Extruded Water Adsorbent APO-Tric for Adsorption Thermal Battery Utilizing Solar Energy

Alenka Ristić[1], Urška Mlakar[2], Suzana Mal[1], Franz Hengel[3], Wim van Helden[3], Uroš Stritih[2], Nataša Zabukovec Logar[1,4]

[1] National Institute of Chemistry Slovenia, Ljubljana, Slovenia

[2] Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia

[3] AEE - Institute for Sustainable Technologies, Gleisdorf, Austria

[4] University of Nova Gorica, Nova Gorica

Abstract

An adsorption thermal battery utilizes the reversible adsorption and desorption of water on porous solids and is of particular interest in combination with solar thermal collectors. The efficiency of this technology depends on the performance of the adsorbents, which should have high water adsorption capacity and, consequently, a high energy storage density, stability under humid conditions, and fast kinetics of adsorption and desorption. New synthetic approaches and improved performance of the adsorbents and the systems are being studied to improve the energy storage performance. The microporous aluminophosphate APO-Tric adsorbent with chabazite structure was shaped into extrudes and granules on laboratory scale, showing higher water adsorption capacity of the extrudes in comparison to the granules. The APO-Tric extrudes were tested in 15 adsorption-desorption cycles between 40 °C and 90 °C at a water vapour pressure of 12.5 mbar and showed good hydrothermal stability under these conditions. Good mass balances between adsorbed and desorbed water were achieved in the sorption cycles. In all cycles, maximum temperatures from 53 to 57 °C were reached during adsorption.

Keywords: APO-Tric extrudes, water adsorption, hydrothermal stability, solar energy, thermal battery, test set up

1. Introduction

The adsorption thermal battery (*Zeng et al., 2023*) utilizes the reversible adsorption and desorption of water on porous solids and is of great interest as it represents an energy storage concept with great potential for the loss-free and long-term storage of thermal energy with high energy density, especially in combination with solar thermal collectors. It offers the possibility of reducing the consumption of fossil fuels for space heating in buildings and achieving net-zero scenarios.

The driving forces for the development of an efficient storage adsorbent with advanced properties are a high water adsorption capacity in the low relative pressure range, a low regeneration temperature of up to 100 °C, good adsorption kinetics and hydrothermal cycling stability under working conditions. New synthetic approaches, improved sorption properties of the adsorbents and the systems should be developed to improve the energy storage performance.

Thermally stable microporous adsorbents such as zeolites, aluminophosphates and metal-organic frameworks are often tested with water as the working fluid for thermal energy storage and/or transformation. (*Ristić,*

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2022) Zeolites are microporous crystalline alkali or alkali-earth aluminosilicates with a 3D framework containing channels and/or cavities with pore openings of 0.3 to 0.8 nm. One of the advantageous properties for thermal energy storage applications is the strong hydrophilicity of zeolites, expressed as a Type I water isotherm, that depends on the Si/Al molar ratio of the zeolite framework, the framework structure type, the type and distribution of exchangeable extra-framework cation, structural defects and the distribution of possible surface silanol groups. (*Ng, Mintova, 2008*) However, the high affinity for water at low partial pressure affects on the desorption temperature in the heat storage cycle, i.e. high desorption temperatures above 300 °C are the result of the strong interactions between the charged framework and water molecules. The most frequently investigated zeolites with a high Al content as thermal energy storage materials are the commercially available zeolites A, X and, more recently, Y. (*Ristić, 2022; Schmit et al., 2024*) Microporous aluminophosphates have shown their advantages over zeolites in terms of lower charging/desorption temperature, higher water adsorption capacity and higher adsorption enthalpy. (*Ristić, 2022*) They have a weaker hydrophilic (water isotherm Type I) or hydrophobic-hydrophilic (water isotherm Type V) character depending on the chemical composition, structure type, framework defects and synthesis approach. The commercially available aluminophasphates AQSOA FAM Z02 (SAPO-34), AQSOA FAM Z05 (APO-5) and AQSOA FAM Z01 (FAPO-5) from Mitsubishi Plastics Ltd. (*Kakiuchi et al., 2005*) are more expensive than above listed zeolites, because expensive organic structural directing agents are used for their production. Of the aluminophosphates, SAPO-34 is the most widely investigated adsorbent for use in the adsorption thermal batteries application, with various energy storage densities being determined as a function of the working conditions. Henninger determined an energy storage density of 177 Wh kg^{-1} at an adsorption temperature of 40 °C and a water vapour pressure of 5.6 kPa as well as a desorption temperature of 95 °C and a water vapour pressure of 1.2 kPa. (*Henninger et al., 2010*) A study by Brancato and Frazzica showed a lower energy storage density (94 Wh kg^{-1}) at a desorption temperature of 90 °C and a water vapor pressure of 1.2 kPa and an adsorption temperature of 35 °C and a water vapor pressure of 4.2 kPa (*Brancato, Frazzica, 2018*). In contrast, a higher energy storage density of 196 Wh kg^{-1} was achieved by Palomba et al. (*Palomba et al., 2017*) under conditions of adsorption temperature (35°C), evaporation temperature (10 °C), desorption temperature (91 °C) and condensation temperature (15 °C) in an open system. In addition to energy storage density, the determination of cycling stability under humid conditions is another important objective in the development of aluminophosphate adsorbents for their use in solar energy storage. Two SAPO-34 prepared by different synthesis routes were tested in short-term adsorption-desorption cycles by Henninger et al. (*Henninger et al., 2011*). The tests were performed directly in a thermogravimetric apparatus that could cycle the adsorbent material between 140°C and 20°C at a water vapour pressure of 5.6 kPa and 1.2 kPa for the desorption and adsorption conditions, respectively, to monitor the change in water adsorption capacity. Frazzica presented the experimental protocol for the long term cycling stability of adsorbents for thermal energy storage applications under realistic operating conditions. SAPO-34 was tested between 90°C and 40°C at a water vapour pressure of 7.3 kPa. (*Frazzica, Brancato, 2018*) in a designed test rig. Freni et al. proposed a protocol to test the hydrothermal stability of adsorbent coatings on heat exchanger, which was carried out in a system with saturated and dry air over samples that were continuously cooled and heated to simulate typical cycles. The adsorption capacity was then checked in a thermogravimetric device to detect possible deterioration of the adsorption capacity. (*Freni et al, 2013*)

