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Proposition of a new concept and characterization of a novel Polydimethylsiloxane-AQSOA Z05 water-sorption composite material for cold thermal energy storage in thermodynamic power plants

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Abstract

In arid regions, dry solutions, including dry thermal energy storage to postpone the evacuation of heat, can be of interest to reduce the water footprint of condenser cooling in thermodynamic power plants like CSP. However, energy efficiency is limited using sensible heat storage for cool air production. In this paper, we propose a new concept of dry cooling solution based on thermal energy storage, based on the coating of a material to take the advantage of both, sensible and sorption heat storage. A novel Polydimethylsiloxane-AQSOA Z05-based composite for coupled heat and moisture storage is proposed, and its behavior and performance are assessed via water vapor adsorption and desorption investigations. The thermodynamic and kinetic data of pure AQSOA Z05 and of the novel composite material (referred to here as SyZ05-47.6) were experimentally measured for temperatures ranging from 20 °C to 60 °C and water vapor pressures up to 160 mbar. The composite material maintains the same behavior at equilibrium as the pure material (i.e., shape of isotherms, maximum uptake and sorption enthalpy) but shows a different kinetic behavior associated with considerably lower adsorption-desorption velocities after the first phase related to the instantaneous sorption stage (or external surface sorption). The sorption enthalpies of the pure and composite materials were assessed by the integration of calorimetric

signals during the adsorption reactions and reached 1 to 1.4 times the enthalpy of vaporization of water at 25°C and atmospheric pressure. The results show that, in operating conditions, the SyZ05-47 coating allows to double the storage capacity of the sensible cold thermal energy storage, enabling its development for future applications.

Keywords

Thermochemical energy storage; Adsorbent coating; Water adsorption/desorption; Sorption isotherms; Sorption kinetics; Sorption enthalpy.

1. Introduction

Wet cooling towers (Figure 2 (a)) are the most efficient choice for condenser cooling in thermodynamic power plants, like CSP, but these are no longer viable solutions in water-scarce regions due to their high water consumption: up to 4 m³/kWh, which may represent 90 to 95% of the water consumed by a power plant [1].

The U.S. government financed a program aiming at maintaining the efficiency of their electric power generation, which otherwise could suffer due to regional water shortages: Advanced Research In Dry cooling (ARID) [2]. The European Commission is also financing projects on the same issue like, for instance, the Water Saving for Solar Concentrated Power Horizon 2020 project [3], [4] and Solving Water Issues for CSP Plants. Horizon 2020 project [5], [6]. Some of the technologies considered to overcome the water scarcity issue in desert locations can be cited:

- Replacing water by a cooling fluid not evaporating in the cooling tower: the tests carried in [7] show that such system is not cost efficient as cooling effect is limited and leakages are too important.
- Using night cold air and dedicated thermal storage system: during night, the temperature is colder than during the day. [8] used a cold and hot water storage tank to store available cold temperature and use it during the hot temperatures time. The system is presented in

Figure 1. The results of these study show that the system is energy-efficiency if the day–night temperature differences is at least 20 °C, which is not realistic most of the time.

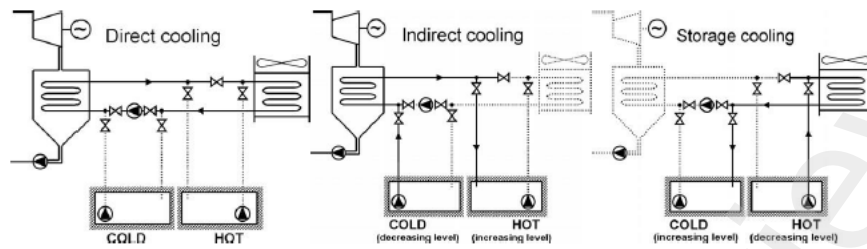
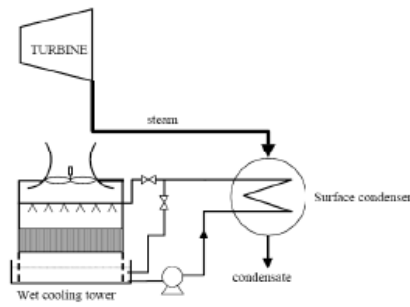


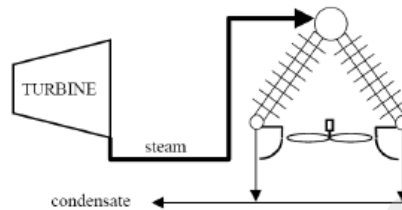
Figure 1: General scheme of the dry-cooling system, where a cold water and a hot water storage tank, are represented – extracted from [8]

- Using radiative cooling: the sky infrared radiative equivalent temperature is always lower than the air temperature. In [9], a simple supercritical carbon dioxide cycle operating at hot source temperature equal 550 °C is studied and the results show a net output of the cycle improved by 5.0 %. Moreover, such daytime radiative cooling requires very specific radiative properties at the absorber. In [10], convection and radiation are used during the night to produce cold water stored in a tank. However, the large water tank volume can be an issue in arid-climate zones.

The use of dry-cooled systems (Figure 2 (b)) can reduce water consumption by up to 80% - 100% [11], but the efficiency of the turbine decreases significantly if the temperature of the ambient air exceeds 15°C [12]. This leads to additional investment and increases the final electricity cost. In this regard, global interest is being directed toward new cooling technologies for reducing the need for water withdrawal and consumption in thermal-based power plants [13], [14] and [15]. It is worth mentioning that this solution also needs less maintenance [16]. From a system point of view, dry cooling tower can be an interesting solution in other systems like, for instance, oil refineries [17].



(a) Schematic Diagram of Wet Heat Rejection System



(b) Schematic Diagram of Dry Heat Rejection System

Figure 2: Wet vs. Dry cooled condenser – extracted from [18]

In the past decade, works on the principle of cTES (for cold thermal energy storage) systems can be considered as a specific realization of previous alternative technology and have shown the potential to enhance air-cooled system performance by storing all or part of the power block heat during the day and evacuating it during the night, when ambient temperatures are colder.

From a scientific literature point of view, Manglik and Jog [19] designed a highly compact thermal energy storage dedicated to dry cooling of thermoelectric power plants. Moser et al. [20] numerically studied the impact of dry cooling systems on technical and economic CSP plant performances. Their results show that even if the investment cost is higher for dry cooling solutions, the optimized overall electricity production with such solution can be of interest. In [21], the numerical modeling lead to the conclusions that high water savings could be obtained by the implementation of dry cooling systems at power plants, and is an economic and technical feasible option in arid regions. Sadafi and al. [22] numerically studied a mixed solution based on dry cooling and water spray to combine the advantages of each solution. A natural draft dry

cooling system was proposed and numerically optimized in [23]. The results from [24] show that such system can increase the thermal efficiency of a 250 MW plant by more than 0.5 %.

