

## Thermal storage systems brought into shape

Scientists are optimising zeolites for use in thermochemical storage systems



*Thermal storage systems that utilise zeolite as an environmentally friendly and cost-effective mineral are still very rare. However, they can store heat very compactly and almost without losses. In a research project, scientists have investigated aluminosilicates for their practical use in thermal storage systems. They have succeeded in significantly improving the energy density, cycle resistance and thermal performance. The research has led to the development of a thermochemical storage system for a CHP power plant.*

Zeolites are produced by the tonne as chemical mass products in different versions. They are modelled on natural minerals. All zeolites have a microporous structure, which enables them to be used for a wide range of applications. Most are used for softening water in washing detergents.

If you moisten zeolite-containing detergent in your hand, you will feel a slight warming. This is caused by adsorption heat being released – water attaches to the surface of the pores. This effect is utilised by zeolite heat storage systems: heat is released when moisture is added to dry zeolite. Conversely, the storage system can be charged by adding heat to drive off the water. This energy can be stored for as long as required. Losses only occur during the charging and discharging processes.

Although the operating principle appears simple, the task of building efficient and durable storage systems with zeolite is extremely complex. This is because zeolite exists in many different modified versions with different properties. In addition, its shaping determines the energy and power density as well as the cycle resistance. In order to develop an adsorption thermal storage system for a CHP plant, engineers from ERK Eckrohrkessel GmbH have been investigating different zeolites and optimising their extrusion in collaboration with Wildau Technical Universi-

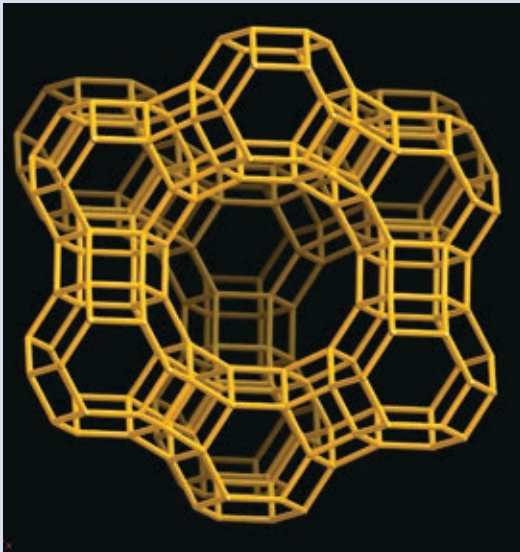
This research project is funded by the

Federal Ministry for Economic Affairs and Energy (BMWi)



## Zeolites

As crystalline aluminosilicates, zeolites form a micro-porous framework structure that has a larger internal surface area as a result of its pores and channels. It is possible for one gram of zeolite to have a 1,000 square-metre surface area. Of the 225 known zeolites with different framework structures, approximately a quarter are found in nature. The most important synthetic zeolites are called A, X, Y and ZMS-5. Each modification has a well-defined pore size. Zeolites can therefore be used for technological purposes as a molecular sieve to separate different sized molecules from one another. As ion exchangers or water softeners, zeolites exchange positively charged ions from the interior of the pores against others. With water softening, this binds the calcium ions. Van der Waals forces are decisive for their function as a thermal storage system. They ensure the adsorption of water on the surface. Accreted water molecules can be removed from the structure by heating or reducing pressure. Anhydrous zeolites are highly hydrophilic and react in a strongly exothermic manner even with the smallest amounts of water vapour.



**Fig.1** Model of the atomic structure for zeolite X. The large entrance window (centre) has a diameter of approx. 0.7 nm.