The water adsorbent APO-Tric has the same chabazite structure as SAPO-34, containing 3-dimensional interconnected pore system with pore openings of 0.38 nm and large ellipsoidal cavities of 0.84 nm. (*Baerlocher et al., 2007*) The adsorbent was developed by (*Ristić et al., 2012)*. It was found that a driving force for the water adsorption process (S-shaped water adsorption isotherm) was formation of highly ordered water clusters in the micropores, which was enabled by an optimal micropore diameter and, rapid and reversible changes in Al coordination associated with synthesis in a fluoride medium. The dehydration of this material is a very complex process and practically all the water can be desorbed at 95 °C, which is another important characteristic for its utilization. Recent calculations of the dynamics of the system by mimicking an in-house solar heat storage system, revealed a complex sorption/desorption dynamics. (*Krajnc et al., 2017*) One consequence of the sudden water uptake in a narrow pressure range was the immediate release of heat. The APO-Tric adsorbent (powder) can store 320 Wh kg^{-1} at working conditions of the adsorption temperature of 30 °C and desorption temperature of 100 °C at a water vapour pressure of 12.5 mbar, which is significantly

higher than the reported stored energy densities for SAPO-34s. The APO-Tric adsorbent is considered an expensive adsorbent when piperidine is used in its synthesis. However, a green synthesis using a low-cost ionic liquid was recently developed (*Mal et al., 2021*), which resulted in the preparation of APO-Tric powder with a more hydrophilic character and an improved water adsorption capacity of 5 %. The reuse of the spent ionic liquid was also confirmed, contributing to the reduction of toxicity and production costs of aluminophosphate synthesis. The powdered form in which these aluminophosphates are produced is not advantageous, as the thermal energy storage systems require compacted and shaped adsorbents, such as bodies a few millimetres in size, due to process requirements such as mechanical stability and mass transport. The powder material limits the separation of powder and gas phase, the permeability of the material and the handling in general and leads to clogging of the valves in the systems. Therefore, thermochemical adsorbent powders must be shaped for the utilization in the systems.

We present here a study on the influence of a shaping process on the water sorption properties of the adsorbent APO-Tric developed for a low temperature solar energy storage application. To this end, the hydrothermal cycling stability in the gravimetric adsorption analyzer and the mass transport in the laboratory test rig were investigated for the first time.

