

ARE THE LESSONS OF THE TECHNO-ECONOMIC STUDIES ON THE SULPHUR-IODINE CYCLE APPLICABLE TO THE OTHER CYCLES?

*F. Werkoff, C. Mansilla, A. Le Duigou**

CEA/DEN/DANS/I-tésé Bât 460 -91191 GIF-SUR-Yvette CEDEX- FRANCE

E-mail address for all correspondence: francois.werkoff@cea.fr

* CEA/DEN/DANS/DPC/SCP GIF-SUR-Yvette CEDEX- FRANCE

Abstract

Nuclear production of hydrogen by thermochemical means is one of the prime candidates for powering the hydrogen economy without producing greenhouse gases. At first glance, a very high temperature reactor coupled with a Sulphur-Iodine (S-I) thermochemical cycle seemed very promising. However investigations in depth on the S-I cycle led to reconsider alternative thermochemical cycles.

The first criteria for choice of an alternative cycle must be the temperature at the core outlet of a previously selected nuclear reactor. The net efficiency of the thermochemical cycle must be higher than a reference value defined from alkaline electrolysis fed by the electricity produced by the selected reactor. The techno-economic evaluations of alternative cycles will have to take into account the excess reactants for reactions that are not spontaneous, the costs of the primary energies and the coupling between the reactor and the chemical plant.

1. Introduction

It is generally accepted that a cost is an opinion, not a fact. This assertion widely applies to the Techno-Economic (TE) studies devoted to assessments of costs of hydrogen production by advanced high temperature processes. These assessments inevitably contain assumptions which have to be identified, as clearly as possible.

The Generation IV International Forum aims at studying advanced nuclear reactors as well as alternative use of nuclear heat. In [1] is clearly indicated that: “ *The economic goals of Generation IV nuclear energy systems, as adopted by Generation IV International Forum (GIF), are to have a life cycle cost advantage over other energy sources, and have a level of financial risk comparable to other energy projects*” .

An advanced high temperature process for hydrogen production will be implemented at the industrial scale only when enough information will be available allowing thinking that they will present an economic advantage with regard to existing ones [1]. This implies two consequences:

1. Comparison between expected production costs for advanced and existing systems will be the decisive criterion.
2. Decision of financial investments in programs of research and development will be based on forecasts which must consider both technical and economical points of view. The technical feasibility of such processes will have to be proven (through R & D programs), and in every important stage of the evolution of researches, the investment costs, as well as consumption costs, must be revalued.

Concerning the present processes for producing hydrogen, whether they are implemented at small scales or they are not sustainable since they consume non renewable energy and reject greenhouse gases (GHG). It is now assuredly expected that during the 21st century the reserves of fossil fuels will decrease. Besides, measures begin to be taken to reduce GHG emissions.

Alkaline electrolysis is an existing process for producing hydrogen. Today it is mainly devoted to niche markets, such as the use of electricity production peaks. Alkaline electrolyzers fed by electricity produced by nuclear plants could be a competitive way to produce hydrogen without rejecting GHG. Third generation nuclear reactors devoted to the production of hydrogen and coupled with large electrolysis plants, offer the perspective of producing hydrogen at a cost slightly higher than 2 €/kg of H₂ indeed [2].

The high temperature delivered from helium cooled reactors led to consider thermochemical cycles to produce hydrogen using heat instead of electricity for the chemical reactions and without consuming other material than water. Among all the possible cycles [3], a major advantage of the Sulphur/Iodine (S-I) was that the temperature needed for the decomposition of the sulphuric acid fits the temperature of the helium at the outlet of the reactor core. Moreover, the Carnot theoretical energy efficiency could be high. For these reasons, in the last years, investigation on the S-I cycle has been done in USA [3], Europe [4], Japan which has built a pilot plant [5], South Korea and China.

In Section 2 we will recall the potentiality of the S-I cycle as it was perceived a few years ago, and we will present more recent information on it and two limits for its competitiveness.

We will examine in Section 3 some alternative thermochemical cycles and their compatibility with various Generation IV nuclear reactors.