More recently, in 2021, Rougé et al. [25] proposed and experimentally characterized an improvement of the cTES concept based on the coupled storage of heat and moisture from ambient air (see Figure 3). The global system consists of a dual-media thermocline tank using humid air as heat transfer fluid and filled with a mixture of glass spheres¹ acting as sensible heat storage material and regular density silica gel grains acting as moisture storage material. The basic principle is to cool the dry atmospheric air during the hottest hours of the day by the cumulative effects of convection and desorption; then, the module is regenerated during the night when sorption occurs, and heat is released (sensible and physisorption). It is worth mentioning that a detailed analysis of atmospheric conditions in different arid regions carried in [25] led to the following operating conditions for the storage system:

- Adsorption / heat release: ambient temperature $< 55^{\circ}\text{C}$ with relative humidity $< 50\%$.
- Desorption / heat storage: ambient temperature $> 30^{\circ}\text{C}$; with relative humidity $> 10\%$.
- Storage duration less than 12 hours.

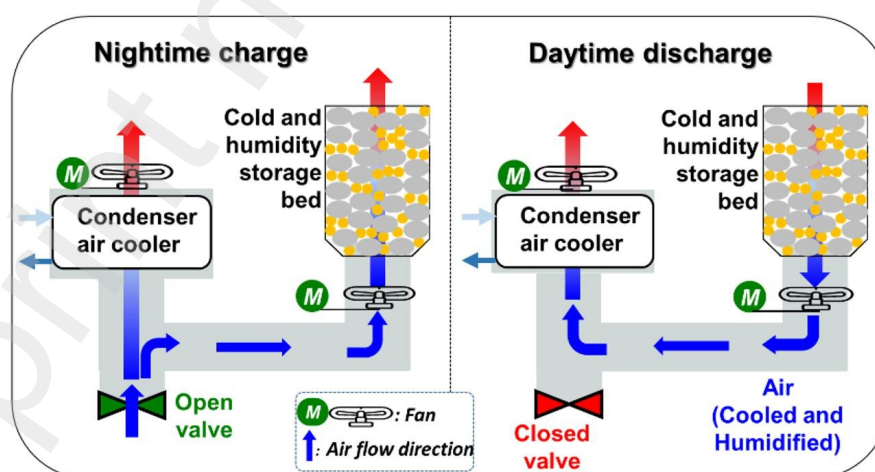


Figure 3: Integration of the storage module in the power plant scheme extracted from [25]

¹ The glass spheres are used as a reference material. In real system, lower price materials will be used.

The experimental tests presented in [25] have proven that coupling sensible heat storage with water adsorption-desorption can be effective for flattening the air temperature variations near night temperatures and optimizing air-cooled systems. However, high pressure drops inside the storage reactor were reported, which were by the different sizes of the filling materials and mostly by degradation of the sorbent during the experiments. In addition, the maximum cooling capacity was never achieved during the experiments since the sorbent never desorbed all the moisture stored during the first cycle. The regular density silica gel is susceptible to have this behavior because of its type I equilibrium isotherm (according to BET theory [26]) with a linear increase between 0% and 90% of the RH [27], [28], which means that complete desorption can only be obtained at 0% RH. Since typical atmospheric conditions during the day/night in some targeted semiarid regions, never reached the extreme 0% RH state, the sorbent was never completely discharged, and part of its sorption energy remained inactive. Consequently, the energy density of the reactor decreased after the first adsorption.

In this paper, we propose a new concept to take advantage of both, sensible and sorption heat storage. The idea is to replace the commercial regular density silica gel used as the moisture storage material with a coated version of an AQSOA Z05 zeolite on the previously mentioned glass spheres. To the authors knowledge, this coating option has never been studied before.

Figure 4 shows the thermodynamic equilibrium data found in the literature [27] for both AQSOA Z05 and regular density silica gel. The AQSOA Z05 shows an S-shaped equilibrium curve (type V according to BET theory [26]), which indicates a behavior corresponding to three phases [27], [29], [30]:

- I. Hydrophobic behavior at low vapor pressure conditions (approximately 20-35% RH depending on the temperature).

- II. A sharp increase in the water uptake occurs when the vapor pressure is higher than the hydrophobic limit (until approximately 25-40% RH depending on the temperature), where the maximum uptake is almost attained.
- III. There was a slight increase in water uptake (approximately 5-10% of the total) at higher vapor pressures (>40% RH).

Therefore, AQSOA Z05 may present higher charge–discharge proportions under the studied operation conditions than regular density silica gel. In addition, the application of a sorbent coating on the glass spheres may considerably reduce the pressure drops inside the storage module not only because it allows the use of a simple granulometry reactor instead of the double granulometry used in [25] but also because it may increase the mechanical stability of the sorbent and avoid its degradation during cycling, which is the main factor responsible for the high pressure drop problems reported in [25].

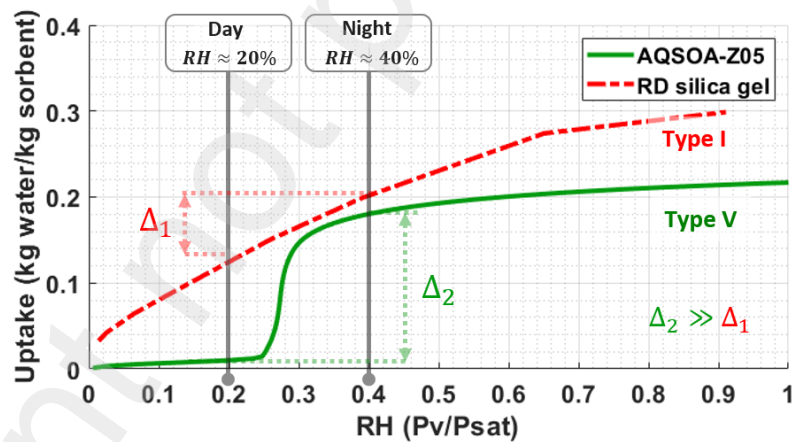


Figure 4: Isothermal sorption data of AQSOA-Z05 and regular density (RD) silica gel at 40 °C extracted from [27]

In this article, a procedure to produce a zeolite-based coating for coupled heat and moisture storage applications is proposed, and its behavior and performance are assessed by means of

water vapor adsorption and desorption investigations. This procedure allows the production of a thin adsorbent membrane that can be used to coat sensible heat storage materials (such as the glass spheres used in [25]) and obtain a unique material that couples both sorption and sensible heat storage properties. The proposed material is composed of a polydimethylsiloxane (PDMS) silicon structure filled with AQSOA Z05 zeolite. The principal criteria for the choice of PDMS as the silicon structure for binding the AQSOA Z05 powder to the surface of glass spheres include glass adherence, low cost of the synthesis process, low weight, large contact surface area, high vapor diffusion permeability and good hydrothermal and mechanical stability under operational conditions. Zeolite-filled PDMS has been investigated in the literature, mainly as a gas separation membrane [31], [32], [33], [34], [35], [36], [37], [38] and these sorbents have shown significant interactions with silicon structures. The results highlight that due to their high surface area, PDMS silicones can obtain a large amount of zeolite coating per unit volume, and the polymer structure also acts as a preferential pathway for vapor diffusion. Although the fabrication procedures and the compositions of these zeolite-filled PDMS materials are well discussed in the literature [31], [32], [33], [34], [35], [37], [36], [38] there is a lack of data on the influence of the silicon structure on the sorption equilibrium (i.e., thermodynamic behavior) and the reaction kinetics. Moreover, no data were found on the AQSOA Z05-filled PDMS.