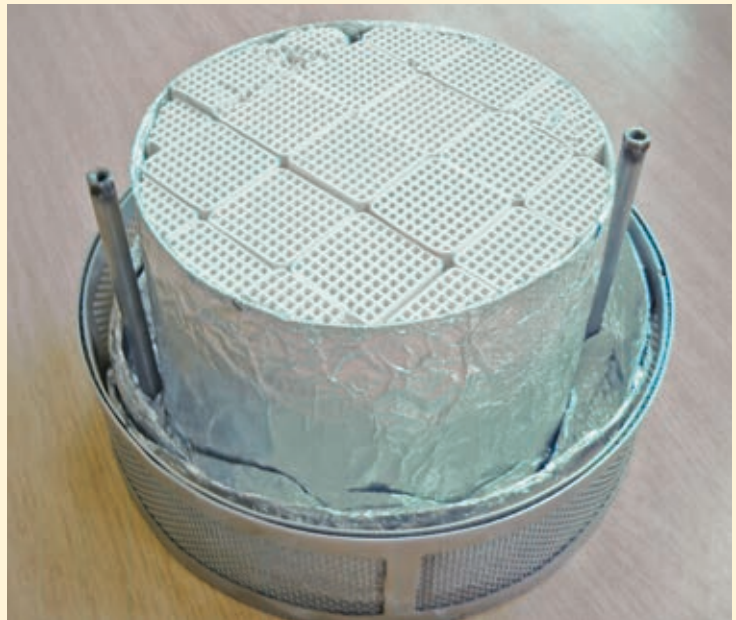
ty of Applied Sciences and other cooperation partners, including Chemiewerk Bad Köstritz GmbH.

### 100 per cent zeolite

Zeolites are extruded for use in thermal storage systems, i.e. shaped with a binding agent to form solid bodies, the extrudate. For example, commercial zeolite beads contain about 10 to 15 % clay. In order to increase their storage density, the researchers searched for a method for producing beads from pure zeolite without additives. They succeeded at Bad Köstritz for type A, X and Y zeolites. In a chemical process, the metakaolin binder was successfully synthesised into zeolite of the same type. The binder-free beads also had an improved pore structure. Through various investigation methods, the researchers



**Fig. 2** Zeolite beads without a binder have a greater active mass and surface area



**Fig. 3** A zeolite honeycomb structure made of zeolite A, fitted into the laboratory storage basket

were able to show that binder-free zeolites have larger macropores and no mesopores. This results in very good dynamic adsorption properties. In total, the adsorption capacity and thus the heat storage capacity improved relative to conventional, clay-bound beads by 15 to 20 %.

### Binder-free zeolites in different shapes

In addition to the energy density, the power density is an important parameter for thermal storage systems. The shape of the storage system determines how fast the heat can be absorbed and released. The scientists were not satisfied with the thermal output that they achieved with beds of zeolite beads. They therefore tried to coat heat exchanger tubes with zeolite. However, despite extensive experiments they were unable to create a well-bonded layer. Very successful were the attempts to produce complex forms from binder-free zeolite. In particular, a honeycomb structure made of 100 % zeolite can be regarded as a world first. In measurements, the honeycomb achieved a significantly better storage performance than bead beds, whereby a computer simulation provided an astonishing explanation: decisive for the better sto-





Fig. 4 Zeolite extrudates made of pure zeolite A in the form of macaroni

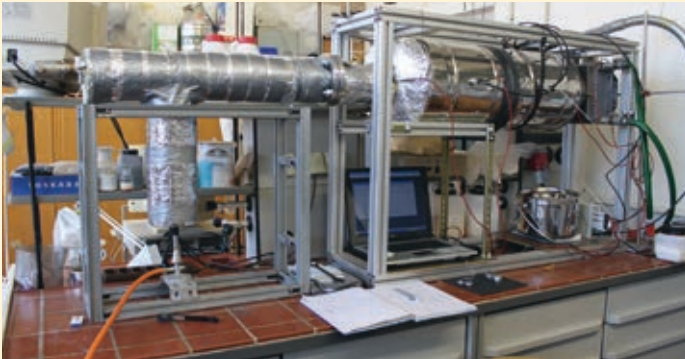


Fig. 5 The laboratory storage system can be filled with 1.5 kg of zeolite for desorption and adsorption measurements.



Fig. 6 An algae reactor utilises CO<sub>2</sub> and heat from the CHP exhaust gas.