2. Materials and methods

The extruded APO-Tric, which was produced using a Caleva Multi Lab extruder (Dorset, UK) at the National Institute of Chemistry in Slovenia, was analysed by X-ray powder diffraction using the PANalytical X'Pert PRO diffractometer (Malvern Panalytical, Almelo, Netherlands) and nitrogen physisorption using Autosorb iQ3 (Quantachrome Instruments, Boynton Beach, FL, USA) to determine the structural properties. The isotherms of water adsorption at 25 °C and the adsorption/desorption cycles were determined using the automatic gravimetric water sorption analyser IGAsorp-XT (accuracy ± 0.1 µg) (Hiden Isochema Ltd., Warrington, UK). Hydrothermal stability (short term) of the small amount of the APO-Tric material (1 g) was determined by the same analyser using the modified sequential method (*Ocvirk et al., 2021; Frazzica, Brancato, 2018*), in which water uptake was measured at 40 °C under humid nitrogen gas flow (80 % relative humidity) and then dried at 90 °C with dry nitrogen flow.

The heat storage performance of a larger quantity of the adsorbent (150 g) was tested in a dedicated laboratory test rig at AEE INTEC in Austria. The test rig is placed in a vacuum vessel and can be divided in two main parts: the evaporator/condenser unit and the material block unit. The cooling system for heat sinks of both units is situated outside the vacuum vessel. Figure 1 shows a schematic representation of the setup, where the blue line represents a cooling fluid. The material block is a coated aluminum block with ribs, in between which the adsorption material is placed. Multiple adsorption-desorption cycles can be performed under vacuum conditions. The masses of the water reservoir and the material block are monitored during the process in order to check the mass balance. To sufficiently monitor adsorption-desorption cycles, temperature and pressure sensors together with mass balances were used.

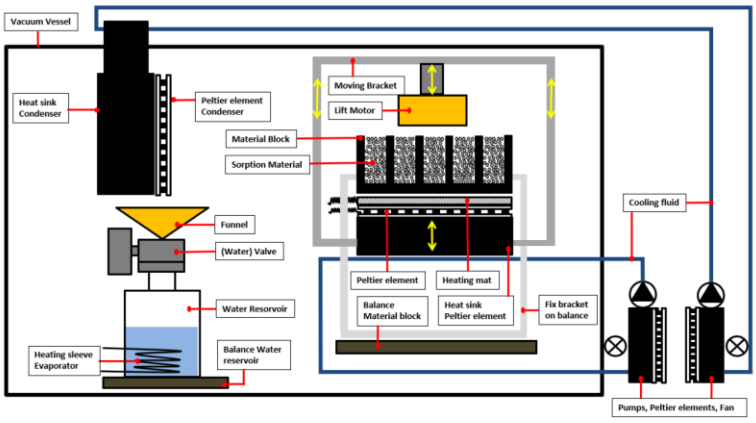

Figure 1: Schematic representation of the material test set up at AEE INTEC

3. Results

A new synthesis approach using cheap and recyclable reactants (*Mal et al., 2021*) has significantly reduced the production cost of the shaped aluminophosphate adsorbent. Figure 2 shows a comparison of the water adsorption isotherms of APO-Tric granules (spheres) and extrudes (cylinders), which illustrates the influence of the shaping process on the water uptake of the adsorbent.

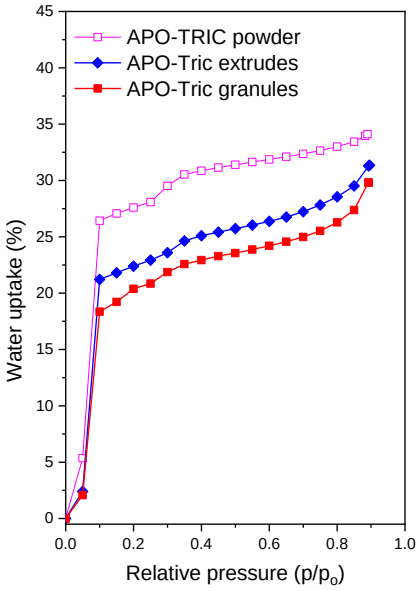

Figure 2: Water adsorption isotherms at 25 °C of shaped APO-Tric and powdered APO-Tric adsorbents

Figure 3 presents good cycling stability of the APO-Tric extrudes and a water loading lift as the difference between the amount of adsorbed water at 40 ºC and desorber water at 90 ºC at a water vapor pressure of 12.5 mbar. The small decrease (3%) in water uptake was observed after 15 adsorption/desorption cycles, which is consistent with the powdered sample. (*Ristić et al., 2012)*

