



Squaring the circle in drying high-humidity air by a novel composite sorbent with high uptake and low pressure-drop

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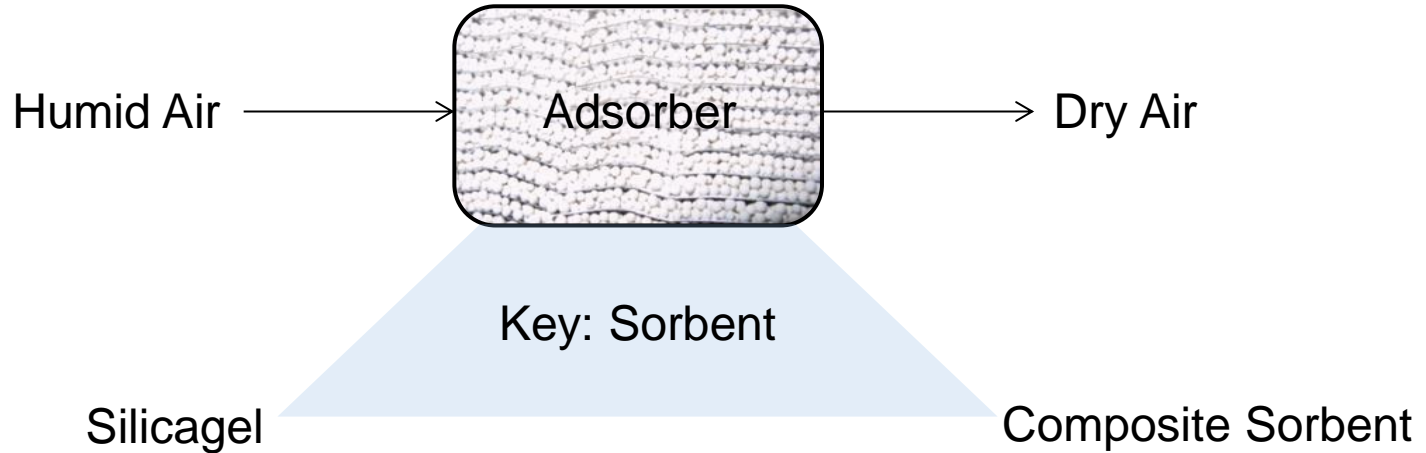
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HPC 2018, 16-19th September



Adsorptive Drying



- Uptake
- Pressure drop
- Dehumidification Rate
- Hydrothermal Stability

Novel Composite Sorbent for Drying

Preparation



Characterization

- Isotherms
- Uptake
- Pressure drop
- Dehumidification Rate
- Hydrothermal Stability

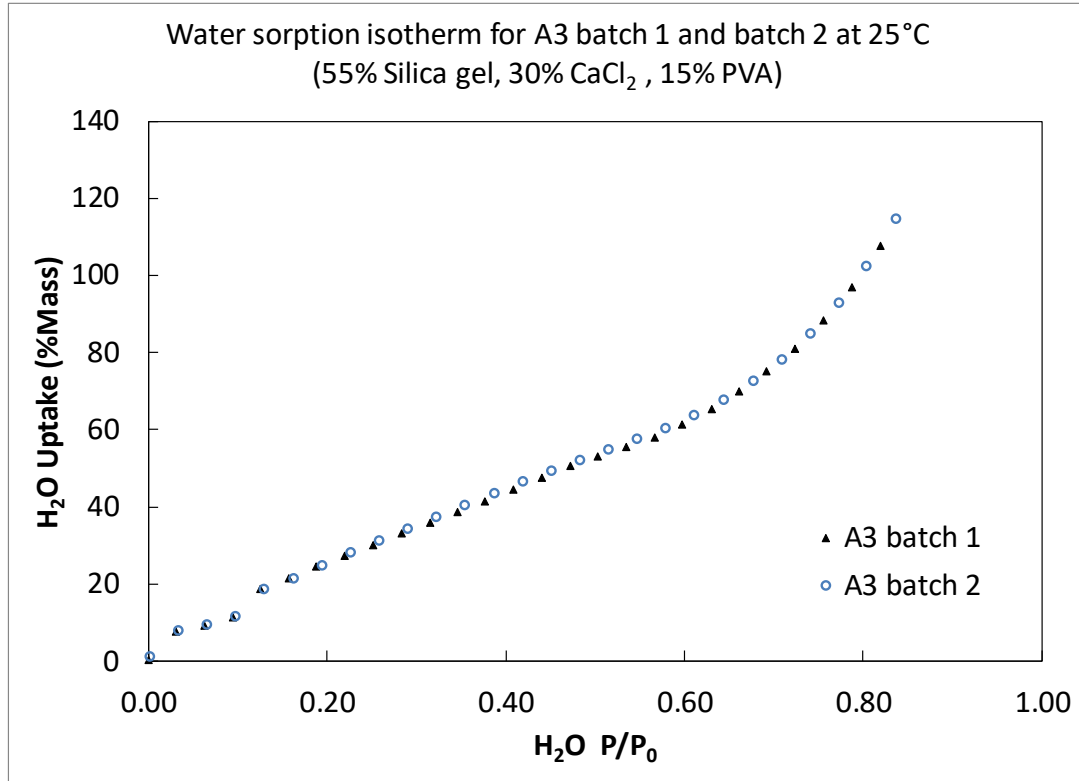
Preparation of Composite Sorbent I/II

- Prepared in batches of 400 g
- 55 wt.% mesoporous silica gel, 30 wt.% CaCl_2 and 15 wt.% polyvinyl alcohol
- PVA (85,000-124,000 MW) combined with anhydrous calcium chloride and dissolved in 600 mL distilled water
- Solution was combined with a mesoporous silicagel
- Oven dried at 80 °C and cured at 150 °C

Porosimetry: $S_{\text{BET}} = 104 \text{ m}^2/\text{g}$, $0.44 \text{ cm}^3/\text{g}$



