Thermogravimetric analysis of water and methanol vapor sorption of silicoaluminophosphate zeolite (AQSOA-Z02)

Claire McCague, Ameer Ismail, and Majid Bahrami

IVth International Symposium on
Innovative Materials for Processes in Energy Systems
Taormina, Sicily, Italy
October 24, 2016

SFU
SIMON FRASER UNIVERSITY
ENGAGING THE WORLD

LAEC
Laboratory for Alternative Energy Conversion

Laboratory for Alternative Energy Conversion

Sorption chiller research (started in 2012):

- Focus: Water-based systems
- Built a 300 W/kg sorption chiller
- Capillary-assisted evaporator
- Adsorber bed heat exchangers

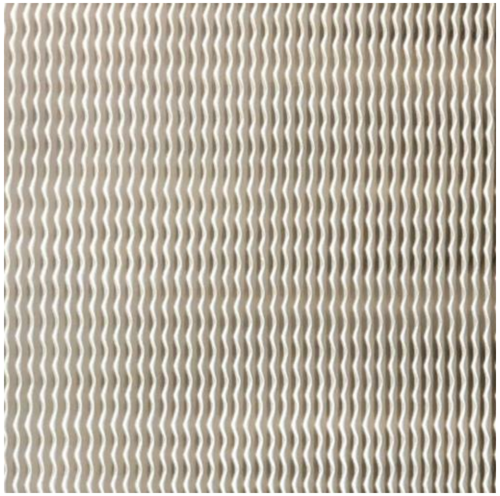
- Transport in PEMFC catalyst and gas diffusion layers
- Passive cooling systems for power electronics
- Thermal management of batteries
- Efficient HVAC-R
- Atmospheric water generation
- Rotary desiccant dehumidifiers
- Adsorption thermal energy storage

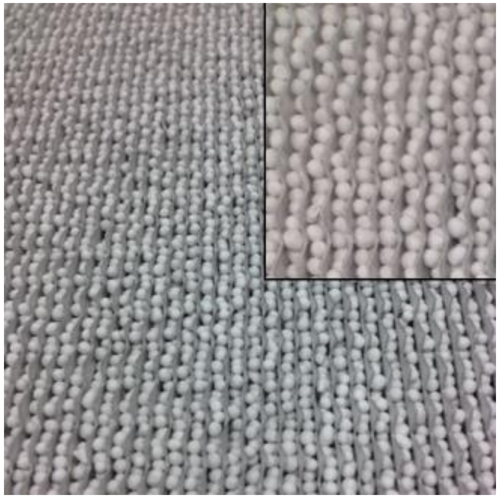
- Sorbent materials:
  - $CaCl_2$-silica gel and **FAM-Z02**
  - Organic binders
  - Graphite flakes

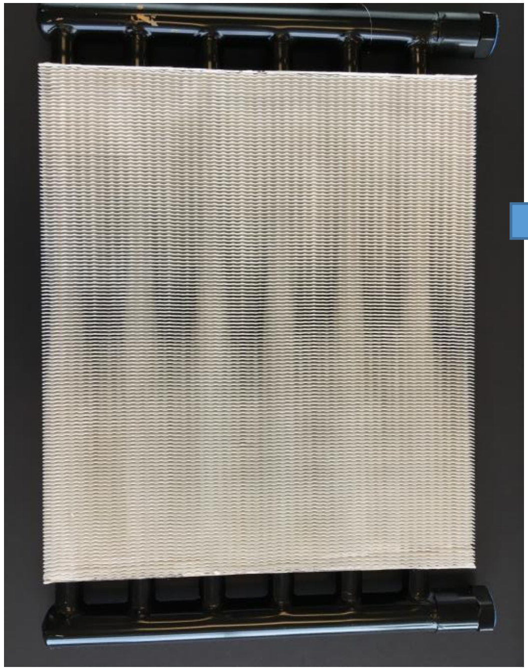
LAEC
Laboratory for Alternative Energy Conversion

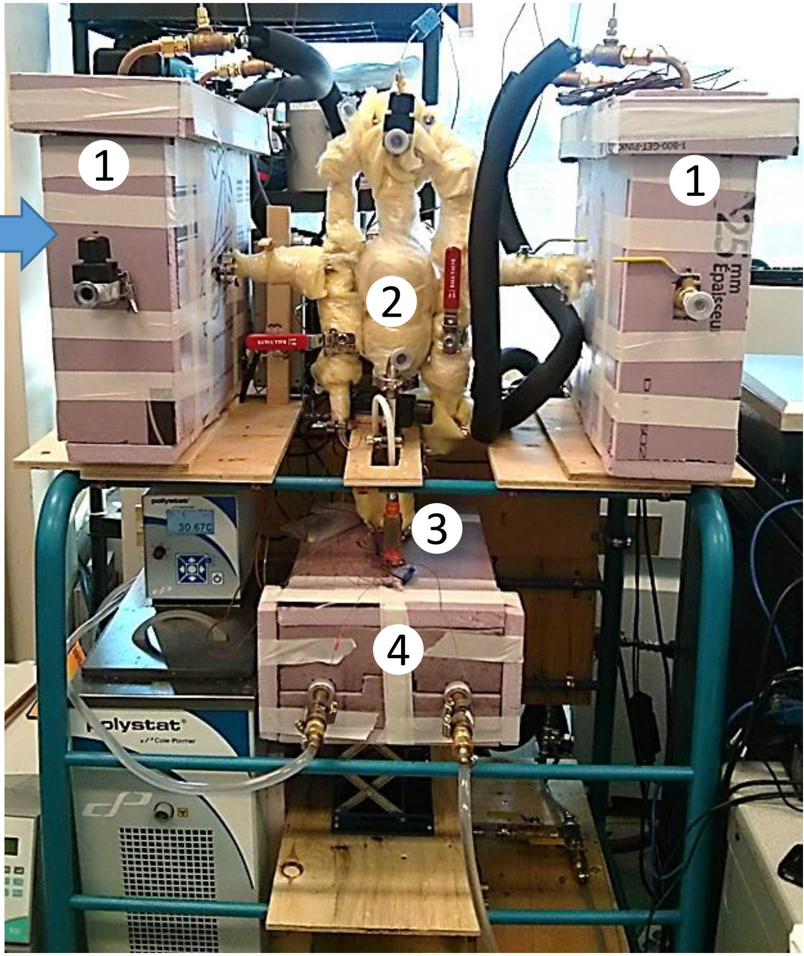
SFU

Lab-scale Sorption Chiller


0.7 kg sorbent coating


1.9 kg sorbent pellets

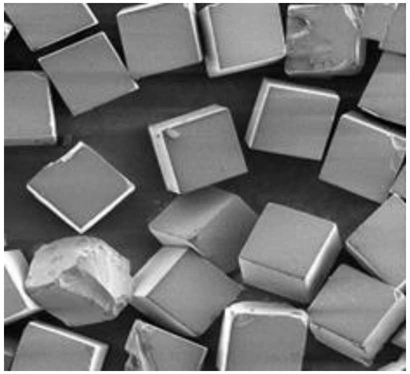

Finned-tube HEx coated or packed with sorbent



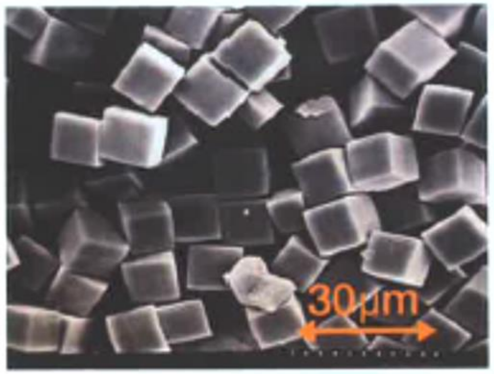
Sorption chiller: 1) two adsorber beds, 2) condenser, 3) expansion valve, and 4) evaporator.

LAEC
Laboratory for Alternative Energy Conversion

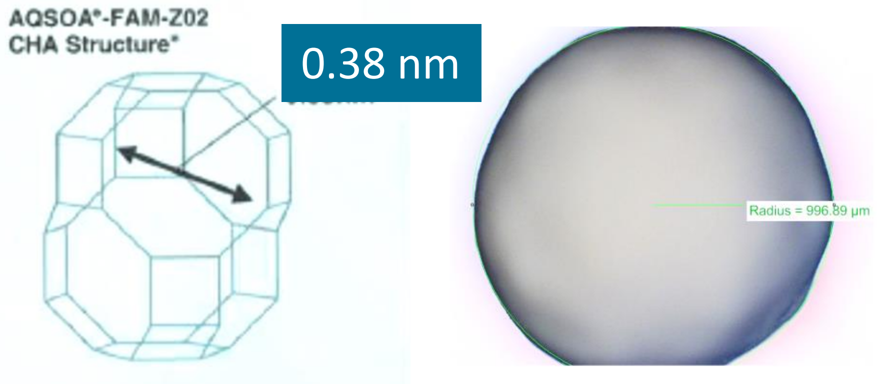
Functionalized Adsorbent Material (FAM)
ASQOA-Z02



SAPO-34 crystallites. Y. Iwase, *Phys. Chem. Chem. Phys.* (2009), **11**, 9268



Mitsubishi



$Si_xAl_yP_zO_2\cdot nH_2O$

$x = 0.05–0.25$, $y = 0.4–0.6$, $z = 0.25–0.50$, $n = 0–1.5$

FAM ASQOA-Z02 is a silicoaluminophosphate developed by Mitsubishi Plastics (similar to SAPO-34)

