Energy Proceedings
Vol 61, 2025
ISSN 2004-2965

Distributed District Heating via Zeolite as Thermochemical Energy Storage#

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ABSTRACT

This study aims at investigating the technical potential of using Zeolite as a thermochemical energy storage in a distributed district heating system. Different storage sizes were simulated and combined with an existing local pellets boiler at a medium sized school building as a case study. A test rig was built to monitor how the Zeolite was charged through desorption where heat was added and then discharged when vapour was added to the Zeolite. The storage sizes were assessed in various scenarios. A seasonal storage unit sized to cover the challenging low-load thermal demand during summer was reasonably sized and weighted. The seasonal storage can also provide heat for almost a week during winter out of a resilience perspective.

Keywords: Thermochemical Energy Storage, Zeolite, District Heating, Waste Heat Recovery, Resilience

NOMENCLATURE

Abbreviations	
AH	Absolute Humidity
DH	District Heating
ED	Energy Density
EED	Effective Energy Density
RH	Relative Humidity
TCES	Thermochemical Energy Storage
Symbols	
c_p	Specific heat capacity [kJ kg^{-1} K^{-1}]
η	Efficiency [%]
m	Mass [kg]
M	Molar mass [g mole^{-1}]
p	Pressure [Pa]
$Q_{des/ads}$	Energy charged during desorption or discharged during adsorption [kWh]
R	Universal gas constant [J mol^{-1} K^{-1}]
ρ	Density [kg m^{-3}]
T	Temperature [K]
t	Time [s] or [h]
$\dot{V}$	Volumetric flow [m^3 s^{-1}]
$\chi_{a/s}$	Steam pressure, Actual or at Saturation

1. INTRODUCTION

District heating (DH) is a geographically confined energy system limited to urban areas where the heat density is sufficiently high. For a DH company, this means that there are potential customers that are challenging to reach with centrally produced heat using conventional methods.

To ensure heat supply to a building where the DH network does not reach, a thermochemical energy storage (TCES) could be implemented together with a local boiler. This could remedy situations with high relative operating costs, e.g., peak load periods or low-load seasons. There is also a potential to reduce primary energy use by charging the Zeolite with residual industrial heat. Overall, this could strengthen the business model for DH companies. The Russian full-scale invasion of Ukraine has caused significant increase in fuel prize of bioenergy which motivates the introduction of alternative methods that both reduce the rely on solid fuel for heat delivery and potentially also increase energy security and resilience in the energy system.

If the heat supply is dependent on a single resource, as this study's school building used as a reference for calculation of storage sizes, the systems become susceptible to disruptions that can cause significant discomfort to the end-user. Currently, the local energy company can deploy oil-fuelled burners to the boiler as a contingency measure, hence the resilience of the system is poor due to low access to redundancy functions.

Zeolite is a material with high adsorption capacity, high energy density and low heat losses, that can be used in a TCES [1], [2]. The TCES is charged through desorption where heat is added, which starts an endothermic reaction that results in the separation of the sorbent, i.e. the Zeolite, and the adsorbate, i.e. water molecules, that were adsorbed to the Zeolite. If the Zeolite is kept in a hermetically sealed space, the added energy is stored. Due to negligible losses, the energy in the material can be stored over a long time. An exothermic reaction

This is a paper for the Resilient-Applied Energy Symposium and Forum: Resilient energy systems (Resilient2025), Sep. 23-25, 2025, Västerås, Sweden.

occurs upon discharge when the adsorbate (i.e. vapour) is added, causing water molecules to re-adsorb to the Zeolite and releasing stored energy as heat.

1.1 Scope and purpose

This study investigates the technical potential of using Zeolite as a TCES as a means for supplying heat to a school building outside of the DH network.

1.1.1 Research questions

1. How would a TCES using Zeolite be dimensioned in terms of energy quantity (weight and volume) and required frequency of replenishing the energy content, given the power requirement and discharge range?
2. How can a TCES using Zeolite increase the resilience of heat supply to a single, medium sized end user outside of the DH network?