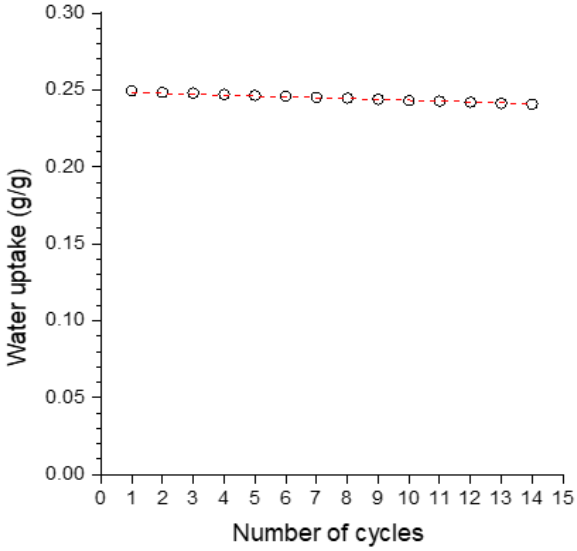

Figure 3: Cycling stability of APO-Tric extrudes of 15 cycles of adsorption and desorption between 40 °C and 90 °C at 12.5 mbar

The APO-Tric extrudes were used for the first time in experiments on a dedicated laboratory test rig. As these were the first experiments with the extrudes, extensive adsorption-desorption cycles were carried out to better understand both the processes with the new material and the interaction of the material in the system. Different conditions were used to find the optimal conditions. For example, the adsorption time was set at 10

hours. When the adsorption cycle started, the valve of the evaporator was opened and water vapour was adsorbed by the APO-Tric material, the temperature of the material initially increased and reached a maximum temperature of 53 °C, while it decreased to 31 °C at the end of the process. During adsorption, the mass of the evaporator decreased by 22.3 g and the mass of the adsorber increased by 22.8 g. With a difference of only 0.5 g, it can be concluded that the balance of masses in the adsorption cycle is very good. During adsorption, it was possible to achieve a temperature lift of 29 °C, starting from 24 °C, the temperature of the material at the beginning of adsorption, up to a maximum temperature of 53 °C, which was reached after 8 minutes. It was observed that the mass of the adsorber reached a maximum after 3 hours and 28 minutes. More detailed results obtained during adsorption are shown in Table 1. They show the time of the start and end of the adsorption cycle, the mass of the evaporator, the mass of the adsorber, the pressure change in the vacuum vessel, the temperature of the material and the temperature lift

Tab 1: Detailed results during the adsorption process

Time [h:min]	m_Evaporator [g]	m_Adsorber [g]	p_Vacuum [mbar]	T_APO-Tric [°C]	T_lift [°C]
15:59	1287	1508.8	3.46	24	29
03:11	1264.7	1531.6	27.21	53	
	-22.3	**22.8**			

Figure 4 shows one of the adsorption processes carried out at 15 °C and a pressure from 3.46 mbar.

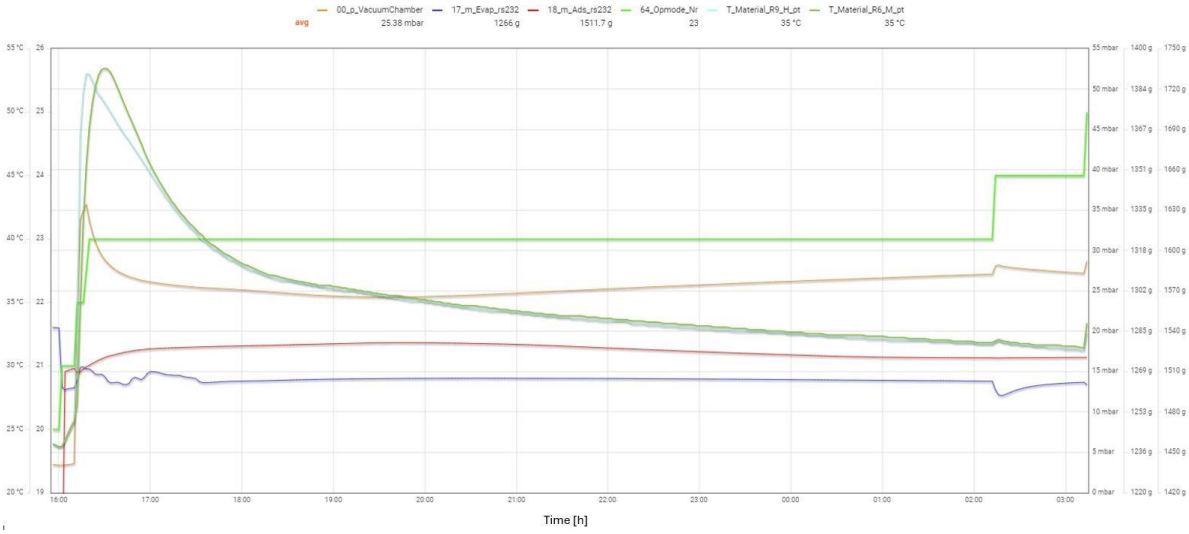

Figure 4: Monitoring of the adsorption at 15 °C and pressure starting at 3.46 mbar

