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SOLID SORBENTS IN HEAT PUMP APPLICATIONS

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1. SOLD SORBENTS IN HEAT PUMP APPLICATIONS

The cumulative waste heat currently released to the environment by the chemical en refining industries in The Netherlands amounts to 110 PJ/a in the temperature window 50 < T(^{o}C) < 200. A huge energy saving potential exists if this waste heat can be upgraded to either industrial cooling levels (T < 10^{o}C) or the middle pressure (MP) steam grid (T > 230^{o}C). Conventional (absorption, compression) heat pumps are not able to provide the necessary temperature lifts in the desired temperature regime, heat pumps based on solid sorption however are. Currently we are working on solid sorption based heat pumps both for cooling and for heating purposes. The former are based on solid/water sorption by either Na_2S (the so-called SWEAT system) or silica, the latter are based on solid/ammonia sorption in metal halides e.g. LiCl or $MgCl_2$. The working principle is based on the reversible desorption (endothermic) and absorption (exothermic) of vapours in solids. In principle two different solids are needed (or the equilibrium between a solid/vapour pair and the condensed vapour), the so-called high and low temperature salt HTS and LTS: $HTS \cdot Vapour + \Delta H' \leftrightarrow HTS + Vapour$ (heat input at waste heat temperature level, e.g. 120^{o}C) and at the same time $LTS + Vapour \leftrightarrow LTS \cdot Vapour + \Delta H''$ (heat output hat ambient temperature, Figure 1.1) and vice versa. In the reverse case heat output occurs at high temperature (MP-steam). Typical efficiencies are about 33%. When the cycle is performed counter clockwise, cooling is achieved with typical efficiencies of 55%. Design of the heat pump process is dependent on the exact knowledge of the p,T-equilibrium lines, phase diagram and kinetics of the specific solid/vapour pairs, as well as heat and mass transport aspects. Vapour pressure and XRD measurements on the different phases of $Na_2S \cdot xH_2O$ and DSC measurements on $LiCl \cdot xNH_3$ and $MgCl_2 \cdot xNH_3$ yielding both thermo-dynamic and kinetic data will be presented (Figure 1.2).

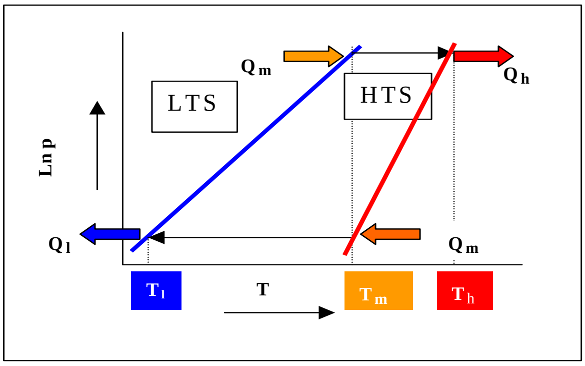


Figure 1.1 *Schematic of a heat pump cycle*

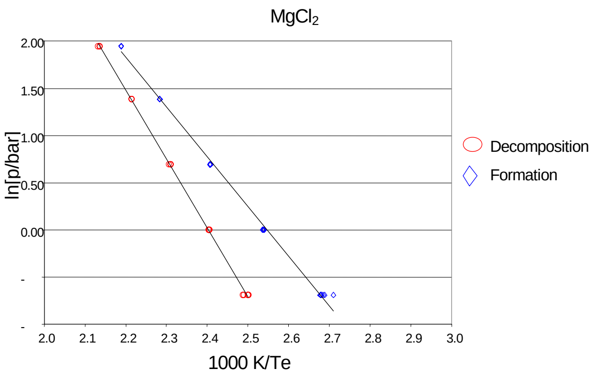


Figure 1.2 *p vs. 1/T equilibrium lines for formation and decomposition of $MgCl_2 \cdot (2 \leftrightarrow 6)NH_3$ (DSC data)*

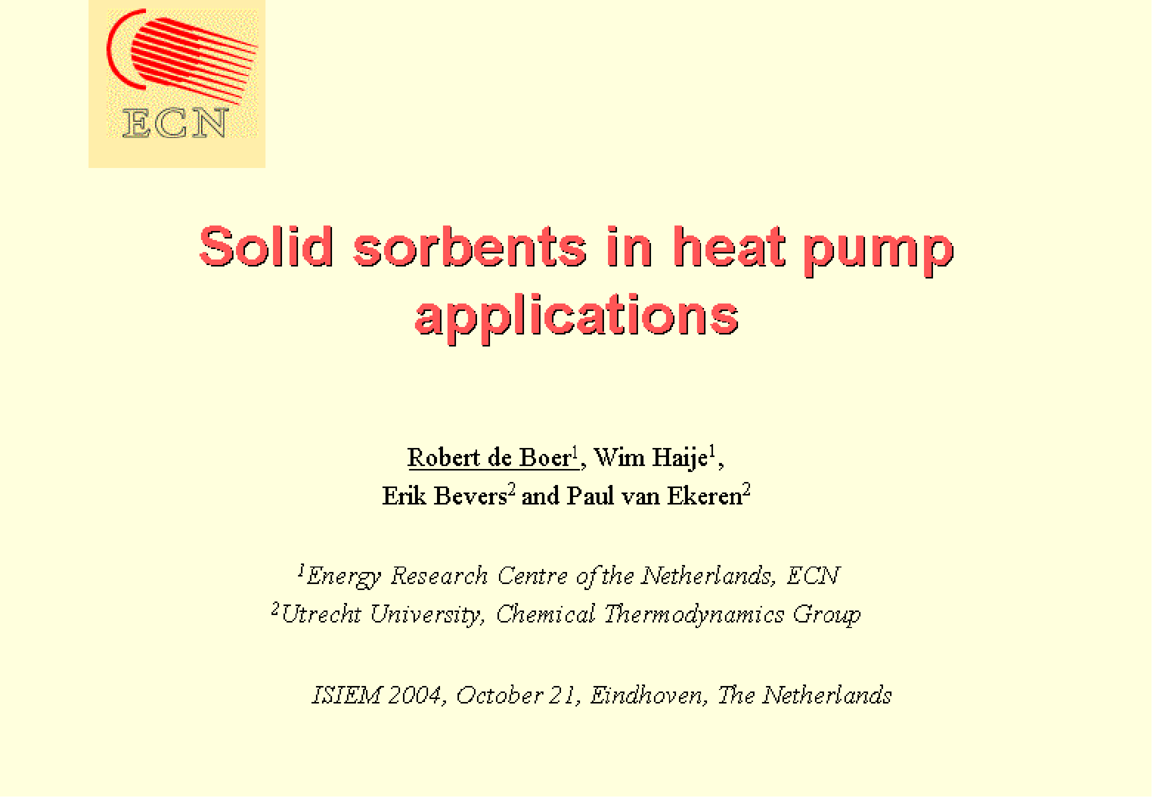
Furthermore a conceptual design on an industrial scale of the high temperature chemical heat pump based on a continuous version of the batch system will be presented. The implementation of such a heat pump is both economically and technically feasible.

