Materials with desirable Thermodynamics Properties for the Storage of Hydrogen Energy using Sponge Metals

Sponge Metals With Desirable Thermodynamic Properties For The Storage Of Hydrogen Energy

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How do we store hydrogen using sponge metal?

We do not store hydrogen itself, rather we store its energy in the form of a metal (a porous metal called a 'sponge').

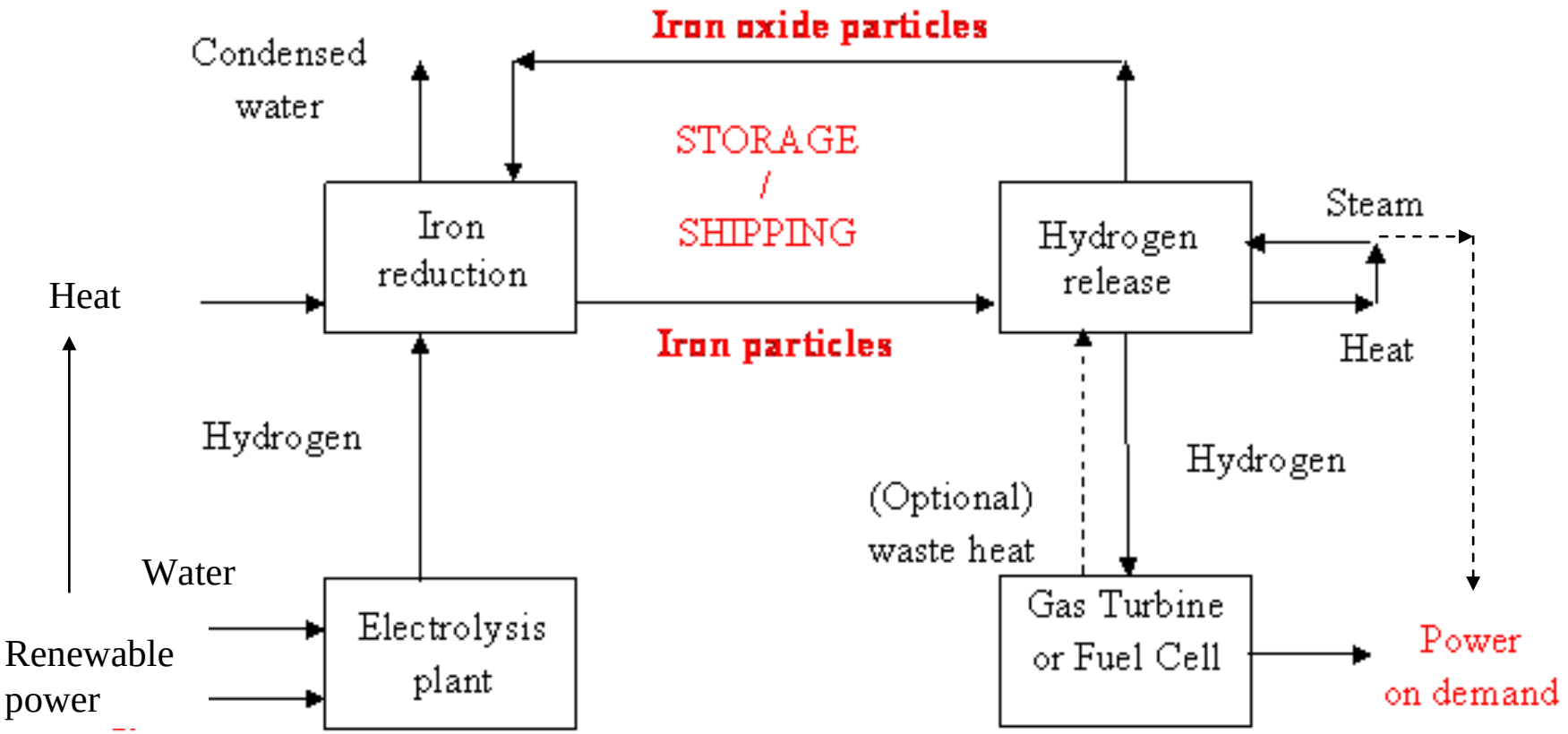
During storage:

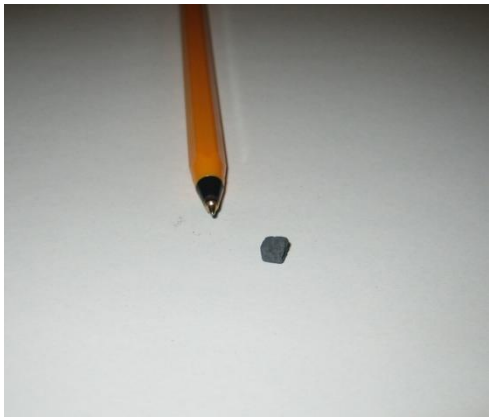
$$H_2 + \text{Metal Oxide} \rightarrow \text{Metal} + H_2O$$

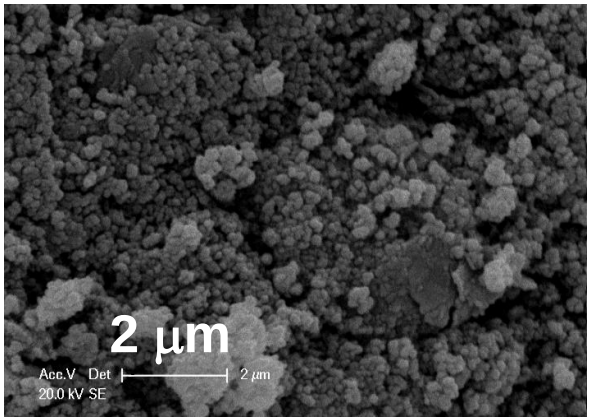
During release:

$$\text{Metal} + H_2O \rightarrow H_2 + \text{Metal Oxide}$$

High temperature reaction (for good kinetics), 600-1000^{o}C.







Suitable particles made by e.g. mechanical mixing, precipitation, sol-gel, etc.

Why using sponge metal?

Up to 3-6 wt.% H_2 capacity – compact stationary storage

No need for pressurized containment

Cheap materials, can be non-toxic (e.g. iron)

Reduction step is a well known metallurgic process ('Direct Reduced Iron'), and the reverse oxidation is facile.

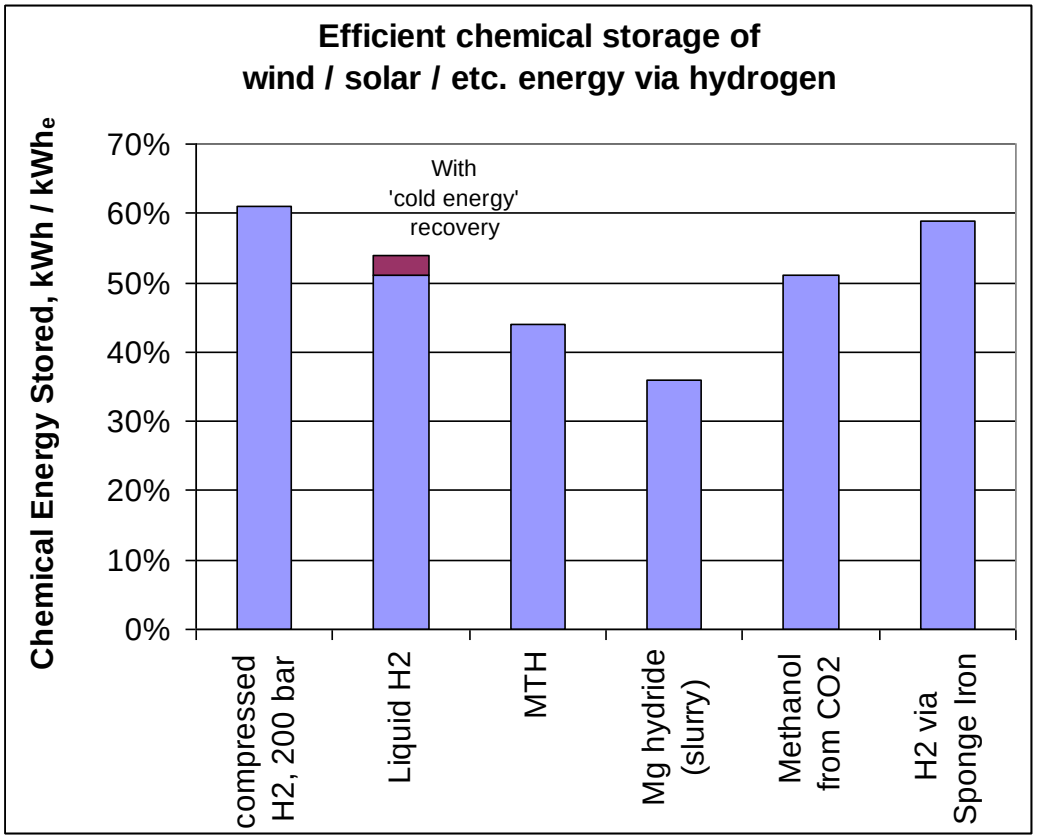
H_2 production from sponge iron was also common practice in the early chemical industry.