Therefore, the aim of this work is to characterize and quantify the behavior and performance of the new proposed material under operational conditions relevant to cTES applications. The thermodynamic and kinetic behaviors of both the pure AQSOA Z05 and its novel composite form (mixed with the PDMS structure) were measured over a wide range of temperatures (20 °C to 60 °C) and relative humidities (10-80 % RH) corresponding to operating conditions [25]. Finally, the enhancement of the coating is assessed in possible operating conditions of the cTES, proven the interest of this material.

2. Materials and methods

2.1. Synthesis of the composite material

The aluminophosphate AQSOA Z05 studied in this work was obtained from Mitsubishi Plastics in powder form with a $D_{90} = 5 \mu\text{m}$. The PDMS used, named Sylgard-184, was obtained from Dow Corning and needs to be prepared using a two-part resin/curing agent kit to obtain its final solid form. The preparation of the novel composite, referred to here as SyZ05-47.6, consisted of mixing the AQSOA Z05 powder (47.6 %wt) with the Sylgard-184 solution immediately after its two-part resin/curing agent kit was added. Several preliminary tests have proved these proportions of materials inside the composite to be optimal since the mixture becomes heterogeneous when the Z05 mass exceeds 47.6 %wt. Moreover, from a material inside reactor point of view, this composition and the developed protocol led to a complete coating and adherence to the spheres with the highest thickness of around 0.5 mm. Figure 5 shows the scheme for the fabrication of the samples. A 10:1 mass ratio of resin to curing agent was mixed with AQSOA-Z05 (step 1). The mixture is then ready for coating any substrate by dip coating (step 2) for the next 30 h, which is the time needed for the final crosslinking between the Sylgard-184 resin and curing agent kit at room temperature, i.e., the time needed to obtain its final reticulated form (step 3). For the experiments presented in this work, the fully cured samples were peeled off from their substrate and cut into strips 2-10 mg and 0.5 mm thick (step 4), which were previously determined to be the optimum sample sizes for the experimental devices [39], [40]. It is worth mentioning that this composite material has been patented by the authors [41].

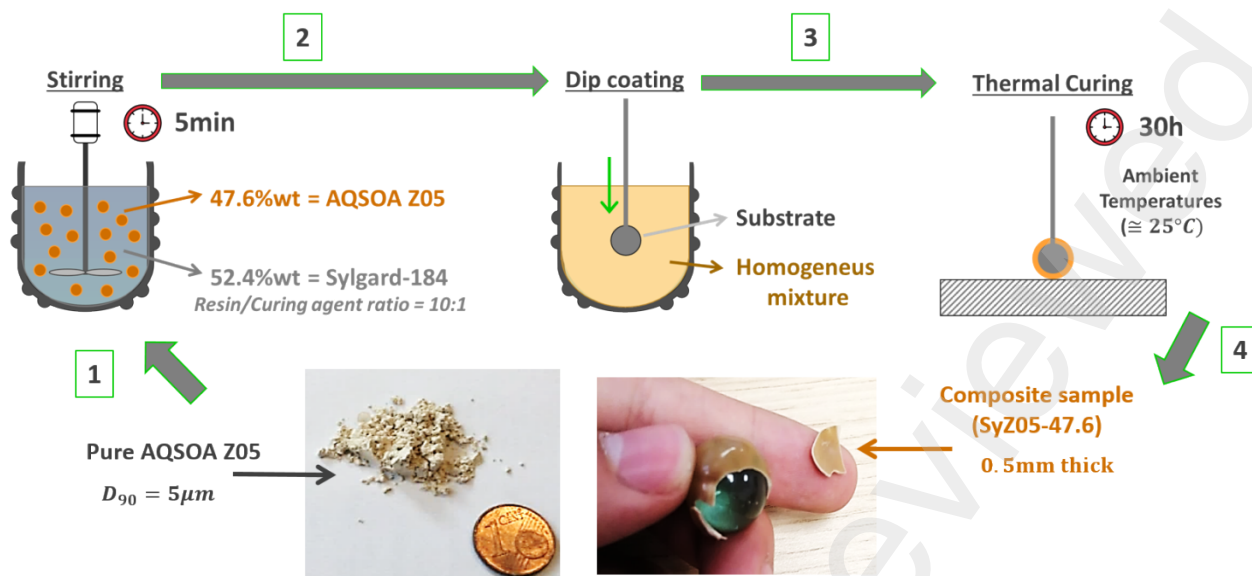


Figure 5: Scheme of the composite fabrication method

2.2. Sorption characterization

The pure AQSOA Z05 and the novel composite SyZ05-47.6 were characterized by means of water up, and down, -take and heat flux measurements over a wide range of temperatures (20 °C to 60 °C) and relative humidities (up to 80% RH), corresponding to the operating conditions relevant to the specific cTES application. Tests with the pure AQSOA Z05 were performed to compare its intrinsic sorption properties against literature data [27], [29], [30] and thus assess the validity of the devices and measurement methods used in the present study. Then, the same tests were repeated with SyZ05-47.6 to analyze the influence of Sylgard-184 and quantify the new properties of the composite.

2.2.1. Experimental setup

Two different devices were employed for the experiments. The first device is a symmetrical suspension-type thermobalance TGA-DSC Sensys Evo from Setaram Inc.. This apparatus enables simultaneous measurement of the mass variation and heat flow as a function of time. The related uncertainties are ± 1 °C for temperature, ± 0.1 % for calorimetry and ± 0.01 % for mass. The humidity of the inert gas was controlled using a Wetsys water-vapor generator from Setaram

Inc., with uncertainties of $\pm 0.01 \mu\text{g}$ for mass and $\pm 0.5 \%$ of reading for pressure. The second device is an automated multi-vapor gravimetric analyzer DVS from Surface Measurement Systems Ltd. with uncertainties of $\pm 0.1 \text{ }^\circ\text{C}$ for temperature and $\pm 0.3 \%$ RH for humidity. This apparatus also has a symmetrical suspension-type thermobalance for measurement of the mass variation as a function of time, but it does not provide heat flux measurements. Due to technical limitations and the limited range of vapor pressures, maximum 40 mbar, the ATG/DSC device was used for all the experimental data obtained below $30 \text{ }^\circ\text{C}$. Then, the DVS device was used to complete the experimental data at higher temperatures with the aim of verifying the influence of temperature and vapor pressure over a wider range of operation conditions, i.e. vapor pressure up to 140 mbar. The experiments were all performed under atmospheric pressure with dry nitrogen mixed with pure water vapor at a flow rate of $20\text{-}30 \text{ mL} \cdot \text{min}^{-1}$. The specified measurement accuracy for both devices is $\pm 1 \text{ }^\circ\text{C}$, $\pm 0.01 \%$, and $\pm 0.8 \%$ RH for the thermocouples, balance and water-vapor pressure, respectively.

The reproducibility of the tests and consistency of the measurements were verified by the repetition of several points with the pure Z05 samples at $25 \text{ }^\circ\text{C}$ with both experimental devices (TGA-DSC and DVS). The results of these tests are presented in Figure 6. Since the results show the same isotherm shape and the same maximum uptakes at equilibrium, the reproducibility is correct. This implies also that both experimental device results are consistent with each other.