REFERENCES

Boer, R. de, W.G. Haije, J.B.J. Veldhuis, *Determination of structural, thermodynamic and phase properties in the* Na_2S-H_2O *system for application in a chemical heat pump, Thermochimica Acta.* 395 (2003): 3-19

Spoelstra, S, W.G. Haije, J.W. Dijkstra, *Techno-economic feasibility of high-temperature high-lift chemical heat pumps for upgrading industrial waste heat, Applied Thermal Engineering 22* (2002): 1619-1630.

APPENDIX A PRESENTATION



Solid sorbents in heat pump applications

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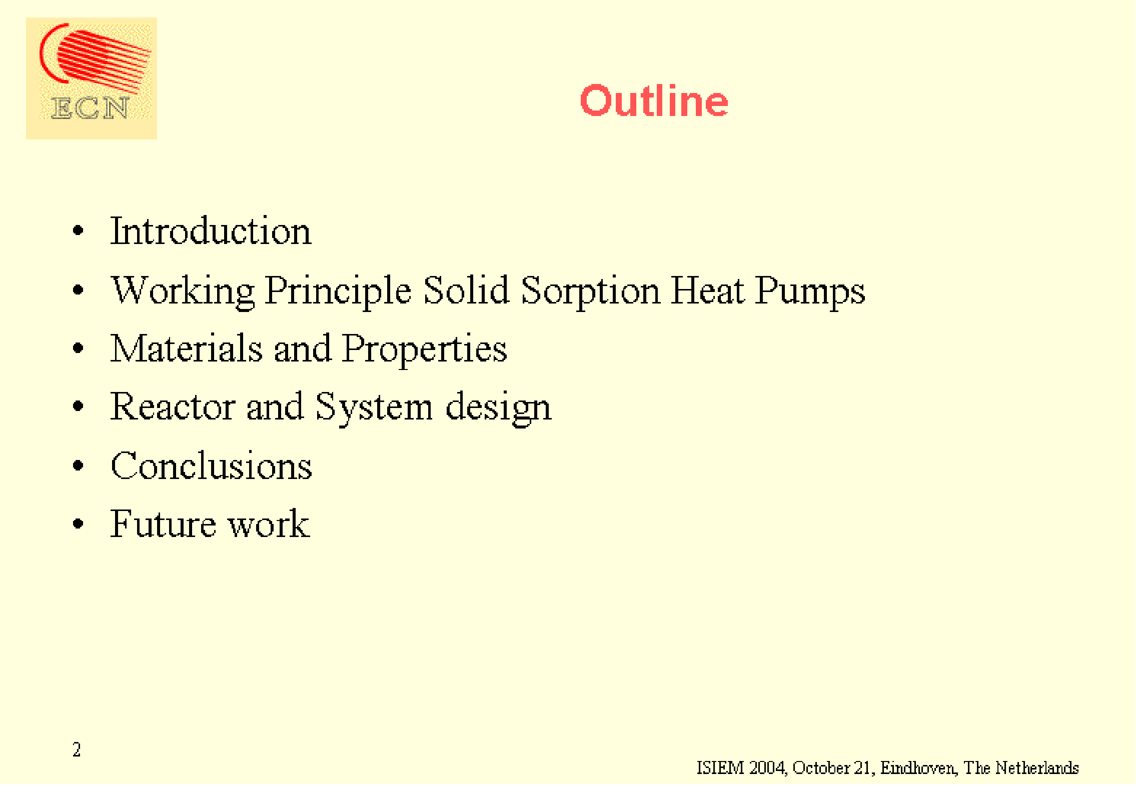
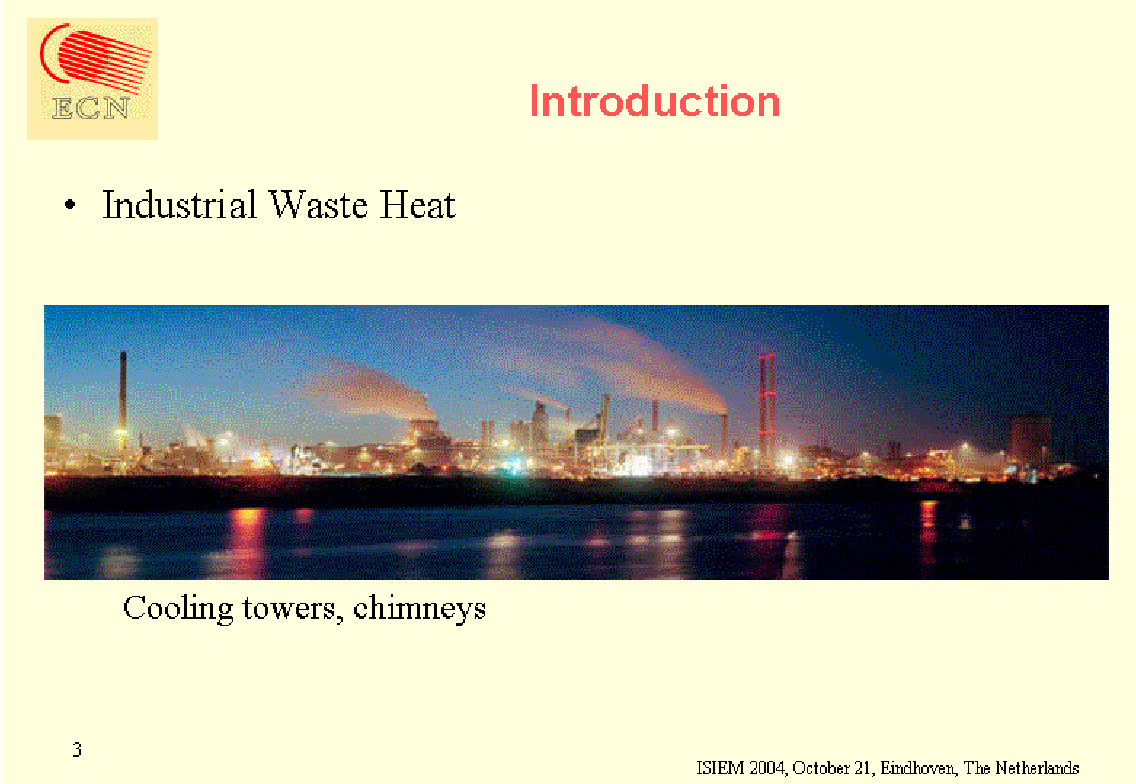