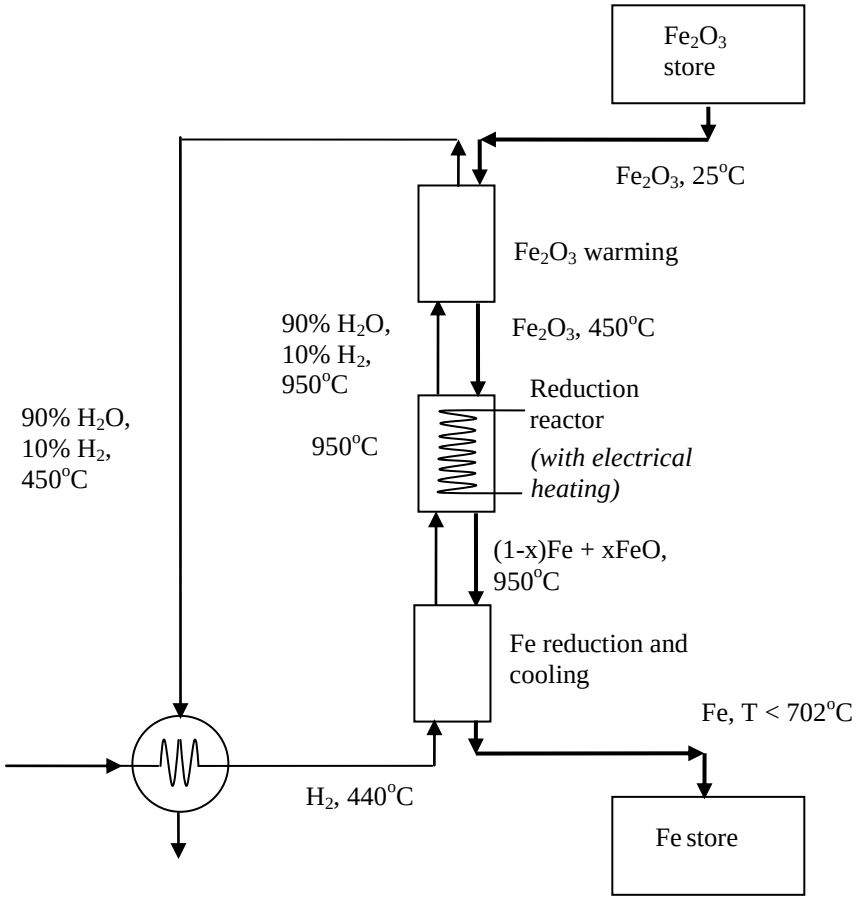
Delivery of pure hydrogen. For example, carbon monoxide would be screened out during the storage of hydrogen, via

$$CO + \text{iron oxides} \leftrightarrow CO_2 + \text{iron}$$

Iron sponge factory, near Alibaug, Maharashtra (India) – (C) Lepley, 2007.

How energy efficient?





(Mignard and Pritchard, *Int. J. of Hydrogen Energy*, 32 (2007), 5039 – 5049)

With suitable heat integration, iron sponge has the best energy efficiency amongst all processes for compact H_2 storage

Why so efficient?

Storing and releasing hydrogen tends to waste energy:

During storage,

$$H_2 + \text{empty carrier} \rightarrow \text{stored } H_2 + \text{energy (LOST)}$$

During release,

$$\text{stored } H_2 + \text{energy (PARASITIC DEMAND)} \rightarrow H_2 + \text{regenerated carrier}$$

The sponge-iron process works the other way round:

$$H_2 + \text{iron oxides} + \text{heat} \leftrightarrow \text{iron} + \text{water},$$

which enables co-storage and co-generation of H_2 + heat.

