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Institute for Advanced Energy Technologies “Nicola Giordano”

Thermally driven adsorption heat pumps: recent advancements and future technical challenges

Giovanni Restuccia

Problématiques Scientifiques et Technologiques dans les Procédés Frigorifiques et Thermiques à Sorption
Paris 7/2/2014

SUMMARY

- Basics
- Current market Situation
- R&D priorities
  - Novel Adsorbent Materials
  - Adsorbent coatings
  - Adsorption machine components
  - Machine optimization and control
- Recent advancement at CNR-ITAE

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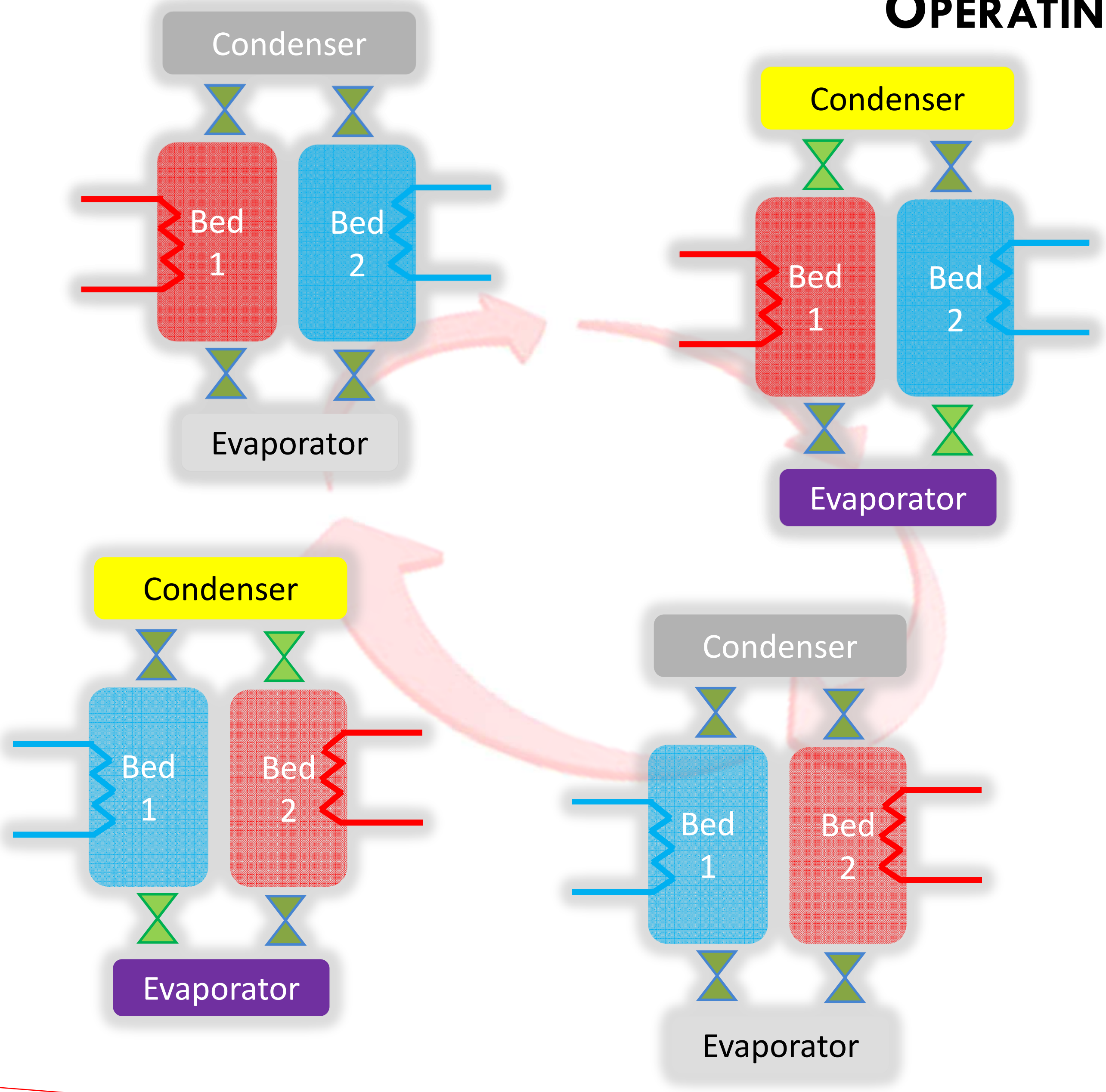
Thermally Driven ADsorption Machines

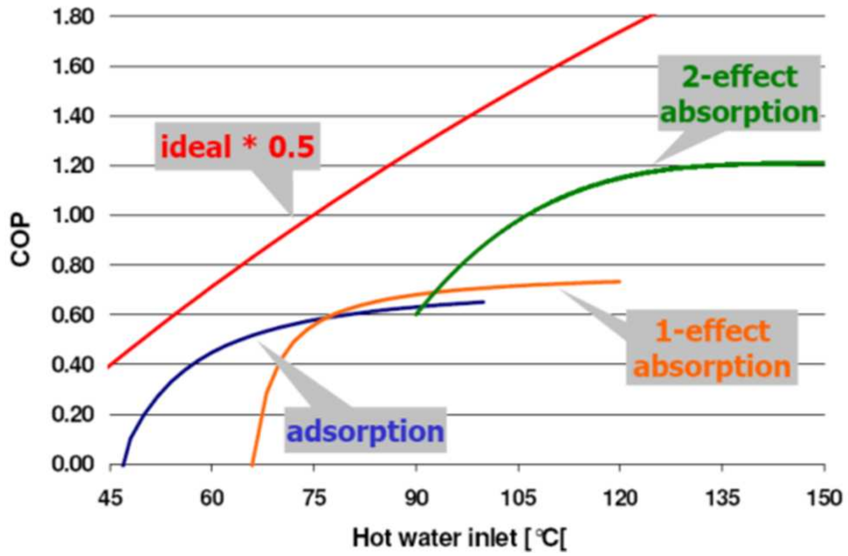
Operating Principle



Thermally Driven ADsorption Machines

PERFOMANCE AND DRAWBACKS

- ☹ Less studied and developed than liquid sorption
- ☹ Not a mature technology
- ☹ Few products on the market



Environmental aspect

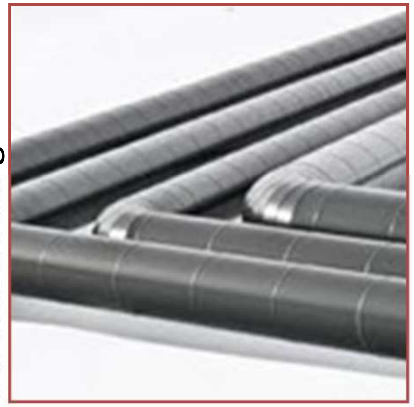
- ☺ Can be efficiently driven by a heat source at a temperature as low as 60- 80 °C
- ☺ Environmental friendly refrigerants (water)
- ☺ Silent operation

APPLICATIONS

Heat Sources for Adsorption Chillers

Automotive waste heat

District heating



Solar collectors

CHP units, process heat

- (Low-grade) waste heat recovery
- Tri-generation
- Air conditioning in vehicles or boats
- Solar cooling

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Brief history of adsorption chiller development

2000 – today

reliable products developed

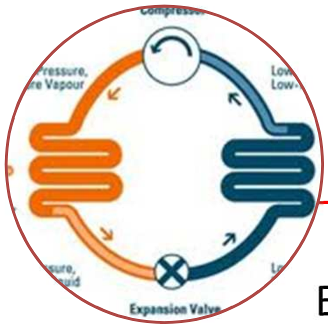
(better heat transfer quality, materials, controls)

Specific Cooling Power ~ 5-10 kW/m^3

1990 – 2000

No commercial products strong enough to survive, apart the Mycom silica gel /water chiller

Specific Cooling Power < 5 kW/m^3



1980 – 1990

Early studies and prototypes

- Meunier, Guilleminot, Pons et al. in Paris (AC/Meth, Zeolite/H2O)
- Tchernev in USA (zeolite/water)
- Shelton in USA (AC/Ammonia)
- Spinner in Perpignan (hygroscopic salts)
- Cacciola and Restuccia in Italy (zeolite/water)
- Groll in Germany (metal hydrides)
- Alefeld in Germany (zeolite/water)

Current market situation

SMALL SIZE UNITS

Vaillant

zeoTHERM VAS
heat pump
gas-fired
zeolite/water
10kW
Germany

SorTech AG

ACS08-15
chiller
water-fired
silica gel/water
8kW - 15kW
Germany

invensor

LTC10-18
chiller
water-fired
zeolite/water
10-18 kW
Germany

上海交通大學 SHANGHAI JIAO TONG UNIVERSITY

SHUANGLIANG

SWAC-10
chiller
water-fired
silica
gel/water
10 kW
China

Before 2012

Current market situation

SMALL SIZE UNITS

SolabCool
Chiller
water-fired
silica gel/water
4kW
Netherlands

SorTech AG

eCoo
chiller
water-fired
silica gel/water
12kW
Germany

VIESSMANN
climate of innovation

Vitosorp 200-F
heat pump
gas-fired
zeolite/water
16kW
Germany

MITSUBISHI PLASTICS

AQSOA
chiller
water-fired
zeolite/water
10 kW
Japan

After 2012

SORPTION ENERGY

heat pump
gas-fired
AC/ammonia
10kW
available in 2014
UK

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Current market situation

HIGH-CAPACITY CHILLERS

MAYEKAWA MYCOM

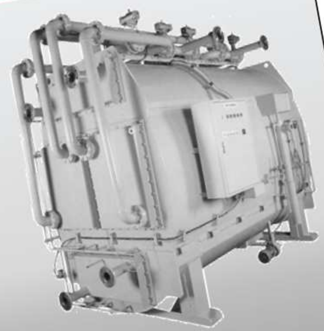
AdRef-Noa
chiller
water-fired
zeolite/water
105kW - 430kW
Japan