Pellets: 1.9 mm
Zeolite: 83-94% wt
SiO_2 binder: 6-17% wt

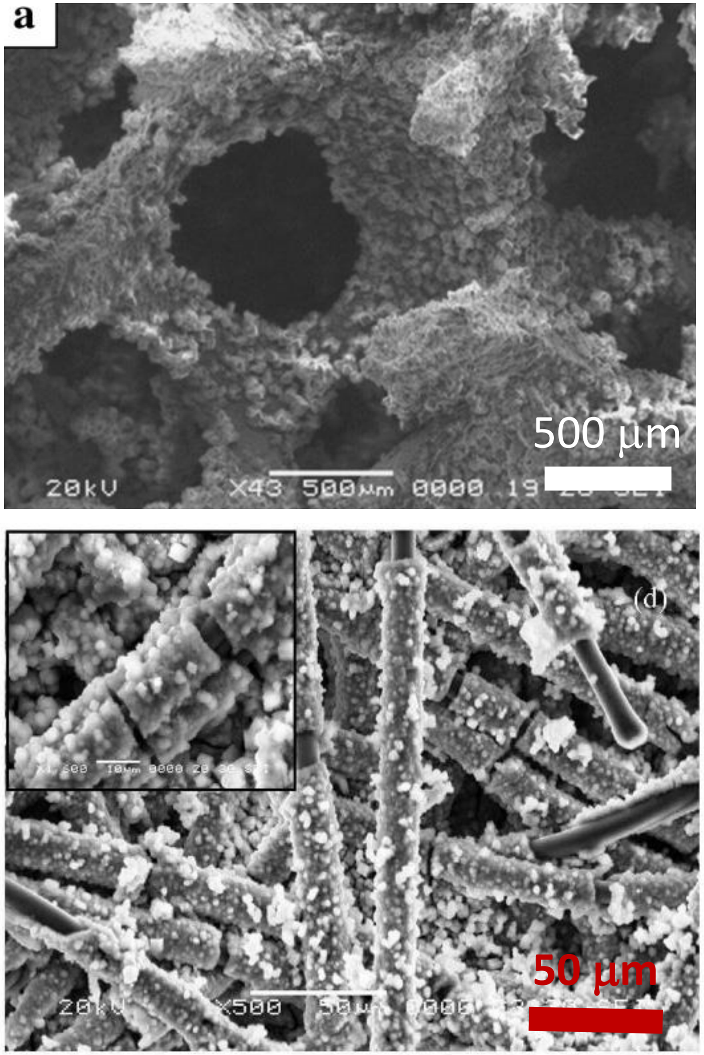
How is SAPO-34 or FAM-Z02 synthesized?

Hydrothermal synthesis
(e.g. 200°C in a pressurized reactor)

- aluminium isopropoxide
- orthophosphoric acid
- silica
- tetraethylammoniumhydroxide

Coating/pellets

- prepare a silane solution (e.g. N-propyltrimethoxy-silane, 5%) and add zeolite powder
- dip coat cleaned and treated substrate
- dry and cure



Direct growth of SAPO-34 on graphite and aluminum

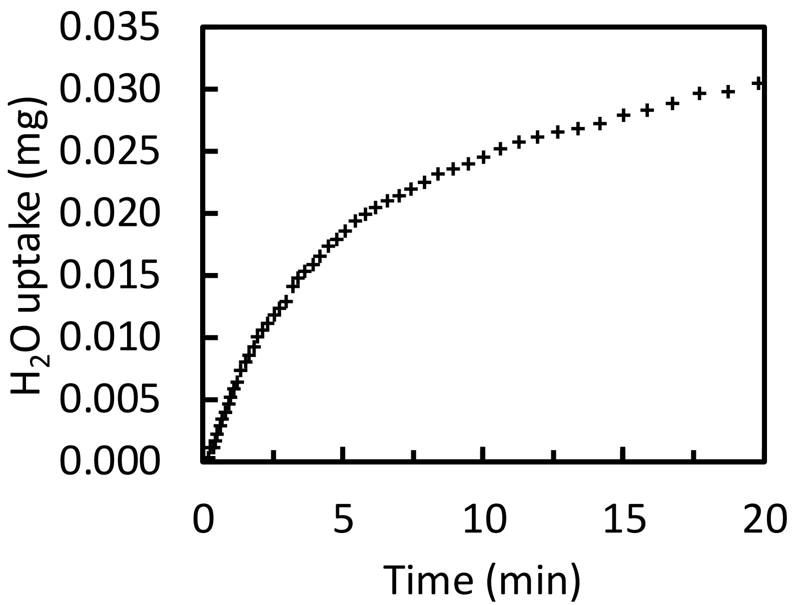
Bonaccorsi et al., *Micropor. Mesopor. Mat.* 167 (2013) 30
Bonaccorsi et al., *J. Energy Chem.* 22 (2013) 245
University of Messina