Current research in the field

Usually, research groups stick to iron, and seek to achieve

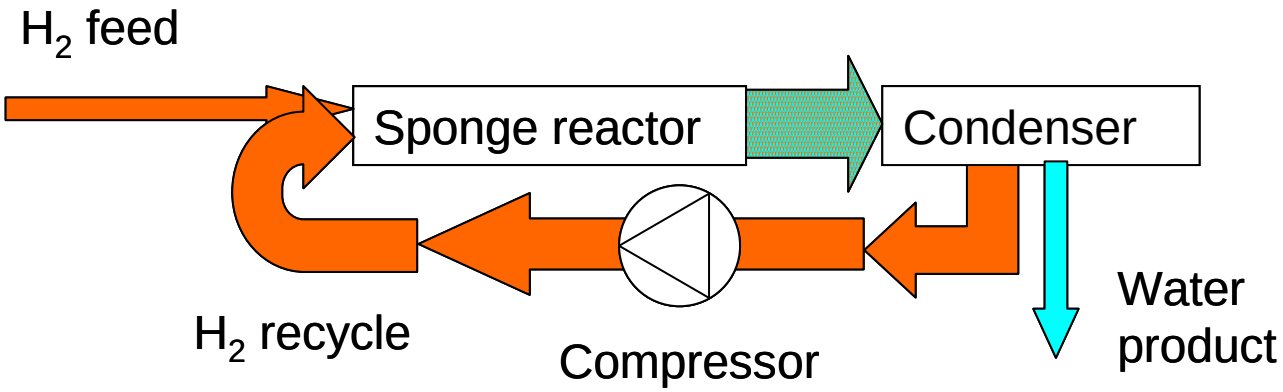
- **Improved resilience to sintering and attrition**
- **Maintained activity over 1000's cycles**
- **Improved kinetics**
- **Lower operating temperature.**

Typically, a hard support (alumina, silica, etc.) is mixed with the iron, together with some metallic additives. Fabrication technique is also important for obtaining stable but active contact mass.

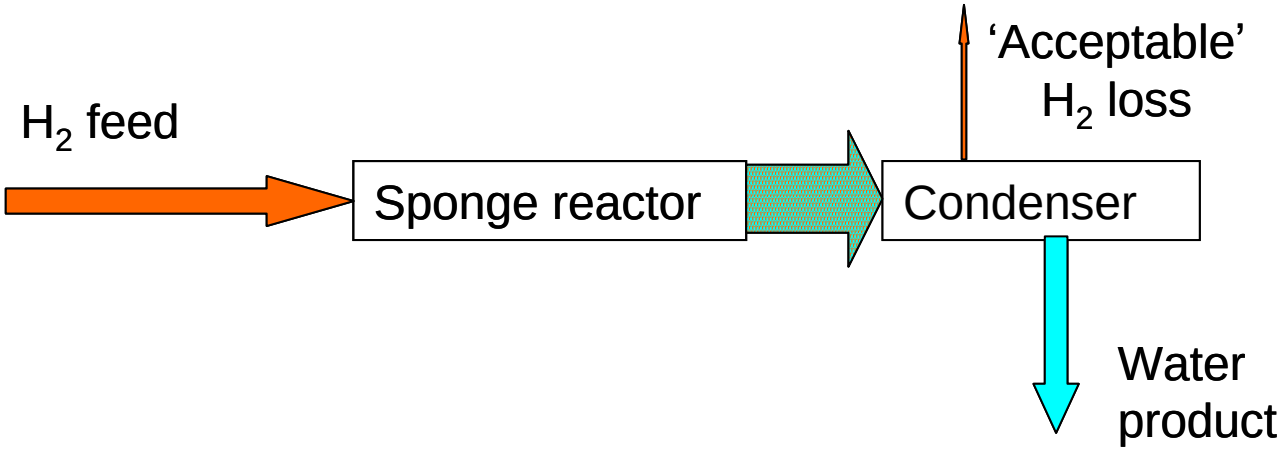
But what about the process? - Our proposal

H_2 storage step requires high conversion per pass!

Low conversion:

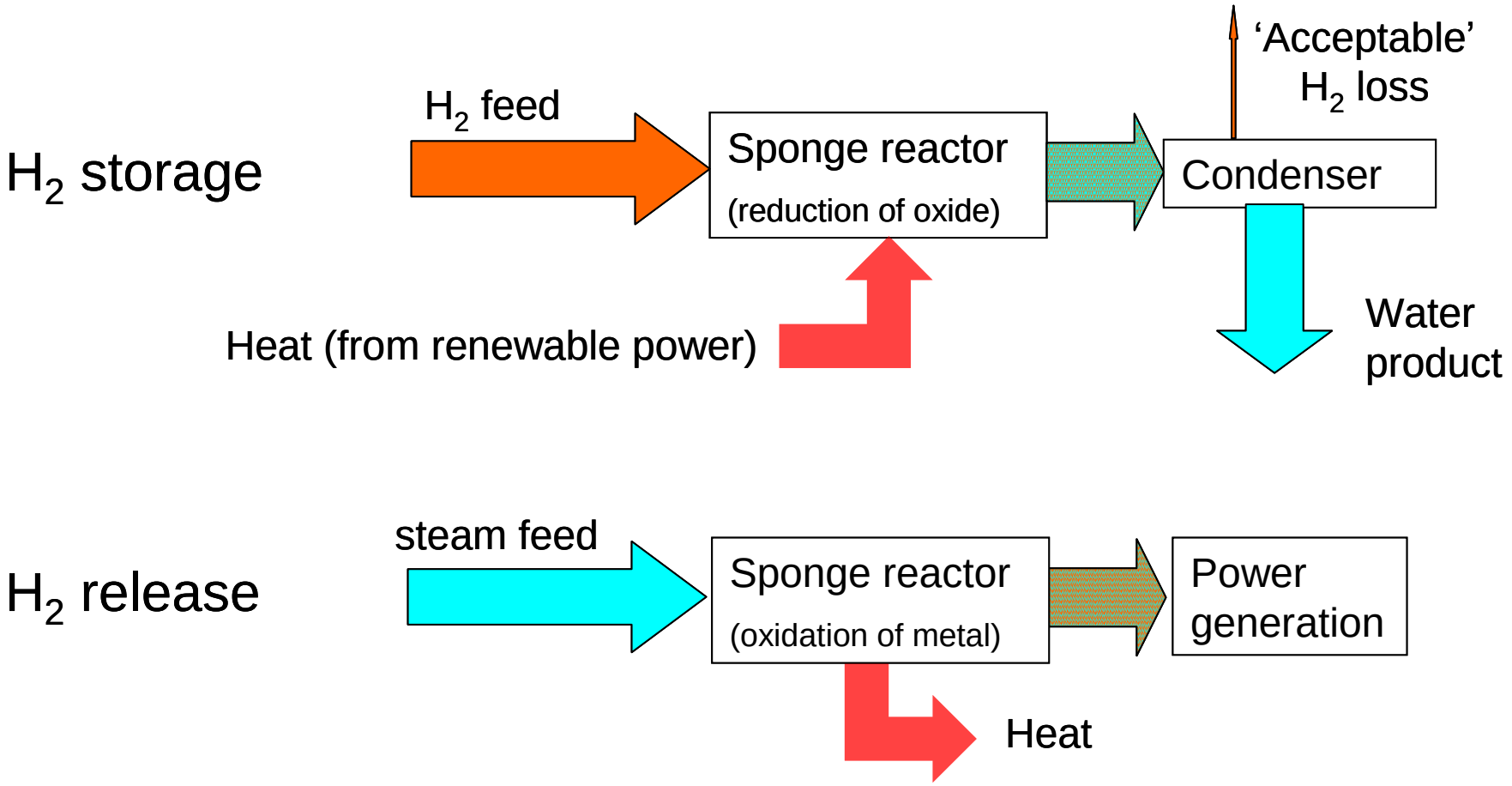


High conversion:



A high H_2 conversion per pass ≥ should make the system cheaper, simpler, more efficient and safer.

A high conversion per pass is not as critical for the H_2 release step (unreacted steam can be used for: heat recovery; proper emission control in H_2 gas turbine; hybrid fuel cell / turbine power generation systems, etc.