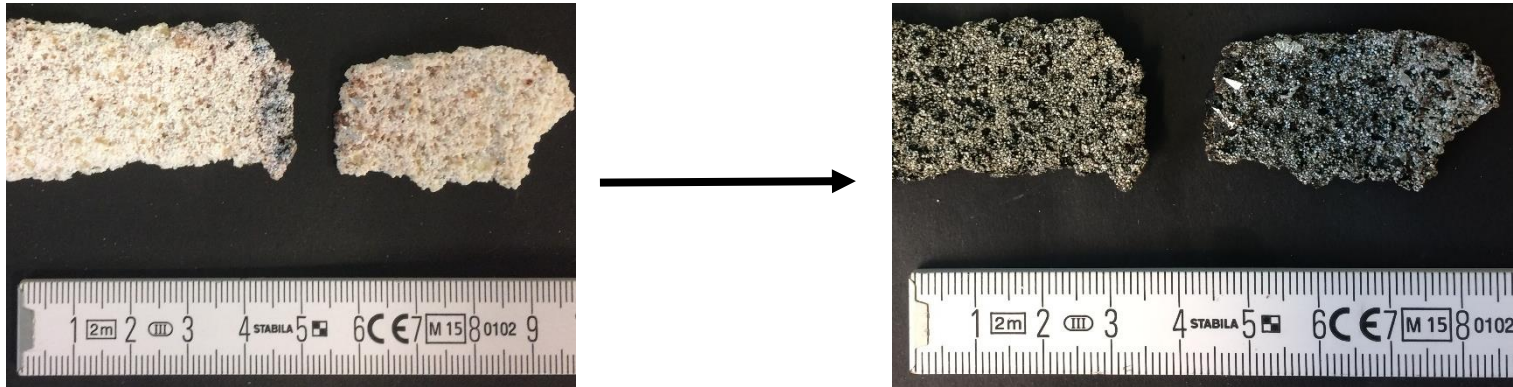
CaCl₂/silica gel composite sent to LTT: Batch 1 & Batch 2



Composite
batch 1

Preparation of Composite Sorbent III/II

- The sorbent was further baked at 250 °C for 24 h, during which it darkened

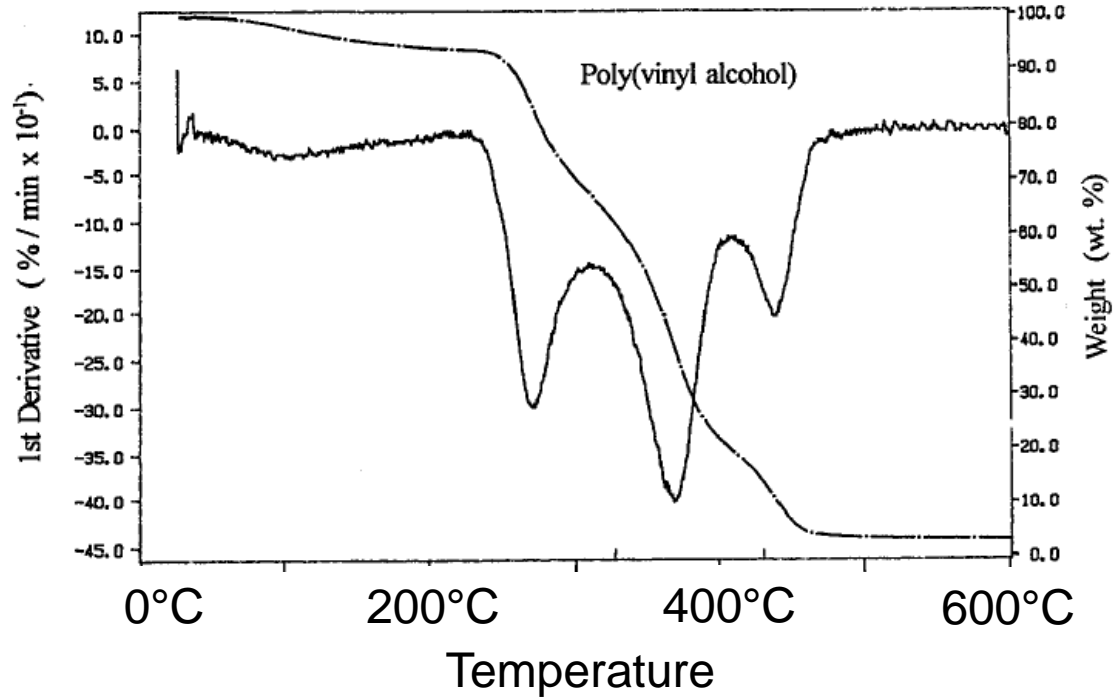
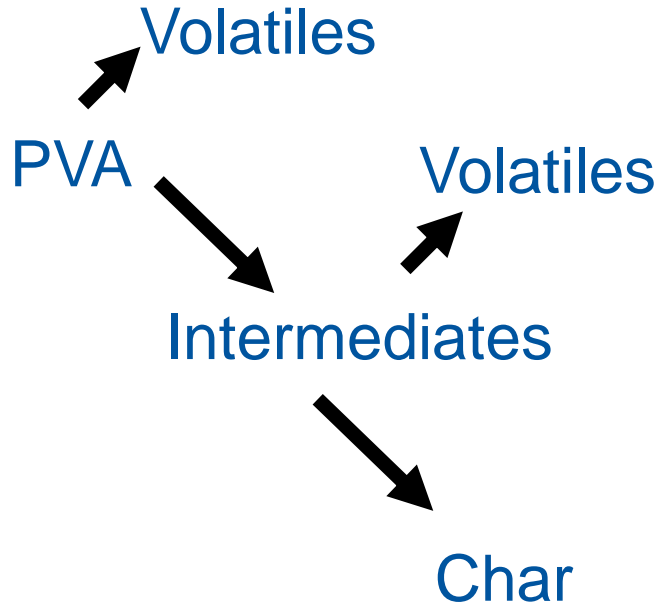


PVA Binder: $T_g = 85^\circ\text{C}$

mp = 180-190°C (partially hydrolyzed), 230°C (fully hydrolyzed)

