Ecole d'ingénieurs du Canton de Vaud

Journée du CUEPE 2006
Geneva, 6th of April 2006

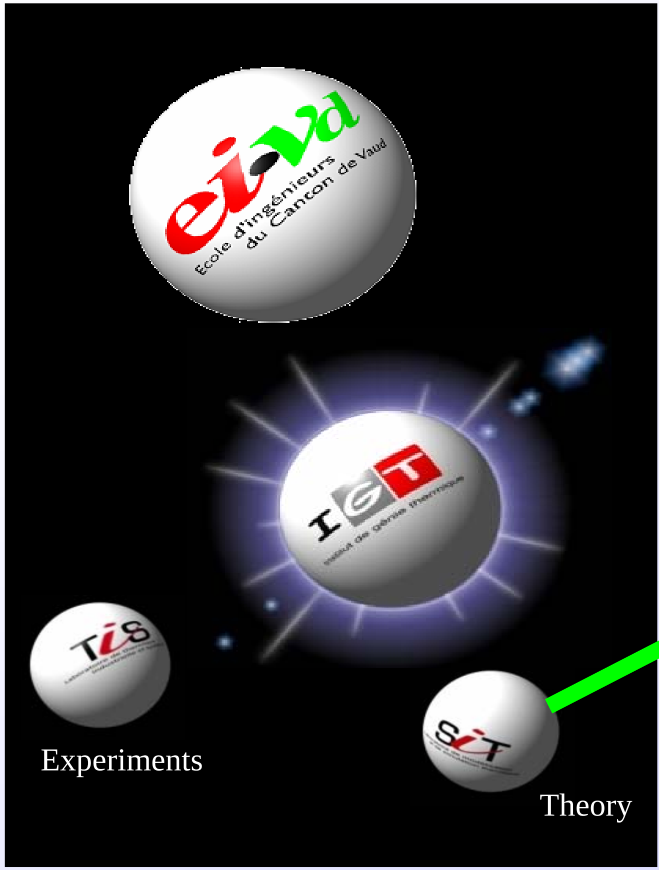
Haute Ecole Spécialisée de Suisse Occidentale

Magnetic heating and refrigeration: A new technology of heat and cold production

University of Applied Sciences of Western Switzerland
Yverdon-les-Bains, Switzerland

Peter W. Egolf

The Divisons TIS and SIT



Thermique Industriel et Systèmes:
O. Sari, N. Erbeau, J. Brulhart, M. Zaghoudi, G. Wyss, G. Chollet, K. Martin-Drezet

Simulation des Systèmes Thermique:
P.W. Egolf, F. Gendre, A. Kitanovski, D. Ata-Caesar, H. Bajpai, K. Winkelmann

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Collaboration and Help

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New name:

heig-vd
Haute Ecole d'Ingénierie et de Gestion
du Canton de Vaud

Route de Cheseaux 1
CH - 1401 Yverdon-les-Bains

- **Prof. Dr. O. Sari**
- **F. Gendre**
- **N. Erbeau**
- **N. Alber**
- **F. Brun**
- **J. Hu**

University of Ljubljana

Prof. Dr. Alojz Poredos
Dr. Andrej Kitanovski
Dr. Alen Sarlah

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„Giant“ magnetocaloric effect

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New materials ... may bring practical magnetocaloric cooling a step closer. A large magnetic entropy change has been found to occur in $MnFeP_{0.45}As_{0.55}$ at room temperature, making it an attractive candidate for commercial applications in magnetic refrigeration.

Nature Highlights

10 th of January 2002

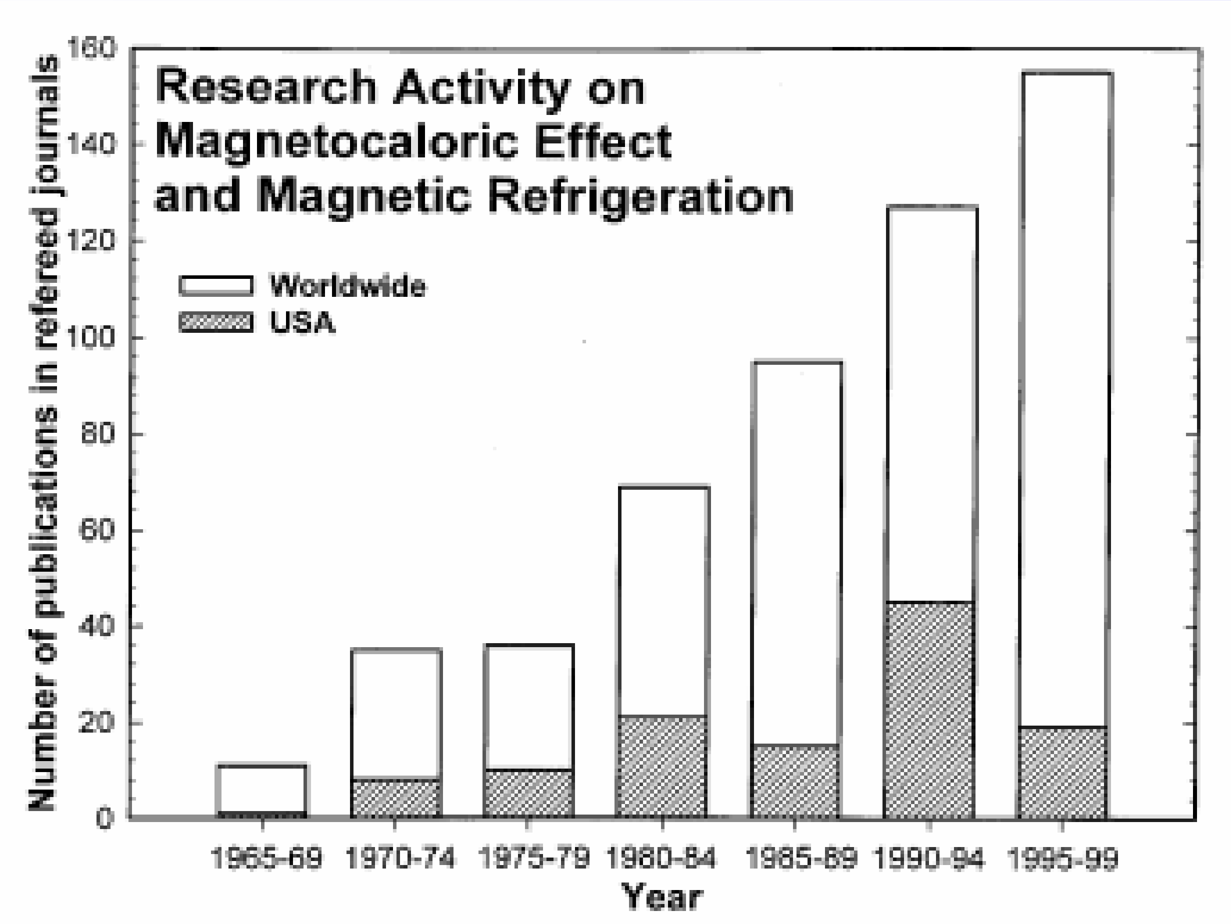
„Giant“ magnetocaloric effect

In an article published in the journal *Nature* last month, scientists at the University of Amsterdam reported that they had created an iron-based compound that also exhibits a large warming effect in a magnetic field. Iron and other ingredients in the compound are considerable less expensive than gadolinium.

The New York Times

9 th of February 2002

„Giant“ magnetocaloric effect



Brief history of magnetocaloric materials and systems

- 1881 : Warburg discovers the magnetocaloric effect in iron
- 1926 : Debye proposes the first practical application at low temperatures. The process is named adiabatic magnetization/demagnetization
- 1927 : Giauque proposes the same process independently of Debye
- Since 1930 : Application of magnetic cooling becomes standard in low temperature physics ($T<<1$ K)
- At present : Discovery of magnetocaloric materials with Currie temperatures T_C around room temperature
- Development of new magnetic cooling systems operating at room temperature: **Promising new technology !**

The magnetocaloric effect

For the entropy of rare earth alloys (no electron phonon interactions) a superposition of the partial entropies is possible (Tishin, 2003):

$$S(H,T)=S_e(T)+S_l(T)+S_m(H,T)$$

The entropy of the electronic (*e*) and the lattice (*l*) subsystems show no dependence on the magnetic field! Then:

$$ds(H,T)=\frac{ds_e}{dT}(T)dT+\frac{ds_l}{dT}(T)dT+\left(\frac{\partial s_m}{\partial H}\right)_T(H,T)dH+\left(\frac{\partial s_m}{\partial T}\right)_H(H,T)dT$$

Some basic thermodynamic relations and definitions:

$$\delta q=Tds \qquad c_\chi=\left(\frac{\delta q}{\partial T}\right)_\chi \qquad c_\chi=T\left(\frac{\delta s}{\partial T}\right)_\chi$$

The magnetocaloric effect

Combining these equations:

$$ds(H,T) = \frac{c_e(T)}{T}dT + \frac{c_l(T)}{T}dT + \left.\frac{c_m(H,T)}{T}\right|_H dT + \left(\frac{\partial s_m}{\partial H}\right)_T (H,T)dH$$

With the Mayxwell relation (e.g. Kitanovski & Egolf, Int. J. Refr. **29**, 3-21, 2006:

$$\left(\frac{\delta s}{\partial H}\right)_T = -\mu_0 \left(\frac{\delta M}{\partial T}\right)_H$$

because:

$$\left(\frac{\delta s_m}{\partial H}\right)_T = \left(\frac{\delta s}{\partial H}\right)_T$$

The magnetocaloric effect

and:

$$c_H = c_e + c_l + c_m$$

In an adiabatic magnetization or demagnetization process:

$$ds = 0$$

Therefore, it follows that:

$$\frac{c_H}{T} dT - \mu_0 \left(\frac{\delta M}{\partial T} \right)_H = 0 \quad \Rightarrow \quad \boxed{\frac{dT}{T} = \frac{\mu_0}{c_H} \left(\frac{\delta M}{\partial T} \right)_H dH}$$

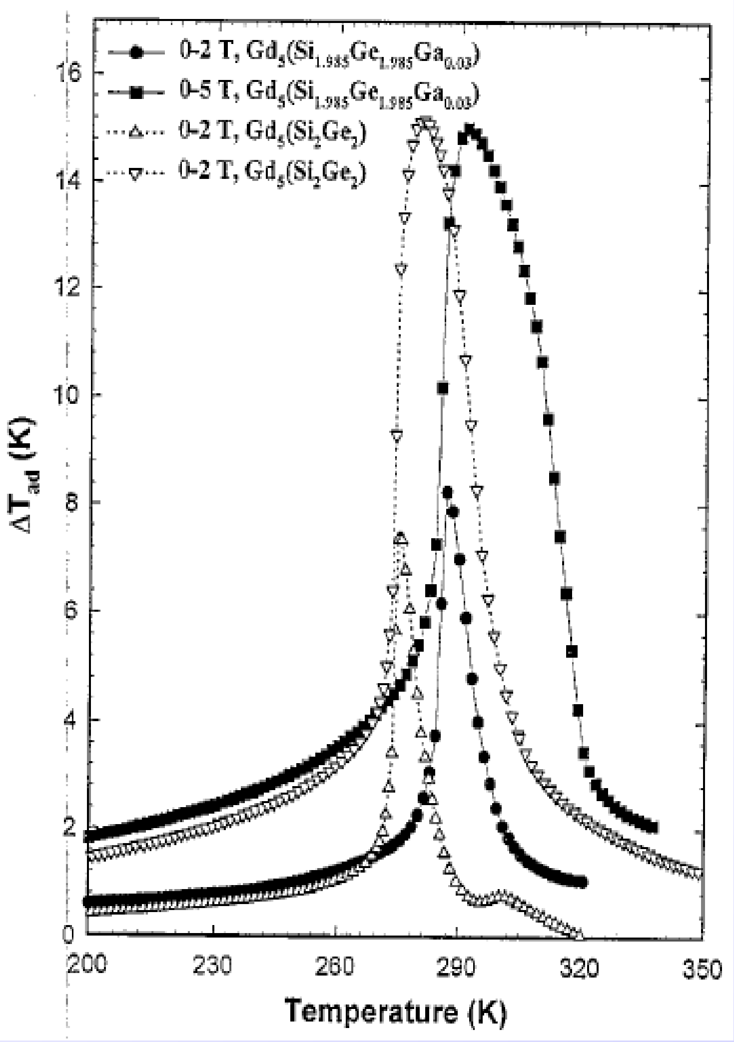
Moving magnetocaloric material into (out of) a magnetic field increases (decreases) the magnetisation and the temperature.

The magnetocaloric effect

The magnetocaloric effect occurs at a phase transition between different magnetic states.

The temperature of phase change is the Curie temperature.

