Lab-scale sorption chiller comparison of FAM-Z02 coating and pellets

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The food cold-chain

World population: 7.3 billion

Food losses due to lack of refrigeration: 25%

Projected population: 8.5 billion by 2030

Developed countries: 627 refrigerators per 1000 people

Developing countries: 70 refrigerators per 1000 people

How much power would be required to provide cold storage to this portion of the world population?

S.J. James, C. James, “The food cold-chain and climate change”, *Food Res. Int.*, **43** (2010) p. 1944
Transportation of refrigerated and frozen food

The current worldwide cold-chain for transport of food uses approximately:

- 1300 refrigerated cargo ships
- 80,000 refrigerated railcars
- 650,000 refrigerated containers
- 1.2 million refrigerated trucks

Heap, 2006; McKinnon & Campbell, 1998; Brodt, Chernoh, & Feenstra, 2007
Review of tests of Z02-water samples and sorption chillers

- Freni et al. (2015): 0.1 mm SAPO-34 (84 g) on aluminium finned flat tube HEx (510 g) with SCP 675 W/kg, VSCP of 93 W/dm³ (5 min cycles under 15 °C/28 °C/90 °C)
- Santamaria et al. (2014): Temperature jump tests on small HEX (70-90 g of Z02 grains) with cooling powers up to 2.3 kW/kg, 6-8 times greater than tests larger prototypes (ie. 280-380 W/kg)
- Dawoud et al. (2013): Adsorption kinetics of Z02 coatings (0.2-0.5 mm) on small substrates and extruded finned-tube and finned-plate Hex.

The specific cooling power of our first runs of Z02 coated heat exchangers in our sorption chiller peaked at a specific cooling power ~200 W/kg, indicating that the overall system needed improvement.
Components
Flow Control

8 solenoid valves for controlling the heating/cooling fluid flow to the beds

Back pressure in a solenoid valve will lead to reverse flow

4-way valves for faster switching and elimination of crosstalk between the chillers

(Actually, reduce crosstalk... we operate with a deliberate switching delay between change of inlet sources, and change of outlet...)

Replaced eight valves with two 4-way valves
Upgrade to gate valves for the evaporator

- Observed 1 kPa pressure difference between evaporator and the bed in early tests

- Larger piping and valves reduce pressure drop between the beds and the evaporator
LAEC Modular 2-Bed Sorption Chiller

Two sorber beds (1,2)
Condenser (3)
Capillary-assisted low-pressure evaporator (4)
Check valves, gate valves, 4-way valves
Four heating/cooling (H/C) circulators
Thermocouples, pressure sensors
Flow meters
Scroll vacuum pump

Graph showing temperature changes over time:
- Temperature (°C) on y-axis
- Time (s) on x-axis
- Temperature ranges: 0 to 100°C
- Time range: 0 to 1800 seconds

Diagram of the system:
- H/C 30°C
- H/C 15°C
- H/C 90°C
- 2 sorber beds labeled 1 and 2
Flow meters don’t like temperature swings

**FIX:** Change the positions of the flow meters so they operate at a single temperature

Flomec (OM015S001-222) meters, rated to 120°C
Temperature jump tests by Glaznev et al. on loose grain silica gel and salt/silica gel composites showed reduction of the adsorption rate even for low partial pressure of residual air (e.g. 0.06 mbar) [1], [2]

The custom-built capillary-assisted low pressure evaporators used in our system has finned copper tubes. It is operated in an aluminum vacuum chamber, therefore corrosion is expected.

When we swing adsorber bed temperature, the valves connecting the adsorber bed to the condenser and the evaporator are both closed for several seconds, allowing us to evacuate residual gas “on the fly” between cycles during runs.

and
Lab-scale Sorption Chiller

- The heat and mass transfer resistances increase with increasing sorbent layer thickness and pellet size.
- This lowers the water uptake rate and the specific cooling power of the system.

FAM AQSOA-Z02 silicoaluminophosphate developed by Mitsubishi Plastics

A. Sharafian, et al., *Energy* 112 (2016) 481
Dawoud, *Appl Therm Eng* 50 (2013) 1645
Adsorber bed heat exchanger

Copper tube (black painted), aluminum fin

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>HEx (L,W,H)</td>
<td>35.2×3.8×30.5 cm³</td>
</tr>
<tr>
<td>Fin spacing</td>
<td>2.54 mm (10 fpi)</td>
</tr>
<tr>
<td>Surface area</td>
<td>2.8 m²</td>
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<tr>
<td>HEx weight</td>
<td>2.51 ± 0.03 kg</td>
</tr>
<tr>
<td>Z02 coating</td>
<td>0.80 kg per HEx</td>
</tr>
<tr>
<td>Z02 pellets</td>
<td>1.97 kg per HEx</td>
</tr>
</tbody>
</table>