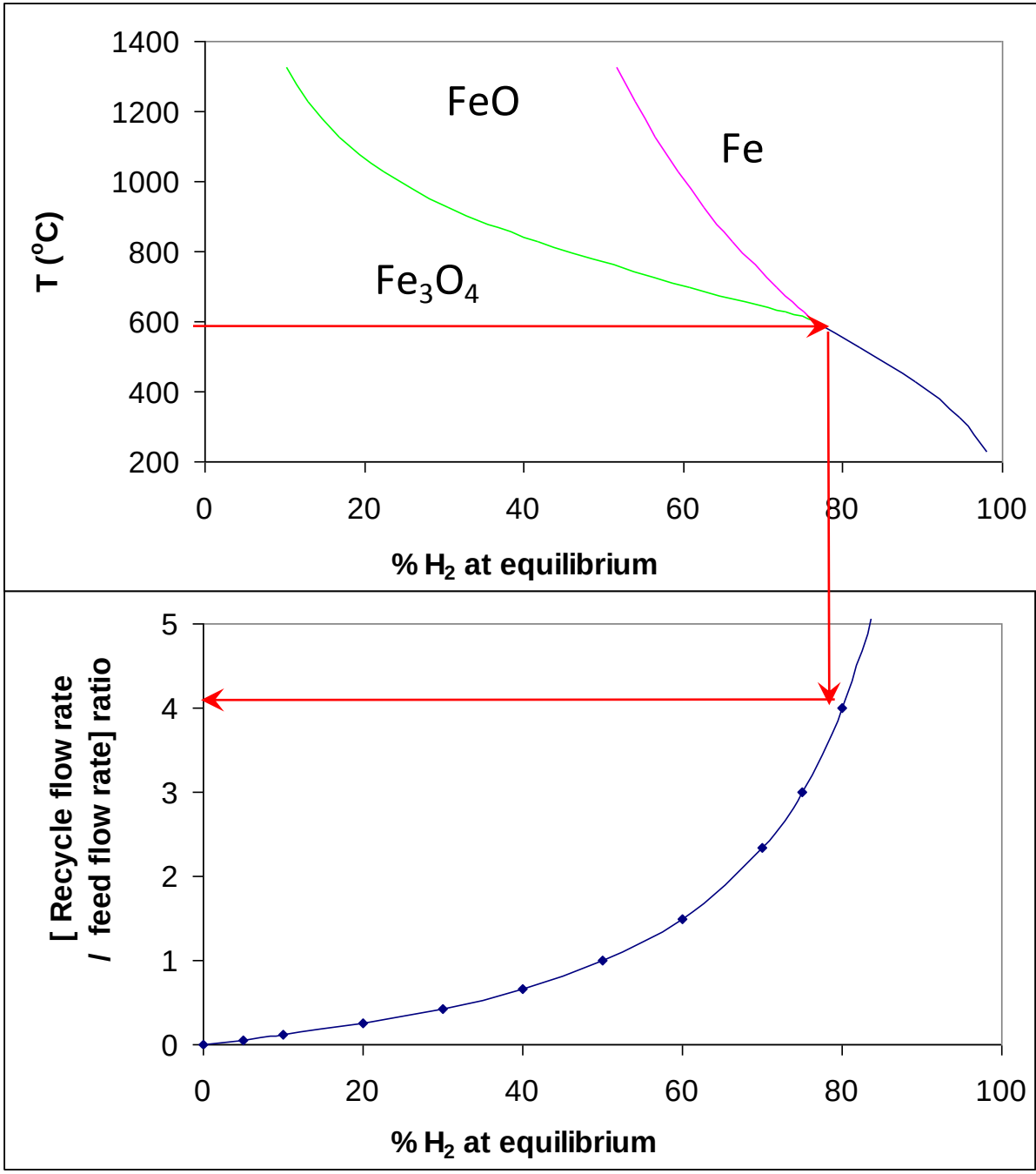


Can we operate at lower temperature?

T ≤ 600 °C good for costs
(and durability,
as we found in the lab!)

However,
lowering T also lowers
the conversion per pass
during H_2 storage.

From that point of view, iron is not the best metal.



TARGETS:

Reduction stage (hydrogen storage), must be endothermic
with **H_2 equil. concentration ≤ 5 % at T = 600 ^oC**

Oxidation stage (hydrogen release), must be exothermic
with **H_2 equil. concentration ≥ 50 % at T = 300 ^oC**

No single, common enough element can do this. We need an alloy of at least two metals M and M', such that for the reaction

$$M_xM'_y + 2H_2O \rightarrow M_xM'_yO_2 + 2H_2$$

the targets set above can be met.

A bit of thermodynamics...

The previous targets are equivalent to setting for the reaction

$$M_xM'_y + O_2 \rightarrow M_xM'_yO_2$$

the following requirements:

$\Delta S^{\ominus}_r \leq -236$ J/mol (standard entropy of reaction)

$\Delta H^{\ominus}_{r,\,298K} \leq -572$ kJ/mol (standard enthalpy of reaction)

Further approximations:

$\Delta H^{\ominus}_{r,\,298K} \sim \Delta H^{f,\ominus}_{298K}(M_xM'_yO_2)$,
the enthalpy of formation of the oxide.