The magnetocaloric effect

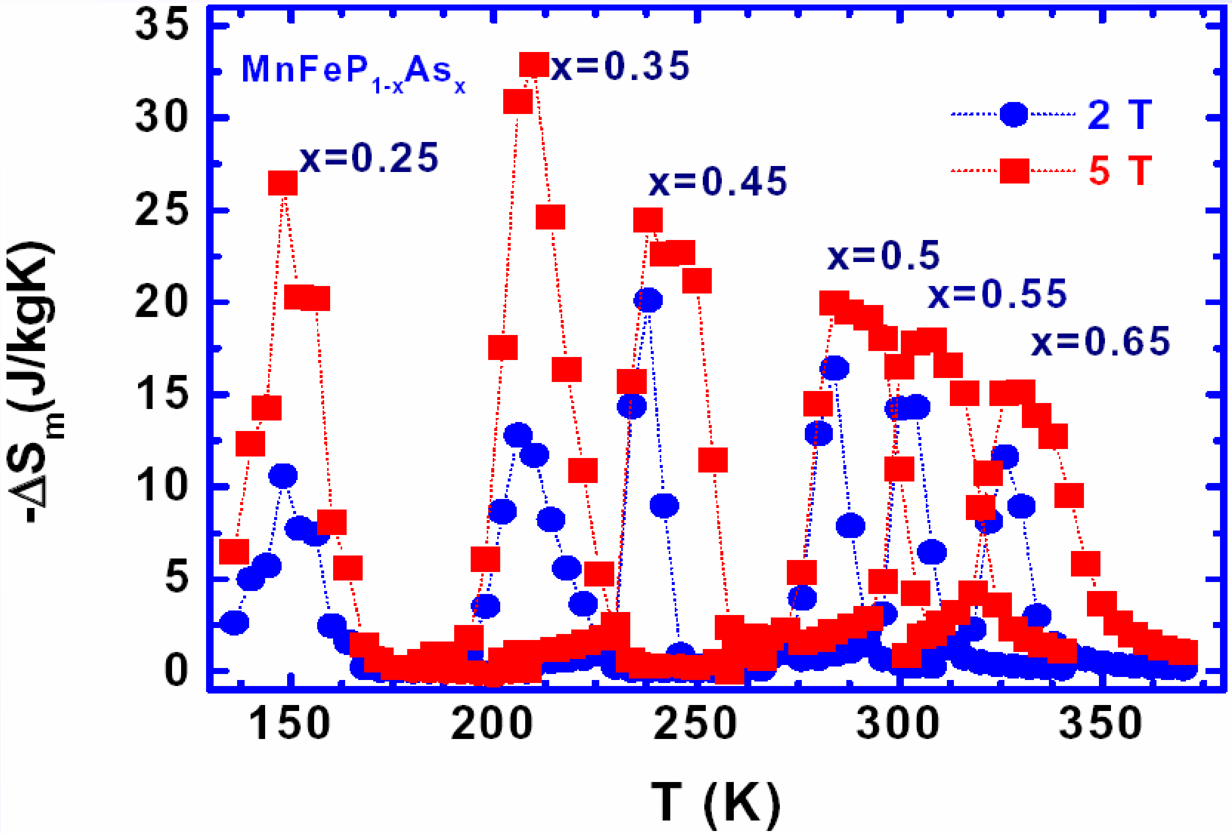


Data from:

Pecharsky VK, Gschneidner KA Jr. *Tunable magnetic regenerator alloys with a giant magnetocaloric effect for magnetic refrigeration from ~ 20 to ~ 290 K.* Applied Physics Letters 1997; 70 (24): 3299-3301.

Still limited temperature differences!

Magnetic heating and refrigeration at room temperature



Tegus, PhD thesis

Van der Waals-Zeemann Institute

University of Amsterdam

2003

Magnetic heating and refrigeration at room temperature

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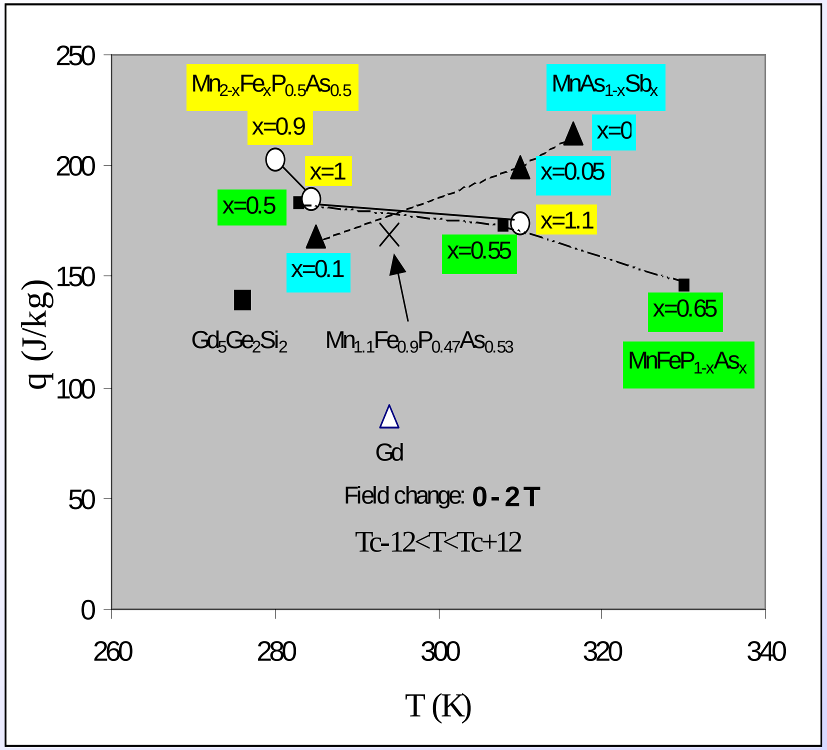
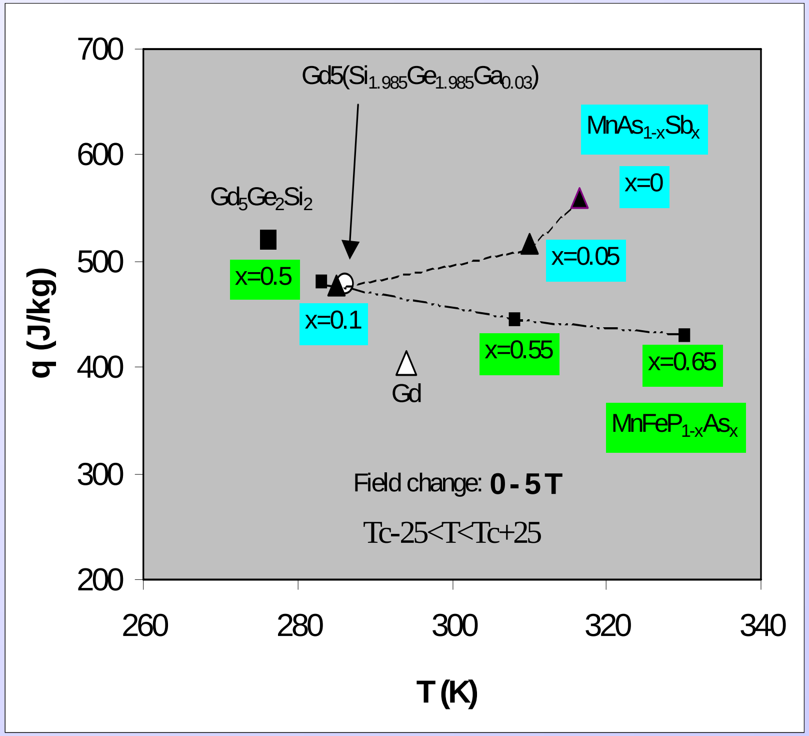
Heating and refrigeration „capacities“:





Tegus et al., 2002

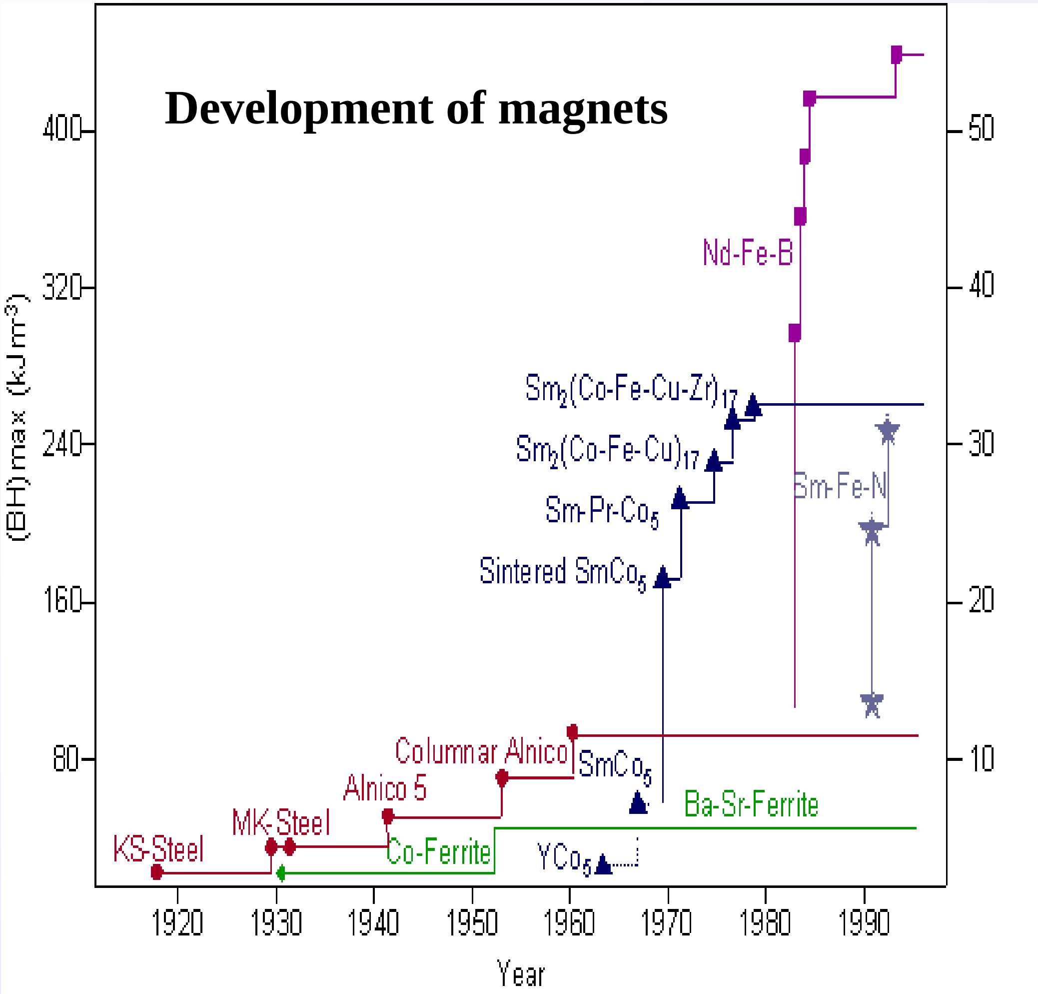
Zimm et al., 2001

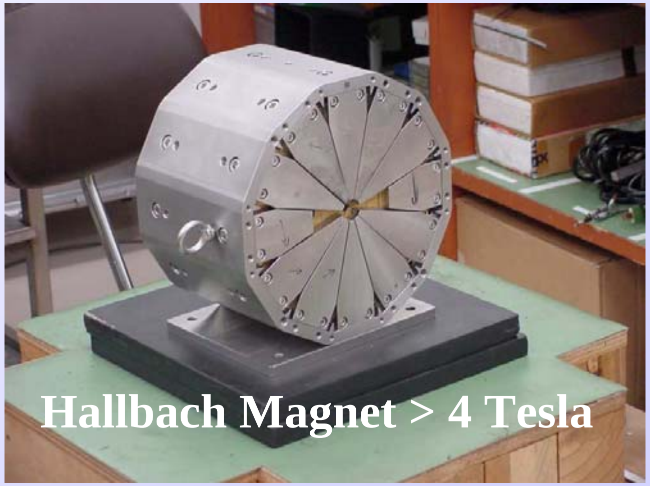
Magnetic heating and refrigeration at room temperature

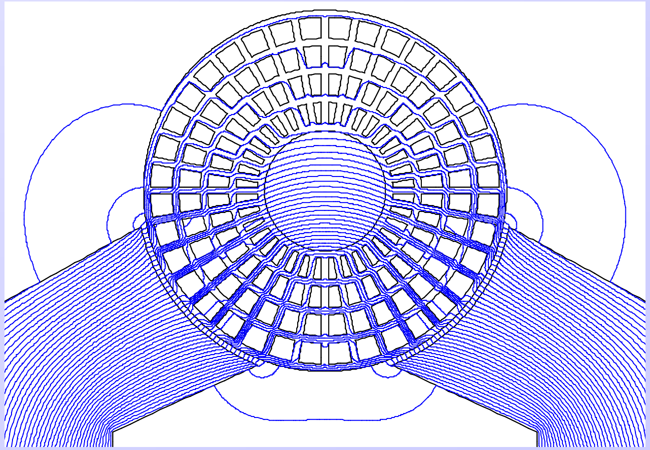
Magnetocaloric materials should (partly by Yu et al., 2003):

- Modest Debye temperature (a high temperature makes the fraction of lattice entropy small correspondingly at a high temperature)
- High temperature difference at phase transition
- Large width of transition
- No magnetic hysteresis (irreversibility of cycle)
- Small specific heat and large thermal conductivity to guarantee fast heat exchange
- Large electric resistance to avoid the eddy current loss
- Fine molding and processing must be possible
- No poison substances (arsenic, etc.) for direct contact applications

