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Hydrogen Production Options for Water-Cooled Nuclear Power Plants

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Hydrogen Production Options

- Almost all H_2 today comes from steam reforming of CH_4.
  - Costs rising with natural gas prices. — >750°C. — *CO_2 emissions.*
- Low-temperature water electrolysis.
  - Energy intensive (i.e., costly).
  - Precious-metal catalysts.
- Thermochemical cycles.
  - Most require high temperatures (800°C - 2000°C) and aggressive chemicals.
- High-temperature steam electrolysis.
  - Solid-oxide fuel cell technology. — Durability?
- Solar hydrogen.
  - Direct solar production: photo-electrochemical cells; artificial photosynthesis.
  - Biomass as feedstock.
- Other options under investigation:
  - Biological/biomimetic hydrogen production.
  - Coal gasification.
  - Direct ceramic-membrane separation of water.

Steam Methane Reforming

- Reforming:
  - $CH_4 + H_2O \longrightarrow CO + 3H_2$, Endothermic (750 – 800$^oC$)
- Shift:
  - $CO + H_2O \longrightarrow CO_2 + H_2$, Exothermic (350$^oC$)
- Cost: $1.00 - $3.50/kg, depending on CH_4 cost.
- Nuclear reactor heat has been proposed, but water-cooled reactors can't reach conventional reforming temperatures.
- But an integrated *catalytic membrane reformer system* could perform both reactions simultaneously at **500 – 600^oC**.
  - Tokyo Gas Company has demonstrated such a system.

Low-Temperature Water Electrolysis

- Commercially available.
  - Solid-polymer / proton exchange membrane (PEM) cells.
  - Liquid-electrolyte (e.g., KOH) cells.
- Energy intensive.
  - Cell efficiency: 65 - 90%.
  - Light water reactor electrical generation efficiency: 32%.
  - Total water electrolysis efficiency: 21 - 30%.
- Noble metal catalysts (e.g., Pt).
  - A strong U.S. program to find alternative catalysts.
- Higher-pressure PEM systems (35 MPa?) can reduce hydrogen compression costs.

High-temperature reactors can reach 44 - 48%

Low-Temperature Water Electrolysis

- DOE research goals:
  - Capital cost: $300/kW for a 250 kg/day plant with 73% efficiency.
  - $2.00/kg hydrogen.
- Implications:
  - No process heat needed, in general.
  - Hydrogen production can be decoupled from electricity generation.
  - Hydrogen/electricity co-generation and off-peak production is possible.

