EC FP 5 Programme 1998-2002

HYSTORY

Hydrogen Storage in Hydrides for Safe Energy Systems

A Consortium of EC FP5, programme 1998-2002, funded for the period 2002-2005

Partners are :

IFE – Norway (coordinator) – WP6	J. Muller, B. Hauback
Stockholms University – Sweden – WP3	D. Noréus
CNRS Grenoble – France – WP1, WP2	D. Fruchart
NCSRD – Greece (management)	T. Stubos
Treibacher Industrie – Austria – WP4	P. Barbic
MCPT – France	M. Jehan
Statkraft – Norway	J.S. Thon
ABB – Sweden – WP5	B. Stridh
Kockums - Sweden / HDW - Germany	J. Stromquist – B. Siegler

Three classes materials were proposed for fundamental studies and research development for applications. (WP1 to 3)

Processing and upscale of the materials and hydrides were planed operating by specialised industrial companies from pilot, then to mass production. Parallel to numerical modelisation of the mass, heat and pressure transfers, developments of metal hydride tanks was proposed. (WP4)

As fuel cells were considered for a practical end-use, a large tank development was made, then for further connection to a multimode safe energy system. (WP5)

HYSTORY

Institute for energy technology
Stockholms universitet
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
Environmental Research Laboratory
TREIBACHER
Innovation is our tradition.
Société Commerciale de Métaux et Minerais
Statkraft
ABB
KOCKUMS

A 1st class metal hydride of BCC type, aims to achieve better than 2 w%, reversible properties at e.g. 80°C in a first step, then even closer to RT. Syntheses were oriented to optimise a multinary aspects of the alloys, in terms of formula and processes (milling and melting), thus to achieve fast kinetics of absorp./desorp. A pilot scale production was also done and critically analysed.

A 2nd class of material considered is Mg-activated hydride, for which the performance of more than 6 w% were fully realised in both the laboratory and in safe industrial pilot process for mass production.

A 3rd class of materials comprises different light materials e.g. Li and Na alanates and more complex types multinary metals hydrides, thus potentially able to develop a max H-uptake ranging from 5 to 10 w%. They were expected to achieve high reversible performances specifically down to 140°-150°C.

HYSTORY

The BCC type hydride was designed for static systems and the latter two classes aim to be used for fuelling mobile applications.

Upscale pilot production of these materials was operated on the basis of optimised properties resulting from basis studies.

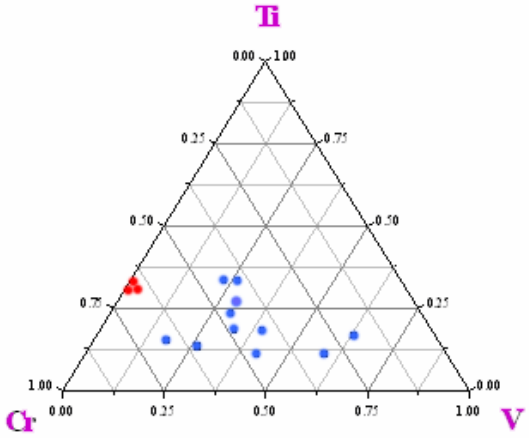
Numerical computation were made using 2D numerical codes to simulate tank working conditions. Development of prototype tanks (lab and factory scale) were realised in order to qualify the active materials, thus monitoring work parameters (pressure, cold and heat transfers, thermal gradient, time…).

A large scale tank was constructed, charged with hydrides then being connected to a fuel cell as a part of a complex energy management system for a 4-floor building in Stockholm.

The major results gained during the first 2 years of the HYSTORY workplan are discussed here after.

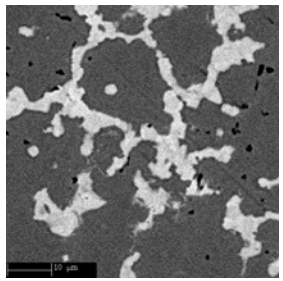
HYSTORY

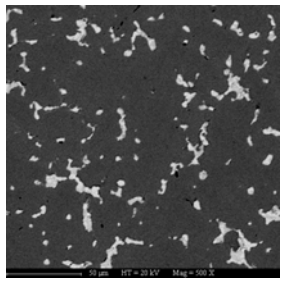
Class A metal hydrides from BCC type alloys

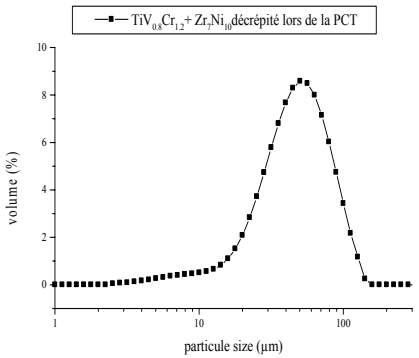


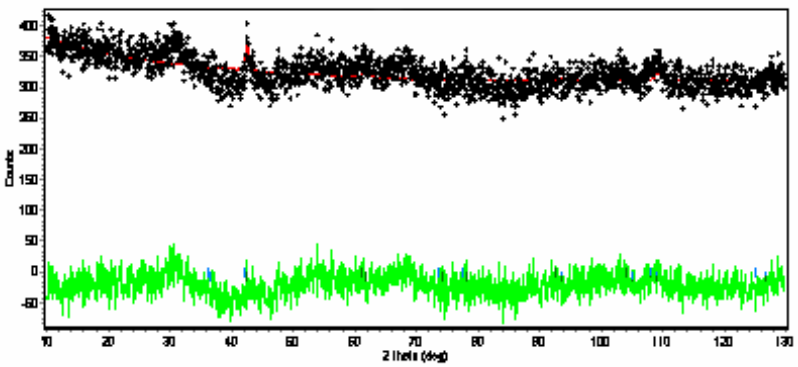
$TiV_{0.8}Cr_{1.2}$ x_{max} ~ 3.1w%.... up to…

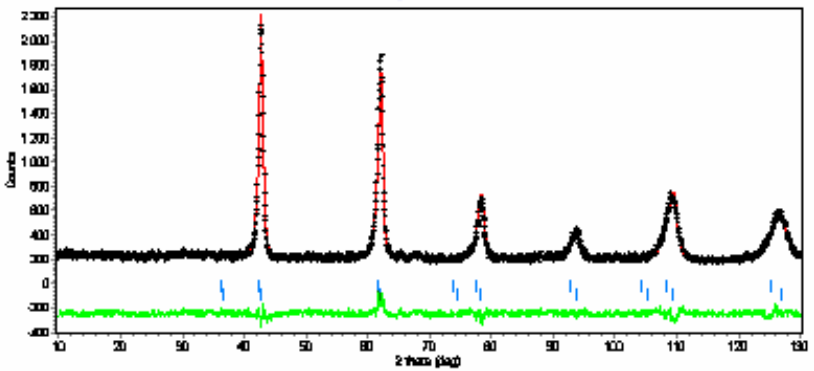
$Ti_{0.5}V_{1.9}Cr_{0.6}$ x_{max} ~ 3.6w%





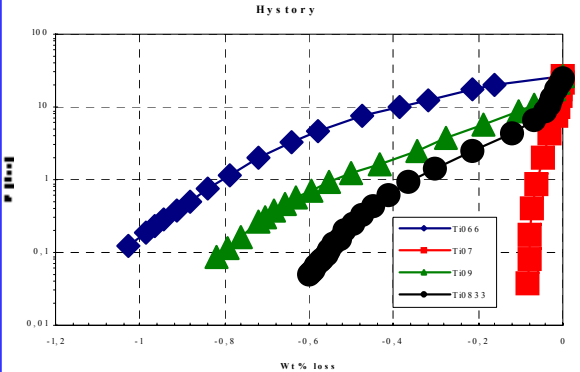


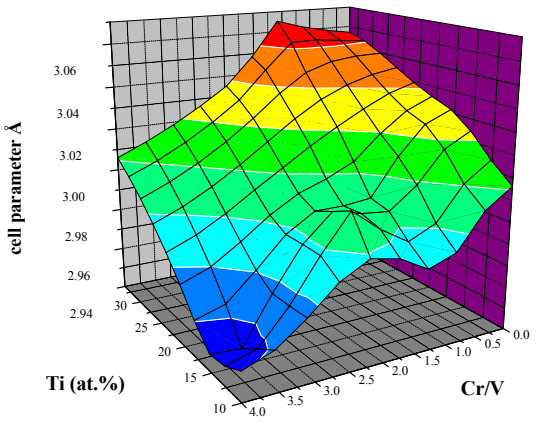


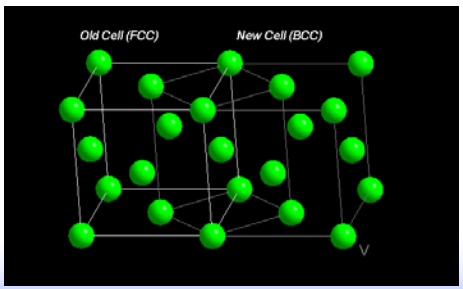


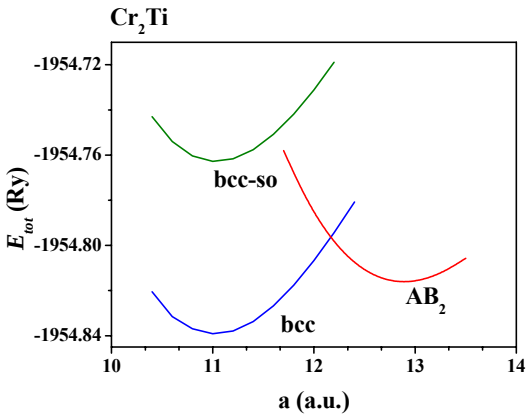
HYSTORY

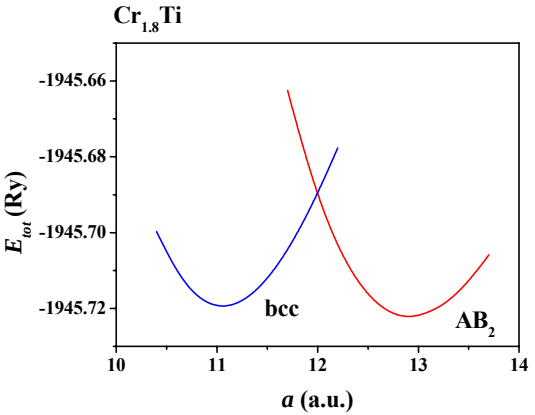
Class A metal hydrides from BCC type alloys

