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MgH_2 nano-structured powders for hydrogen storage

Metals
Composites
Powders
MCP serbien

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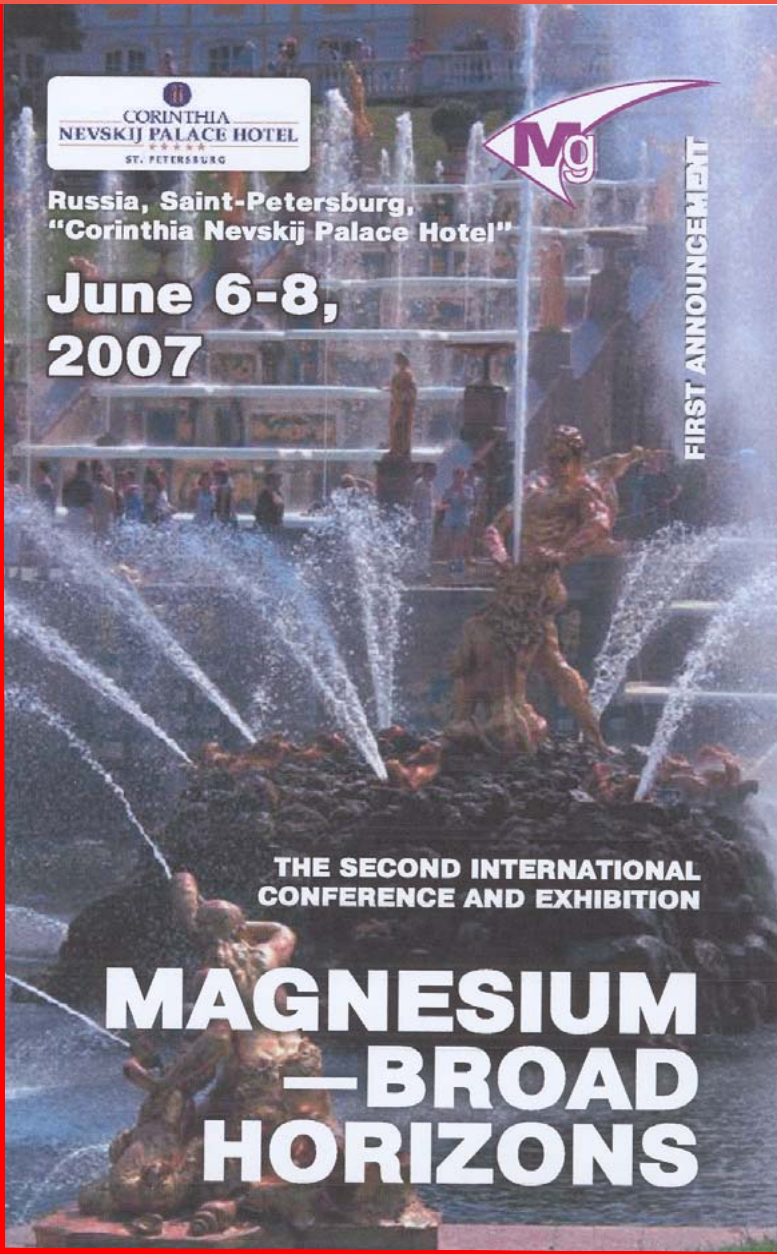

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MCP Mg-Serbien SAS

Production unit at Romans (Drôme), 90 km south Lyons. France

Plant at Romans - Drôme

Company developed by M. Jehan 1995

MCP Mg-Serbien produces granules, powders and chips of pure Mg and its alloys, aluminum and other alcaline-earths

Specific sieving of reacting powders

(e.g. nuclear application powders)

Continuous production

24 hours a day / 6 days a week.

Certification ISO 9001: 2000

Membre IMA

Production team : 22 personnes on a certified site (DRIRE).

Mg present capacity : 6 000 M tons

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Equipements and processes at MCP Mg-Serbien - Romans

- Production up to 500 tons a year
- of granules and powders
- Morphologies suited for steel production and chimistry (metal-organics, vitamines)
- Granules of Mg-alloys for “Thixomoulding”

- One of the two large facilities in Western-Europe for transformation of Mg into fines particles
- Automatised equipements
- Laboratory complet for caracterisation by laser granulometer

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Production of Mg hydrides

- **Cooperation with Centre National de la Recherche Scientifique – Grenoble** to synthesise and produce activated Mg-hydride for reversible hydrogen storage
- **Goal : industrial scale production**

- **European Projects**
  HYSTORY « 6th PCRD : Energy, Environment and Sustainable Development » High Energy ball-milling of nanostructured MgH_2

- **NESSHY** « 7th PCRD Novel Efficient Solid Storage of Hydrogen » Production of MgH_2 powders with catalysts
- International patent MCP-CNRS

- **Other Projects**
- **Requests :** More than 1000 MTons a year of MgH_2
- **French Label ENERDIS**

High Energy Industrial Ball-Milling

Mecanosynthesis of MgH_2 with transition metal under controlled atmosphere

Industriel scale production (on request)

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Other equipements

Isostatic cold pressing up to 4000 bars

Pilot ball miller in liquid or gas

Controlled atmosphere glove boxes

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Metals
Composites
Powders
MCP serbien S.A.

MgH_2 nano-structured powders for hydrogen storage

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HYSTORY

EC FP 5 Programme 1998-2002

Institute for energy technology	N
Stockholms universitet	S
CNRS	F
Environmental Research Laboratory	GR
TREIBACHER	AUS
Société Commerciale de Métaux et Minerais	F
Statkraft	N
ABB	S
KOCKUMS	D

ACI – Hymet

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Cluster Energy

CNRS Grenoble
LMI - UCBL

RhôneAlpes Région

Patents 2006
FR0651478
FR0601615

NessHy

EC FP6

NESSHY Novel Efficient Solid Storage for H_2

NCSR Demokritos	GR
University of Salford	UK
Air Liquide	F
EC-Joint Research Centre	NL
Stockholms Universitet	S
Institut For Energiteknikk	N
University of Fribourg	CH
University of Birmingham	UK
Vrije Universiteit Amsterdam	NL
CNRS Grenoble	F
Daimler Chrysler AG	D
GKSS Geesthacht GmbH	D
University of Iceland	IS
Johnson Matthey PLC	UK
ForschungZentrum Karlsruhe	D
Max-Planck MPI-MF	D
Technical University Denmark	DK
METU Ankara	T
INETI	PT
IFW Leibniz Gemeinschaft	D
Delft University of Technology	NL
Southwest Research Institute	USA