Fig. 7 The two zeolite containers are alternately charged and discharged.

rage behaviour was not just the outer storage geometry – the more open pore architecture of the honeycomb wall relative to zeolite beads had an even greater effect. In further development steps, they also managed to produce and test binder-free extrudates, for example in the shape of macaroni, produced from the zeolites 13X and NaY. The high adsorption capacity of the extrudates for all three zeolite types confirmed that the binders had also been completely synthesised here.

### Using natural zeolites

Natural zeolites are much cheaper than synthetic ones. But are they just as efficient? To answer this question, the researchers studied natural minerals. The result was clear. The samples only absorbed about half as much water in direct comparison. The material is therefore only suitable to a limited extent for energy-based systems. The researchers can envisage, however, applications for the construction industry due to the low price. As aggregate in external render, natural zeolites can smooth out the temperature profile in buildings. When the sun shines the zeolite desorbs the moisture stored

in the render and dissipates heat. During the night, the zeolite reabsorbs the air moisture and warms up the render.

Similar concepts have already been implemented with paraffins as latent heat storage systems. Theoretically, however, the storage capacity of zeolite considerably exceeds that of paraffin. A further advantage is that zeolites do not increase the fire load in buildings. Whether the concept proves itself in practice must be shown by further tests.

### Condensing boiler technology with zeolites

Standard condensing boiler technology utilises the condensation heat from moist exhaust gas by condensing the moisture on a cooler heat exchanger. This method of gaining energy by means of dehumidification is also possible with zeolites. Three different zeolites were tested using a laboratory storage system. It was found that Y-zeolite is best suited for cooling or dehumidifying gases and, due to its extremely high temperature lift, A-zeolite removes a particularly large amount of heat from exhaust gases. X-zeolite achieves a high adsorption rate. It is therefore well suited for storage systems that are intended to achieve a high level of performance.

### A practical test

With a laboratory storage system filled with 1,500 cubic centimetres of zeolite, the researchers tested how moisture can be removed from flue gas and used to produce heat. Based on this experience, they integrated two adsorption storage systems with about 100 litres of storage material in the exhaust system of a small CHP plant. The two storage systems were filled with the innovative, binder-free molecular sieves 4ABF and 13XBF and successfully tested. The adsorptive properties from the laboratory experiments were also successfully reproduced. The CHP plant forms a virtually closed loop system with an algae cultivation system and a bio-refinery, whereby the algae reactor utilises both the heat from the cogeneration plant for temperature control as well as the carbon dioxide from the flue gas as a source of carbon for photosynthesis. The sunlight required in the test facility is simulated by high-performance diodes.

Whereas the CHP plant is used for generating electricity, the algae cultivation system is used to produce biomass. This is further processed in a bio-refinery to form high-grade products such as cosmetics, fatty acids or dyes. The cycle is closed with a biogas reactor. As part of an anaerobic digestion process, it uses the remaining biological residues from the treatment process to generate methane that is deployed as fuel for the CHP plant.

The two zeolite storage systems provide a twin benefit: primarily they dehydrate the flue gases from the CHP plant but they also provide additional heat for temperature controlling the biological process. For continuous operation, the zeolite containers are alternately charged and discharged. The system is currently being prepared for utilisation on an industrial scale.



## Sorption processes in research and practice

Until now, sorption technology utilising zeolites has only been available in a few commercial products. These include a dishwasher in which an integrated zeolite storage system temporarily stores heat from the heating process and supports the final drying process with heat and by dehumidifying the air.

With support from the German Federal Ministry for Economic Affairs and Energy, two German manufacturers have developed gas-operated zeolite heat pumps. In a cycle of adsorption and desorption, environmental heat is transformed to a usable temperature level. Both systems have now successfully established themselves in the market. Hamm's waste incineration services have tested a mobile zeolite storage system for industrial applications. Here, an articulated truck transports a roughly 8 metre-long steel cylinder with 12 tonnes of dry zeolite to an industrial user. This enables around 3 megawatt-hours of thermal energy to be transported with each trip.