$\Delta S^{\ominus}_r = -205 + S^{\ominus}(M_xM'_yO_2) - S^{\ominus}(M_xM'_y)$

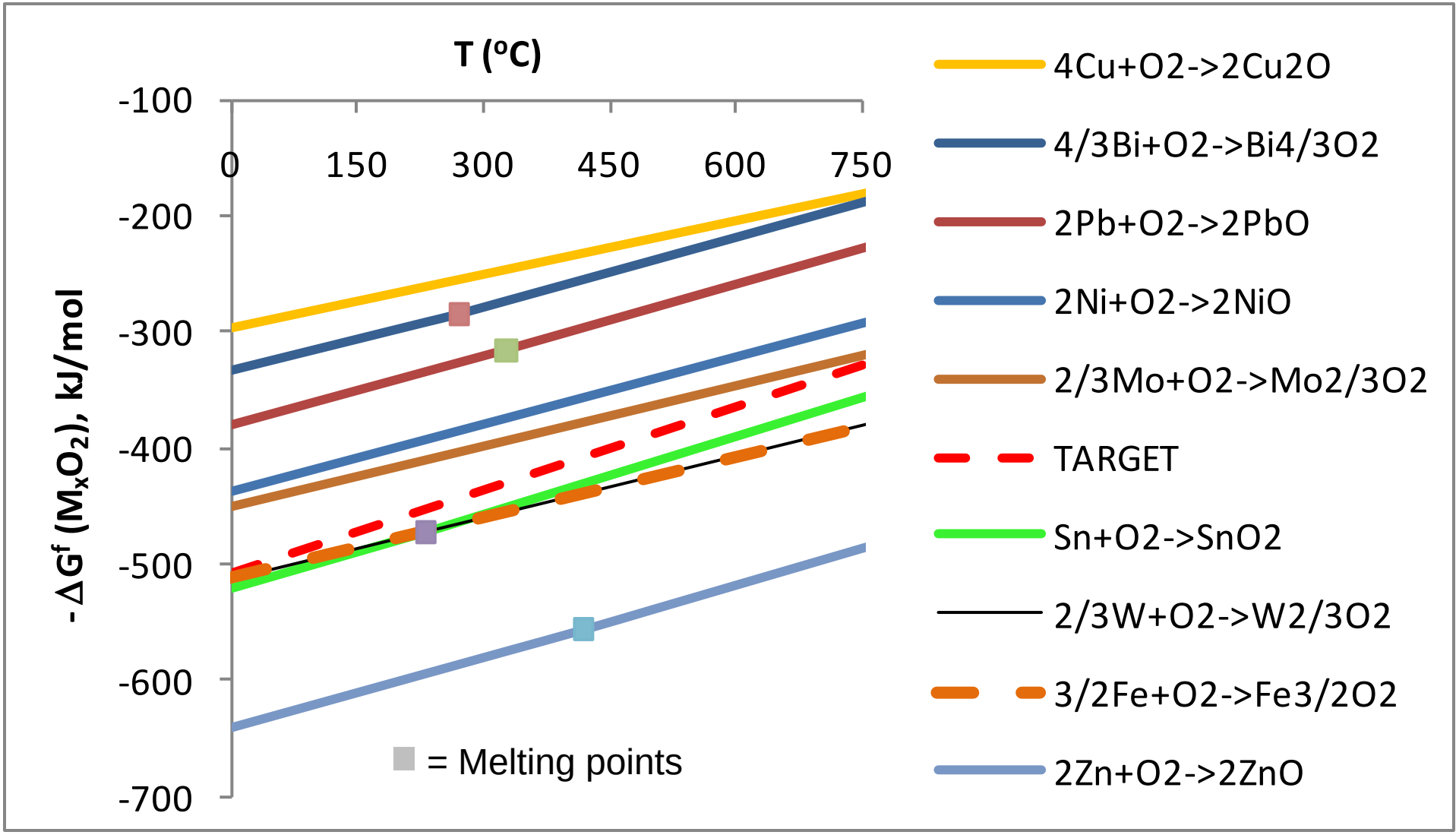
Hence the target properties of the alloy and the mixed oxide:

$$S^{\ominus}(M_xM'_yO_2) - S^{\ominus}(M_xM'_y) \leq -31 \quad J/mol$$

$$\Delta H^{f,\ominus}_{298K}(M_xM'_yO_2) \leq -572 \quad kJ/mol$$

(The first condition seems tough,
and may need to be relaxed somewhat)

Let's take y = 0 and check a few elements
– we visualize this on a Ellingham diagram (next slide)



No single element is suitable...
Tentatively, mixtures of
Iron, Tin, Tungsten, Molybdenum, Nickel
could be considered – beware of melting points!

Can we *engineer* the right alloy/mixed oxide?

A wealth of literature for the prediction of enthalpies of formation and entropies.