2. BACKGROUND AND THEORY

Thermal energy storage can be classified into three categories: sensible, latent, and thermochemical methods [1]. Thermochemical storage, although more expensive, offers higher capacities, energy densities, and efficiencies [1], [3]. Sorption systems and chemical reactions are common types of thermochemical storage. These systems utilize physical or chemical bonds to store energy, resulting in higher energy density and fewer heat losses compared to sensible storage technologies [2].

Sorption systems can be designed in two ways: open systems and closed systems [2], [1]. Open systems, as in this study, exchange both mass and energy with the environment. The system operates at atmospheric pressure and requires neither a condenser nor evaporator, but fans to transport humid air to the sorption tank and possibly humidifiers to achieve the desired sorption vapor pressure [2], [1].

Closed systems consists of a heat exchanger, condenser, and evaporator [1]. In closed systems, the sorbent and sorbate are separated throughout the process and only energy exchange occurs with the ambient surrounding [2]. Closed systems operate with clean steam under vacuum conditions where no energy is lost to the environment [1].

Zeolite is an adsorbent material and thus by definition the sorbent in a sorption system [2] and can be used in a thermochemical energy storage system. Zeolite is a natural material consisting of porous crystalline aluminosilicates of alkali or alkaline earth elements, e.g., sodium, potassium, and calcium built up in a tetrahedral form. In commercial use, it is usually synthetic and classified as molecular sieve.

Zeolite has been tested in earlier projects where especially two are of specific interest and related to the current study. In Münich in 2015, ZAE Bayern initiated a full-scale test with a 14-ton mobile Zeolite storage that were charged using steam from a waste incineration unit and then transported to an industry 7 km away to release process heat [1], [4]. They showed the importance of high temperature during desorption and challenges with design of Zeolite-modules [4]. Narwal et al. [5] also investigated the potential of a mobile Zeolite-storage solution. Their results emphasized the importance of providing a sufficient relative humidity during adsorption (discharge of heat) [5]. In Table 1 a summary of other studies is shown to provide a context of the materials potential ([4], [5], [6], [7], and [8]).

2.1 Theory

The energy storing capacity for desorption (charging) and/or adsorption (discharging), $Q_{des/ads}$, of the Zeolite is given by

$$Q_{des/ads} = \dot{V} \int_{t_{start}}^{t_{end}} \rho_{air} \times c_{p,air} \times |T_{out} - T_{in}| \mathrm{dt} \quad (1)$$

where $\dot{V}$ is the volumetric flow of air in m³/s and T is temperature in K at in- and outlet of the Zeolite chamber. The density of air, ρ_{air}, is given via the ideal gas law

$$\rho_{air} = \frac{pM}{RT_{out}} \quad (2)$$

where p is atmospheric pressure, M is molar mass of air, and R is the universal gas constant. The specific heat capacity of air, $c_{p,air}$, is a function of the humidity ratio, x, and is given by

$$c_{p,air} = c_{p^{dry\ air}} + x \times c_{p^{moist\ air}} \quad (3)$$

x is given by the pressure, temperature out of the Zeolite chamber, and χ_a.

*Table 1: Characteristics of previous Zeolite-based thermal energy storage studies. * = calculated using a density for Zeolite of 700 kg/m³ [6].*

Reference	$m_{zeolite}$ [kg]	T_{charge} [°C]	$T_{discharge}$ [°C]	T_{out} [°C]	Capacity [kWh]	Energy density [kWh m^{-3}]
ZAE Bayern, 1997 [7]	7 000	130 – 180	25 – 30	100	1 300 – 1 400	124
ZAE Bayern, 2015 [4]	14 000	130	60	160	2 333.35*	115*
MONOSORP [8]	61.5	180	19	41	-	120
Prototype STAID [8]	50	-	-	-	-	103
Experiment, STAID [8]	80	180 / 120	20	-	13.5*	114
Narwal [5]	0.27*	200	20 – 23	45 – 55	0.042*	110