Zeolites achieve storage densities of around 0.3 kWh/kg and operate at temperatures of 130 °C when discharging and 300 °C when charging. Silica gel adsorbent achieves comparable storage densities but at much lower operating temperatures of between 40 °C (discharging) and 100 °C (charging). In addition to adsorbents, absorbents are also used for technological purposes. For example, aqueous solutions of lithium chloride are good for air conditioning tasks. The concentrated solution can store heat or dehumidification capacities. The concept has been tested in a Munich Jazz club.

### Energy Storage Research Initiative

Storage technologies could become an important element of energy policy in the next few years. To ensure that they are available when required, the German Federal Ministry for Economic Affairs and Energy and the German Federal Ministry of Education and Research have launched the Energy Storage Research Initiative. In addition to electricity storage systems and Power-to-Gas technologies, thermal storage systems also form a research focus. The main applications include storage systems for conventional and solar thermal power plants as well as for electricity-led CHP plants, seasonal storage systems for buildings as well as storage systems that facilitate the management of heating networks. A special focus is on latent thermal and sorption storage systems. The [forschung-energiespeicher.info](http://forschung-energiespeicher.info) website documents the research initiative's research approaches and findings.

## Imprint

### Project organisation

Federal Ministry for Economic Affairs and Energy (BMWi)  
11019 Berlin  
Germany

Project Management Jülich  
Forschungszentrum Jülich GmbH  
Dr Hendrik Wust  
52425 Jülich  
Germany

### Project number

0327439B

### ISSN

0937-8367

### Publisher

FIZ Karlsruhe · Leibniz Institute  
for Information Infrastructure GmbH  
Hermann-von-Helmholtz-Platz 1  
76344 Eggenstein-Leopoldshafen  
Germany

### Author

Dr Franz Meyer

### Copyright

Cover image, Fig. 2 – 6: TH Wildau  
Fig. 1: Ch. Baerlocher and L.B. McCusker,  
Database of Zeolite Structures,  
[www.iza-structure.org/databases/](http://www.iza-structure.org/databases/)  
Fig. 7: Roberto Lisker, TH Wildau

Text and illustrations from this publication can only be used if permission has been granted by the BINE editorial team. We would be delighted to hear from you.

## Project participants

- » **Project management:** ERK Eckrohrkessel GmbH, Berlin, Prof. Dr-Ing. Udo Hellwig
- » **Project partners:** Wildau Technical University of Applied Sciences, Wildau, Dr Jochen Jänchen; ZeoSolar e. V., Berlin; La Mont-Kessel GmbH & Co. KG, Wildau, Germany

## Links and literature (in German)

- » Jänchen, J; Hellwig, U.: Entwicklung eines thermochemischen Wärmespeichers für den Einsatz in einem Blockheizkraftwerk. Schlussbericht. Förderkennzeichen 0327439B. ERK Eckrohrkessel GmbH, Berlin (Hrsg.). 2013. 90 S.
- » Hauer, A.; Hiebler, S.; Reuß, M.: Wärmespeicher. FIZ Karlsruhe GmbH. BINE Informationsdienst, Bonn (Hrsg.). Stuttgart: Fraunhofer IRB-Verl., 2013. 152 S., ISBN 978-3-8167-8366-4, 29,80 Euro (Print), 3,80 Euro (E-Book), BINE-Fachbuch

## More from BINE Information Service

- » Heating with gas adsorption heat pumps. BINE-Projektinfo brochure 03/2015
- » This Projektinfo brochure is available as an online document at [www.bine.info](http://www.bine.info) under Publications/Projektinfos.

BINE Information Service reports on energy research projects in its brochure series and newsletter. You can subscribe to these free of charge at [www.bine.info/abobo](http://www.bine.info/abobo)

## Contact · Info

Questions regarding this Projektinfo brochure? We will be pleased to help you:

**+49 228 92379-44**  
**[kontakt@bine.info](mailto:kontakt@bine.info)**

### BINE Information Service

Energy research for application  
A service from FIZ Karlsruhe

Kaiserstraße 185-197  
53113 Bonn, Germany  
[www.bine.info](http://www.bine.info)

Supported by:



Federal Ministry  
for Economic Affairs  
and Energy

on the basis of a decision  
by the German Bundestag