Outline

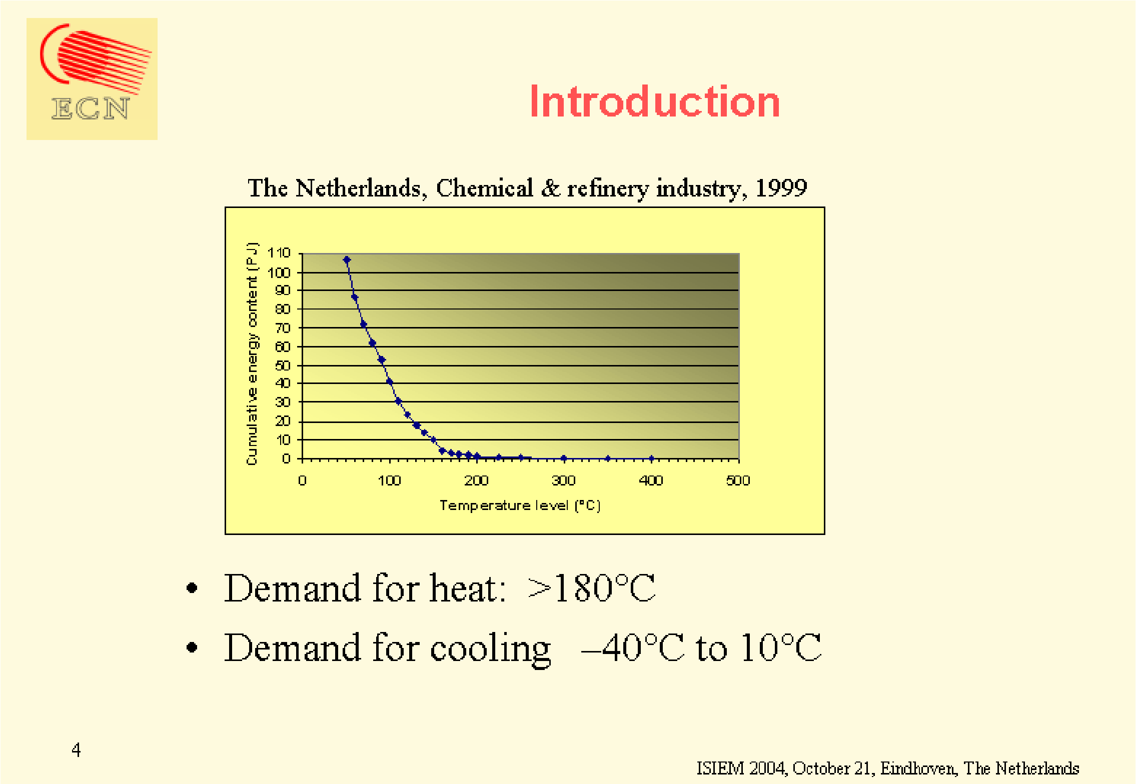
- Introduction
- Working Principle Solid Sorption Heat Pumps
- Materials and Properties
- Reactor and System design
- Conclusions
- Future work