Magnetic heating and refrigeration at room temperature

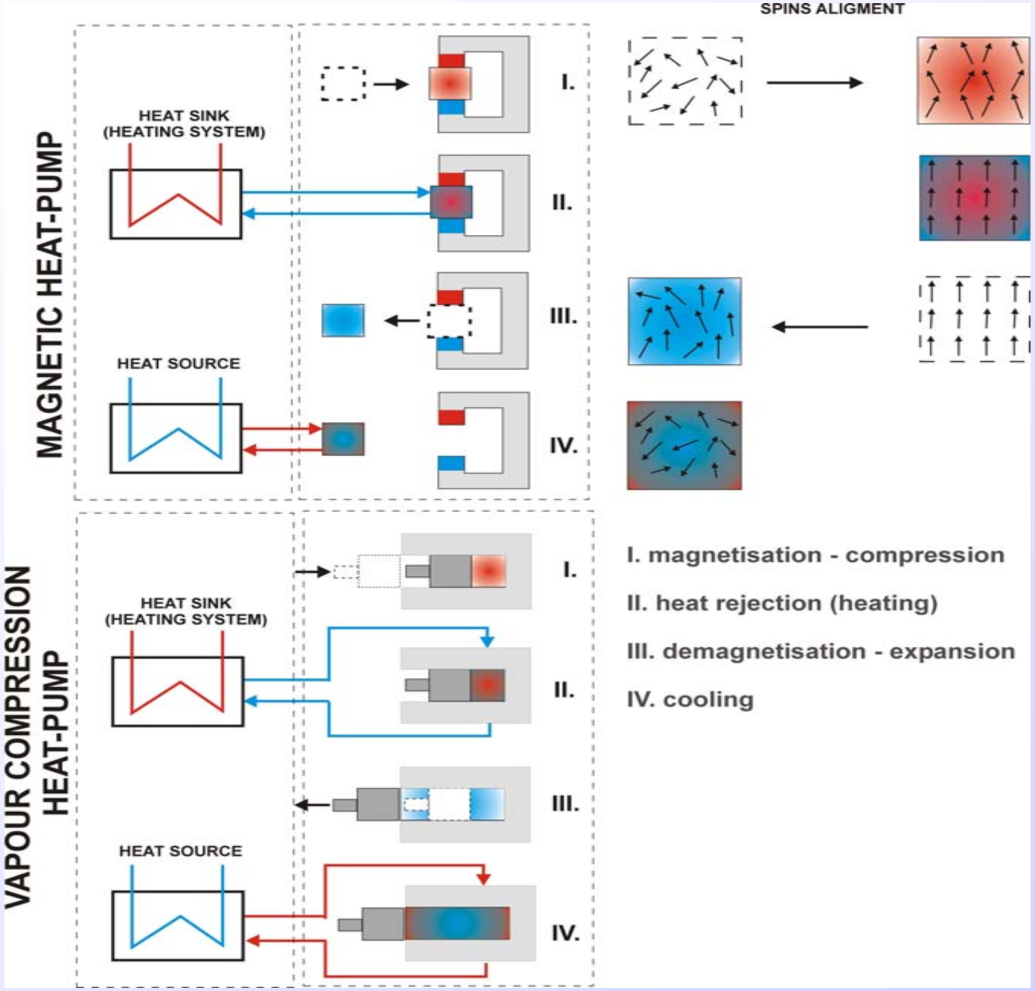






High flux line density

Magnetic heating and refrigeration at room temperature



Four stage process each:

A) Magnetic heat pump:

1) Increase of magnetic flux density
2) Rejection of heat for heating purpose at high temperature level
3) Decrease of magnetic flux density
4) Injection of heat at low level to the heat pump

B) Conventional heat pump:

1) Compression (Increase of pressure)
2) Rejection of heat for heating purpose at high temperature level
3) Expansion (decrease of pressure)
4) Injection of heat at low level to the heat pump

Magnetic heating and refrigeration at room temperature

Advantages:

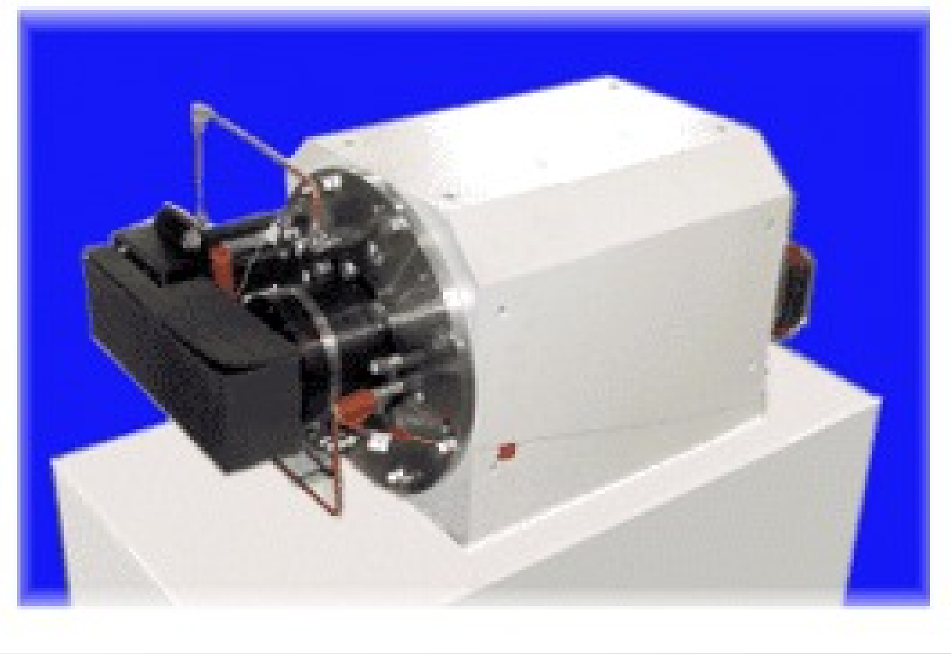
- Green technology (no use of conventional refrigerants)
- Noise-less technology (no compressor)
- Very high thermodynamic efficiency (20-30% higher than in conventional cycles due to the reversibility of the magnetocaloric effect)
- Lower energy consumption
- Simple construction
- Low maintenance costs
- Low pressures (operation at atmospheric pressure, advantage e.g. for air-conditioning applications and refrigeration systems in automobiles)

Magnetic heating and refrigeration at room temperature

Disadvantages:

- Strong magnetic fields with not completely known influences on living creatures
- Protections to avoid disturbances of electronic components
- The field strengths of permanent magnets are still limited, superconducting magnets are too expensive
- The temperature differences are still not so high
- In moving material applications the precision of the machine must be high (small gap between magnet and magnetocaloric material)

Existing prototypes

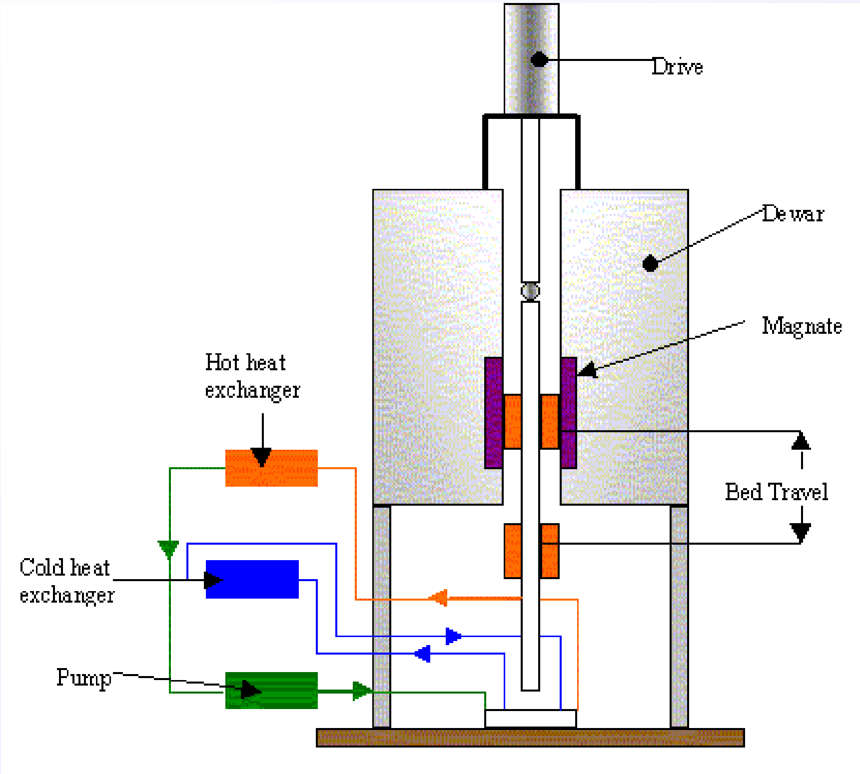


A development in Japan

Chubu – Toshiba (2000)

This machine consists of a cascade with three pistons of different magnetocaloric materials. A low magnetic field of B=0.7 T is induced by permanent magnets.

Existing prototypes



Development in the USA

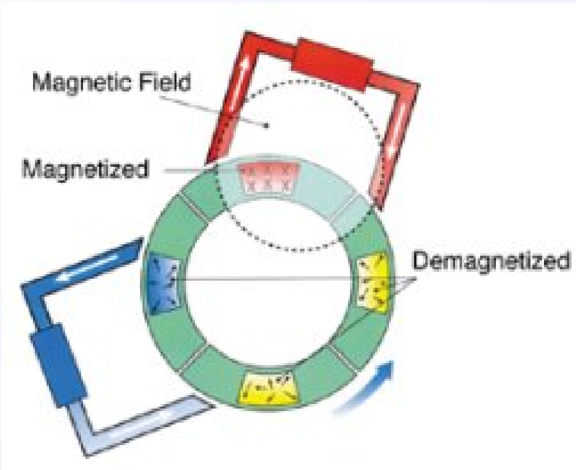
AMES Laboratory - 1997

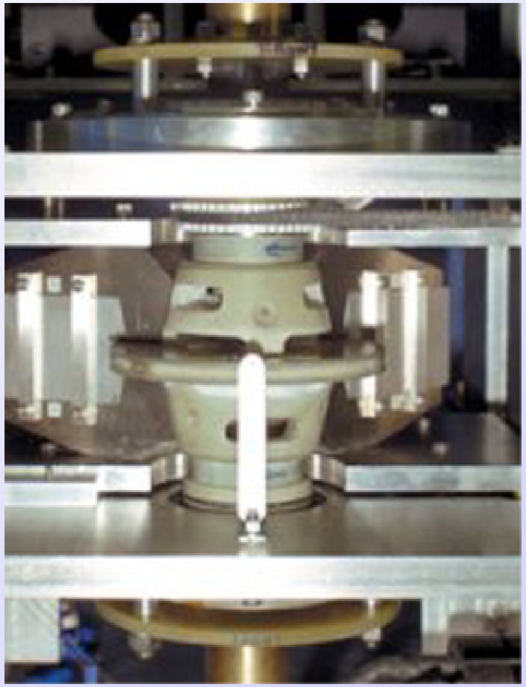
The kernel are two pistons of packed beds of gadolinium spheres. A superconducting magnet with a high magnetic field is applied.