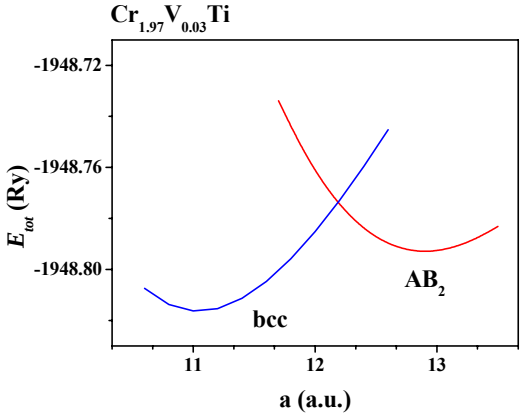


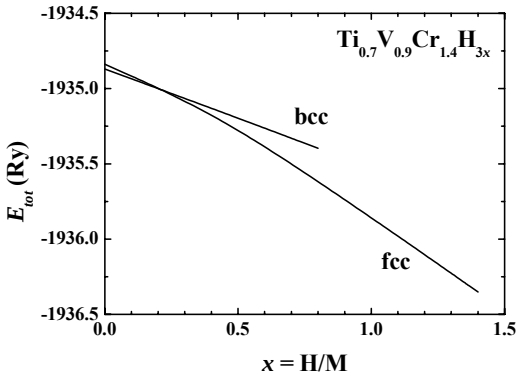












HYSTORY

Institute for energy technology

Stockholms universitet

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Environmental Research Laboratory

TREIBACHER
Innovation is our tradition.

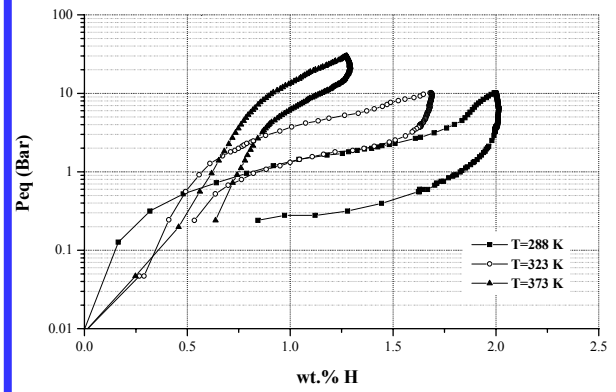
Société Commerciale de Métaux et Minerais

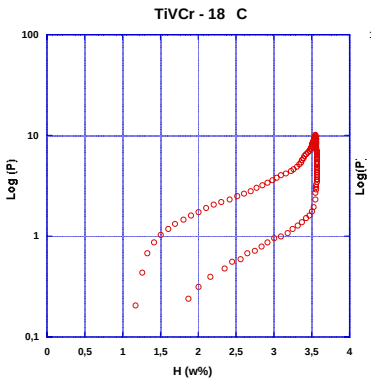
Statkraft

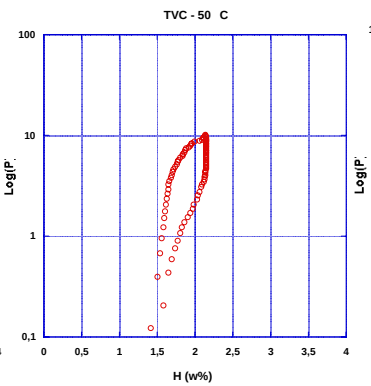
ABB

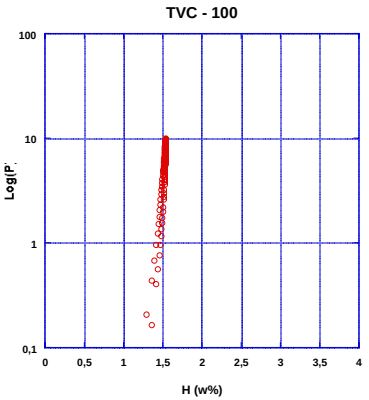
KOCKUMS

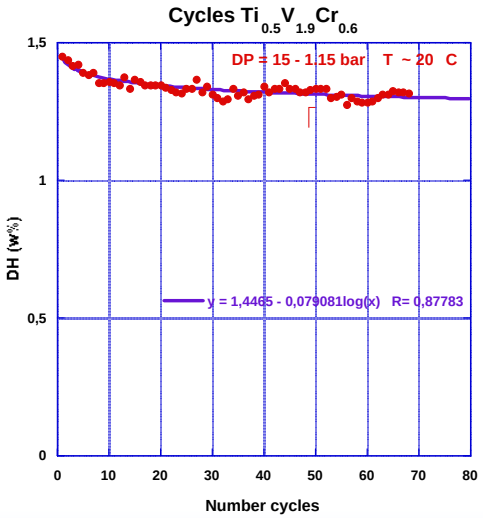
Class A metal hydrides from BCC type alloys

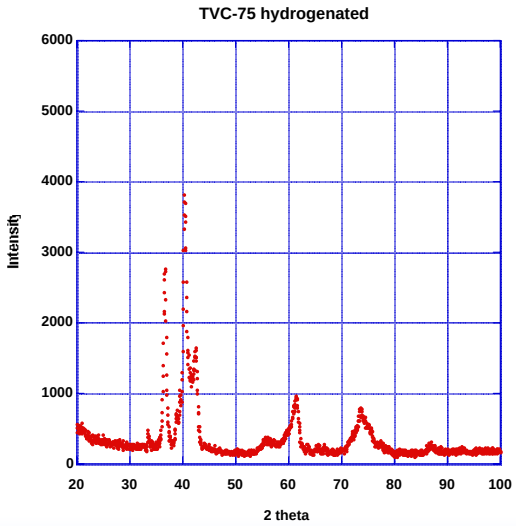


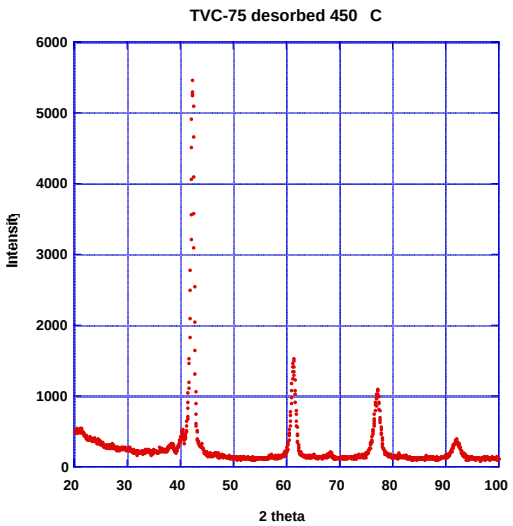






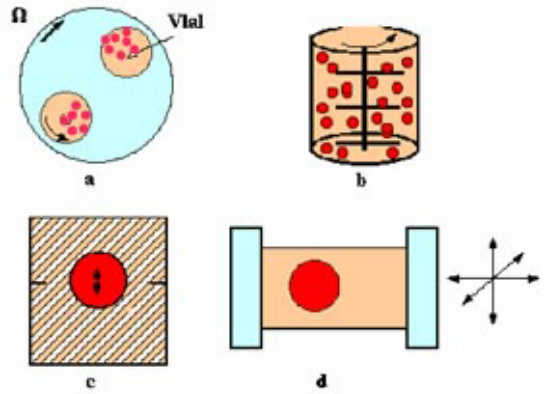






HYSTORY

Class B metal hydrides as activated $Mg(X)H_2$

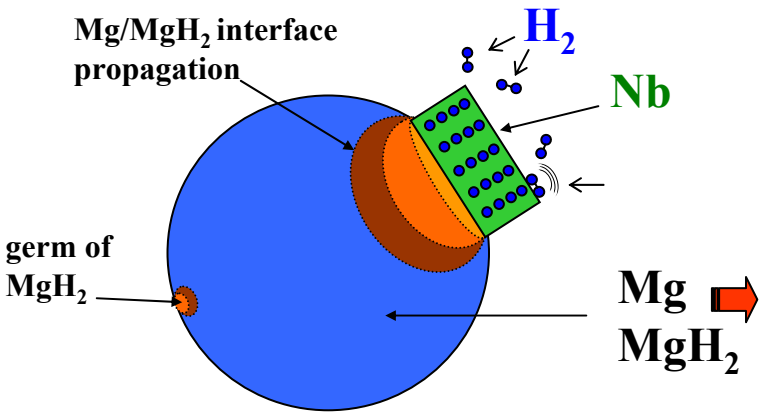


Co-milling of MgH_2 powders with activating early d-metal or d-metal compoundse.g. oxides….