ECO-MAX adsorption chillers

Ad3
chiller
water-fired
silica gel/water
35 to 600 kW
USA

GBU

NAK/NAK-C
chiller
water-fired
silica gel/water
50 to 430 kW
Germany



NET new energy transfer

NUS-VEG
chiller
water-fired
silica gel/water
35 to 500 kW
Poland

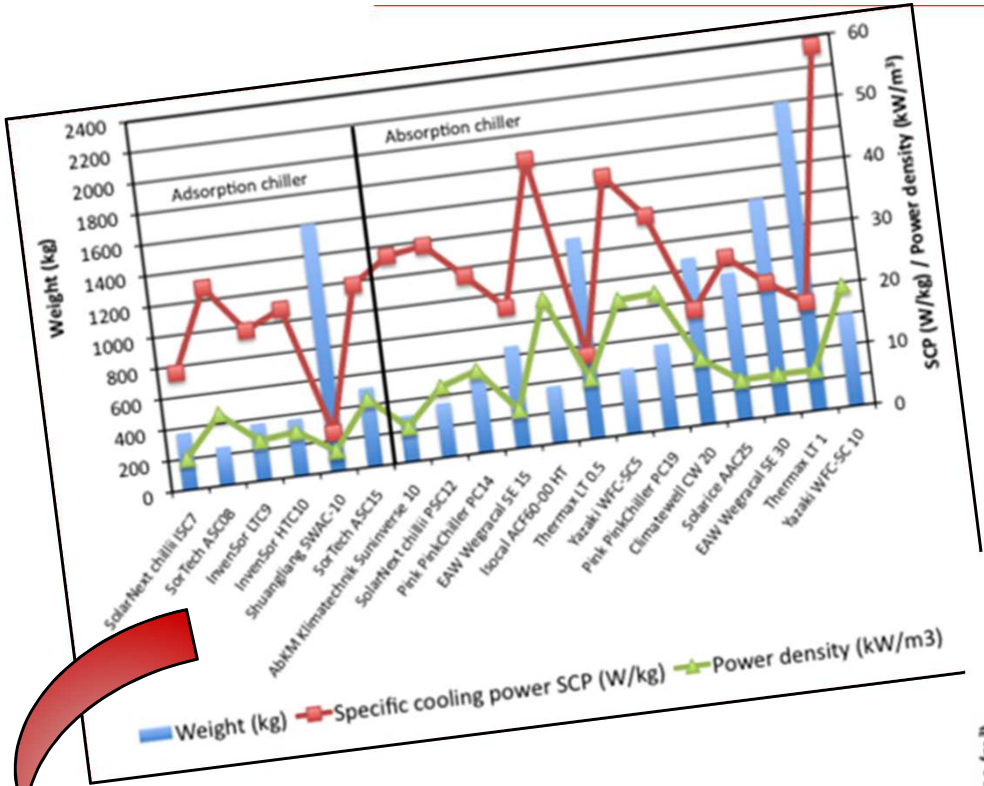
National Research Council of Italy

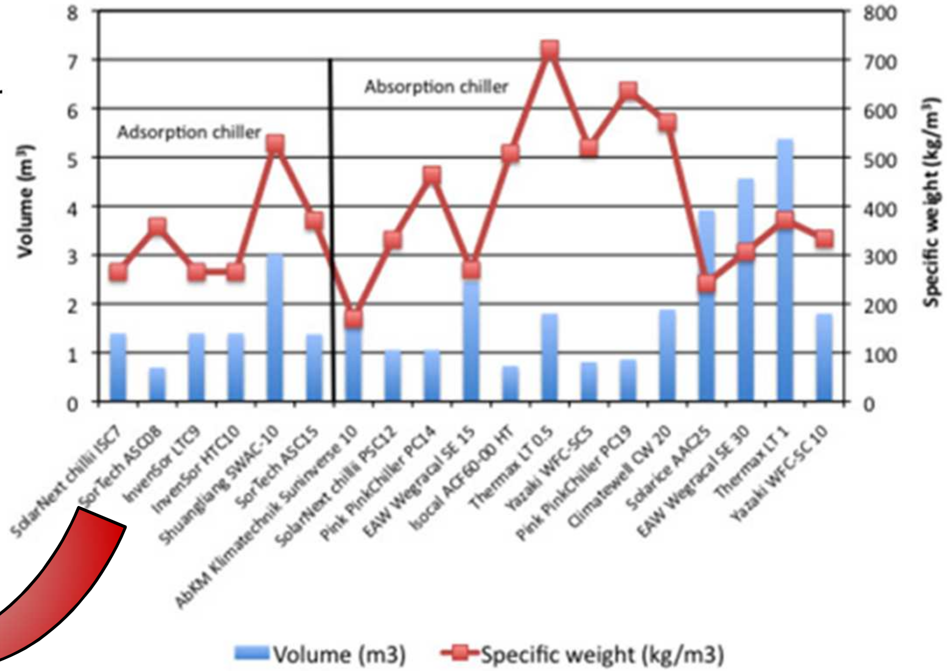
Current market situation

COMPARISON

The current market for solid sorption heat pumps is very small, due to:

- High capital costs
- Still too big and too heavy to compete with conventional systems
- Lower thermal efficiency and power density than liquid sorption systems





Advanced prototypes realized at:

Warwick University (UK)
ECN (NL)
SJTU (Ch)
CNR ITAE (IT)

Adsorption chillers/heat pumps development

MAIN ACTORS INVOLVED

THE UNIVERSITY OF WARWICK

ECN

UNIVERSIDAD POLITECNICA DE VALENCIA

Cnam

ITAE

Vaillant

VIESSMANN

Fraunhofer ISE

green chiller.de

ASIA

- 上海财经大学 Shanghai University of Finance & Economics
- Nagoya University
- MITSUBISHI PLASTICS

SUMMARY

- Basics
- Current market Situation
- **R&D priorities**
  - Novel Adsorbent Materials
  - Adsorbent coatings
  - Adsorption machine components
  - Machine optimization and control
- Recent advancement at CNR-ITAE

Future challenges

Materials

- Today a limited number of materials is used!
- New or modified adsorbents needed
- Stability over several thousand cycles

Components for adsorption machines

- Compact, lightweight, high surface area HEXs and adsorbent reactors
- Compact and low cost evaporator and condenser
- Coated adsorbent reactors

Machine optimization control & integration

- Advanced control strategies
- Compact and modular system designs

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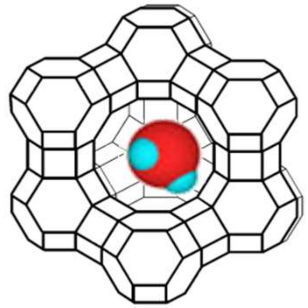
Development of advanced adsorbent materials

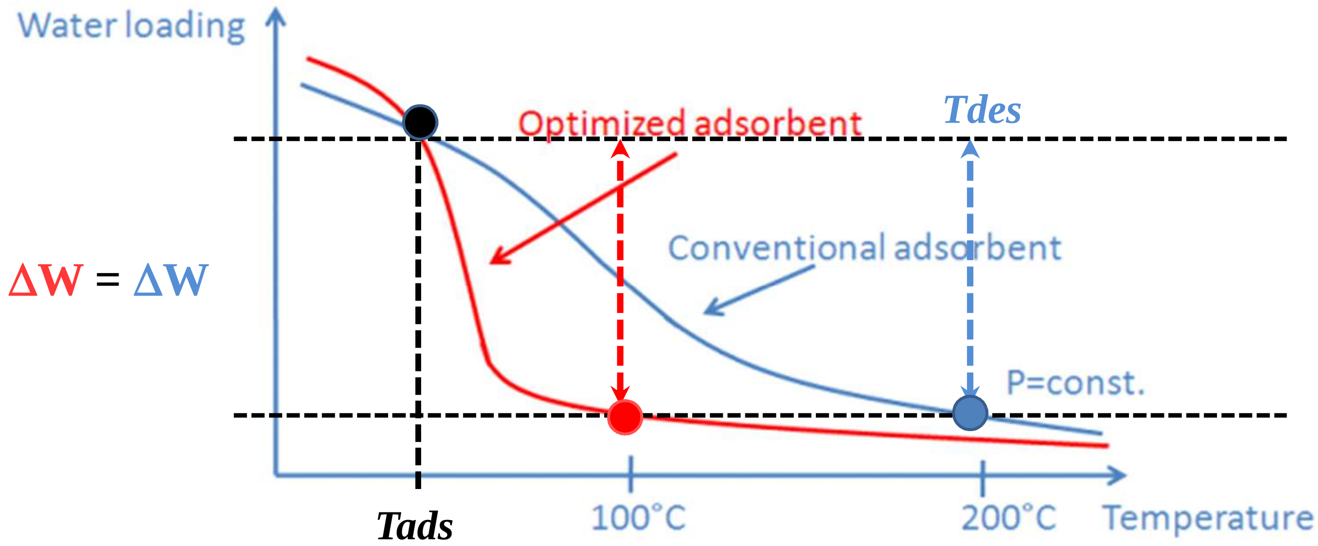
The adsorbent material is a key-element of an adsorption machine

Initially, adsoption heat transformers were realized using not optimized adsorbents

(Zeolite 4A, X, silica gel)



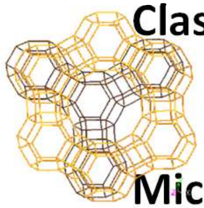
New generation of adsorption machines requires novel adsorbent materials with optimal adsorption properties



"New" adsorbent materials

- Composite Adsorbents «salt in matrix» (Selective Water Sorbents)
- Modified Zeolites (dealuminated zeolites, MeAPO)
- Metallic Organic Frameworks (MOFs) (Major trend)

The solution must be stable and cheap.



