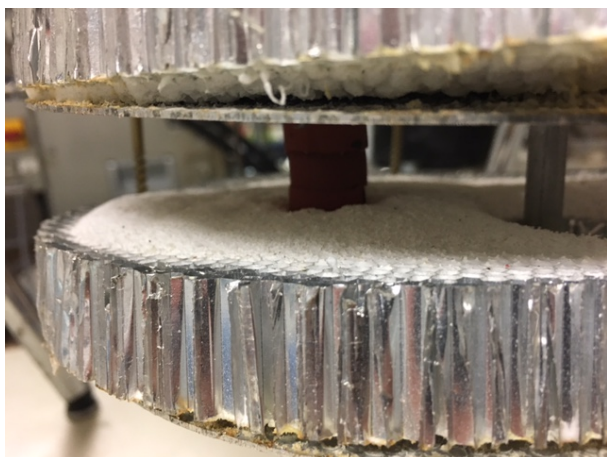

Fig. 6. Calcium chloride volume expansion from methanolation lead to forces high enough to destroy the adhesive bond between the honeycomb plate (20 mm high) and the bottom plate.

The temperature was measured in the salt in both honeycomb plates and increased by 40 K to 60°C in the first of five sorption phases (the temperatures over time of all five cycles can be seen in Fig. 7). In the round-bottom flask serving as the evaporator for the liquid methanol (for the generation of cold), temperature first dropped from 18°C to 4°C and then stayed at 7.3°C in the first sorption phase. Thus, achieved cooling effectivity was around 10 K below ambient. Methanol evaporation was 211.48 g (1.02 mol methanol per mol calcium chloride). Desorption over 49 hours yielded no more than 8.75 g condensed methanol in the round-bottom flask. During the second sorption phase, an amount of 165.35 g methanol was evaporated with temperatures in the methanol dropping from 19°C to $\approx$ 10°C. Under the assumption that the methanol evaporated under vacuum equals the amount of methanol sorption by the storage salt, a mass of 368.08 g methanol (1.85 mol methanol per mol calcium chloride) was absorbed after the second sorption phase.
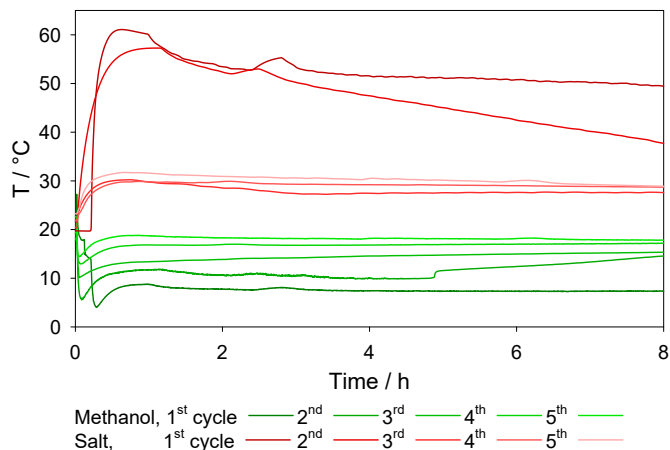

Fig. 7. Discharging phases of five cycles performed in a lab-scale reactor with the working pair calcium chloride / methanol. The green lines show the temperature drop in the round-bottom flask (=evaporator), the red lines show the temperature rise in the sorption bed absorbing methanol.

Subsequent cycles showed a significantly lowered additional sorption of methanol along with lower temperature rise in the salt and lower cold production (TABLE I) with methanolation state exceeding $CaCl_2 \cdot 2\,CH_3OH$. In cycles 3-5 the desorption temperature pair was not sufficient to reverse methanolation below 2 mol/mol.