Thermogravimetric vapor sorption analyzer

Isotherms and isobars

Hiden Isochema IGA-002

TGA vapor sorption kinetic data for a single point of an isotherm

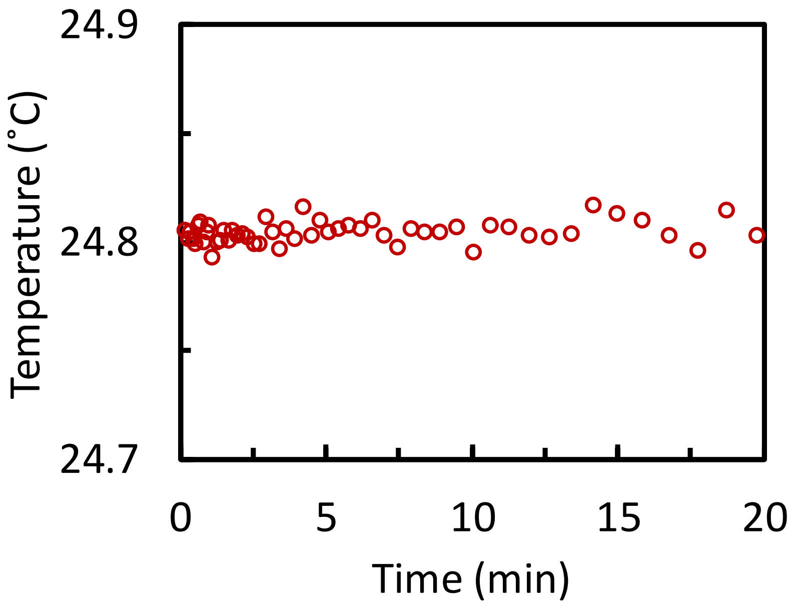


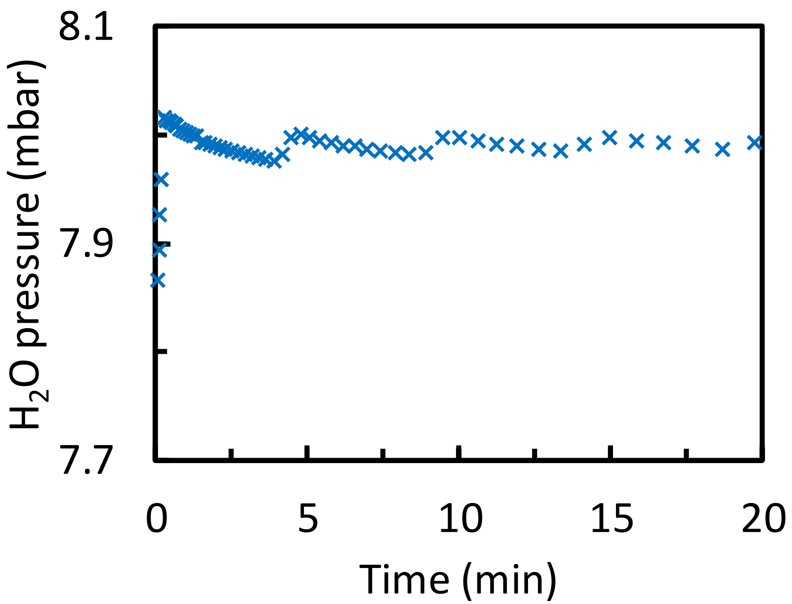
7.5-8.0 mbar step of a 25°C isotherm

Sample: Five 1.9 mm pellets
(19.3 mg) of ZO2 in a
conical wire mesh basket

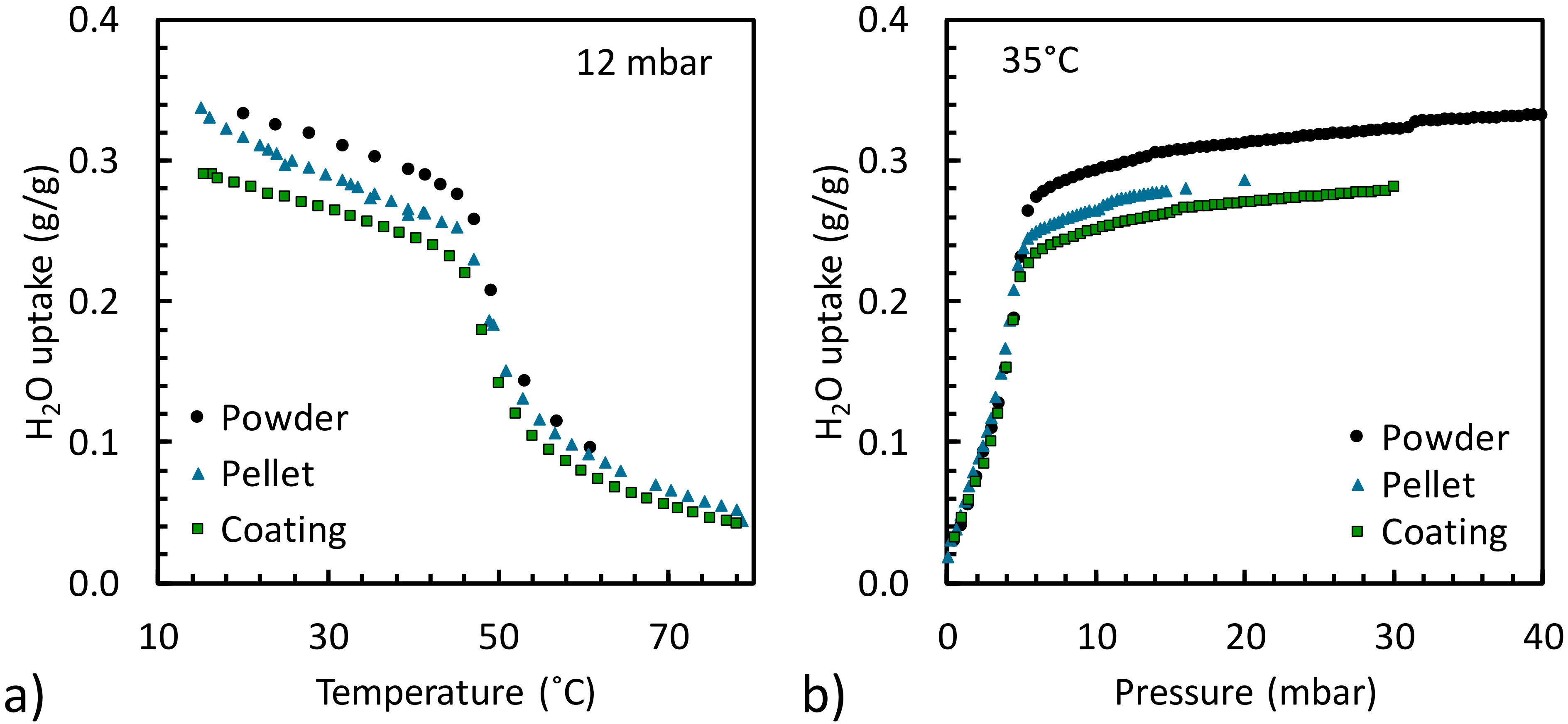
Pressure ramp 2-8 mbar/min

Active pressure control





Isobar and Isotherm for FAM-Z02

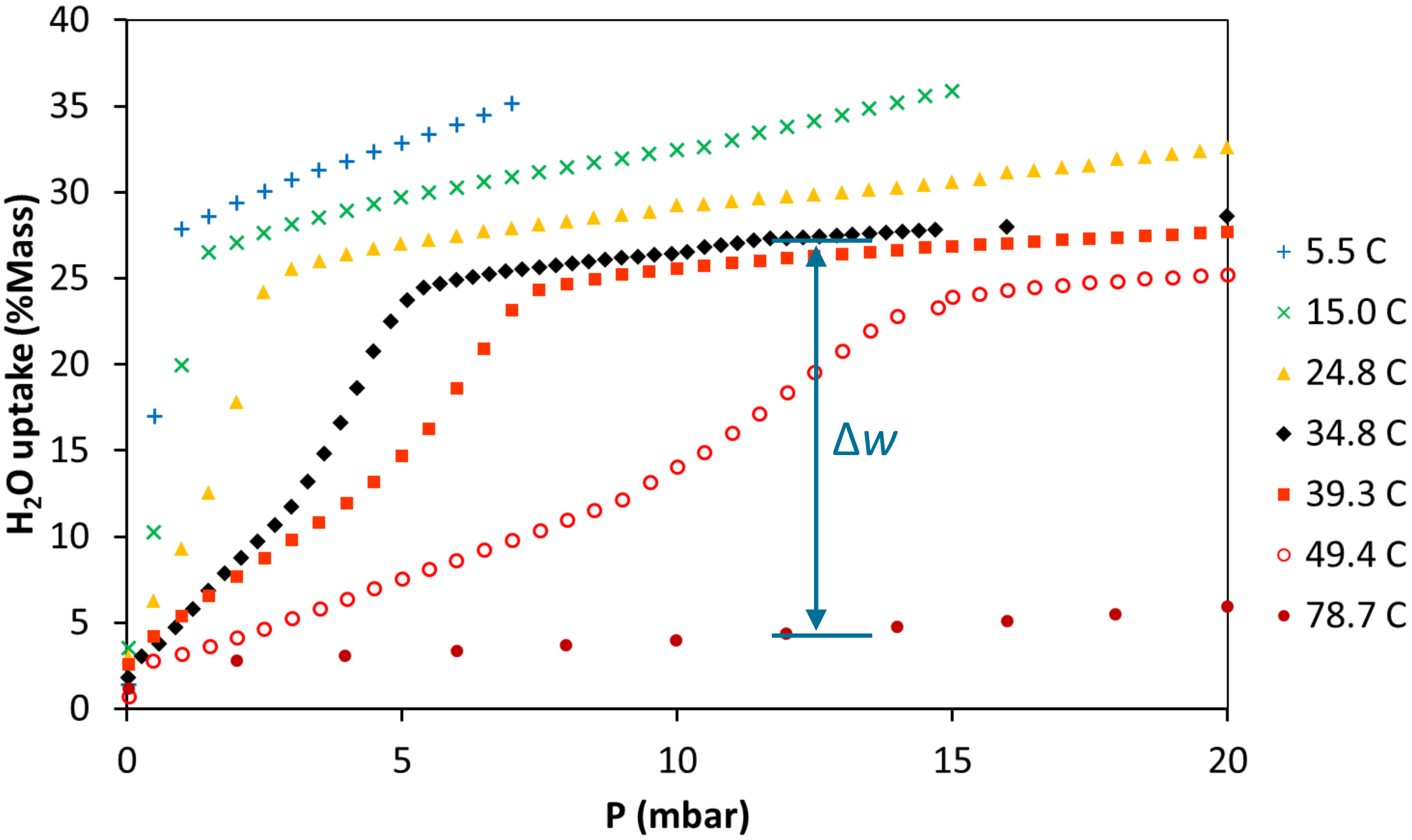


- The Z02 pellets adsorbed ~9% less than the Z02 powder
- The Z02 coating adsorbed ~ 13.6% less that the Z02 powder

LAEC
Laboratory for Alternative Energy Conversion

SFU

Water sorption isotherms for FAM-Z02

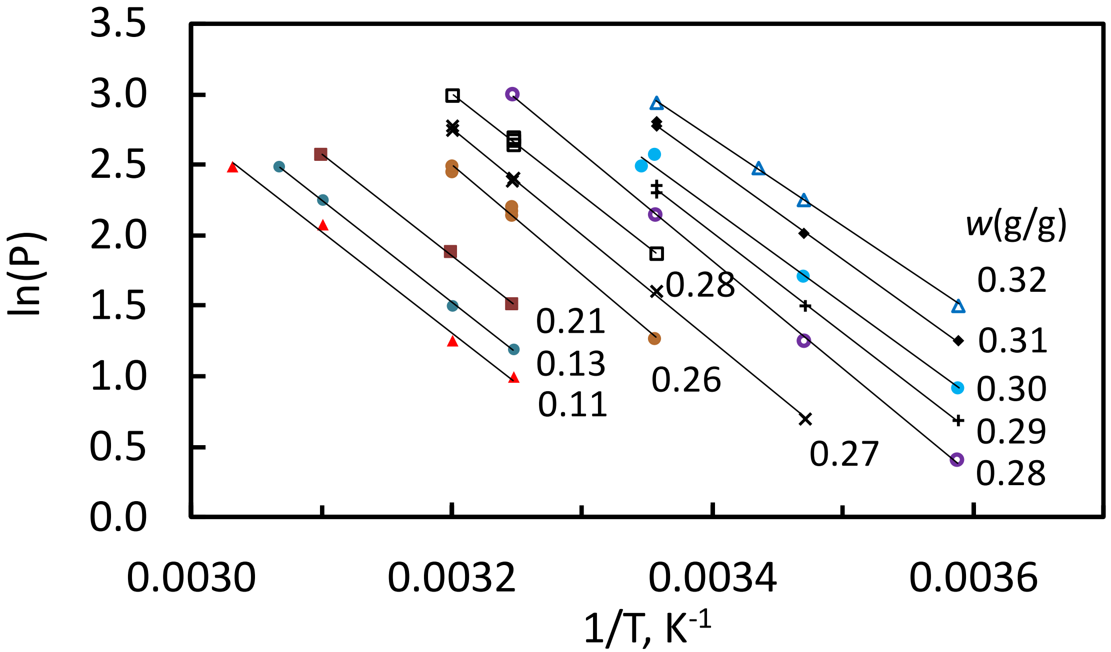


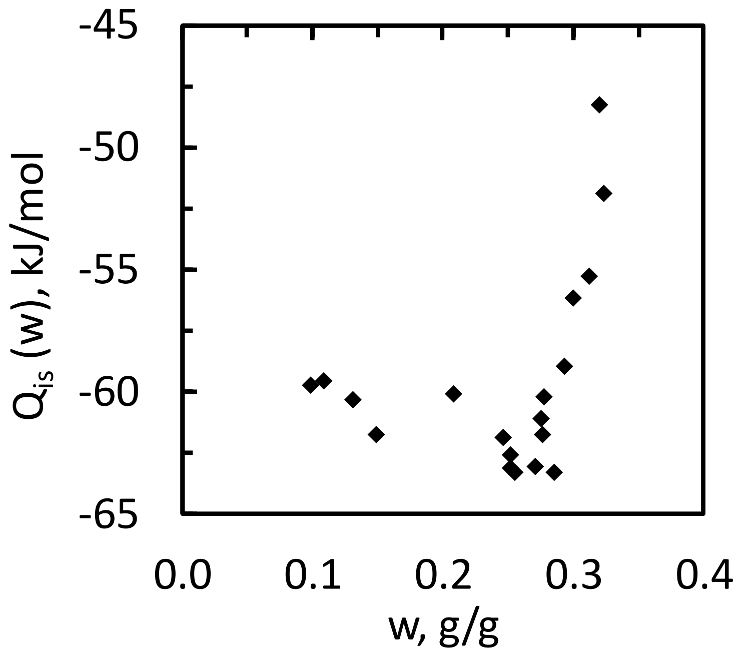
Uptake

w = $\text{mass}_{\text{adsorbate}}/\text{mass}_{\text{dry adsorbent}}$)

LAEC
Laboratory for
Alternative Energy
Conversion

Isosters for water sorption of FAM-Z02 pellets





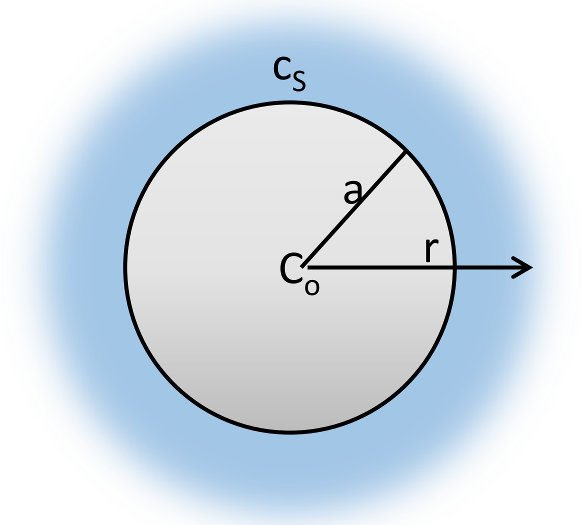
Isosteric heat of adsorption
van't Hoff equation

$$Q_{is}(w) = R\frac{d(lnP)}{d(1/T)}$$

Q_{is} (*w*) ~ 61 ± 2 kJ/mol
for *w* range 0.1 to 0.3 g/g

Attempt to determine effective diffusivity from small pressure step TGA kinetic data

