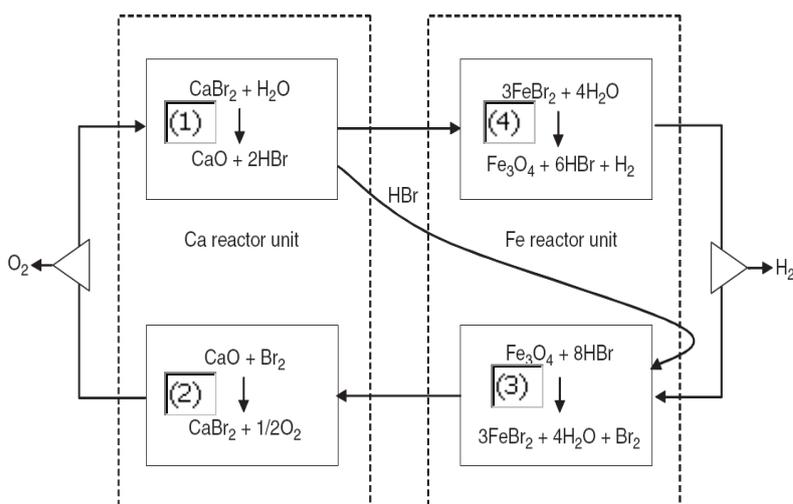
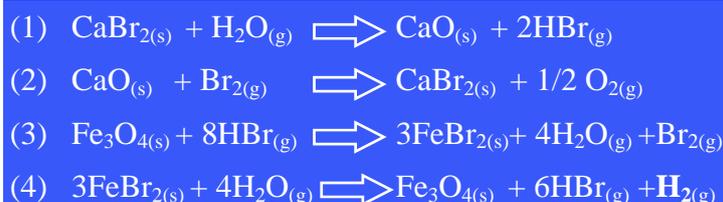


UT-3 cycle

Process principle



UT-3 cycle flowsheet for the Mascot pilot facility⁷



UT-3 cycle

Process description :

- (1) Hydrolysis of Ca at 1033 K (endothermic)
- (2) Bromination of Ca at 845 K (exothermic) : rate-limiting for the whole cycle
- (3) Bromination of Fe at 493 K (endothermic)
- (4) Hydrolysis of Fe at 833 K (exothermic)

Heat source :

Nuclear or Solar heat source

Materials :

- zirconia-silica composite coated membranes

Efficiency :

- Nuclear : second law efficiency = 53.2%¹
- Solar : - thermal efficiency = 49.5%
- exergetic efficiency = 52.9%.³

Current status :

The UT-3 (University of Tokyo, Ca-Br-Fe) cycle is a pathway for high temperature hydrogen production. It has been developed by Kameyama and Yoshida¹ and has been studied both theoretically and experimentally since being proposed in 1978. Nowadays, UT-3 thermochemical cycle is one of the most studied thermochemical hydrogen production cycles in the world.²

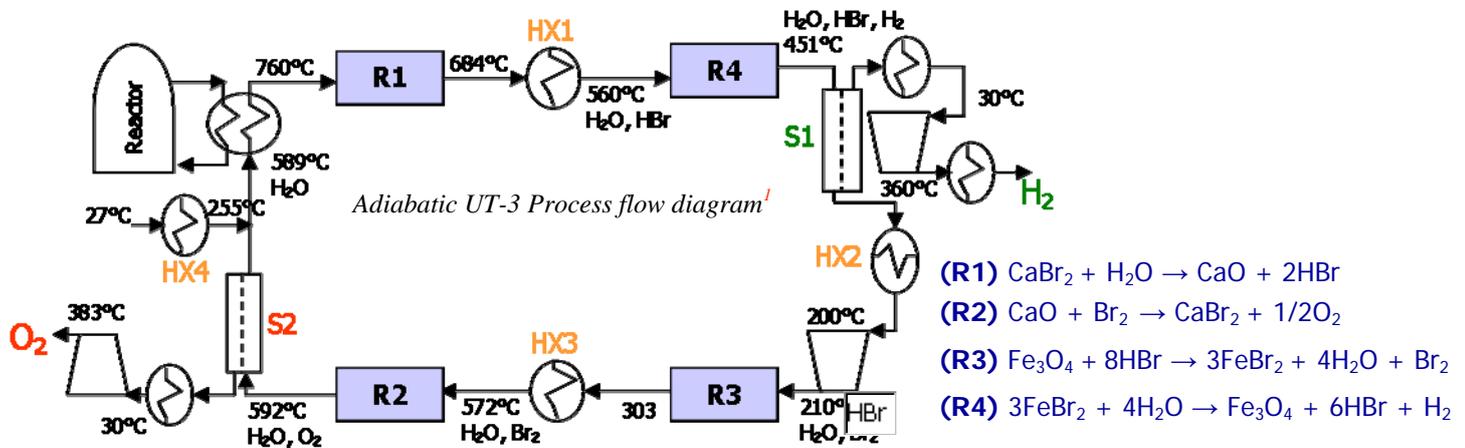
Advantages :

- Easy gas-solid separation
- Circulation of gases only

Challenges :

- Possible scale-up difficulties for H₂ and O₂ removal via membranes
- Necessity to compress H₂ and O₂ produced at sub-atmospheric pressures
- Lower efficiency and possible solid attrition in non steady-state operation
- Limited potential for improvement: already at melting point of CaBr₂

Flow-sheet



The four chemical reactions take place in four adiabatic fixed bed chemical reactors, R1-R4, that contain the solid reactants incorporated in a titanate matrix for the calcium, and a silica matrix for iron, connected in series in a loop where gaseous substances circulate.