Finally, recommendations will be expressed for guiding the selection of alternative cycles, having in mind the competitiveness targets.

2. On the potentiality of the S-I thermochemical cycle

The clearest description of the thermodynamic principle of the thermochemical cycles has been given in [6], at the beginning of the 1980's.

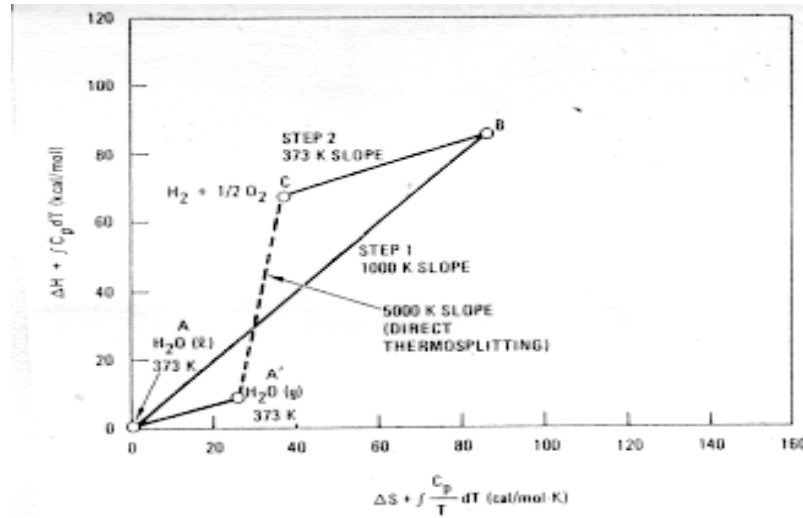


Figure 1: From [6]. In the Mollier diagram, water splitting starts from point A (liquid water) to point C ($H_2 + 1/2 O_2$). In an ideal two-step cycle, the initial step is a high-temperature endothermic reaction creating O_2 which inserts a quantity of entropy upon the addition of heat (AB line in the Figure), but it must be completed by a second step which backs to the original cycle reactants and creates H_2 . From an idealized theoretical point of view, this second step could be either exothermal or endothermic.

If the temperature at which O_2 is created is sufficiently high, the value of Carnot energetic efficiency will be high and then a first glance analysis may suggest that the energy efficiency (that we will define, following the High Heating Value [HHV] of hydrogen) could be high and then the production cost of hydrogen could be low.

In the case where the work (W) and the heat (Q) necessary for the production process of hydrogen are produced from the reactor, it is necessary to take at least $Q_T = Q + (W/\eta_{el})$ from the heat source, where it is considered that the electricity needed is produced with an energetic efficiency of η_{el} . It is possible to define a global efficiency η_T , if W and Q are normalized to a unity of produced hydrogen:

$$\eta_T = HHV / Q_T = \frac{HHV}{Q + (W/\eta_{el})} \quad (1)$$

To assess the economic interest of a thermochemical cycle coupled with a nuclear reactor, it is necessary at first, to compare it with a reference chain defined by:

Heat from the reactor \rightarrow electricity \rightarrow hydrogen from alkaline electrolysis.

Due to the complexity of all the thermochemical cycles, they would lead to investment and maintenance costs higher than those of the reference chain. Consequently, to be competitive one day, η_T the net efficiency of a thermochemical cycle will have to be higher than that of the reference chain defined by:

$$\eta_{Ref} = \eta_{el} \times \eta_{\text{electricity} \rightarrow \text{hydrogen}} \quad (2)$$

This allowed us to propose a first limit to the competitiveness for a thermochemical cycle coupled with a dedicated reactor:

$$\eta_T > \eta_{Ref} \quad (3)$$

Analysis of the existing alkaline electrolyzers [7, 2] showed that the NorskHydro company has developed devices with $\eta_{\text{electricity} \rightarrow \text{hydrogen}} = 73\%$, including the work necessary for the compression until 30 bar.