- Uniform initial adsorbate concentration, C_o, in the particle
- Constant adsorptive concentration, c_s, at the surface of the particle
- Good mass transfer around particle and constant mass diffusivity
- Uptake is controlled by diffusion mass transfer
- Solid-side resistance on surface of sphere
- Radial diffusion of adsorbate
- Isothermal process



Spherical particle, showing boundary conditions

$$\frac{\partial c}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right)$$

Mass balance

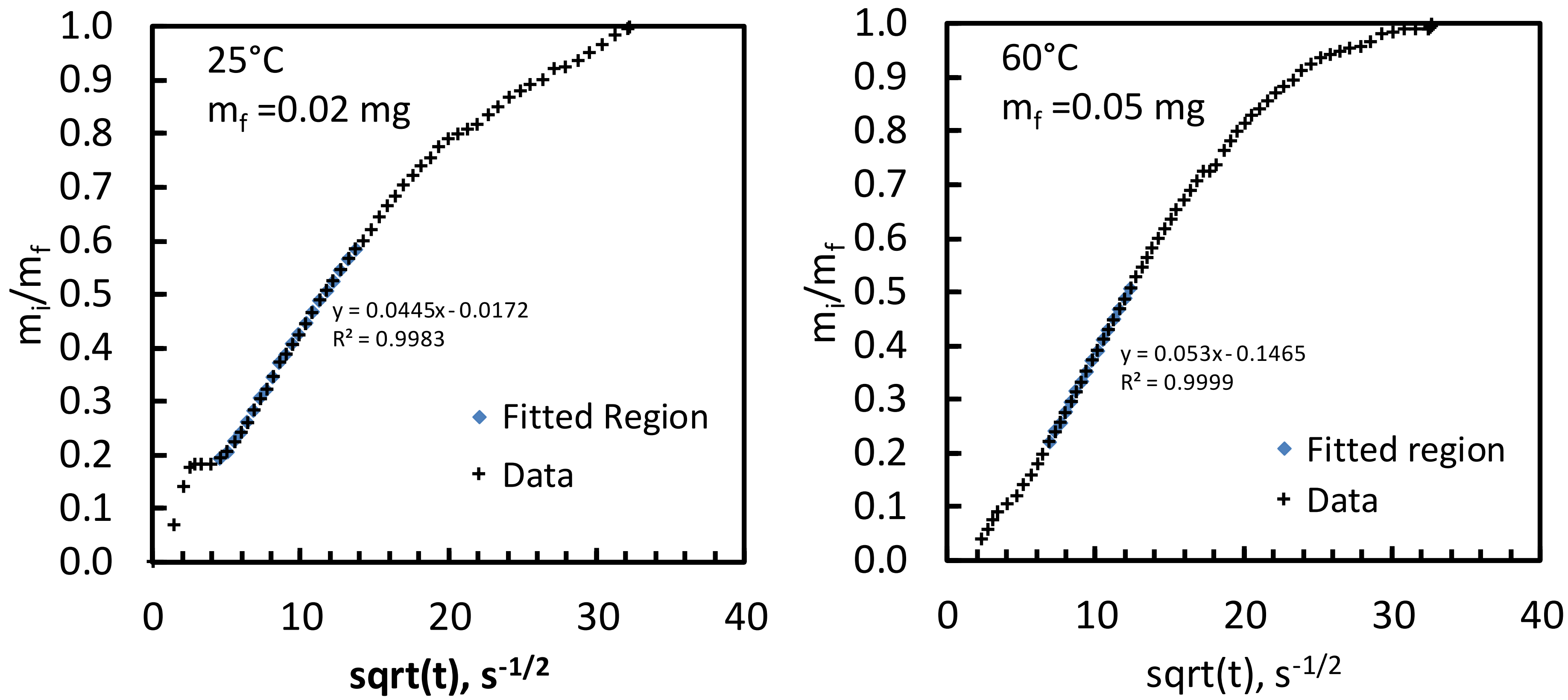
$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 D_{eff}\, t}{r^2}\right)$$

$$\frac{m_t}{m_\infty} \approx \frac{6}{\pi}\sqrt{\left(\frac{D_{eff}\, t}{r^2}\right)}$$

for small times

Strategy: Fit the initial linear portion the kinetic curves for small pressure steps (e.g. 0.3 or 0.5 mbar) plotted as a function of sqrt(t)

