Ricerche National Council of Research

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Institute for Advanced Energy technologies, "Nicola Giordano"



Adsorption heat pumps, research activitities at CNR ITAE ANGELO FRENI

> Workshop "Heat pumps in the Italian energy system" IEA HPP ExCO meeting - Rome, 4 November 2009



Summary

Introduction

Background Adsorption machines: current state of the art Key factors for further development

CNR-ITAE activity on adsorption chillers

Materials, Heat transfer improvement Components Modeling Prototypes

Challenges for the future



Introduction

Background

Worldwide the cooling and air conditioning market is growing

Vapor compression units need a high amount of electric energy

The high consumption of electricity leads to peak loads, malfunction of the power grid etc

Thermally-driven cooling systems could be an answer

Two technologies:

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absorption chillers

Cold is generated through the process of sorption by liquid solution

LiBr/water and NH₃/water

Mature technology

Several products on the market

adsorption chillers

Cold is generated through the process of adsorption on porous material Silica gel/water, zeolite/water, AC/ammonia

Developing technology

Few products on the market

History of adsorption machines^{Ricerche}

USA 1929: Silica gel – SO2 adsorption refrigerator

Wait for 40 years... Vapour compression units and CFC's are dominating the market

1980-1990: New interest in heat driven systems due to oil price shocks, resource limitations

1990-2000 : First commercial products, no strong enough to survive

2000-today

Solid products developed in the EU Many contributions from China and Japan Still very little in USA











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Scientific production









An overview on the market



Company	Nominal Cooling capacity (kW)	Useful effect (cold water), C	Working pair	Heat source (hot water) T _{in} /T _{out} (C)	СОР
Nishiyodo (Japan)	70-1000	14/9	Silica gel/ water	85/79.4	0.6
SorTech AG (Germany)	8-15	10-18	Silica gel/ water zeolite/ water	75/67	0.6
Solamext (Germany)	5-15	6-8	Silica gel/ water zeolite/ water	90/83	n.a.
DY Refrigeration (China)	14	n.d./≥-25 C	Zeolite/ ammonia	98/93	n.a.





Best adsorption chillers applications

(Low-grade) waste heat recovery Solar cooling Tri-generation Automotive AC

Main benefit: higher performance at low driving temperature



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Open issues to improve the machine performance

International R&D is mainly focused on the following subjects:

Improvement of adsorption capacity of adsorbent materials -Higher COP and specific power-Volume and weight reduction

Heat transfer intensification through the adsorbent bed

-Shorter cycle time

- Higher specific power

Engineering and control strategy

-Cost reduction
-Machine reliability
-Maximization of performance

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The CNR-ITAE activity on adsorption machines





Ricerche Development of advanced adsorbent materials

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

First adsoption heat transformers were realized usign adsorbents (Zeolite 4A, X, silica gel) not – optimized

MATERIAL

LEVEL



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



Ricerche MATERIAL ITAE's activity: new composite sorbents

In collaboration with Boreskov Institute of Catalysis (BIC) – Russian Academy of Science

Selective Water Sorbents **SWSs**: Two-component materials based on a porous host matrix with a salt inside its pores

Benefits:

LEVEL

Superior sorption capacity and low desorption T Tailoring of the adsorption properties



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Designation	SWS-1L	Designation	SWS-8L	Designation	CS-9L
Host matrix	Mesoporous silica gel	Host matrix	Mesoporous silica gel	Host matrix	Mesoporous silica gel
Pore volume of the silica	1 cm ³ /g	Pore volume of the silica	1 cm ³ /g	Pore volume of the silica	1 cm ³ /g
Salt	Calcium Chloride – CaCl ₂	Salt	Calcium Nitrate - Ca(NO ₃) ₂	Salt	Lithium Chloride (LiCl)
Salt content	33 wt.%	Salt content	45 wt.%	Salt content	30 wt.%
Max water loading	0.7 g/g	Max water loading	0.4 g/g	Max MeOH loading	0.7 g/g
Optimal Tdes	100-110°C	Optimal Tdes	80-90°C	Optimal Tdes	80-90°C

Best SWSs for cooling applications

Ricerche ITAE's activity: new zeolites

In collaboration with University of Messina

development of new zeolites and (*silico*)aluminophosphates (AlPO, SAPO)

- -Hydrothermal synthesis
- Microwave synthesis

MATERIAL

LEVEL

- Direct synthesis over metal substrates (finned tubes, foams, fibers, etc)

In collaboration with Mitsubishi Chemical – Japan Characterization of novel AQSOA – FAM materials, specifically realized for utilization in adsorption machines.