Decomposes above 200°C; undergoes pyrolysis at high temperature

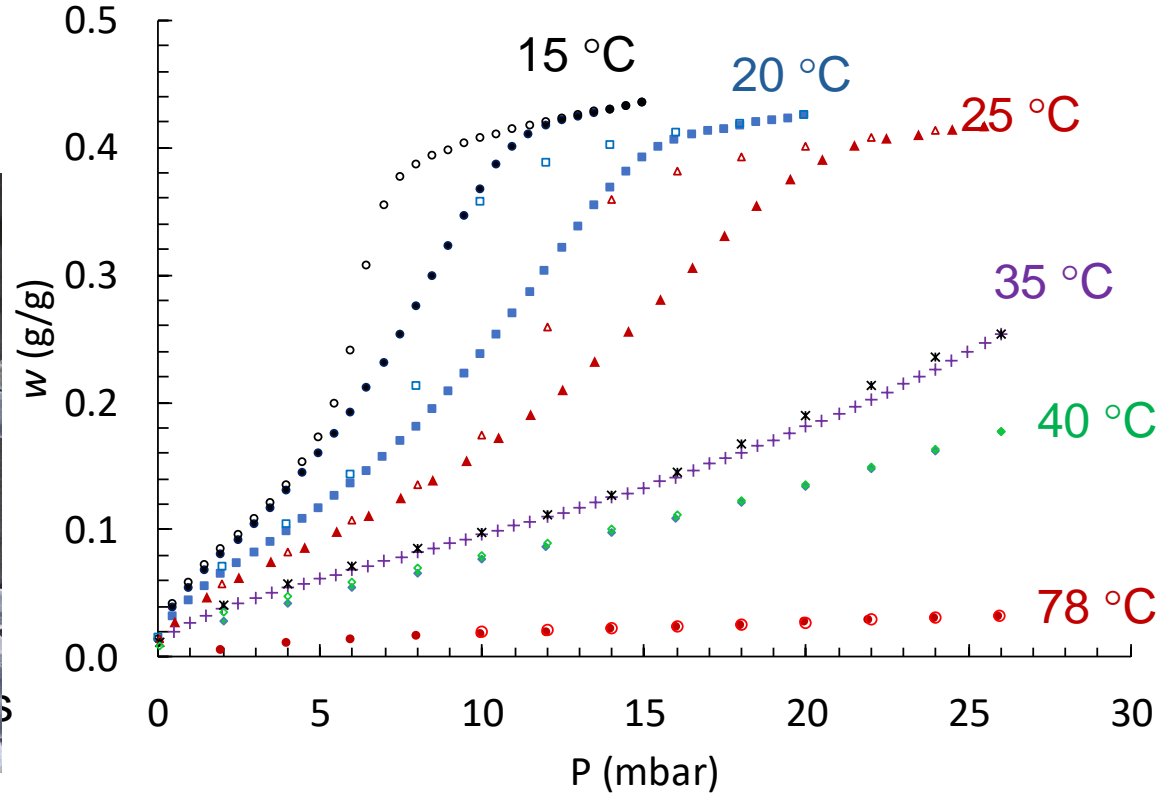
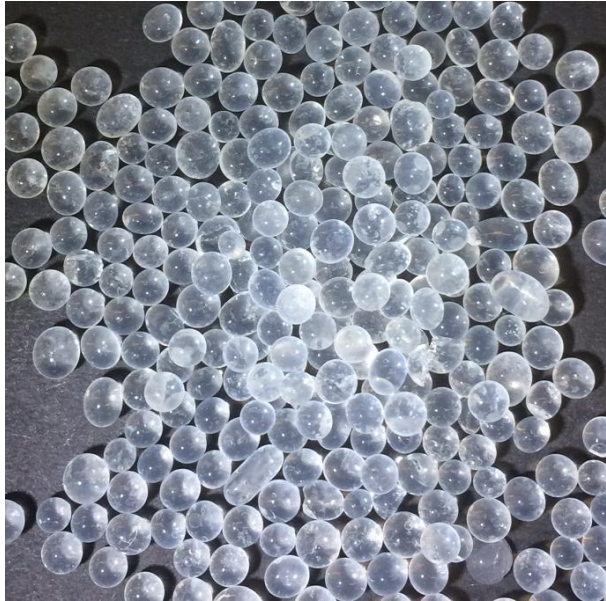
Pyrolysis of PVA Binder



Gilman et al, Thermal decomposition chemistry of poly(vinyl alcohol), ACS 1995

Silica Gel “Grace Sylobead B127” isotherms

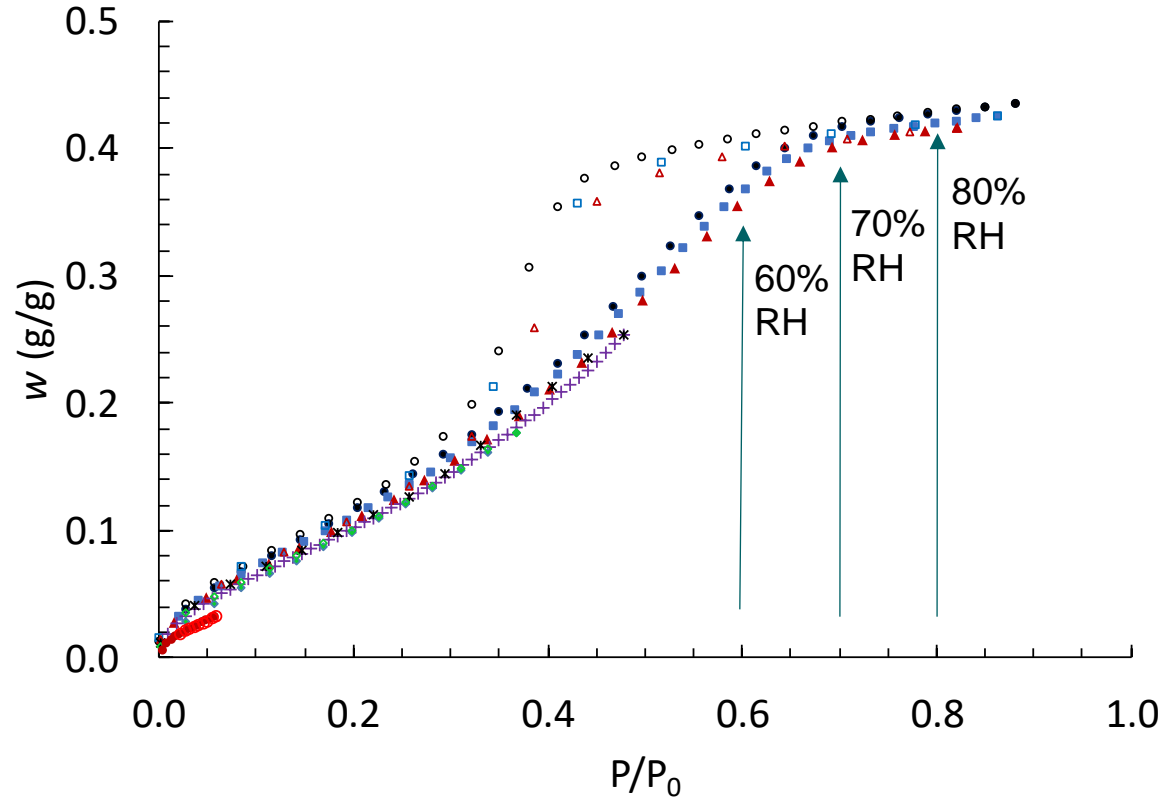
- Silica gel provided by RWTH Aachen team