T = Ti, V, Nb.. are active (larger is the valence state better the d-metal is active).
WE CHOOSE PURE METALS SINCE OXIDES (V_2O_5, Cr_2O_3..) ARE KNOWN HIGH CARCIGEN..!

Several aspects in ball-milling :
- creation of high density of defects
- creation of nanoscale M/MgH_2 interfaces

Important :
- energy of co-milling
- time of milling
- amount of activant
- ….

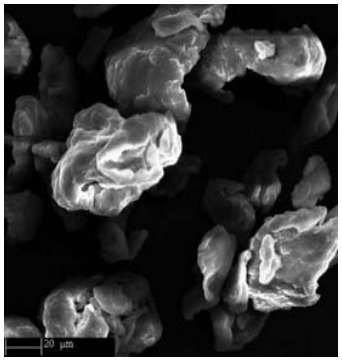
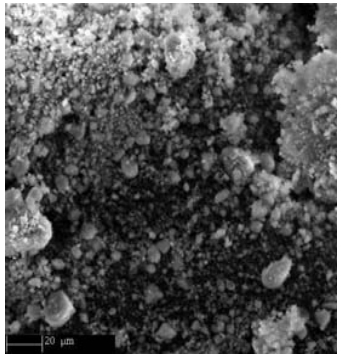
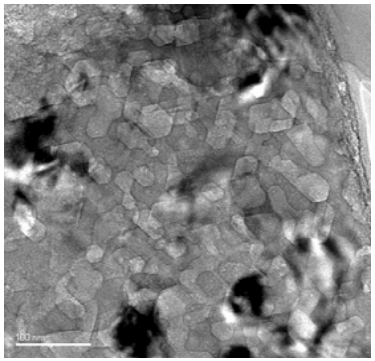
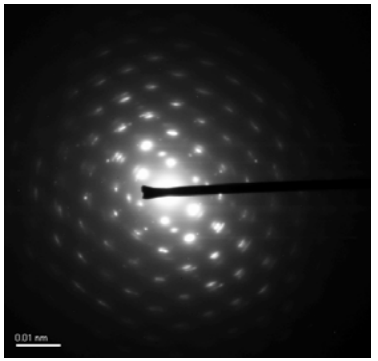


Scheme for a Nb nano-particle interfacing a micrometric Mg grain

HYSTORY

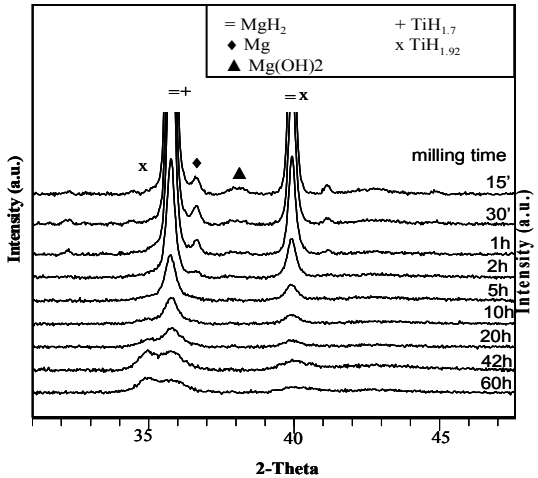
Institute for energy technology
Stockholms universitet
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
Environmental Research Laboratory
TREIBACHER
Innovation is our tradition.
Société Commerciale de Métaux et Minerais
Statkraft
ABB
KOCKUMS

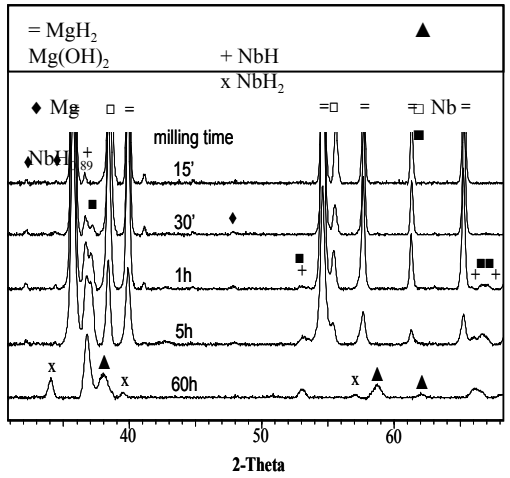
Class B metal hydrides as activated $Mg(X)H_2$

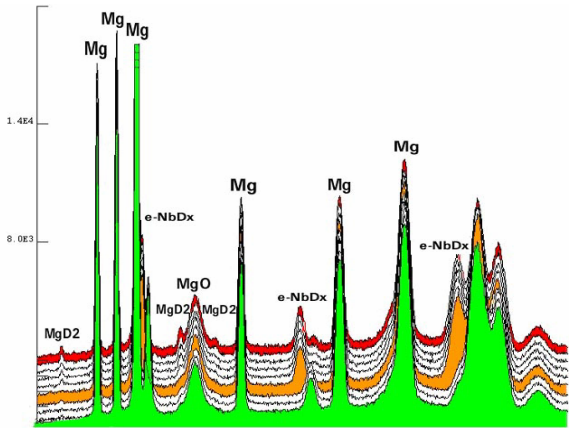





a - SEM picture of as received MgH2, the mean grain size is up to 40 µm,, b – SEM picture of a 100 hour ball milled MgH2 the mean size distribution range from 0.2 to 10 µm.

c - HREM picture of a 60 hour ball milled MgH2, which defects and nano crystalline state is transformed to well shaped and homogeneous size crystals after evacuation under beam; mean grain size ~ 20 nm.d – Electr. diffraction picture of in-situ well recrystallised Mg from MgH2 precursor.





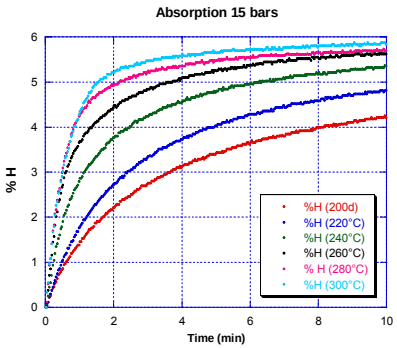


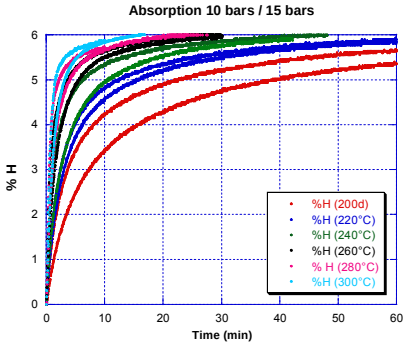
X-ray and neutron diffraction experiments revealing the formation of MHx phase during the ball-milling (activation), and at hydrogen absorption/desorption process (active interface)

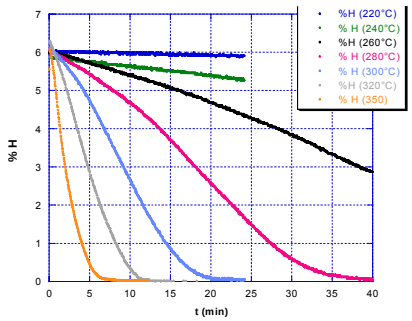
HYSTORY

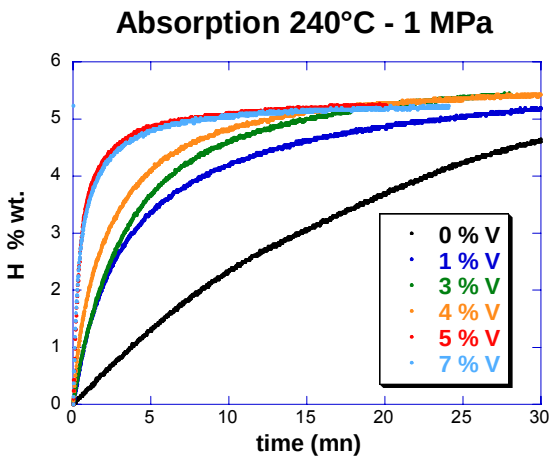
Institute for energy technology
Stockholms universitet
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
Environmental Research Laboratory
TREIBACHER
Innovation is our tradition.
Société Commerciale de Métaux et Minerais
Statkraft
ABB
KOCKUMS

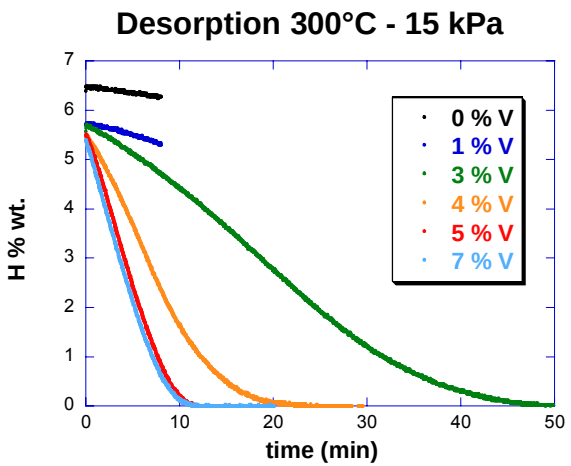
Class B metal hydrides as activated $Mg(X)H_2$











<u>Optimised activated materials :</u> 1 - $Mg(V)H_2$ leads to react promptly at 50°C for absorption, 2 - desorption can be promoted significantly fast at 220°C