\[ Q_{evap} = \int_{0}^{\tau} mc_p (T_{in} - T_{out}) dt \]

\[ \text{COP} = \frac{Q_{evap}}{Q_{heat}} \]

\[ \text{SCP} = \frac{Q_{evap}}{(m_{ads} \cdot t_{cycle})} \]

\[ VSCP = \frac{Q_{evap}}{(V_{ads} \cdot t_{cycle})} \]
Functionalized Adsorbent Material (FAM)  
ASQOA-Z02


\[ \text{Si}_x\text{Al}_y\text{P}_z\text{O}_2\cdot n\text{H}_2\text{O} \]

\[ x = 0.05–0.25, \quad y = 0.4–0.6, \quad z = 0.25–0.50, \quad n = 0–1.5 \]

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

Pellets: 1.9 mm  
Zeolite: 83–94% wt  
\( \text{SiO}_2 \) binder: 6–17% wt
- The Z02 pellets adsorbed ~9% less than the Z02 powder
- The Z02 coating adsorbed ~ 13.6% less than the Z02 powder
Water isotherms for Z02 pellets: Adsorption curves
Z02 pellet characteristic curve

\[ \Delta F = -RT \ln \left( \frac{P}{P_0} \right) \ (kJ/mol) \]

- 5.5 C
- 15.0 C
- 24.8 C
- 34.8 C
- 39.3 C
- 49.4 C
- 78.7 C
Water sorption isotherms for Z02 powder:
Adsorption and desorption curve
Coating and pellet isotherms: Adsorption curves at 35°C

FAM ASQOA-Z02
\[ \Delta w_{\text{coating}} \approx 0.17 \text{ g/g} \]

Uptake
\[ 0.17 \text{ g/g} \times 804 \text{ g} = 136 \text{ g H}_2\text{O} \]

\[ \Delta w_{\text{pellet}} \approx 0.18 \text{ g/g} \]

Uptake
\[ 0.19 \times 1972 \text{ g} = 375 \text{ g H}_2\text{O} \]

But sorption chiller performance depends on uptake rate not capacity

Ignoring the complications....
Specific cooling power as a function of cycle time

Performance of two adsorber bed sorption chiller, testing of two Z02 coated beds and two Z02 pellet beds

Heat Transfer at the Evaporator

\[ Q_{evap} = \int_0^\tau m c_p (T_{in} - T_{out}) dt \]

Specific Cooling Power

\[ SCP = \frac{Q_{evap}}{m_{ads} \cdot t_{cycle}} \]

Volumetric Specific Cooling Power

\[ VSCP = \frac{Q_{evap}}{V_{ads} \cdot t_{cycle}} \]

Operating conditions: \( T_{evap} = 15^\circ C, T_{cond} = T_{ads} = 30^\circ C, \) and \( T_{des} = 90^\circ C \)
Evaporator cooling power can be used to calculate the water uptake rate of the sorbent.
吸附动态

字符时间，τ，通过无维吸附量随时间的拟合得到

\[ X(t) = 1 - e^{-t/\tau} \]

\[ \tau = 194 \pm 2 \text{ s} \]
Comparison to other tests of similar thickness Z02 coating (small samples and heat exchangers)

0.3 mm on small aluminum plate

300 s = 0.113 g/g = 66% equil.

Z02 coated (803.5 g) HEx
600 s = 0.163 g/g = 96% equilibrium uptake

Z02 COATING

Summary and Future Work

- The sorption chiller system performance is now satisfactory
- Two Z02 coated HEx operated with 10 min cycles at 15, 30, 90 °C operating conditions had a SCP of 456 W/kg (90 kW/m³) and COP of 0.27
- We have since tempted fate, running CaCl₂-silica gel adsorber beds in the lab scale chiller (some good data, and then, during downtime, corrosion in the evaporator accelerated beyond reason)
- The aluminum evaporator chamber was bead blasted and cleaned, and an anti-corrosion coating and a thin Teflon liner have been added
- Restart tests have been conducted with a Z02 coated bed and a loose grain microporous silica gel bed (Grace 408)
- Future test work includes new composites, new evaporator designs, new adsorber bed designs and difference chamber configurations
Thank you for your attention!

Sorption chiller testing is a team effort.

Mina & Ecem have talks in the 14:15 session this afternoon (H31)
Specific Cooling Power: CaCl\(_2\) composite tests

**SCP and System Power**

CaCl\(_2\) 0%G: 242 W/kg (630 ± 20 W)

CaCl\(_2\) 20%G: 192 W/kg (580 ± 20 W)

8 min cycles

NEXT:
- Swap the beds.
- Increase uptake capacity.
- Increase thermal conductivity.
- Review data.
- Think.