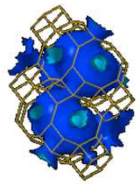
Classical zeolites (4A, 13X, DDZ 70 UOP)

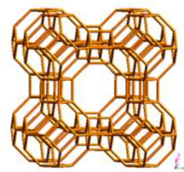
Microporous silica gel (e.g. Fuji Davison type RD)

Commercially available

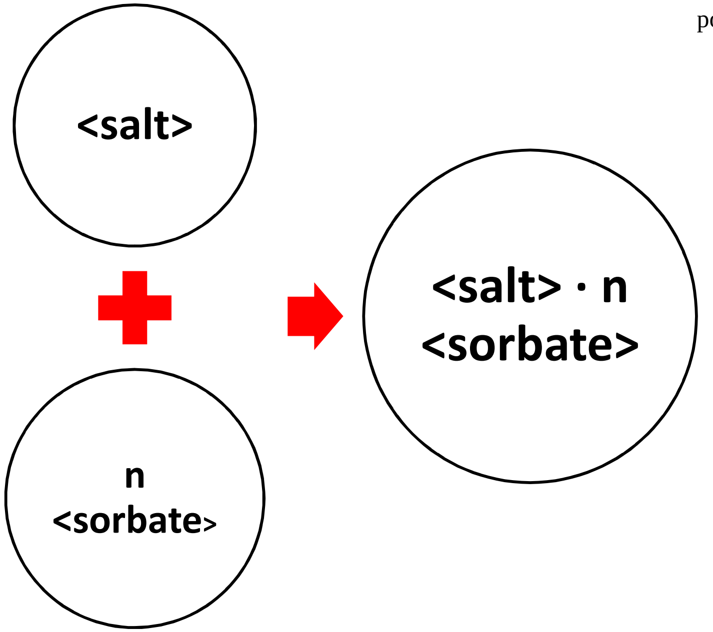
Aluminophosphates (SAPO34, AQSOA FAMZ02 from MITSUBISHI Plastics)

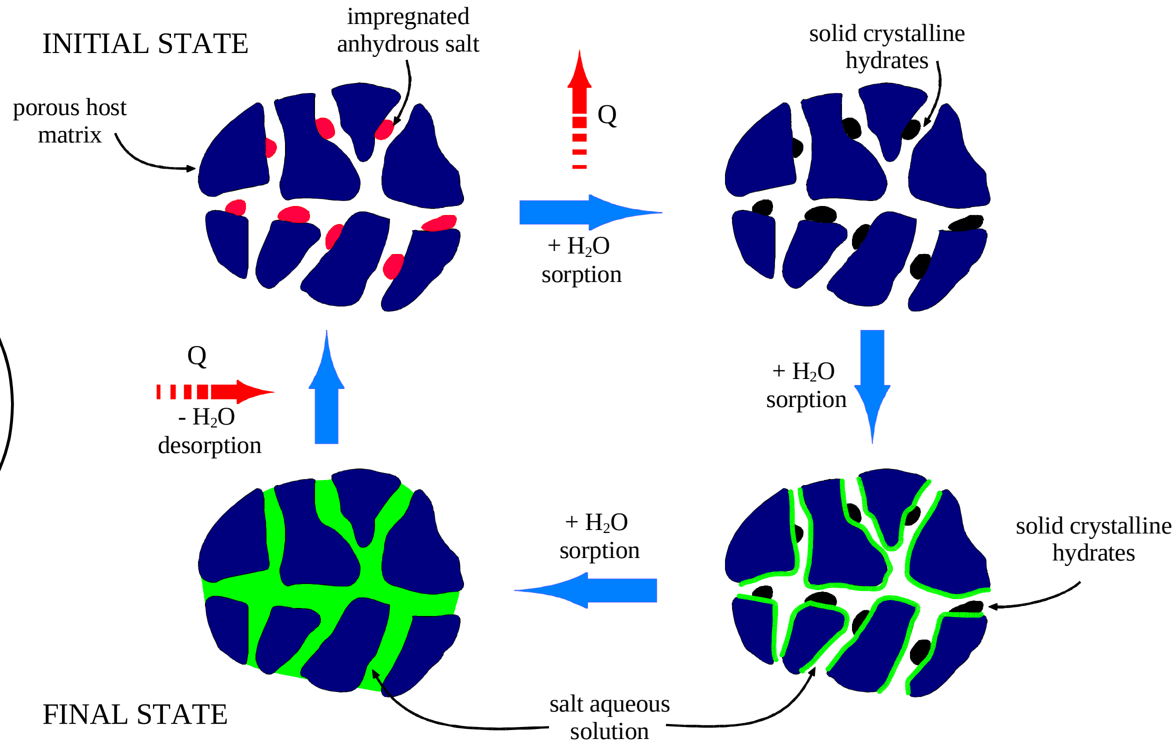
Porous Carbons (ammonia and alchools adsorbate)