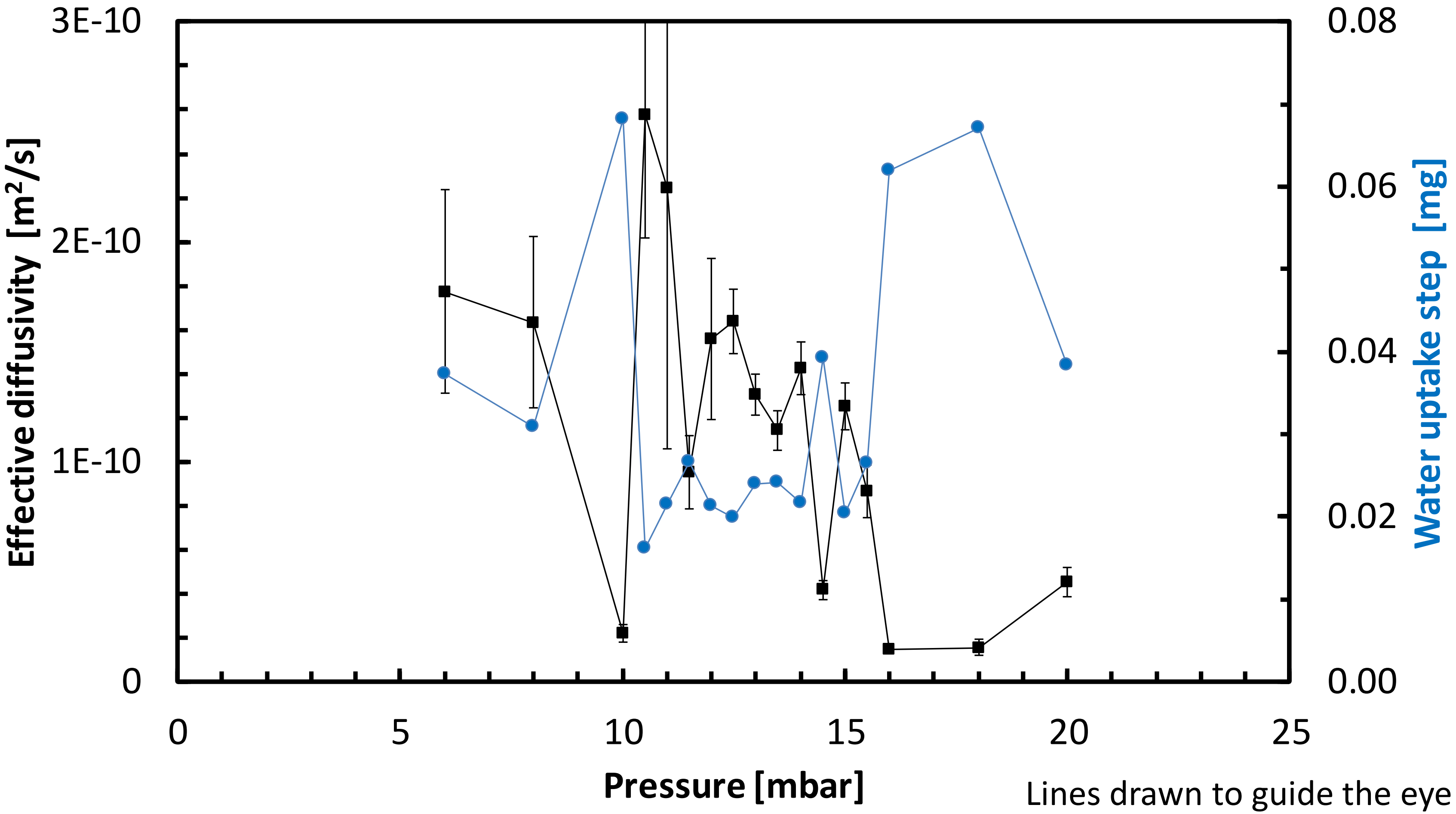
FAM-Z02 kinetic data fit



FAM-Z02 water uptake kinetics for
11.5 to 12 mbar pressure steps

SFU

Effective diffusivity from 25°C isotherm with 0.5 mbar steps

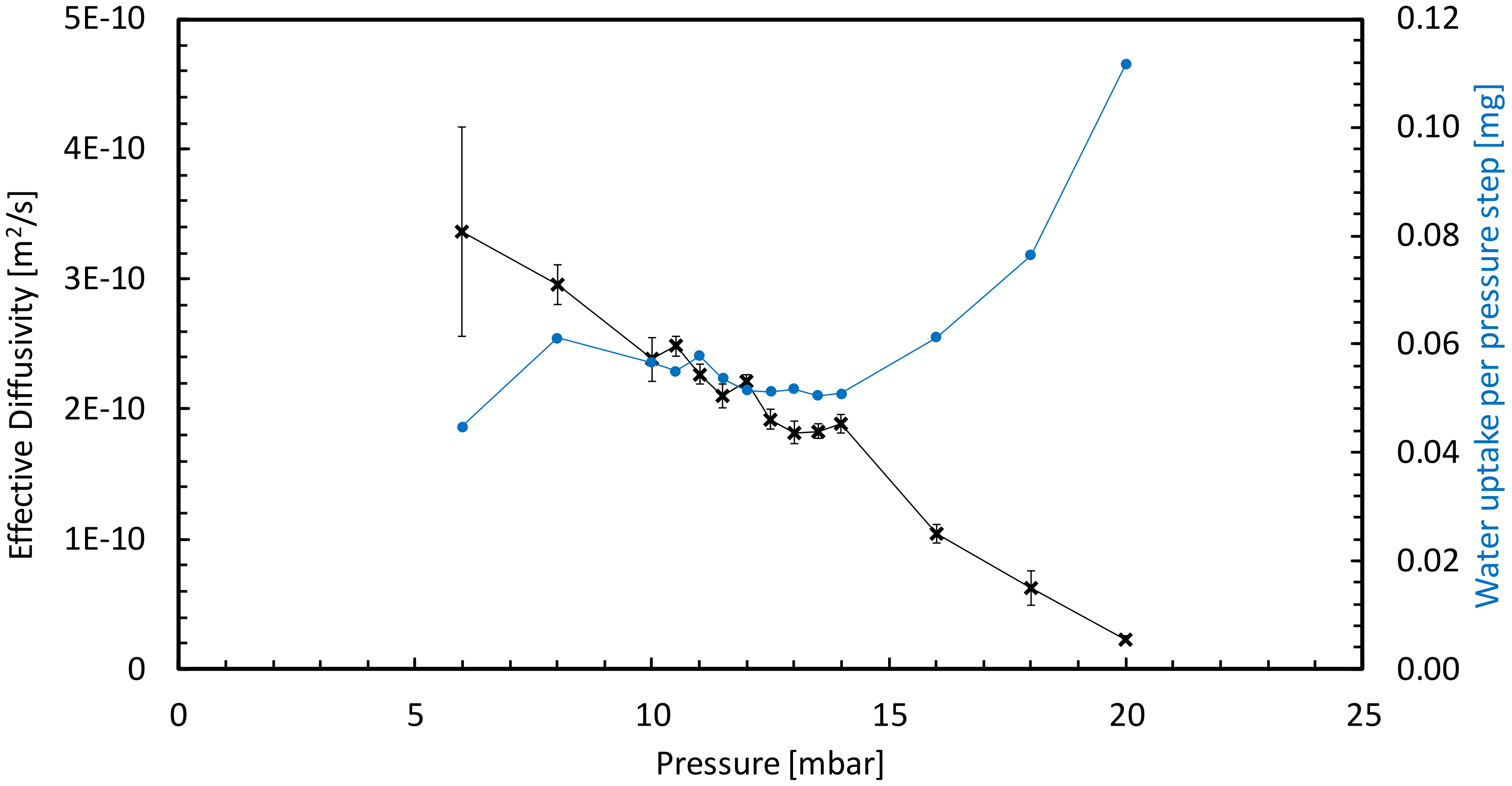


Lines drawn to guide the eye

- The highest effective diffusivities were calculated from fits for 0.5 mbar pressure steps where the least amount of water was adsorbed (e.g. 0.02 mg adsorbed by a 20 mg sample)

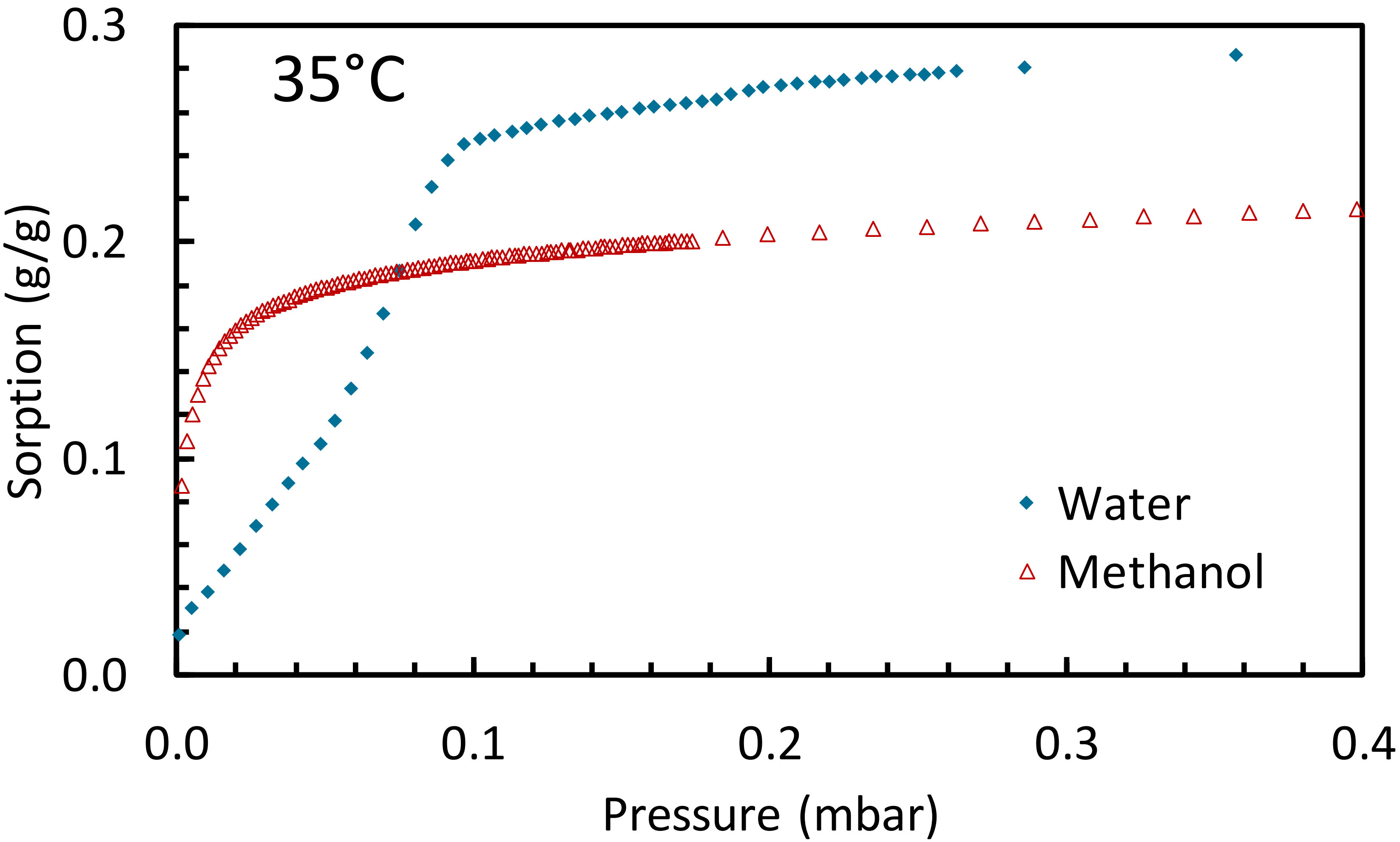
LAEC Laboratory for Alternative Energy Conversion

Effective diffusivity from a 60°C isotherm with 0.5 mbar steps



- The uptake rate observed is clearly influenced by the rate of heat dissipation to the constant temperature low pressure vapor surrounding the sample

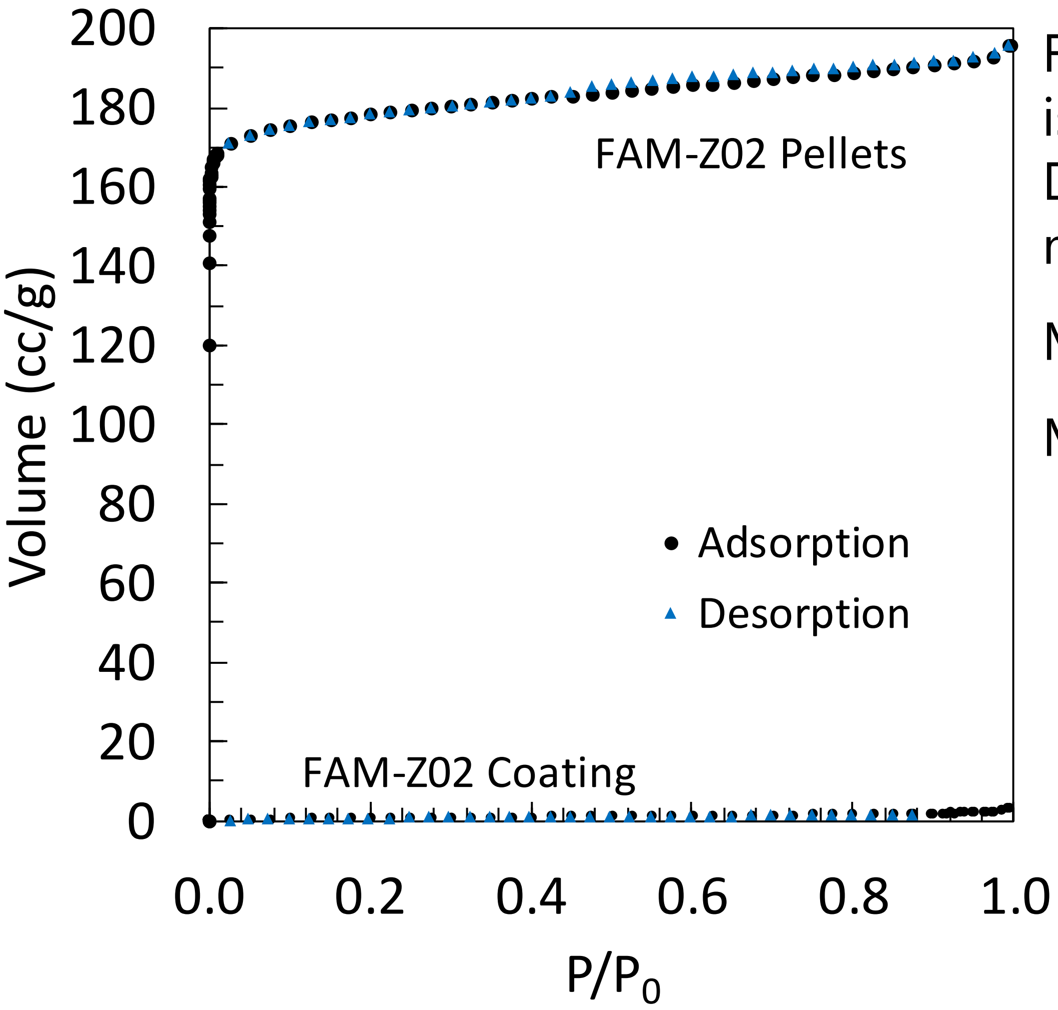
FAM-Z02 water and methanol adsorption isotherms



- FAM-Z02 is not a useful adsorbent for a methanol-based sorption cycle

SFU

Nitrogen adsorption porosimetry of FAM-Z02



FAM-Z02 nitrogen adsorption isotherm (Type I curve) fit with Dubinin–Radushkevich (DR) method.