If the nuclear reactor is a VHTR (Very High Temperature Reactor), it is generally assumed [1] that $\eta_{el} = 47\%$ and then, for the corresponding reference chain: $\eta_{Ref} = 34\%$.

However the perspective of a high energy efficiency value cannot guarantee the competitiveness of a process. Different studies estimated that in the future, the new processes for producing hydrogen would reach **a target between 2 to 3 \$/kg of H₂ [8]. This provided a second limit for the competitiveness of the S-I cycle coupled with a HTR.** In a previous work [2], we also estimated that large alkaline electrolysis plants coupled with dedicated EPRs could reach such a target. Therefore, it is often considered that a value of 2 €/kg of H₂ should be considered as a target and that the R&D programs related to advanced processes for producing hydrogen would have for objective to reach this target value.

The preliminary investigations for the S-I cycle coupled with a helium cooled reactor were very encouraging. For instance, in [3] it was indicated: at 850°C: $\eta_T = 42\%$ and 1.53-2.01 \$(2002)/kg of H₂; at 950°C: $\eta_T = 52\%$ and 1.42-1.87 \$(2002)/kg of H₂. Somewhat later, a deeper investigation indicates that a realistic efficiency of the S- I cycle is $\eta_T \sim 37\%$ [4], a value which do not include the coupling to the Very High Temperature Reactor. More recently, assessments performed for the European HYTECH project [9] which include the coupling to the VHTR have been done. Two cases were presented:

- a) By trying to give preference to the global efficiency, values of $\eta_T = 30\%$ and 5.3€(2006)/kg of H₂ have been obtained.
- b) By trying to reduce the production cost, values of $\eta_T = 26\%$ and 4.2€(2006)/kg of H₂ have been obtained. From the previous case, these values correspond to increases of pinch values of the heat recovery exchangers in the H₂ production step section, which leads to increase the need in primary energy but also to reduce the dimensions of devices and significantly capital costs.

The coupling scheme of [9] includes a cooler (60 MWth) downstream the final heat exchanger between the secondary helium loop and the S_I cycle, currently being removed so that a 3 to 4% increase in efficiency could be obtained.

Besides the HYTHECH assessments, CEA is currently performing its own evaluation which will be available in 2008.

There are several reasons for the reduction of the value of η_T through more precise estimations: one is that the second law of thermodynamics does not allow recovering all the heat produced by exothermic reactions. Moreover chemical reactions are usually not complete; as a matter of fact, the consumption of energy needed for the decomposition of HI is higher than expected in preliminary evaluations. Besides, it was pointed out in [3] that the excess of water and iodine at the outlet of the Bunsen reactor are needed to avoid miscibility of HI and H₂SO₄ acids. These lead to higher material circulation and higher heat needs than a preview may suggest. A method for assessing the consequences in term of energy

consumptions of using excess reactants for reactions that are not spontaneous are presently under investigations [10].

Cost accounts concerning advanced systems such as the S-I cycle are characterised by uncertainties. In [11] an economic evaluation of only four main economic parameters that determine the production cost of hydrogen by the S-I process has been performed: investment costs, maintenance costs, iodine costs and the amount of hydrogen produced. Standard numerical operations' fuzzy equivalents have been applied to existing data of the S-I cycle, available in October 2006, to obtain a fuzzy set on the cost of the hydrogen produced by the S-I cycle (see Figure 1).

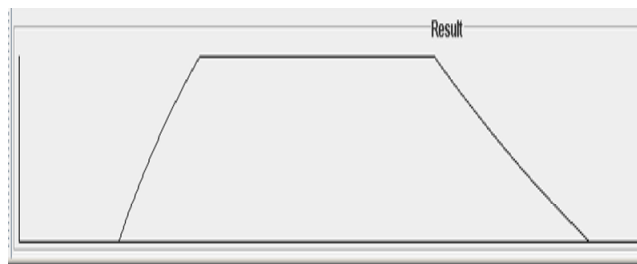


Figure 2: Assessment of the total production cost for the S-I cycle coupled with a HTR, from [11]. The horizontal axis corresponds to the possible values of the hydrogen production cost. The minimum value is 1.6 €/kg of H₂, the maximum value is 9.4 €/kg of H₂. Between them the horizontal segment is bounded by a most certain minimum value equal to 3. €/kg of H₂ and a most certain maximum value equal to 6.8 €/kg of H₂. The vertical axis corresponds to non normalized probabilities of occurrence linked to each production cost value.