SWS-Selective Water Sorbents





<sorbate> = water, methanol, ethanol, ammonia

$Ca(NO_3)_2$ + 2 H2O = $Ca(NO_3)_2 \cdot 2H_2O$

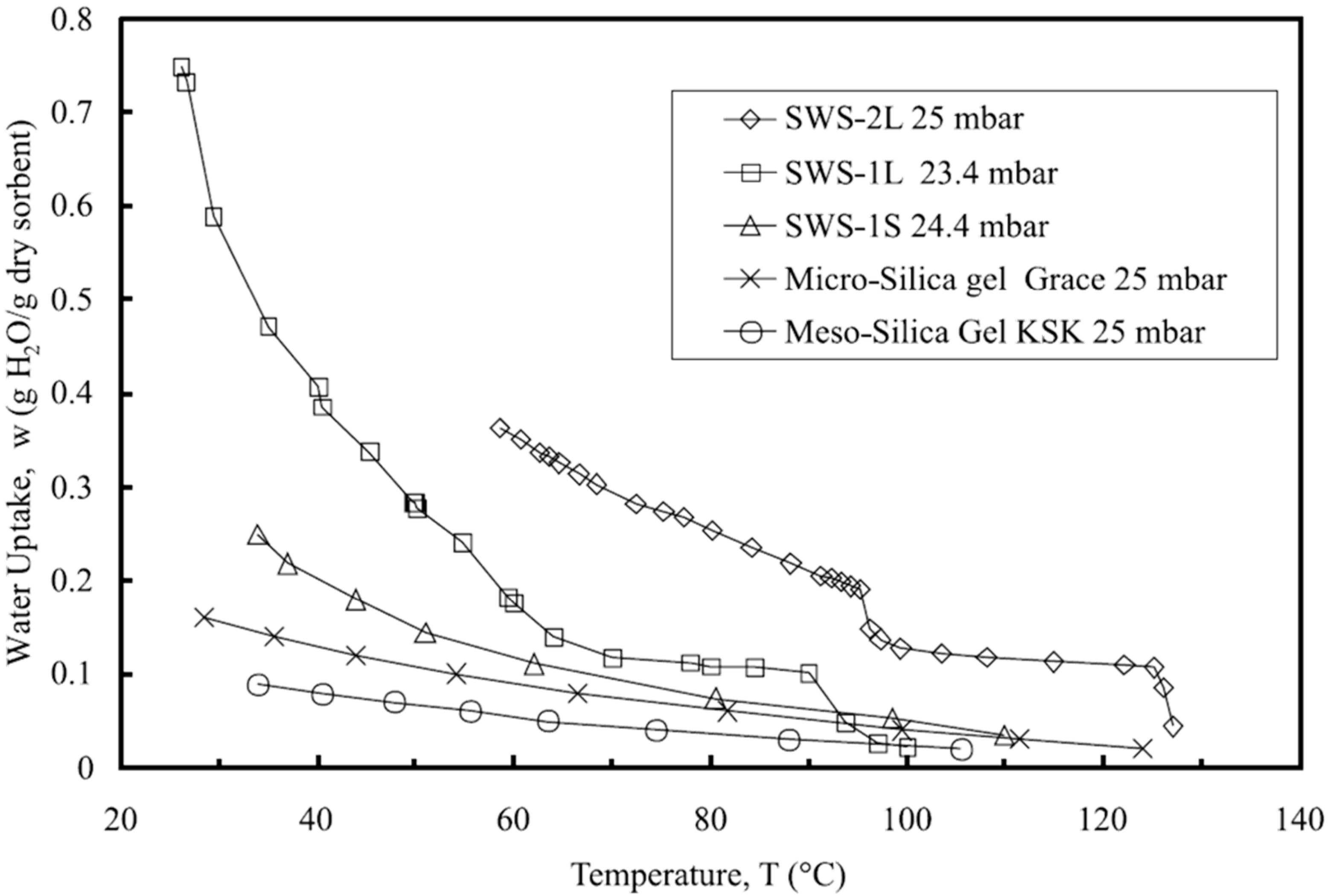
$BaBr_2 + 8\ NH_3 = BaBr_2 \cdot 8NH_3$

$LiCl + 3\ CH_3OH = LiCl \cdot 3CH_3OH$

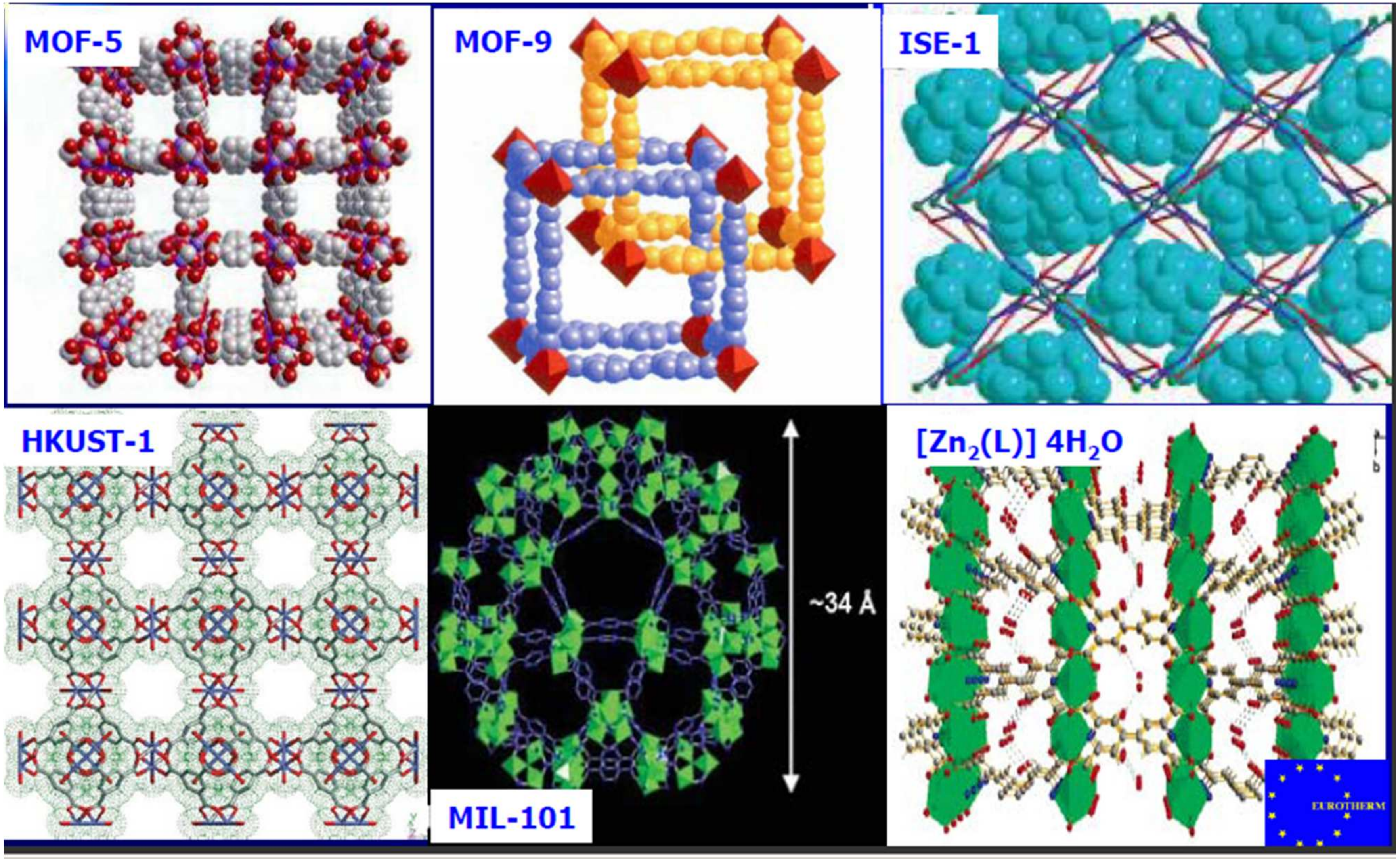
$LiBr + 3\ C_2H_5OH = LiBr \cdot 3C_2H_5OH$

SWS-Selective Water Sorbents

SORPTION CHARACTERISTICS

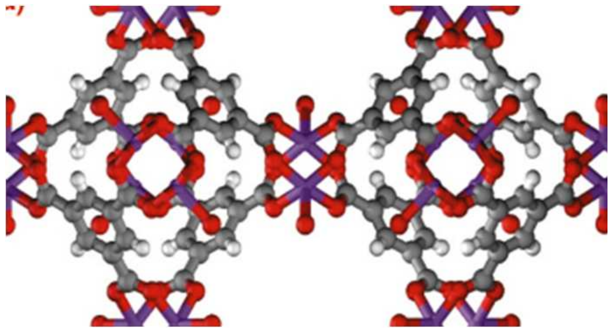


MOF-Metall Organic Frameworks



MOF-Metall Organic Frameworks

Commercially available MOFs: (BASF - Basolite®)



● Oxygen ○ Carbon ○ Hydrogen ● Copper

Basolite C300 (HKUST-1) structure

Basolite® C300 (HKUST-1): Copper-based MOF, trimesate trianions as linkers. It is also known as Cu(BTC).

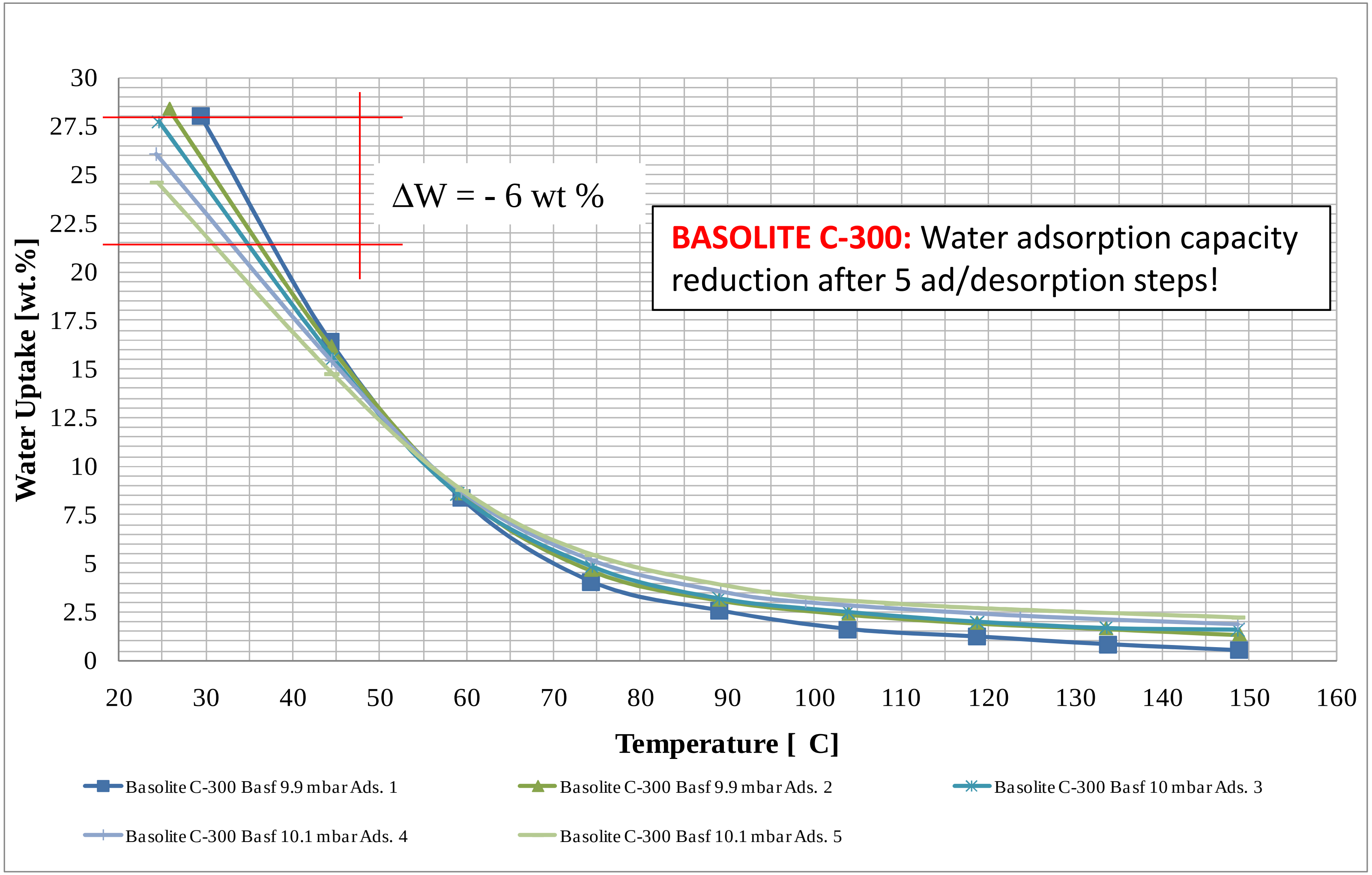
Particle size distribution	15.96 µm
Surface area	BET surf. area 1500-2100 m2/g
Bulk density	0.35 g/cm3
Cost	~ 95 €/(10 g)

Basolite® F300: Iron-based MOF, trimesate trianions as linkers.