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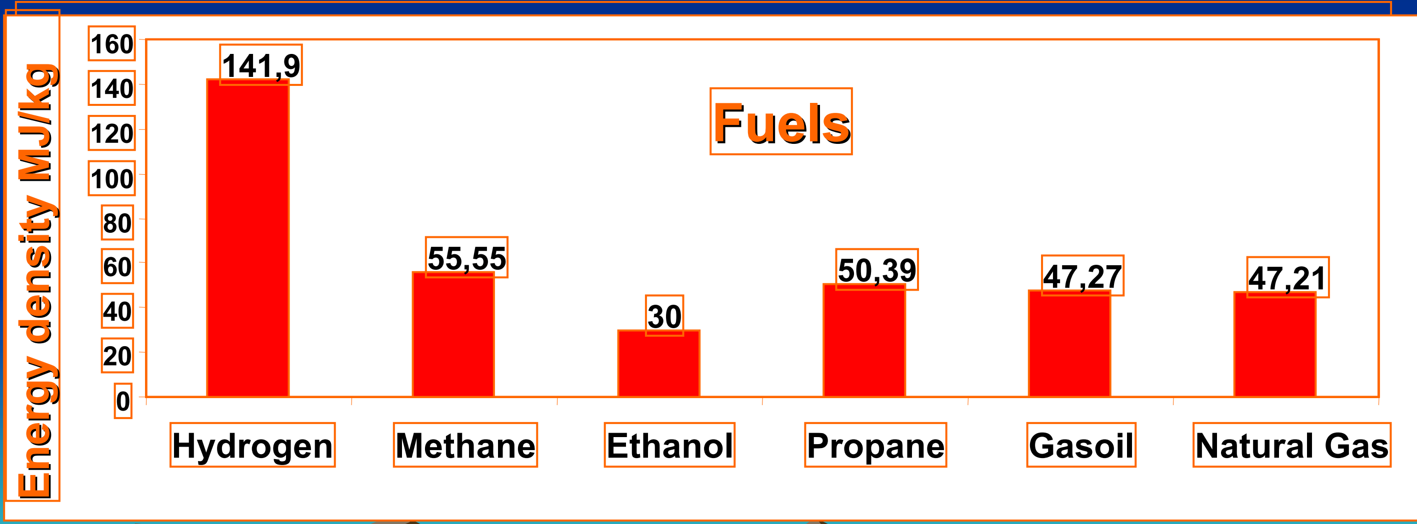
Why store hydrogen ?

- Oil : cost increases, resources decrease, greenhouse effect…
- Renewable energies (solar, wind,…) : irregular availability

Hydrogen : Energy-carrier for the futur ?

- Electric energy storage
- Fuel Cell
- ICE



Hydrogen storage in safe conditions
High gravimetric density of energy (142 MJ/kg)

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Reversible Metal Hydrides

- **Compressed gas** (350-700 bars)
- **Cryogenic liquid** (20 K)
- **Chemical hydrides**

	kg H_2 / m^3	Weight %
H_2 gas 700 b	62	100 *
H_2 liquid	70	100 *
$LaNi_5H_6$	123	1.4
Ti-V-Cr	205	3.5
$AlNaH_4$	96	7.5
MgH_2	106	7.6

+ **High volume density of hydrogen**
+ **Safe solution (low pressure, endothermic release)**
+ **Large-scale production**
+ **Purity of Hydrogen (Fuel Cells)**

– **Low weight density !**

* not comprising mass of tank

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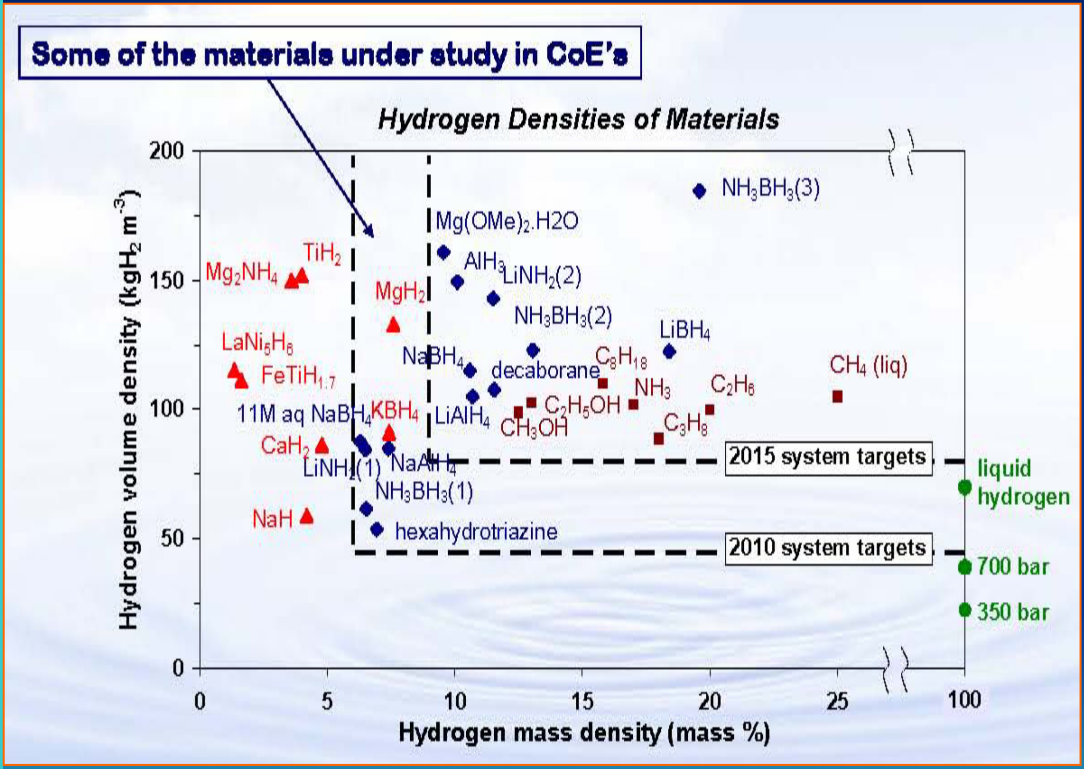
Why metal hydrides ? Why MgH_2 ?