This method enables to provide lower and upper bonds for expected production costs. Tighter limits are also given to estimate the cost which is more likely to be achieved, considering today's R& D results.

3. Alternative thermochemical cycles and their compatibility with various nuclear reactors.

The GIF has retained six innovative concepts of nuclear reactors with technological breakthroughs, for which domains have been defined for T_{oc} , the temperature at the outlet of the reactor core [1]:

- 1) the Gas Fast Reactor (GFR) $T_{oc} \in [550-850^{\circ}\text{C}]$,
- 2) the Molten Salt Reactor (MSR) $T_{oc} \in [640-850^{\circ}\text{C}]$,
- 3) the Lead Fast Reactor (PbFR) $T_{oc} \in [520-620^{\circ}\text{C}]^1$,
- 4) the Sodium Fast Reactor (SFR) $T_{oc} \in [500-640^{\circ}\text{C}]$,
- 5) the Supercritical Water Reactor (SCWR) $T_{oc} \in [380-500^{\circ}\text{C}]$,
- 6) the Very High Temperature Reactor (VHTR) $T_{oc} \in [880-1000^{\circ}\text{C}]$.

In a recent study [12] a selection was done for promising alternative thermochemical or hybrid cycles. The hybrid cycles, in which hydrogen is produced by an electrolysis step is beyond the scope of our present work. However, at the restart of the interest for the cycles, they were considered less promising in terms of energy efficiency than pure thermochemical

¹ There is an alternative Lead-Bismuth reactor, for which the temperature outlet core's could be as high as 800°C. However [13] points out that the bismuth world's reserves are so low that cycles that contain bismuth are not likely to be economic. This argument should also be applicable to reactors.

ones [3]. The pure thermochemical cycles retained by [11] and the corresponding temperature of the associated hotter point T_h for each cycle are:

- Cerium-Chlorine (Ce-Cl) $T_h = 850^\circ\text{C}^2$,
- Magnesium-Iodine (Mg-I) $T_h = 600^\circ\text{C}$,
- Iron-Chlorine (Fe-Cl) $T_h = 739^\circ\text{C}^3$,
- Vanadium-Chlorine (V-Cl) $T_h = 770^\circ\text{C}^4$.

We can examine the compatibility of nuclear reactors and thermochemical cycles, by taking into account the domains of temperature at the outlet of nuclear reactor core and that T_{oc} should be at least 40°C higher than T_h , for taking into account a reasonable pinch temperature in the heat exchanger between the reactor and the thermochemical cycle. The results are given in Table 1.

	Ce-Cl	Mg-I	Fe-Cl	V-Cl
GFR	No	Yes [+]	Yes [+]	Yes [+]
MSR	No	Yes [- +]	Yes [+]	Yes [+]
PbFR	No	No	No	No
SFR	No	Yes [+]	No	No
SCWR	No	No	No	No
VHTR	Yes [+]	Yes [- +]	Yes [- +]	Yes [- +]

Table 1: Compatibility between Nuclear Reactors and Thermochemical Cycles.

+ corresponds to the upper bound among the studied values for the outlet core temperature,
- to the lower bound.

It appears that, **at the present stage of knowledge**, all the alternative cycles selected in [12], would be compatible with the VHTR, none of them with the PbFR and the SCWR. The Magnesium-iodine (Mg-I) is compatible with the SFR as well as with the GFR and MSR, which are both compatible with Fe-Cl and V-Cl.