Class B metal hydrides as activated $Mg(X)H_2$

Empirical kinetics laws : x (t, T, P)

x = fraction of Mg transformed to MgH_2 at a time t

Absorption : Jander law

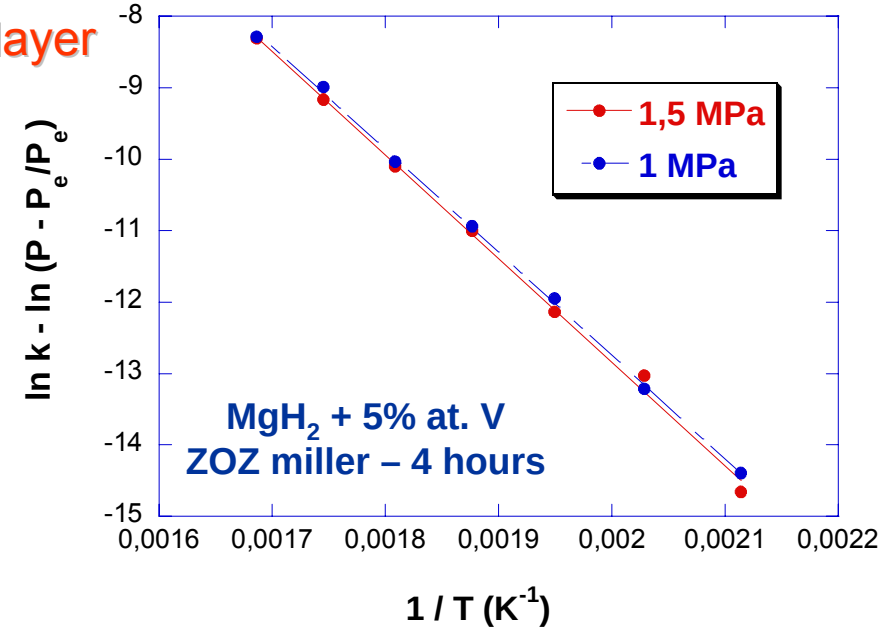
hydrogen diffusion through the MgH_2 layer

$$(1 - (1-x)^{1/3})^2 = k \cdot t$$

$$k = k_0 \cdot (P - P_e)/P_e \cdot \exp(-E_a/RT)$$

E_a = 120 kJ / mol H_2

k_0 = 9.9 10^6 s^{-1}



Desorption :

$$(1-x)^{1/3} = k \cdot t$$

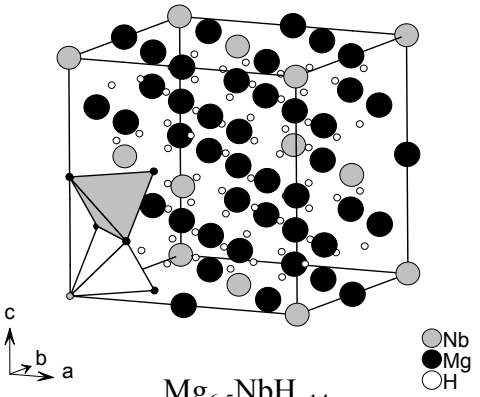
$$k = k_0 \cdot \exp(-E_a/RT)$$

E_a = 95 kJ / mol H_2

k_0 = 0.25 10^6 s^{-1}

Class B Mg-based metal hydrides

FCC structure (metal structure: Ca_7Ge type structure)



$Mg_{6.5}NbH_{\sim 14}$
(a = 9.548(1) Å and V = 870.49 Å^3)

Crystallographic parameters for $Mg_{6.5}NbH_{\sim 14}$ in space group Fm-3m (No. 225) and Z = 4

Atom	Site	x	y	z	B_{iso}	Occupancy
Nb	4a	0	0	0	1.2(1)	1.00
Mg1	4b	1/2	1/2	1/2	0.5(1)	0.52(2)
Mg2	24d	0	1/4	1/4	0.5(1)	1.00
H1	32f	0.127(4)	0.127(4)	0.127(4)	3.0	1.00
H2	32f	0.360(3)	0.360(3)	0.360(0)	3.0	1.00

The new metal hydrides with FCC structure have high hydrogen contents

$Mg_{6.5}NbH_{\sim 14}$: 5.7 wt. %
$Mg_7TiH_{\sim 16}$: 6.8 wt. %
$Mg_6VH_{\sim 14}$: 6.6 wt. %

HYSTORY

Institute for energy technology
Stockholms universitet
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
Environmental Research Laboratory
TREIBACHER Innovation is our tradition.
Société Commerciale de Métaux et Minerais
Statkraft
ABB
KOCKUMS

Class C : Alanates as light metal hydrides

	Dehydrogenation temperature (°C)	Hydrogenation		Hydrogen content (wt.%)
		Temperature (°C)	Pressure (bar)	
$LiAlH_4$	-	-	-	10.5
$NaAlH_4$	< 160	120-130	< 120	7.4
$KAlH_4$	300	> 300	100	5.7

$NaAlH_4$: High hydrogen contents & reversible

$$NaAlH_4 \leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \leftrightarrow NaH + Al + H_2$$

Ti-catalyst

3.7 wt. % 1.8 wt. %

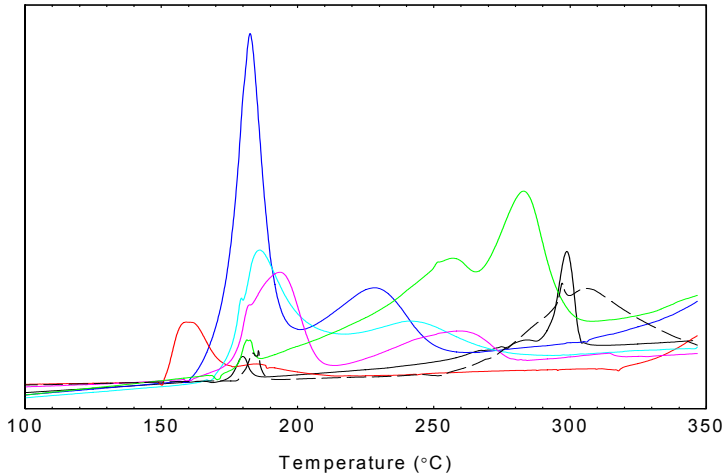
5.5 wt. % (3-4 wt.%)

$LiAlH_4$: low stability and poor reversibility
$NaAlH_4$: looks the best candidate
$KAlH_4$: high temperature dehydrogenation for low H content
Main problems : low kinetics! needs catalytic activation!
-> What catalysts? Mixed alkali-metal systems : structure and kinetics

HYSTORY

Class C : Alanates as light metal hydrides

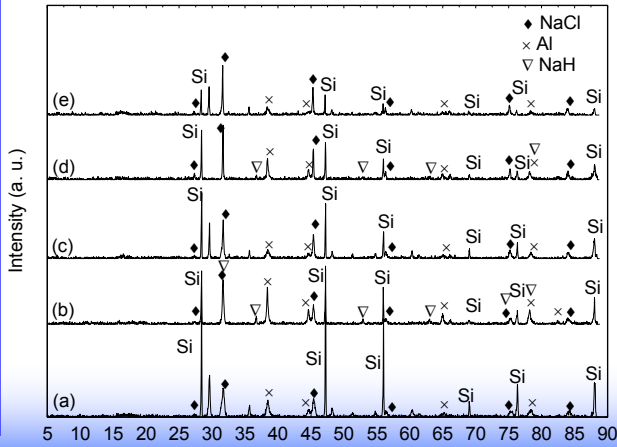
Dehydrogenation kinetics for Ti-catalyst doped/undoped $NaAlH_4$



*heating rate: 10 °C/min in Ar gas flow

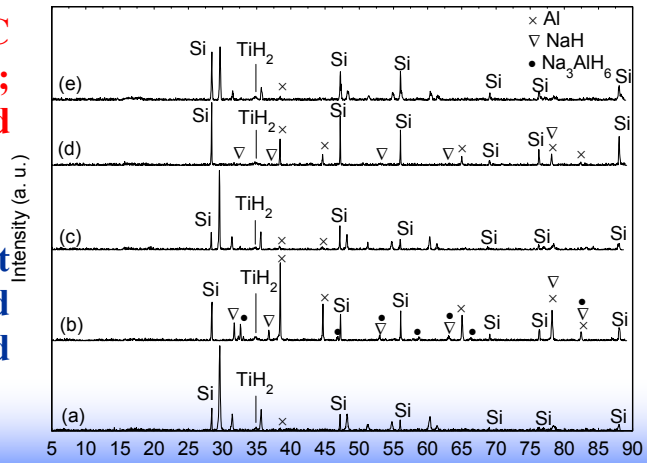
Catalyst	Onset temperature (°C)
Pure $NaAlH_4$ (...)	177.31
Ball milled $NaAlH_4$ (—)	175.66
Ti (—)	178.14
★ Nanosized activated Ti (—)	**159.31**
TiH_2 (—)	176.66
TiC/TiN (—)	166.52
★ $TiCl_3$-1/3$AlCl_3$ (—)	**151.24**

Cycling



Dehydrogenation: 160°C and 1 bar for 2 h; Hydrogenation: 125°C and < 110 bar in H_2 for 24 h.