Advantages with Mg

Mg is the 7th most abundant element on earth
Mg is cheaper than… Al
Mg metallurgy is easy
Mg is non-toxic
Mg is re-cyclable
MgH_2 is mono-metal element system: no demixtion
MgH_2 uptake is 7.6 w%

Difficulties with Mg

H-reaction kinetic are said low, but…
Temperatures of reaction are high, but…

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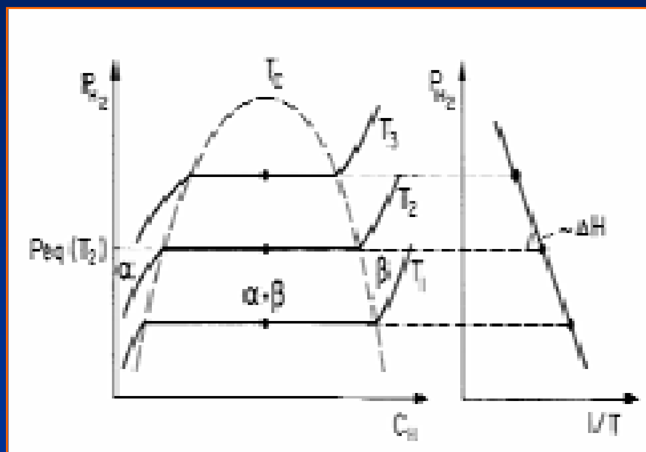
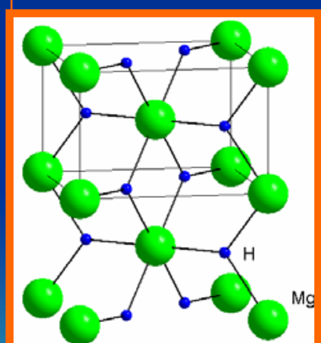
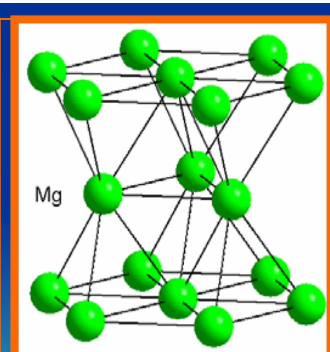
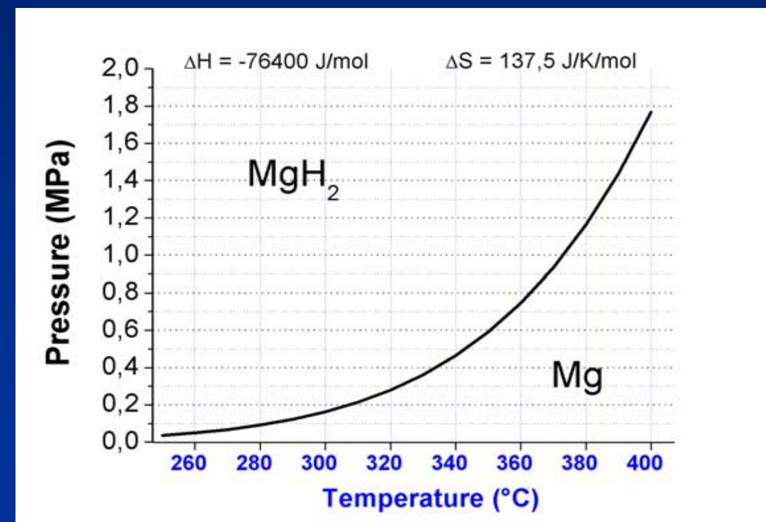
MgH_2 towards nano-structured powders







$Mg + H_2 \leftrightarrow MgH_2$



+ High weight storage capacity (7.6 wt. % H_2)

- High thermodynamic stability

T > 300°C, but heat flow control…

- Slow diffusion kinetics, but…

Ball-milling (BM) with catalysts (transition metals or oxides)

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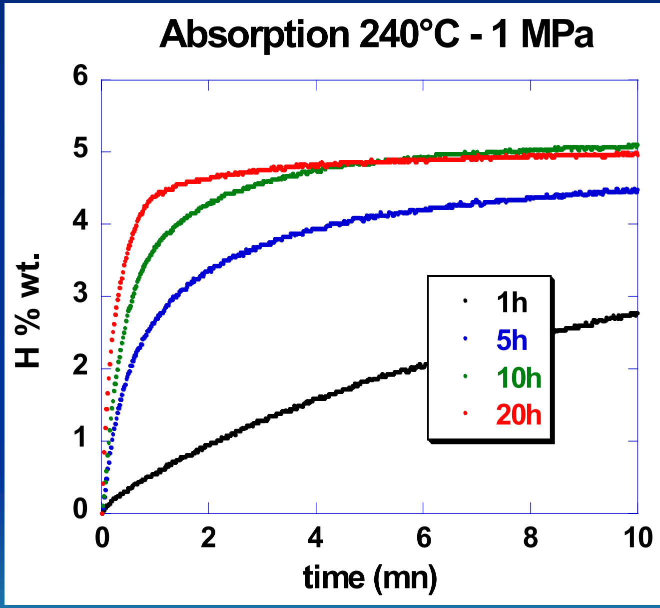
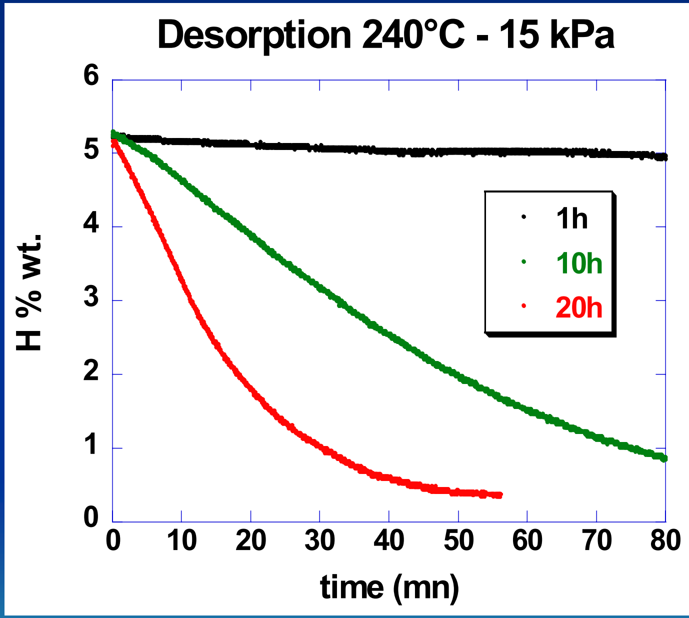
Co-milling process vs BM time