χ_a is given by the relation with the relative humidity of air, *RH*, and the saturation vapour pressure, χ_s

$$\chi_a = \frac{RH \times \chi_s(T_{RH})}{100}. \quad (4)$$

At *T*>0°C χ_s is approximated by Bucks equation as

$$\chi_s(T) = 6.1121 e^{\frac{\left(18.678-\left(T/_{234.5}\right)\right)T}{257.14+T}} \quad (5)$$

with good reliability up to 100°C [9]. Finally, the efficiency, η, is given by the ratio of Q_{ads}/Q_{des}, that is useful energy extracted from vs stored to the Zeolite, and the energy density (ED) is the ratio between released energy and the volume of Zeolite in kWh/m^3. The heating system in the school used as a reference for dimensioning the Zeolite storage is assumed to require a minimum temperature of 60°C. The effective energy density (EED) is hence calculated from $Q_{ads}^{T_{out}>60°C}$ and the volume of the Zeolite chamber.

3. MATERIAL AND METHODS

3.1 Experimental setup

The experimental tests are carried out at the University of Gävle, where laboratory technicians built a test rig to enable the desired measurements to be made on the Zeolite. Measurement data is recorded with LabVIEW and exported to MatLab for analysis, calculations, and simulations. A schematic of the experimental setup is shown in Fig. 1.

Measurements during the experimental tests are done as shown in Fig. 1 and Table 2. Temperature will be measured at 11 points in the set-up, where point ① and ② measures temperature before and after the addition of vapour, located prior to the measurement of RH_1 in point ③. Furthermore, five measuring points for temperature will be evenly distributed within the Zeolite bed with one additional measuring point at the inlet to the Zeolite chamber. Downstream of the Zeolite bed and the single-leaf damper holds an additional measure point, ⑤, placed next to the measuring of RH_2 in point ⑥. Finally, ambient temperature will be measured in the laboratory, point ⑧, and between the outside of the Zeolite-chamber and the enclosing insulation, point ④, to track heat loss out through the chamber wall.

Table 2 Performed experimental tests. In all tests the air flow is 11 l/s.

	Desorption/Charging		Adsorption/Discharge		
Test	**Application**	T_{in}[°C]	**Application**	T_{in}[°C]	RH_1[%]
1	Waste heat	90	Ventilation	25	50
2	Waste heat	90	Ventilation	25	80
3	Waste heat	90	District Heating	40	50
4	Waste heat	90	District Heating	40	80
5	Heat pump	60	Ventilation	25	80
6	Flue gas	120	Ventilation	25	80
7	Flue gas	120	District Heating	40	80

Temperature and RH in and out of the Zeolite bed, i.e., measuring points T_1 and T_5 inside the chamber as well as points ③ and ⑥, will be used to calculate charging/discharging time. Flow (point ⑦) and RH (points ③ and ⑥) will be used to establish a controlled laboratory environment. Together with T_1 and T_5 these are necessary input parameters when calculating the heat energy. The air flow will be kept the same while RH will be varied between different tests to investigate how the charge/discharge is affected. T_1 will also be varied by regulating the power of the heater.

3.2 System configuration

For dimensioning calculations, the heat demand of a school building will be used. Currently the school's heating demand is supplied by a pellets-fired boiler located approximately 100 m from the school building, delivering heat by underground pipes connected to a substation as in an ordinary DH system. The boiler is operated to maintain a certain level of thermal energy in an accumulator tank from which the end-user extract heat. Peak demand is 100 kW_{th} and annual demand is 190.2 MWh_{th} as shown in Fig. 2, top panel. Calculations will be made for three scenarios:

1. *Annual*, covers the entire heat demand
2. *Seasonal*, covers only the low load season (orange section in Fig. 2, top panel)
3. *Peak*, covers peak load supply (red shaded area in duration graph in Fig 2, top panel).