Ball milled (a), after 1st dehydrided (b), 1st cycled (c) 10th dehydrided (d) and 11th cycled (e) sample



HYSTORY

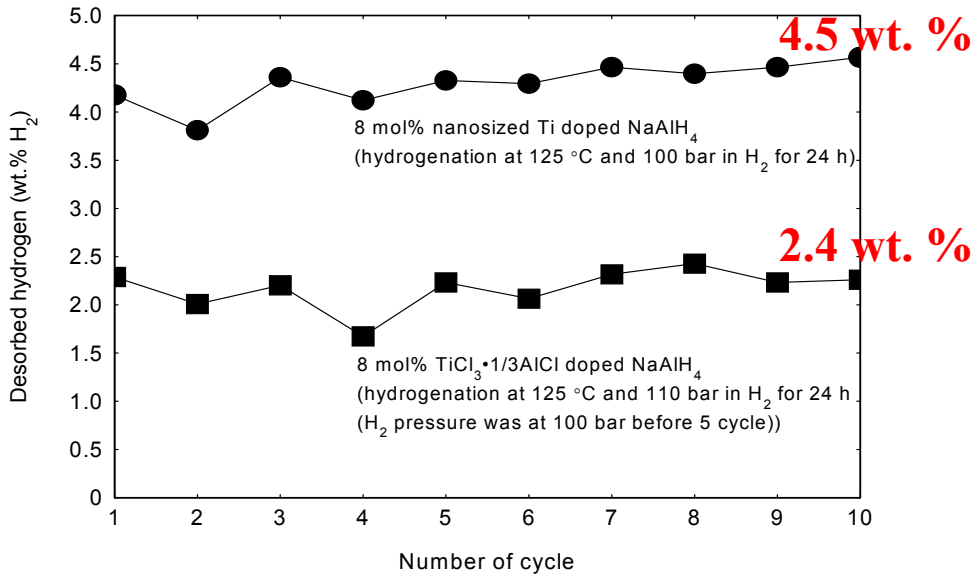
Class C : Alanates as light metal hydrides

Amount of desorbed hydrogen

Ball milled ordinary Ti doped $NaAlH_4$

≤ 3.75 wt. %

(P. Wang and C. M. Jensen, *J. Phys. Chem. B* 2004, 108, 15827.)



Conclusions

$NaAlH_4$ with dispersed Ti (< 100 nm)
Better reversiblity and high hydrogen content (4.5 wt. %)
Desorption (160 °C/1 bar for 2h)/Absorption (125 °C/100 bar for 24h)
Large amounts of the sample can be made by ball milling

$KAlD_4$ and studies of Al phases and crystal quality related to the reactions

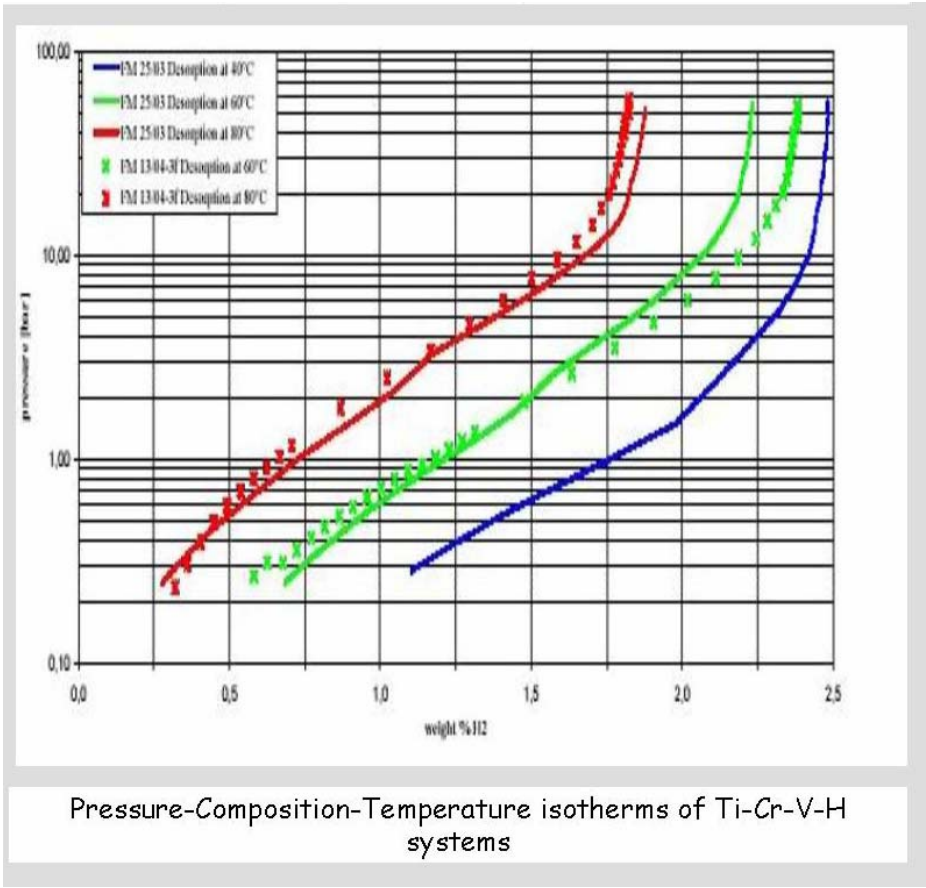
The life cycling operation was performed up to 10 cycles

HYSTORY

Upscale class A materials

Presently, batches of ~ 20 kg have been produced at Treibacher Industry plant. However the first alloys as studied in the Hystory project were not formulated specially for fuel-cell operation. New batches are under synthesis, developped from the most recently prepared formulas (temperature range : 20-60°C)

Small scale tank designed for testing the new materials within the HYSTORY project.



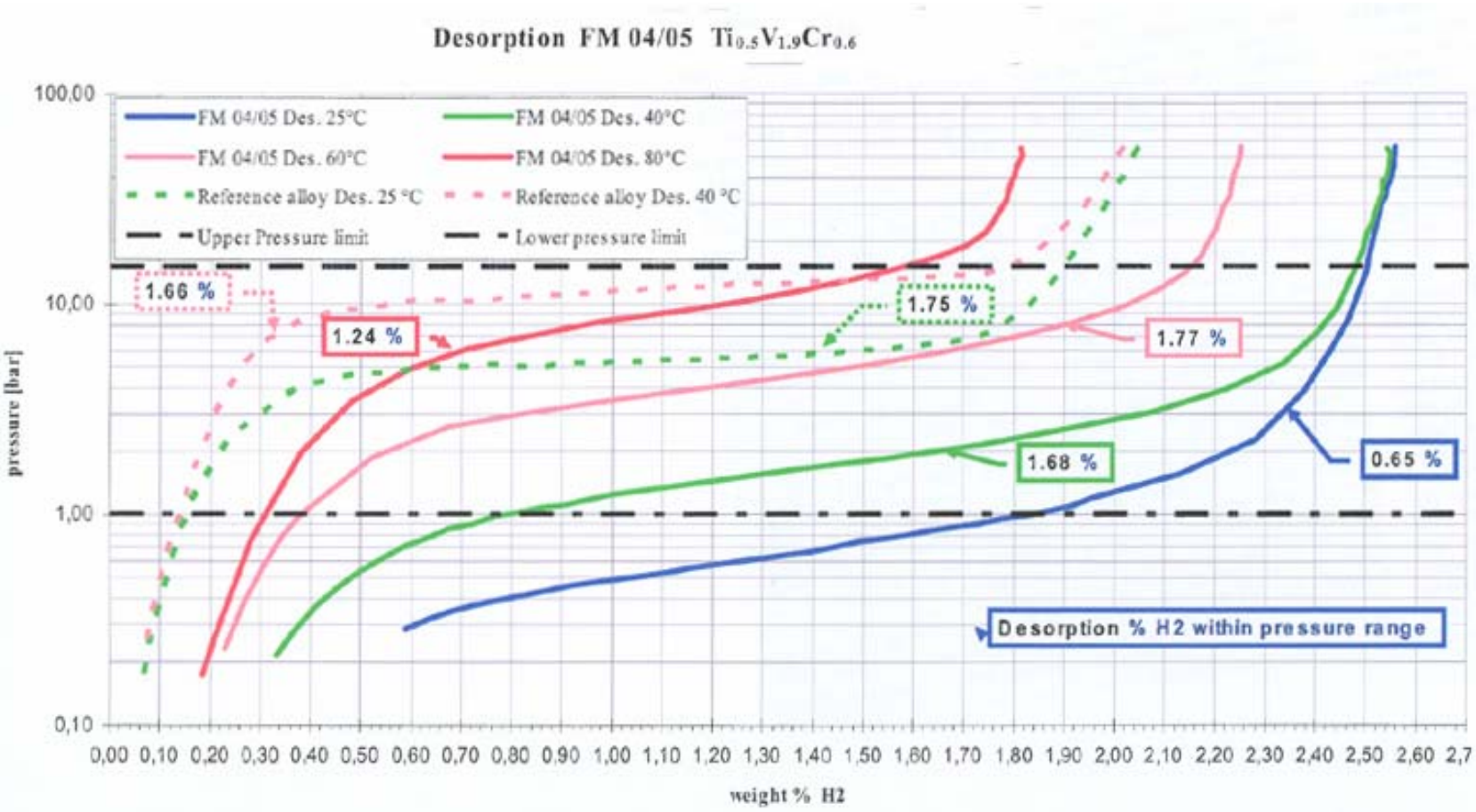
Pressure-Composition-Temperature isotherms of Ti-Cr-V-H systems

PCT measurements on a Ti-rich BCC alloy as prepared at Treibacher Industrie

HYSTORY

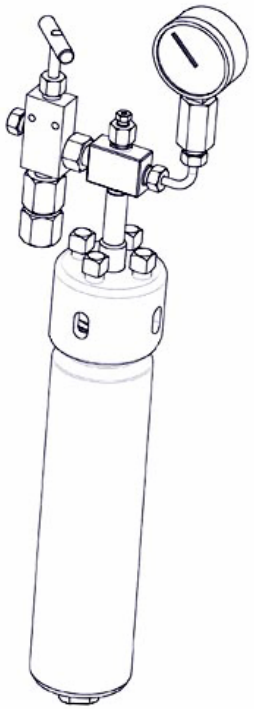
Upscale class A materials

A new BCC type hydride behave better than the « conventionnal » AB_2H_x as delivered for the large tank designed for fuel cell application.