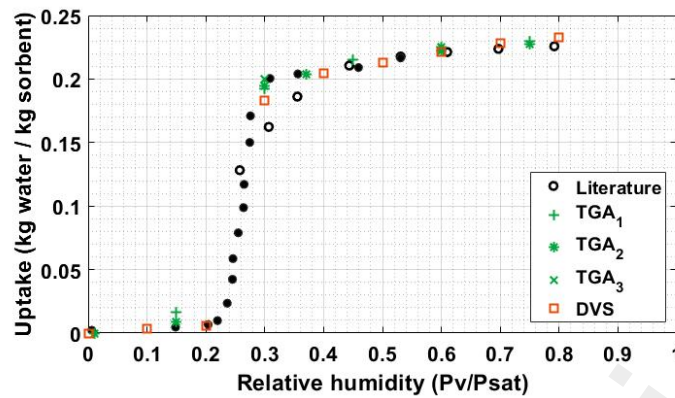


Figure 6: Sorption isotherms at 25 °C for Pure Z05 measured by TGA 3 times and DVS 1 time – literature data from [27]

2.2.2. Experimental conditions

Two types of experimental investigations are performed for each sample:

- I. **Isothermal sorption experiments**, i.e., determination of the equilibrium isotherms according to the temperature and relative humidity conditions.
- II. **Kinetics characterization**, i.e., quantification of the time needed to reach the equilibrium state and, by calculation, the isosteric heat of sorption (i.e. the reaction enthalpy). It is worth mentioning that the time needed to reach the equilibrium state is, of course, not strictly the reaction rate. However, this value is of interest for comparisons between different materials and different temperature and relative humidity conditions.

The operating parameter of the tests performed to date are summarized in Table 1.

Table 1: Summarize of the experimental protocols

Type test	Measure device	Operating cond.	Adsorption or Desorption
Isothermal sorption tests	TGA-DSC	20-25-30 °C	
		up to 70 %RH	Adsorption
		(Pv ≤ 30 mbar)	

	DVS	25-45-60 °C	
		up to 80 %RH (Pv ≤ 140 mbar)	Adsorption & Desorption.
Kinetic tests	TGA-DSC	20 °C	Adsorption
		50 %RH	
		25 °C	Adsorption
		25-50 %RH	
		30 °C	Adsorption
		30-40-65 %RH	
		45 °C	Desorption
		10-15 %RH	
		50 °C	Desorption
		15 %RH	

2.2.3. Kinetics evaluation

The kinetics of the adsorption and desorption reactions were analyzed by means of charge–discharge rate measurements with a TGA-DSC apparatus. In this protocol, all the experiments were performed under isothermal and isobaric conditions at a flow rate of 30 mL·min⁻¹ to measure the intrinsic sorption kinetics. The aim was to reach equilibrium from (-and to) extreme states, i.e., from completely charged to completely discharged and vice versa.

2.2.4. Energy storage density measurement

The thermal energy of the adsorption and desorption reactions can be experimentally calculated with a thermogravimetric analysis (TGA)-differential scanning calorimetry (DSC) apparatus,

which has a calorimetric sensor around crucibles that allows simultaneous measurement of the heat flow signal and mass variations. Therefore, the energy storage density linked to water sorption can be evaluated based on the heat flow measurements during kinetic experiments. First, the specific heat capacity (c_p) of the samples was measured by flowing dry nitrogen between 30°C and 100 °C at a heating rate of 1 °C/min. Then, the adsorption and desorption steps were measured at different temperatures and water vapor pressures (as indicated in Table 1). The small differences in heat flux and mass data due to reactor characteristics are used for correction before each test by performing a blank test with no sample in the crucible. The blank test allows the subtraction of unexpected measurements of mass variation and DSC that may occur during the thermal cycle with no sample due to uncontrolled events related to temperature evolution, such as buoyancy effects or small DSC signals due to heat flux imbalances between crucibles. The sorption enthalpy is thus calculated with the following equation:

$$H_s = (\Delta Q_{exp} - \Delta Q_{blank})/m_{H2O} \quad (1)$$

With H_s the sorption enthalpy [J/g_{water}], ΔQ_{exp} and ΔQ_{blank} the integration of the DSC signal during the sample characterization [J] and the blank test, respectively, and m_{H2O} the water uptake measurements [g].

3. Results and discussion

3.1. Adsorption and desorption equilibrium isotherms

This section is dedicated to the characterization of pure Z05 and SyZ05-47.6 under static conditions of temperature (isotherm). It should be noted that preliminary thermodynamic tests using the TGA-DSC device were realized with Sylgad-184 alone, and neither noticeable water vapor uptake nor heat flux variations were measured. This is consistent with the data from the literature which reported that PDMS silicon structures present very low water uptakes (approximately 0.07 %wt, [42], [43]), which are negligible in comparison with the reported

AQSOA Z05 water uptakes (approximately 23 %wt [27], [29], [30]). Those results highlight that the Sylgard-184 matrix does not participate in the uptake/reduction of water by the new composite material at this study scale (sample mass: 2-10 μg). However, it was necessary to assess this assumption for the novel composite developed in this article.

For comparison purposes between pure Z05, SyZ05-47.6 and data from literature, the up and down -takes are always calculated as the ratio of the mass of water adsorbed to the mass of dry AQSOA Z05 [$\text{kg}_{\text{H}_2\text{O}}/\text{kg}_{\text{dry,sorbent}}$]. Of course, in the application, those values must be regarded as the ratio of the mass of water adsorbed to the mass of composite SyZ05-47.6, i.e. [$\text{kg}_{\text{H}_2\text{O}}/\text{kg}_{\text{SyZ05-47.6}}$]. The relation linking those two units is straightforward.

Figure 7 shows the experimental data obtained for the adsorption of water vapor at 25 °C, 45 °C and 60 °C and for water vapor pressures up to 160 mbar. The experimental data of Goldsworthy [27], Teo et al. [29] and Shimooka et al. [30] are included here for comparison, and the dotted lines connecting our pure Z05 data were added for better visualization. As observed in Figure 7, both materials pure Z05 and SyZ05-47.6 present the same S-shaped equilibrium isotherm (type V, according to the BET theory [26]) and the same hydrophobic lengths, which increase to 20 % RH at low temperatures (25 °C) and then increase to 30% RH at higher temperatures (45 °C). When the vapor pressure is higher than this value, the water uptake increases sharply. The maximal water uptake is slightly reduced when the temperature increases. Moreover, the presented experimental data for pure Z05 shows good agreement with the literature for the isotherm shape, the hydrophobic length and for the maximum uptake. At 60 °C, our experimental data are between two different datasets found in the literature but seems to have better agreement with the data presented in the work of Goldsworthy [27] because of the isotherm shape at the end of the hydrophobic length. The behavior of SyZ05-47.6 also shows good agreement with the shape of the isotherm but with slightly reduced uptake at equilibrium (but higher than measurement accuracy). Those results highlight that Sylgard-184 does not interfere with the

sorption reactions within AQSOA-Z05 since the composite maintains the same shape of the equilibrium isotherm and nearly 95 % of the maximum uptakes of pure Z05 are found for AQSOA-Z05.