MgH_2 MCP + 5 % at. V (40 µm)

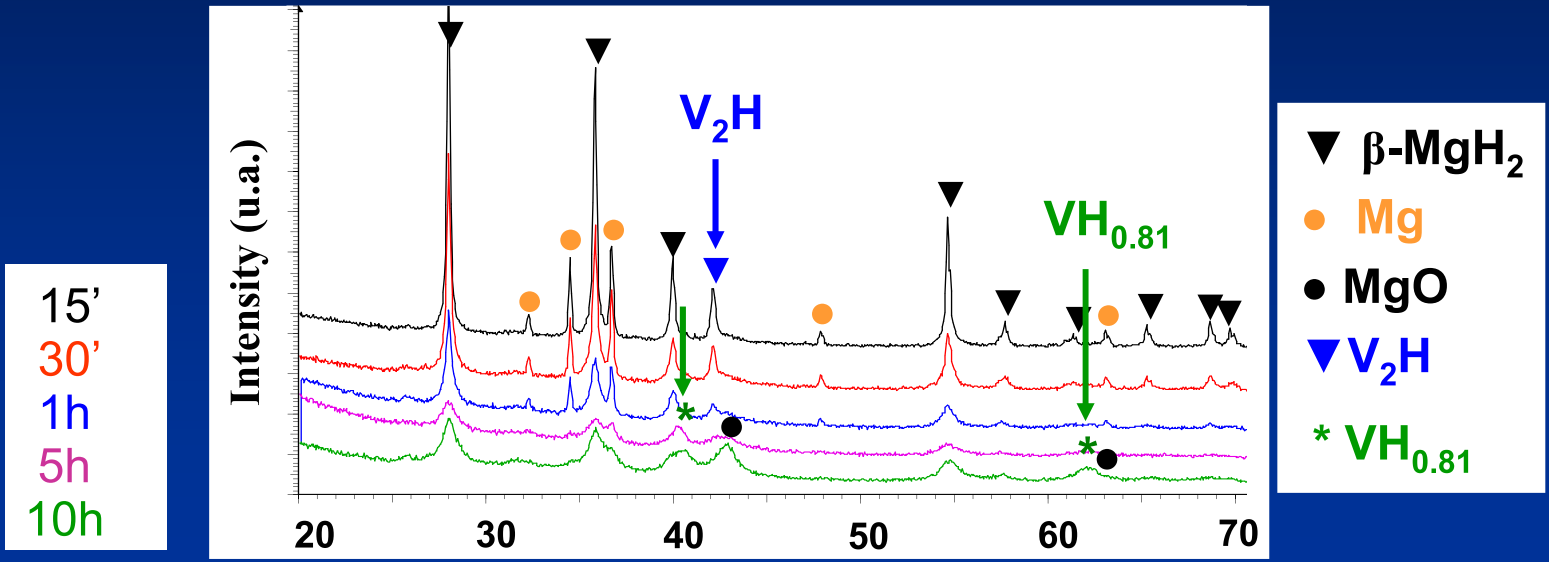




Large impact of the milling time, especially at desorption

Optimum ≈ 20 hours milling time with catalysts

MgH_2 and M transformation on BM



- High density of defects
- Reduction to nanosize MgH_2 crystallites
- Progressive MH_x formation from MgH_2

$V \rightarrow V_2H \rightarrow VH_{0.81}$

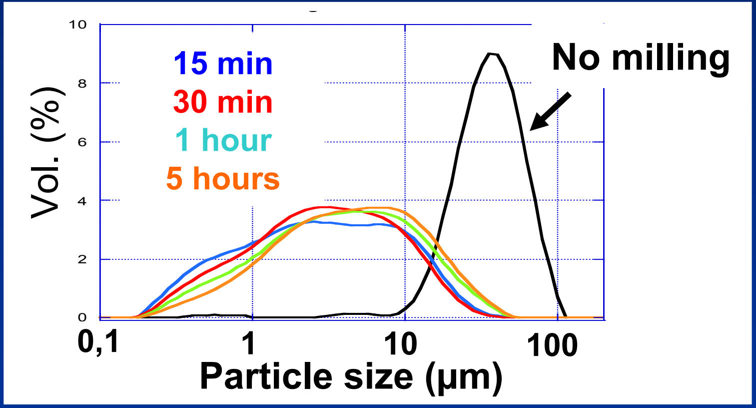
$Nb \rightarrow NbH_{0.89} \rightarrow NbH_2$

$Ti \rightarrow TiH_{1.7} \rightarrow TiH_{1.7} + TiH_{1.92}$

Interfaces between MgH_2 grains and M particles

Microstructural evolution on BM

- **Granulometry measurements**



Starting powder : 20 – 80 µm
After 15 min. milling time : 1 – 10 µm
No further evolution

- **Crystallites size of the β-MgH_2**

After 15 min. milling time : 30 nm
Further crystallites size reduction with increasing milling time