HYSTORY

Upscale class B materials



Rotating furnace and autoclave with its ancillary equipments installed at MCPT to prepare the MgH_2 precursor from Mg powder

HYSTORY

Institute for energy technology

Stockholms universitet

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Environmental Research Laboratory

TREIBACHER
Innovation is our tradition.

Société Commerciale de Métaux et Minerais

Statkraft

ABB

KOCKUMS

Upscale class B materials

Large scale energetic ball miller (ZOZ) used to prepare kg batches of M-activated MgH_2

HYSTORY

Institute for energy technology

Stockholms universitet

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Environmental Research Laboratory

TREIBACHER
Innovation is our tradition.

Société Commerciale de Métaux et Minerais

Statkraft

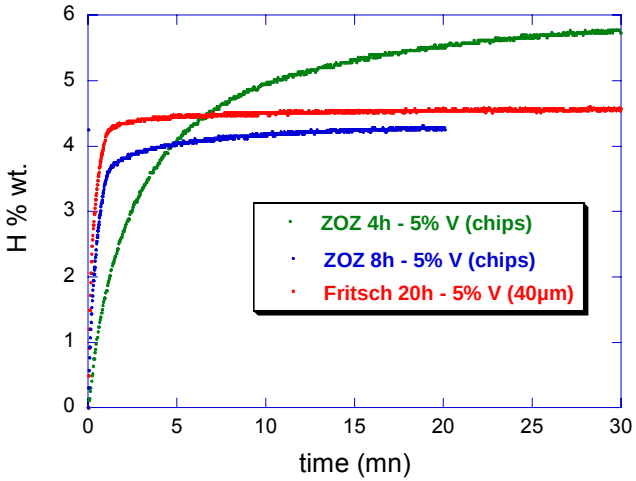
ABB

KOCKUMS

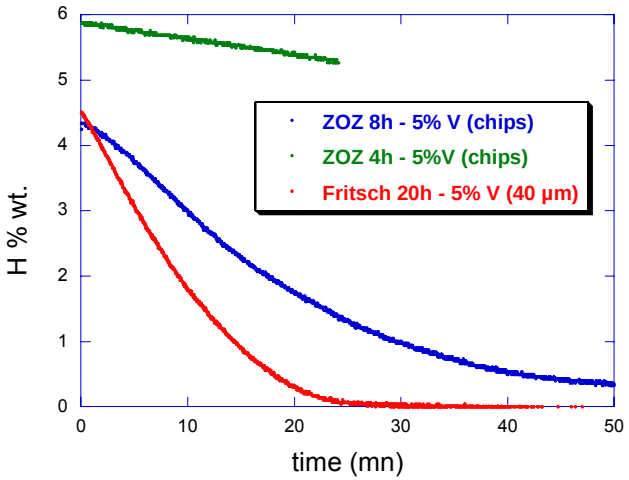
Upscale class B materials

Comparisons Institute/Industry

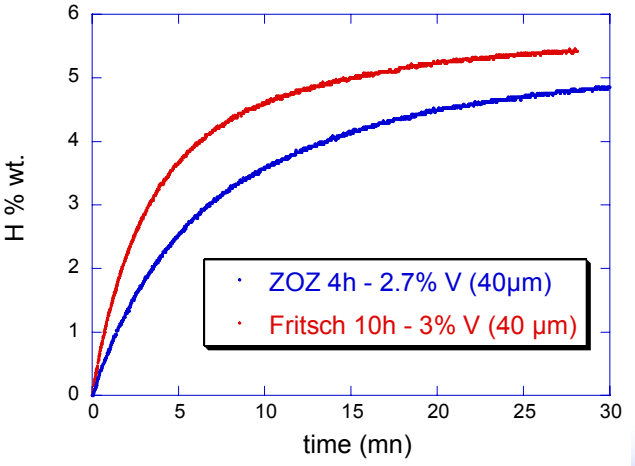
Absorption 240°C - 1 MPa



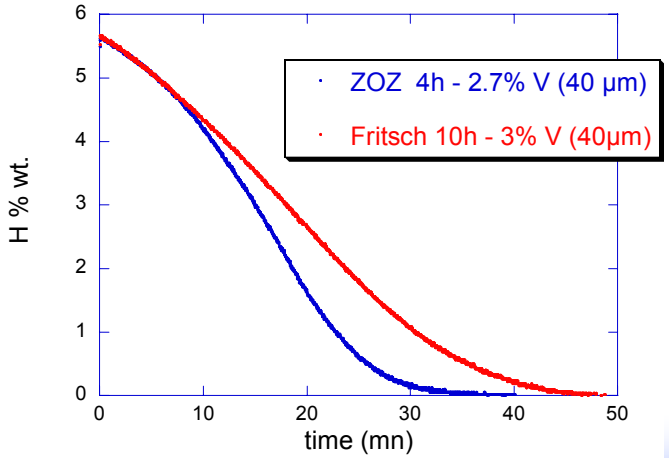
Desorption 240°C - 15 kPa



Absorption 240°C - 1 MPa



Desorption 300°C - 15 kPa



Simulation of tank in working conditions

Need for optimal/safe heat management strategies and novel cost effective design options (develop new 2-D models and utilize recent advances in Dynamic Optimisation)

Bed filled with a metal hydride alloy surrounded by a cooling jacket:

- **Solid and gas temperatures equal**
- **Axial and radial dispersion included**
- **Axial and radial velocity calculated through Darcy's law or the Blake-Kozeni equation**
- **Ideal gas law in the gas phase**

Mass balance of hydrogen in the gas phase (bulk of the reactor)

Pressure Drop Equations

Energy Balance

Mass balance of hydrogen in metal phase

Definition of Equilibrium Pressure (Jemni and Nasrallah, 1995)

Other auxiliary expressions

Boundary conditions

Initial Conditions

Institute for energy technology

Stockholms universitet

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Environmental Research Laboratory

TREIBACHER
Innovation is our tradition.

Société Commerciale de Métaux et Minerais

Statkraft

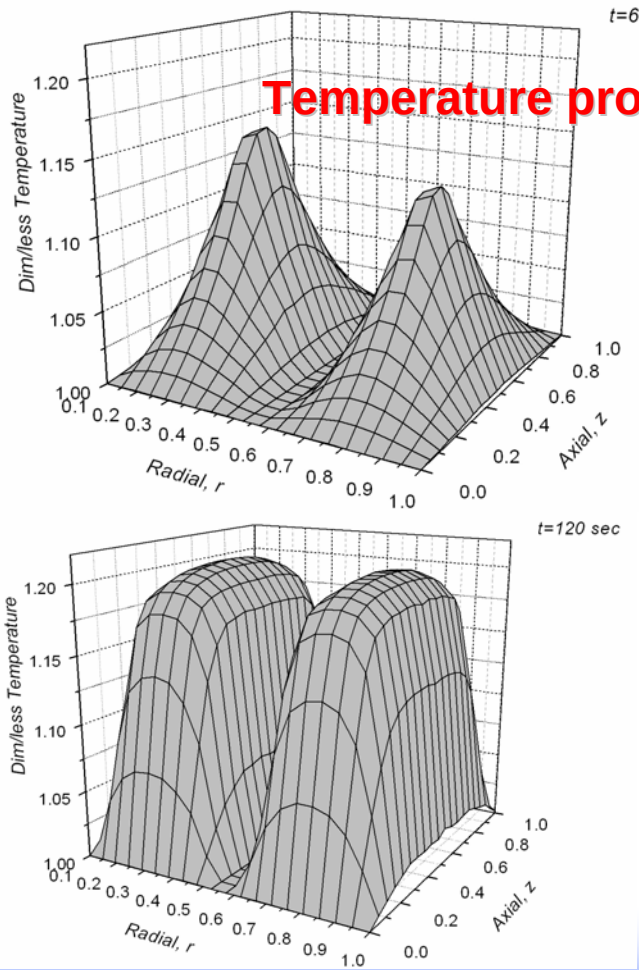
ABB

KOCKUMS

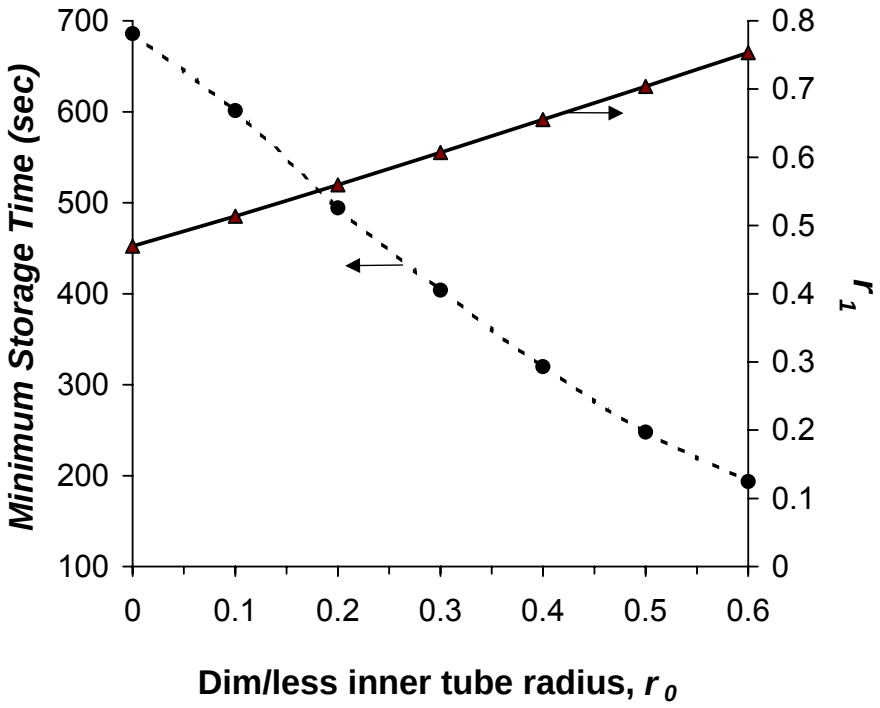
Simulation of tank in working conditions