Particle size distribution	~ 20 µm
Surface area	BET surf. area 1300-1600 m^2/g
Bulk density	0.35 g/cm^3
Cost	~ 85 €/(10 g)

MOF-Metall Organic Frameworks

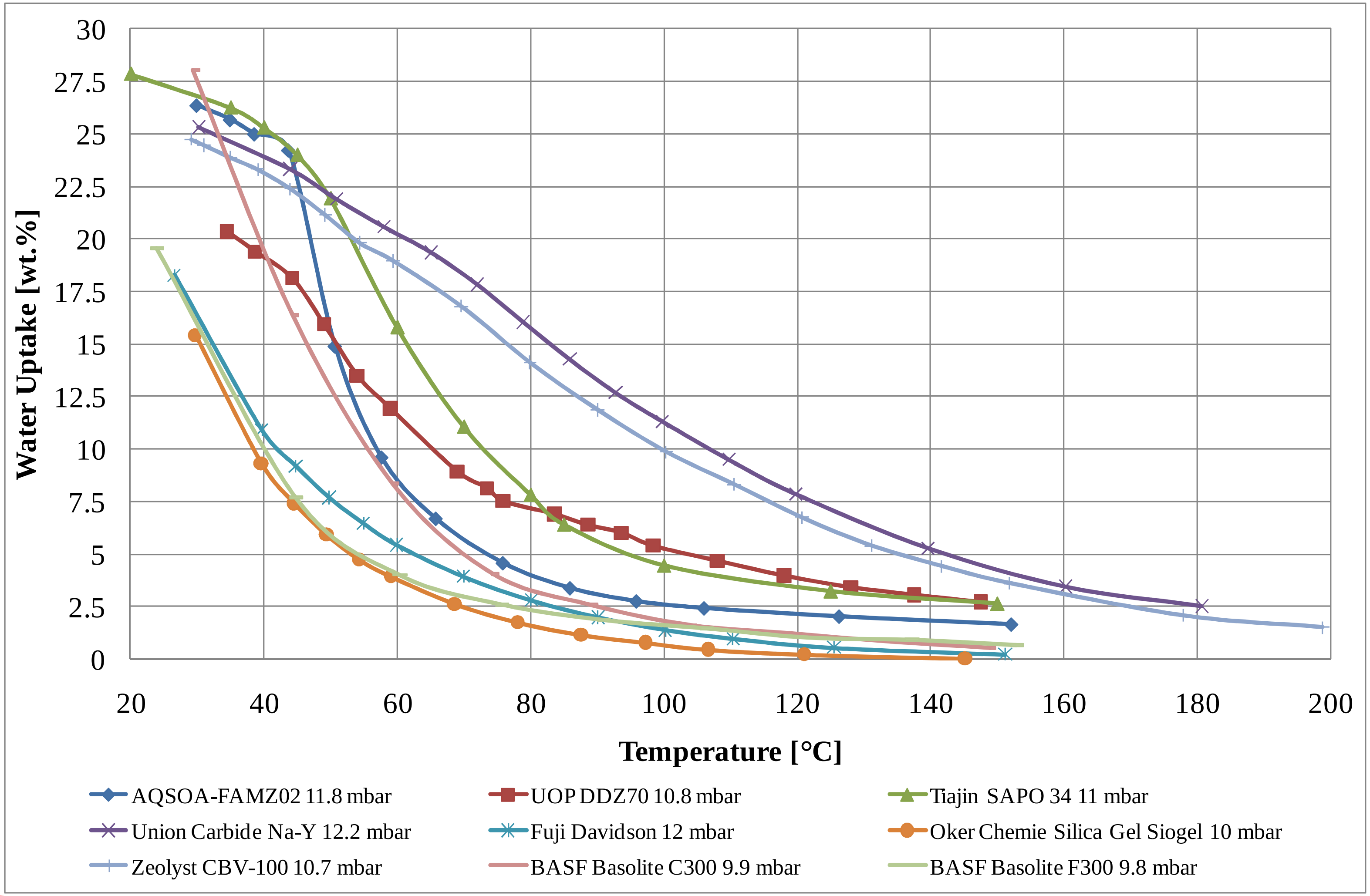
Stability Issue



Database of Adsorbent Materials

A DATABASE of adsorbent materials was created within the *IEA - Annex 34 "Thermally Driven Heat Pumps for Heating and Cooling"*

Databasing of adsorbents is continuing within the new Annex 43 "fuel driven sorption heat pumps".



Overall comparison of adsorbents

Material	Ability to be regenerated at low T	Maximum adsorption capacity	Hydrothermal stability
AQSOA – Z02	+	+	+
NaY UnionCarbide	-	+	+
NaY CBV-100	-	+	+
DDZ70	-	+	+
Fuji Davidson	+	-	+
Basolite C300	+	+	-
SAPO 34	+	+	-
Siogel	+	-	+
Basolite F300	+	-	-

AQSOA Z02 is the best material for low T application

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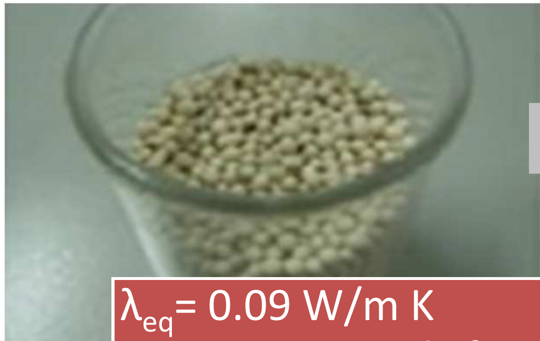
Coated adsorbers

Heat transfer characteristics

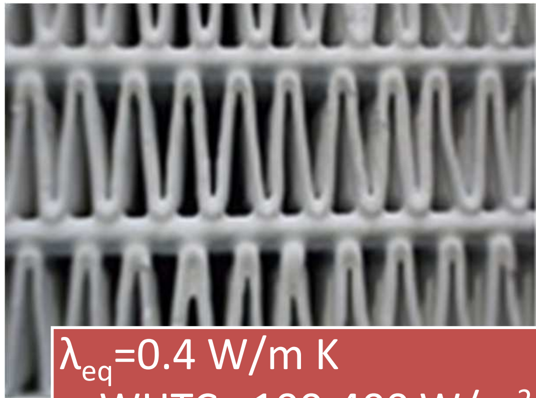
Granular (loose grains)	Consolidated (mechanically compressed)	Coated HEXs (dip coating) (direct synthesis)

Intensification of the heat transfer quality in adsorbers is a key-factor for development of dynamically efficient adsorption refrigeration and heat pump systems