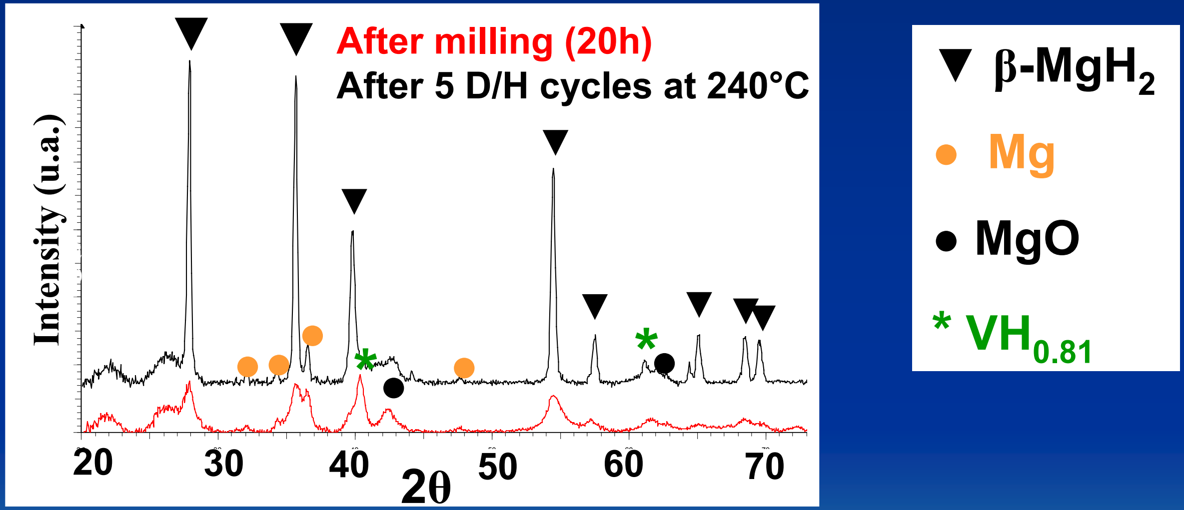
Milling Time	Crystallite sizes (nm)
15 min	29,(3)
30 min	14,(2)
1 h	12,(2)
5 h	10,(9)

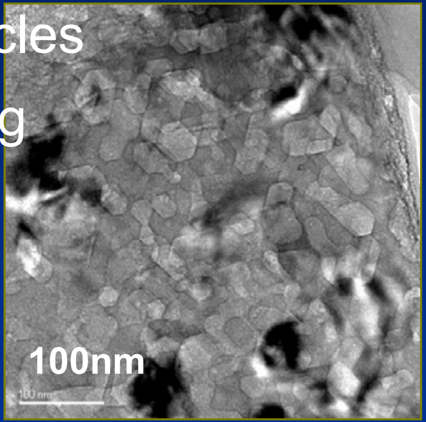
Hydrogen sorption properties not correlated to powder grain size, but to the crystallites size

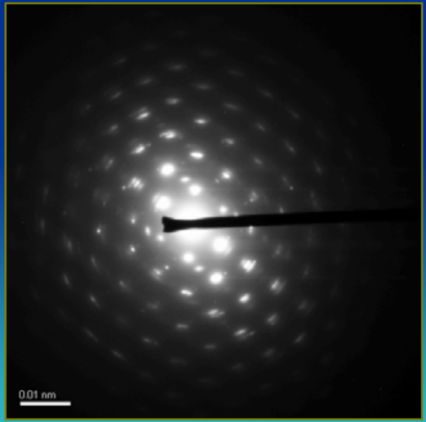
Microstructure evolution on cycling

The high density of defects disappears after D/H cycles

Recristallisation of hexagonal single cristallites of Mg





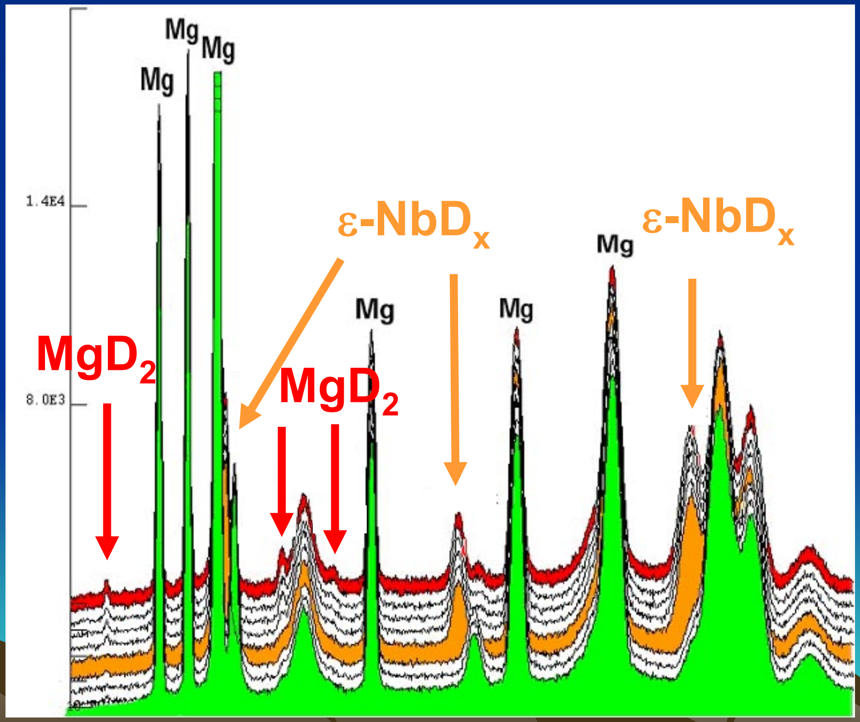


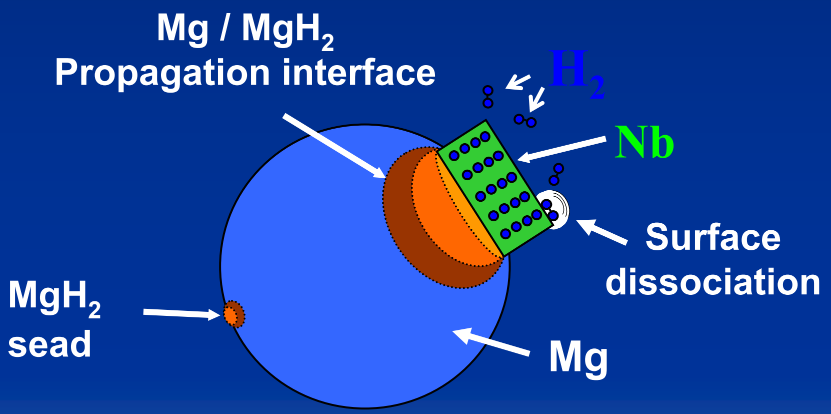
Fast hydrogen diffusion results from the very large amount of boundaries developed between nanometric crystallites