20% graphite

0% graphite

20% graphite

322 W/kg (517 W)

Z\(_{\text{02}}\) coating

Z\(_{\text{02}}\) pellet

103 W/kg (404 W)

CaCl\(_2\) 0%G

150 W/kg (453 W)

CaCl\(_2\) 20%G
Performance of Sorption Chiller Composite Beds
CaCl$_2$, B150 silica gel, PVA with 0% or 20% graphite flakes

Sorption Chiller Performance

15°C, 30°C, 90°C
20 min (1200 s) cycles

214 ± 2 W/kg CaCl$_2$ composite with 0 wt% graphite flakes

150 ± 2 W/kg CaCl$_2$ composite with 20 wt% graphite flakes

The difference in SCP for long cycles (beds adsorbing and desorbing to near equilibrium) reflects the difference in uptake capacities between the beds.
Expectations from sorption isotherm data

For a long cycle, we get 70% SCP from the graphite containing composite with 60% uptake capacity.

Sorption Chiller Performance for 15/30/90°C and 600 s cycles

- 15°C/30°C $P/P_0 = 0.06$
- 30°C/90°C $P/P_0 = 0.40$

0% graphite composite
$\Delta w = 0.45 - 0.08 = 0.37 \text{ g/g}$

20% graphite composite
$\Delta w = 0.30 - 0.08 = 0.22 \text{ g/g}$

214 ± 2 W/kg CaCl$_2$ composite with 0 wt% graphite flakes
150 ± 2 W/kg CaCl$_2$ composite with 20 wt% graphite flakes
Adsorption dynamics studied by a gravimetric large temperature jump method
Tested small scale adsorbers, based on commercial heat exchangers (HExs) filled with loose grains of the adsorbent AQSOA™-FAM-Z02.

- The experimental uptake curves are exponential
- Adsorption rate is extremely sensitive to traces of residual air
- The effect of hydrogen is less dramatic as compared with air
<table>
<thead>
<tr>
<th></th>
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<th>Cycle times</th>
<th></th>
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<tbody>
<tr>
<td>HEx (L,W,H)</td>
<td>35.2×3.8×30.5 cm³</td>
<td>5, 10, 20, 30 min</td>
<td></td>
</tr>
<tr>
<td>Fin spacing</td>
<td>2.54 mm (10 fpi)</td>
<td>(T_{\text{desorption}})</td>
<td>75, 80, 90 °C</td>
</tr>
<tr>
<td>Surface area</td>
<td>2.8 m²</td>
<td>(T_{\text{adsorption}})</td>
<td>20, 30, 40 °C</td>
</tr>
<tr>
<td>HEx weight</td>
<td>2.51 ± 0.03 kg</td>
<td>(T_{\text{condenser}})</td>
<td>20, 30, 40 °C</td>
</tr>
<tr>
<td>Z02 coating</td>
<td>0.80 kg per Hex</td>
<td>(T_{\text{evaporator}})</td>
<td>5, 10, 15 °C</td>
</tr>
<tr>
<td>Z02 pellets</td>
<td>1.97 kg per Hex</td>
<td></td>
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Sorption System Schematic
The temperature of the beds switch at the programmed cycle time, but adsorption only begins once the pressure in the adsorber drops to the trigger point for opening the gate valve.

The pressure drop time for Bed 1 and Bed 2 differ significantly.
Example of non-condensable gas effect in our system

30 min and 20 min cycles

- High condenser pressure decreased both uptake rate and total water uptake per 10 min half cycle.

20 min cycles

- 327 W/kg
- 210 W/kg
Temperature jump kinetic tests on loose grain silica gel and salt/silica gel composites:

- Reduction of the adsorption rate was revealed even at a partial pressure of residual air as low as $0.06 \text{ mbar}$.
- Dependence of the characteristic adsorption time on air partial pressure was found to be linear for partial pressures greater than $0.4 \text{ mbar}$, with the slope depending on the adsorbent nature.
- Desorption stage was less affected by the residual air.

A. Sapienza, et al. Dramatic effect of residual gas on dynamics of isobaric adsorption stage of an adsorptive chiller


Adsorption rate for SWS-1L loose grains 0.8–0.9 mm (1) and 1.4–1.6 mm (2) in the presence of different partial pressure of air ($P_A$). Symbols = experimental data; lines $m_t = m_0 + (m_f - m_0)[1 - \exp(-t/\tau_{\exp})]$.

Left to right $P_A = 0, 0.4, 1,$ and $4.7 \text{ mbar}$
For tests with short cycles and high SCP, the heater on circulator for desorption can be overwhelmed.

Desorption temperature drops with repeated cycling, resulting in a SCP decrease.

A rise in condenser temperature (and therefore pressure) can also be observed for individual cycles.