λ_{eq}= 0.09 W/m K
- WHTC= 10 W/m^2 K

λ_{eq}= 10 W/m K
- WHTC= 20 W/m^2 K

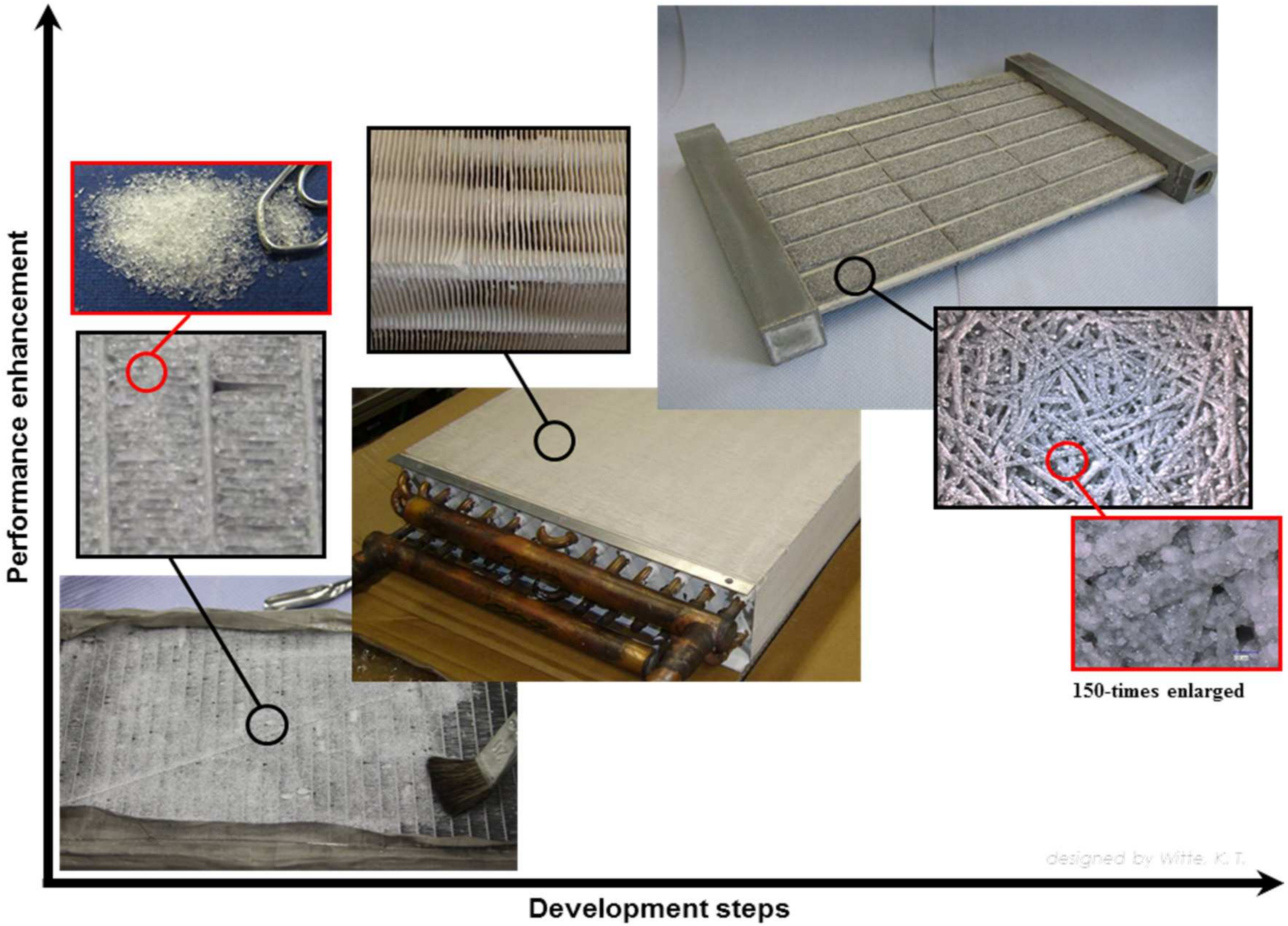


λ_{eq}=0.4 W/m K
- WHTC= 100-400 W/m^2 K

λ_{eq}=0.6 W/m K
- WHTC= >1000 W/m^2 K

Coated adsorbers

Development Steps



Grains - coating - synthesis

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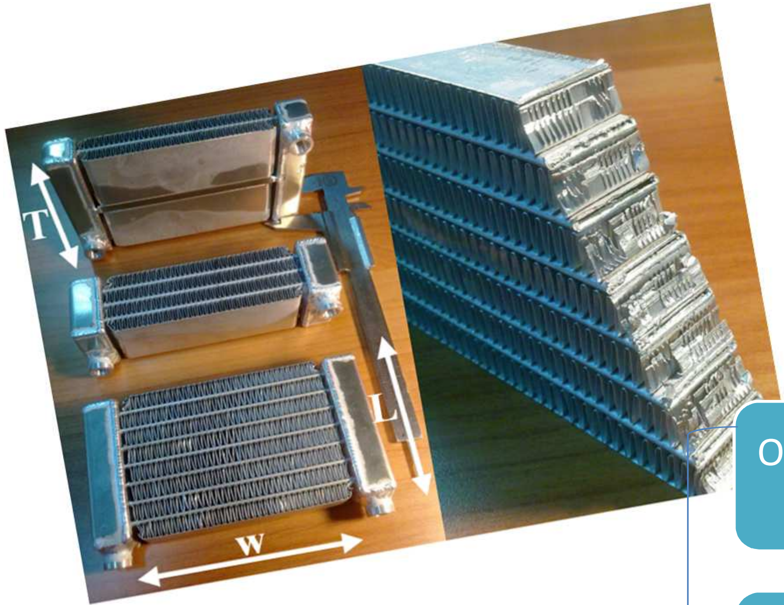
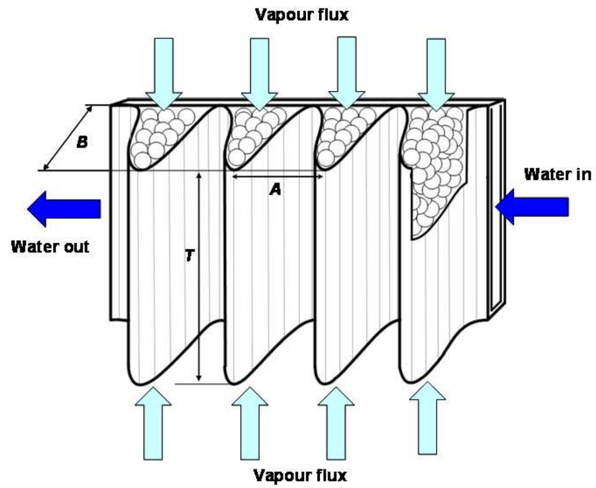
Components for Adsorption Machines

Utilization of compact, lightweight, high surface area HEXs is mandatory for realization of dynamically efficient adsorbent beds



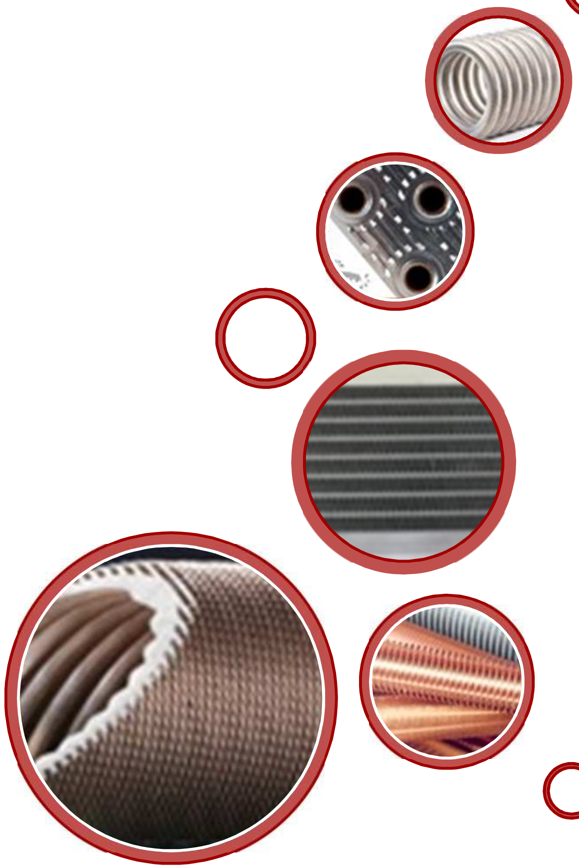


OPEN ISSUES

Optimization of the HEX design	• (H&M transfer properties, thermal mass, flow field)
Optimal configuration of the "adsorbent – HEX" (AdHex) unit	• Optimal adsorbent mass per 1 m^2 of HEX • Optimal size of the adsorbent
Corrosion	Is it a real issue? Coatings offer a barrier effect

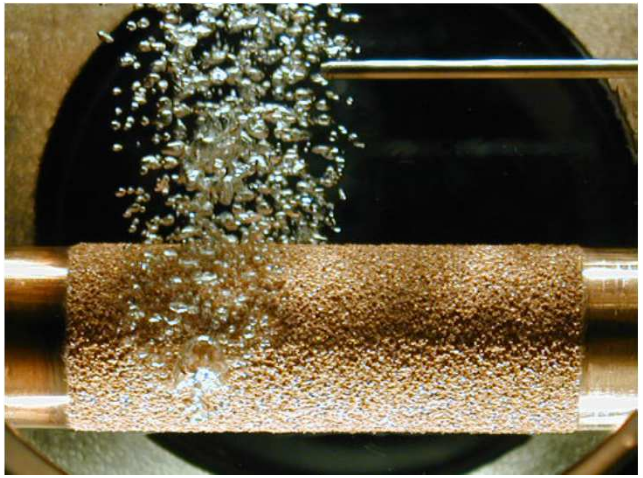
Components for Adsorption Machines

Increased dynamic efficiency of the AdHex unit asks for compact and efficient evaporator and condenser



The heat transfer between tube wall and refrigerant and between tube wall and chilled water circuit have to be increased through:

- Increasing of the specific surface area
- Improvement of the heat transfer coefficient
- Increasing the volume flow and the turbulence inside the tube



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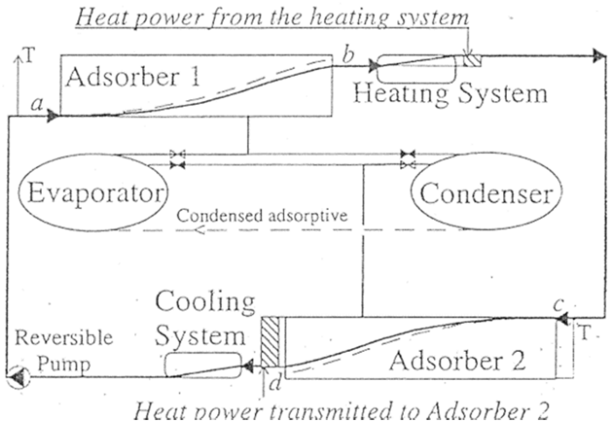
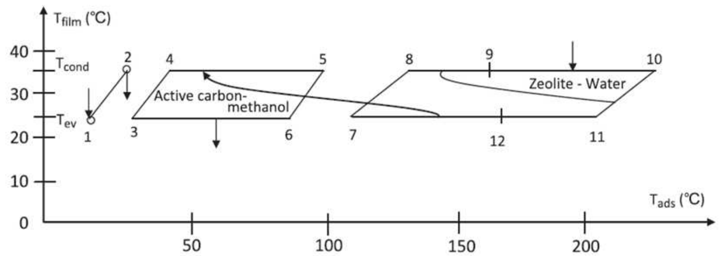
Machine optimization

Improved cycles

Early studies on improved cycles for high regenaration T

- Thermal wave
- Heat and/or mass recovery
- Cascades cycles
- Multiple beds



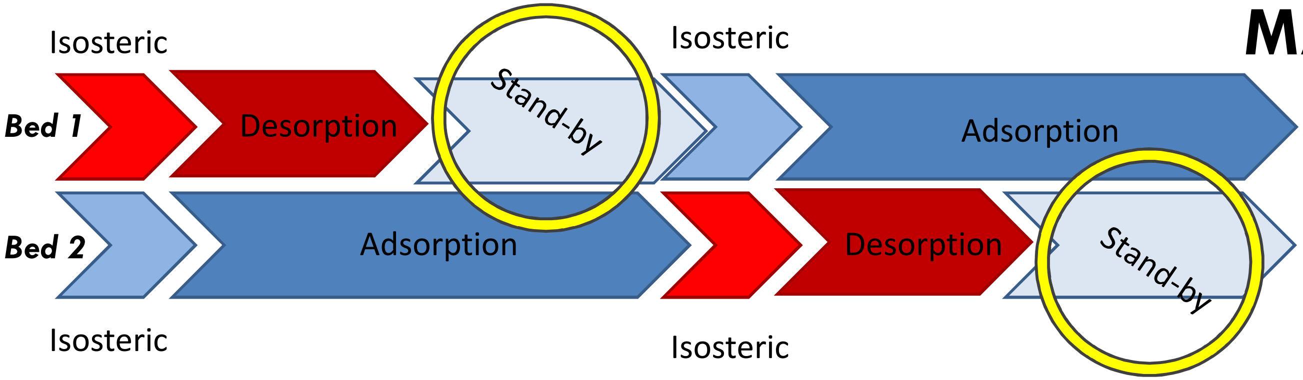


Today the trend is to use low regeneration T.

