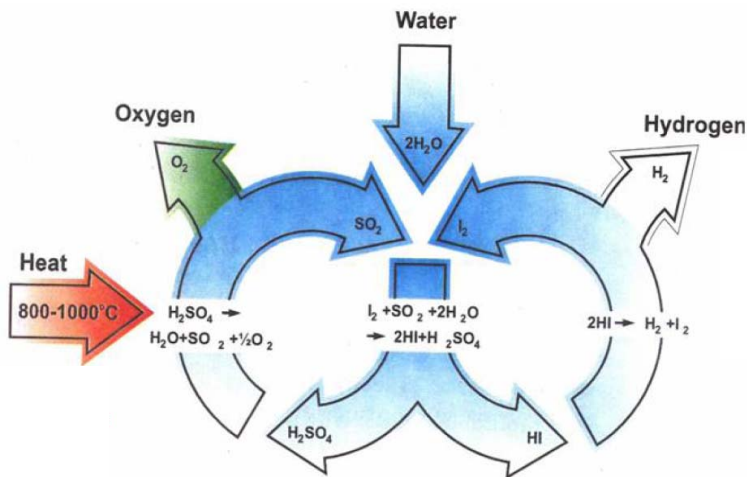


Sulfur-Iodine Cycle

Process principle



Current status :

The sulfur-iodine thermo-chemical cycle is considered to be one of the most promising routes for massive hydrogen production^{1,2}.

- Process demonstrated at lab scale,
- Large scale implementation under study :
 - ◊ Coupling with nuclear or solar heat source,
 - ◊ Material selection and testing.

Advantages :

- All fluid fluxes,
- Chemicals all recycled ; no effluents,
- Projected efficiency \approx 40%.

Challenges :

- **Process :**
 - ◊ Iodine inventory,
 - ◊ Iodine solidification at cold points.
- **Materials :**
 - ◊ High temperature process,
 - ◊ Corrosive media,
 - ◊ Amounts of Pt-based catalysts.

Sulfur-Iodine Cycle

Process description³ :

- (1) Bunsen reaction to produce HI and H₂SO₄ (exothermic) between 20 and 120 °C
- (2) H₂SO₄ decomposition (endothermic) in a catalytic reactor between 800 and 850 °C
- (3) HI decomposition in a catalytic reactor between 300 and 400 °C

Heat source : Nuclear or Solar furnace

Materials :

- Aluminized Incoloy 800H, SiC, glass-lined steel for H₂SO₄ decomposition,
- Titanium, zirconium, tantalum, niobium and molybdenum metals or their alloys for HI decomposition.

Efficiency : at 850 °C \approx 40 %

Cost evaluation :

The SI cycle is expected to produce hydrogen with a cost between 6.7 and 10.7 €/kg depending on flow-sheet hypotheses¹².

Flow-sheet

General Atomic report GA-A24266

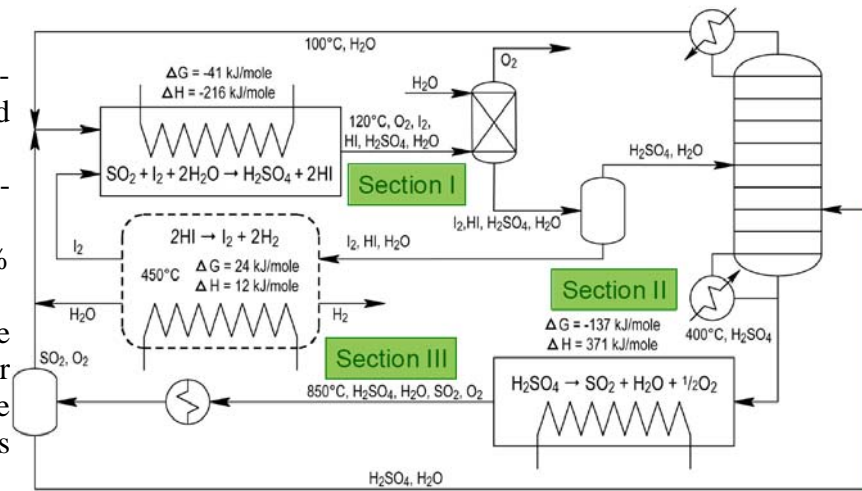
Section I : Bunsen section⁴

This spontaneous reaction occurs at low temperature (20 -120 °C). SO₂ at 1 atm is oxidized to SO₃ in presence of iodine.

An excess of iodine and water makes the reaction irreversible.

SO₃ is absorbed into water to form 48 wt.% H₂SO₄.⁵

As the two acids are almost immiscible, the separation of H₂SO₄ and HI takes place under gravity. The upper phase contains most of the H₂SO₄ and the dense lower phase contains most of HI.



Section II : H₂SO₄ decomposition

This section appears to be the most understood because of the experience gained in the sulfuric acid industry.

H₂SO₄ is concentrated through a series of flashes starting from low pressure. Then it is dehydrated. The partial SO₃ decomposition into SO₂ occurs on a catalytic bed. Undecomposed SO₃ is recombined with water, which allows recovery of its heat content. The reaction, which requires a temperature around 850 °C, takes place in a reactor.

