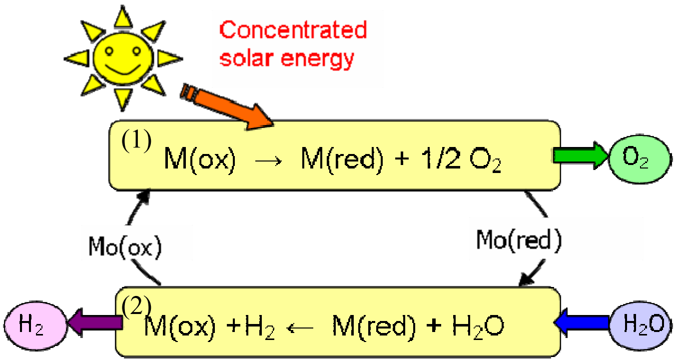
IEA/HIA TASK 25: HIGH TEMPERATURE
HYDROGEN PRODUCTION PROCESS

Metal/Metal Oxide cycle

Process Principle



(1) *Solar thermal decomposition* (2) *Water splitting*
M: Ti, Ni, Fe, Mn, Co, Ce, Cd...

TWO-STEP CYCLES

Fe_3O_4/FeO

(1) $3FeO + H_2O_{(g)} \rightarrow Fe_3O_4 + H_2$	850 K
(2) $Fe_3O_4 \rightarrow 3FeO + 1/2\ O_{2(g)}$	1900 K

Cd/CdO

(1) $Cd_{(s,l)} + H_2O \rightarrow CdO_{(s)} + H_{2(g)}$	298-573 K
(2) $CdO_{(l)} \rightarrow Cd_{(g)} + 1/2\ O_{2(g)}$	1773 K

CeO_2/Ce_2O_3

(1) $2CeO_{2(s)} \rightarrow Ce_2O_{3(s)} + 1/2O_{2(g)}$	2300 K
(2) $Ce_2O_{3(s)} + H_2O_{(g)} \rightarrow 2CeO_{2(s)} + H_{2(g)}$	700 K

THREE-STEP CYCLES: main cycles

Fe_2O_3/Fe_3O_4

(1) $3Fe_2O_3 \rightarrow 2Fe_3O_4 + 1/2O_2$	1600 K
(2) $2Fe_3O_4 + 6KOH \rightarrow 6KFeO_2 + H_2 + 2H_2O$	673 K
(3) $6KFeO_2 + 3H_2O \rightarrow 3Fe_2O_3 + 6KOH$	373 K

Mn_2O_3/MnO

(1) $Mn_2O_3 \rightarrow 2MnO + 1/2O_2$	> 1873 K
(2) $2MnO + 2NaOH \rightarrow H_2 + 2NaMnO_2$	900 K
(3) $2NaMnO_2 + H_2O \rightarrow Mn_2O_3 + 2NaOH$	> 373 K

Advantages:

- H_2 and O_2 gases are removed in separate steps (no high temperature separation step needed),
- No explosive formation gas mixture.[1]

Challenges:

- Low efficiency (irreversibility and transfer between stages),
- Low energy yields.[1]

	Reduced	Oxidised	T (K)
Non-volatile metal oxide	Fe_2O_3	Fe_3O_4	1500
	FeO	Fe_3O_4	1900
	Mn_2O_3	MnO	1750-2000
	Co_3O_4	CoO	1600
Volatile metal oxide	CdO	Cd	1750-1800
	CeO_2	Ce_2O_3	2300

Mo, Sn Ti, Mg, Ca cycles are not mentioned since their reactions occur at temperatures above 2500 K.[2]
Zn/ZnO cycle is described in another flyer.

Metal/Metal Oxide

Process principle:
(1) Thermal decomposition using solar energy,
(2) Hydrolysis (water splitting step).

Heat source: Solar[1]

Expected efficiency:

- Fe_2O_3/Fe_3O_4: 18.6 %,[3]
- Fe_3O_4/FeO: 17.4 %,[3]
- Mn_2O_3/MnO: 16-2 %,[1]
- Cd/CdO: 48.3 % (LHV),[4]
- Ce_2O_3/CeO_2: NA*.

Cost evaluation: (\$/kg H_2)

- Fe_3O_4/Fe_2O_3: 8.4,[3]
- Fe_2O_3/FeO: 7.86 to 14.75,[3]
- Mn_2O_3/MnO: NA*,
- Cd/CdO: 4.5 in 2015,[4,5]
- Ce_2O_3/CeO_2: NA*.