Lower-Temperature Hybrid Thermochemical Cycles

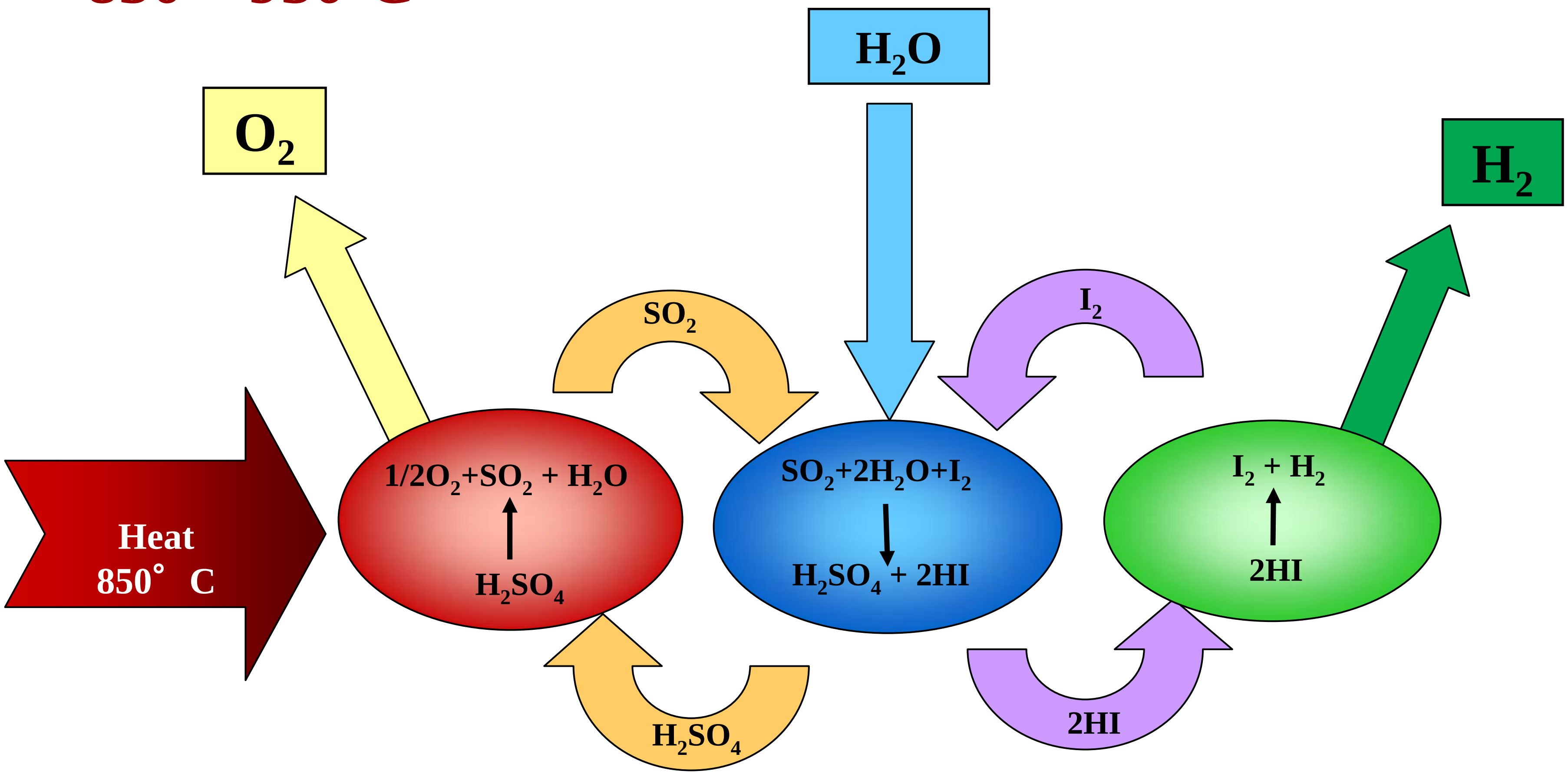
- Hundreds of thermochemical and thermo-electrochemical hydrogen production cycles have been identified.
  - Net reaction: H_2O + energy → H_2 + ½O_2.

- A recent review found 11 with maximum reaction temperatures below 550°C — compatible with supercritical water reactor temperatures.

- Five cycles have recently been explored.
  - Hybrid sulfur with SO_3 electrolysis (500 - 600°C).
  - Copper-chloride (530 - 550°C).
  - Active-metal alloy cycle (475 - 675°C)
  - Magnesium-chloride (500 - 600°C).
  - Heavy-element halide (300°C).

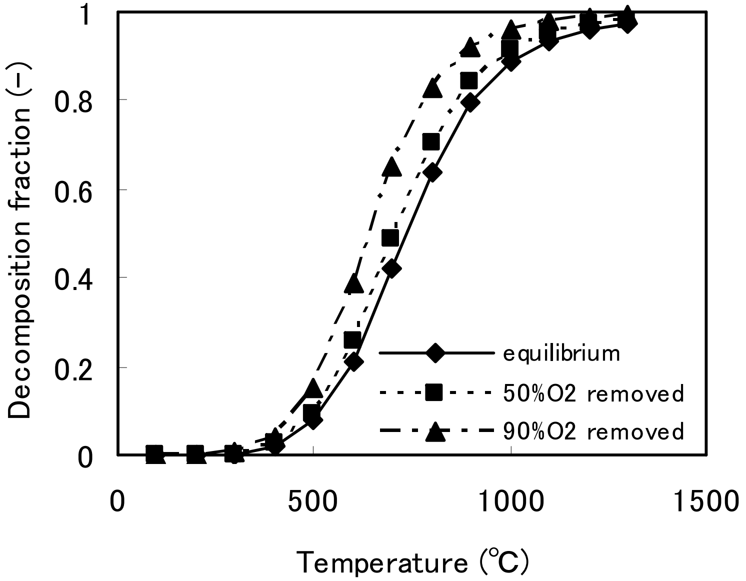
The Sulfur–Iodine Thermochemical Cycle

850 – 950ºC



Sulfur-Based Hybrid Cycle Eliminates Iodine, but Still Requires High Temperatures for O_2 Production

$2\ H_2O + SO_2 \rightarrow H_2SO_4 + H_2 - \textit{electricity}$	80ºC	(1)
$H_2SO_4 \rightarrow H_2O + SO_3$	>450ºC	(2)
$SO_3 \rightarrow SO_2 + \frac{1}{2}\ O_2$	850 - 950ºC	(3)