Most developers are using the simple cycle, especially for low temperature applications

Machine optimization

MANAGEMENT STRATEGY

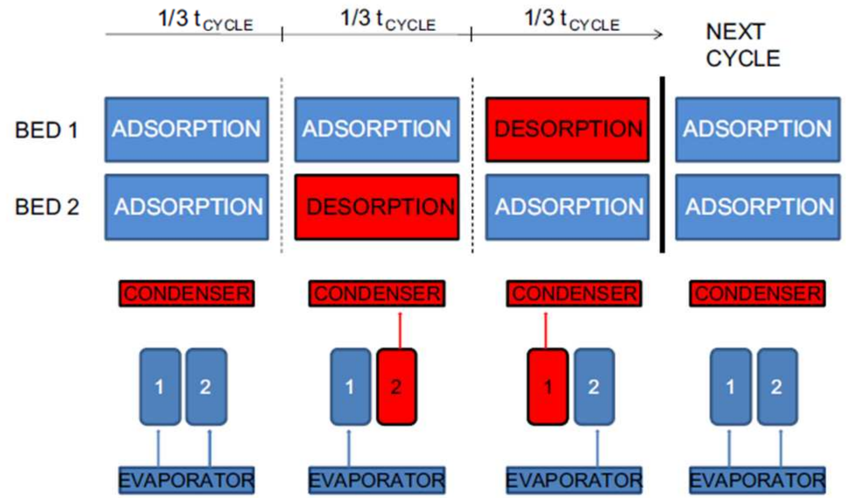


UP TO 30% COP INCREASING

Desorption rate is faster than adsorption, due to higher temperature and vapor pressure

Very short duration of the isoteric stages

Identification of the optimal cycle time for a given operating condition



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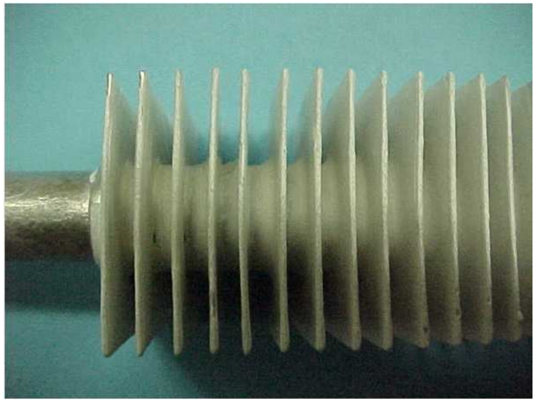
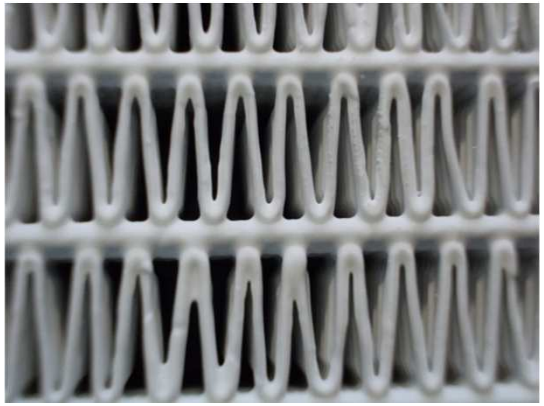
ITAE's Coating Technique



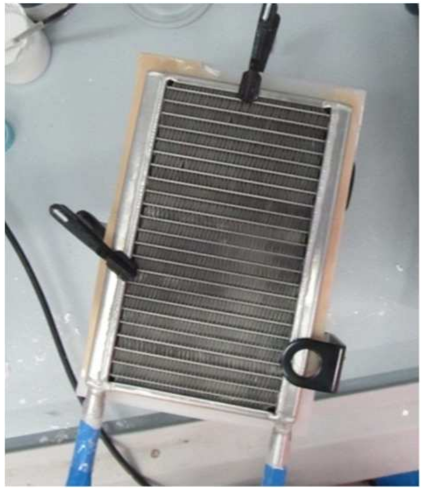
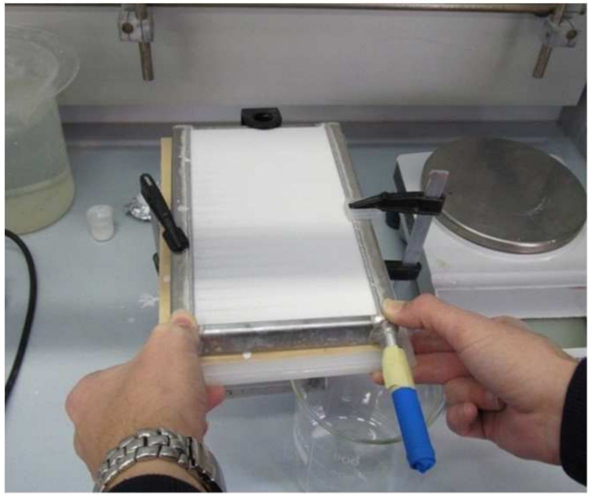


Inorganic (clay-based) binder

Organic binder – in collaboration with UNIME

Preparation of the Coated Adsorbers

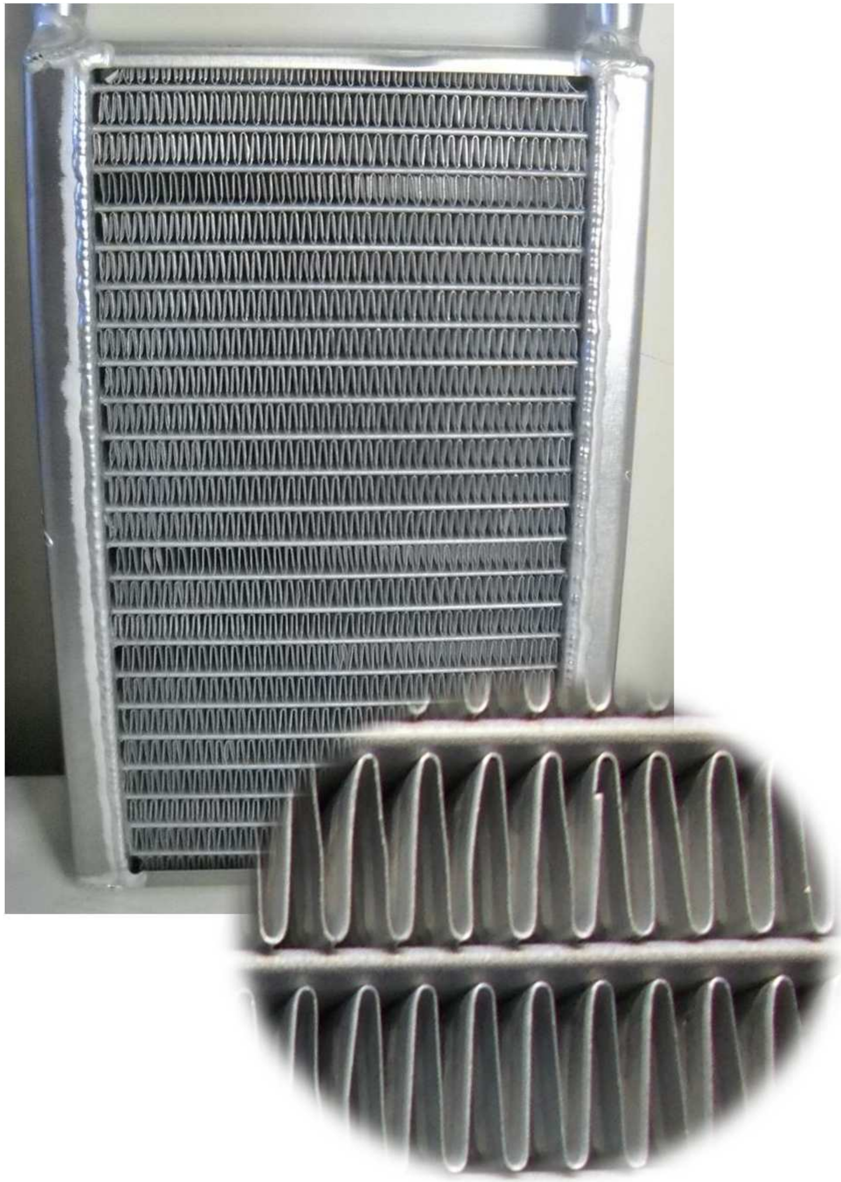
Coating technique: The original lamella HEX in aluminum was coated by pouring a SAPO-34 zeolite – polymeric binder (5 wt.%) solution through the lamellas …

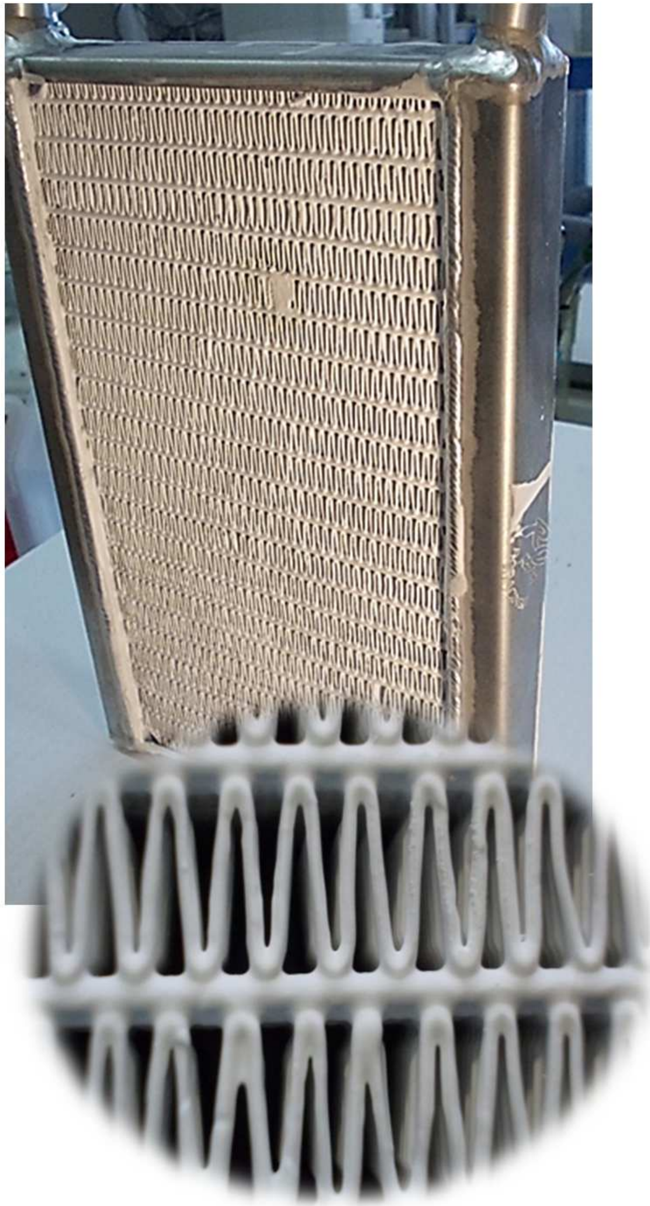




…drying at room temperature, then heating at 120 °C in oven.