The middle and bottom panel of Fig. 2 shows the energy demand per week and month respectively, which is used for dimensioning the Zeolite-modules in scenario 1, *Annual*. Desorption/charge of Zeolite is assumed to either take place elsewhere and be transported to site or

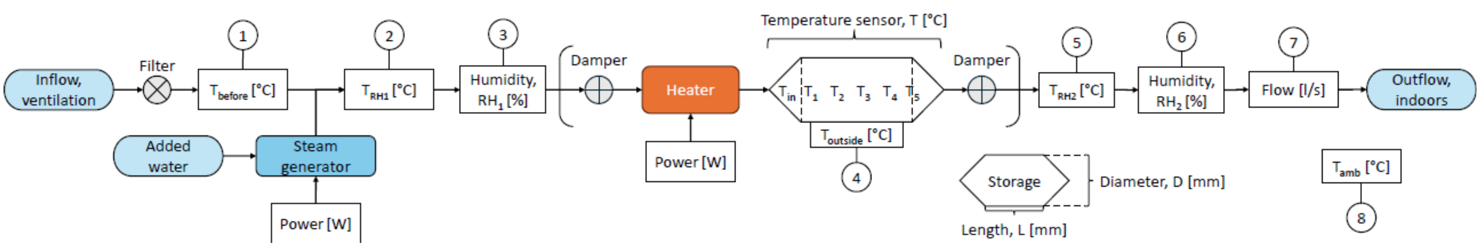

Fig. 1 Schematic representation of the experimental setup.

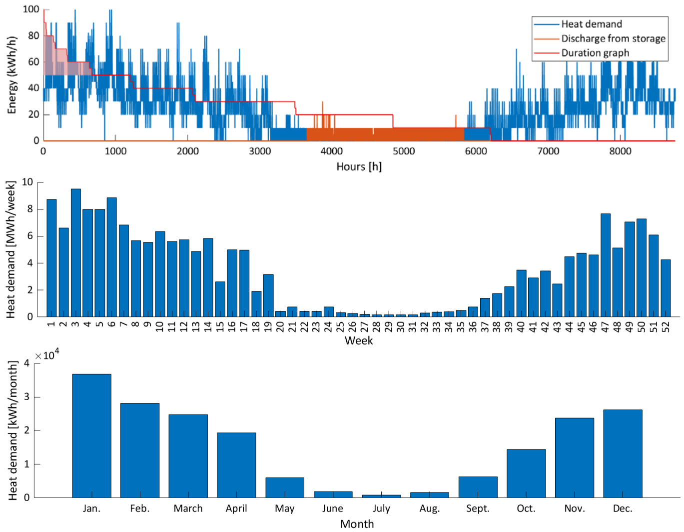

Fig. 2 Top panel shows the duration (red) and time series (blue) of the heat demand with the low load period indicated in orange. In the duration graph is the peak load marked as a red area. Middle and bottom panel show energy demand per week and month respectively.

use heat from the flue gas from the boiler on site. No flue gas recovery is currently installed. Fig. 3 a and b show the assumed schematic system solution for desorption and adsorption that is used as basis for dimensioning calculations. In Fig. 3 a, it is exemplified how the evaporation heat during desorption can be used for residential heating to improve the system efficiency.

3.3 Economic calculations

The maximum cost of Zeolite, c_{zeo}, based on the desired payback period is calculated as follows

$$c_{zeo} = \left(\left(c_{fuel} \times t_{PB}\right) - c_{aux}\right) \times \left(m_{zeo}\right)^{-1} \quad (6)$$

where c_{fuel} is the fuel cost saved, t_{PB} is desired payback period, c_{aux} is investment cost for peripheral equipment, and m_{zeo} is the mass of Zeolite.

4. RESULTS

4.1 Experimental setup

Table 3 shows results from the experimental setup. For the dimensioning calculations, data from tests 6 and 7 are used with the assumption that desorption is done

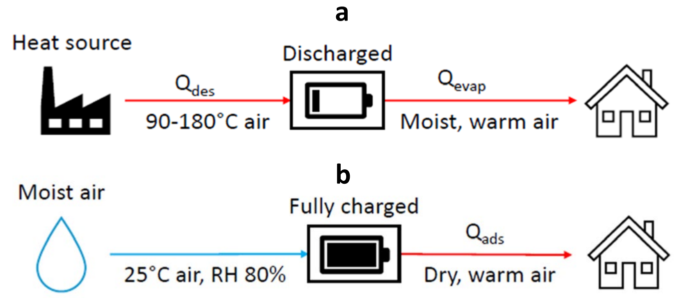

Fig. 3 In top figure (a) is the desorption conceptually shown and bottom figure (b) shows the adsorption.

