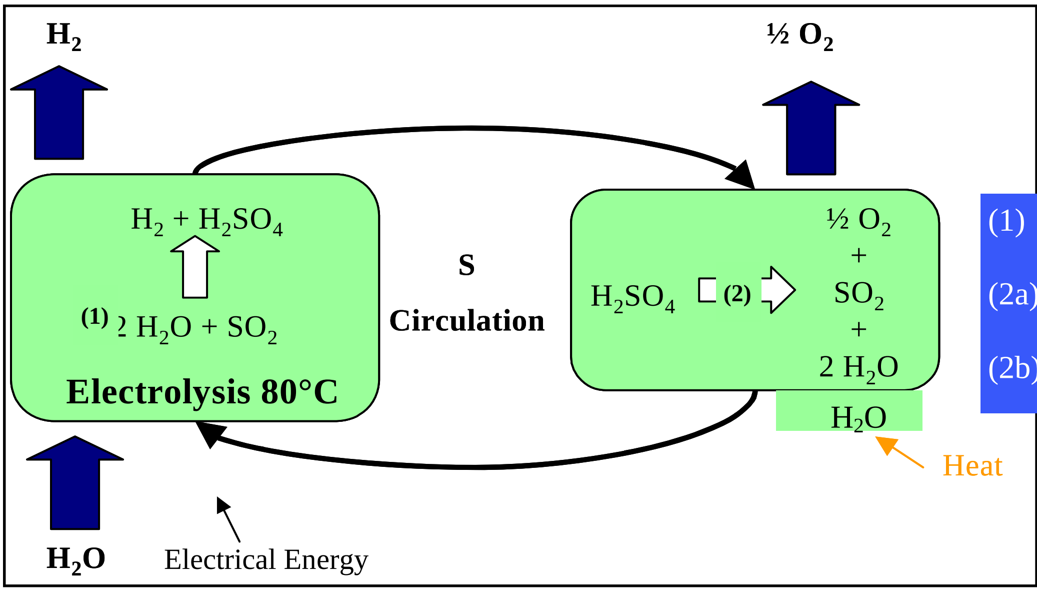
IEA/HIA TASK 25 : HIGH TEMPERATURE HYDROGEN PRODUCTION PROCESS

Hybrid Sulfur cycle

Process principle



(1) $2\ H_2O + SO_2 \longrightarrow H_2SO_4 + H_2$

(2a) $H_2SO_4 \longrightarrow H_2O + SO_3$

(2b) $SO_3 \longrightarrow SO_2 + \frac{1}{2}\ O_2$

Current status :

The Hybrid Sulfur (Westinghouse) Cycle is a two-step thermochemical cycle for decomposing water into hydrogen and oxygen. Sulfur oxides serve as recycled intermediates within the system.

- Significant research activity for nuclear and solar.
- Chemical reactions all demonstrated.

Advantages :

- Uses common / inexpensive chemicals.
- Cycle has the potential for achieving high thermal efficiencies.
- Only one intermediary species (oxides of sulfur).

Challenges :

- Requires high temperature.
- Corrosion by H_2SO_4.

Hybrid Sulfur

Process description :

(1) SO_2 electrolysis at 80° C
(2) H_2SO_4 decomposition : (2a) Starts at 450° C
(2b) Starts at 800° C

Heat source :

Nuclear or Solar heat source

Materials :

Electrodes : carbon-supported platinum catalysts
H_2SO_4 Decomposition : Ceramics such as silicon carbide, silicon nitride and cermets

Efficiency :

The cycle efficiency is 42 % which has the potential to be increased to 48.8 % [1].

Cost evaluation :

Between 4.4 and 6.8 $/kg for a nuclear heat source[12]
Between 1.6 and 5.6 €/kg for a solar heat source[13,14]

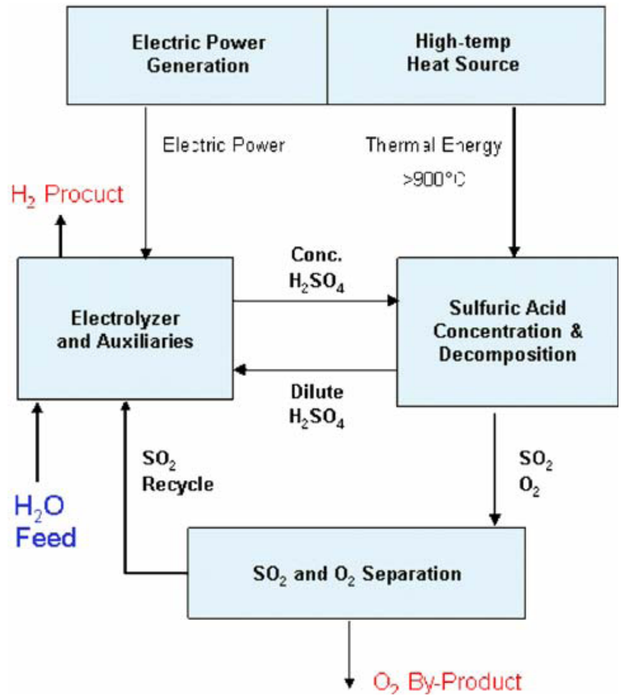
Flow-sheet

The Hybrid Sulphur cycle, also named Ispra Mark 11 cycle or Westinghouse Sulphur cycle was developed in the 70's by Westinghouse Electric corporation.
The stages of this two-step process are :

- produce hydrogen and sulphuric acid from the electrolysis of a solution of sulphur dioxide in sulphuric acid;
- decompose sulphuric acid to regenerate sulphur dioxide (thermochemical step).