In-situ neutron diffraction study (ILL - D20)

In-situ hydrogenation (T ~ 280°C, P = 2 MPa)

ε - $NbD_{0.75}$ rapid formation prior to the MgD_2 formation





Role of the TM additives ~ "gates" favoring H_2 dissociation, then H diffusion

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Up-scaling powder production @ MCP-Serbien

1. **Synthesis the MgH_2 precursors from Mg powder**
2. **Co-milling MgH_2 + M additives**

Large scale energetic ball miller (25 l)

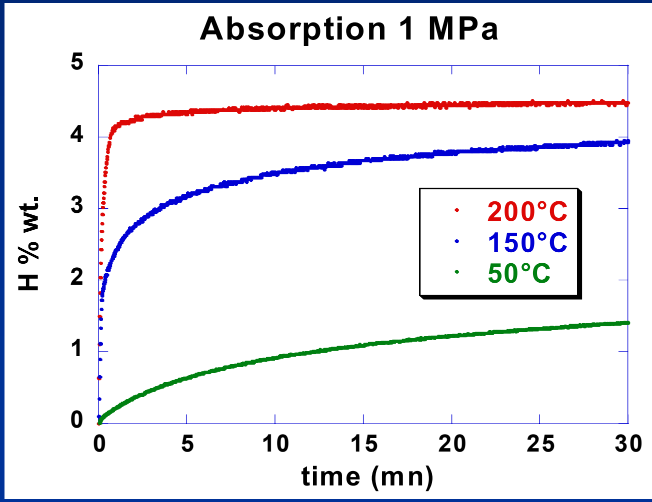
Batches of 1 kg of activated powders

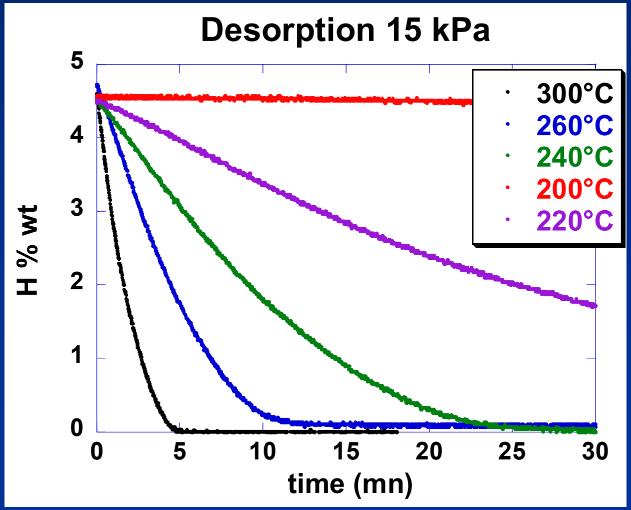
Very reactive powder in air (to handle under Ar gas)

Patent FR 06-51478

Kinetics characterisation vs T

MgH_2 MCP + 5 at.%V (40 µm)   ZOZ Miller - 8 h





Absorption can be initiated at 50°C, reasonably faster at 150°C
4% wt. in 1 minute at 200°C

For 15 kPa :
only 20 min at 240°C
(1 h at 220°C)

Highly reactive powders

Stability of the sorption properties on cycling

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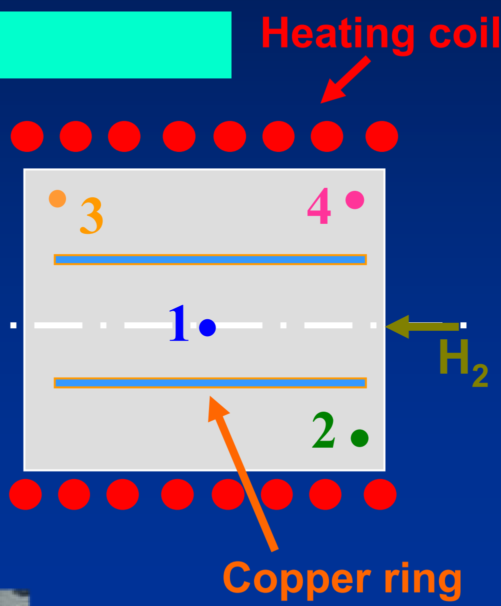
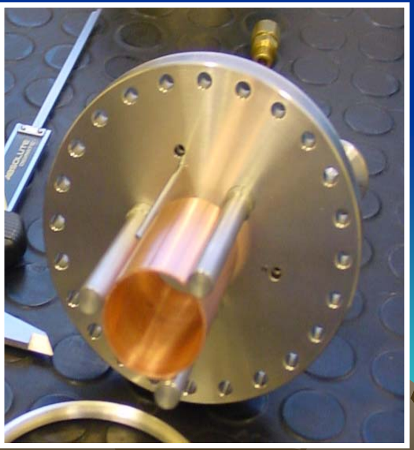
MgH_2 pilot tank development

Main problem = <u>control of the heat transfers</u>

- Strong <u>exothermic</u> Mg hydrogenation
- Low thermal conductivity of MgH_2 powder —

Equilibrium conditions are immediately reached, thus stopping hydrogenation





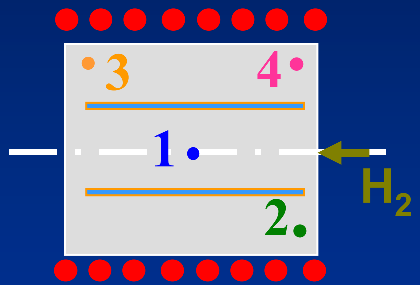
120 g of MgH_2
(6 gr H_2 / 0.86 MJ)