Simulation results: 2-D H_2 storage with annular ring heat exchanger

Temperature profiles

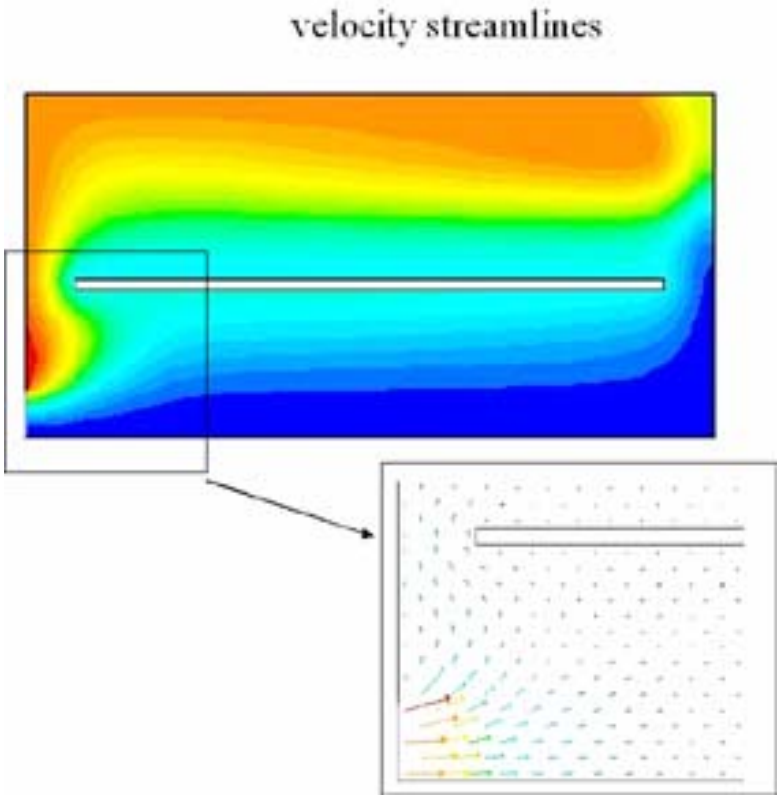


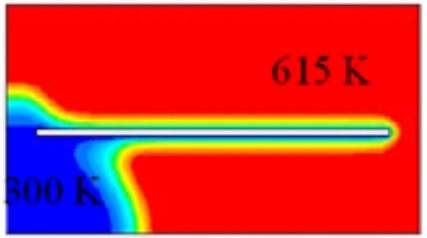
Optimal Design of the annular ring heat exchanger