TABLE I
METHANOLATION/DEMETHANOLATION RATES DURING AND CUMULATIVE METHANOLATION STATE AFTER THE CYCLES

Cycle	t / h		$\frac{dm}{dt}$ / $\frac{g}{h}$		$\frac{n(\text{CH}_3\text{OH})}{n(\text{CaCl}_2)}$ / $\frac{mol}{mol}$	
	sorp[a]	des	sorp[b]	des[b]	sorp[c]	des[c]
1	8	49	26.44	0.18	1.06	1.02
2	8	30	20.67	0.07	1.85	1.84
3	8	78	11.34	0.76	2.29	2.00
4	8	56	3.93	0.42	2.15	2.03
5	24	59	3.61	1.14	2.47	2.13

[a]sorp: sorption, des: desorption; [b]assuming linearity; [c]cumulative

B. Demonstrator tests

Peak cooling power was 0.3-0.4 kW/kg sorbent with an average of 0.1-0.2 kW/kg sorbent and COP values of 0.6–0.75. The first sorption phase of reactor A generated 5 kWh cooling energy (550 W over 9 hours; this corresponds to a quarter of the theoretical power). T_{evap} was 5 K below ambient, which is suitable for the cooling of buildings.

Cold production in the subsequent cycles was only $\approx$ 1-2 kWh/cycle due to insufficient temperature in the salt and/or too high condenser temperatures. During the desorption, temperature in the salt reached up to 82.4°C (inlet temperature: 85°C). Fig. 8 displays the temperature change in reactor A during desorption. The plots belong to different points within the four aluminum plates (1-4) of the reactor. Contrary to the observations in the laboratory tests (Fig. 6), no visible volume
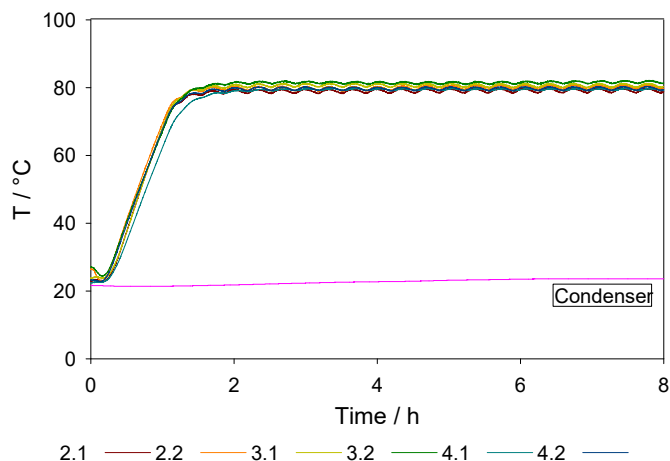
Fig. 8. Temperatures in the salt and condenser during charging phase (desorption) of the working pair calcium chloride / methanol in a technical scale reactor.

expansion by the salt out of the honeycombs was observed in an inspection after the demonstrator tests.

IV. DISCUSSION

Overall, the working pair calcium chloride/methanol shows attractive results for thermochemical generation of cold at laboratory and technical scale. While other authors (using water as the sorbate) identify a main limitation in the heat transfer at the interface between the heat exchanger surface and the reactive salt [7], the results of the presented demonstrator show a good heat transfer into the salt.

The temperature varied only slightly between the different points of measurement ($\pm$ 1.2%, without correction for the accuracy of the temperature sensor, cf. Fig. 8). This indicates an even distribution of heat. Over the first sorption phase of the demonstrator tests using the oven-dried salt, a cooling energy of 5 kWh was generated. This reflects overstoichiometric sorption and is in line with TABLE I, which shows that sorption in the laboratory experiments was overstoichiometric at the end of cycles 3-5. A promising finding from the laboratory setup is that cold generation continued over more than 8 hours, which is well suitable e.g. for cooling in office buildings (cf. Fig. 7).

During the desorption phase in the demonstrator, the required onset temperature of $\approx$ 90°C to reach peak demethanolation (cf. Fig. 1, [3]) was not met. The temperatures in the salt reached only 80.67 ($\pm$ 0.98)°C (Fig. 8). For both, laboratory and demonstrator experiments, the salt remained at minimum in the state of dimethanolate from the second or third cycle on. This is concluded from the observations that temperature rise in the salt during methanolation was low and that cold production in the methanol was substantially lowered; with $\approx$ 1-2 kWh/cycle, falling below the calculated values. The finding indicates that the charging of the material (desorption) was not as successful in the respective set-ups compared to charging (drying the material) in the laboratory oven.