Control of maximum reaction temperatures is ensured by use of three heat exchangers, HX1-HX3. The flow of gas products is in the clockwise direction.

The bromination is carried out in R2 and R3, producing $\text{CaBr}_{2(s)}$ and $\text{FeBr}_{2(s)}$ respectively. Hydrogen and oxygen are separated as products, each in separator (S1 and S2). Water to decompose is fed into the loop after the separation of O_2 at separator S2.

Kinetic studies show that to achieve 100% conversion of the first reaction at low pressure, excess of

H_2O at 1033K takes approximately 1 hour.¹

Reaction 2 requires about 10 min, and the third and fourth reactions less than 1 hour each at the temperature given above.

Therefore, after approximately 1 hour, the complete cycle is achieved.

At the end, the direction of the cycle is reversed. The process runs at 2.0 MPa, the pressure of hydrogen is assumed to be 2.5 MPa, while that of the oxygen 1.8 MPa.²

Excess steam or steam + N_2 is used to operate the process in an adiabatic equipment. Using an inert gas such as N_2 is to make sure that membrane separators S1 and S2 function as required.³

Experimentation or existing prototype

A bench scale plant was built and operated to produce hydrogen continuously for 200 h² and a reaction model was proposed⁴. For the reactor, studies using honeycomb-shaped solid reactant were conducted.^{1,3}

The Model Apparatus for the Study of Cyclic Operation in Tokyo (MASCOT) pilot was operated in the late 80's.⁵

For a plant producing 30,000 Nm³/h or 2.68 GJ H₂ per year, the plant sizing has been carried out.

Sizing of a solar hydrogen plant producing 2000 Nm³/h of hydrogen has also been reported.³

Nevertheless, the process has the double disadvantage of requiring a reagent preparation unit and increasing the quantity of material by adding an inert phase representing 33-50% of the reactive load.⁶

Thus, a new process implementing two vertical asymmetric torus reactors involving fluidized beds of solid reactants was experimented. The kinetic of CaBr_2 hydrolysis is enhanced by UV radiation. The cycle is improved by adding a recalibration system, and magnetic properties are used to separate the iron loop products within a single reactor.⁷

Description of heat source

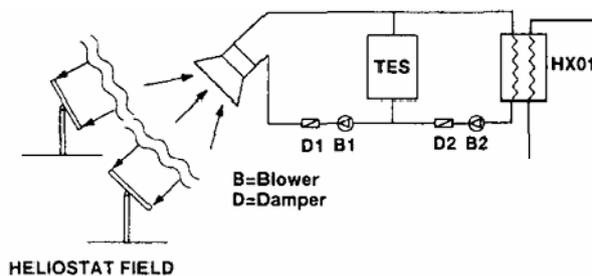
Nuclear heat energy

General Atomics selected the adiabatic UT-3 cycle as one as the best potential cycles for hydrogen production using nuclear power.⁸

Solar heat energy

During daytime operation or sunshine hours, a part of the solar heat collected in a Central Receiver System (CRS) is directly used in heat exchanger HX01 to run the process. The rest is stored in a Thermal Energy Storage system (TES).

Blowers B1, B2 and dampers D1, D2 are used to



Solar heat energy in UT-3 process³

regulate the energy flow. During night-time operation or cloudy periods, the necessary thermal energy is supplied from TES.³ In the new process, UV radiation is used in the Ca loop to enhance the kinetics of the direct dissociation of Br₂.⁷

Material

The hydrolysis of calcium bromide (R1)

This reaction is known to be the rate-limiting step due to the melting point of calcium bromide and the large volume expansion (76%). For these reasons, numerous studies were lead on the reactant, for example :

- calcium titanium oxide matrix,
- fluidized bed reactor instead of packed bed reactor,
- an innovative concept base on the molten calcium bromide with molten calcium oxide,
- calcium oxide reactant dispersed and immobilized on a fibrous yttria woven mat⁹.

Membrane separation process

Initially, hydrogen and oxygen were separated by conservative condensation method from the respective gas mixtures.⁸ Investigation on zirconia-silica composite membranes coated on porous ceramic tubing were conducted up to 733 K. The membranes were applied to separate hydrogen in the presence of HBr and abundant steam at 473-673 K.

The membranes were durable in the H₂-H₂O-HBr atmosphere at 673 K¹⁰⁻¹¹.

Expected efficiency

For the MASCOT pilot, the first law efficiency of the cycle was determined as 48.9 % and the second law efficiency as 53.2 %¹.

For solar operation an overall thermal efficiency of 49.5 % and an exergetic efficiency of 52.9 % were reported³. A critical assessment of the actual energy efficiency that could be realized in a thermochemical cycle, taking the UT-3 cycle as the basis for the study, was reported in 2005¹². It was concluded that

the upper efficiency for this process would be of 39.9 % and 12 % if solar efficiency is included. With the toroidal reactor, the process efficiency is about 15 % using fractionated condensation for gas separation, and 22.5 % using dedicated membranes.⁷

Cost evaluation

It would be premature to calculate the cost of hydrogen per GJ for the thermochemical cycle given the multitude of assumptions for plant sizing and price quotes that are organizational dependent.

In the absence of this information, process efficiency is taken to be the best indicator for the prospects of the technology.¹²

IEA/HIA task 25 : High Temperature Hydrogen Production Process

UT-3 hydrogen production cycle

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

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