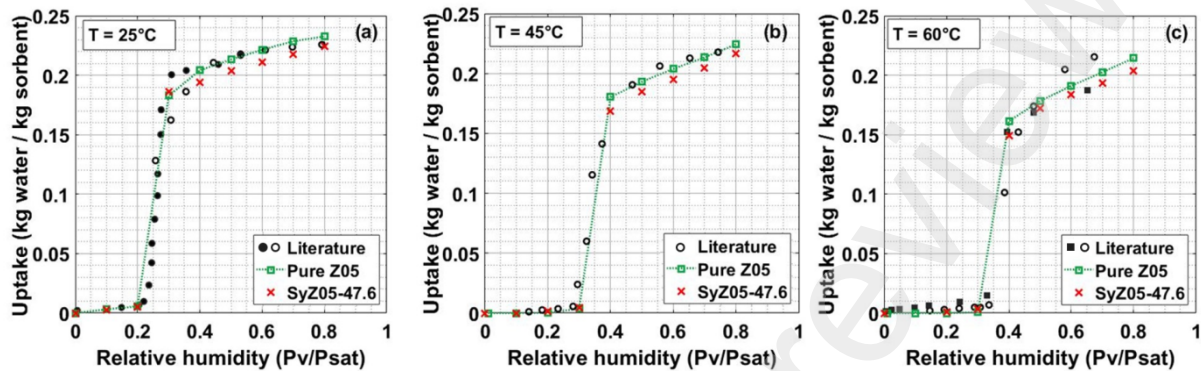


Figure 7: Equilibrium isotherms – Comparison of Pure Z05, SyZ05-47.6 and Literature at 25 °C (a), 45 °C (b) and 60 °C (c)

■: Goldsworthy [27]; ○: Teo et al. [29]; ●: Shimooka et al. [30]

Figure 8 shows the influence of possible hysteresis (hydration and dehydration) on the thermodynamic equilibrium of pure Z05 and SyZ05-47.6. Hence, the adsorption curve (blue) is obtained by the adsorption of water vapor on the anhydrous sample, and the desorption curve (red) is obtained by dehydration of the fully hydrated sample. The lines and dots connecting the isotherm data were added for better visualization. The normalized root mean square difference between adsorption and desorption were 3.3 % and 2.9 % for pure Z05 and SyZ05-47.6, respectively. This indicates a slight hysteresis behavior in the adsorption-desorption curve and is consistent with the results of [29], who studied the sorption equilibrium of pure AQSOA Z05-type zeolites and found that a hysteresis effect may exist but is not large because of the narrow distribution of relatively uniform pores. According to [29], this occurs because the desorption process is not complete, and some residual water remains trapped in the AQSOA Z05 powder. Since the hysteresis effects have minor effects on the isotherm shape and the uptake at equilibrium, they are not further investigated.

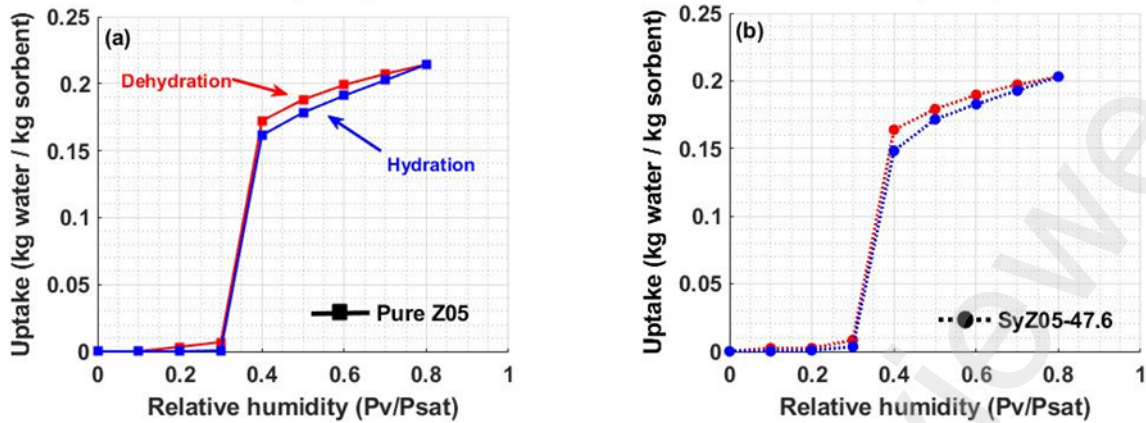


Figure 8: Adsorption and desorption isotherms at 60°C for a) pure Z05 and b) SyZ05-47.6

3.2. Modeling of the equilibrium isotherms

The modeling of equilibrium isotherms of the composite material is of utmost interest for the modeling of the whole storage system. The authors that present the experimental data on the water uptake of pure AQSOA Z05 under static conditions also proposed models for the adsorption isotherms according, of course, to the temperature and vapor pressure conditions. It should be noted here that there is no mention of potential hysteresis in their work, which is in agreement with the conclusions from Figure 8. Consequently, a single model is used to model the equilibrium isotherms for both adsorption and desorption.

Goldsworthy [27] used an equation based on the least squares method to determine spline fit coefficients of the thermodynamic behavior (equilibrium isotherms and sorption enthalpy) from experimental data obtained between 20 °C and 60 °C (over the range of $P_v \leq 140$ mbar). Teo et al. [29] selected 3 well-known theoretical models (the Langmuir, [44] and [45], Langmuir-Modified [46] and Dubinin-Astakhov [47], [48], [49] equations) and fitted some parameters related to the entropy of adsorption, the hydrophobic length and the slope of the isotherm curve to their experimental data.

Figure 9 shows a comparison between those models and some of the experimental data from the literature and from our study. The experimental data presented in [27] and [29] have similar

isothermal shapes, but the proposed models diverges under the studied conditions. The three models presented by Teo et al. [29] fail to reproduce the influence of temperature on the measured hydrophobic lengths. The Langmuir equation shows an effect of temperature, which is opposed to that observed in the experimental data, since this model predicts that the hydrophobic length decreases when the temperature increases. The models based on the modified Langmuir and Dubinin-Astakhov models show almost no influence of temperature, which is neither verified in our experiments nor in the literature, including the data used by the authors to develop and validate these models. The model developed by Goldsworthy [27] shows good agreement with our data on both the general shape and the influence of temperature on the hydrophobic length. Consequently, this model is then an appropriate choice to model the equilibrium behavior of our composite.