with heat from flue gasses (≈120°C). In Fig. 4 the full cycle from test 7 is shown. The desorption, in the upper panel, is shown by a calculated AH in red. The AH is calculated based on the ideal gas law, a given temperature, and χ_a. At inlet the AH (AH_{T1}, in solid red) is at low levels and in steady state, while the AH at outlet (AH_{T5}, in dashed red) is elevated and changing over time. When AH_{T5} approaches AH_{T1} the desorption is completed. Similarly, the temperature at the inlet, T_1, shown in solid blue line, is held steady at 120°C while the temperature at outlet, T_5, shown with dashed blue line, stays at ambient temperature (approximately 22°C) for approximately one hour before the temperature front has moved through the Zeolite and T_5 starts to increase. When T_5 approaches T_1 the desorption is completed. For adsorption (discharge) the relations are reversed, shown in Fig. 4 lower panel.

4.2 Dimensioning simulations

The simulations of supplying the heat demand via Zeolite were done for three scenarios. In Table 4 key parameters are given from the simulations. Based on the experimental results shown in Table 3 a scaling factor was determined for the upscaling of the experimental Zeolite bed (cassette). It was assumed that the operation of the cassette would stay unchanged with moderate increase in size. Hence, a module with Zeolite for mobile heat supply was assumed to correspond to 8.2 times the experimental cassette's size for scenario 1 and 2 and 9.0 for scenario 3. Scenario 1 and 2 use experimental results from test 6 and scenario 3 use results from test 7 where

Table 3 Results from the performed experimental tests. In all tests the air flow was 11 l/s. Shelf time is time between charge/discharge.

	Desorption/Charging			Adsorption/Discharge					Full cycle			
Test	T_{in} [°C]	t [h:m]	Q_{des} [kWh]	T_{in} [°C]	RH_{in} [%]	T_{out} [°C]	t [h:m]	Q_{ads} [kWh]	Shelf time [d:h:m]	η [%]	EED [kWh/m³]	ED [kWh/m³]
1	91	3:15	1.65	23.3	53	49.0	4:06	0.76	2:18:51	46.4	41.2 – 54.0	89.0 – 117
2	95	3:14	1.85	22.8	79	65.5	2:56	0.81	4:16:03	43.7	43.6 – 57.2	99.8 – 131
3	97	4:12	2.15	40	50	62.4	2:44	0.54	0:16:22	25.0	29.0 – 38.1	116 – 152
4	92	3:27	1.51	40	80	72.5	1:52	0.48	6:15:56	32.0	26.1 – 34.2	81.4 – 107
5	62	3:49	0.87	27.1	75	53.4	3:11	0.38	7:15:50	43.2	20.3 – 26.7	46.9 – 61.5
6	123	2:09	1.84	28.4	80	82.6	3:53	1.36	3:16:42	73.8	73.2 – 96.0	99.2 – 130
7	123	4:24	2.32	40	78	95.5	2:36	1.15	1:15:11	49.5	62.1 – 81.4	125 – 164