General Atomics (GA) identified Fe₂O₃ (US patent pt 4,131,982) and Pt/TiO₂ was found to be an acceptable catalyst.⁶

Section III :

HI can be decomposed over relatively stable activated carbon catalyst.⁶ The decomposition is incomplete

and slow.⁷

The HI extraction from HI_x is the main difficulty, because the presence of an azeotrope in the mixture, prevents simple distillation.

- *Extractive distillation:* of HI with H₃PO₄. This was proposed by GA. The introduction of H₃PO₄ induces first the separation of iodine, and then allows simple distillation of HI. HI is then decomposed in gaseous (or possibly liquid) phase around 450°C to yield H₂ which has to be separated from the gaseous mixture using membranes.⁸
- *Reactive distillation:* This was proposed in the 80s by RWTH Aachen.⁸ HI_x distillation and HI decomposition are performed in the same reactor at 350°C. A liquid–gas equilibrium is obtained in the middle of the column, I₂ is dissolved in the lower liquid phase and a mixture of gaseous H₂ and water is recovered

Experimental programmes and prototypes

The cycle was invented in the 1970s by GA.

A bench scale test facility for hydrogen production using the IS process has been established at Japan Atomic Energy Authority (JAEA).¹⁰

The CEA-GA-SNL I-NERI loop

Sandia National Laboratories (SNL), General Atomics Corporation (GA) and the Atomic Energy Commission (CEA) are participants in a international collaborative effort to construct a laboratory-scale Sul-

fur-Iodine (S-I) process capable of producing 100-200 L/h of hydrogen. This project is being conducted as an International Nuclear Energy Research Initiative (I-NERI).

CEA has constructed a Bunsen reaction device, SNL has constructed the sulphur acid decomposition device, and GA has constructed the iodhydric acid decomposition device. The process has been constructed at General Atomics facility in San Diego, CA and testing are ongoing.¹¹

IEA/HIA TASK 25: HIGH TEMPERATURE HYDROGEN PRODUCTION PROCESS



BUNSEN REACTION DEVICE



H₂SO₄ DECOMPOSITION DEVICE



HI DECOMPOSITION DEVICE

Description of heat source

JAERI expects to utilize nuclear heat from their High Temperature Reactor as primary thermal energy for the SI process.¹² The original design in the 1970s was to couple the SI cycle with a high tem-

perature reactor or fusion reactor. More recently the coupling schemes with solar thermal plants have been proposed.^{13,14}

Materials

Materials for section II :

Aluminized Incoloy 800H has demonstrated excellent integrity and has been selected as the candidate material for heat exchangers to contain the H₂SO₄ decomposition sub process at temperatures up to 900°C.¹⁵ Ceramic (SiC, Si₃N₄, Al₂O₃) have also been investigated. Tests show a good resistance at

high temperature (up to 1500 °C) in a corrosive environment.

Materials for section III :

Titanium, zirconium (up to 100°C), tantalum, niobium and molybdenum metals or their alloys (Fe-14 wt.% Si alloy (Durichlor 51) have shown excellent resistance to corrosion in HI_x.^{16,17}

Thermal efficiency

General Atomics (GA) expects a high thermal efficiency of approximately 50 %. By a revision of the first flow sheet reported in 1976 an overall thermal efficiency of 41.4 % has been calculated. Preliminary improvements indicate that revised flow sheets will have an overall thermal efficiency of at least 45 %¹⁸. A more detailed flow-sheet analysis, taking

into account plausible values of efficiencies of components such as pumps or compressors, leads to a value between 34 % and 37 %, depending on the pinch assumed for heat recovery in Section III.⁸ This is slightly lower than that predicted by Roth and Knoche (42 % at 850 °C).⁹

Cost evaluation

Materials used in this cycle have a significant impact on capital cost. Moreover, iodine is an expensive raw chemical product.¹⁵

A first evaluation based on the reference flow-sheet (efficiency 36 %) and of the pre-conceptual design of the plant has led to a production cost in the range 4-5 €/per kg : about 30 % for energy consumption, 30 % for maintenance and 40 % for paying off the investment (the iodine section representing about 60

% of the investment). A revisited evaluation taking into account the expected result of research and development (efficiency 50 %, simplified Bunsen and iodine sections) with realistic hypotheses of cost cuts (coated materials instead of solid, new catalysts, etc.) leads a new cost between 6.7 and 10.7 €/kg (50-60% due to energy consumption)¹⁹. Hydrogen production costs are tightly related to techno-economic models.

IEA/HIA task 25 : High Temperature Hydrogen Production Process

Sulphur-Iodine cycle

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<https://www-prodh2-task25.cea.fr>

Main initiatives

USA : The Sandia National Laboratory
www.sandia.gov , GA www.ga.com

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

France : CEA (HYTHEC : HYdrogen
THERmochemical Cycles), www.cea.fr

Italy : ENEA (TEPSI) : Technologies and
Innovative Processes for the Transition to the
Hydrogen System future), www.enea.it

Japan : The Japan Atomic Energy Authority
(JAEA), www.jaea.go.jp/english/index.shtml

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