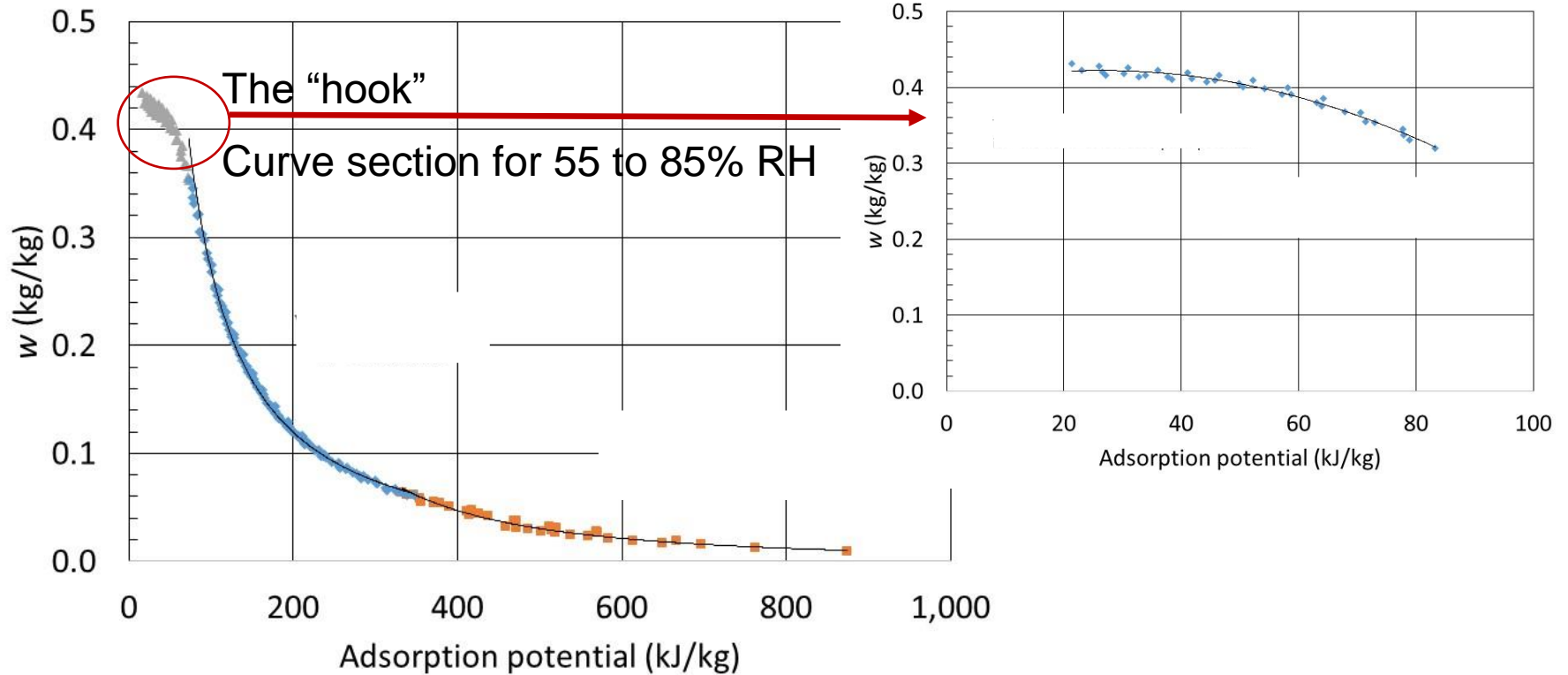
Silica gel isotherm set plotted as a function of P/P_0

- P/P_0 plots are easy to read
- Equilibrium uptake capacity for 60, 70, and 80 RH%
- The data can also be plotted as a function of adsorption potential

$$\Delta F = -RT \ln(P/P_0)$$



Silica gel uptake characteristic curve



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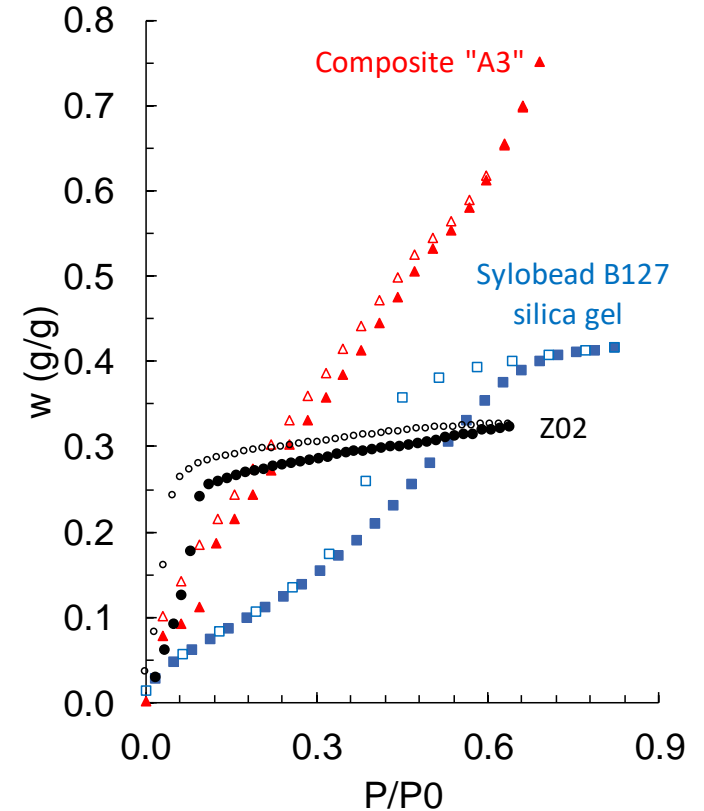


Characterization

- Isotherms
- Uptake
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- Hydrothermal Stability

Isotherms of Composite Sorbent and Silicagel

- The composite sorbent takes up more than twice the water as silicagel
- For high humidity air (> 80 % RH), the composite sorbent reaches a maximum uptake of more than 1 kg/kg