Energy is supplied to the system as high temperature heat (approximately 1173 K) and electricity. Advanced nuclear reactors (Generation IV) or central solar receivers can be the source of the primary thermal energy.
Direct electrolysis of water requires 1.23 V while SRNL estimated that the theoretical reversible cell voltage required to dissociate water in a 50 % acid media at 289 K is only 0.29 V[3,4].
Moreover, in 1976 [5,6], a NASA conceptual design calculated a cell voltage of 0.48 V and a cell current density of 200 mA/cm² under an acid concentration of 80 % w., at 2586 kPa and 361 K.

Nevertheless, this cell voltage level seems to be unrealistic. Recent SRNL works[4] on lab-scale electrolysers indicate that only a cell voltage around 0.6 V can be attained.



A simplified flow-sheet of the Westinghouse Sulfur Cycle

Experimental programs and prototypes

The hybrid-process was studied at an early stage in Los Alamos Scientific Laboratory (LASL) Thermochemical Hydrogen Program. In the USA and in Italy, active development has been undertaken by Westinghouse and Euratom.

The HyS cycle has been also experimentally investigated at the Research Centre Jülich, in close cooperation with Joint Research Centre (JRC) ISPRA. This led to a three-compartment electrolysis cell with a hydrogen production rate of 10 Nl/h successfully operated in a 600 h test run. The cell conditions were 353 K at 1.5 MPa[8]. With an improved tungsten carbide coated cathode a reduction of the cell voltage to 550 mV at 100 mA/cm² was obtained [7].

Recent studies[9] have shown that the chemical decomposition of sulfur trioxide is achievable without catalyst at a temperature range over 1300 K. Without catalyst the reaction cannot occur below 1123 K. With the use of catalysts (such as Ag-Pd or Fe_2O_3) it has been experimentally demonstrated that the decomposition starts at about 773 K and is almost complete at 1100 K.

Description of heat source

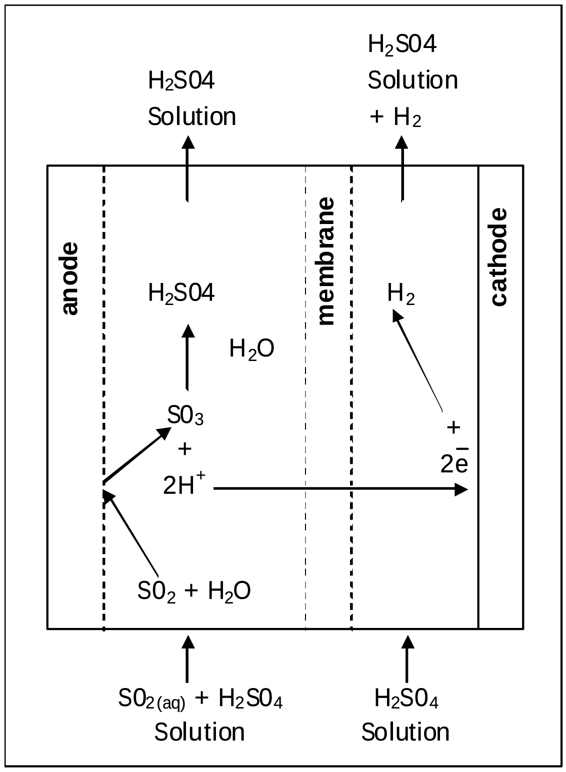
A European cooperation (DLR, DIMI, EA, CEA,USFD), within the scope of HYTHEC project, studied the possibility of coupling the chemical process to a solar central receiver system[10]. The H_2SO_4 splitting at temperatures up to 1473 K was proved using concentrated solar radiation.

Westinghouse used helium from a very high temperature nuclear heat source (VHTR). The heat was transported to the process via an intermediate heat transfer loop at temperatures sufficiently high to permit peak process temperatures of 1144 K.

Materials

Electrolysis :
For SO_2 electrolysis, carbon-supported platinum catalysts were employed to prepare the electrodes[8].

Thermal Decomposition :
Ceramics such as silicon carbide, silicon nitride and cermets possess excellent resistance to sulphuric acid corrosion at ambient temperature and at low acid concentration.



hydrogen.energy.gov/pdfs/review05/pdp_45_summers.pdf

SO_2 depolarized electrolysis

Expected efficiency

Optimal efficiency of the cycle is reached with a concentration of 65 % w/w sulphuric acid in water. The cycle efficiency is 42 % which has the potential to be increased to 48.8 % if the electrolysis is conducted in several stages[1].
The NASA conceptual design has an overall thermal efficiency of 45.2 %[5,6,11].

Cost evaluation

Summers et al.[1] and McLaughlin et al.[2] have studied the efficiency and the cost of hydrogen production using Helium as the heat source. McLaughlin has primarily estimated the cost of hydrogen production at 2.32 $ /kg while Summers has estimated this cost at 1.60 $/kg. Recently those costs were estimated at about 4.4 to 6.8 $/kg for a nuclear heat source[12], and between 3,9 and 5,6 €/kg if a solar heat source[13] is used. Hydrogen production costs are tightly related to techno-economic models.

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Hybrid Sulfur Process

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Main initiatives

Hythec in Europe : www.hythec.org

EC : HycycleS-Hydrogen thermoCycleS-(DLR) Germany, www.dlr.de

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