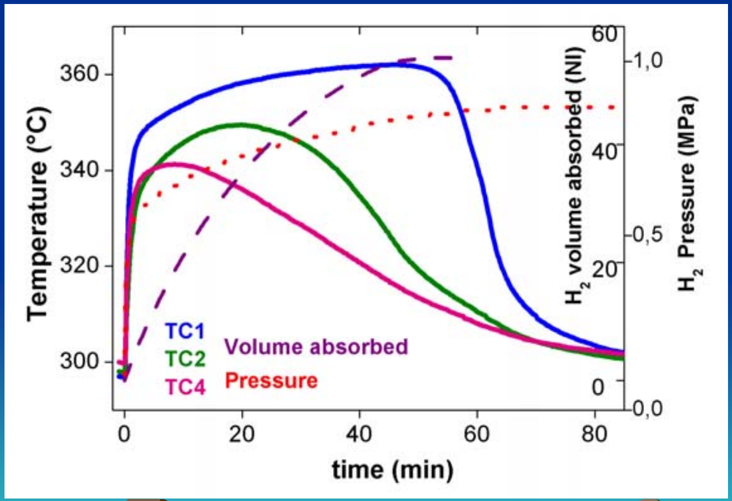
Charging process (initial 280°C / 8 bars)

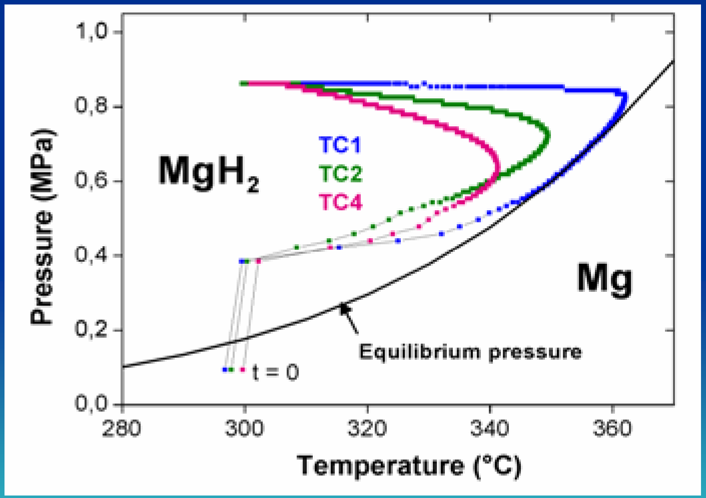
Without cooling fluid :

Huge increase of temperature (+ 80°C)

Total charging : 50 min. - 57 Nl (5 wt. %)





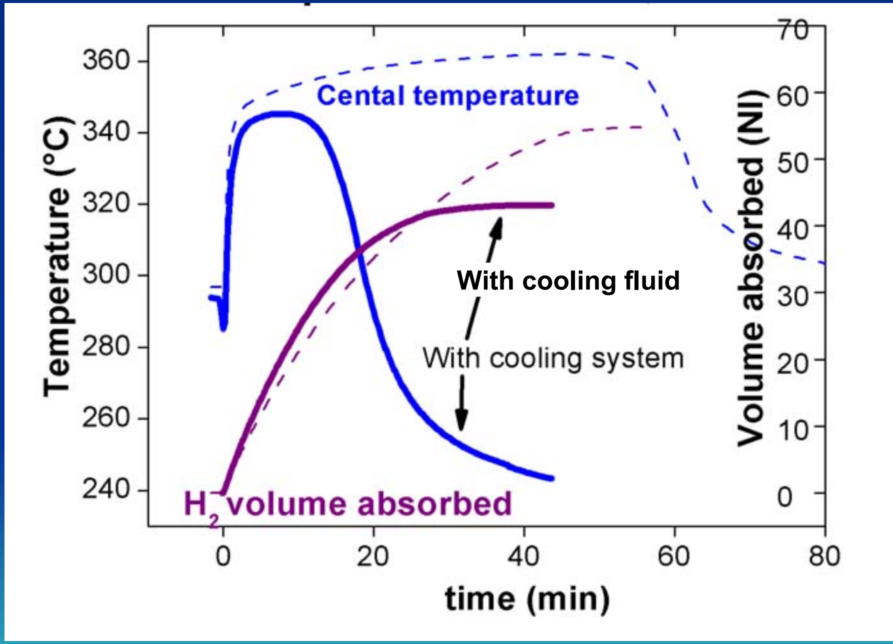


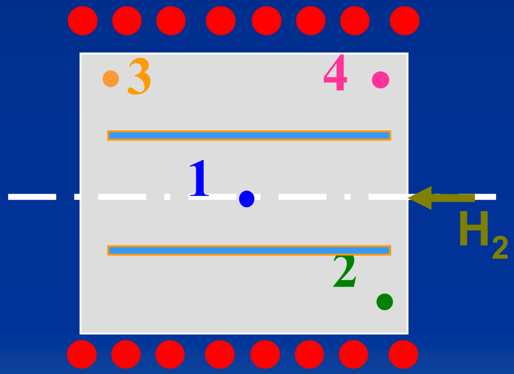
The central part of the tank follows the thermodynamic equilibrium up to the end of reaction, slowing H_2 absorption

Charging process (starting 280°C / 8 b.)

With forced air as cooling fluid

Charge in 30 min. - 42 Nl (3.6 % wt.)





A cooling system reduces the tank loading-time

(managing the cooler is needed to complete the charge)

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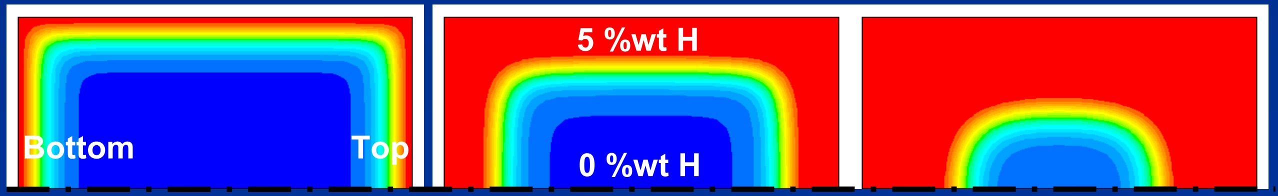
Numerical modeling

Fluent® software

- hydrogenation reaction
- H_2 consumption
- heat generation
- thermal conductivity
- gradient of pressure

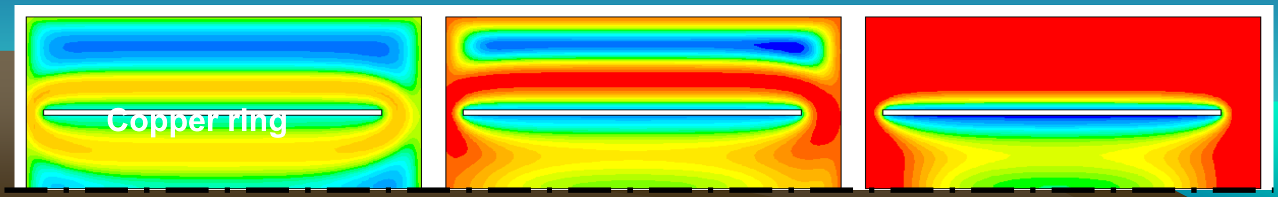
Hydrogenation rate without cooling system

After 600 s **2200 s** **5200 s**



Hydrogenation rate with forced air cooling system

After 400 s **800 s** **1400 s**



Fuel Cell - PAXITECH

120 g MgH_2 (6 gr H_2 / 0.86 MJ) : lightening for ~ 72 h.