When the adsorption was complete, the valve on the evaporator was closed and after 1 hour a desorption process began with the heating of the material to 100 °C. The water vapour desorbed from the material condensed on the surface of the condenser and collected in the water reservoir. The desorption process lasted 1 hour and 3 minutes. During this time, the temperature of the material changed from 31 °C to 105 °C and also reached the maximum temperature of 116.5 °C at the end of desorption. During desorption, 25.5 g of water was desorbed from the material, while 14.8 g of water was stored in the water reservoir. There is a difference in the mass balance between the adsorber and the water reservoir because the remaining water that condensed during desorption was still dripping into the funnel even though the valve was already closed (this can be seen in Figure 5 as a jump in the curve showing the mass of the evaporator at the end of desorption). Further results obtained during desorption can be found in Table 2.

Tab 2: Results during desorption temperature of 100 °C

Time [h:min]	m_Evaporator [g]	m_Adsorber [g]	p_Vacuum [mbar]	T_Material [°C]	T_lift [°C]
3:11	1264.7	1531.6	27.21	31	84
4:14	1279.5	1506.1	30.82	105	
	14.8	**-25.5**			

The monitoring of the desorption process is shown in Figure 5.

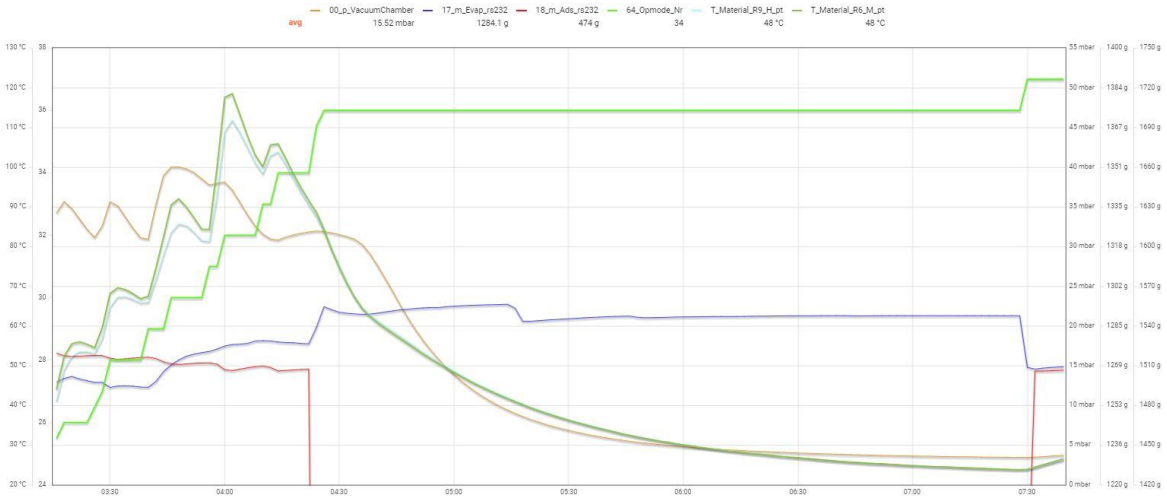

Figure 5: Monitoring of desorption at 100 °C and pressure starting at 27.21 mbar

The highest value of water uptake achieved during adsorption was 27.2 g, and 27.6 g of water vapour was desorbed during the associated desorption. This was achieved at an adsorption temperature of 15 °C and a pressure range of 3.36 mbar to 32.13 mbar. At the desorption temperature of 100 °C, a maximum pressure of 54.94 mbar was reached, which fell to 39.20 mbar by the end of desorption.

4. Conclusions

In order to develop and optimize TCMs and storage systems, a multi-level approach is required, ranging from the material level to the component and system level. When a new material is introduced into an existing pilot plant or system, extensive adsorption-desorption testing is required to determine the interaction between the material and the system.

In this work, newly developed extrudes of APO-Tric were investigated and tested in a 150-gramme laboratory test rig to demonstrate the potential of water adsorption for low-temperature heat storage applications. Due to the hydrophobic inorganic binder in the extrudates, the shaped materials were found to have lower water uptake than the powdered material. After 15 cycles with a small amount of the material (1 g), a 3% decrease in water uptake was observed, which is consistent with a decrease in specific surface area. The mass balance during adsorption was in good agreement in most tests, while larger mass differences were observed during desorption. Therefore, further analyses need to be carried out to determine the cause of the discrepancies in mass balance in some of the adsorption-desorption cycles.

5. Acknowledgments

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