Fixed Packed Bed

Composite Sorbent



Open porous sponge structure formed inside adsorber

108 g dry weight inside adsorber

Adsorber

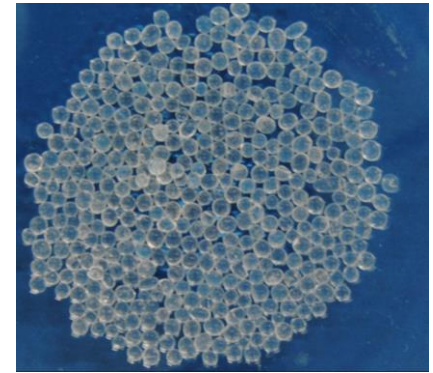


Diameter: 100 mm

Length: 50 mm

Volume: 0.393 L

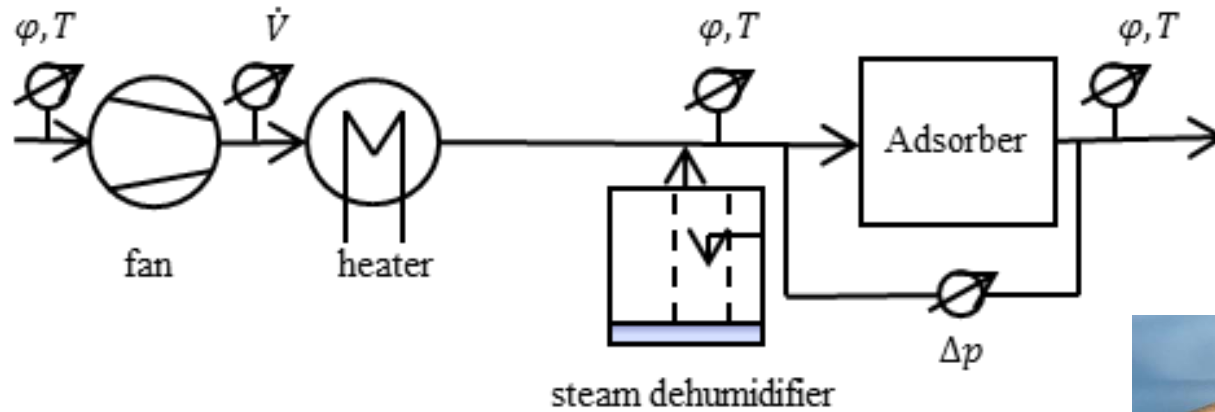
Silica gel



Spherical beads of ~2 mm in diameter

332 g dry weight inside adsorber

Process Parameters & Experimental Setup

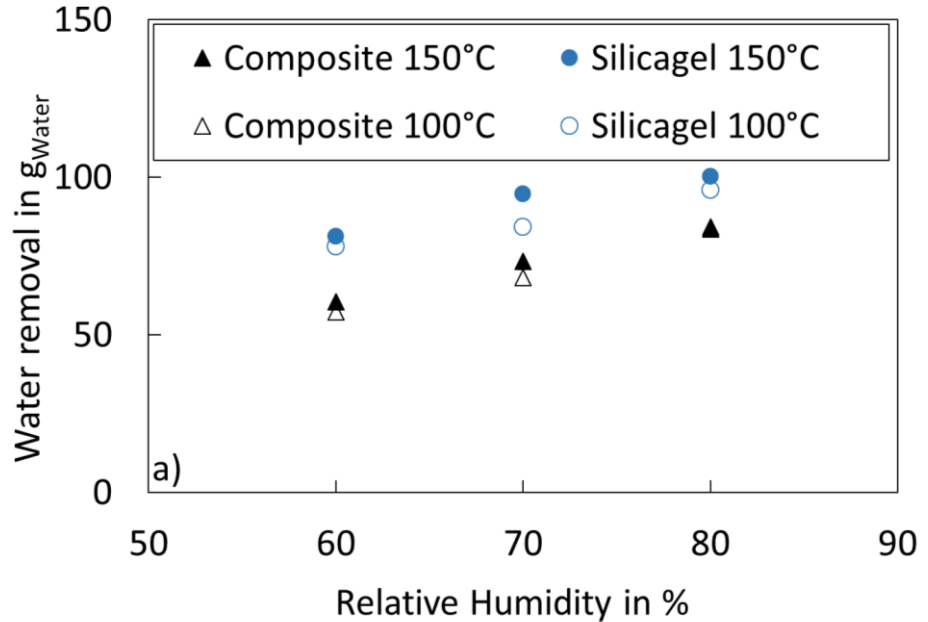


Adsorber

- Adsorption temperature of 40 °C
- 60, 70 and 80 % RH
- Regeneration temperatures of 100 °C and 150 °C
- Air flow of 40 m³/h

Water Removal

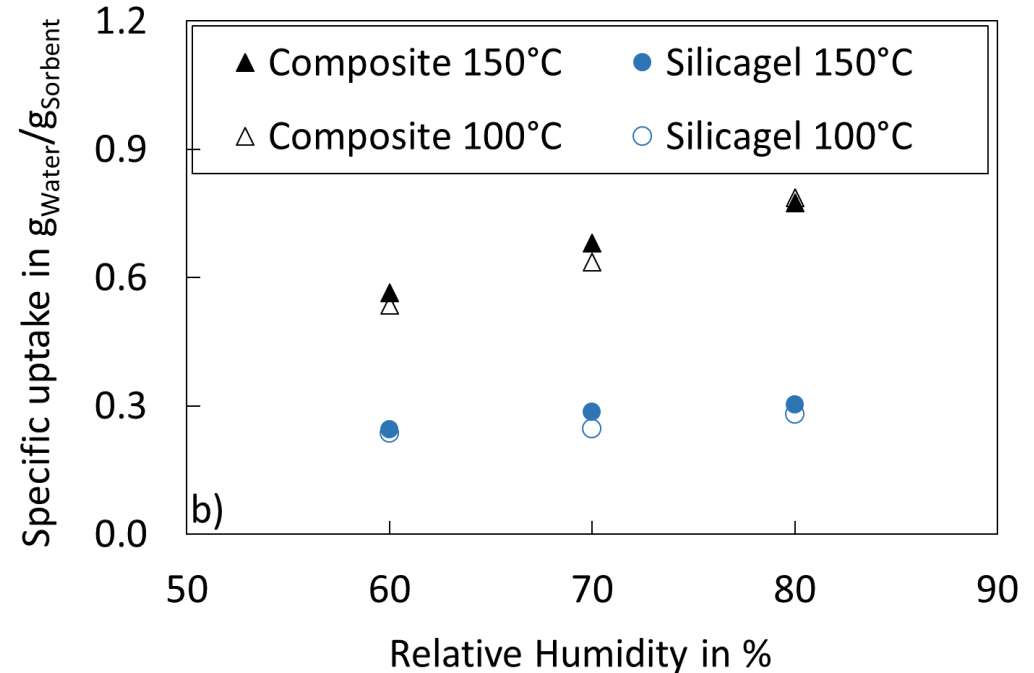
- Water removal of composite sorbent
 - 37 % lower than silica gel (> 60 % RH)
 - 20 % lower than silica gel (> 80 % RH)
- Water removal of silica gel higher because bulk density is about 3 times higher compared to composite sorbent