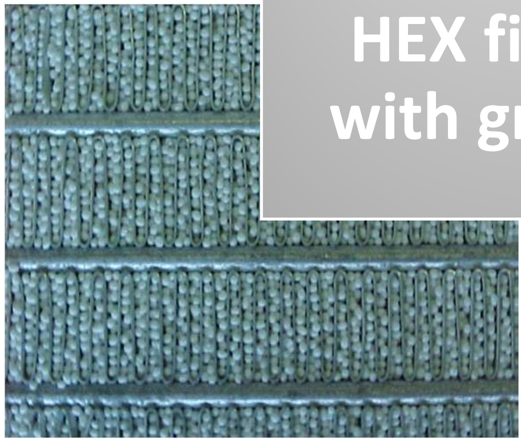
- binder thermally resistant in the T-range of application
- coating thickness can be controlled (0.1- 0.7 mm) by **multi-layer deposition**

The prepared adsorbers





ITAE coating performance evaluation



HEX filled with grains

Coated HEX

10	**Cycle time, min**	5
10	**Wall Heat Trans. Coeff., W/m^2K**	100
20	**Specific cooling power W/kg_{ads}**	300

Adsorption Chiller for Automotive Applications

Thermally OPerated Mobile Air Conditioning Systems

ToPMACS

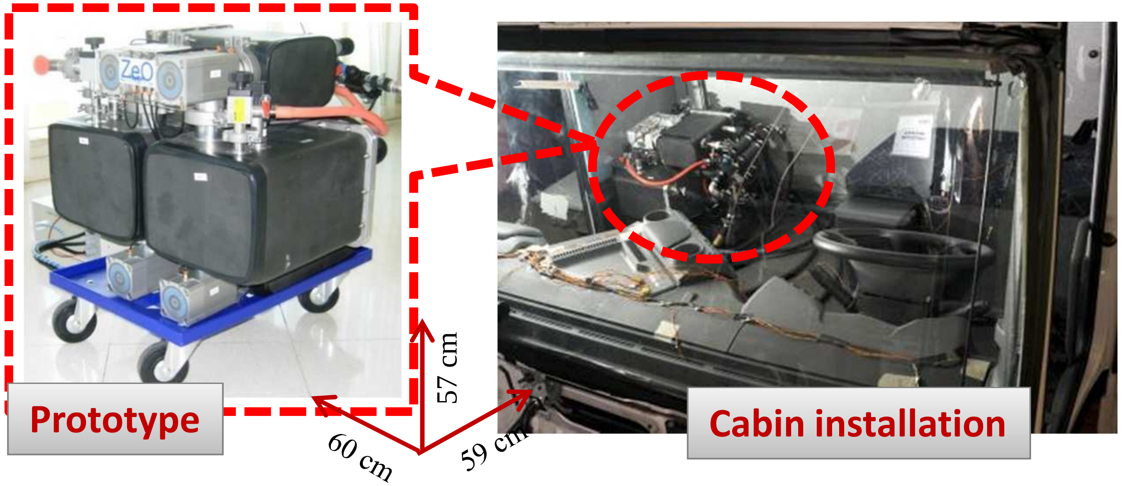
Thermally OPerated Mobile Air Conditioning Systems

IVECO TORINO

STRALIS 520

Overall volume	150 L
Overall weight	59 kg
Chilling capacity	2,3 kW
Min, air temperature	9 °C
COP	0,2
Regeneration temp.	80 °C
Adsorbent	Zeolite

- **SCP: up to 600 W/kg**
- **Very competitive weight considering commercial products!**
- **Volume density higher than 10kW/m³!**

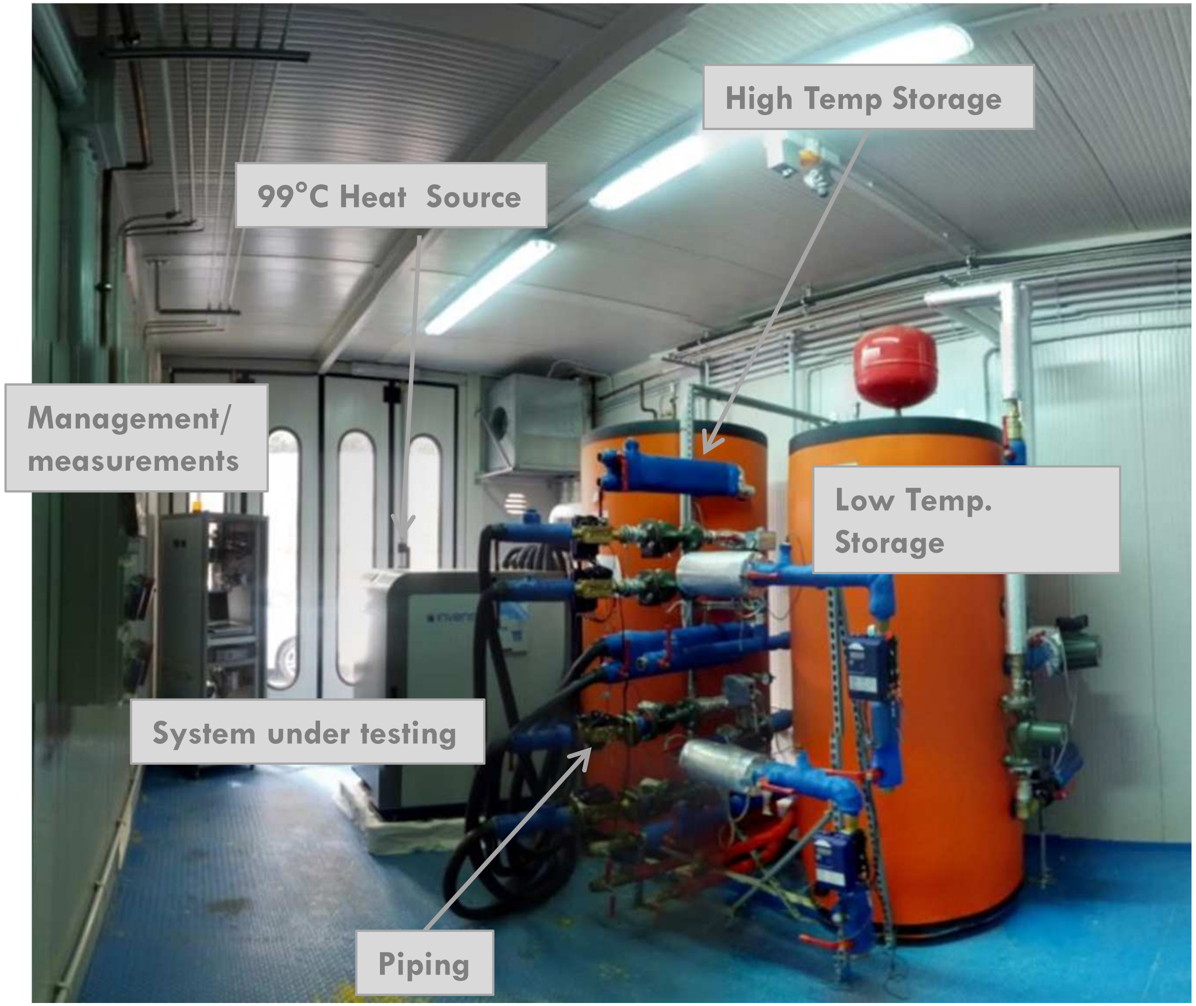


Solar Cooling System for Residential Application

Technology of solar thermal collectors	Evacuated tubes
Number of evacuated tubes	90
Total thermal collectors area [m²]	9.6
Heat storage volume [m³]	0.5
Tilt angle [°]	20
Gas Boiler nominal Power [kW]	20
AHP cooling Power [kW]	8
Required Cooling Load [max, kW]	2.43
Cold delivering system	Flat radiant panel
Overall radiant surface [m²]	28

Test facility for Trigeneration Systems

- 75 kW heat source up to 99 °C
- 15 – 50 °C discharging T ability
- 2 – 20 °C Low T simulation ability
- 1500 litres High Temperature Storage
- 1000 litres Low Temperature Storage
- Variable flow hydraulic pumps
- High accuracy sensors
- Pressure drop measurements
- Full automatic operation (overnight tests!)
- UNI-EN 12977 – III (possible tests on storages for solar application)



Testing of chillers up to 35-40 kW cooling

Thermal energy storage test (max charging rate 75 kW – discharging 63 kW

ICE or Fuel cell Cogenerator

Conclusions

Development will be mainly technological

- Better materials
- Enhanced heat transfer/HEX
- Optimized management strategy
- Techno-economic optimization

Scientific issues

- Material science (adsorbents, etc.)
- From thermodynamic to adsorption dynamics

Thank you!