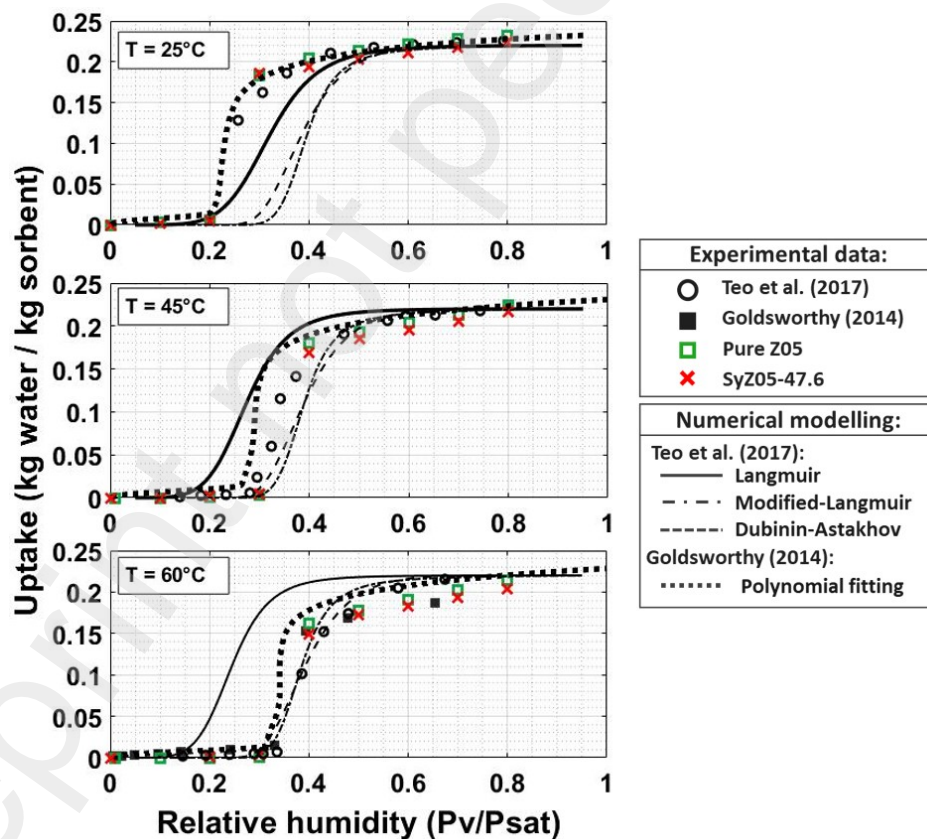


Figure 9: Comparison of equilibrium isotherm models and experimental data

■: Goldsworthy [27]; ○: Teo et al. [29]; □: Pure Z05; ×: SyZ05-47.6

3.3. Adsorption and desorption kinetics under operating conditions

This section is dedicated to the analysis of the adsorption and desorption rates. Figure 10 shows the mass variations as a function of time for a complete hydration–dehydration cycle at 19 mbar and different temperatures between the adsorption (25 °C) and desorption (50 °C) cycles. The mass uptake during the first 20 minutes was similar between pure Z05 and SyZ05-47.6. The same behavior is observed for desorption at 50 °C. These first minutes contribute to 30 % and 40 % of the water uptake and decrease, respectively. Later, the behaviors change, and the reaction rates are considerably reduced for the SyZ05-47.6 composite, which can take up to ten times more time to reach equilibrium than pure Z05 under the same experimental conditions. A comparison between the adsorption and desorption rates is not easy as the experiments were not performed under isothermal conditions, and both sorption and diffusion kinetics have been shown to be strongly influenced by temperature and relative humidity [42], [43], [50], [51], [52], [53], [54], [55].

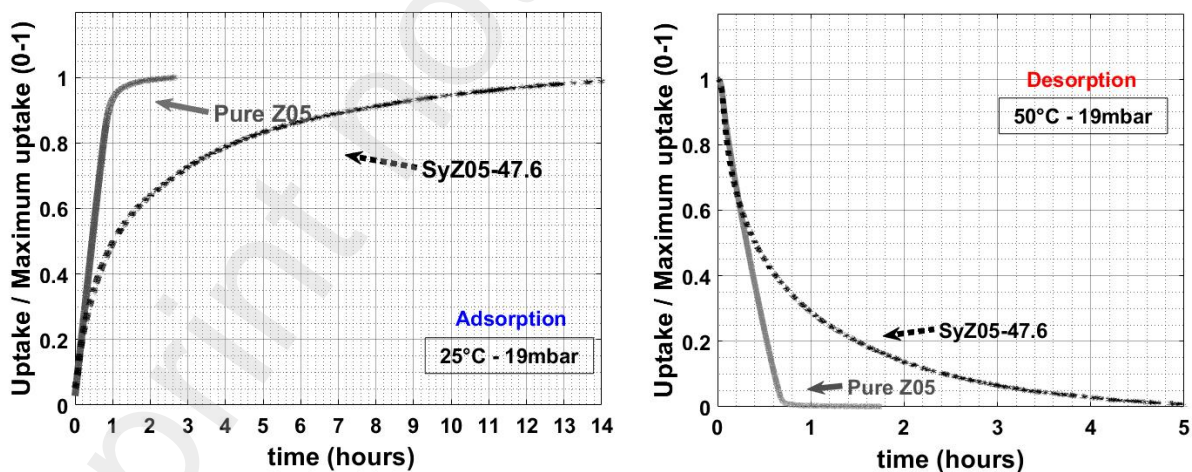


Figure 10: Kinetics of pure Z05 and SyZ05-47.6 during adsorption (left) and desorption (right)

Figure 11 shows the influence of temperature and relative humidity on water uptake during adsorption. These results indicate that the velocity of adsorption increases when the temperature and relative humidity. Under iso-RH conditions, both materials present a slight increase in adsorption velocity when the temperature increases (Figure 11-a). Under isotherm conditions, the velocity considerably increases when the relative humidity increases (Figure 11-b). Moreover, as was already observed in (Figure 10), both materials present the same slope in the first phase, which contributes to only 25 % of the total composite uptake, and then the composite adsorption velocity is considerably reduced until the maximum uptake is reached.

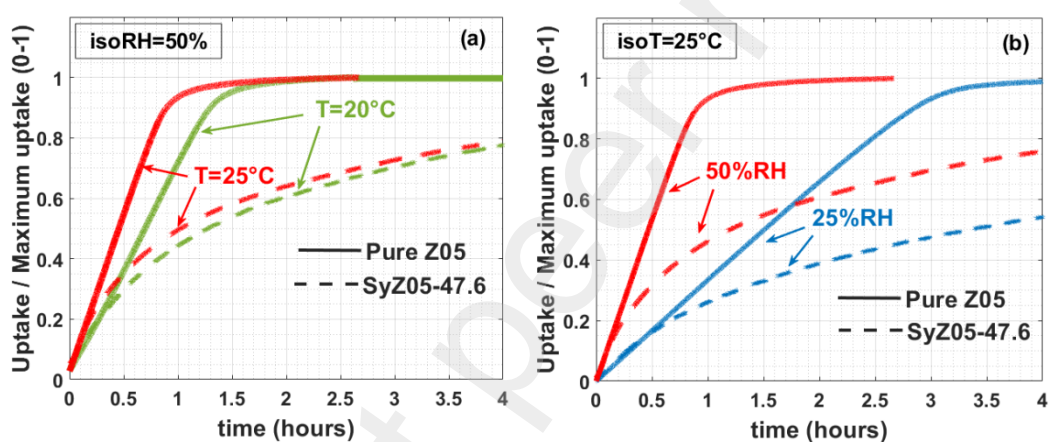


Figure 11: Influence of temperature and relative humidity on the adsorption kinetics.