Adsorption temperature of 40 °C

Specific Uptake

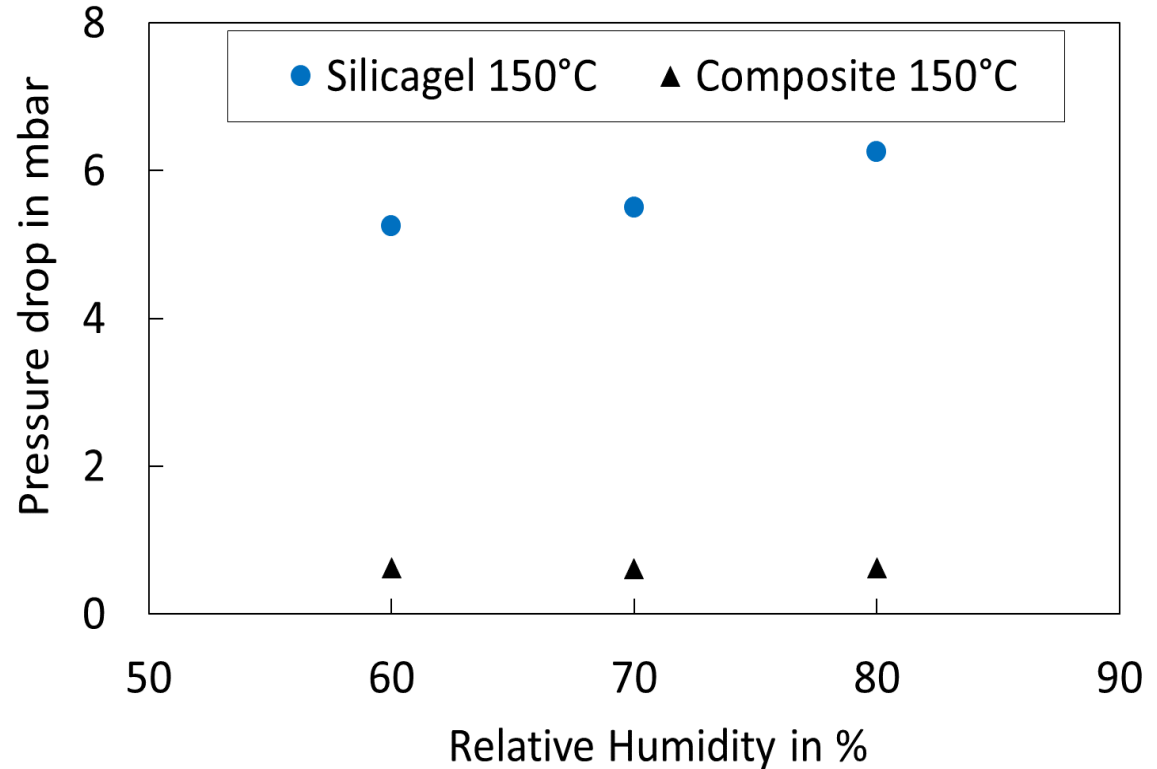
- Uptake of composite sorbent more than twice as high as for the silica gel
- For high humidity air (> 80 % RH), the composite sorbent had a maximum uptake of about 0.78 kg/kg and absorbs 2.6 times more than silica gel



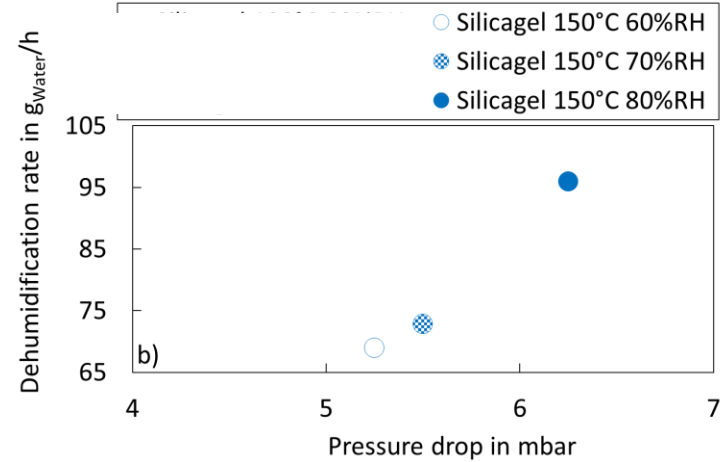
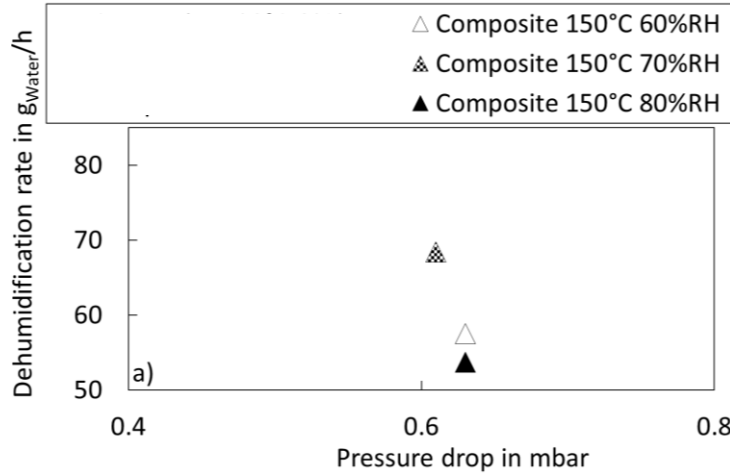
Pressure Drop across the Bed

Composite sorbent has a 8-10 times lower pressure drop than silica gel

→ Due to sponge structure inside the adsorber instead of packed bed of 2 mm beads