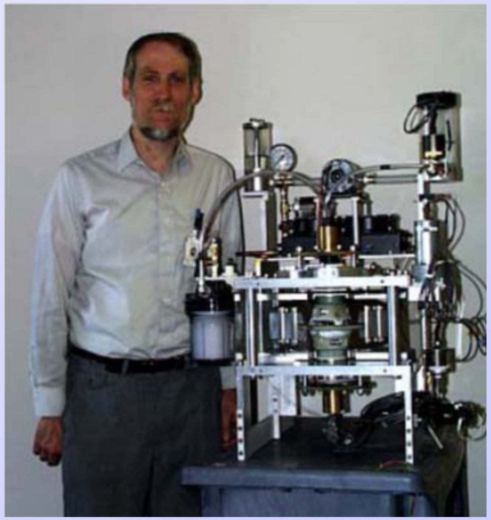
Existing prototypes

Development in the USA

AMES Laboratory - 2001

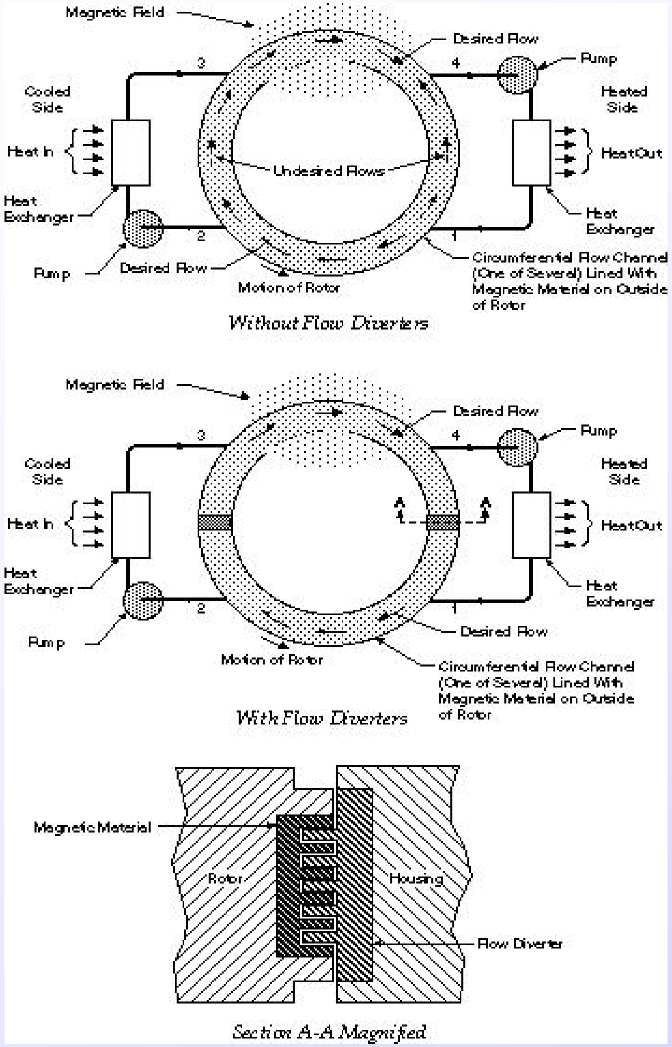






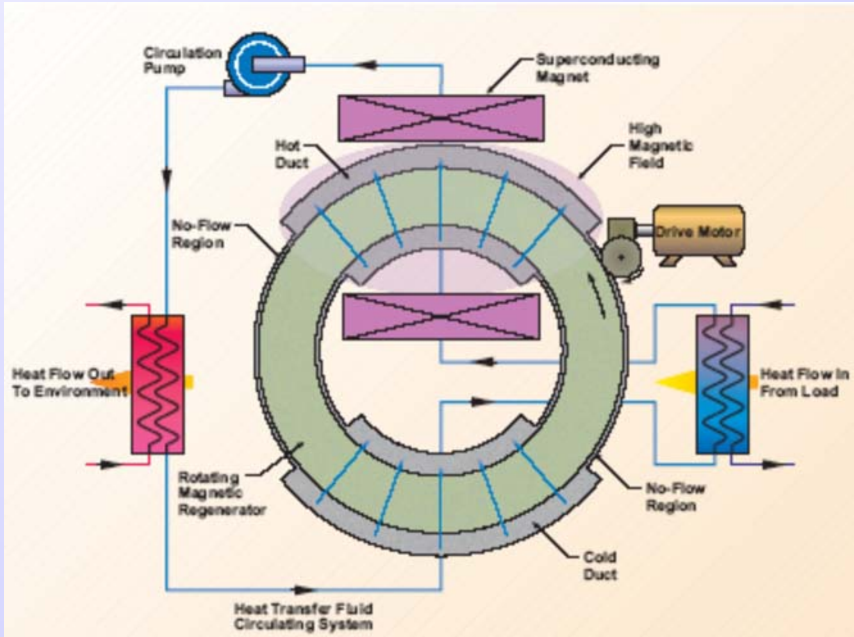
Rotary magnetic refrigerator with permanent magnets
(with complicated fluid switches)

Existing prototypes



Developments in the USA

University of Victoria



Magnetic forces and thermodynamic potentials

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A. Lange, *Kelvin force in a layer of magnetic fluid.*
J. Magn. Mat. 2001; 241: 327-329:

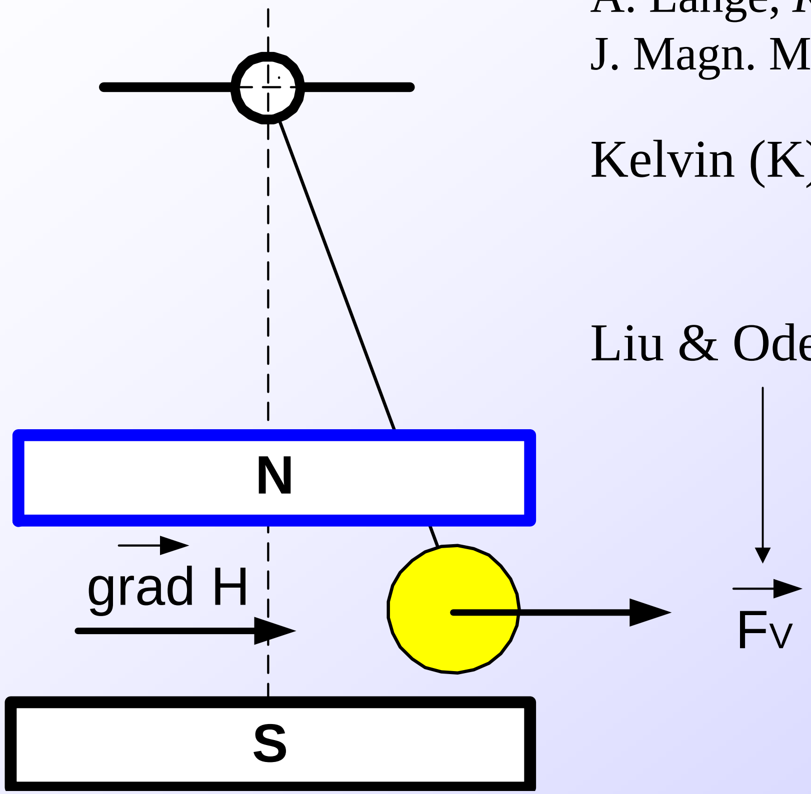
Kelvin (K): $$\boxed{\vec{F}_K = \mu_0 \int_\Gamma M_i \nabla H_i \, dV}$$

Liu & Odenbach (V): $$\boxed{\vec{F}_V = \mu_0 \int_\Gamma M_i \nabla B_i \, dV}$$

extensive vector analytical treatment

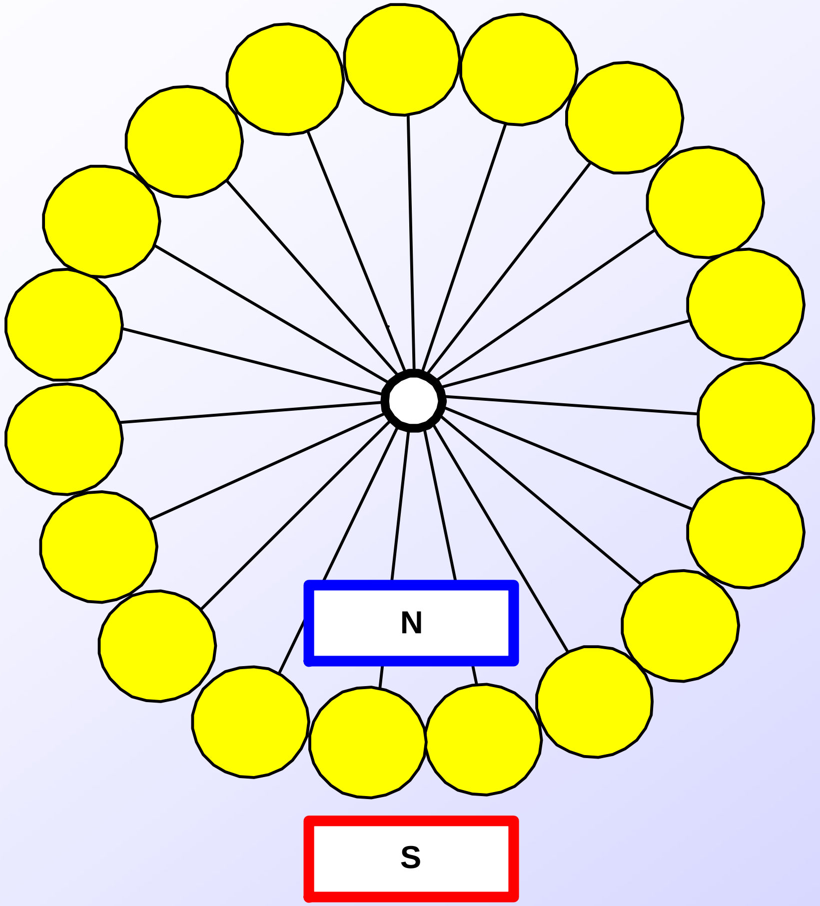
$$\boxed{\vec{F}_V = \mu_0 \int_\Gamma H_{0i} \nabla M_i \, dV}$$

Kitanovski & Egolf, 2005 (in print)



Dilute limite only (ferrofluids)!

Magnetic forces and thermodynamic potentials



What is the difference?

We still may have the external work:

$$dw_1^{(ext)} = -\mu_0 H_0 dM$$

But now additionally a flux of magnetisation occurs. Its infinitesimal change is:

$$dw_1^{(abs)} = -\mu_0 d\left(H_0 M\right)$$

Then the technical work is:

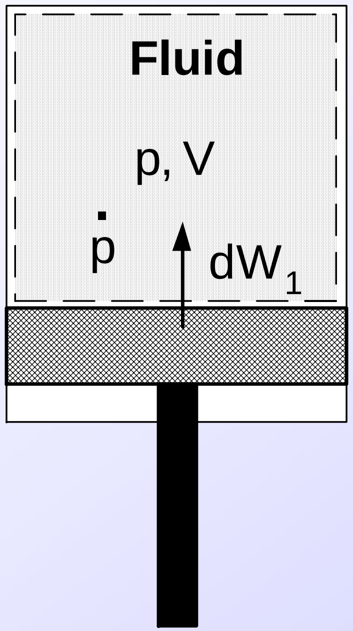
$$dw_1^{(tech)} = -\left(dw_1^{(abs)} - dw_1^{(ext)}\right) = \mu_0 M dH_0$$

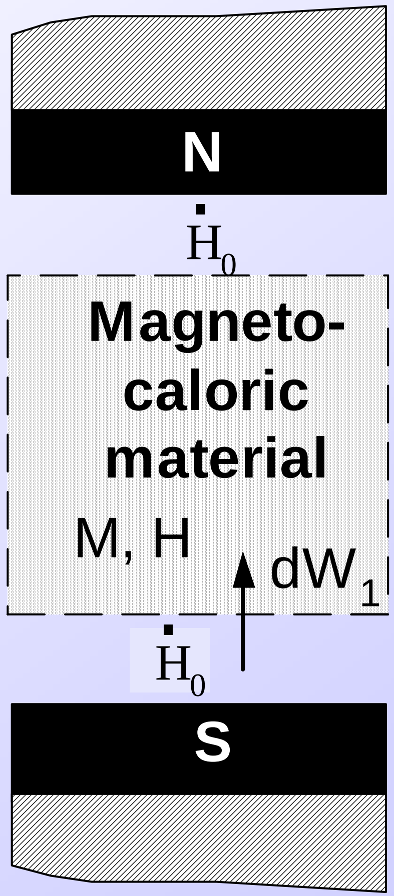
In turbo machinery this work is also named shaft work

Magnetic forces and thermodynamic potentials

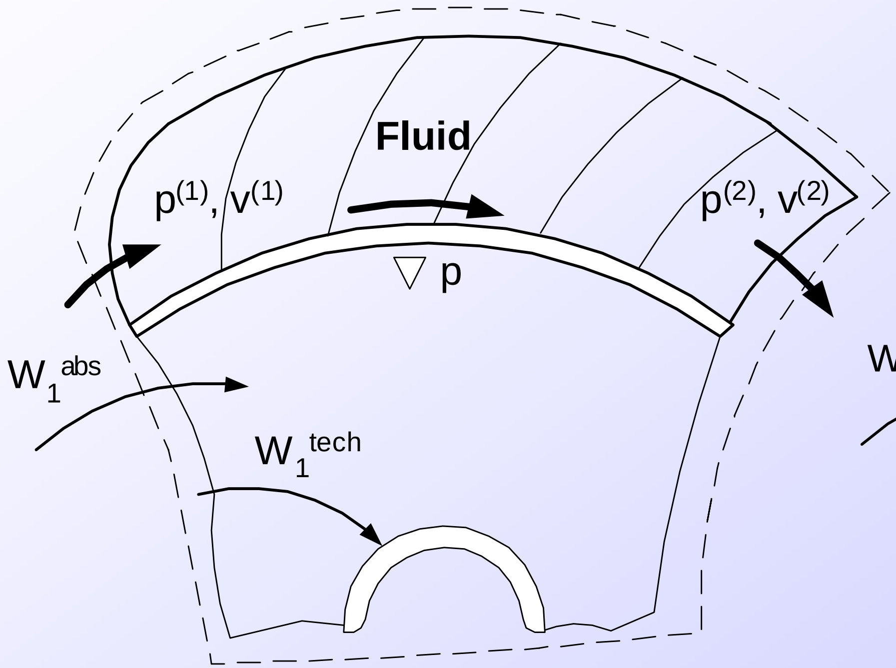
Quantity	Gas thermodynamics	Magneto-thermodynamics
Driving "force" (stress parameter)	Pressure p	Field H_0
Order parameter (reaction of system)	Specific volume v	Magnetization M (orientation of spins)
External work (closed system)	$dw_1^{(ext)} = -p dv$	$dw_1^{(ext)} = -\mu_0 H_0 dM$ (related to force of Liu)
Technical work (open system)	$dw_1^{(tech)} = v dp$	$dw_1^{(tech)} = \mu_0 M dH_0$ (related to Kelvin force)