Figure 12 shows the influence of temperature and relative humidity on water loss during desorption. These results indicate that the reaction velocities for desorption slightly increased when the temperature increased and the relative humidity decreased, even if these parameter variations were not large.

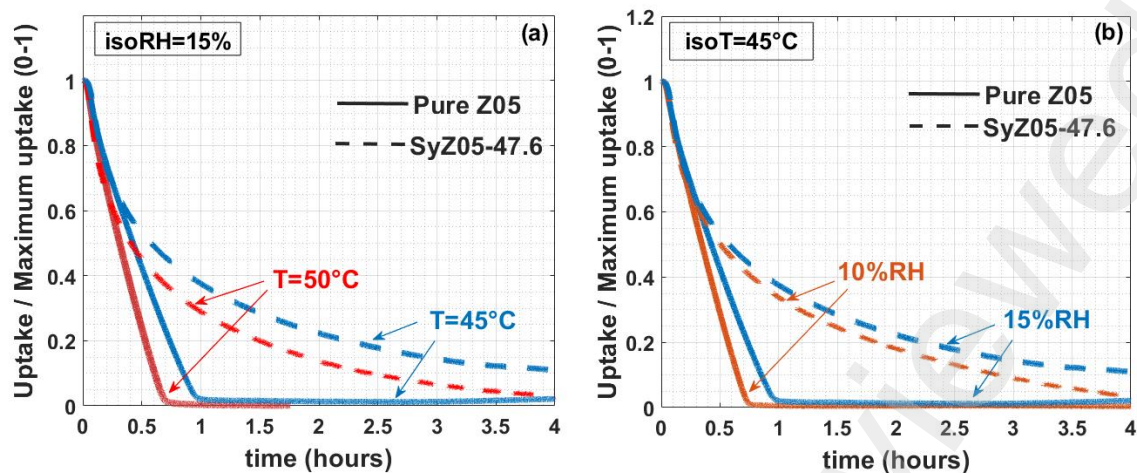


Figure 12: Influence of temperature and relative humidity on desorption kinetics

As observed for adsorption, the kinetic characterization results show that both materials present a similar slope for mass increase (-down) at the beginning of the reactions, but then the shape changes and the reaction velocities are considerably reduced for the SyZ05-47.6 composite. From phenomenological aspects, the first phase, where both materials show the same adsorption and desorption rates, can be related to the instantaneous sorption stage on available sorption sites and contributes to approximately 20 to 30 % of the total up(-down) takes for SyZ05-47.6. The second phase, in which SyZ05-47.6 takes up to ten times more time to reach equilibrium than pure Z05, can be related to the higher water diffusion resistance through Sylgard-184, which makes it more difficult for water molecules to reach the internal sorbent particles and be adsorbed (and desorbed). This is partially assessed by a previous study on PDMS diffusion and vapor permeation behavior [51] that showed a maximum vapor permeation of approximately $40 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 40°C . This means that a SyZ05-47.6 sample with a total mass of 4-5 mg and a thickness of 0.5 mm would have a maximum water flow rate passing through the silicon structure of approximately $0.2 \text{ mg}\cdot\text{h}^{-1}$, which is independent of the vapor flow rate inside the reactor. If the vapor permeation rate is assumed to be constant, the value proposed in [51] results in a minimum of 3 hours for completely charging the sorbent inside the silicon structure. This conclusion goes

on the direction of using the composite coating developed in this study as the desorption, i.e. cooling stage, lasts during at least 6 hours in a real system

3.4. Energy storage density

Measurement

Figure 13 (a and c) shows an example of the experimental data obtained at 20 °C and 50 % RH on the sorption enthalpy of both pure Z05 (a) and the SyZ05 composite (c). Figure 13 (b and d) shows the calculated sorption heat and enthalpy for both pure Z05 (b) and the SyZ05 composite (d). First, the sorption heat (black line in Figure 11 b-d) is calculated by integrating the calorimetric data obtained by the DSC device (red line in Figure 11 a-c). Then, the sorption enthalpy (red line in Figure 11 b-d) is calculated by dividing the sorption heat by the absolute quantity of adsorbed water (black line in Figure 11 a-c). These results reaffirm that diffusion resistance through Sylgard-184 deaccelerates the reactions and thus reduces the absolute sorption power. However, the total energy is maintained, and both materials present similar sorption enthalpies ranging from approximately 2800 J.g⁻¹ water for pure Z05 to approximately 3100 J.g⁻¹ for SyZ05-47.6. The limited discrepancy is attributed to the very long duration of test for the SyZ05-47.6 tests (up to ten times greater than that for pure Z05), which leads to the integration over time of the signal uncertainty of the measurement device. Moreover, one can also notice that the sorption enthalpy may be overrated at the beginning of the experiments for both materials because the mass variations are very small compared to the high calorimetric signals measured.