Introduction

- Industrial Waste Heat

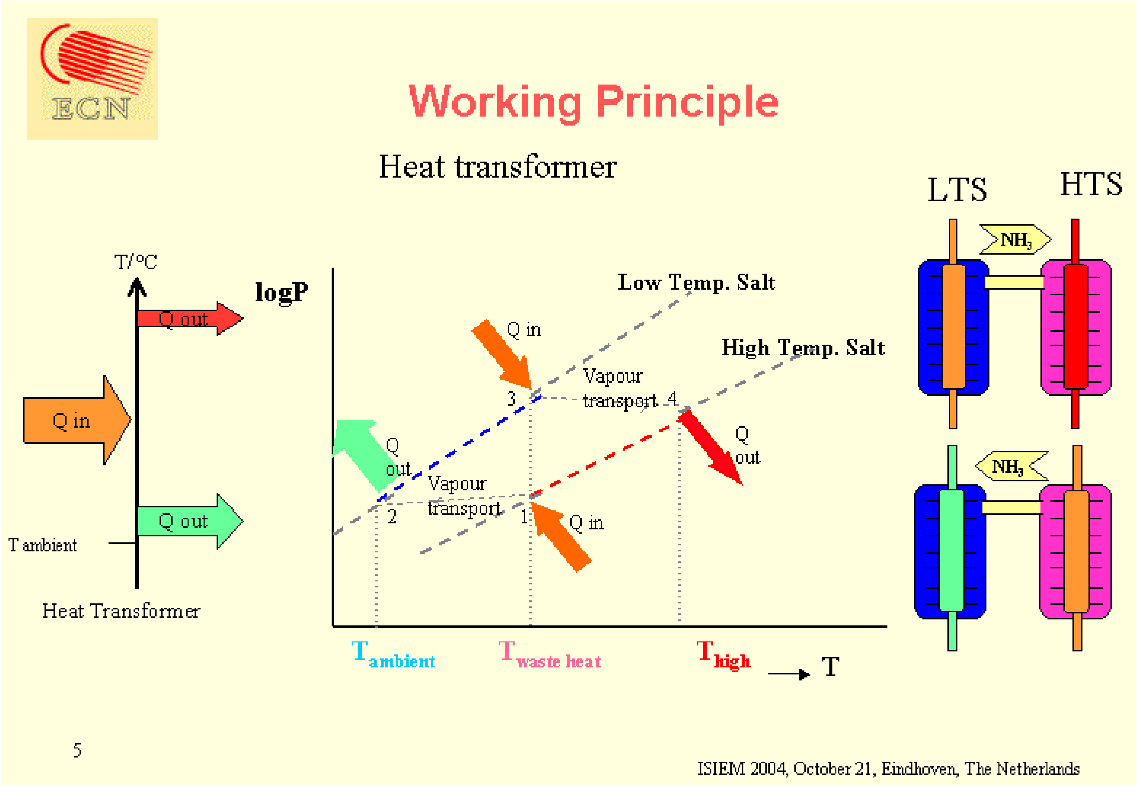
Cooling towers, chimneys



Introduction

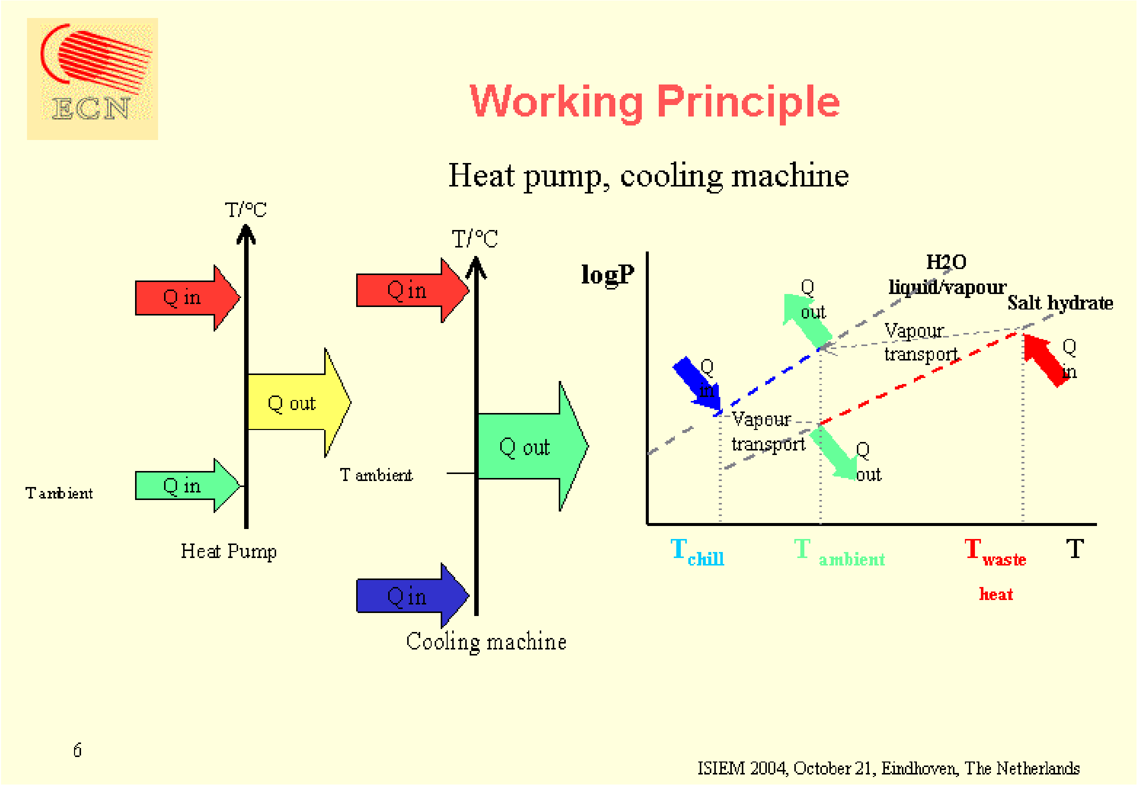
The Netherlands, Chemical & refinery industry, 1999