Source: GENES4/ANP2003, Sep. 15-19, 2003, Kyoto, JAPAN

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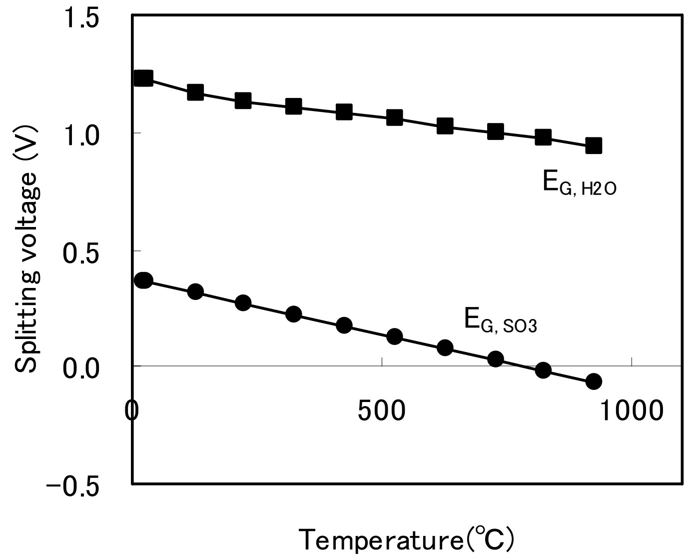
Alternative: Electrolysis of SO_3

$SO_3 \rightarrow SO_2 + 1/2\ O_2 - \textit{electricity}$ **500-600ºC**

- Lowers maximum operating temperature of cycle to <600ºC.
- Low electricity requirement compared to steam electrolysis.
- Simple process flow.
  - Does not require decomposition and separation processes.
  - Does not require separation of O_2 from a gas mixture.
- Decreased corrosion of structural materials.



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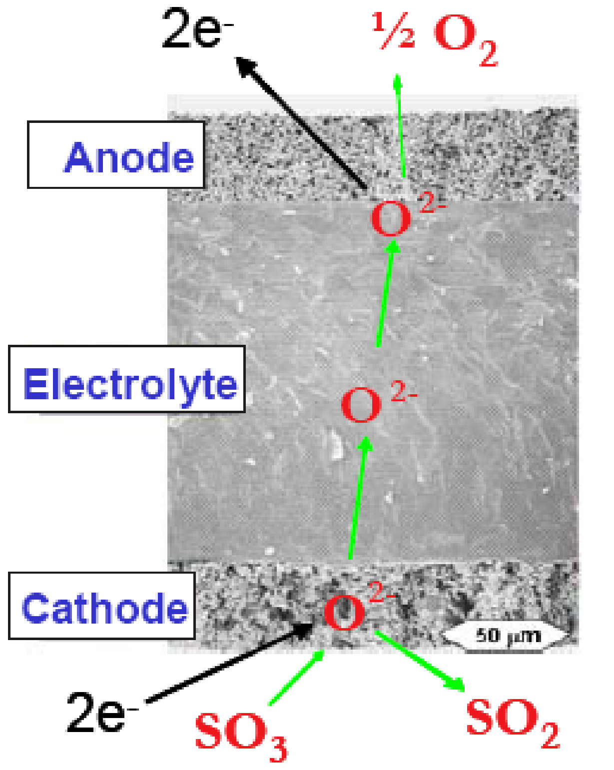
SO_3 Electrolysis Cell Component Requirements

- **Oxygen Electrode**
  - Compatible with electrolyte.
  - Electronic and ionic conductor.
  - Catalytically active for oxygen evolution.
- **Electrolyte**
  - Stability in electrolyzer environment:
    Cathode: SO_3, SO_2, steam.
    Anode: oxygen.
  - High oxygen ion conductivity.
  - Workable, low-cost material.
- **SO_3 Electrode**
  - Stability in corrosive SO_3 and steam.
  - Tolerant of impurities (e.g., HI).
  - Electronic and ionic conductor.
  - Catalytically active for SO_3 reduction.



Copper-Chloride Cycle

- The most mature of the lower-temperature cycles.
- Four primary steps:
  - $2Cu + 2HCl(g) \longrightarrow H_2(g) + 2CuCl$, T = 430 - 450^{o}C
  - $4CuCl \longrightarrow 2Cu + 2CuCl_2$, Electrolytic
  - $2CuCl_2 + H_2O(g) \longrightarrow CuO{*}CuCl_2 + 2HCl(g)$, T = 325 - 375^{o}C
  - $CuO{*}CuCl_2 \longrightarrow 2CuCl + \frac{1}{2}O_2(g)$, **T = 530 - 550^{o}C**
- Estimated efficiency: 40% (lower heating value).