Micropore volume: 0.265 cc/g

Micropore surface area: 746 m^2/g

Adsorption cross sections:

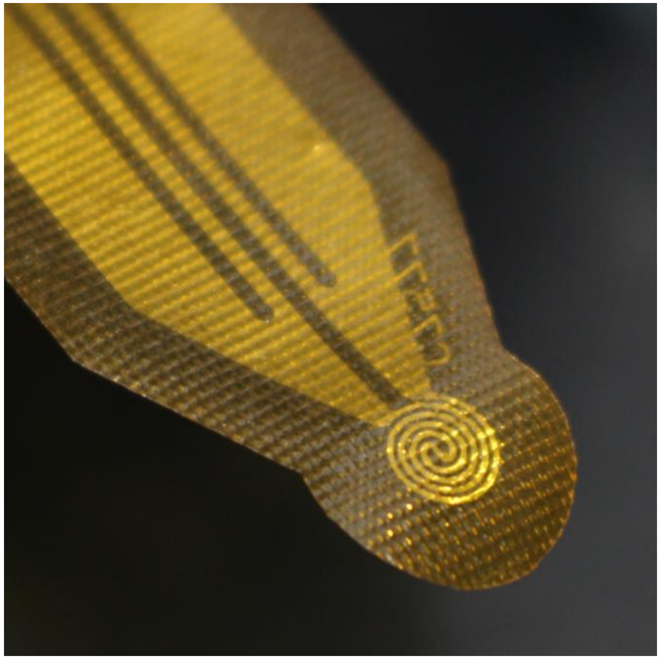
N_2 σ = 0.162 nm^2

H_2O σ = 0.106 nm^2

LAEC Laboratory for Alternative Energy Conversion

SFU

Transient plane source (TPS) thermal analysis



Kakiuchi et al. 2005
0.117 W/m·K at 30°C
0.822 J/g·K

A thin foil double-spiral of nickel is used to resistively heat the sample and monitor the temperature change as a function of time.

Three samples of 2 mm FAM-Z02 pellets, each measured five times.

Thermal conductivity

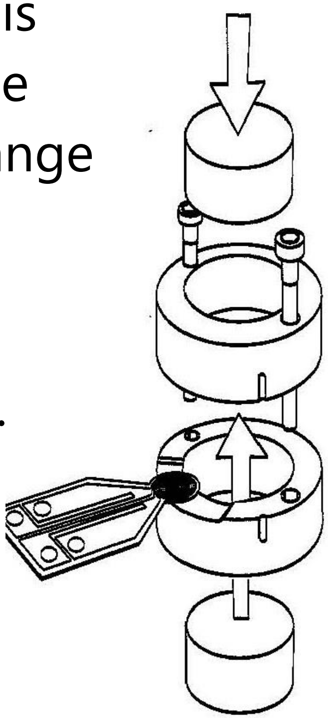
0.139 ± 0.005 W/m·K

Thermal diffusivity

$0.33 \pm 0.5\ \mathrm{mm^2/s}$

Specific Heat

$0.42 \pm 0.5\ \mathrm{MJ\ m^3/K}$
0.56 J/g·K (pellets ~757 g/L)



Powder Cell

LAEC
Laboratory for Alternative Energy Conversion

Conclusions

- The binder in FAM-Z02 pellets and coatings reduces the water sorption capacity by 9% and 14%, respectively

- Nitrogen adsorption data indicates that the binder in FAM-Z02 coatings appears to impact the width of the surface pores

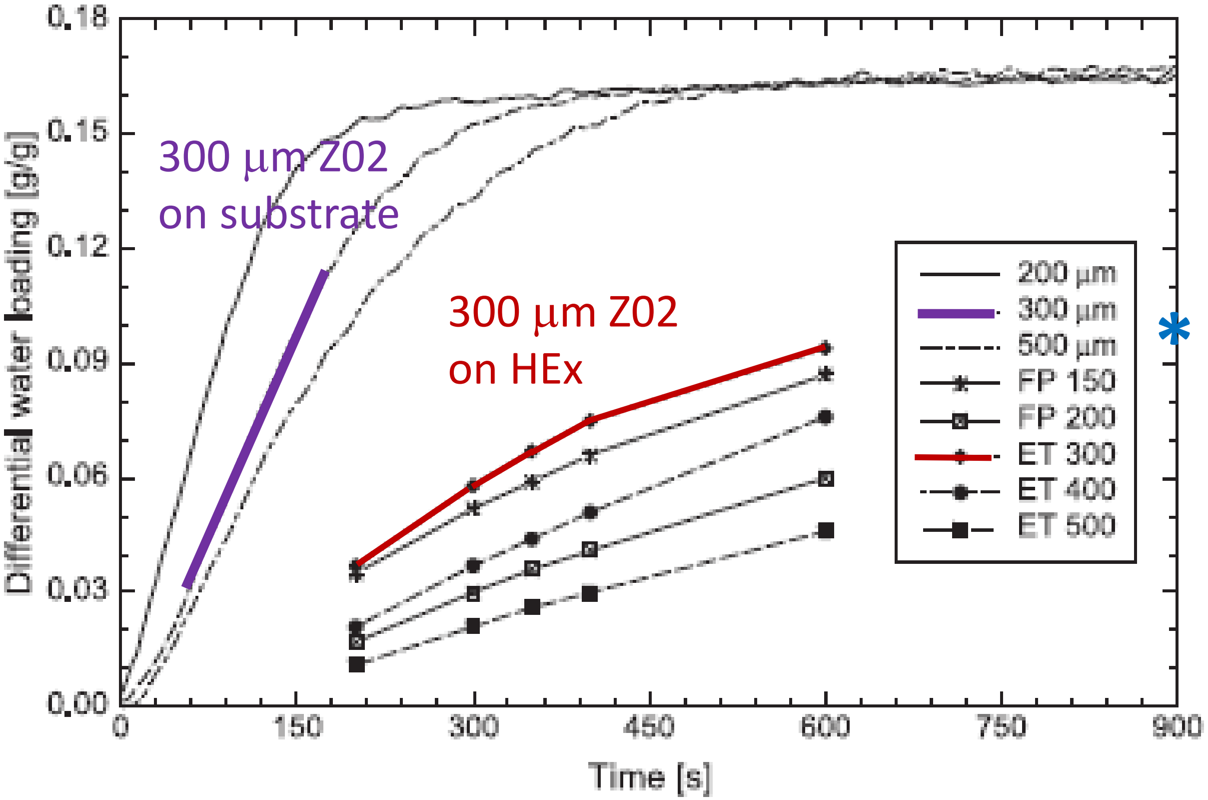
- The effective diffusivities calculated from the kinetic data from our pressure step gravimetic sorption curves are heat dissipation limited

- FAM-Z02 can adsorb a significant amount of methanol, however the regeneration temperature would be to great for an effective sorption cycle

Characteristic Curve

Adsorption kinetics of ZO2 coated heat exchangers

Dawoud, *Appl. Therm. Eng.* 50 (2013) 1645



Small aluminum substrates coated with 200, 300 and 500 μm thick FAM-Z02.

Aluminum HEx coated with by 150-500 μm FAM-Z02 (1.5-2.5 kg adsorbent on 5.6-6.6 kg HEx)

Resistance increase of electrically heated disk as a function of time:

$$R(t) = R_0\{1 + \alpha \cdot [\Delta Ti + \Delta Tave(\tau)]\}$$

R_0 = initial resistance of the nickel sensor
α = temperature coefficient of resistivity
ΔTi = constant temperature difference over the thin Kapton insulating layers covering both sides of the nickel hot disk sensor
$\Delta Tave(\tau)$ = sample surface temperature increase

Time-dependent temperature increase:

$$\Delta Tave(\tau) = \frac{P_0}{\pi^{3/2} \cdot a \cdot \Lambda} \cdot D(\tau)$$

P_0 = power output of sensor
a = sensor radius
Λ = thermal conductivity
$D(\tau)$ = Dimensionless time function

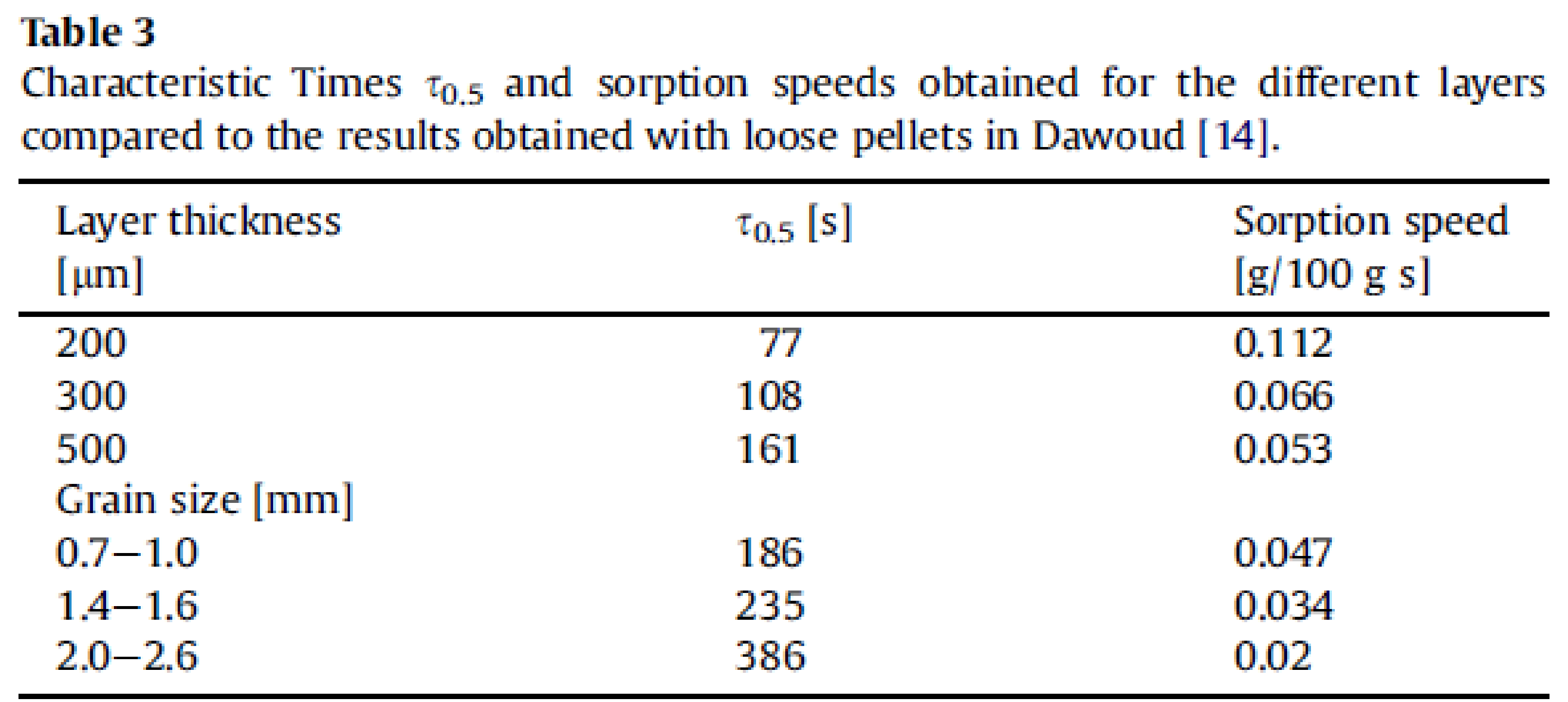


Table 3

Characteristic Times $\tau_{0.5}$ and sorption speeds obtained for the different layers compared to the results obtained with loose pellets in Dawoud [14].