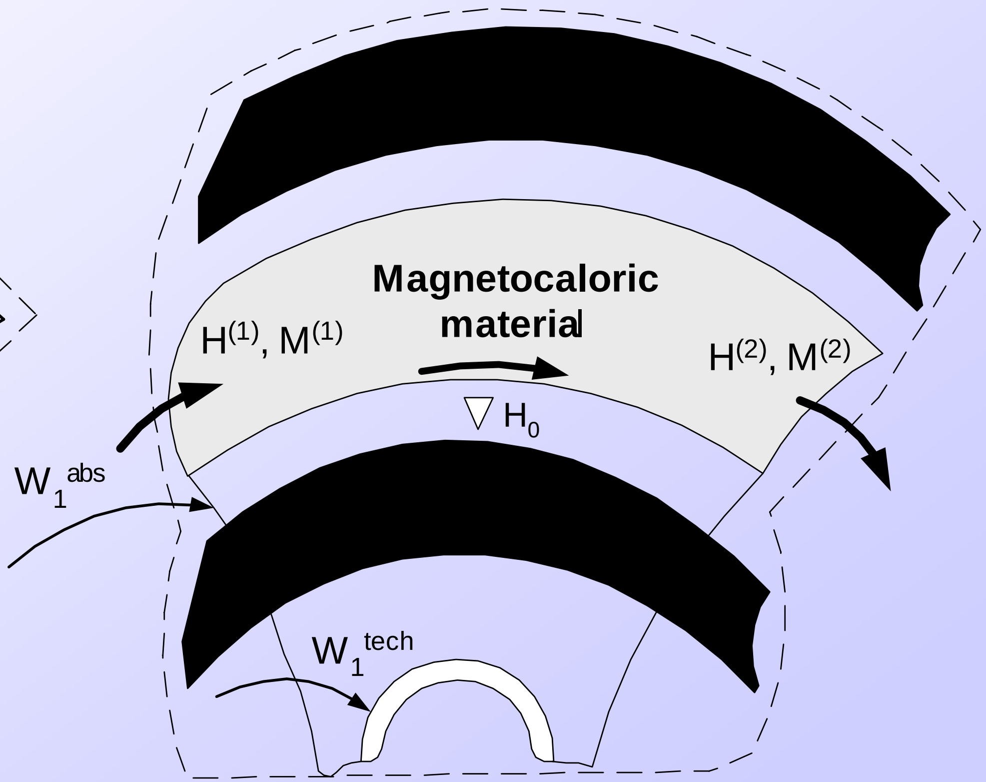
Possible Systems





Possible systems:
Open systems

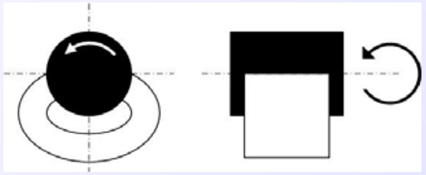




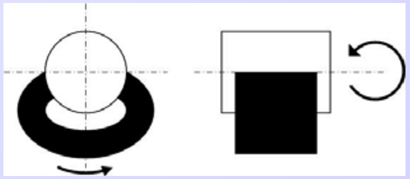
Possible systems

1) Static system with two storage blocks and valves
2) Linear movement
3) Rotational movement

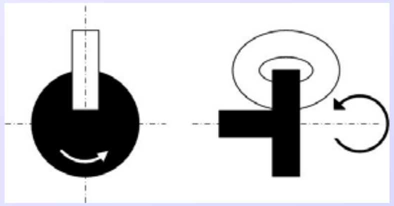
Solution A:
Rotary wheel, magnet fixed, axial current.



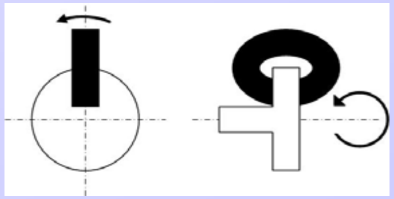
Solution B:
Wheel fixed, rotating magnet, axial current.



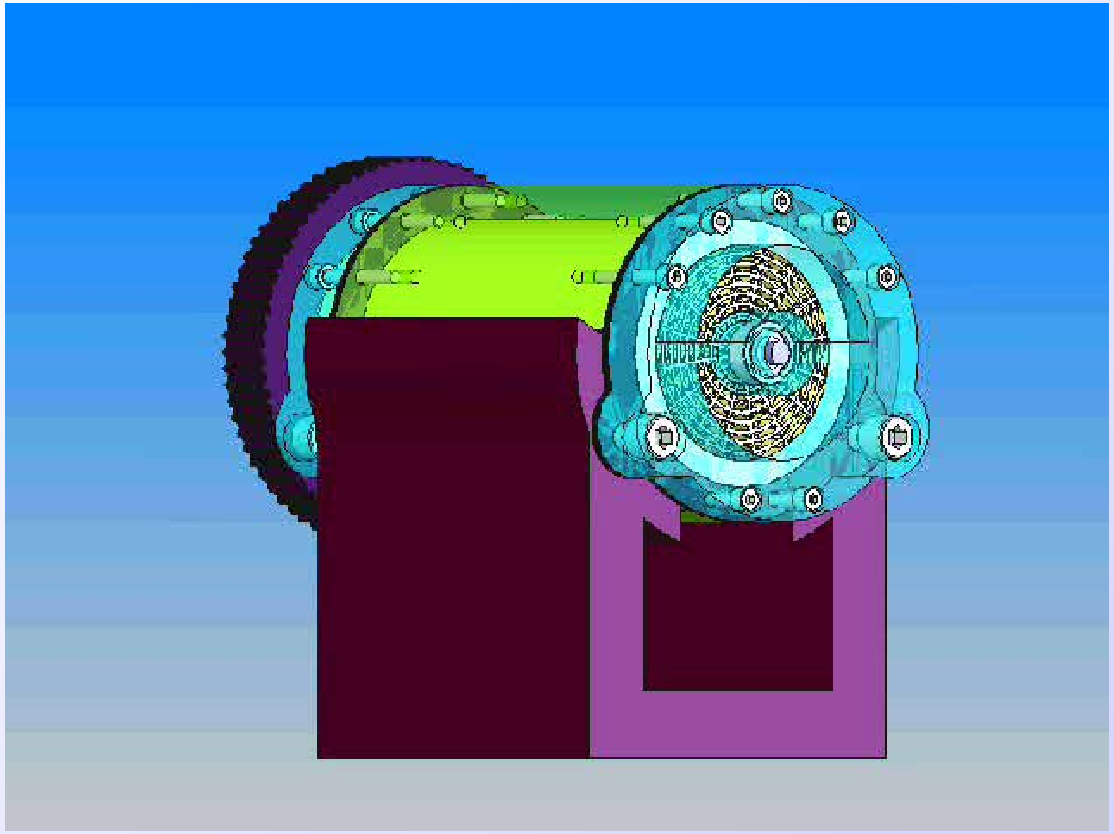
Solution C:
Rotary wheel, fixed magnet, radial current.



Solution D:
Fixed wheel, rotary magnet, radial current.



Porous rotary magnetic refrigerator

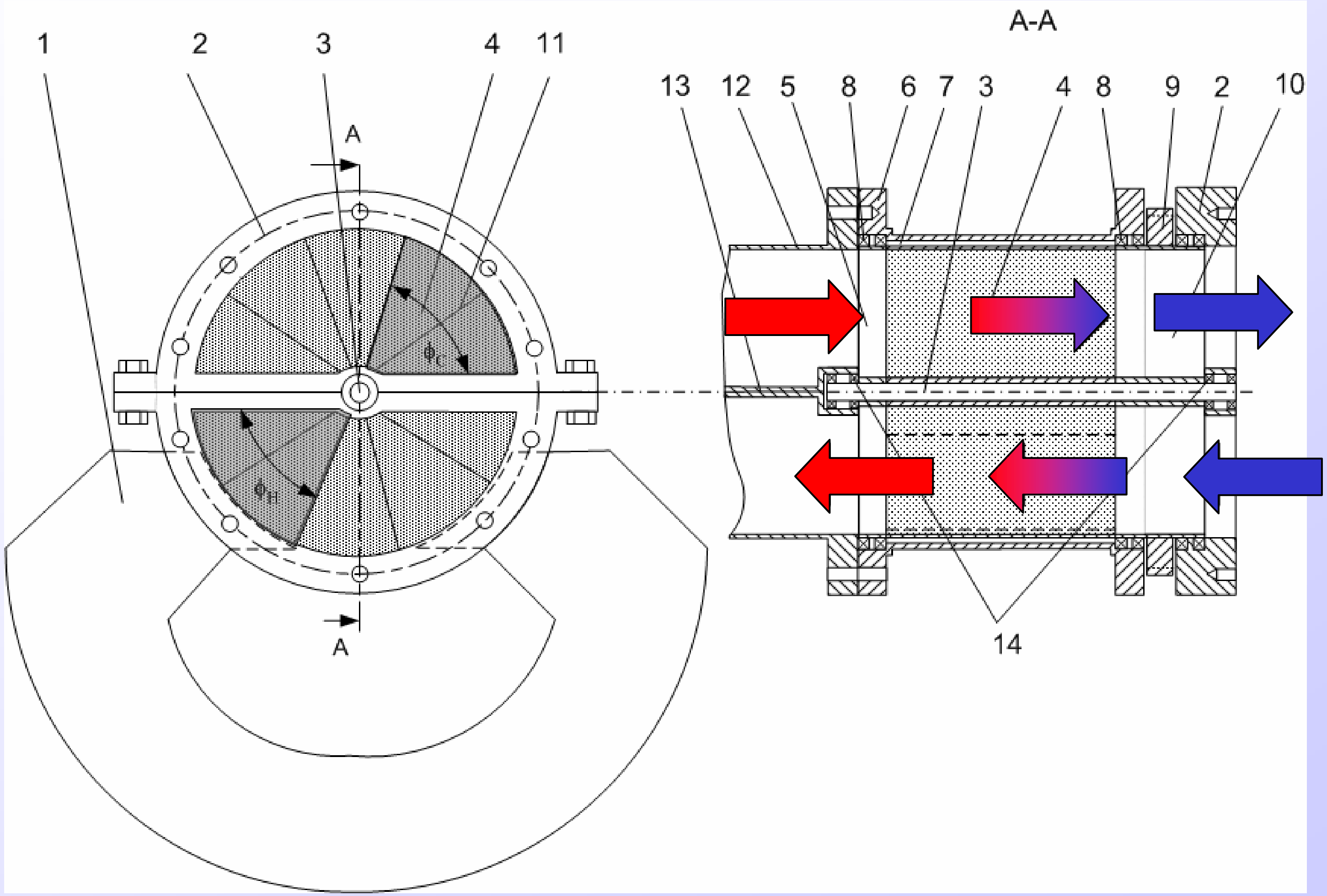


A. Kitanovski, P. W. Egolf, O. Sari, 2003. *Procédé et dispositif pour generer en continue du froid et de la chaleur par effet magnetique.*

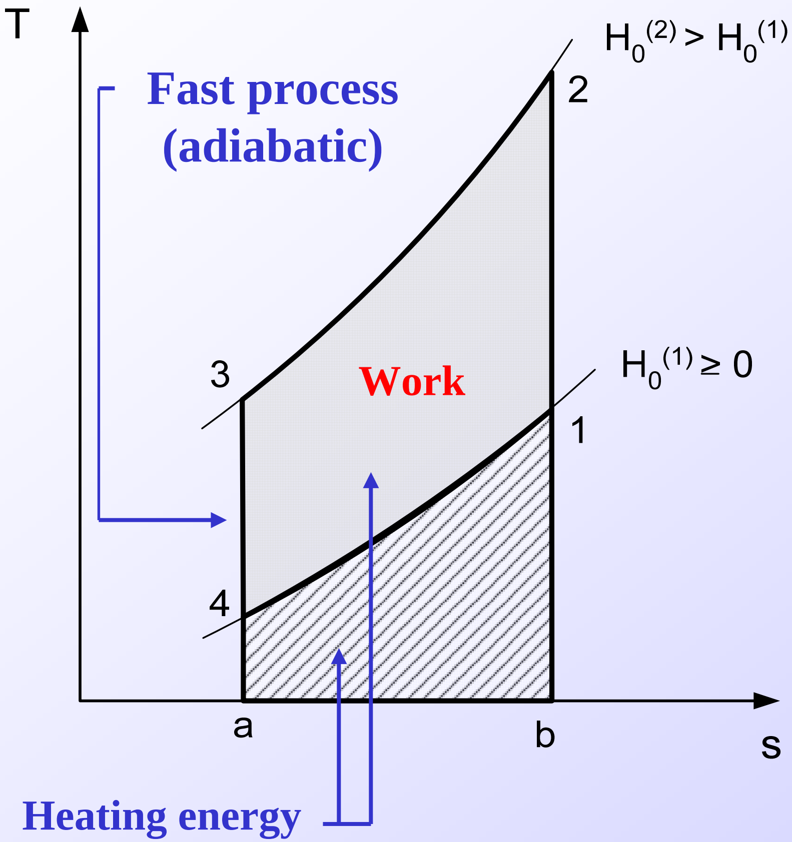
PCT BR – 10’463 - IN

Four functions are realized in a very simple manner!