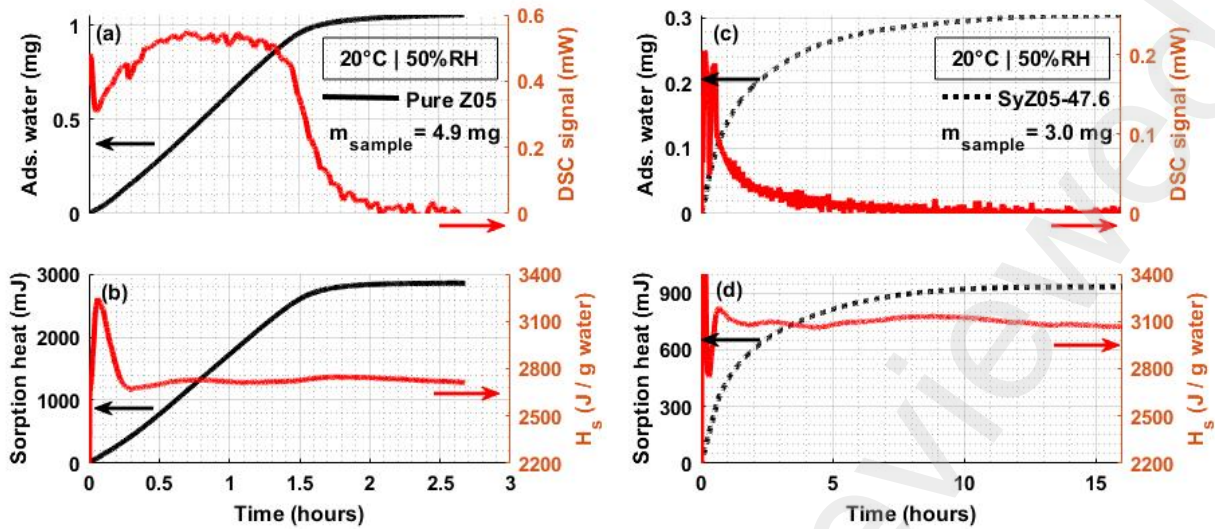


Figure 13: Sample sorption enthalpy measurements at 20 °C and 50 %RH

The sorption enthalpy ΔH_s can also be calculated for different mass uptakes via the Clapeyron diagram, which represents the Napierian logarithm of vapor pressure, $\ln(Pv)$, as a function of minus 1 over the temperature, $-1/T$, [27], [29], [56]. Using this method, the literature has shown that AQSOA Z05 zeolites present an average sorption enthalpy between $2800 \text{ J} \cdot \text{g}_{\text{H}_2\text{O}}^{-1}$ [27] and $2880 \text{ J} \cdot \text{g}_{\text{H}_2\text{O}}^{-1}$ [29]. These values are in fair agreement with our experimental calorimetric measurements for pure AQSOA-Z05, for which an average value of approximately $2902 \text{ J} \cdot \text{g}_{\text{H}_2\text{O}}^{-1}$ was obtained. Figure 14 shows a comparison of the experimental data for both the pure Z05 and the SyZ05 composite and the literature data obtained from the Clapeyron diagram [27], [29]. These results show that the literature data are in good agreement until the uptake reaches 0.17 %, but Teo et al. [29] reported a decrease in sorption energy at higher uptakes, while Goldsworthy [27] reported an increase. From our experimental data, however, the sorption enthalpy remained almost constant during the experiments with pure Z05 (see Figure 14-a). Moreover, from Figure 14-b, one can notice that the SyZ05-47.6 data show an increased sorption enthalpy compared to that of pure Z05, but we suppose that this is only due to the integration of measurements over

time, as discussed previously (see Figure 13). Furthermore, at 25 °C and 50 % RH, both materials show unexpected increases in sorption enthalpy compared to the other materials.

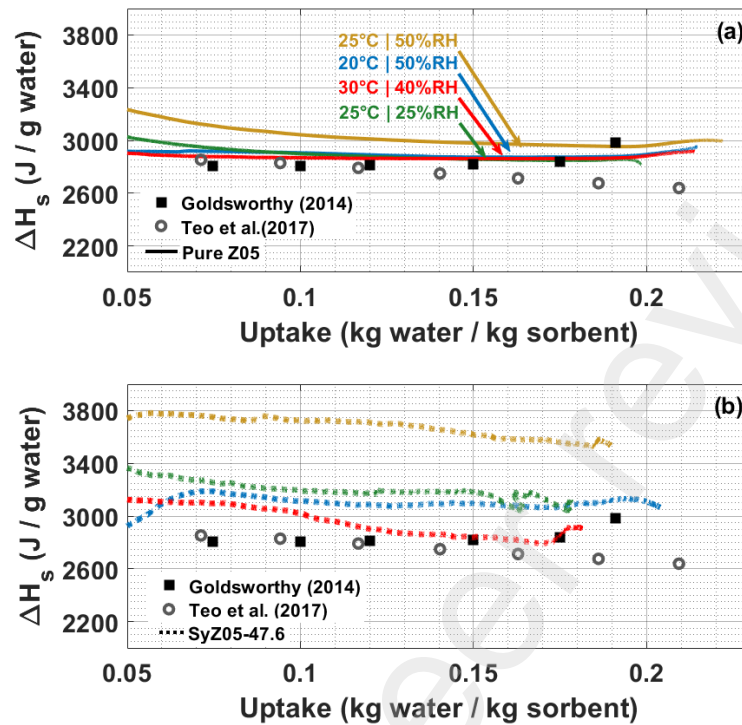


Figure 14: Sorption enthalpy as a function of uptake: experimental vs. literature
 (a) pure Z05 and (b) SyZ05-47.6

From these results, if we assume an average sorption enthalpy of $2900 \text{ J.g}_{\text{water}}^{-1}$ (Figure 14 – for comparison water heat of vaporization is 2257 J.g^{-1}), the maximum energy storage density of the samples can be calculated as:

$$\Delta E_{\text{Pure Z05}} = 440.1 \text{ kWh.m}^{-3}$$

$$\Delta E_{\text{SyZ05-47.6}} = 257.6 \text{ kWh.m}^{-3}$$

Assessment of cooling performance enhancement in operating conditions

The objective being to coat the sensible material in the cooling storage tank, the energy density must be assessed for the operating conditions (see section 1):

- Adsorption at 25 °C & 50 %RH => $0.21 \text{ kg}_{\text{water}}.\text{kg}_{\text{sorbent}}^{-1}$ (Figure 7)

- Desorption: 60 °C & 15 % RH => 0.008 kg_{water}.kg_{sorbent}⁻¹ (Figure 7)
- Assuming an average sorption enthalpy of about 2900 J.g_{water}⁻¹ (Figure 14)

Then the resulting energy density in real conditions is 585.8 kJ.kg_{sorbent}⁻¹ or 383.2 kWh.m_{sorbent}⁻³.

The sensible only storage, tested in [25], is made of glass beads of 16 mm diameter. Using the data from [25], it is possible to evaluate the storage energy of one bead of glass, in the operating conditions given above, to 174.4 J. We developed the composite SyZ05-47 so that a coating of the beads of 0.5 mm is resistant enough for an upscaled real application. With the previous data using the operating conditions, this coating has a storage capacity of 163.5 J, i.e. 94% of the storage capacity of glass alone. This result means that, in operating conditions, **our novel coating can nearly double the cooling storage capacity of the initial sensible system, by only modifying the solid storage material.**

4. Conclusions:

In this work, a new concept of dry cooling solution is proposed, based on the coating of a material to take the advantage of both, sensible and sorption heat storage. The thermodynamic and kinetic data of pure AQSOA Z05 and a novel composite material (referred to here as SyZ05-47.6) were experimentally measured in operating conditions, at temperatures ranging from 20°C to 60°C and a water vapor pressure of up to 160 mbar. The addition of the AQSOA Z05 powder to the Sylgard-184 matrix is a favorable approach for obtaining effective and adsorptive coatings with good mechanical and adhesive properties under targeted environmental conditions. Compared with its pure form, AQSOA Z05 remains 95 to 100% active when embedded in the novel composite since it maintains the same isotherm shape and accounts for approximately 95% of the maximum uptake. However, the low vapor diffusivity of Sylgard-184 creates some resistance for the reactions illustrated by a different shape of kinetic behavior associated with considerably

lower adsorption-desorption velocities after the first phase related to the instantaneous sorption stage (or external surface sorption). However, this change in reaction rate is not a real issue in the aimed application.

The sorption enthalpy is assessed by the integration of calorimetric signals during the adsorption reactions and can reach 1 to 1.4 times the enthalpy of vaporization of water at 25°C and atmospheric pressure, which is consistent with literature data obtained by the application of the Clapeyron diagram to the adsorption equilibrium isotherms of pure AQSOA-Z05. The results show that, in operating conditions, the SyZ05-47 coating allows to double the storage capacity of the sensible cTES, enabling its development for future applications!

The next steps include new experimental campaigns at the reactor scale with 270 kg of the novel hybrid sensible/sorbent material, which is composed of 16 mm diameter glass spheres coated with the SyZ05-47.6 membrane studied in this work. To investigate reactor behavior and quantify reactor performance, a reactor containing the novel material was installed on the experimental bench presented in [25]. The goal is to use the experimental data for validating a new version of the numerical 1D model presented in [57] and assess the performance of the new reactor configuration. The development and validation of this model are highly important for analyzing what happens inside the storage reactor and enhancing its operation and control. Such a validated model is necessary to test different configurations depending on the location and related weather and to assess the techno-economic interest of the concept.

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