This could have two major causes: methanol vapor pressures during desorption and mass transfer of methanol from the salt. The former could have been due to a too high condenser temperature. Fig. 1 shows the relation of temperatures in the salt and the condenser and respective vapor pressures. Desorption and mass transfer of methanol require a sufficient vapor pressure gradient. In the applied setup, the vapor pressure gradient was insufficient according to the theoretical data (Fig. 1). With 82°C in the salt, much lower condenser temperatures, i.e. below 15°C would have been necessary. Depending on the application, the design of the device can be modified as follows:

a) higher regeneration temperatures

b) lower condenser temperatures

c) an actively controlled pressure gradient between the sorbate and condenser/evaporator (to tackle the issue of mass transfer)

Thanks to the modular design of the honeycomb plates, upscaling of the system for applications in need of higher cooling power is easily achievable.

The employed desorption temperature equals industry waste heat levels. When using higher temperatures (e.g. >100°C from solar thermal energy), it has to be considered that fully continuous operation may be challenging due to a necessary cool down phase when switching between sorption reactors. The necessary cool down would result in higher losses and lowered thermal COP. A solution for this could be the use of more than two reactors. Option b) can be considered if a) is not possible.

The optimization option c) with an actively controlled pressure gradient seems to be most promising as it enables active control of the reaction progress and of the cold output as well as regeneration. The ability to align the two halves of the cycle process is crucial for continuous operation.

Replacement of the radial blower between reactors and condenser with mechanical compression would require additional electrical energy consumption, as estimated in equation (5). However, the amount would still be lower compared to installations using other types of refrigeration than chemisorption.

$$P_{\text{compressor}} = \frac{\dot{V} \cdot \Delta p}{\eta}$$

$$= \frac{27\,\text{m}^3}{3600\,s} \cdot 2 * 10^4\,\frac{kg}{m\,s^2} \cdot \frac{1}{0.7} \quad (5)$$

$$\approx 214\,\frac{kg\,m^2}{s^3} = 214\,\text{W}$$

with:

$P_{\text{compressor}}$ = compressor power / W
$\dot{V}$ = volumetric flow rate / m³ h⁻¹
Δp = differential pressure / mbar

η = compressor efficiency, here estimated to be close to the mechanical efficiency due to low pressure difference and therefore low thermal loss

Estimated electrical COP of such chemisorption installations with mechanical compression would likely reach 10 or higher. In case of solar thermal cooling (a combination of a) and c)), the higher desorption temperatures lower the required mechanical compression power. Still, such a concept needs to be tested. To compare the proposed system other storage options, it can be stated that the above cited value of 250 kJ per kg of zeolite [17] is low compared with the 1188 kJ kg^{-1} from the present study. In comparison with ice storage, even optimized ice storage systems which combine a heat pipe-based seasonal ice storage system with a chilled water storage system, have a lower cold storage density (0.087 kWh kg^{-1} [22]) than the CaCl$_2 \cdot$ xCH$_3$OH system presented in this work (0.32 kWh kg^{-1}).

Note that the presented demonstrator was installed in an uninsulated vehicle trailer. Since fluctuations of the ambient temperature influenced the performance, the test environment was not optimal. The envisaged future application will be inside buildings with stable/predictable temperatures. The integration of a prototype into a residential building or factory needs to be investigated in future research. Improvements regarding the material could be the use of composites with e.g. expanded vermiculite or biochar [3]. A review of techniques to enhance the heat and the mass transfer in solid/gas sorption systems is given in [14]. These additives are meant to improve diffusion of methanol and cycle stability, as well as to avoid agglomeration. In this study, there was no indication that the volume expansion of the salt is problematic, after reducing the height of the honeycomb plates from 20 mm to 15 mm.

V. Conclusions

Overall functionality of solid sorption refrigeration with calcium chloride methanolates was demonstrated with a closed prototype on technical scale. The main challenges are identified in the desorption of the absorbate (methanol) and in the transfer of the absorbate. Optimizations are:

1) Higher desorption temperatures ≈ 90°C
2) Lower condenser temperatures
3) Reduction of pressure (cost intensive)
4) Use of compression (better control and higher cooling power)

Depending on the use case (e.g. with CHP heat, solar thermal/electrical energy, biomass combustion engines), 1, 3 or 4 should be considered for plant optimization. Upscaling is possible via greater amounts of absorber material. It is possible to either enhance storage capability and therefore duration of a uniform cold output or to enhance cooling performance using a bigger absorber. Optimization potentials and upscaling options are realized in a follow-up project. Furthermore, future research should address the system integration.

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