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Conclusion

- **Systematic investigation of the ball-milling process**

  - Activation role of the transition metal hydride directly evidenced

- **Highly reactive powders available by kg batches**

  - Stability of the sorption properties on cycling

- **Small scale tank tested with success (6 gr H_2 / 0.86 MJ)**

  - Loading process : P < 10 bars, starting at 150°C

  - Loading time strongly dependent of the cooling efficiency

  - Overall weight capacity to be optimized

New metallurgy routes (Severe Plastic Deformation : ECAP)

Pilot tank development 5 kg MgH_2 (250 gr H_2 / 36 MJ)

Recycling waste heat (SOFC, thermal engines, factories)

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Fuel = Hydrogen

ICE
Thermal engine

PEMFC
Low temperature Fuel Cell

SOFC
High temperature Fuel Cell

Hydrogen storage

Reforming

Gasoline

Gasoil/gas

High pressure
30 to 70 MPa

Cryogenic liquid
20 K

Solid
hydrides

MgH_2

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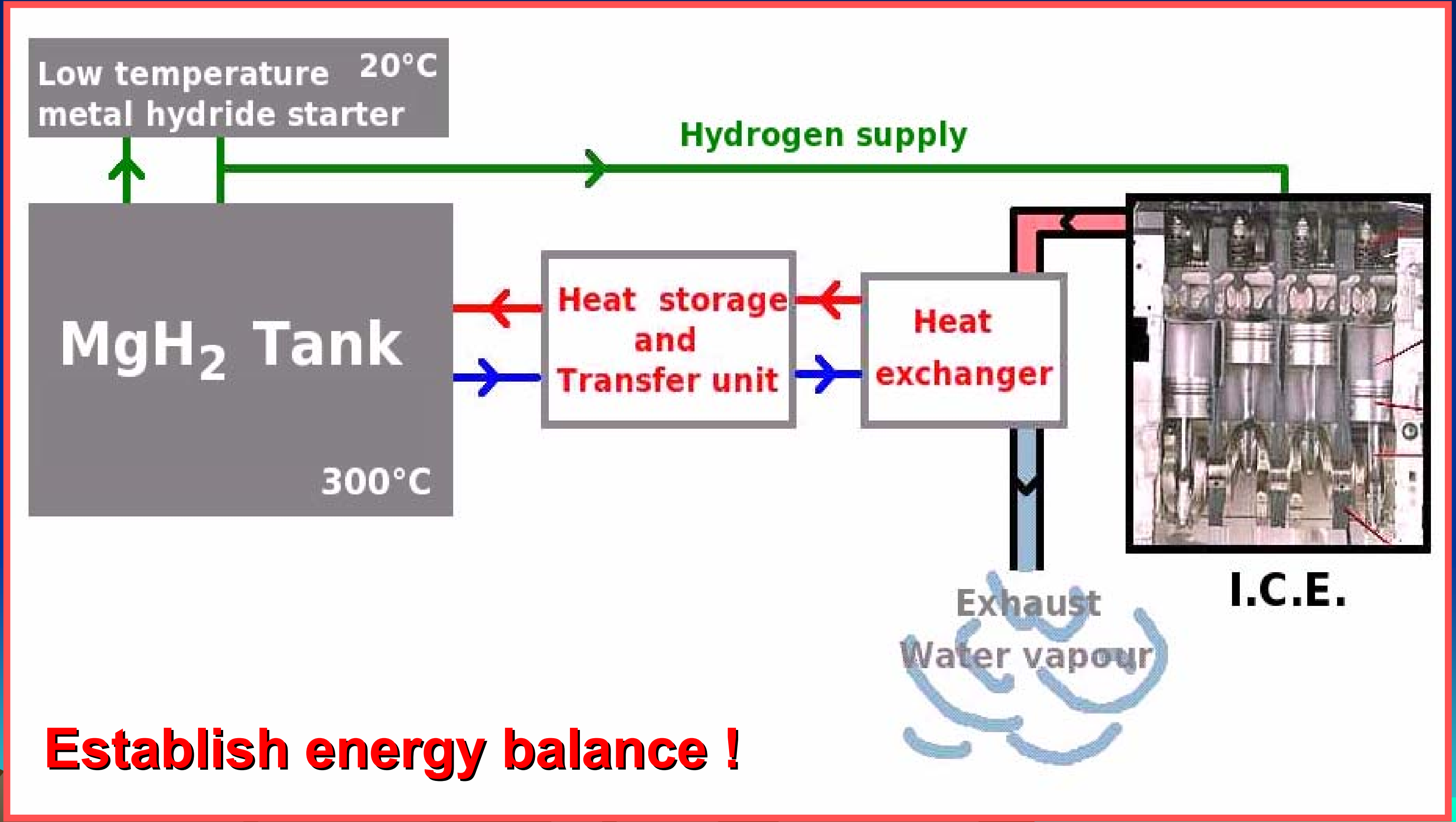
Integrated Project :
Energy regenerating ICE / MgH_2 tank



~ 100 kg MgH_2 for ~ 250 – 300 km with ICE car

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What could be promising for Mg technologies ?

10^8 ICE cars being equipped with MgH_2 tanks

250 kg MgH_2 for 700 km autonomy

20 years shift from gazoline to hydrogen civilisation

Needs for more than 10^6 tons Mg a year during more than 20 years !

NB - fuel cell : 0.3kW/kg, large volume, very expensive, very fragile, short life, ressources of Pt, Rh ????

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