4. The alternative thermochemical cycles and the competitiveness targets.

At present, the investigations were not equally distributed between the various reactors and the various cycles. Therefore the efficiencies η_{el} for producing electricity from these reactors are not known with the same precision. However from [1], we can get η_{el} estimations for the reactors which are compatible with at least one alternative cycle. Following the relation between η_{el} , $\eta_{\text{electricity} \rightarrow \text{hydrogen}}$, η_T (3) and considering a NorskHydro alkaline electrolyser with $\eta_{\text{electricity} \rightarrow \text{hydrogen}} = 73\%$, it is possible to define values that η_T the net efficiency that an alternative cycle coupled with a given reactor must exceed. The results are given in Table 2.

	η_{el} [%]	η_T [%]
GFR	42	> 31
MSR	29	> 21
PbFR	44	> 32
SFR	40 ⁵	> 29
VHTR	47	> 34

Table 2: Electric efficiencies and limits of efficiencies that the alternative cycles will have to exceed.

² An alternative with 750°C is currently investigated (F. Lemort: private communication).

³ There is an alternative with 650°C , whose feasibility is questionable.

⁴ The VO-Cl alternative with 610°C does not work from a thermodynamic point of view.

⁵ K. Tucek et al. (*Comparison of sodium and lead-cooled fast reactors regarding severe safety and economical issue*. In proceedings of Icone 13-50397, Beijing, May 2005) pointed out that $\eta_{\text{electricity} \rightarrow \text{hydrogen}}$ could reach a 46% value.

The second limit for the competitiveness of an alternative cycle coupled to a Generation IV reactor, although more severe, appears somewhat more complex to express. As a matter of fact, there are many unknown factors on the economic data needed to perform a realistic evaluation of the cost of hydrogen produced from non-demonstrated systems such as Generation IV reactors and thermochemical cycles. However it is possible to have an idea of the costs of heat and electricity produced by a Generation IV reactor, by optimistically supposing in an optimistic way that the production cost of the electricity by a Generation IV reactor is close to that of a Generation III reactor (in similar contexts: dedicated reactors). Besides, in order to assess the cost of the heat produced by a given reactor, it is possible to assume that the ratio between the costs of heat and electricity would be equal to the inverse of η_{el} . The estimation of the cost of the hydrogen produced by all the combinations of nuclear reactors and thermochemical cycles would be somewhat tedious; however it is possible to highlight certain problems which if not correctly handled, could lead to additional costs for the hydrogen produced:

- The energy consumption must be very carefully estimated, particularly for the secondary reactions of the thermochemical cycles. The reactions that produce hydrogen, are not spontaneous, the production of hydrogen from chemical reactions is an extremely rare phenomenon in nature. As observed for the S-I cycle and explained in [10], it is often necessary to use excess reactants and to optimise incomplete conversion reactions. Still it is possible to recover some heat from exothermic reactions: heat management will be optimised in order to reach a correct balance between the recovery of the heat and the size of the apparatus.
- The cost of energy consumption must be compared, in the most possible relevant way, with the electric consumption by large alkaline electrolysis plants fed by a Generation III reactor. If the electric efficiency η_{el} can provide a first approximation of the ratio between the unit costs of heat and electricity, there are only incomplete data on the production cost of the electricity by breeder reactors like five of the six Generation IV reactors. The situation is somewhat different for the VHTR which appears from Table 1 probably the most compatible with the thermochemical cycles. However, it was recently pointed out in [13] that the cost of the electricity produced by a VHTR could be 24 % greater than that of a Generation III reactor. Besides, the total failure probability of a S-I hydrogen plant was calculated to be 0.0241 for a 24-h mission time [14]. This failure probability being considerably higher than expected for the reactor power source, this would imply either an increase in the out of operation periods or the implementation of a power cut circuit and therefore an additional investment. Overall, the cost of the energy produced by the reactor would be higher.
- The cost of the coupling between the reactor and the thermochemical cycle must be investigated in terms of investment, additional energy consumption and safety consideration. The cost of the coupling should be appreciably greater than for an alkaline electrolyser plant, as pointed out in [15]: *“The interface between the electrolyser unit and the nuclear plant only requires the transfer of electricity, since current water electrolyser technology does not require heat input...This feature allows the electrolyser to be placed at a large distance from the reactor if required for safety reason”*.
- Finally, the impact in the public opinion of three combined risks: nuclear + chemical + hydrogen will also have to be considered.