Porous rotary magnetic refrigerator



Thermodynamic cycles, cascades, regeneration



A. Kitanovski, P.W. Egolf
International Journal of Refrigeration
***Thermodynamics of Magnetic Refrigeration* (in print):**

Internal energy:

$$du_1 = T\,ds - \mu_0 \vec{H}_0 d\vec{M}$$

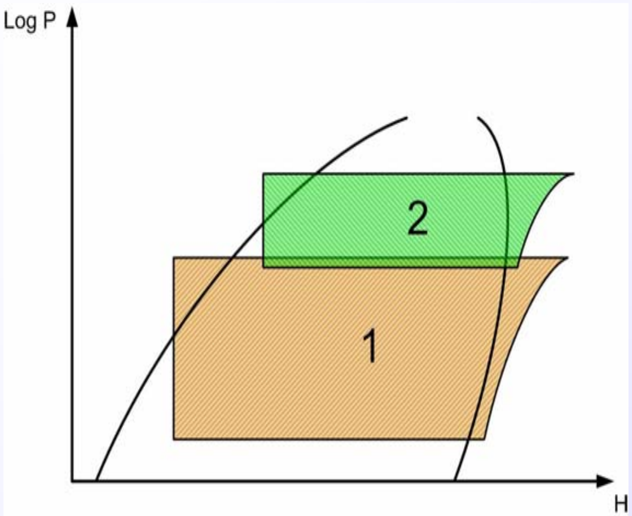
Legendre Transformation:

$$h_1 = u_1 + \mu_0 \vec{H}_0 \vec{M} \quad \Rightarrow \quad dh_1(s, H_0) = T\,ds + \mu_0 M dH_0$$

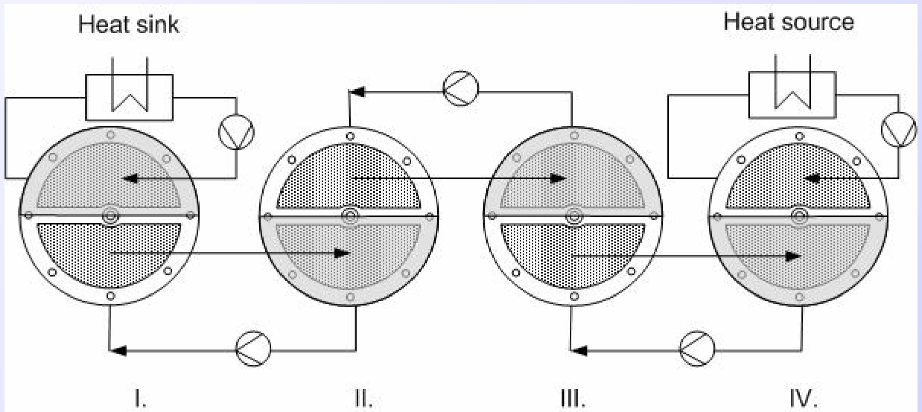
„Coefficient of performance“:

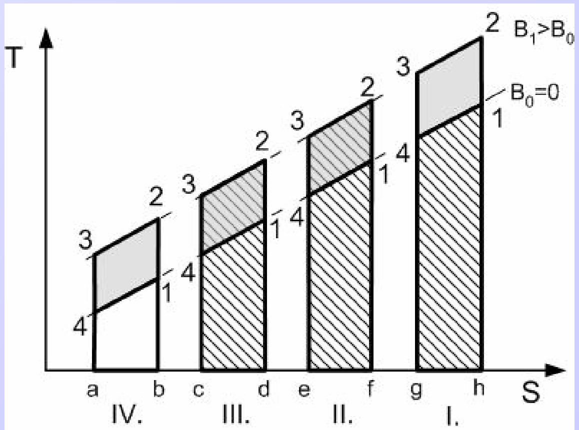
$$COP_{Brayton} = \frac{\left[h^{(1)} - h^{(4)}\right]}{\left[h^{(2)} - h^{(1)}\right] + \left[h^{(4)} - h^{(3)}\right]}$$

Thermodynamic cycles, cascades, regeneration



To improve the available temperature differences cascade systems..





Thermodynamic cycles, cascades, regeneration

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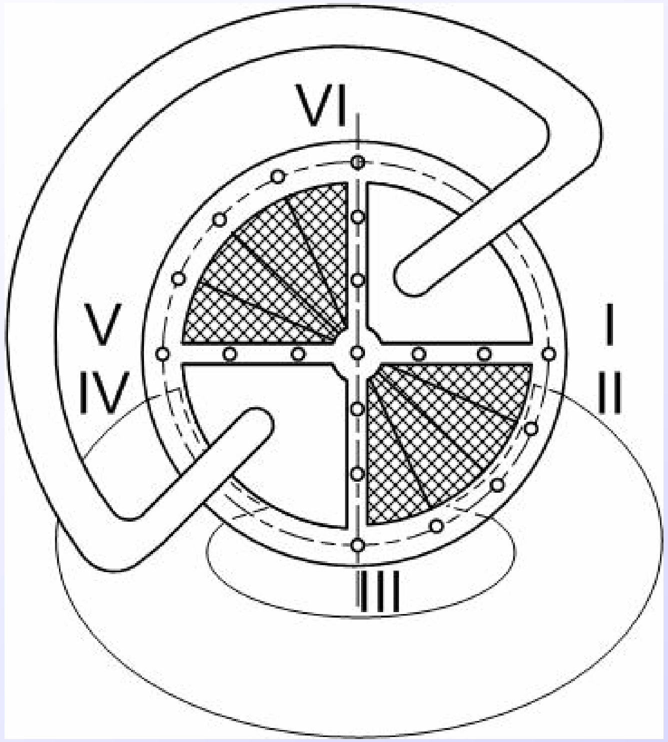
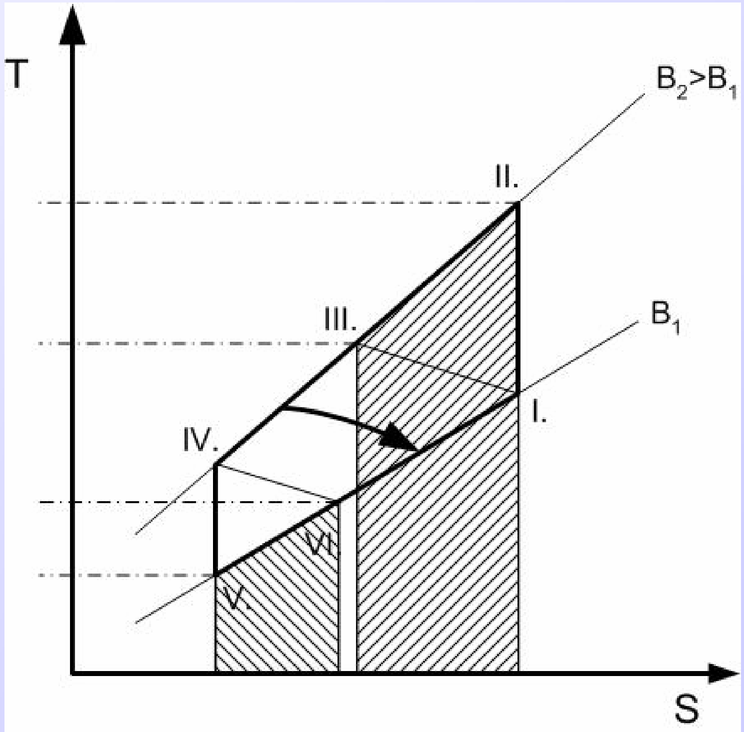
...or regeneration systems are required!





Numerical method and simulations

Energy conservation: $$\rho\left(\frac{\partial\Lambda}{\partial t}+\omega\frac{\partial\Lambda}{\partial\phi}+v\frac{\partial\Lambda}{\partial z}\right)+\frac{1}{r}\frac{\sum_{i=1}^{n}\dot{q}_{\chi}{}_{\phi}^{(i)}}{\partial\phi}+\frac{\sum_{i=1}^{n}\dot{q}_{\chi}{}_{z}^{(i)}}{\partial z}$$

Mapping of a cylinder to a square:

Thermal inertia and conductivities negligible!

$$\rho_F\, v\, c_p\frac{\partial T_F}{\partial z}+\frac{\alpha\,\xi}{L}\left(T_F-T_R\right)=0$$

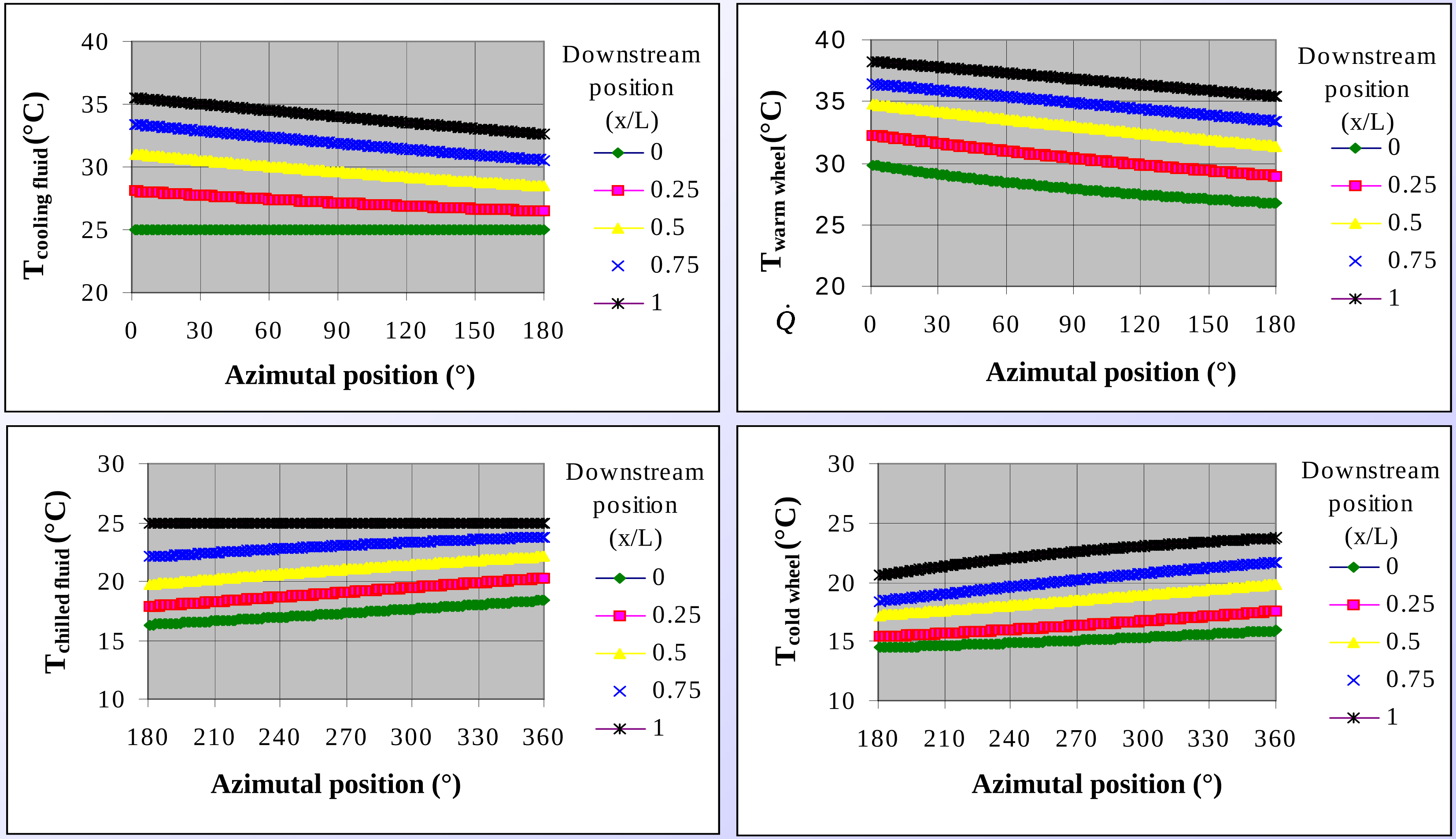
$$\rho_R\omega\, c_H\frac{\partial T_R}{\partial\phi}\psi+\frac{\alpha}{\delta}\left(T_R-T_F\right)=0$$

$$TF(\phi,L)=TF_{in}^{(hot)},\quad TR(\phi,L)=TR_{in}^{(hot)}+\Delta T^{(hot)},\quad \pi<\phi\leq 2\pi$$

$$TF(\phi,0)=TF_{in}^{(cold)},\quad TR(\phi,0)=TR_{in}^{(cold)}+\Delta T^{(cold)},\quad 0<\phi\leq\pi$$

$$TR(2\pi,z)=TR(0,z),\quad 0\leq z\leq L$$ (Periodicity condition)

Numerical method and simulations

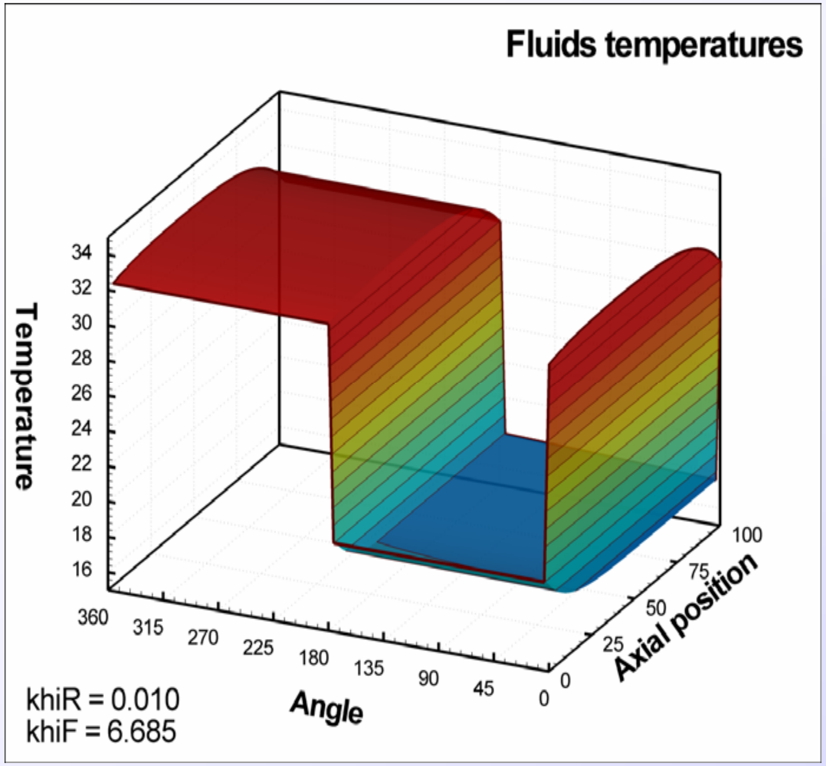


Without optimi-sation:

***COP*=5.8**

Temperature distributions in a steady state condition: L=0.2 m, D=0.198 m., v_{cold}=v_{warm}=6 m/s, ω=0.6 s^{-1}, $\dot{Q}$=704 W, m_{wheel}=8.09 kg, ΔB= 5 Tesla. Material: $Gd_5(Si_{1.985}Ge_{1.985}Ga_{0.03})$

Newest work: Analytical optimization



More simple (also analytical) models:

$$\chi_R = \frac{h}{\psi \ \delta \ \rho_R \ f \ c_H} = \frac{1}{\psi} \frac{L}{\delta} \frac{St_R}{S_r},$$

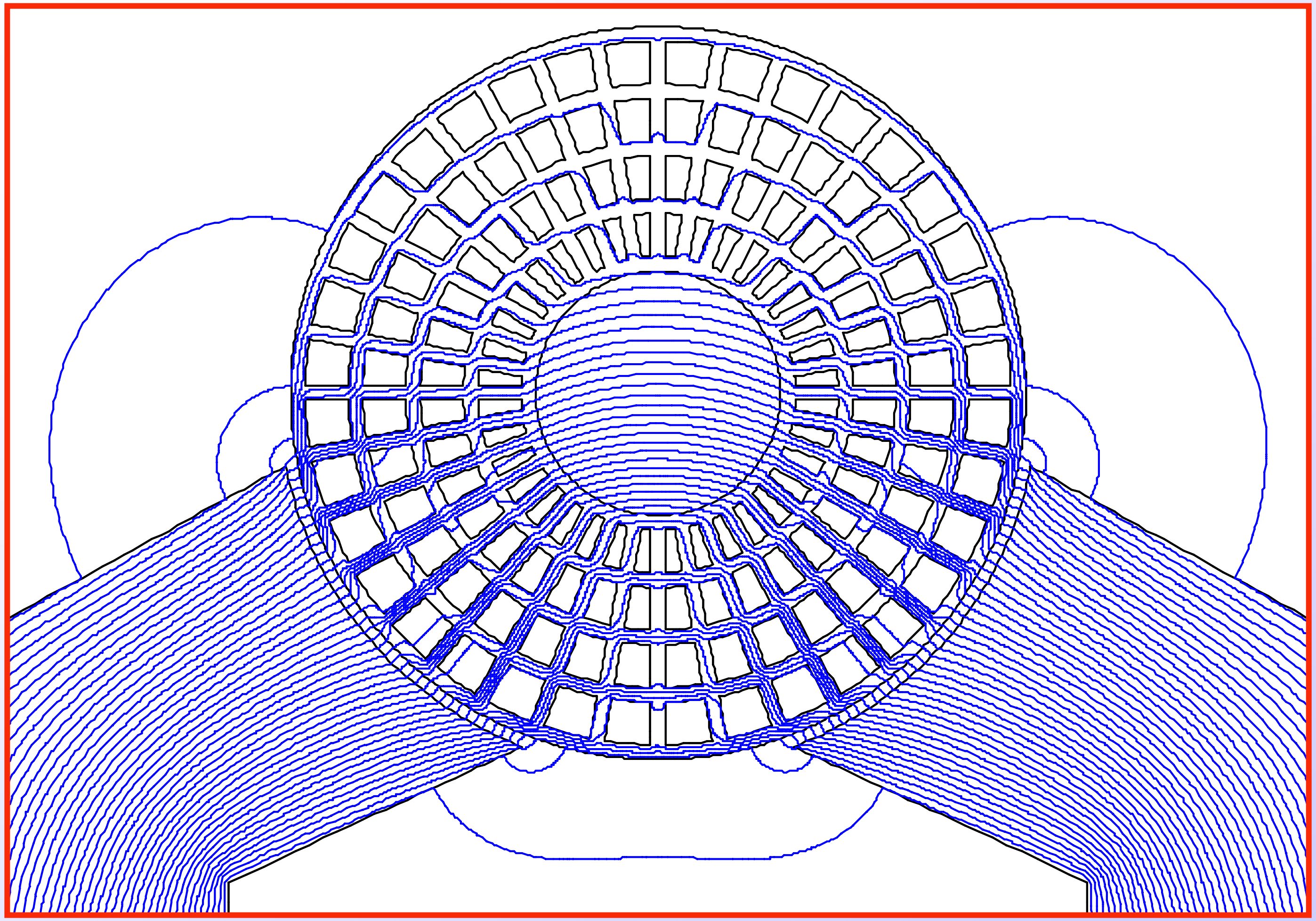
$$St_R = \frac{h}{\rho_R \ c_H \ v}, \qquad S_r = \frac{f \ L}{v} << 1$$

$$\chi_F = \frac{h \ \xi}{\rho_F \ v \ c_{pF}} = \xi \ St_F = NTU \ ,$$

$$St_F = \frac{h}{\rho_F \ c_{pF} \ v}$$

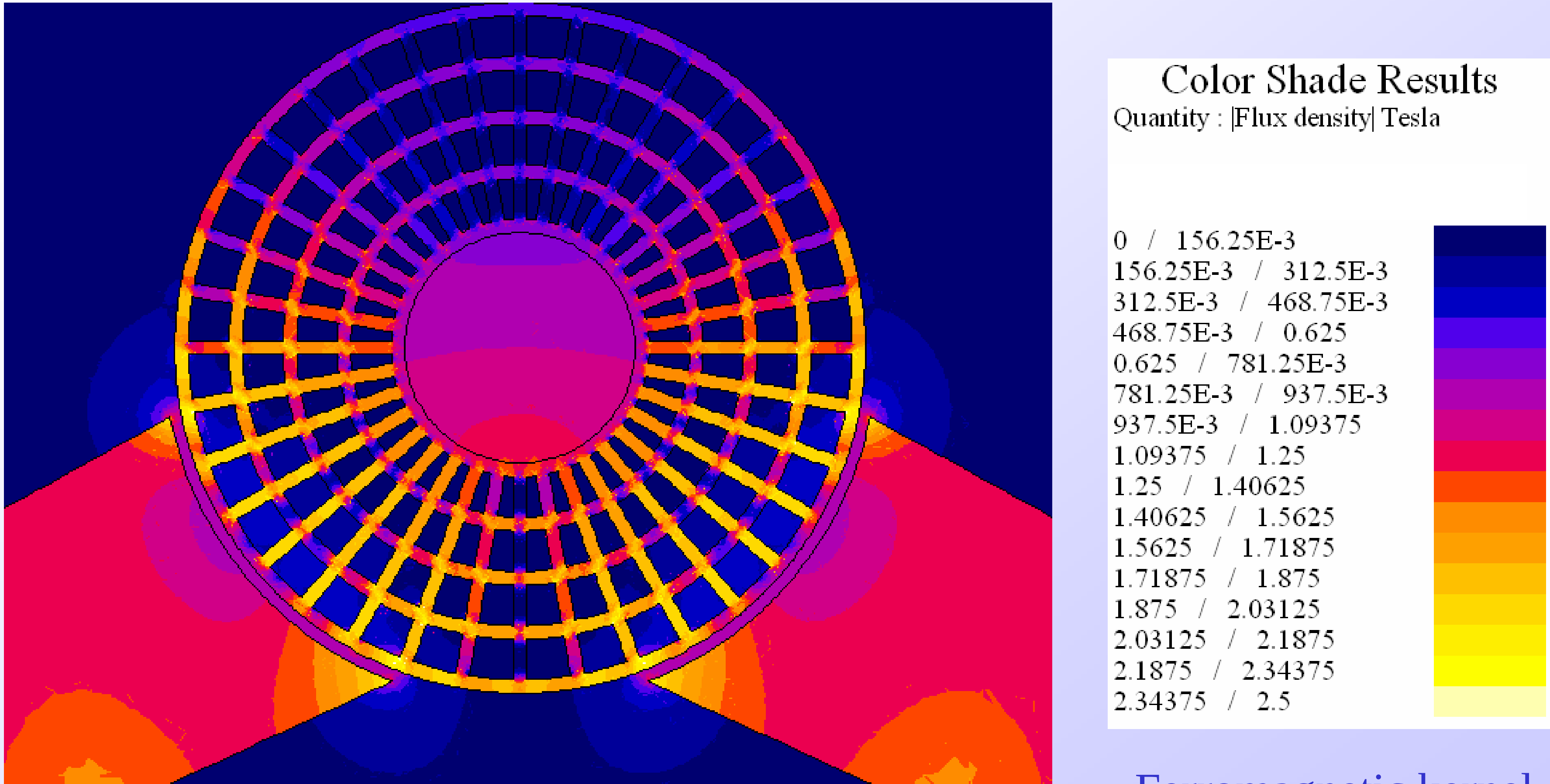
$$COP = \frac{1}{2} \underbrace{\frac{\chi_R^{(hot)}}{\chi_F^{(hot)}} \left(1 - e^{-\chi_F^{(hot)}}\right)}_{\leq 1} \underbrace{\left(1 - \frac{T_{F,\ in}^{(hot)}}{T_R^{(hot)}}\right)}_{\leq 1} COP_{Carnot} \ , \qquad COP_{Carnot} = \frac{T_R^{(hot)}}{T_R^{(hot)} - T_R^{(cold)}}$$

Numerical method and simulations



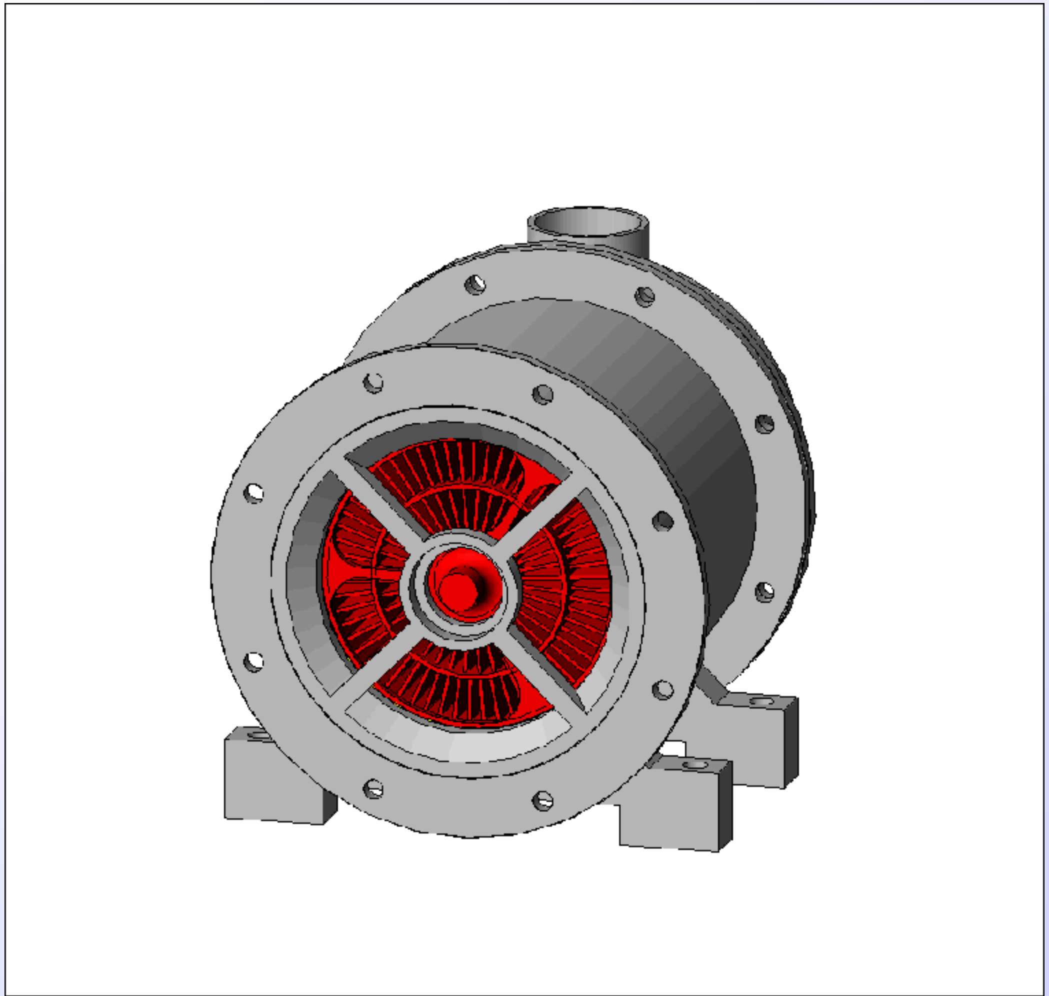
Vertical slabs are very bad!