- Demand for heat: >180°C
- Demand for cooling –40°C to 10°C



Working Principle

Heat transformer



Working Principle

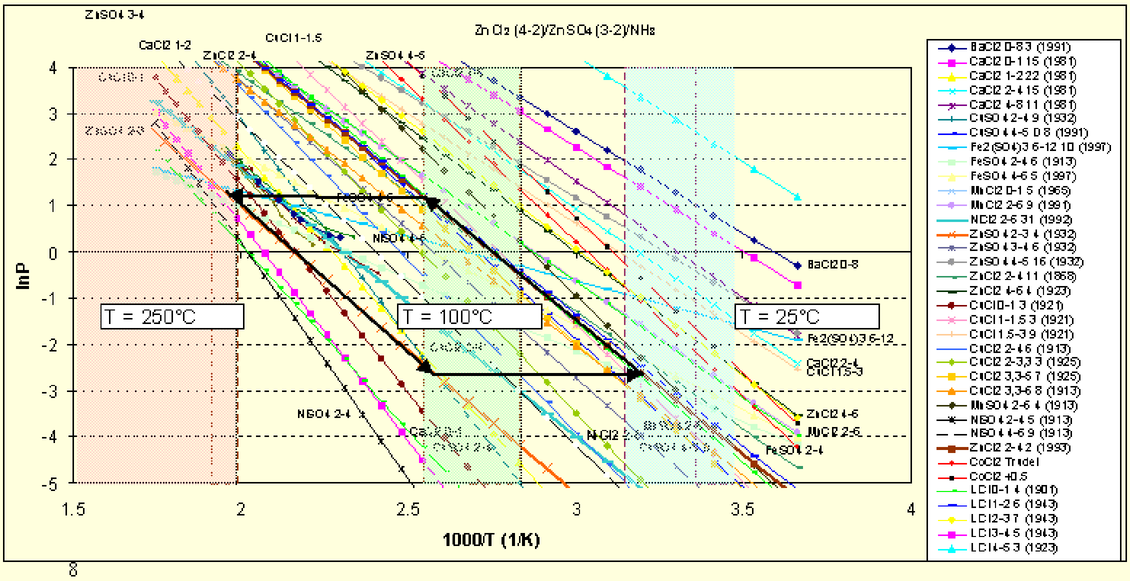
Heat pump, cooling machine

Materials and Properties

- Materials Requirements
  - Reversible sorption reactions
  - High heat of reaction, similar for both salts, high theoretical efficiency
  - Long term mechanical and chemical stability under thermal cycling
  - Good reaction kinetics, small hysteresis
- Process requirements
  - T-lift
  - Operational T-P window → Working pair selection
  - small thermal mass (reaction heat/sensible heat), Low Cp

Working pair selection

Salt-Ammonia systems



Materials Properties

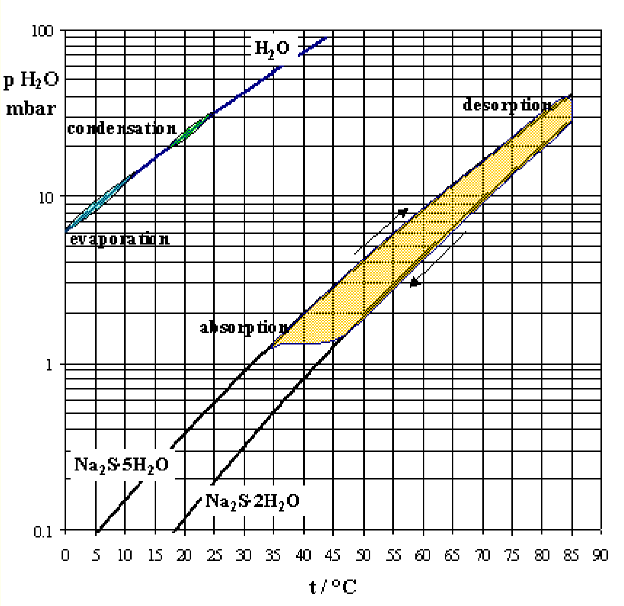
Properties

- Pressure-Temperature equilibria
- Reaction stoichiometry
- Enthalpy and Entropy of reaction, heat capacity
- Reaction Kinetics
- Hysteresis
- Crystallographic phases

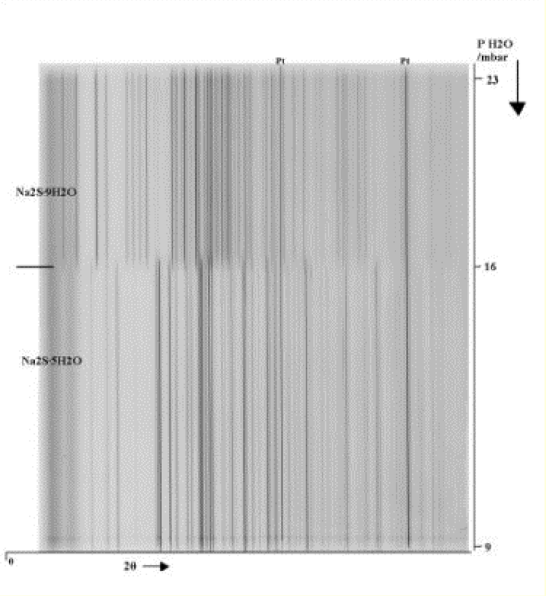
Measurements

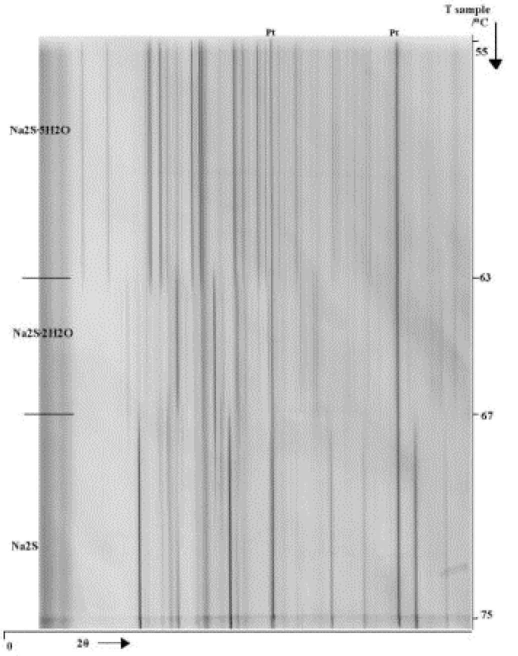
- Vapour pressure measurement
- Differential Scanning Calorimetry
- TG-DTA
- X-ray / neutron diffraction