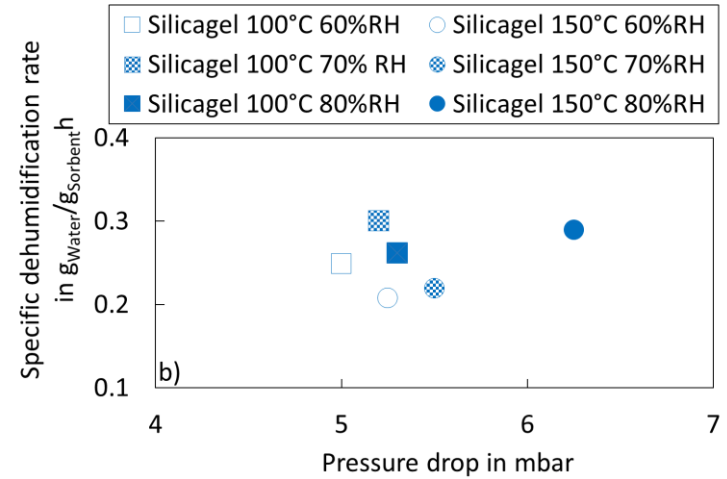
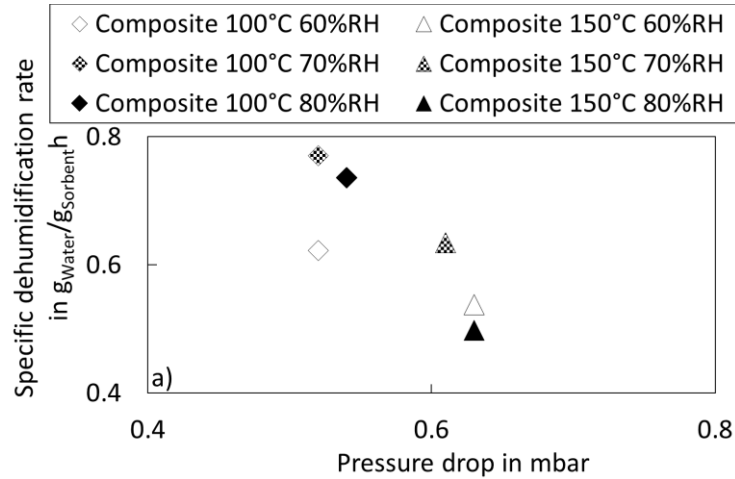


Dehumidification Rate (DR)



- DR lower for higher regeneration temperature, due to longer cooling period
- Highest DR for both adsorbents at 100 °C and 70 % RH
Composite ≈ 83 g_{Water}/h Silica gel ≈ 103 g_{Water}/h
- DR of silica gel about 24 % higher for the best case

Specific Dehumidification Rate (SDR)



- Range of SDR

Composite $\approx 0.5 - 0.77 \text{ g}_{\text{Water}}/\text{g}_{\text{Sorbent}} \text{ h}$

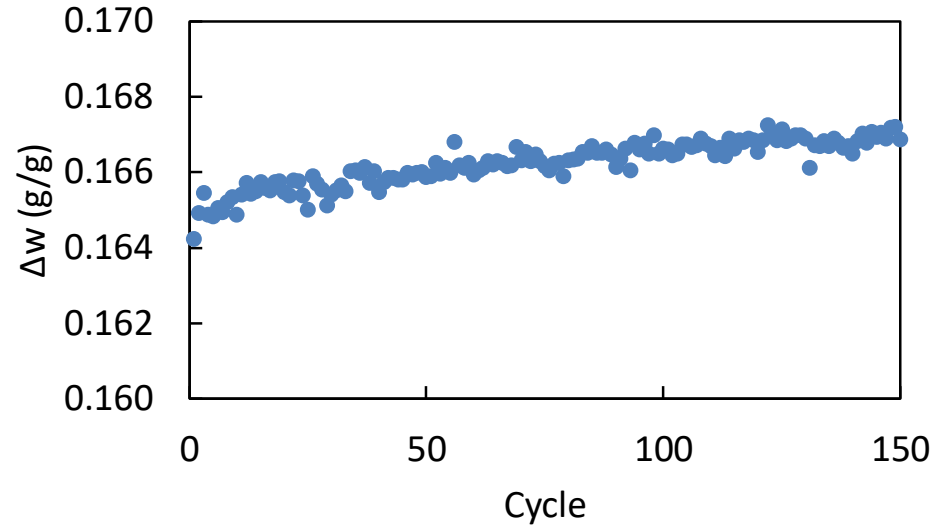
Silica gel $\approx 0.2 - 0.3 \text{ g}_{\text{Water}}/\text{g}_{\text{Sorbent}} \text{ h}$

- SDR of silica gel about up to 2-3 times lower compared to SDR of composite

Hydrothermal Stability

Thermogravimetric vapor sorption analysis:

- 0 to 1.2 kPa swings in water vapor pressure
- 40 minute cycles at 35 °C
- Average change in water content per cycle was 0.1662 ± 0.0006



→ no measurable loss in uptake capacity across 150 cycles

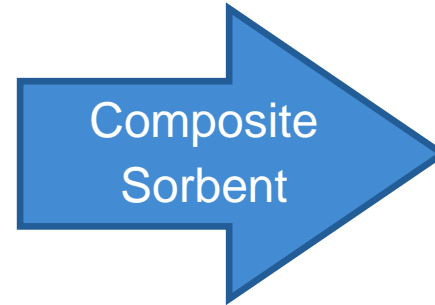
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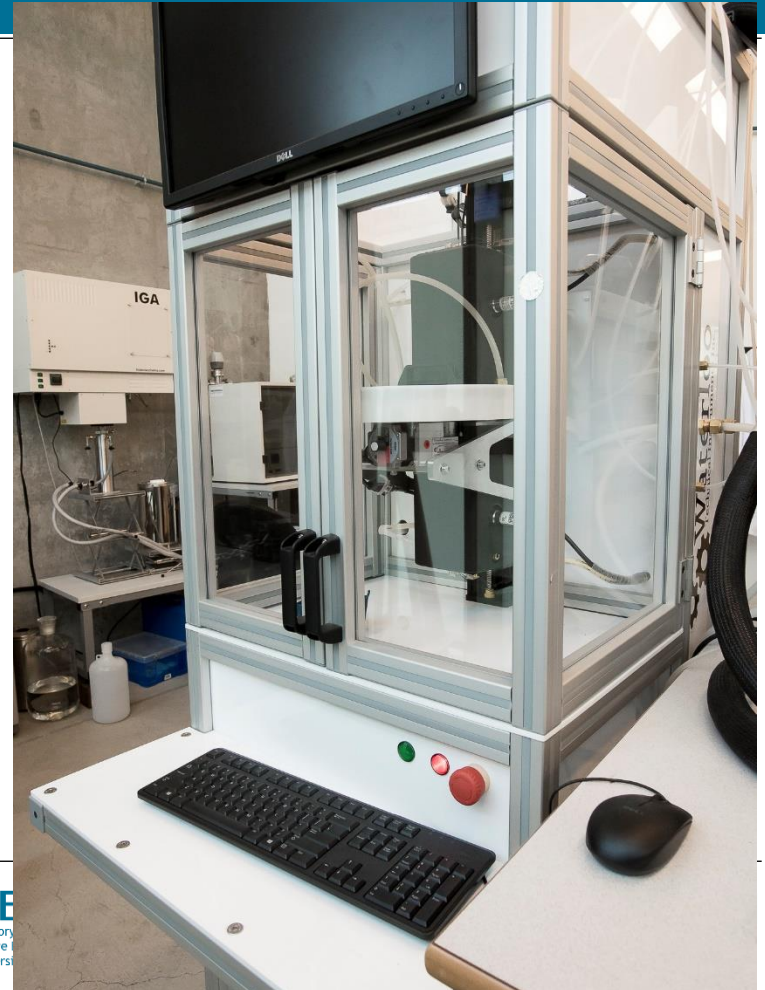
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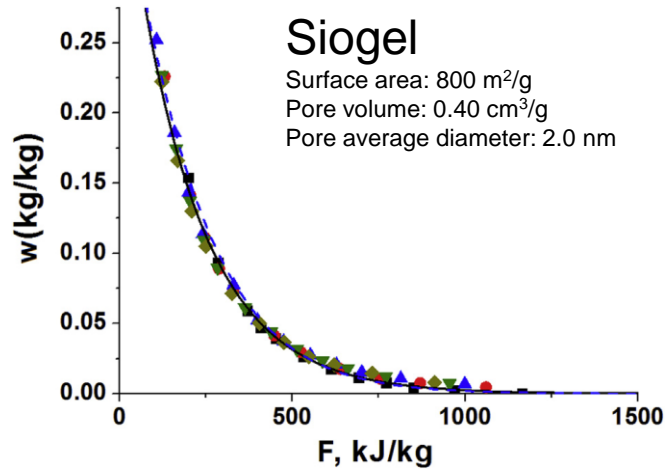