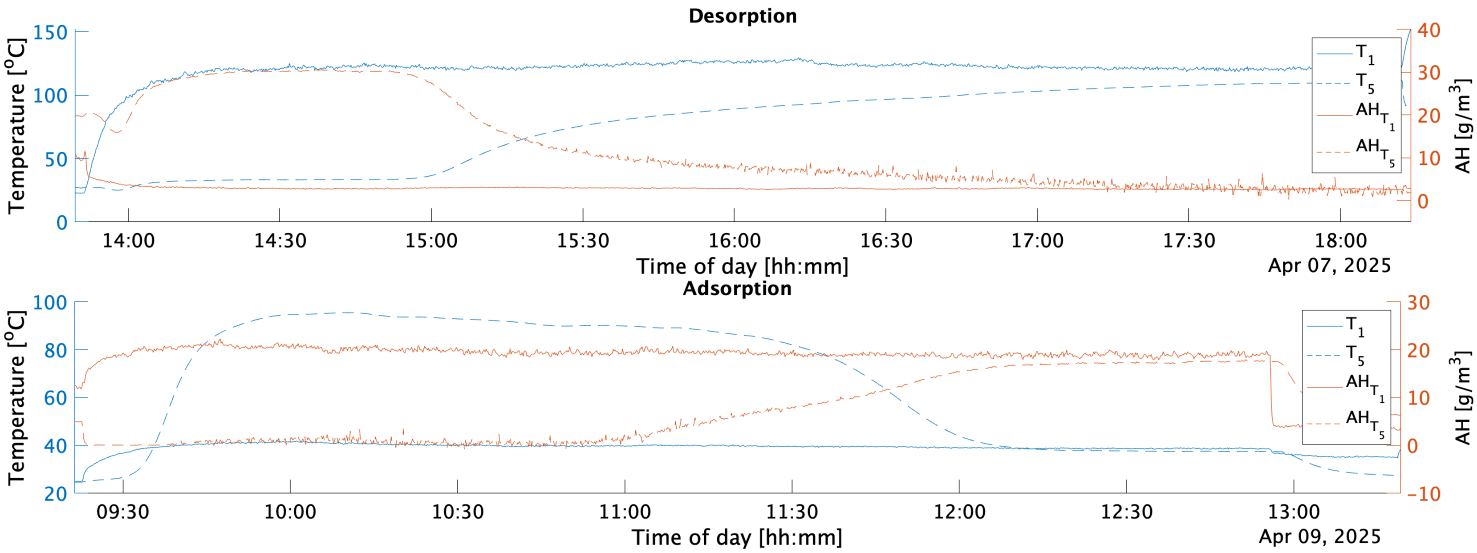

Fig. 4 Cycle from test 7. Temperature at inlet (T_1) and at outlet (T_5) is shown in solid and dashed blue lines. Absolute humidity, AH, at inlet and at outlet is shown in solid and dashed red lines. Between T_1 and T_5 a temperature front moves through the Zeolite (not shown in the figure).

Table 4 Results from simulation of Zeolite-modules.

Parameter \ Scenario		1. Annual month	1. Annual week	2. Seasonal	3. Peak
Boiler	*MWh*	-	-	185.93	178.49
Zeolite	*MWh*	190.2	190.2	4.33	11.71
Unit capacity	*MWh*	2×36.9	2×9.51	1×4.3	1×0.5
Modules	*#*	3 686	951	434	46
Rotation	*y^{-1}*	6	20	1	1
m_{module}	*kg*	49.1	49.1	49.1	42.8
P_{module}	*kW*	5	5	5	5
Q_{module}	*kWh*	10	10	10	10
Bulkiness	*ton*	350.1	90.3	41.2	4.8
	m^3	428–561	110–145	50.4–66.1	5.85–7.67

the latter has a slightly lower Q_{ads}. The discharge power capacity for a module is based on data from Table 3 and is calculated by dividing Q_{ads} with the approximate time of discharge rounded up to 4 h and 3 h for test 6 and 7 respectively. The modules are assumed to be assembled into units yielding the required capacities.

For scenario 1. *Annual* the units are either dimensioned by the heat demand per week or per month, yielding two different configurations. It is assumed that the units will be alternated during the year so that one unit is charged at a heat resource elsewhere, i.e., off site, while the other unit is discharged on site. For the week-based configuration, week number 3 of the year became the dimensioning week with a heat demand of 9.51 MWh, while for the monthly-based configuration January where the dimensioning period with a heat demand of almost 36.9 MWh.

Fig. 5 shows the duration of the discharge for the Zeolite-units for scenarios 1-3. It shows how the units are alternating for the weekly and monthly configurations of scenario 1. *Annual*, but for 2. *Seasonal* there is only one