* NA: Not Available

TWO-STEP CYCLES

Flow-sheet

The most prominent cycles are:

Fe$_3$O$_4$/FeO

(1) $3FeO + H_2O_{(g)} \rightarrow Fe_3O_4 + H_2$ 850 K

(2) $Fe_3O_4 \rightarrow 3FeO + 1/2\ O_{2(g)}$ 1900 K

Cd/CdO

(1) $Cd_{(s,l)} + H_2O \rightarrow CdO_{(s)} + H_{2(g)}$ 298-573 K

(2) $CdO_{(l)} \rightarrow Cd_{(g)} + 1/2\ O_{2(g)}$ 1773 K

Hydrolysis (1)

The hydrolysis occurs as steam bubbles through a static pool of molten cadmium.[4] Hydrolysis efficiency increases in the presence of CO$_2$.[6] A quenching step is required to limit oxygen recombination.

Solar thermal decomposition (2)

A window-enclosed decomposer using “beam-down” optics enables the use of inert gas and sub-atmospheric pressure to reduce the decomposition temperature.

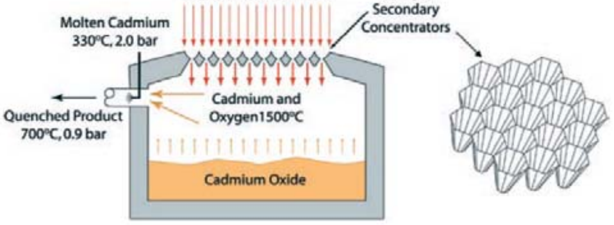
-CeO$_2$/Ce$_2$O$_3$

(1) $2CeO_{2(s)} \rightarrow Ce_2O_{3(s)} + 1/2O_{2(g)}$ 2300 K

(2) $Ce_2O_{3(s)} + H_2O_{(g)} \rightarrow 2CeO_{2(s)} + H_{2(g)}$ 700 K

This cycle has never been studied before 2006 but seems to be a promising cycle. Experiments were conducted at lab-scale.[2]

Schematic of a Beam-Down Multi-Concentrator Cadmium Decomposer Design [4]



Description of heat source

Fe$_3$O$_4$/FeO

A ferrite reactor (Counter Rotating Ring Receiver Reactor Recuperator) has been designed by SNL[13]. The goal is to use large dish mirrors.

Cd/CdO

A CdO central plant concept solar field has been developed, to permit ground-level operation of all chemical processes using a beam-down collector/concentrator.

A 24-hour hydrogen plant concept was designed. One part of the plant operates under solar radiation, and the second part during solar off-hours with thermally stored energy.[4]

CeO$_2$/Ce$_2$O$_3$

The high temperature needed could be achieved with dish or tower technologies.[2].

Expected efficiency

Fe$_3$O$_4$/FeO

Steinfeld obtained theoretical efficiencies at 61 % at 1900 K to 42 % at 2500 K[7].

The global efficiency (incorporating all steps from sun to hydrogen) is estimated at 12.7 %[8] and could reach 17.4 % in optimized conditions.[3]

Cd/CdO

In 2008, the DOE project estimated the thermal efficiency at 48.3 % (LHV).[4]

Cost evaluation

Fe$_3$O$_4$/FeO

A small size advanced tower plant (32 MW) has been designed to product 100 kg/h of H$_2$ at $12.5/kg.[8] An economic assessment gave hydrogen production cost ranging form $ 7.98/kg to $ 14.75/kg of H$_2$ depending on the level of optimisation considered and on the targeted hydrogen productivity.[3]

Cd/CdO

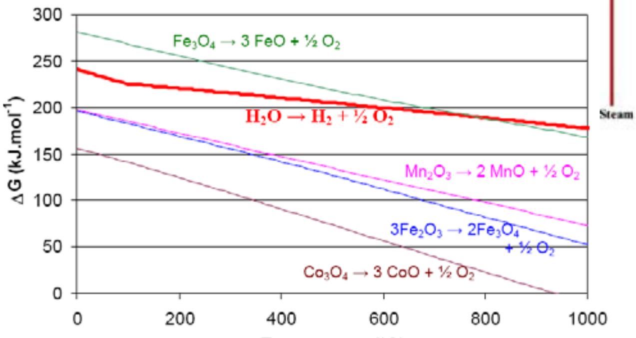
H2A analysis leads to an estimated cost range of H$_2$ /kg of $3.08 to $ 4.20.[5]

Furthermore, hydrogen plant components have been sized for 100,000 kg/day and the gate-cost based on a 2015 case, was calculated to be around $ 4.50/kg.[4]