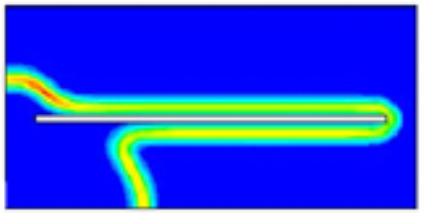
HYSTORY

Simulation of tank in working conditions

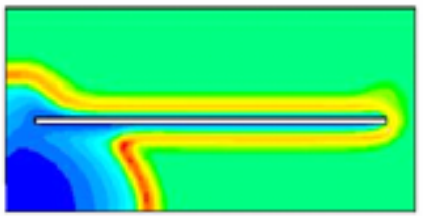




Contours of temperature



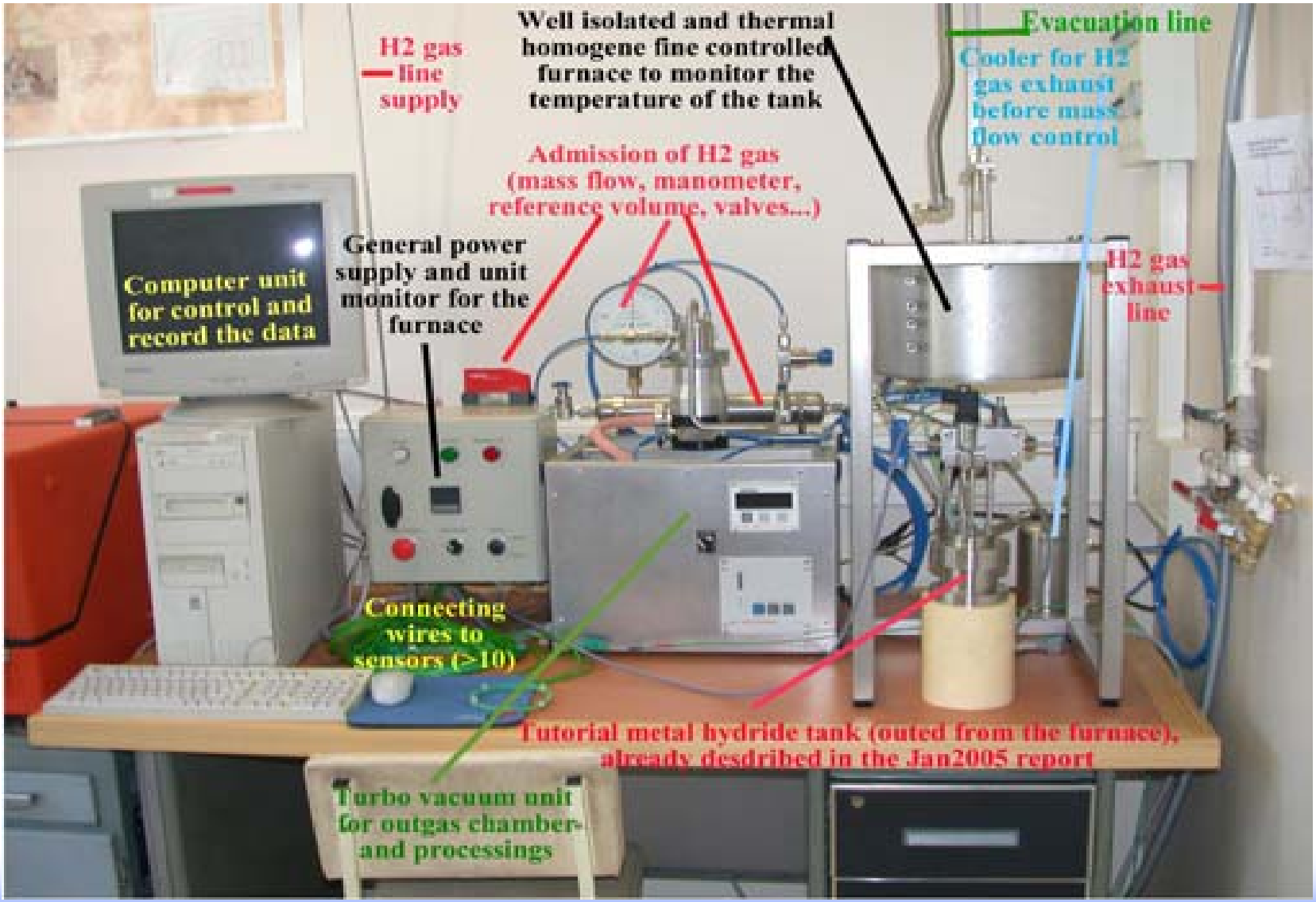
Contours of reaction rate



Contours of hydriding fraction

HYSTORY

Development of a tutorial tank



HYSTORY

Development of a tutorial tank

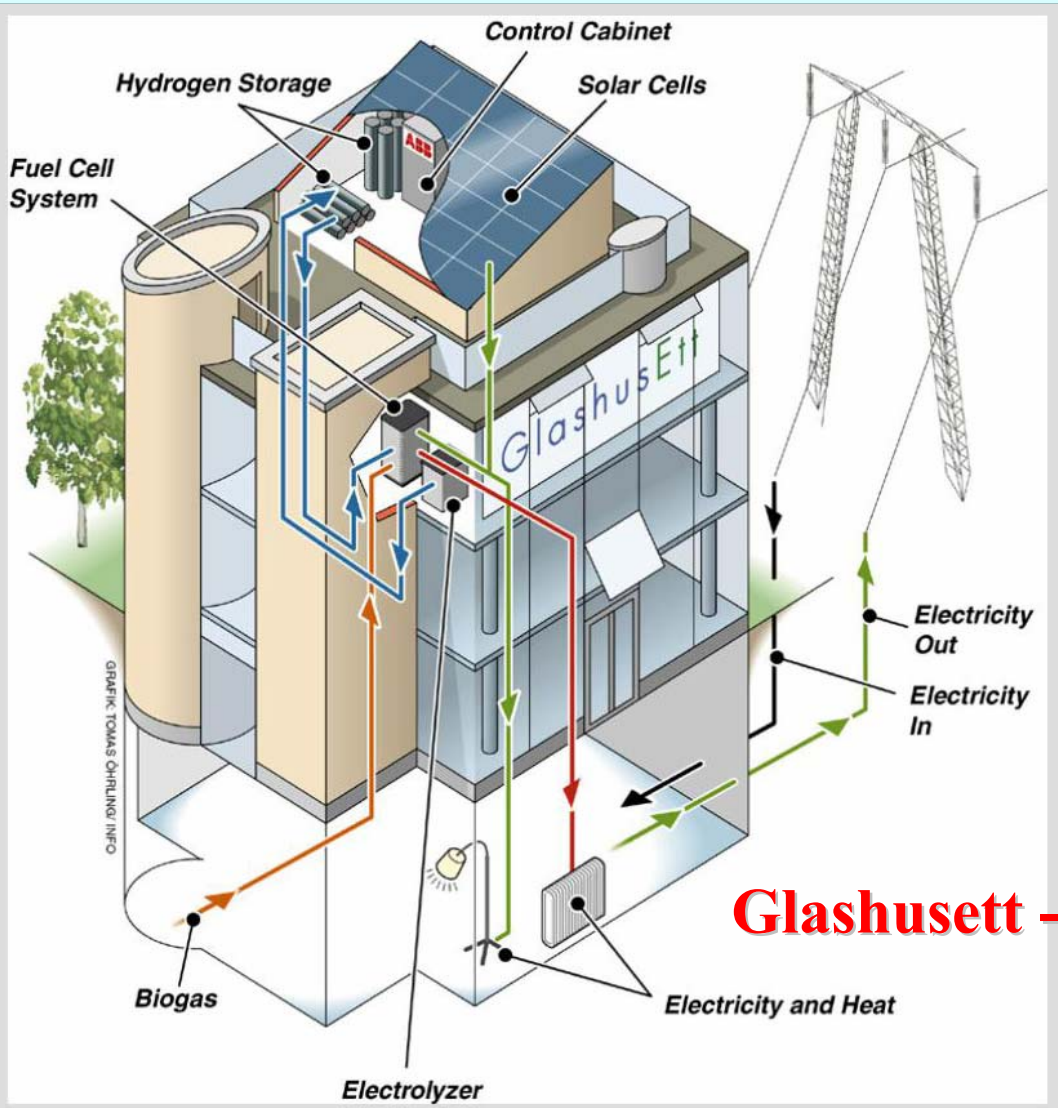
Tutorial tank (1/4 liter), axis-symmetrical. It can be as well heated (cool) at periphery or cool (heated) from the internal copper cylindar

HYSTORY

Development of a full scale tank

HYSTORY

Institute for energy technology
Stockholms universitet
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
Environmental Research Laboratory
TREIBACHER
Innovation is our tradition.
Société Commerciale de Métaux et Minerais
Statkraft
ABB
KOCKUMS



Glashusett - Stockholm

GlashusEtt in Hammarby Sjöstad, Stockholm, Sweden. Schematic drawing showing the components and the energy flow in the alternative energy system in GlashusEtt.

HYSTORY

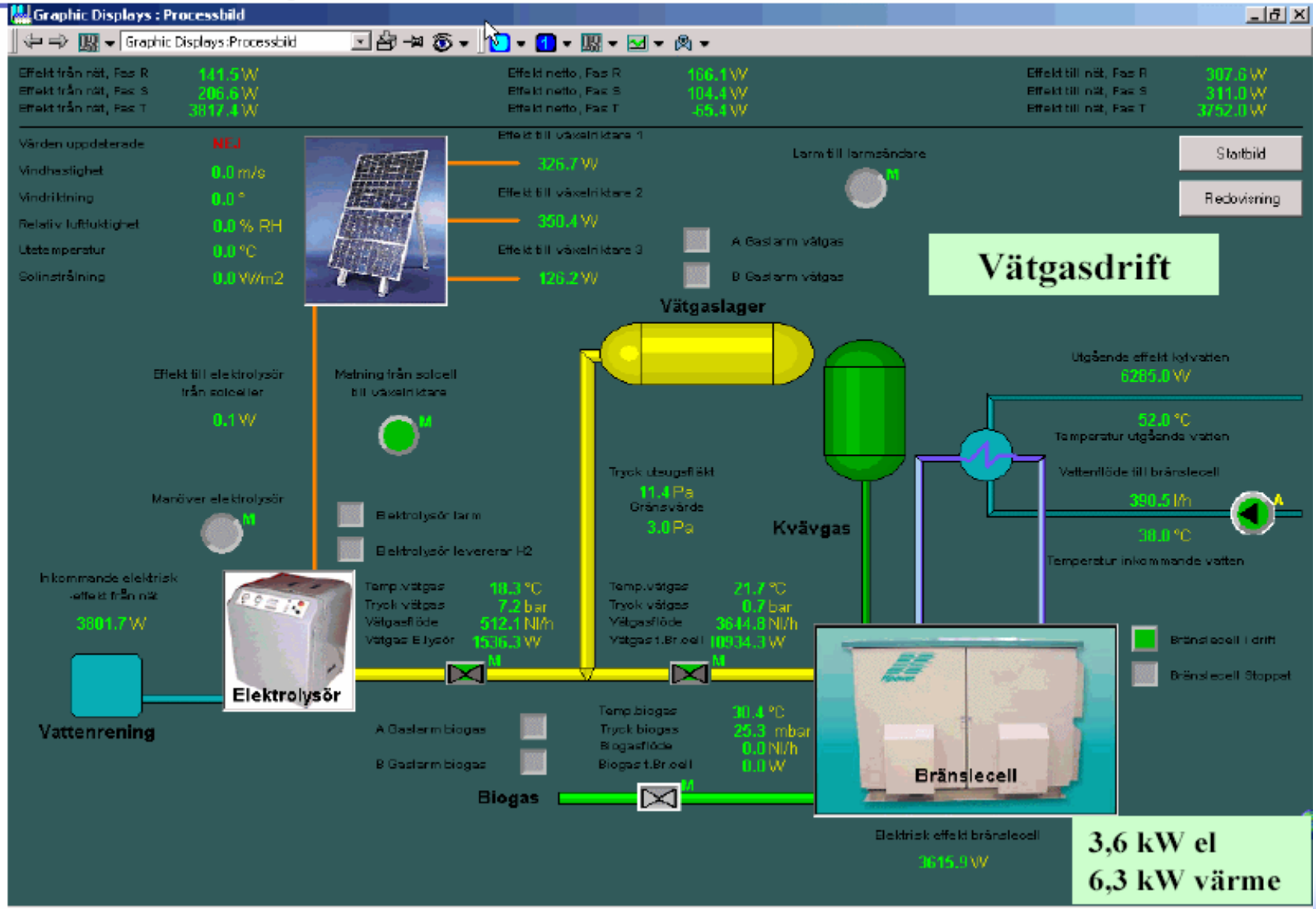
Glashusett - Stockholm

Current hydrogen storage unit in GlashusEtt: Conventional H_2 storage consisting of 22 bottles, each with a water volume of 50 litres, giving a total volume of 1100 litres. At 14 barg this storage contains 15 Nm^3 of H_2.

Large scale metal hydride tank designed to store 15 Nm^3 of H_2. The outer volume of the tank is approximately 90 litres. This tank is shortly to be installed in GlashusEtt.

HYSTORY

Kontrollsystem – Processbild



© ABB, Corporate Research - 21

HYSTORY

Institute for energy technology

Stockholms universitet

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Environmental Research Laboratory

TREIBACHER
Innovation is our tradition.

Société Commerciale de Métaux et Minerais

Statkraft

ABB

KOCKUMS

To Achieve

Optimised formula in the Ti-V-Cr systems with a large FCC-hydride ~ RT
Upscaling the BCC type of alloys and hydrides
Development of a prototype large tank

Nature and structure of the M/MgH_2 active interface (Ti-Mg hydride?)
Better and new catalysts for Mg-activation
Upscaling the Mg(M)H_2 production
Simulation and experience in tank management (matter and heat exchange…)
Development of large tank (~ 5 kg MgH_2)

Mixed alkali-alanates
About the Ti catalytic effect in alanates (Al metastable alloy)
Experience in tutorial tank

HYSTORY

Institute for energy technology
Stockholms universitet
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
Environmental Research Laboratory
TREIBACHER
Innovation is our tradition.
Société Commerciale de Métaux et Minerais
Statkraft
ABB
KOCKUMS

EC FP 5
Programme
1998-2002

HYSTORY

Institute for energy technology

Stockholms universitet

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Environmental Research Laboratory

TREIBACHER
Innovation is our tradition.

Société Commerciale de Métaux et Minerais

Statkraft

ABB

KOCKUMS

EC FP 5
Programme
1998-2002

HYSTORY

Institute for energy technology

Stockholms universitet

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Environmental Research Laboratory

TREIBACHER
Innovation is our tradition.

Société Commerciale de Métaux et Minerais

Statkraft

ABB

KOCKUMS