Numerical method and simulations



Ferromagnetic kernel

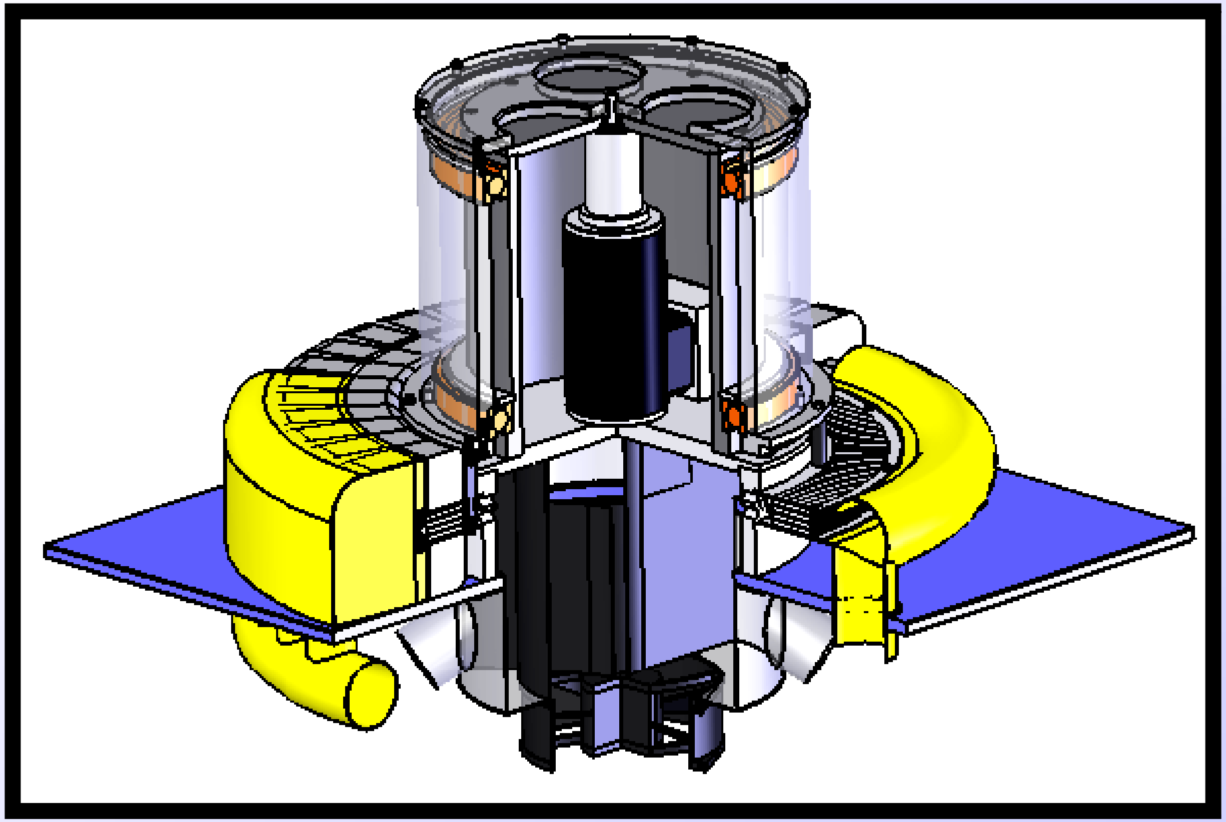
Alternative machines



MMagnetic Refrigerator or Heat Pump

Second generation
of a rotative proto-
type with regeneration.

Alternative machines



A system with radial flow is being built and will be presented at the Hannover industrial exhibition 2006.

Magnetic heat pumps for Switzerland?

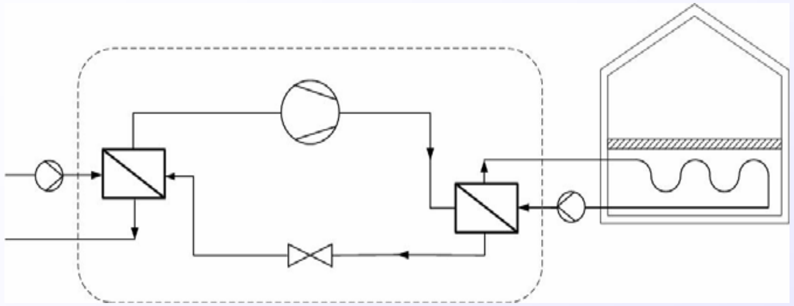
Heat pumps for new buildings with floor heating

Fluids:	**Brine/water (brine: 25 % ethylen-glycol)**
Temperature primary side:	**0 °C (e.g. water of a river)**
Temperature secondary side:	**35 °C**
Power:	**8 kW**

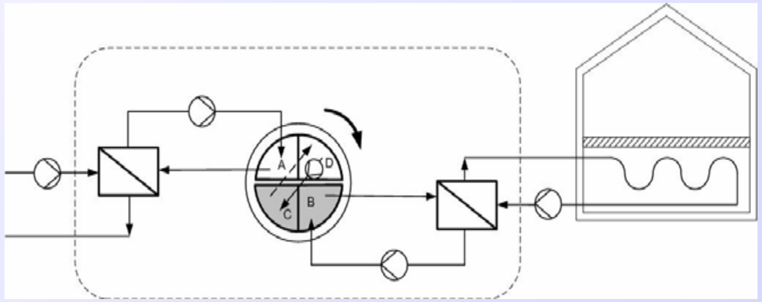
Renovation building with radiator heating

Fluids:	**Air/water**
Temperature primary side :	**-7 °C**
Temperature secondary side :	**50 °C**
Power:	**15 kW.**

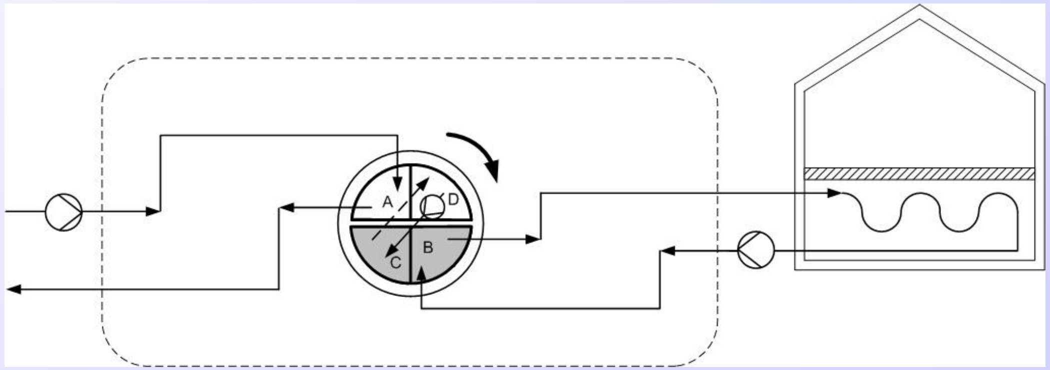
Magnetic heat pumps for Switzerland: New building with floor heating



Conventional heat pump application

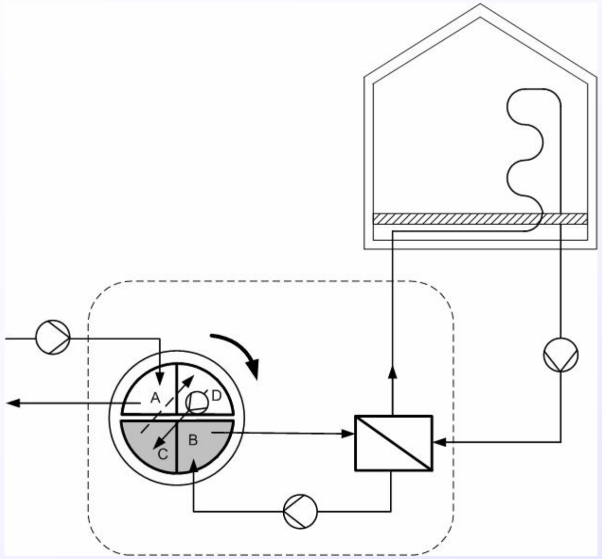


Analogous design of a magnetic heat pump

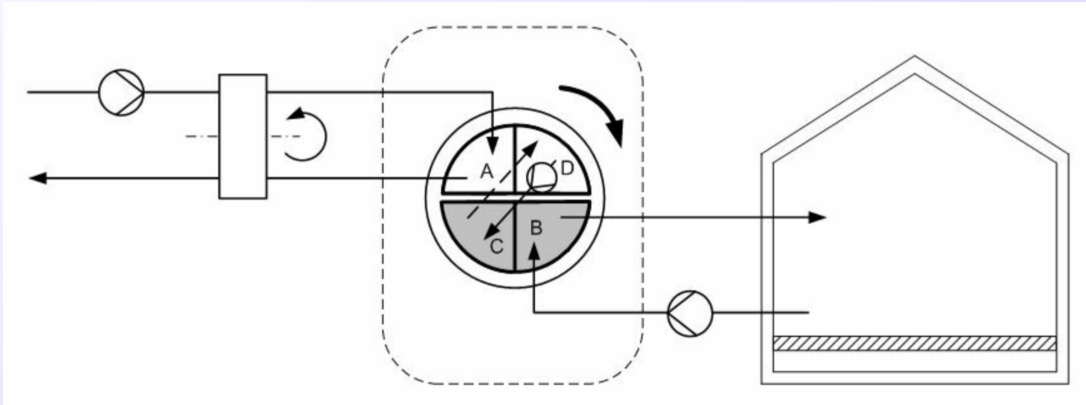


Simple magnetic heat pump system with only two pumps. A requirement is identical fluids in the two circuits, e.g. water/glycol.

Magnetic heat pumps for Switzerland: Renovation building with radiator heating

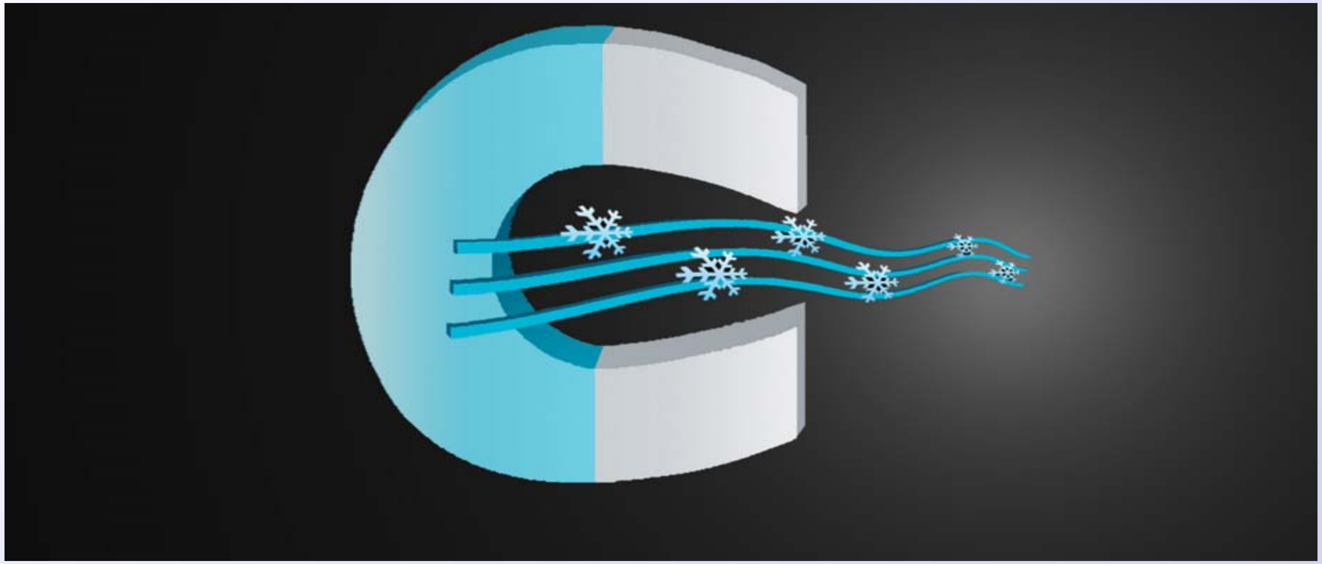


The system shows an air/water heat exchanger, a pump in the small heating cicuit and two air ventilators.



Schematic drawing of a complete heating system with a magnetic heat pump. By the heat recovery system the required temperature difference becomes smaller and a magnetic heat pump appplication becomes realistic.

New IIR Working Party on Magnetic Refrigeration



See on the web:
www.iifiir.iifiir.org

First Int. Conf. on Magnetic Refrigeration at Room Temperature

27-30. September 2005
in Montreux Switzerland

Interested:
Coca Cola, Néstle,
Daewoo, Danfoss,
Peugeot, Citroen,
Axima, Arcelik,…

Next conference:
Protorosz, Slovenia
11-13 April 2007

Swiss Technology Award 2006
First prize

Conclusions and Outlook

- Magnetic refrigerators at room temperature have been designed (and several patents for different systems submitted)
- The basic theory has been established, but will be further prepared
- First numerical simulations results have been made available
- Experimental validation is planned to be performed
- Optimisation calculations are very important to reach high COP values and are still missing
- More powerful systems as cascades and systems with regene-ration must be designed, their behaviour measured and modeled.

Thank you for your attention!

Magnetic cooling
at room temperature:

A future major
evolution in
refrigeration?