Static vapour pressure measurement



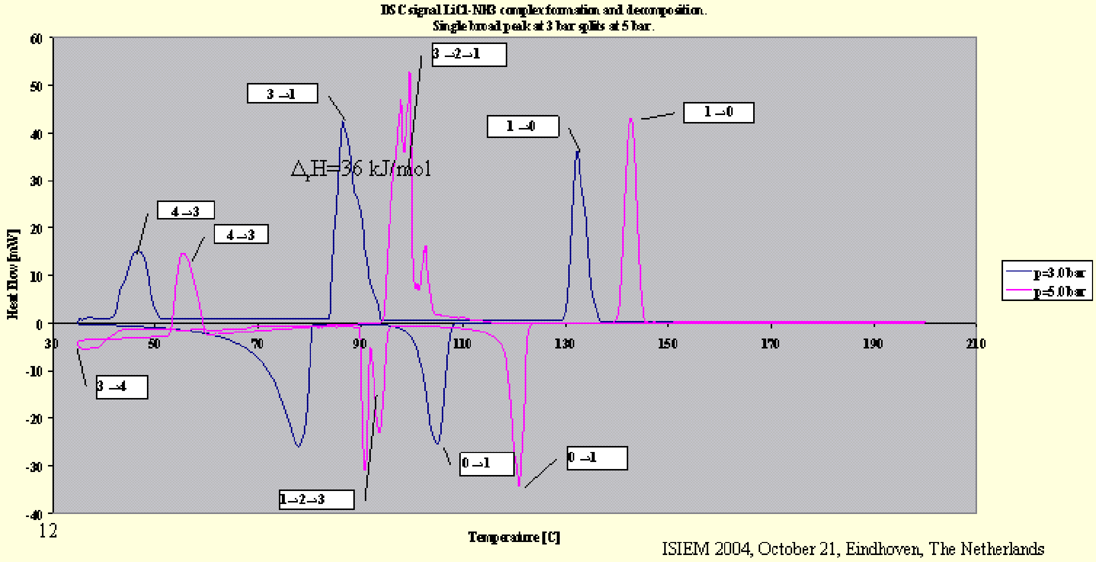
X-ray diffraction

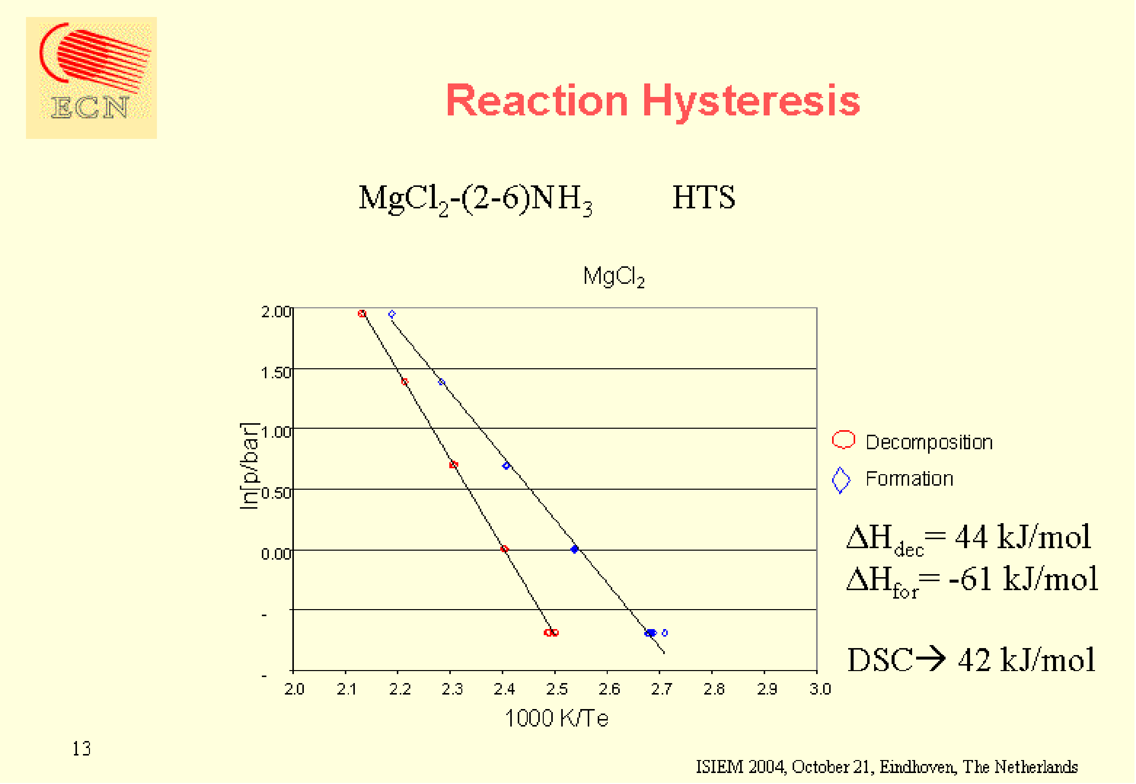




High Pressure-DSC measurements

LiCl-NH_3 LTS



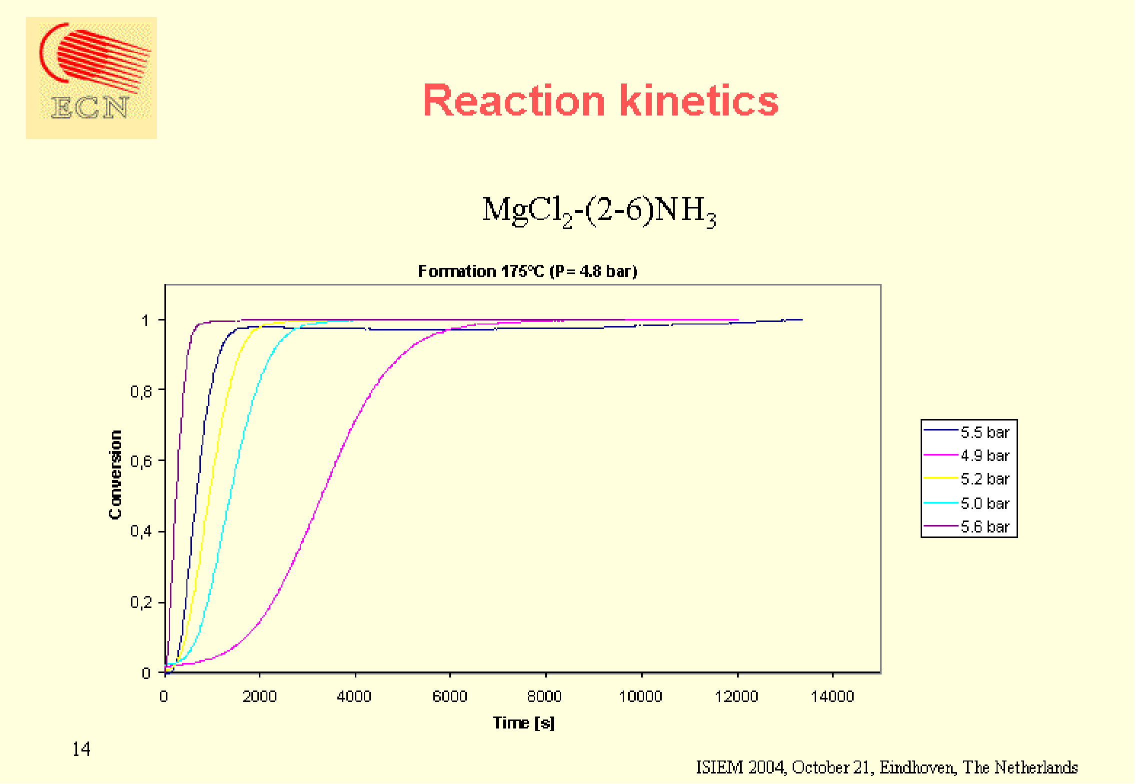


Reaction Hysteresis

$MgCl_2$-(2-6)NH_3 HTS

ΔH_{dec} = 44 kJ/mol
ΔH_{for} = -61 kJ/mol

DSC→ 42 kJ/mol



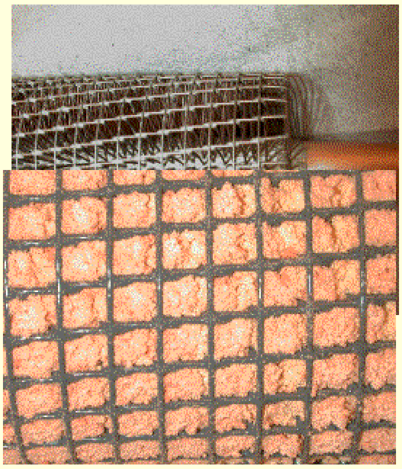
Reaction kinetics

$MgCl_2$-(2-6)NH_3

Reactor design

- Batch proces
- Heat and mass transfer
- Salts - Poor thermal conductivity
- 1)Design for heat transfer, 2) check on mass transfer, 3) assume reaction kinetics not limiting
- Porous structure of salt mass, high surface area
- Solid Sorbent + heat exchanger integrated
- Porous heat conducting support