5. Conclusions

Among the promising thermochemical cycles studied with a view to produce hydrogen from nuclear reactors, and at the present of knowledge, most of them should only be compatible only with VHTRs. The future of these cycles should strongly depend on the VHTRs. In any cases, the sets reactor + thermochemical cycles will be confronted with limits of competitiveness. The experience gained from the recent works on the S-I cycle allows from now to identify critical points applicable to each of the cycles, which shall be examined by CEA during the next years, as well as generic improvements of the basic operations common to the thermochemical cycles. CEA will realize a complete assessment of the thermochemical cycles at the end of 2008.

References

- [1] *A technology Roadmap for Generation IV*. Report U.S. DOE 03-GA50034 and GF-002-00, December 2002. (<http://gif.inel.gov/roadmap/>).
- [2] F. Werkoff, et al. *Processes of hydrogen production, coupled with nuclear reactors: economic perspectives*, Proceedings of the European Nuclear Conference (ENC), (paper n° 227) 11-14 December 2005, Versailles (France).
- [3] L.C. Brown et al. *High efficiency generation of hydrogen fuels using nuclear power*. General Atomics, GA-A24285, Rev.1, 2002.
- [4] A. Le Duigou et al. *HYPHEC: An EC funded search for a long term massive hydrogen production route using solar and nuclear technologies*. International Journal of Hydrogen Energy. In Press, 2007.
- [5] Y. Miyamoto et al. Research and Development Program of Hydrogen Production System with High Temperature Gas-Cooled Reactor, In Proc. of the ICONE11 Conf. Paper n° 3639. Tokyo. April 20-23, 2003.
- [6] D.R. O'Keefe, J.H. Norman and D.G. Williamson. *Catalysis research in thermochemical water-splitting processes*, Catal. Rev.-Sci. Eng., Vol.22, Part 3, pp. 325-369. 1980.
- [7] J. Ivy. *Summary of Electrolytic Hydrogen Production, milestone completion report*, National Renewable Energy Laboratory/MP-560-36734. September 2004.
- [8] P. Davis. *Hydrogen Production R &D*, slides presented at the DOE annual meeting, May 16, 2006.
- [9] G. Cerri et al. *HYPHEC-Importance and impact of large scale H₂ production processes industrial scale-up and cost analysis*. In proceedings of the 3rd European Hydrogen Energy Conference, 18-22 June 2007, Maastricht (the Netherlands).
- [10] MJ. Bagajewicz, S. Mullin and J. Traver. *A New Methodology to Screen Water Splitting Cycles for Hydrogen Production*. In Proceeding of the 2006's Aiche annual meeting. November 2006.
- [11] T. Baerecke et al.. *Fuzzy sets for assessing the profitability of hydrogen production by the sulphur-iodine thermochemical cycle*. Proposed for publication in the International Journal of Energy, Environment and Economics.

[12] M.A. Lewis, J.G. Masin and A. Taylor. *Evaluation of Promising Alternative Thermochemical Cycles*. In Proceeding of the 2006's Aiche annual meeting. November 2006. See also: M.A. Lewis. *2006 DOE Hydrogen Program- Evaluation of Alternative Thermochemical Cycles*. (http://www.hydrogen.energy.gov/pdfs/review06/pdp_21_lewis.pdf).

[13] D. Barbier. *Private communication*.

[14] E.A. Harvego et al. *An evaluation of reactor cooling and coupled hydrogen production processes using the modular helium reactor*. Nuclear Engineering and Design 236 (2006) 1481-1489.

[15] B. Yildiz et al. *Configuration and Technology Implications of Potential Nuclear Hydrogen System Applications*. ANL-05/30, July 2005
(http://www.dis.anl.gov/ceeesa/documents/NuclearHydrogen_ANL0530Final.pdf).