Copper-Chloride Cycle

- An alternative, 3-step approach:
  - $2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2(g)$, Electrolytic
  - $2CuCl_2 + H_2O(g) \rightarrow CuO{*}CuCl_2 + 2HCl(g)$, $T = 325 - 375^oC$
  - $CuO{*}CuCl_2 \rightarrow 2CuCl + ½O_2(g)$, **$T = 530 - 550^oC$**
- Hydrogen can be produced directly without the need for copper metal.
- The efficiencies and the capital costs of the two alternatives need to be further evaluated.

Copper-Chloride Cycle

- Proof of principle has been demonstrated.
  - Copper production and hydrogen production have been demonstrated.
    - Work is ongoing on both types of electrochemical cell.
- Hydrolysis reaction is currently being studied.
  - Excess water is required, but how much is not known yet.
  - Potential competing reaction: decomposition of $CuCl_2$.
    - Conditions to minimize this competing reaction are being identified.
- Other reactions are straightforward.

Hybrid Active Metal Alloy Cycle

- Representative cycle consists of two reactions:
  - $\frac{1}{3} K_3Bi(l) + H_2O(g) \longrightarrow KOH(l) + \frac{1}{2} H_2(g)$, **T = 475 - 675^{o}C**
  - $KOH(l) + \frac{1}{3} Bi(l) \longrightarrow \frac{1}{2} H_2(g) + \frac{1}{2} O_2(g) + \frac{1}{3} K_3Bi(l)$
    Electrolytic
- Single-vessel reactor?
- Little thermodynamics/chemistry known;
  no experimental data.
- LHV Efficiency = 29 - 46%?
- Alternative: Na-Sn cycle.

Magnesium-Chloride Cycle

- Three primary steps:
  - $MgCl_2 + H_2O \rightarrow 2HCl + MgO$, T = 450°C
  - $MgO + Cl_2 \rightarrow MgCl_2 + \frac{1}{2}O_2$, **T = 500°C**
  - $2HCl \rightarrow H_2 + Cl_2$, Electrolytic
- Zeolite support structure for $MgCl_2$ reactions.
- Limited testing.
- Side products may require higher reaction temperatures.
- Research effort shifted to *MgI* cycle (600°C).

U-Eu-Br Heavy-Element Halide Cycle

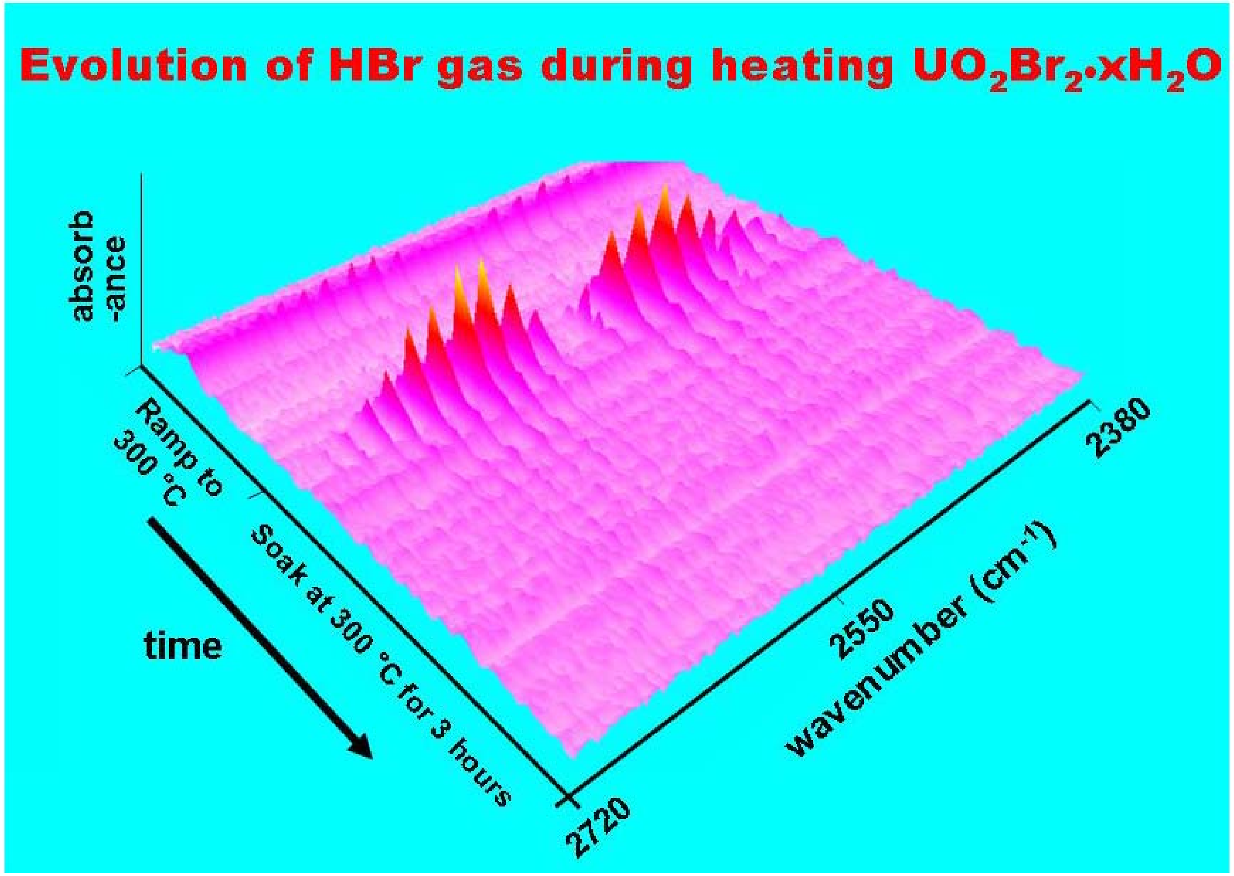
- Four steps:
  - $2(UO_2Br_2{*}3H_2O) \rightarrow 2(UO_3{*}H_2O) + 4HBr + 2H_2O$, T = 300$^oC$
  - $4EuBr_2 + 4HBr \rightarrow 4EuBr_3 + 2H_2$, Exothermic
  - $4EuBr_3 \rightarrow 4EuBr_2 + 2Br_2$, T = 300$^oC$
  - $2(UO_3{*}H_2O) + 2Br_2 + 4H_2O$
    $\rightarrow 2(UO_2Br_2{*}3H_2O) + O_2$, Exothermic