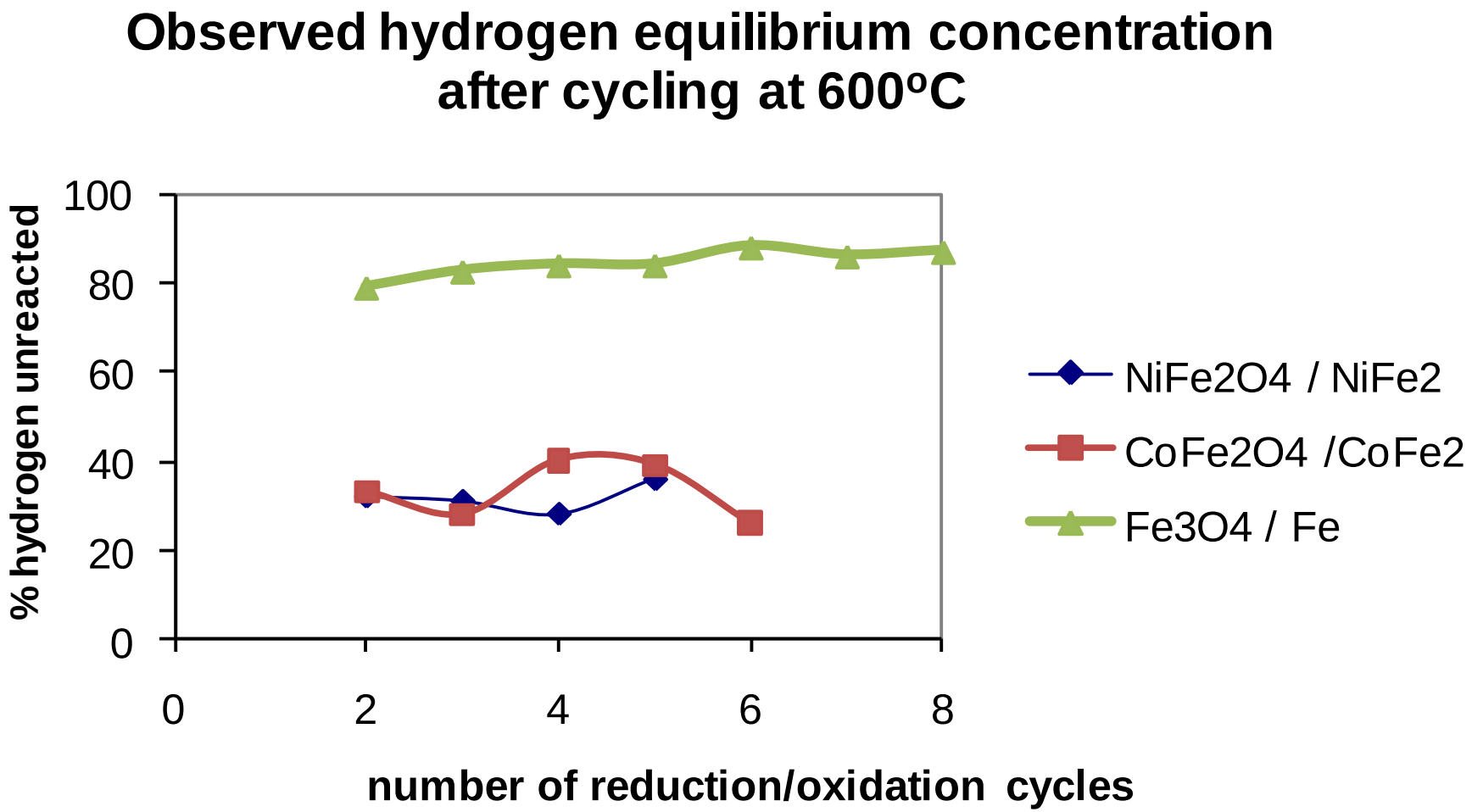
Some are accurate within a few %, e.g.

Schwitzgebel, Lowell and Parsons, 1971 (J. Chem. Eng. Data, 16(4), 418-423) predict $\Delta H^{f,\ominus}_{298K}$ *of binary oxides from a rather empirical model, but within a few % of exp. values.*

Holland, 1989 (American Mineralogist, 74, 5-13) predicts $S^{\ominus}$ *from molar volumes and coordination within a few %.*

A universal but less accurate (up to ~ 10% error) method for $S^{\ominus}$ *was demonstrated by Jenkins and Glasser, 2003 (Inorg. Chem., 42, 8702-8708) based on no more than the density.*

Preliminary results - Experimental Validation



Challenges ahead

- stability of the mixed oxide
and phase segregation of the metal

- emissions?

- thermal management for maximum efficiency
(heat recovery + insulation)

Thank you for your attention