Layer thickness [μm]	$\tau_{0.5}$ [s]	Sorption speed [g/100 g s]
200	77	0.112
300	108	0.066
500	161	0.053
Grain size [mm]		
0.7–1.0	186	0.047
1.4–1.6	235	0.034
2.0–2.6	386	0.02

- Water uptake rate of ZO2 is faster in films than in loose grains
- Thinner films and smaller grains have highest uptake rate
- Attributed to increase of both heat and mass transfer resistances with increasing the layer thickness

Note: Adsorption systems never operate from x_0

$$V_S = \frac{(x_{0.5} - x_0)}{\tau_{0.5}}$$

LAEC
Laboratory for
Alternative Energy
Conversion

Dawoud, Appl Therm Engi 50 (2013)1645
Dawoud, J. Chem. Eng. Jpn. 40 (13)1298 & IMPRES conference 2007

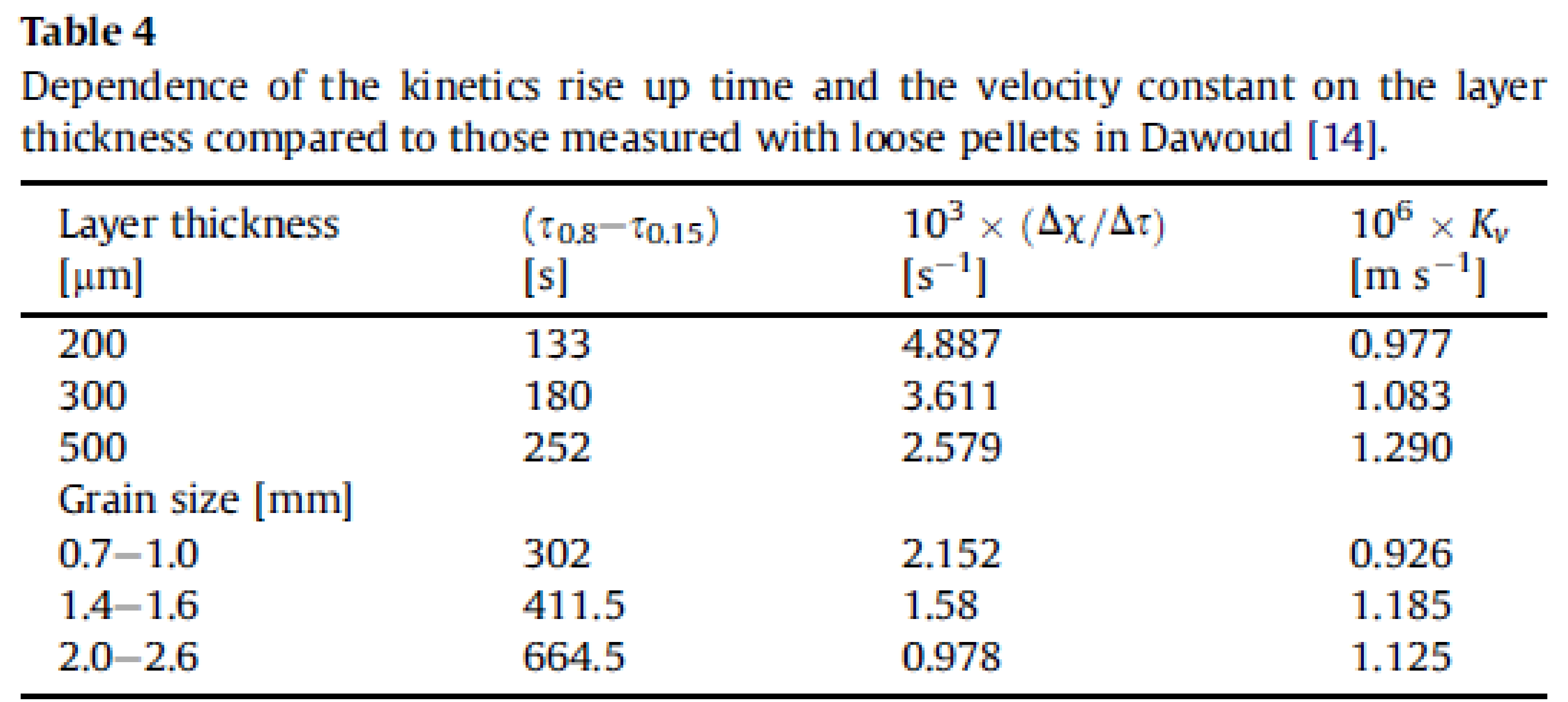


Table 4

Dependence of the kinetics rise up time and the velocity constant on the layer thickness compared to those measured with loose pellets in Dawoud [14].

Layer thickness [μm]	$(\tau_{0.8}-\tau_{0.15})$ [s]	$10^3 \times (\Delta\chi/\Delta\tau)$ [s^{-1}]	$10^6 \times K_v$ [m s^{-1}]
200	133	4.887	0.977
300	180	3.611	1.083
500	252	2.579	1.290
Grain size [mm]			
0.7–1.0	302	2.152	0.926
1.4–1.6	411.5	1.58	1.185
2.0–2.6	664.5	0.978	1.125

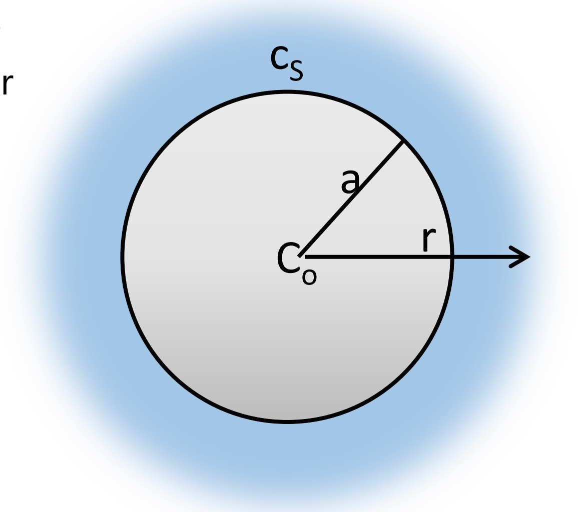
Dawoud, Appl. Therm. Eng. 50 (2013)1645
Dawoud, J. Chem. Eng. Jpn. 40 (13)1298 &
IMPRES conference 2007

Adsorption kinetic data fitting

- <u>Key Assumptions:</u>[1]

- Initial adsorbate concentration (c_o) is uniform throughout particle
- Constant concentration of adsorbate (c_s) at surface of adsorbent particle
- Adsorbate uptake is controlled by diffusion mass transfer
- Solid-side resistance on surface of sphere
- Radial diffusion of adsorbate
- Constant mass diffusivity
- Isothermal process
- Good mass transfer

  around particle
- *Fickian* process



$$\frac{\partial c}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)^{[1,2]}$$

Mass balance

↓

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 D_{eff}t}{r^2}\right)$$

Series solution

↓

$$\frac{m_t}{m_\infty} \approx \frac{6}{\pi}\sqrt{\left(\frac{D_{eff}t}{r^2}\right)}^{[2]}$$

(on small times = t)

↓

Linearizing, where: $x = \sqrt{t}$

$$\frac{m_t}{m_\infty} = \left(\sqrt{\left(\frac{6}{\pi}\right)^2\left(\frac{D_{eff}}{r^2}\right)}\right)x$$

Plotting uptake data vs. SQRT(time), we perform linear regression on multiple intervals on “short” times, picking interval with highest r^2, yielding our coefficient.

↓

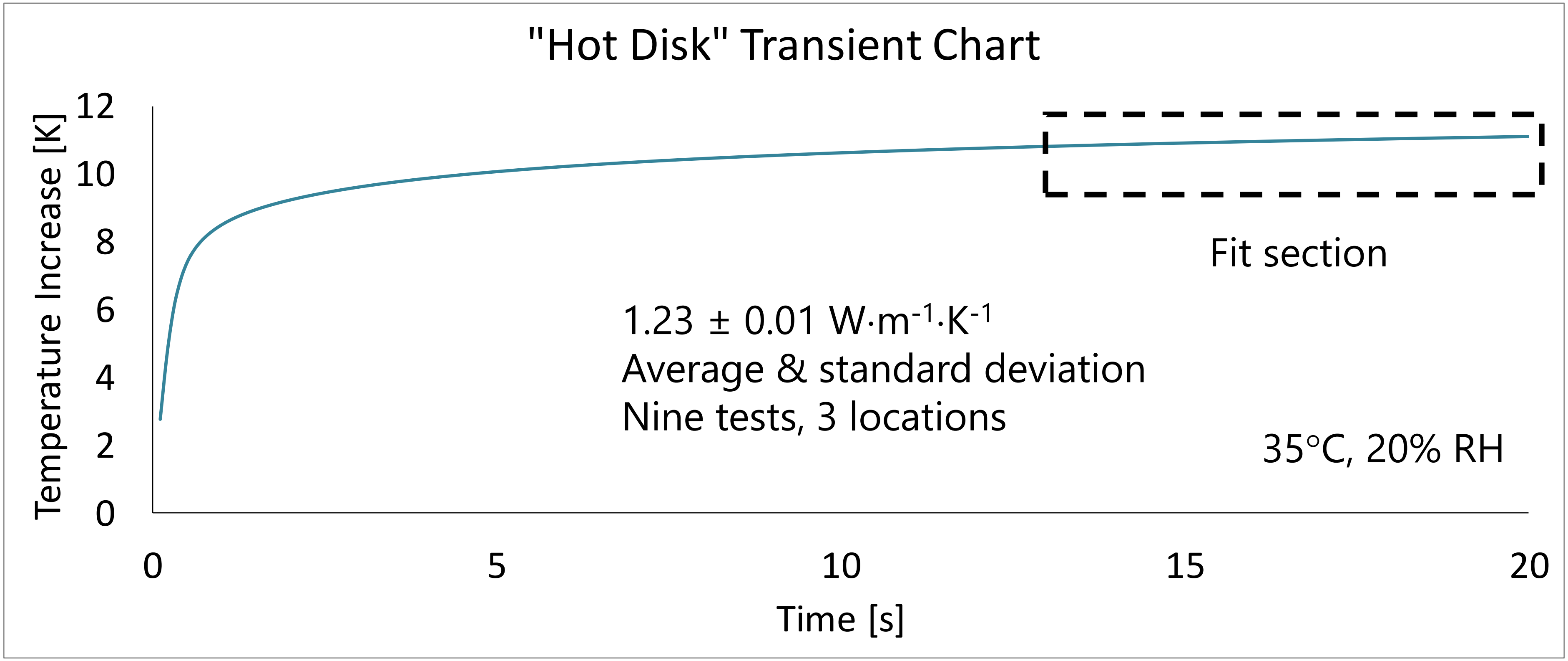
$$F_O = \frac{D_{eff}t}{r^2}$$

Mass Fourier number

↓

$$\frac{m_t}{m_\infty} = 1 - \exp(-15F_O)^{[1,3]}$$

(on F_O greater than 0.1)