THREE-STEP CYCLES

Flow-sheet

The redox reaction between reduced metal oxide and water is thermodynamically possible only if the Gibbs free energy (G) of the metal oxide redox couple is higher than the G of water reduction. The G curves show that water-splitting is only possible with FeO below 800 °C. MnO, CoO and Fe_3O_4 are not able to split water spontaneously. An additional energy is necessary to run the reaction ($\Delta G>0$).[9]



Gibbs free energy of reduction reactions [9]

The main cycles are:

1) Fe_2O_3/Fe_3O_4

(1) $3Fe_2O_3 \rightarrow 2Fe_3O_4 + 1/2O_2$ 1600 K
(2) $2Fe_3O_4 + 6KOH \rightarrow 6KFeO_2 + H_2 + 2H_2O$ 673 K
(3) $6KFeO_2 + 3H_2O \rightarrow 3Fe_2O_3 + 6KOH$ 373 K

2) Mn_2O_3/MnO

(1) $Mn_2O_3 \rightarrow 2MnO + 1/2O_2$ > 1873 K
(2) $2MnO + 2NaOH \rightarrow H_2 + 2NaMnO_2$ 900 K
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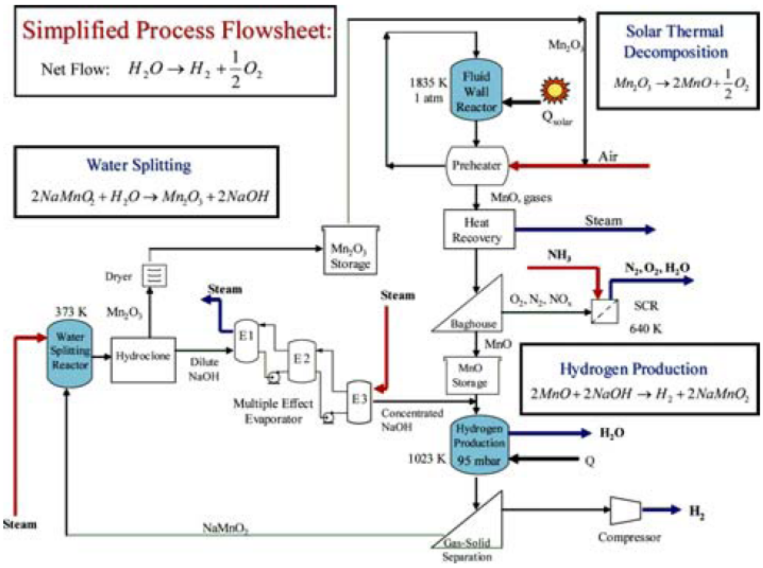

Simplified manganese cycle flow-sheet[10]

Flow-sheet of Mn_2O_3/MnO

The reactants are preheated and fed under pressure into the solar thermal reactor to reach 80 % conversion. The products then pass through four heat exchangers and a filter. The solid stream is sent via a solid conveying system to a storage tank. The gas stream is mixed with NH_3 at 620 K and fed to the selective catalytic reduction system to reduce NOx. The MnO is mixed with a 50 % NaOH solution and reacts in two rotary furnaces to produce H_2. The vapour is cooled and sent to a series of compressors, heat exchangers and separators. This product, 99.5% H_2, is sent to a hydrogen pipeline.

The solid product reacts with water in the third reactor to form Mn_2O_3 which is recycled. [10]

Description of heat source

Fe_2O_3/Fe_3O_4: the most suitable concentrating system is a solar tower with a heliostat field (tracking mirrors) in front of the tower.

Mn_2O_3/MnO: solar energy would be supplied from three 8 MW_{th} heliostat fields[10] .H_2 can be produced during off-sun periods (MnO can easily be stored[11]).

Expected efficiency

Fe_2O_3/Fe_3O_4

The optimized global process efficiency (from solar energy to hydrogen) is estimated to reach 18.6 %.[10]

Mn_2O_3/MnO

Sturzenegger and Nuesch calculated efficiencies of 26-51 %, ignoring separation steps, and 16-21% taking all steps into consideration.[12]

Cost evaluation

Fe_2O_3/Fe_3O_4: to produce 250 kg h^{-1} of hydrogen, the price is 8.4$/kg with current solar towers[3].

Mn_2O_3/MnO: Data not available

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Metal/Metal Oxide

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Main initiatives

SHGR Project (US DOE) –"CR5" reactor.
http://www.sandia.gov

France : PROMES-CNRS
http://www.promes.cnrs.fr

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