-Measurement of adsortion kinetics and equilibrium curves

-Evaluation of the material thermodynamic and dynamic performance





Material + Component LEVEL

Ricerche ITAE's characterization activity

Standard equipments for analysis of adsorbent materials, such as XRD, DTA-DSC/TG, SEM, BET, Hg porosimetry

 adsorbent/adsorbate equilibrium curves and kinetics (1 Chan Balance + 2 Rubotherm balances)

•adsorbents specific heat (calorimetric technique)

- adsorbents thermal conductivity (Transient hot-plate method)
- adsorption **diffusion coefficients** and **permeability (self-made apparatuses**)
- adsorbents hydrothermal stability (self-made apparatus)







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measurement of **COP and cooling capacity of full- scale adsorbent beds**

1 kW chiller test-rig

Development of thermally efficient adsorbent beds

Main problem of state-of-the-art of adsorbent beds:

-Commonly, adsorbent beds are realized using the adsorbent in grains (low thermal conductivity).

-Heat transfer is dominated by point-contacts



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COMPONENT LEVEL

Modification of the adsorbent configuration is needed!

Ricerche ITAE's coating technique evolution

L. Pino, Yu. Aristov, G. Cacciola, G. Restuccia, Composite materials based on zeolite 4A for adsorption heat pumps, Adsorption, (3), 33-40, 1996



From simple supports....

COMPONENT

LEVEL

To more sophisticated configurations....

To scale-up.

COMPONENT LEVEL

Ricerche ITAE's coating technique today

Dip coating:





Spray coating:



thickness 0.2-1 mm





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HEX filled with grains

LEVEL



Coated HEX



20	Cycle time, min	8
10	Wall Heat Trans. Coeff., W/m ² K	150
20	Specific cooling power W/kg	300



Ricerche Direct synthesis of zeolite over metal

In collaboration with University of Messina

Advantages No binder required Perfect contact zeolite – metal

Zeolite A synthesized on copper foam

COMPONENT

LEVEL



Copper Heating/cooling foam fluid

Zeolite SAPO synthesized on Aluminium foam



Drawbacks Zeolite layer thickness < 0.1 mm Low zeolite loading



Ricerche ITAE's activity on mathematical modelling

Three levels:

Material + component +

system

Detailed simulation of the adsorption process
Main aim: Optimization of the adsorber configuration
Coupled H&M transfer through the adsorber
Accurate knowledge of H&M diffusion coeff.
Implementation: numerical methods for PDE
(Fortran), FEM analysis by COMSOL

Simulation of the adsorption machine

Main aim: Design of efficient machines Energy and mass balance for machines components **Lumped parameters**: Global heat and mass transfer coefficients **Implementation:** Matlab- Simulink

Simulation of the whole energetic system Main aim: System performance, control strategy Performance-map of the system components Super-lumped parameters Implementation: Trnsys



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Evolution of ITAE's prototypes

SYSTEM

LEVEL

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2.5 kW zeolite-water chiller for automotive applications



(Iveco Stralis)



The ITAE on-board air conditioner



Innovative features

- Novel double-bed adsorber
- Adsorbent material: AQSOA Z02 (Mitsubishi Chemical)
- Compact aluminium HEX
- Compact design of condenser and evaporator



SYSTEM

LEVEL









Testing in a real IVECO truck cabin



SYSTEM

LEVEL



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Performance evaluated: Delivered cooling power: 1-2.3 kW Cooling COP: 0.25-0.4

Specific Cooling Power: up to 600 W/kg

The ITAE solar-assisted air conditioner

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Project "solar cooling" (founded by Ministero Attività Produttive):

SYSTEM

LEVEL

design and the realization of a demonstrative solar cooling system using a self-made adsorption chiller



The ITAE solar-assisted air conditioner



SYSTEM

LEVEL



Key features

Double-bed adsorption machine with heat recovery Thermally driven by low temperature heat source (70-90°C) Adsorbent bed: compact plate-fin type HEX Evaporator/condenser: copper finned coils Fully automatic

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Performance evaluated:

Delivered cooling power: 2.5-3.5 kW

Cooling COP: 0.43-0.55 for Tdes = **78 °C - 90 °C and** Tamb = **30-35°C**



Challenges for the future

KEYWORDS for a further development

<u>Materials:</u> -Database -Cheap adsorbents -Stability

Components:

- Scale-up of coating techniques
- Evaporator design

Machine:

- Advanced cycles
- Control strategy
- System integration



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THANK YOU!