- Purely thermochemical — no electrolysis.
- Maximum temperature = **300^{o}C**.

Heavy-Element Halide Cycle: Proof of Concept Reaction 1

$$UO_2Br_2 \cdot 3H_2O(s) \xrightarrow{\Delta} UO_3 \cdot H_2O(s) + 2HBr(g) + H_2O(g)$$

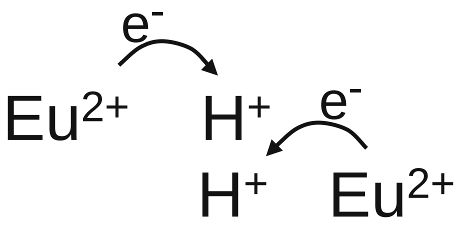
- Fourier Transform Infrared Analysis confirms that the reaction goes to completion at 300°C.



Heavy-Element Halide Cycle: Proof of Concept Reaction 2

$$4EuBr_2 + 4HBr \rightarrow 4EuBr_3 + 2H_2(g)$$

- H_2 generation has been demonstrated, but the reaction rate is slow.
- Evidence for a simultaneous, concerted four-center reaction:



- Catalysis is being considered to improve the kinetics.

H_2 gas bubble evolution from the heavy metal halide reaction.

Heavy-Element Halide Cycle: Proof of Concept Reaction 3

$$2EuBr_3 \xrightarrow[300\ ^\circ C]{\Delta} 2EuBr_2(s) + Br_2(g)$$

- Vacuum pyrolysis allows the reaction to proceed without the complications that can arise from entrained water.

Heavy-Element Halide Cycle: Proof of Concept Reaction 4

$$2UO_3{\cdot}H_2O(s) + 2Br_2 + 4H_2O \rightarrow 2(UO_2Br_2{\cdot}3H_2O)(s) + O_2$$

- Br_2 and water can react to form HBr and HOBr ("bromine water"):

$$Br_2 + H_2O \rightarrow HBr + HOBr$$

- HOBr can interfere with the desired reaction.

Summary

- Many hydrogen production options exist, but none have demonstrated economic competitiveness with steam methane reforming.
  - Nuclear power could support steam methane reforming to reduce CO_2 emissions.
- Low-temperature water electrolysis is a currently available technology for hydrogen production through nuclear power.
  - Reductions in electricity and system costs would be needed (or a carbon tax) for low-temperature water electrolysis to compete with today's costs for steam methane reformation.
- A limited number of thermo-electrochemical cycles have heat requirements consistent with water-cooled reactor technology.
  - Only a small number are seeing active research.
  - All are at an early stage of research; significant technical issues still exist.