Examples of reactor designs



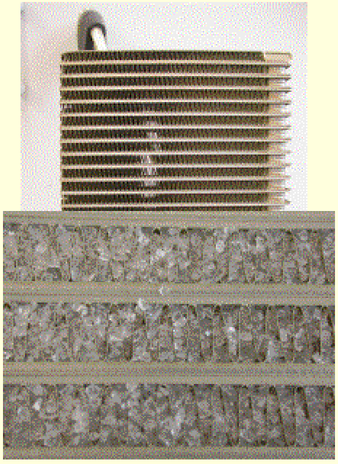


Plate-fin HEX

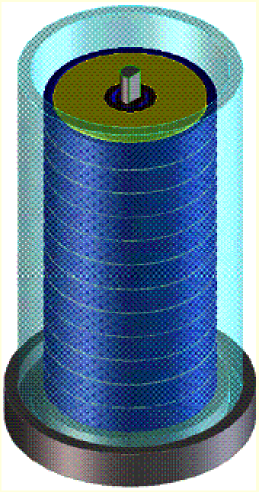
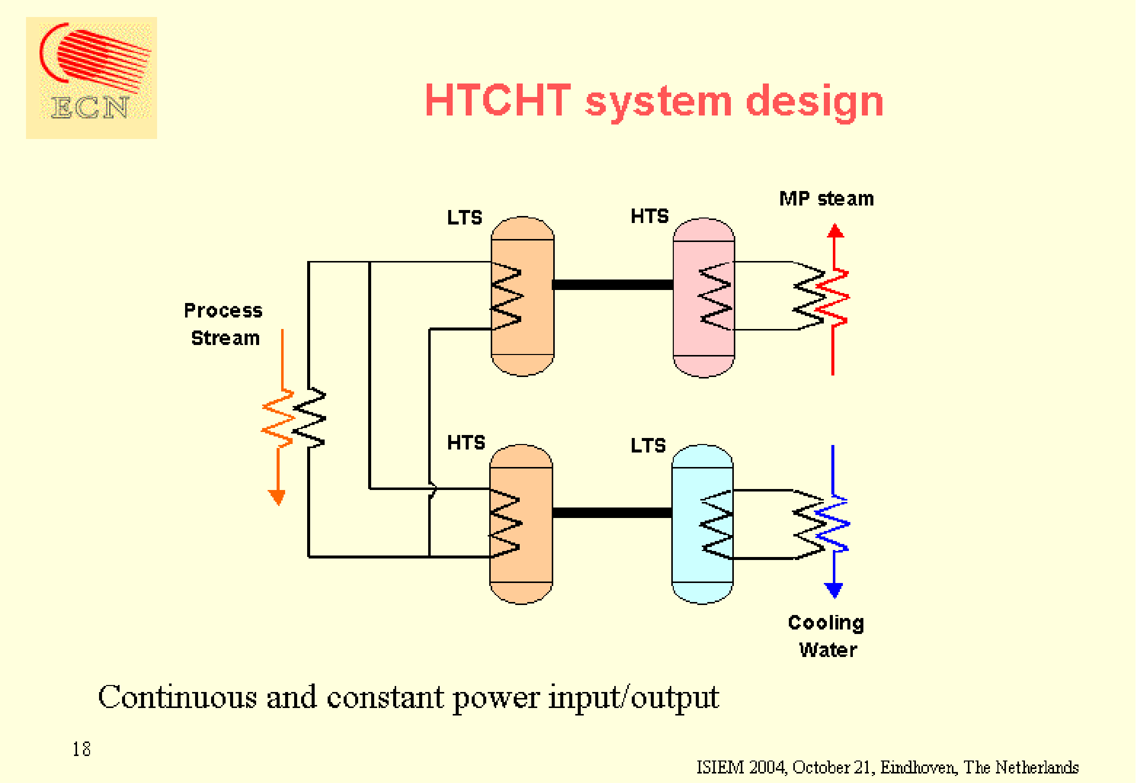


Plate-shell HEX

Support material



HTCHT system design

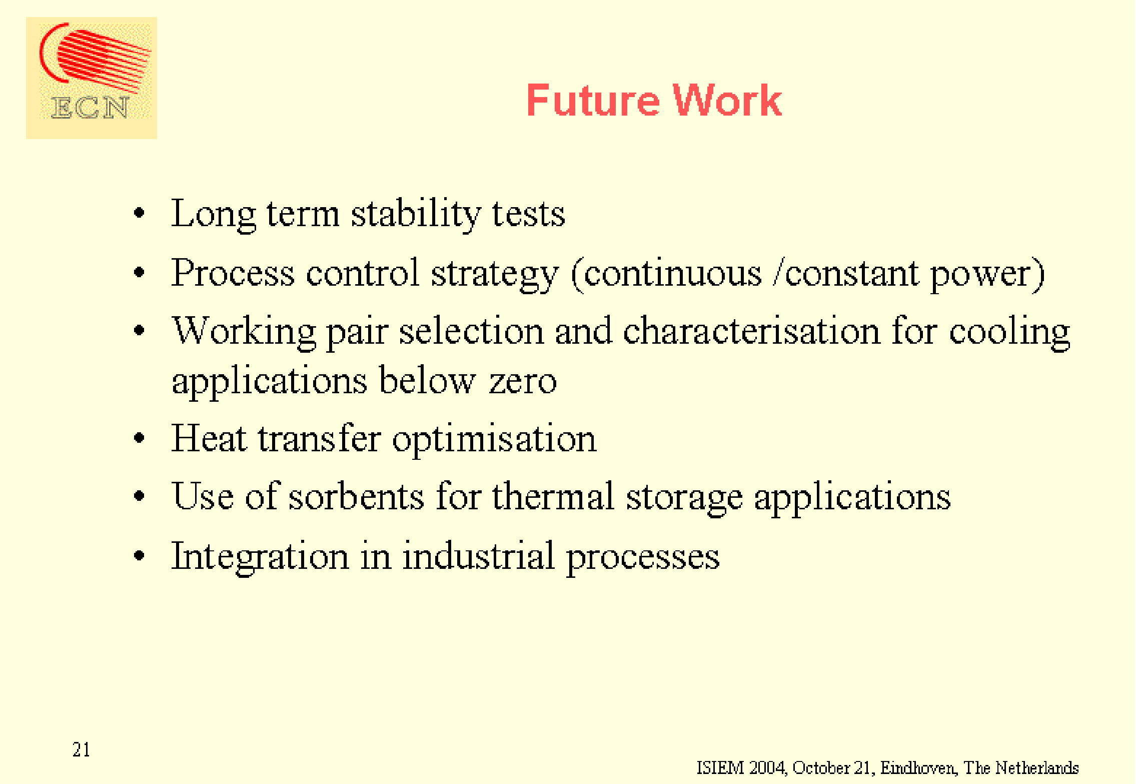
Continuous and constant power input/output

HTCHT: Techno-Economic Evaluation

- Cost estimation:
  - 5 MW thermal input at 140°C
  - 1.7 MW Mid-Pressure steam at 239°C output
  - Shell&fin-tube reactor design
  - U = 1000 W/m^{2}K
  - Total capital investment: 1.3 M€
- Pay out time 2-5 years
- Primary Energy saving 17 PJ/a
- CO_2 emission reduction 950 kTonne/a
- NOx emission reduction 1 kT/a

Conclusions

- Chemical heat pumps are technologically and economically a viable concept for saving large amounts of primary energy in industry and built environment
- Working pairs not off the shelf→ extensive experimental checking necessary.
- Reaction kinetics (salt –ammonia) not limiting for performance
- Focus on heat transfer optimisation
- Poor mechanical stability of the salt-ammoniates
- Each application requires specific working pair



Future Work

- Long term stability tests
- Process control strategy (continuous /constant power)
- Working pair selection and characterisation for cooling applications below zero
- Heat transfer optimisation
- Use of sorbents for thermal storage applications
- Integration in industrial processes

Thanks for your attention
questions?