- **Sample:** 8 mm thick, 30%wt $CaCl_2$, 30%wt silica gel, 25%wt graphite flakes, 15%wt polyvinylpyrollidone (binder, 40,000 MW)
- Specific heat measured & value entered for fit

- **TPS test**
  - Sensor radius 3.189 mm
  - Pulse 0.15 W, 20 s
  - Temperature rise 0.4 s
  - Penetration depth ~ 6 mm

Thermodynamic data for “sorptive-sorbent” pairs

- *Polanyi potential theory.*
  - Considers the adsorption similar to condensation; the adsorbed state behaving like a liquid.
  - The principle of temperature invariance:

$$T_a \ln(h_a) = T_b \ln(h_b)$$

at temperatures, T_1 and T_2, equal uptake at the gas pressures, P_1 and P_2, linked as in the equation above.

$h = P/P_0$ relative pressure of the adsorbate

- *Dubinin.*
  - Free energy of adsorption or adsorption potential

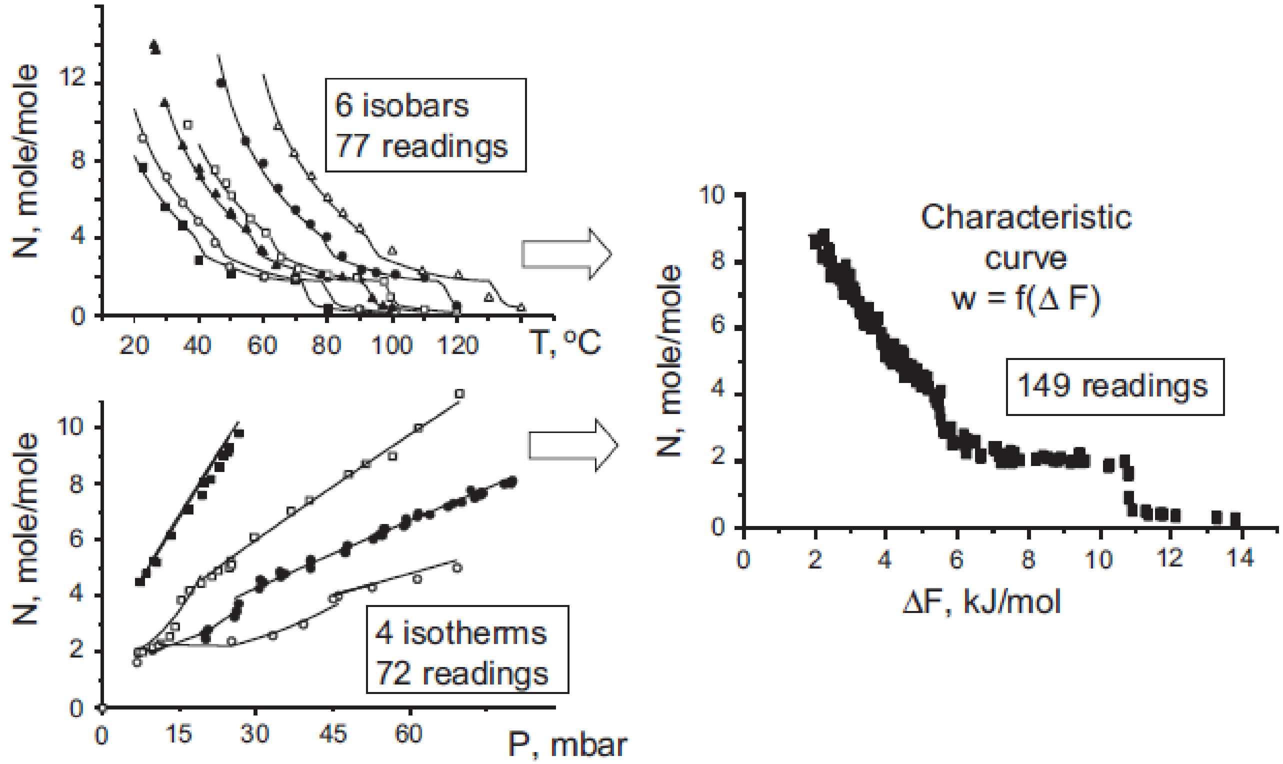
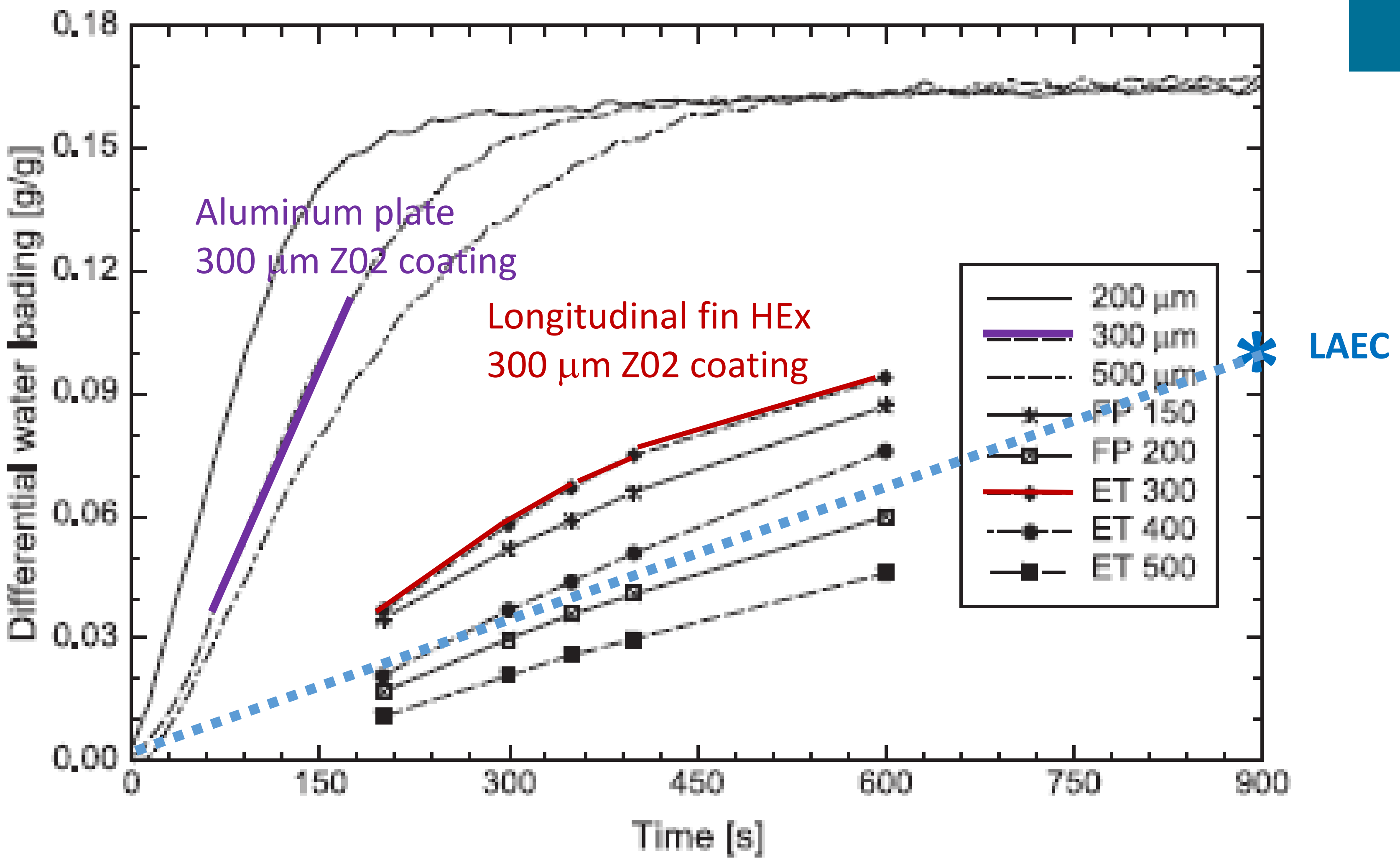


Fig. 2. The experimental isobars and isotherms of water sorption on the composite "$CaCl_2$/silica gel KSK" taken from [4] and [27] and the characteristic sorption curve.

Table 1

Approximation functions $f(\Delta F)$ and appropriate ΔF-ranges (composite $CaCaCl_2$/silica [24]).

No	ΔF, kJ/mol	w [g/g] = $f(\Delta F)$
1	> 5.32	$-0.267795\ln(\Delta F) + 0.672705$
2	5.32–5.78	$-0.121753(\Delta F) + 0.87626$
3	5.78–10.50	$0.00324043(\Delta F-10.5)^2 + 0.0999768$
4	10.5–10.84	$-0.1451285(\Delta F) + 1.623655$
5	10.84–11.15	$-0.689315(\Delta F) + 0.79816$
6	> 11.15	$3.065205\exp(-0.4155\Delta F)$



Aluminum plate
300 μm Z02 coating

Longitudinal fin HEx
300 μm Z02 coating

LAEC

We only have one point for comparison to this graph. The 15 minute point in an uptake cycle from dry to equilibrium for 1.5 kg pellet Z02.

NOTE: Our uptake rate was evaporator power limited.

Also, our T_{evap}=10°C vs Dawoud's experiments with T_{evap}=5°C