Suitable
&
highly promising
for drying high humidity air

Thank you for your attention!



Water - Silica Siogel™ working pair for adsorption chillers: Adsorption equilibrium and dynamics, A. Sapienza, Renew. Energy 2016



Temperature-invariant curve of adsorption
Equilibrium uptake, w [kg/kg], vs the Dubinin-Polanyi potential
 $F = -RT \ln(P_{H_2O}/P_s)$

Equilibrium loading w can be precisely described by the simple exponential expression w [kg/kg] = $w_0 \cdot \exp(-b \cdot F)$ where $w_0 = 0.4031$ kg/kg and $b = 0.0051$ kg/kJ are fitting parameters determined from the experimental equilibrium data.

By comparison, the Dubinin-Astakhov approximation, w [kg/kg] = $w_0 \cdot \exp[-(F/E)^n]$, has three fitting parameters $w_0 = 0.38$ kg/kg, $E = 220$ kJ/kg, and $n=1.1$.

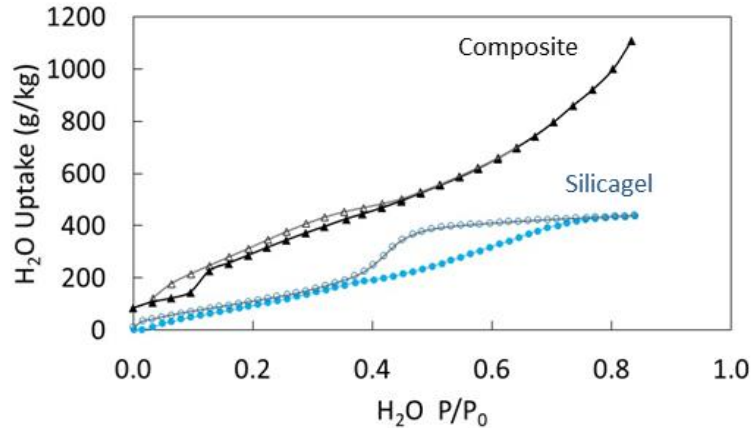
Both approximations have almost the same standard deviations. Therefore, they provide a good analytical description of the whole set of experimental data and can be used for modeling.

Only w_0 has a physical meaning (maximal mass of water that can be adsorbed).

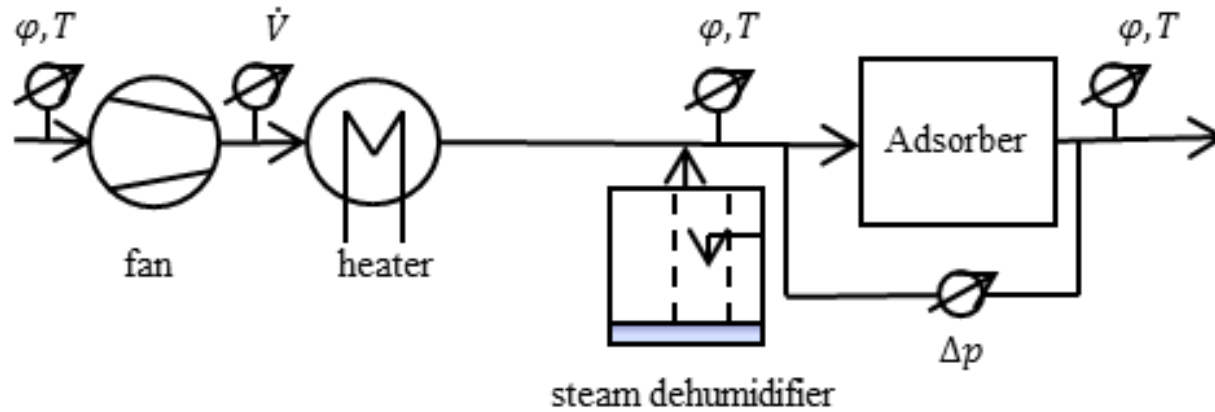
CaCl₂ in silica gel porosimetry

No.	Silicycle <i>SiliaFlash</i> Type	Mean pore diameter (nm)	Pore vol. (cm ³ g ⁻¹)	No.	Mean pore diameter (nm)	Pore vol. (cm ³ g ⁻¹)
S4	B40	4	0.58	CaCl ₂ -S4	7	0.27
S6	B60	6	0.75	CaCl ₂ -S6	9	0.37
S9	B90	8	0.83	CaCl ₂ -S9	10	0.58
S15	B150	16	1.10	CaCl ₂ -S15	18	0.60

Isotherms of Composite Sorbent and Silicagel



- The composite sorbent takes up more than twice the water as silicagel
- For high humidity air (> 80 % RH), the composite sorbent reaches a maximum uptake of more than 1 kg/kg



Conditions: $T_{\text{Desorption}} = 150^{\circ}\text{C}$

$T_{\text{Adsorption}} = 40^{\circ}\text{C}$, RH ~60%

Volume flow: 40 m³/h

Sorbent sample: 34.5 wt% CaCl₂
in Sylobead B 127

~170 g, diameter

100 mm

- 30 wt% CaCl_2 , 55 wt% SiliaFlash B150 silica gel (~15 nm pores, 0.2-0.5 mm irregular grains, Silicycle Inc.), 15 wt% polyvinyl alcohol (PVA) binder (85,000-124,000 MW)
- Open performance tests by Meltem
- 250°C baking at Aachen (partial pyrolyzation of binder)