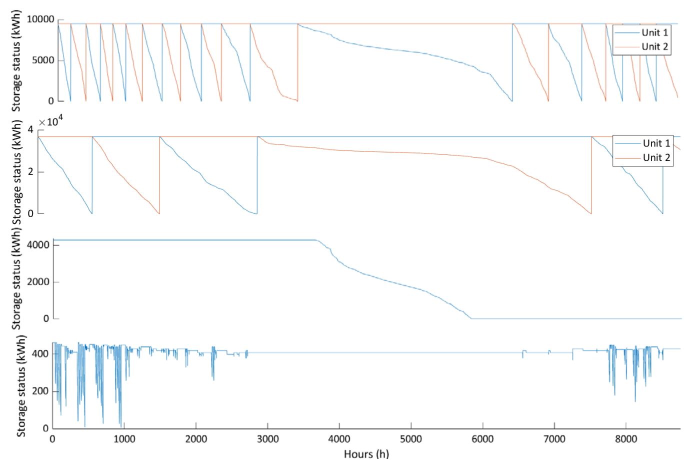

Fig. 5 Duration graphs over the Zeolite unit's discharge at end-user. The top two panels show the Annual scenarios alternating units per week and month respectively. The third and fourth panel show the scenarios Seasonal and Peak.

unit that discharges during the low-load period. This unit is assumed to be charged during the high-load period. For scenario 3. *Peak*, the storage is assumed to be charged when heat is available from the boiler.

4.3 Economics

The parameterised Zeolite cost is shown in Table 5 with the most promising outlook for scenario 3. *Peak.*

5. DISCUSSION

A possible "memory-effect" where the temperature used in the adsorption phase affects the level of starting condition of the Zeolite for the following desorption. When a discharge was performed with an airflow with the temperature of 40°C the following desorption showed reduced storage capacity. This could probably be explained by that the Zeolite require less energy to become fully charged when starting the desorption at a

Table 5 Estimated maximum costs for Zeolite relative payback time.

Scenario / t_{PB}		1. Annual month	1. Annual week	2. Seasonal	3. Peak
10 y	€/ton	67.8	508.3	-	1 060.5
20 y	€/ton	226.2	1 121.9	28.4	2 481.8

temperature above 30°C. A plateau is observed at around 30°C for T_5 during desorption, but when starting at 40°C this plateau is about halved, meaning that less energy and time is needed for the process. However, the experimental test results are not conclusive on this since it seems like the best charging capacity appeared when prior discharge used temperatures around 27 - 28°C.

The test rig used in the studies met the requirements of the initial study, but for further studies, the rig's construction with insulation and air leakage etc. could be improved. The EED for the tested Zeolite varies from 20.3 to 96.0 kWh/m^3 where the lowest EED occurs when the storage is charged with the lowest temperature. The highest EED occurs when the storage is charged with the highest temperature and discharged with high RH but low temperature. Differences in ED and EED between the experimental tests and literature (Table 1) could be explained by what range of outlet temperatures and RH that is considered.

The results show that Zeolite TCES can be used for the investigated building. The bulkiness for using Zeolite as an annual storage system, both for weekly or monthly storage sizes, might cause logistical and/or technical issues but the volumes of Zeolite for covering the seasonal (summer) case or to cover the peak demand is more manageable. The Peak scenario furthermore showed the most positive costs for Zeolite. From a resilience perspective, a Zeolite TCES could reduce supply disruptions together with the accumulator or act as a heat back-up in case of a major disturbance where the TCES can be used for a longer time. A TCES dimensioned for the summer season can deliver 4.3 MWh which during wintertime can be enough to supply the heat demand up to a week, especially if the indoor temperature is allowed to be lower than the set-point.

6. CONCLUSION

It is possible to use Zeolite TCES for all three scenarios investigated. For the annual scenario where both weekly and monthly supplies of charged Zeolite is investigated, the supply on weekly basis is 90.3 tons and on monthly basis 350.1 tons. Both scenarios are technically and logistically challenging. A Zeolite TCES to cover the summer season needs 41.2 tons of Zeolite with an estimated volume of 50-66 m^3 which is a more manageable volume. To cover the peak demands in the system, only 4.8 tons of Zeolite with an estimated volume of 5.9-7.7 m^3 is needed.

A Zeolite TCES designed as a trade-off between peak and seasonal supply is most economically promising. The Zeolite TCES can also act as a heat back-up in case of a major disturbance where a TCES dimensioned for the summer season can be enough to supply the heat demand up to a week during winter, and even longer if the indoor temperature is allowed to be reduced during that time.

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